Dynamic restructuring of coordinatively unsaturated copper paddle wheel clusters drives CO₂ reduction efficiently

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Abstract

Coordinatively unsaturated metal sites in metal–organic frameworks (MOFs) hold promises for improving activity and selectivity of catalyst. As the building unit of many MOFs, copper paddle-wheel (CPW) is of great interest to function as activity sites for CO₂ reduction due to the ability of copper cations to attract and activate CO₂ molecules. However, little is known about the real structure of these active sites for their dynamic structural changes under realistic operating conditions. Here, we apply to design defect metal–organic framework HKUST-1 with coordinatively unsaturated copper paddle wheel through a facile “atomized trimesic acid” strategy, reveal its dynamic behaviour during electrochemical reconstruction and prove its superior CO₂ reduction activity. Through comprehensive analysis of various in situ spectroscopy characterizations, it is demonstrated that unsaturated copper paddle wheel clusters [CU-CPWC, Cu₂(HCOO)₃] are finally formed during electrochemical reconstruction and act as the real active sites. Mechanistic studies based on density functional theory calculations reveal that the higher d band center in CU-CPWC compared with that in CPW accelerates the electron transport from copper atoms to CO₂ molecules, which can be exploited to improve the CO₂ reduction performance.

Background

Coordinatively unsaturated metal sites in metal–organic frameworks (MOFs) hold promises for improving activity and selectivity of catalyst. As the building unit of many MOFs, copper paddle-wheel (CPW) is of great interest to function as activity sites for CO₂ reduction due to the ability of copper cations to attract and activate CO₂ molecules. However, little is known about the real structure of these active sites for their dynamic structural changes under realistic operating conditions. Here, we apply to design defect metal–organic framework HKUST-1 with coordinatively unsaturated copper paddle wheel through a facile “atomized trimesic acid” strategy, reveal its dynamic behaviour during electrochemical reconstruction and prove its superior CO₂ reduction activity. Through comprehensive analysis of various in situ spectroscopy characterizations, it is demonstrated that unsaturated copper paddle wheel clusters [CU-CPWC, Cu₂(HCOO)₃] are finally formed during electrochemical reconstruction and act as the real active sites. Mechanistic studies based on density functional theory calculations reveal that the higher d band center in CU-CPWC compared with that in CPW accelerates the electron transport from copper atoms to CO₂ molecules, which can be exploited to improve the CO₂ reduction performance.

Due to the constituents' geometry, size, and functionality can be flexibly varied, metal–organic frameworks (MOFs) materials represent ideal platforms that can control the interplay between efficiency, activity and selectivity in a single catalytic system.^{1–4} HKUST-1 is the prime example of MOFs based on copper paddle wheel (–Cu₂(COO)₄, metal node) and 1,3,5-benzene-tricarboxylic acid (H₃BTC, organic link), which has the potential to be used in whole catalysis world.⁵ Interest in the reactivity of metal copper and copper based MOFs stems from its unique electrochemistry CO₂ reduction selectivity toward higher-value hydrocarbons beyond CO.^{6–15} Defect engineering in MOFs, such as missing linker defects, has attracted considerable research attention since it offers a means to construct coordinatively unsaturated metal

sites, which is generally considered to be the active sites, and thus has important implications for improving the catalytic performance.¹⁶⁻²³ Therefore, constructing coordinatively unsaturated copper paddle wheel in HKUST-1 may be served to facilitate the catalytic activity. So far, there has been rare report about it.

A critical question remaining to be addressed here is that little is known about the real structure of these active sites. Exploring the dynamic restructuring of electrocatalysts has been of interest for a long time, which is crucial to understand structure-reactivity correlations in many catalysis systems.²⁴⁻²⁹ But it has proved challenging to relate local electronic and geometric structure of these open metal sites to catalytic function. The difficulty arises from the dynamic change of electrocatalyst structure in local coordination under electrochemical reactive environments.^{10,30} The changes in structure and surface composition control catalytic function. Especial challenge is identifying the real active sites of MOFs-based catalysts owing to the complexity of their structure, but it may lead to shift the catalyst design from trial-and-error paradigm to a rational approach.

Herein, we report a defect-engineered metal-organic framework HKUST-1 with coordinatively unsaturated copper paddle wheel, which is named “quasi-MOF (QMOF)”, as pre-catalyst for electrocatalytic CO₂ reduction and reveal its dynamic behaviour during electrochemical reconstruction. Several unique aspects of this work are worth highlighting up in front: (1) defect metal-organic framework HKUST-1 with coordinatively unsaturated copper paddle wheel was synthesized through a facile “atomized trimesic acid” strategy; (2) unsaturated copper paddle wheel clusters [CU-CPWC, Cu₂(HCOO)₃] were identified as real catalytic active site thanks to experimental results using a series of quasi-in situ and in situ characterization methods; (3) a boost in reaction activity for CO₂ reduction was observed owing to the structure with the superior CO₂ activation ability.

Results

Synthesis and structural characterization of QMOF. Previous investigation has indicated that the crystallization of the MOFs undergoes Ostwald ripening process, during which unsaturated metal sites (UMS) may be observed.³¹ With this in mind, retarding the crystal ripening process can generate more UMS in MOFs, so as to obtain more open metal sites for electrocatalytic reaction. The synthetic procedures of catalysts are illustrated in **Figure 1a** and **b**, and the experimental details are summarized in Supplementary Information. Cu(OH)₂ nanowires (NWs) with smooth surface were first grown on Cu foil based on a reported chemical oxidation method.³² Subsequently, Cu(OH)₂ sample was reacted with atomized 1,3,5-benzenetricarboxylic acid (trimesic acid, H₃BTC) solution for 60 s to form uniform quasi-MOF (QMOF) clusters on Cu(OH)₂ NWs surface, as illustrated in **Figure 1a**. The electrochemical reconstruction was undertaken by electrochemically reducing QMOF in 0.1 M KHCO₃ electrolyte at -0.4 V vs reversible hydrogen electrode (RHE) to form CU-CPWC catalyst. For comparison, Cu(OH)₂ sample was reacted with sufficient H₃BTC solution to form complete MOF crystal (CMOF), as illustrated in **Figure 1b**.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirmed the synthesis of a smooth-surface nanowire structure (Supplementary Figure S1 and S2). X-ray diffraction (XRD) patterns verified the presence of a crystalline $\text{Cu}(\text{OH})_2$ phase (**Figure 1c**), which was further evidenced by Raman spectroscopy (**Figure 1d**). Note that no diffraction peaks for HKUST-1 were detected in QMOF (**Figure 1c**), suggesting an amorphous structure may be formed.

In order to investigate the surface structure of samples, we performed Raman and Fourier transform infrared (FT-IR) analysis. The high-frequency region ranging from $700\sim 1200\text{ cm}^{-1}$ is dominated by bands associated with the organic part of HKUST-1 (**Figure 1d**).^{33,35} The band at 1006 cm^{-1} corresponds to C=C symmetric stretching of benzene ring. At 827 and 748 cm^{-1} , the out-of-plane ring (C-H) bending vibrations are recognized in QMOF and CMOF.^{33,35} QMOF exhibits weaker bands in high-frequency region than CMOF, suggesting UMS of QMOF. In the low-frequency region, the doublet at 458 and 505 cm^{-1} is related to Cu-O stretching modes involving oxygen atoms of carboxylate bridges, which is consistent with previous reports, suggesting the metal-organic coordination in the samples.^{7,35} Vibrational properties of the samples were further investigated by FT-IR spectroscopy. As shown in **Figure 1e**, the QMOF and CMOF exhibit the significant peaks ranging from 1100 to 1800 cm^{-1} compared with $\text{Cu}(\text{OH})_2$ NWs.

Characteristic peaks assigned to vibrations of the carboxylate group in HKUST-1 are observed: 1370 and 1419 cm^{-1} corresponding to the symmetric vibrations of $-\text{COO}$ groups and 1450 , 1592 and 1646 cm^{-1} attributed to the asymmetric vibrations of $-\text{COO}$ groups.^{8,34,36} The peak at 1114 cm^{-1} is assigned to C-O vibration in the HKUST-1. In addition, the peaks at 732 and 762 cm^{-1} are observed in CMOF, which can be ascribed to the bonding of Cu with BTC linker molecules (**Figure 1e**).⁷ A weak peak at 1545 cm^{-1} is also found in CMOF, which is due to water coordinated with Cu in the MOF.³⁴ Meanwhile, for the QMOF, two features of the FT-IR spectrum are worth noting. Firstly, notable shifts to lower wavenumber are observed for the peaks of asymmetric vibrations of $-\text{COO}$ groups, suggesting an elongation of the associated bonds. Secondly, the peaks at 1545 cm^{-1} (water coordinated with Cu in the MOF), 1419 cm^{-1} (one of the symmetric vibrations of $-\text{COO}$ groups) and 732 cm^{-1} (one of the Cu with BTC linker molecules) in QMOF are undetectable, which indicates that a defective HKUST-1 structure with UMS or distorted metal nodes may be formed in QMOF.

Notably, SEM and TEM images of QMOF reveal that the uniform nanowire structure with many small clusters on the surface (**Figure 2a-e**). As shown in **Figure 2d and e**, small clusters are clearly observed in the high-resolution TEM (HR-TEM) images. **Figure 2f-j** show the scanning TEM (STEM) and corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping images of QMOF, confirming the existence and uniform distribution of elemental Cu, O and C in the nanowires.

Moreover, the structural evolution of the $\text{Cu}(\text{OH})_2$ NWs in the presence of the atomized H_3BTC was explored. As shown in Supplementary Figure S3, the controllable structural evolution from QMOF clusters to complete MOF crystal (CMOF) is achieved through controlling the reaction time with “atomized H_3BTC ”. In order to prove the superiority of “atomized H_3BTC ” method, common “immersed method” was

performed, that is, $\text{Cu}(\text{OH})_2$ NWs precursor was submersed into liquid H_3BTC solution to synthesize HKUST-1. As a contrast, only CMOF is obtained by the ordinary “immersed method” even in a short time of 10 s (Supplementary Figure S3d). SEM image of CMOF reveals a typical octahedral HKUST-1 morphology (Supplementary Figure S3c), which is consistent with previous reports.³⁷⁻³⁹ High

magnification SEM and TEM images identify $\text{Cu}(\text{OH})_2$ NWs trace in CMOF (Supplementary Figure S4), further revealing the structural evolution from $\text{Cu}(\text{OH})_2$ NWs to CMOF.

The surface hydrophilicity and CO_2 capture capability of the samples were characterized by contact angle and CO_2 -temperature programmed desorption (TPD) measurements (Supplementary Figure S5 and S6). Contact angle measurements illustrated that $\text{Cu}(\text{OH})_2$ surface is the most hydrophilic. The surface clusters of QMOF decrease the hydrophilicity of $\text{Cu}(\text{OH})_2$, but increase the CO_2 capture capability.

Electrochemical reconstruction of QMOF and CMOF. Attention was then paid to the structural changes of QMOF and CMOF during the electrochemical reconstruction process. X-ray photoelectron spectroscopy (XPS) tests under *ex-situ* (Figure 3a-c) and *quasi-in situ* (Figure 3d-e) conditions were first performed to reveal the electronic configuration of each catalyst before and after electrochemical reconstruction.

The *ex-situ* XPS spectra of C 1s for QMOF and CMOF are shown in **Figure 3a**, which can be divided into four peaks, including sp^2 carbon in benzene ring (284 eV), sp^3 carbon (C-C, 284.8 eV), C-O (286 eV) and C=O (289 eV).⁴⁰⁻⁴³ The metal node $[-\text{Cu}_2(\text{COO})_4]$ defect of QMOF is further confirmed by the lower binding energy shift of C-O peak compared with that of CMOF. Note that an additional O 1s peak at 533.2 eV is clearly observed in QMOF, which is related to H_2O molecule (**Figure 3b**).^{44, 45} This result has been confirmed by FT-IR peak at 1545 cm^{-1} , corresponding to water coordinated with Cu in the MOF, as described above. O 1s spectra of QMOF and CMOF both display two peak regions at approximately 530.5 and 531.8 eV, which can be assigned to the Cu-O and -COO groups.⁴³ As expected, the QMOF sample exhibits the lower binding energy of Cu-O and -COO than CMOF for the defect of metal nodes $[-\text{Cu}_2(\text{COO})_4]$ in QMOF. XPS data for the Cu $2\text{p}_{3/2}$ exhibit Cu^{2+} and Cu^{1+} characteristic peak (Supplementary Figure S7).^{41, 46} Previous report suggests the conversion of Cu^{2+} to Cu^{1+} in CMOF is induced by the exposure of MOF to X-ray source and charge neutralizer during XPS data collection.⁴⁶ Note that Cu Auger ($L_3M_{45}M_{45}$) region shows that a reduced oxidation state for the Cu species in QMOF, which may be attributed to the lower coordinatively unsaturated Cu atoms (**Figure 3c**).⁴⁷

Furthermore, the electronic structures and chemical bonding of Cu atoms in their local environment were investigated by X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The QMOF sample exhibits lower-energy edge position as compared with CMOF, indicating a reduced oxidation state for the Cu species (Supplementary Figure S8), which is consistent with XPS auger spectrometry (**Figure 3c**). The dominant coordination peaks in EXAFS can be ascribed to Cu-O (EXAFS, Supplementary Figure S9).

Overall, a comprehensive study of ex-situ XPS, XAS, FT-IR, and Raman provides clear evidence that *quasi* MOF with UMS has been formed in QMOF sample.

Significant changes were observed in the XPS spectra for CU-CPWC and CPW under *quasi-in situ* condition, of which the detail is shown in Experimental Section. C 1s spectra in **Figure 3d** shows that sp^2 carbon in benzene ring (284 eV) is not detected in the samples, indicating the loss of organic coordinating ligands (linkers) during electrochemical reconstruction. But the peaks corresponding to C-O and C=O in the metal nodes $[-Cu_2(COO)_4]$ still show up (**Figure 3d**). Figure 3e displays that the -COO groups peaks (532.0 and 532.2 eV) in CU-CPWC and CPW have shifted towards higher binding energy compared with those in QMOF and CMOF, suggesting that the lost organic coordinating ligands may be replaced by hydrogen during electrochemical reconstruction. The peaks at 536.2 ~ 537.0 eV assigned to CO_2 molecule are also observed (**Figure 3e**), due to the superior CO_2 adsorption capacity.⁴⁴ The presence of Cu^0 and Cu^{1+} characteristic peak indicates a reduced oxidation state for the Cu species (Figure 3f). Based on these findings, it is suggested that $[Cu_2(HCOO)_4]$ cage and defective low-coordinated $[Cu_2(HCOO)_{4-x}]$ ($0 < x < 4$) cage may be formed in CMOF and QMOF respectively after electrochemical reconstruction.

In order to further gain insight into the dynamic electronic structures and chemical state of the Cu active site during CO_2RR , *in situ* XAS were investigated under real operating conditions at -0.4 V vs RHE in aqueous CO_2 -saturated 0.1 M $KHCO_3$. **Figure 4a** presents the schematic of XAFS set-up and recording processes for the *in situ* spectro-electrochemistry experiment. **Figure 4b** shows the Cu K-edge XANES spectra with electron transitions from $1s$ to $4p$ states, including $1s \rightarrow 4p_z$ transition (A), and the $1s \rightarrow 4p_{x,y}$ transition (B, C).^{25,48-51} The higher absorption edge position and the lower $1s \rightarrow 4p_z$ transition intensity indicate a gradually oxidized Cu species.⁵⁰⁻⁵² Furthermore, FT-EXAFS spectra in **Figure 4c** reveal detailed

information regarding the local coordination environment of Cu. The dominant peak at approximately 2.2 Å, which is assigned to the coordination of Cu-Cu, is clearly observed in Cu foil, ER-Cu(OH)₂ and CU-CPWC. Note that the existence of Cu-O coordination peak suggests the oxygen-bearing copper clusters may be formed in CU-CPWC. Meanwhile, the Cu-O coordination (approximately 1.5 Å) is the main peak in CPW (**Figure 4c**). A straight comparison of XAS data before and after electrochemical reconstruction is shown in Supplementary Figure S10, highlighting the changes of coordination environment in the samples.

An additional analysis of Morlet wavelet-transform (WT) was performed to better understand the local structure of Cu atoms. As shown in **Figure 4d**, ER-Cu(OH)₂ exhibits an intensity maximum at approximately 7.2 Å^{-1} , which is very close to that in the reference Cu foil. Note that a slightly higher WT maximum at about 8.1 Å^{-1} is observed in QMOF, indicating the influence of oxygen on the local coordination environment of copper. Furthermore, two intensity maximums at 5.2 and 9.8 Å^{-1} , corresponding to Cu-O and Cu-Cu shells, is visible in CU-CPWC.

To better understand the stepwise structure evolution process of HKUST-1, more in-depth localized observations were performed by *in situ* Raman and *in situ* FT-IR. **Figure 4e** shows *in situ* Raman spectra measured at -0.4 V vs RHE in aqueous CO₂-saturated 0.1 M KHCO₃ and a time resolution of about 30 s. The nethermost spectrum is the first collected data. *In situ* Raman results show that the peak attributed to C-H and C=C peaks disappeared, indicating the loss of organic ligands during electrochemical reconstruction. In pursuit of a molecular-level understanding of electrochemical reconstruction for catalyst, advanced *in situ* ATR FT-IR was employed to dynamically monitor the structure evolution at the fixed potential of -0.4 V (Supplementary Figure S11 and S12). As shown in Supplementary Figure S12, the peak at 1370 cm⁻¹ corresponding to the symmetric vibrations of -COO groups in [Cu₂(HCOO)_{4-x}] cage becomes stronger as the reaction progresses. This further confirms the loss of organic ligands and [Cu₂(HCOO)_{4-x}] cage is exposed during electrochemical reconstruction.

Based on the above results, we can reasonably speculate about the structure of the [Cu₂(HCOO)_{4-x}] cage in CU-CPWC and perform quantitative EXAFS curve-fitting analysis to reveal the quantitative coordination configuration of Cu atoms. A previous investigation has shown that Cu easily forms paddle-wheel dinuclear Cu(ii) carboxylate coordination compounds.⁵³ A good fitting of the experimental FT-EXAFS data is achieved by the simulated EXAFS based on tricoordinated [Cu₂(HCOO)₃] cage model for CU-CPWC (Supplementary Figure S13c). The typical tetracoordinate copper paddle wheel [Cu₂(HCOO)₄] cage model fits well with experimental FT-EXAFS data of CPW (Supplementary Figure S13d).

In order to clarify the details of the adsorption and activation of CO₂ on CU-CPWC, *in situ* XAS data were recorded in aqueous CO₂ and Ar-saturated 0.1 M KHCO₃, respectively. It can be found that the Cu K-edge of CU-CPWC shows the lower 1s → 4p_z transition intensity in CO₂-saturated KHCO₃ solution under -0.4 V compared with that in Ar-saturated KHCO₃ solution (**Figure. 4f**), which suggests an increase in the Cu oxidation state as a result of the charge transfer from Cu to the carbon 2p orbital in CO₂ to form a CO₂^{δ-} species.^{54, 55} The Cu-Cu coordination peak slightly decreases in CO₂-saturated KHCO₃ solution (**Figure. 4g**), which further confirms the increase in the Cu oxidation state compared with that in Ar-saturated KHCO₃ solution.

The SEM image of CPW shows that the octahedral morphology has collapsed into irregular nanoparticles after electrochemical reconstruction (Supplementary Figure S14). These changes indicate the organic links are removed from HKUST-1 frames during reconstruction, resulting in large cleavages and structural collapse. The morphological change is also shown for CU-CPWC, as revealed in Supplementary Figure S15.

On the basis of these results from *quasi-in situ* XPS, *in situ* XAS, *in situ* Raman and *in situ* FTIR, it is concluded that the CU-CPWC sample surface has been modified by oxygen-bearing copper clusters based on coordinatively unsaturated [Cu₂(HCOO)_{4-x}] cage. In order to verify whether the defect oxygen-bearing copper clusters promotes electrochemical CO₂ reduction, we carried out CO₂RR assessments on target catalyst CU-CPWC and the control samples including Cu foil, ER-Cu(OH)₂ and CPW.

Electrochemical activity of catalysts in CO₂ reduction. We evaluated the electrochemical CO₂ reduction activity using a gas-tight H-cell system filled with 0.1 M KHCO₃ solution. Prior to CO₂RR testing at a given potential, all of the samples were subjected to a potential of -0.4 V vs RHE in CO₂-saturated KHCO₃ solution for activation. As indicated by the linear sweep voltammetry (LSV) curves shown in **Figure 5a**, CU-CPWC shows the lower overpotentials at fixed current densities, suggesting the improved activity. The CO₂ reduction product distribution of the four catalysts was investigated under various potentials (Supplementary Figure S16). As shown in **Figure 5b and c**, the CU-CPWC exhibits dramatically increased CH₄ and C₂H₄ Faradaic efficiency among the four catalysts, benefiting from the superior CO₂ capture and activation capability. Significantly, the total Faraday efficiency of CO₂ reduction to CH₄ and C₂H₄ has reached approximately 80.5 % at -0.90 V.

Electrochemical impedance spectroscopy (EIS) tests were performed to investigate the kinetics of electrochemical processes. CU-CPWC exhibits the smaller Nyquist semicircle diameter than the control samples (Supplementary Figure S17), suggesting the fast charge-transfer kinetics in CRR. Cyclic voltammetry (CV) measurements were then performed to determine the double-layer capacitances (C_{dl}) (Supplementary Figure S18 and S19), which is related to electrochemical active surface area (ECSA). Not surprisingly, CU-CPWC exhibits the higher C_{dl} than the control samples, indicating the larger ECSA, which is also an important contributor to the enhanced activity. In addition, LSV tests of the four samples in Ar-saturated and CO₂-saturated KHCO₃ electrolyte were performed as well (Supplementary Figure S20). The higher current density in CO₂-saturated KHCO₃ electrolyte demonstrated that the carbon source for the evolved hydrocarbons comes from CO₂, which provides a direct evidence for the reduction of CO₂.

For clarifying the origin CO₂RR mechanisms of CU-CPWC and CPW, the first principles-based density functional theory (DFT) calculations were performed. The CU-CPWC and CPW models have been built and optimized, the detail of which is shown in Supporting Information. The spin-orbit projected 3d density of states of CU-CPWC and CPW are shown in **Figure 5d**. From this figure, the CU-CPWC presents obvious spin properties with asymmetrical spin distribution around the Fermi level. The d band center of CU-CPWC and CPW is -1.16 and -1.96 eV respectively from the calculations, which indicates that the level change of d band center can be the intrinsic origins of the different CO₂RR performance.⁵⁶ In addition, there are more states around the Fermi level for Cu-CPWC model with CO₂ adsorption (**Figure 5e**) than those of CU-CPW model as shown in **Figure 5f**. It means that the CU-CPWC model has better electron transport behavior than that of CPW model, which can help to accelerate the reaction process. The data shown in Supplementary Figure S21, further support the statement.

CU-CPWC catalyst also exhibits good stability for CH₄ and C₂H₄ generation under continuous CO₂ electroreduction, as shown in Supplementary Figure S22. The Cu K-edge XANES spectra before and after stability testing reveal that the valence state shows negligible change after the constant-potential electrolysis (Supplementary Figure S23a), which is further confirmed by the first-derivative spectra of XANES (Supplementary Figure S23b). In addition, FT-EXAFS spectra show that the distinct Cu-O peak is

still present after stability testing, indicating the structure stability of the CU-CPWC (Supplementary Figure S24).

Conclusions

Our results demonstrate that defect metal–organic framework HKUST-1 with coordinatively unsaturated copper paddle wheel, that is quasi-MOF clusters (QMOF), can be constructed through a facile “atomized trimesic acid” strategy. The restructuring mechanism based on hydrion substituting organic ligand during electrochemical reduction is revealed through a series of *ex-situ*, *quasi-in situ* and *in situ* characterization analysis, which indicates that unsaturated copper paddle wheel clusters $\text{Cu}_2(\text{HCOO})_3$ plays a key role in the catalytic function by facilitating CO_2 activation on the CU-CPWC. It is expected that such facile “atomized” strategy and the coordinatively unsaturated copper paddle wheel clusters reported here are not unique to HKUST-1, but have general implications for other MOFs based catalyst systems.

Methods

Chemicals and materials. Trimesic acid (H_3BTC), acetone, ethanol ($\text{C}_2\text{H}_5\text{OH}$), sodium hydroxide (NaOH , AR), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98%), hydrochloric acid (HCl , AR), potassium bicarbonate (KHCO_3 , 99.7%), Copper foil (99.99%, 0.2 mm thick), carbon dioxide (CO_2 , 99.99%), argon (Ar, 99.999%), and helium (He, 99.99%) were used as received. All chemicals were used directly without further purification. Deionized water was used for the preparation of all aqueous solutions.

Synthesis of $\text{Cu}(\text{OH})_2$ nanowires. In a typical synthesis, a uniform layer of blue $\text{Cu}(\text{OH})_2$ nanowires was firstly prepared by chemical oxidation of Cu foil. Each Cu foil piece was initially washed with hydrochloric acid (36%) for 2 min to remove its native oxide layer, followed immediately by an ultrasonic cleaning in acetone, ethanol, and deionized water for 5 min sequentially. The cleaned Cu foil was immersed into 100 mL of an aqueous solution containing 5.2 g NaOH and 2.282 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 35 min at around 3 °C. Then, the Cu foil was taken out of the solution, thoroughly rinsed with ultra-pure water, and dried with nitrogen. Thus, blue $\text{Cu}(\text{OH})_2$ nanowires were obtained.

Synthesis of quasi-metal–organic frameworks HKUST-1 (QMOF) and complete-metal–organic frameworks HKUST-1 (CMOF) through “atomized method”. The ligand solution (H_3BTC) was prepared by mixing 10 mL of water, 20 mL of ethanol mixture, 0.20 g of H_3BTC at room temperature. Subsequently, 15 mL H_3BTC solution was atomized through a mini atomizer at room temperature (Philips, BSC601/05). Meanwhile, the Cu foil with a layer of $\text{Cu}(\text{OH})_2$ nanowires was reacted with atomized H_3BTC solution for 60 s, obtaining QMOF. To investigate the evolution of the MOFs growth, $\text{Cu}(\text{OH})_2$ nanowires was reacted with atomized H_3BTC solution for 120, 240 and 480 s. When the reaction time was 480 s, CMOF sample was obtained.

Synthesis of complete-metal–organic frameworks HKUST-1 (CMOF) through “immersed method”. For comparison, the Cu foil with a layer of $\text{Cu}(\text{OH})_2$ nanowires was immersed into the mixed H_3BTC solution for different time for the final formation of CMOF.

Material characterizations.

(1) Fourier Transform Infrared Spectroscopy (FT-IR) and *in situ* Raman. FT-IR was carried out on Thermo Scientific Nicolet iN10 FTIR Microscope (Thermo Nicolet Corporation, Madison, WI, USA). *In situ* Raman scattering spectra were recorded on a LabRAM HR JY-Evolution microscope using a 532 nm argon ion laser. A customized in situ cell was employed for collecting in situ Raman data under atmosphere pressure in CO_2 -saturated 0.1 M KHCO_3 aqueous electrolyte. The laser power was set to 50 % and the acquisition time was 30 s.

(2) Temperature programmed reduction (TPR)- CO_2 . The TPR- CO_2 experiment was carried out on a BELCAT II (Microtrac BEL). The sample (0.5 g) was loaded into a quartz tube and swept with argon at 100 °C for 120 min. After being cooled down to 40 °C, the sample was loaded with CO_2 at 50 °C for 180 min. Subsequently, a temperature desorption was programmed at 5 °C/min. The CO_2 signal was detected using a thermal conductivity detector (TCD).

(3) Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were obtained on a JEOL JSM-6700 scanning electron microscope at 6 kV with the software package for automated electron tomography. Samples were prepared for TEM by dropping and drying ethanol dispersions of catalysts onto carbon-coated gold TEM grids at room temperature. TEM images were obtained by using a Titan G2 60-300 with an image corrector.

(4) X-ray photoelectron spectroscopy (XPS). For XPS, samples were thoroughly rinsed with deionized water and immersed into liquid nitrogen immediately after being removed from the electrochemical system. This effectively preserved the valence state and structure of the samples during the sample transfer. The samples were vacuum-dried and stored until the X-ray measurements were performed. XPS data were collected on an ESCALAB250Xi photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al K α X-ray beam (1,486.6 eV). All binding energies were referenced to the C 1s peak (284.6 eV).

(5) X-ray absorption spectroscopy (XAS) data collection and analysis. XAS spectra at the copper K edge were measured in fluorescence mode at the X-ray absorption station (beamline 1W2B) of the Beijing Synchrotron Radiation Facility (BSRF) in China using a double crystal Si (111) monochromator. The storage ring was working at the energy of 2.5 GeV with an average electron current of 150 mA. The incident and output beam intensities were monitored and recorded using ionization chambers filled with pure nitrogen.

An *in situ* home-made cell was employed for collecting *in situ* XAFS data. As-prepared $\text{Cu}(\text{OH})_2$ NWs, QMOF, and CMOF on Cu foil samples (1 × 5 cm) were put into ethanol-filled hermetic containers (8 mL)

separately and ultrasonic stripped for 30 min to obtain suspension containing superficial $\text{Cu}(\text{OH})_2$ NWs, QMOF, and CMOF powder, respectively. For each, 100 μL of catalyst suspension and 25 μL of 5 % Nafion 117 solution were sonicated for 5 min. Each catalyst ink was then uniformly loaded onto a fresh piece of thin carbon paper (2 cm $\times$ 5 cm, thickness of 500 nm) and allowed to dry in vacuum. The $\text{Cu}(\text{OH})_2$ NWs, QMOF, and CMOF powder on the thin carbon paper served as the working electrode, was in contact with a slip of copper tape, and was fixed with epoxy glue to the exterior of the wall of the cell, over the 0.8 cm hole, with the OFC or OBC layer facing inward. A Pt foil (1 cm $\times$ 1 cm $\times$ 0.2 cm) and a Ag/AgCl electrode (KCl sat.) were used as the counter electrode and reference electrode, respectively.

The copper XAFS raw data processing was carried out by using ATHENA (Demeter 0.9.25, an interface to IFEFFIT) and ARTEMIS (Demeter 0.9.25) by the standard procedures. The k^3 -weighted $\chi(k)$ data in the k -space ranging from 2.0 to 12 $\text{\AA}^{-1}$ were Fourier-transformed to real (R) space using a Hann window ($dk = 1.0 \text{ \AA}^{-1}$) to separate the EXAFS contributions from different coordination shells. To obtain the detailed structural parameters around the Cu atom in the as-prepared samples, quantitative curve fittings were carried out for the Fourier-transformed $k^3\chi(k)$ in R-space using the ARTEMIS module of IFEFFIT. During curve fittings, the Debye–Waller factor (σ^2) and bond length (R) were treated as adjustable parameters. No R factors yielded are larger than 0.01, indicating the good fitting quality. The Morlet wavelet was chosen as the mother wavelet for the basic functions and the parameters ($\sigma = 2$, $\eta = 5$) were used to achieve better resolution in the wave vector k .

(6) *In situ* IR Measurements. For *in situ* IR measurements, as-prepared QMOF sample was put into ethanol-filled hermetic containers (8 mL) separately and ultrasonic stripped for 30 min to obtain suspension containing superficial powder. 100 μL of catalyst suspension and 25 μL of 5 % Nafion 117 solution were sonicated for 5 min. Then 100 μL of QMOF ink solution was casted onto the Au film coated Si prism. A homemade spectro-electrochemical cell (Figure S4) with three-electrode system was employed for collecting *in situ* IR data. The QMOF powder on the Si prism served as the working electrode. A coiled Pt wire served as counter electrode and a Ag/AgCl electrode (KCl sat.) served as reference electrode. *In situ* IR measurements were performed on a Thermo Scientific Nicolet iS50 FT-IR spectrometer with attenuated total reflection (ATR) configuration using a liquid nitrogen cooled MCT-A detector. All spectra were collected at a resolution of 4 cm^{-1} at a bottom-up incidence angle of ca. 67°. The FT-IR spectrometer was purified with high-purity argon for one hour. Before the test, the electrolyte was purified with high-purity CO_2 for 30 min. Time-resolved IR measurements at a fixed potential of -0.4 V (vs RHE) were carried out with a time resolution of ~ 2 s. A CHI 660E electrochemistry workstation (CH Instruments, Inc.) was used for potential control.

Electrochemical measurements. Electrochemical measurements were performed at ambient temperature and pressure in a customized gastight H-type glass cell separated by a Nafion 117 membrane (Fuel Cell Store). A CHI 660e potentiostat was employed to record the electrochemical response. A typical three-electrode cell configuration was employed with a piece of platinum foil (1 cm $\times$ 1 cm $\times$ 0.2 cm) and a Ag/AgCl electrode (KCl sat.) serving as the counter electrode and reference electrode, respectively. The

area of the working electrode was fixed at 1 cm^2 ($0.5\text{ cm} \times 1\text{ cm} \times 2$). All potentials measured were calibrated to the RHE scale as follows: $V_{\text{RHE}} = V_{\text{Ag/AgCl(KCl sat.)}} + 0.197\text{ V} + 0.059\text{ V} \times \text{pH}$. Ultrahigh purity CO_2 (99.99%) was purged into the 0.1 M KHCO_3 solution for at least 30 minutes to make a CO_2 -saturated 0.1 M KHCO_3 aqueous solution ($\text{pH} = 6.8$). In a typical experiment, 145 mL of CO_2 -saturated 0.1 M KHCO_3 aqueous solution was magnetically stirred in the cathodic compartment with a headspace of 50 mL . The electrode was held at a constant bias using chronoamperometry for 5 C of charge, after which a $500\text{ }\mu\text{L}$ gas sample was taken by a syringe (Hamilton) from the headspace. The gas was injected into a gas chromatograph instrument (GC-2014, Serial No. C11484403556 SA, Shimadzu, Japan) equipped with a flame ionization detector (FID) for detection of organic compounds and a gas chromatograph instrument (Serial No. C11485013433 SA, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) for detection of inorganic gases. Ultrahigh purity N_2 (99.99%) was used as the carrier gas. The concentration of product gases was determined using calibration curves from standard gases (Newradar special gas). Linear sweep voltammetry (LSV) was conducted with a scan rate of 5 mV/s . For comparison, LSV measurements were performed in an Ar (99.99%)-saturated 0.1 M KHCO_3 aqueous solution. All current densities were normalized to the geometrical area of the electrode.

The Faradaic efficiency can be calculated as follows: **see formula 1 in the supplementary files.**

where n_i is the number of electrons required to produce an i molecule, which is 2, 2, 8, and 12 for CO , H_2 , CH_4 , and C_2H_4 , respectively; F is the Faradaic constant ($96,485.33289\text{ C mol}^{-1}$); P_0 is the atmospheric pressure ($1.013 \times 10^5\text{ Pa}$); T_0 is the reaction temperature (298 K); R is the ideal gas constant ($8.314\text{ J mol}^{-1}\text{ K}^{-1}$); V_0 is the total headspace volume (typically 50 mL); V_i (vol %) is the measured volume concentration of product i from the electrochemical cell at a given passing charge (typically 5 coulombs); Q_{total} is the total amount of charge Q (in units of coulombs) passed through the sample (5 coulombs); and Q_i is the amount of charge Q to produce species i from CO_2 .

DFT calculations. By using the Cambridge Serial Total Energy Package (CASTEP) in Materials Studio, all density functional theory (DFT) calculations were performed with the plane-wave pseudopotential method to apply first-principles-based quantum mechanics simulations. In this work, the spin generalized gradient approximation (SGGA) within Perdew-Burke-Ernzerhof (PBE) form was setup as an exchange-correlation function. A $3 \times 3 \times 1$ Monkhorst-Pack k-points grid was used for k-points sampling, and 900 eV plane-wave expansion was setup for energy cut-offs. These parameters were carefully tested. The $\text{Cu-}3\text{d}^{10}4\text{s}^1$, $\text{O-}2\text{s}^22\text{p}^4$, $\text{C-}2\text{s}^22\text{p}^2$, and $\text{H-}1\text{s}^1$ were setup for valence states. A vacuum slab of about $15\text{ \AA}$ was maintained in the super-cell configuration that was large enough for the calculations. The SCF tolerance for geometrical optimization and phonon calculations was less than $1\text{e-}6\text{ eV}\cdot\text{atom}^{-1}$.

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Declarations

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Author contributions

Y.Y., L.M. and Z.Y. supervised the project. W.Z. designed and synthesized the nanomaterials and performed most of the experiments. W.Z., C.H. and R.Y. performed electron microscopy tests. W.Z. and J.Z. performed FT-IR and Raman tests. W.Z., J.Z. and P.A. performed the XAFS measurements. Y.W, Q.Z. and M.Q. conducted and discussed the theoretical calculations. W.Z. wrote the initial draft of the manuscript. All authors discussed the results and edited the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

Electrocatalyst design and structural characterizations. a, b Schematic illustration of the synthetic procedures for CU-CPWC and CPW electrocatalyst. c XRD patterns of pristine Cu foil, Cu(OH)₂, QMOF and

CMOF. d Raman spectra of pristine Cu(OH)₂, QMOF and CMOF. e FTIR spectra of pristine Cu(OH)₂, QMOF and CMOF.

Figure 2

SEM and TEM characterizations of QMOF. a,b SEM images of QMOF. c-e HRTEM images of QMOF. f, HAADF-TEM image of QMOF. g-i The corresponding elemental mapping.

Figure 3

Structural characterizations of samples by XPS spectroscopy. a-c Ex-situ XPS spectra of pristine QMOF and CMOF samples in C 1s, O 1s and Cu Auger region. d-f Quasi-in situ XPS spectra of CU-CPWC and CPW samples in C 1s, O 1s and Cu Auger region.

Figure 4

Structural characterizations of samples by in situ XAS and in situ Raman. a Schematic illustration of the in situ XAS experiment. b Normalized Cu K-edge XANES spectra of four samples under -0.4 V in CO₂-saturated 0.1 M KHCO₃ aqueous solution. c Corresponding k₃-weighted FT-EXAFS spectra. d Morlet WT of the k₃-weighted EXAFS data for the four samples with parameters of $\sigma = 2$ and $\eta = 5$. e In situ Raman spectra of QMOF under -0.4 V in CO₂-saturated 0.1 M KHCO₃ aqueous solution. f Normalized Cu K-edge XANES spectra of QMOF under -0.4 V in CO₂-saturated and Ar-saturated 0.1 M KHCO₃ aqueous solution. g Corresponding k₃-weighted FT-EXAFS spectra.

Figure 5

Evaluation of catalytic activity by electrochemical measurements and DFT simulations. a LSV curves of Cu foil, ER-Cu(OH)₂, CU-CPWC and CPW. b,c Faradaic efficiencies for CH₄ and C₂H₄ respectively at selected potentials on the four samples. d Spin-orbit projected 3d density of states of CU-CPWC and CPW. e Spin-orbit projected density of states of CU-CPWC with CO₂ adsorption. f Spin-orbit projected density of states of CPW with CO₂ adsorption.

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