Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

Supplementary Information

Accelerated proton transmission in metal-organic frameworks for efficient reducing CO₂ in aqueous solution

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Control samples preparation

The MOFs of PCN-222 was prepared according to the report.¹ Specifically, dissolving ZrCl₄ (70 mg, 0.3 mmol), FeTCPPCI (50 mg, 0.06 mmol), and benzoic acid (2700 mg, 22.1 mmol) into 8 mL N,N-diethylformamide (DEF) solution, and the mixture was sealed in a 20 mL glass vial and heated to 120 °C for 48 h in an oven. The needle-shaped crystals could be obtained and activated with fresh DEF and acetone for 3 times at 60 °C, and then dried in vacuum oven under 80 °C. For preparing FeTCPP/CB (FeTCPPCI loaded carbon black) sample, 5 mg carbon black was dispersed into 2 mL water/alcohol (V_{water}:V_{alcohol} = 1:1) through ultrasonic dispersion, then mixed with 300 µL DMF containing 0.3 mg FeTCPPCI. The mixture was subsequently stirred for 24 h. The product was washed with DMF and water by centrifugation, and then dried in vacuum oven under 80 °C.

Electrode preparation

All the samples were drop coated onto the carbon paper substrate (1 cm × 2 cm) as electrodes for the further measurements. Before the coating, carbon papers were cleaned with concentrated HNO₃ through refluxing under 100 °C for 6 h, then washed with plenty of deionized water and dried for further measurements. The electrodes were manufactured as follows: the mixture of catalyst (5 mg) and carbon powder (5 mg) suspended in 2-propanol solution (250 μ L) containing Nafion[®] solution (50 μ L) by sonication dispersing. After sonication for 30 min, the slurry (100 μ L) was dropped onto carbon paper and formed a 1 cm × 1 cm uniform coating, then dried naturally under ambient temperature for overnight. The final loading quantity of FeTCPPC1 molecule is about 5.7×10⁻⁸ mol cm⁻² for the FeTCPP⊂UiO-66 and UiO-66/FeTCPP catalysts.

Calculation method of Faradaic efficiency

The Faradaic efficiencies (FE) of the products (CO and H₂) were calculated as following equation (1):

$$FE_{CO/H2} = \frac{2x_{CO/H2}pGF}{IRT}$$
(1)

Two-electron process is involved in reducing CO₂ to CO and generating H₂ reactions. x (vol%) is the volume fraction of the target product in the gas flow. I is the total current at the specific applied potential. p (gas pressure) = 1.013×10^5 Pa, G (flow rate) = 5 mL min⁻¹, F (Faradaic constant) = 96485 C mol⁻¹, R (molar gas constant) = 8.314 J mol⁻¹ K⁻¹, T (temperature) = 298.15 K.

Theoretical calculations

For the simulated model, the Gibbs free energy at 298.15 K ($G_{298.15 K}$) can be obtained through the total energies from DFT calculations with thermodynamic correction by the following equation (2).

$$G_{DFT,298.15K} = E_{DFT,0K} + ZPE + \int C_p dT - TS$$
(2)

And the Gibbs free energy change of the reaction (ΔG) can be obtained by the following equation (3).

$$\Delta G = G_{products} - G_{reactants} \quad (3)$$

For the simulation of CO₂RR pathways, the CPET pathway was calculated based on the computational hydrogen electrode (CHE, $2H^+ + 2e^- \rightarrow H_2$) model, and the SPET process was simulated according the constant potential model.²⁻⁵ During the electrode reacting, the curve of net charge to work function could be fitted by adjusting the amount of additional charge to the model while keeping the electric potential unchanged. Hence, the energy under real condition could be obtained by adjusting the working function of all species to the reaction potential. In this work, the work function used 4.09 V (at the potential of - 0.56 V) with the reference of 4.65 V of U_{RHE} .⁶⁻⁸



Fig. S1 The *in-situ* XAS electrochemical CO₂RR measurement system, in which the fluorescence model is adopted for collecting spectra. The beam path of X-ray is also marked with red arrows, irradiating the electrode while voltage is applied and CO₂ gas bubbling into electrolyte.



Fig. S2 (a) FT-IR data of the UiO-66, UiO-66/FeTCPP, FeTCPP⊂UiO-66, and FeTCPPCI. (b) Local magnified spectra of the rectangle section in (a). The characteristic peak at 1700 cm⁻¹ reveals the free - COOH group of ligands. No obvious intensity change at 1700 cm⁻¹ for UiO-66/FeTCPP and FeTCPP⊂UiO-66 compared with UiO-66 reveals that the FeTCPPCI ligands are immobilized into MOFs framework through coordination bond.



Fig. S3 (a) Zr *K*-edge extended XAFS oscillation function $k^3\chi(k)$. (b) The corresponding $FT|\chi(R)|$. FeTCPP⊂UiO-66 and pristine UiO-66 samples present the same local atomic arrangement, differing from the UiO-66/FeTCPP.



Fig. S4 The morphology of UiO-66 catalyst after electrolysis for 1.5 h at reducing potentials (a) -0.51 V, (b) -0.56 V, (c) -0.61 V, and (d) -0.71 V in the CO₂-saturated 0.1 M KHCO₃. The intact octahedral MOFs indicates that UiO-66 can survive from the electrolysis condition in the aqueous solution.



Fig. S5 (a) Zr K-edge *in-situ* EXAFS oscillation function $k^3\chi(k)$ and (b) the corresponding $FT|\chi(R)|$ for the UiO-66 without bias and under potentials of -0.51, -0.56, and -0.61 V. The negligible change for the spectra with potential bias compared with the pre one exhibits that the local structure of MOFs can remain stable during electrolysis.



Fig. S6 In-situ XANES data at the Zr K-edge for the FeTCPP⊂UiO-66.



Fig. S7 *In-situ* XANES data at the Zr K-edge of the UiO-66/FeTCPP. The Zr-O cluster might degrade to other piece from typical Zr_6O_8 octahedron of UiO-66.



Fig. S8 SEM image of the FeTCPP⊂UiO-66 after electrolysis for 3 h under -0.56 V.



Fig. S9 (a) XRD pattern for the prepared PCN-222(Fe) compared with the simulated PCN-222. (b-c) SEM images for PCN-222(Fe) catalyst coating onto the carbon paper pre and post electrolysis in the CO₂-saturated 0.1 M KHCO₃ electrolyte under -0.56 V for few minutes. The hole leaved by the decomposed MOFs can been observed in the SEM image. The results reveals that the PCN-222 MOFs would not be qualified for electrochemical CO₂ reduction in aqueous solution.



Fig. S10 (a) Cyclic voltammetry curve and (b) Faradaic efficiency for hydrogen evolution of the UiO-66 catalyst. The UiO-66 MOFs show poor electrochemical activity for CO₂RR and HER.



Fig. S11 The *in-situ* XANES Fe K-edge for the FeTCPP \subset UiO-66. The inset is the local magnification for the dotted line frame. The oxidation states of iron are reduced with the application of potential bias, indicating that the CO₂RR active sites might situate on iron porphyrin.

Catalysts	Product	Medium and cathode material	Potential [overpotential]	Faradaic efficiency
FeTCPP⊂UiO-66 This work	СО	Aq. KHCO ₃ (0.1 M, pH 6.7); Carbon paper	-0.56 V vs. RHE [450 mV]	~100%
Cu ₃ (BTC) ₂ MOFs ⁹	НООССООН	DMF + TBATFB (0.01 M) Glassy carbon	-2.5 V vs Ag/Ag ⁺ [n. r.]	51% (HOOCCOOH)
Fe-MOF-525 ¹⁰	СО	DMF + TFE (1 M) TBAPF ₆ (1 M); FTO	-1.3 V vs. NHE [n. r.]	54 ± 2%
Re-SURMOF ¹¹	СО	MeCN + TFE (5 vt.%) + TBAH (0.1 M); FTO	-1.6 V vs. NHE [n. r.]	93 ± 5%
Zn-BTC MOFs ¹²	CH ₄ CO	BmimBF ₄ ; Carbon paper	-2.2 V vs. Ag/Ag ⁺ [250 mV]	80.1% (CH ₄) 7.9% (CO)
Al ₂ (OH) ₂ TCPP-Co MOFs ¹³	СО	Aq. KHCO ₃ (0.5 M, pH 7.3); FTO	-0.7 V vs. RHE [590 mV]	76% (CO)
HKUST-1 ¹⁴	CH ₃ OH C ₂ H ₅ OH	Aq. KHCO ₃ (0.5 M, pH 7.3); FTO	n. r.	15.9% (CH ₃ OH + C ₂ H ₅ OH)
Co-PMOF ¹⁵	СО	Aq. KHCO ₃ (0.5 M, pH 7.3); Carbon cloth	-0.8 V vs. RHE [690 mV]	94% (CO)
Fe-PMOF ¹⁵	СО	Aq. KHCO ₃ (0.5 M, pH 7.3); Carbon cloth	-0.7 V vs. RHE [590 mV]	28.8% (CO)

Table S1 Comparison of the electrocatalytic performance of reported MOFs catalysts for CO₂ reduction.

TBATFB: tetrabutylammonium tetrafluoroborate;

TBAPF₆: tetrabuthtylammonium hexafluorophosphate;

TBAH: tetrabutylammonium hydroxide;

TFE: trifuoroethanol;

BmimBF₄: 1-butyl-3-methylimidazolium hexauorophosphate.

Abbreviation of n. r. means that not be reported or not calculated due to limited data reporte.



Fig. S12 Cyclic voltammetry curves at different scan rates (1-10 mV s⁻¹) in a non-Faradaic region of +0.08 V to +0.18 V vs. RHE in the CO₂-saturated 0.1 M KHCO₃ for (a) FeTCPP/CB, (b) UiO-66/FeTCPP, and (c) FeTCPP⊂UiO-66. (d) Plots used for the calculations of the C_{dl} for FeTCPP/CB, UiO-66/FeTCPP, and FeTCPP⊂UiO-66. The linear slope is equivalent to the twofold C_{dl} .



Fig. S13 Work functions of the species as functions of the net charge added into the systems. The dot line denotes the experimental work function (4.09 eV) with the reference of 4.65 V of U_{RHE} .



Fig. S14 The optimized geometric structure and charge distribution image for the CO_2^{*-} intermedia involved in calculation on the Fe site.

Notes and references

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