Hydrophobic perfluoroalkane modified metal-organic frameworks for the enhanced electrocatalytic reduction of CO$_2$

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Abstract
The electrochemical reduction of CO$_2$ to value-added chemicals would be an efficient way to utilize CO$_2$ and mitigate greenhouse gas emission. However, the associated competitive hydrogen evolution reaction (HER) in aqueous electrolytes usually leads to poor selectivity for the CO$_2$ electroreduction reactions (CO$_2$RR). Due to their high specific surface areas and tunable single active sites, metal-organic frameworks (MOFs) are considered as promising candidates for CO$_2$RR. Herein, the Fe-porphyrin based Zr-MOF, PCN-222(Fe), was treated with perfluorocarboxylic acid to afford the hydrophobic F$_n$-PCN-222(Fe) ($n$ = 5 and 7, $n$ is the number of fluorine atoms in the perfluoroalkyl chain) for improving the selectivity CO$_2$RR via inhibiting the HER. Owing to the single active Fe sites were positioned in a hydrophobic microenvironment, the optimal F$_5$-PCN-222(Fe) shows a high Faradic efficiency of 97% toward production of CO at $-0.7$ V versus reversible hydrogen electrode. Meanwhile, F$_5$-PCN-222(Fe) achieved a high turnover frequency value of 3850 h$^{-1}$ at $-0.8$ V, which was almost 3.6 times higher than that of PCN-222(Fe) and surpassed most of other reported MOFs. This study paves a new way to improve the selectivity of the CO$_2$RR via inhibiting the associated HER by increasing the hydrophobicity of the electrocatalysts.

KEYWORDS
CO, CO$_2$ electrocatalysis, hydrophobicity, metal-organic framework, perfluoroalkyl chain
1 | INTRODUCTION

The excessive emissions of the greenhouse gas CO$_2$ have triggered serious climate and environmental problems such as sea-level rise.\textsuperscript{1-4} There are many different approaches to mitigate CO$_2$ emissions including CO$_2$ capture and subsequent storage and catalytic conversion into valuable chemicals and fuels. Compared with the physical adsorption methods, the chemical conversion of CO$_2$ to produce valuable-added fuels and chemicals can realize the recycling of carbon resources. To date, several methods have been adopted for CO$_2$ conversion such as thermo-catalysis,\textsuperscript{5,6} photochemical,\textsuperscript{7-10} biochemical,\textsuperscript{11} and electrochemical\textsuperscript{12-16} methods. Among them, the CO$_2$ electroreduction reaction (CO$_2$RR) is considered to be a promising strategy owing to its simple procedures and ambient operation conditions. In addition, this technology coupled with renewable energy sources, such as wind or solar energy, could produce fuels and industrial chemicals including C$_1$ products (CO, formate, methane, and methanol),\textsuperscript{17-21} C$_2^+$ products (ethylene, ethane, and ethanol).\textsuperscript{22-24} Among all of the products, CO is one of the important chemical raw materials and is widely used in many aspects such as Fischer–Tropsch synthesis.\textsuperscript{25} However, the complex electroreduction processes involve multiple protons and electrons transfer steps and the associated competitive hydrogen evolution reaction (HER) in aqueous electrolytes usually leads to poor selectivity for the CO$_2$ electroreduction reactions (CO$_2$RR) toward production of CO. In recent years, extensive efforts have been devoted to exploit highly efficient electrocatalysts for the electrochemical CO$_2$-to-CO conversion. The electrode materials such as Au-, Ag-, Cu-based metals,\textsuperscript{26-28} Fe, Co, Ni-based single-atom catalysts (SACs),\textsuperscript{29-33} metal-free carbon materials\textsuperscript{34-36} have been developed. However, the drawbacks including high cost of noble metals, difficult to prepare SACs in large-scale synthesis restricted their commercial applications in the CO$_2$RR. Thus, developing new efficient electrocatalysts for CO$_2$RR with high selectivity is still highly desirable.

In the recent years, porous crystalline metal-organic frameworks (MOFs) constructed by metal nodes and functional ligands have attracted widespread attention in gas storage, separation, catalysis, sensors, and biomedicine,\textsuperscript{37-45} and are considered as good candidates for CO$_2$RR due to their high surface areas, large adsorption uptakes of CO$_2$ and abundant accessible single sites.\textsuperscript{46-51} Nevertheless, the selectivity of the reported MOF electrocatalysts toward the CO$_2$RR is still far from the commercial standards because the competitive HER is usually occurred in aqueous electrolyte. It is believed that the local environment of the active centers including coordination structure and electrolyte environment,\textsuperscript{52-56} plays an important role in adjusting the catalytic performances of the CO$_2$RR. As we know, most of the pores in MOFs are hydrophilic, which are more favorable for the contaction between active centers and aqueous electrolyte, thus leading to intensive HER. In this regard, the increase of the hydrophobicity in the pores and outer surfaces of MOFs would inhibit the HER and enhance the selectivity of the CO$_2$RR.

Herein, the perfluoroalkyl chains were grafted to the Z$_{10}$ clusters in the Fe-porphyrin-based MOF, PCN-222(Fe), to afford the hydrophobic F$_n$-PCN-222(Fe) ($n = 5$ and 7, $n$ is the number of fluorine atom in perfluoroalkyl chains) for enhancing the selectivity of the CO$_2$RR toward the production of CO via inhibiting the HER. The hydrophobicity of the perfluoroalkyl chains modified PCN-222(Fe) can be tuned by introduction of the different perfluoroalkyl chains length. Compared to the pristine PCN-222(Fe) with 53% of CO Faradic efficiency (FE$_{CO}$) at $-0.7$ V versus HER (all the mentioned potentials in this study are referenced to HER), the optimal hydrophobic F$_5$-PCN-222(Fe) has almost doubled the FE$_{CO}$ and reached 97% at $-0.7$ V.

2 | EXPERIMENTAL SECTION

2.1 | Syntheses of samples

PCN-222(Fe) was synthesized according to literature method.\textsuperscript{57,58} ZrOCl$_2$·8H$_2$O (300 mg, 0.93 mmol) and benzoic acid (2700 mg, 18.7 mmol) were dissolved in 20 ml of N,N-diethyl formamide (DEF) in a 250 ml round-bottomed flask. Then, [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]-Fe (Fe-TCP, 115 mg, 0.15 mmol) was added to the solution and dissolved under ultrasound. The mixture was heated at 120°C for 12 h under stirring, and cooled down to room temperature. The solid was collected by centrifugation, washed with DMF and acetone until the liquid became colorless. The obtained powder was redispersed in a solution containing 60 ml of DMF and 5 ml of 12 mol/L HCl and refluxed at 120°C for 12 h. After centrifugation, the solid was washed with DMF and acetone for several times and then soaked in acetone overnight. Then the powder was collected by centrifugation and dried at 70°C under vacuum.

2.2 | Synthesis of F$_n$-PCN-222(Fe) ($n = 5, 7$)

The perfluoroalkyl chains modified PCN-222(Fe) was synthesized according to a referenced procedure.\textsuperscript{59,60} A quantity of 100 mg activated PCN-222(Fe) was put into
a 20 ml vial. Subsequently, 5 ml 0.1 mol/L DMF solution of perfluoroalkyl acid was added to the above vial and then sealed and heated at 70°C for 24 h with occasional swirling. By centrifugation, the solids were washed with DMF (60 ml, three times) and acetone (80 ml, four times). Finally, the sample was dried at 70°C under vacuum for 12 h to obtain Fₙ-PCN-222(Fe).

3 | RESULTS AND DISCUSSION

The robust mesoporous Zr-MOF, PCN-222(Fe), has two large pores of 1.3 and 3.7 nm, in which the Fe-porphyrin active sites can be easily accessible for the electrolyte and CO₂ molecules. Furthermore, the perfluoroalkyl functionalized Fₙ-PCN-222(Fe) can be easily prepared by postsynthetic modification (PSM) of the parent PCN-222(Fe) via esterification reactions of CF₃CF₂COOH or CF₃(CF₂)₂COOH and hydroxyl (-OH) groups on the Zr₆ cluster (Scheme 1).

To confirm the successful introduction of perfluoroalkyl chains into PCN-222(Fe), the Fourier transform infrared (FT-IR) spectroscopy and ¹⁹F nuclear magnetic resonance (¹⁹F-NMR) measurements were performed. As shown in Figures 1A and S1, the broad peak related to the –OH of the perfluorocarboxylic acids at 3130 and 3120 cm⁻¹ disappeared and the C=O at 1760 and 1765 cm⁻¹ moved to 1658 and 1656 cm⁻¹ in F₅-PCN-222(Fe) and F₇-PCN-222(Fe), respectively. Meanwhile, the peaks of C–F at the range of 1100–1300 cm⁻¹ can be observed in the IR of the two perfluoroalkyl chains modified MOFs. As shown in Figures S2 and S3, the ¹⁹F-NMR of the digested samples of Fₙ-PCN-222(Fe) in H₂SO₄/DMSO showed obviously ⁹F signals, which were consistent with the chemical shifts of the CF₃CF₂COOH and CF₃(CF₂)₂COOH (Figures S4 and S5). These results proved the successful introduction of perfluoroalkyl chains into PCN-222(Fe), which linked to the Zr-based nodes with covalent bonds (Scheme 1).

Powder X-ray diffraction (PXRD) was used to investigate the crystallinity of PCN-222(Fe) and Fₙ-PCN-222(Fe). As shown in Figure 1B, the as-synthesized Fₙ-PCN-222(Fe) and PCN-222(Fe) displayed the same diffraction patterns with the simulated one, indicating that its primal crystalline structure was remained after the introduction of perfluoroalkyl chains in the frameworks. To study the morphological changes of PCN-222(Fe) before and after modification, scanning electron microscope (SEM) and transmission electron microscope (TEM) were tested. The SEM images of F₅-PCN-222(Fe) and F₇-PCN-222(Fe) displayed similar rod-like morphology (Figures 1C and S6) with the pristine PCN-222(Fe) (Figure S7A). The smooth surfaces and the diameters of Fₙ-PCN-222(Fe) were similar to those of PCN-222(Fe) (Figure S7A), which further confirmed that the PSM process did not destroy the original structure. The TEM images also proved that the rod-shaped morphology and structure remained after modification (Figures S8 and S9A). Additionally, energy dispersive X-ray spectroscopy (EDS) elemental mapping analysis
indicated that C, N, O, Fe, F, and Zr elements were uniformly distributed in the entire F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) (Figures 1D and S9B), which confirmed that the perfluoroalkyl chains were uniformly grafted into PCN-222(Fe). The ICP-AES revealed that the Fe contents (mass fraction) in PCN-222(Fe), F$_5$-PCN-222(Fe), and F$_7$-PCN-222(Fe) were 3.47%, 3.03%, and 2.93%, respectively (Table S1), which was in agreement with the EDS results (Table S2). The EDS and X-ray photoelectron spectroscopy (XPS) results (Table S3) demonstrated that high F content of the two samples, which also suggested that the perfluoroalkyl chains were inserted in the frameworks.

The porous structures of all the samples were investigated by N$_2$ adsorption–desorption experiments at 77 K. As shown in Figure 2A and Table S2, the
PCN-222(Fe) has a high Brunauer–Emmett–Teller (BET) surface area of 2244 m$^2$/g and two large pores of 1.3 nm and 3.7 nm (Figure S10), which was in consistent with the crystal structure analysis (Scheme 1). Compared with that of PCN-222(Fe), slightly decreased N$_2$ adsorption uptakes for the F$_n$-PCN-222(Fe) samples were observed due to parts of the pores were occupied by the perfluoroalkyl chains, but F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) still had large surface areas of 2014 and 1924 m$^2$/g, respectively. Compared with F$_7$-PCN-222(Fe), F$_5$-PCN-222(Fe) with shorter perfluoroalkyl chain has larger BET and pore volume of 1.19 cm$^3$/g (Table S4). Such high BET surface areas and pore volumes for these mesoporous MOFs made them have high CO$_2$ adsorption capacities. Notably, although the introduction of perfluoroalkyl chains led to the decrease of surface areas and pore volumes, the CO$_2$ adsorption capacity of F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) did not decrease significantly and showed large CO$_2$ adsorption uptakes of 39 and 37 cm$^3$/g at 298 K, respectively due to the affinity of C-F to CO$_2$ (Figure 2B).$^{61,62}$ The results suggested the successful introduction of perfluoroalkyl chains.

To further investigate the elemental compositions and chemical states in all samples, the XPS was conducted. As shown in Figure S11, the XPS spectrum revealed the existence of C, N, O, Zr, Fe and Cl elements in PCN-222(Fe), which was consistent with the EDS result (Figure S7B). Besides, the F element could be detected in the XPS spectra of F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe). The peak centered at 688.7 eV in F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) was ascribed to C-F (Figure 3A).$^{63}$ The results suggested the successful introduction of perfluoroalkyl chains. To investigate the Fe states in all samples, the high resolution XPS spectra were further analyzed. As shown in Figure S12, the Fe 2p$^{3/2}$ spectra of the three samples exhibited a characteristic peak at ca. 710.8 eV that related to Fe$^{3+}$, which would be facilitate in the CO$_2$RR.$^{64,65}$

![Figure 3](image-url) (A) X-ray photoelectron spectroscopy spectra of F in F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe). (B) The normalized Fe K-edge X-ray absorption near edge structure spectra of F$_7$-PCN-222(Fe), Fe-TPPCN, Fe foil, FeO, and Fe$_2$O$_3$. (C) Fourier transform EXAFS spectra of different samples. (D) First-shell fitting of the Fourier transformed EXAFS spectrum of F$_5$-PCN-222(Fe). EXAFS, extended X-ray absorption fine structure.
To acquire information regarding the oxidation state and local coordination environment of Fe centers in F$_5$-PCN-222(Fe), the X-ray absorption spectroscopy (XAS) test was carried out. As shown in the Fe K-edge of the X-ray absorption near edge structure (XANES) in Figure 3B, a weak pre-edge peak at 7113.4 eV was appeared in the curves of F$_5$-PCN-222(Fe) and the 5,10,15,20-tetrakis(4-cyanophenyl)porphyrinato]-Fe(III) chloride (Fe-TPPCN) molecule, which was assigned to the transition from 1s to 4pz. The result revealed that charge was transferred from the TCPP ligand to Fe centers and existed the square-planar Fe-N$_4$ porphyrin structure in F$_5$-PCN-222(Fe). The absorption threshold of F$_5$-PCN-222(Fe) was far from that of FeO but close to that of Fe$_2$O$_3$ (Figure 3B), indicating the existence of Fe$^{3+}$ in F$_5$-PCN-222(Fe), which was consistent with the result of the XPS spectra. As shown in Figure 3C, the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra exhibited a dominant peak located at 1.62 Å related to the Fe-N coordination path, which was similar to that of the Fe-TPPCN reference sample. Furthermore, no peak at 2.18 Å was observed, which demonstrated no Fe nanoparticles in F$_5$-PCN-222(Fe) (Figure 3C). The above results suggested that the Fe center in F$_5$-PCN-222(Fe) was coordinated with four nitrogen atoms and one chlorine atom in the axial direction perpendicular to the Fe-N$_4$ plane. To prove this hypothesis, the Fe-N$_4$Cl coordination model was used for EXAFS fitting of F$_5$-PCN-222(Fe). As shown in Figure 3D, the fitting curve of F$_5$-PCN-222(Fe) was consistent with the measured data and the fitting parameters were in appropriate range. The EXAFS fitting result revealed that the coordination numbers of Fe-N and Fe-Cl were 3.87 and 1.01 of F$_5$-PCN-222(Fe), respectively (Table S5), further confirmed the Fe centers with the FeN$_4$Cl coordination structures.

The electrocatalytic CO$_2$RR performances for PCN-222(Fe), F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) were conducted in CO$_2$-saturated 0.5 mol/L KHCO$_3$ aqueous solution using a standard two-chamber and three-electrode H-type electrochemical cell separated by a proton exchange membrane. As shown the linear sweep voltammetry (LSV) curves in Figure 4A, PCN-222(Fe) and F$_5$-PCN-222(Fe) have more positive onset potentials and much larger current densities in CO$_2$-saturated 0.5 mol/L KHCO$_3$ aqueous solution than those in N$_2$-saturated corresponding electrolyte, indicating their activities may be originated from CO$_2$RR. Besides, both F$_5$-PCN-222(Fe) and F$_7$-PCN-222(Fe) exhibited higher current densities than PCN-222(Fe) in a wide potential range from $-0.5$ to $-0.9$ V, which demonstrated the vital influence of hydrophobicity environment in improving ability of F$_n$-PCN-222(Fe) toward CO$_2$RR. To further determine the selectivity of these catalysts for the CO$_2$RR, gas chromatography (GC) and $^1$H-NMR were used to detect the gas products and liquid products, respectively. Notably, only...
CO and H₂ were detected and no liquid was found (Figure S13). As shown in Figures 4B and S14, the total Faradic efficiency (FE) of CO and H₂ was near to 100%. Interestingly, both F₅-PCN-222(Fe) and F₇-PCN-222(Fe) showed higher selectivity for the conversion of CO₂ to CO than those of the pristine PCN-222(Fe) at every potential in the range of −0.6 to −0.9 V. The result strongly suggested that the Fe centers in the hydrophobicity environment indeed could improve the selectivity of CO₂RR toward the production of CO via inhibition of HER. It was noticed that the FE of CO of the F₅-PCN-222(Fe) exceeds 80% in the range of −0.6 to −0.8 V, and achieved 97% at −0.7 V, which was positioned at the state-of-the-art electrocatalysts for CO₂RR.67-69 Furthermore, F₅-PCN-222(Fe) exhibited a threefold higher CO partial current density (3.36 mA/cm²) than that of PCN-222(Fe) (1.06 mA/cm²) at −0.8 V (Figure 4C), which was due to the hydrophobicity of F₅-PCN-222(Fe) and improved the performance of CO₂RR. Notably, compared with F₅-PCN-222(Fe), the more hydrophobic F₇-PCN-222(Fe) exhibited slightly low selectivity and current density F₇-PCN-222(Fe) (Figure 4B,C), which might be ascribed to its smaller BET surfaces (Figure 2A) and CO₂ uptake (Figure 2B) and thus inhibiting the availability of electrolyte and protons to the active sites during the CO₂RR.70 To confirm whether the Fe centers were active sites in the CO₂RR, the Fe-free PCN-222 was also prepared and applied for the CO₂RR under the same condition. As shown in Figure S15, H₂ was the predominant product and little CO was produced at the potentials of −0.8 to −1.1 V. This result proved that the CO₂-to-CO conversion was originated from the Fe centers. Thus, the turnover frequency (TOF) of PCN-222(Fe) and F₇-PCN-222(Fe) can be calculated based on the contents of Fe. As shown in Figure 4D, F₅-PCN-222(Fe) presented a high TOF of 3850 h⁻¹ at −0.8 V, which was almost 2.6-fold higher than that of PCN-222(Fe) (1063 h⁻¹) and outperformed than most of MOFs and COFs (Figure S16). To evaluate the stability of the catalysts, the time-dependent total current density curves were performed. The long-term stability of F₅-PCN-222(Fe) was conducted at −0.7 V in CO₂-saturated 0.5 mol/L KHCO₃ (Figure S17). The total current density slightly decreased by only −0.6 mA/cm² and the FE of CO remained over 90% within 10 h. Moreover, as shown in Figure S18, the PXRD patterns of F₅-PCN-222(Fe) and F₇-PCN-222(Fe) revealed that the crystallinity was unchanged after the CO₂RR.

To confirm the intermediates during the CO₂RR, in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) at −0.7 V in 0.5 mol/L KHCO₃ was performed. As shown in Figure 5A, the real-time FTIR spectra of the CO₂RR on F₅-PCN-222(Fe) electrodes showed two major bands at 1400 and 2330 cm⁻¹, which were assigned to the *COO⁻ peak intensity increased with CO₂ adsorption before 280 s, and kept constantly after that, which suggested that *COO⁻ is the key intermediate for the formation of CO.71,72 To prove that CO is derived from the CO₂RR,¹³C-labeled carbon dioxide isotope experiments through gas chromatography–mass spectrometry (GC-MS) at −0.7 V in KH¹²CO₃ and KCl electrolytes were conducted. As shown in Figure 5A,B, when the CO₂RR was conducted under ¹³C-labeling CO₂ in 0.5 mol/L KH¹²CO₃, both the signal of ¹²CO and ¹³CO was observed, while only ¹³CO was observed when KH¹²CO₃ electrolyte was replaced by KCl electrolyte. The results revealed that the CO₂ dissolved in KHCO₃ solution was the carbon source of the CO₂RR.

4 | CONCLUSION

In conclusion, we develop a hydrophobic strategy to enhance the selectivity of the CO₂RR via decoration of the pore walls of PCN-222(Fe) electrocatalyst with perfluoroalkyl chains. The obtained optimal hydrophobic F₅-PCN-222(Fe) present higher selectivity toward the conversion of CO₂ to CO with high FE of 97% at −0.7 V in comparison with the parent PCN-222(Fe). The high TOF of 3850 h⁻¹ for F₅-PCN-222(Fe) was achieved, which was 2.6-times higher than that of...
PCN-222(Fe). The high performances can be attributed to the suppression of the HER caused by the hydrophobicity of catalysts as revealed by water contact angles. Our work presents an effective strategy to enhance the selectivity of MOF in the CO₂RR by the hydrophobic engineering, which provides a new choice for the application of modified MOF in CO₂RR.

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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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