Organic frameworks confined Cu single atoms and nanoclusters for tandem electrocatalytic CO2 reduction to methane

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Abstract
The electrochemical reduction reaction of carbon dioxide (CO2RR) is considered to be an effective way to realize carbon neutrality. As a type of intensively studied materials, covalent organic frameworks (COFs) with a tunable pore structure and various functional groups are promising catalysts for CO2RR. Herein, COF synthesized by 2,6-diaminoanthraquinone and 2,4,6-triformylphloroglucinol is employed to assist the synthesis of electrocatalysts from Cu single atoms (SAs) to nanoclusters by controlling the electrodeposition. A tandem catalyst for CO2-to-CH4 conversion is thus achieved by the Cu nanoclusters dispersed among the isolated Cu SAs in the COF network. It is proposed that CO2 is first reduced to CO over the atomically isolated Cu SAs, followed by diffusion onto the neighboring Cu nanoclusters for further reduction into CH4. In addition, mechanistic analysis suggests that the coordinated K+ ions on the COF network promote the activation of CO2 and the adsorption of reaction intermediates, thus realizing the suppressed hydrogen evolution reaction and selective production of CH4. This study presents a new insight of COFs for the confined synthesis of a tunable SA to nanocluster electrocatalysts, disclosing the great potential of COFs in electrocatalysis.

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1 | INTRODUCTION

With increasing global energy demand and continuous consumption of fossil fuels, the CO₂ concentration in the air has reached 418 ppm in 2022 and continues to rise according to the National Aeronautics and Space Administration (https://climate.nasa.gov/vital-signs/carbon-dioxide/. Accessed February 11, 2022). CO₂ is a heat-trapping gas, causing global warming and climate change. Therefore, carbon neutrality achieving net-zero CO₂ emissions has been enshrined into law as a 2050 long-term strategy and agreed by all parties to the Paris Agreement, which drives the post carbon economy. Carbon credits emerge as a component of national and international attempts to offset the CO₂ emissions. Among efforts toward carbon neutrality, the electrochemical reduction reaction of CO₂ (CO₂RR) into value-added chemicals by using clean energy and water is a promising route to simultaneously enable a closed carbon energy cycle and curtail dependency on fossil fuels.

To date, Cu is found to be the only metal electrocatalyst to produce hydrocarbons and oxygenates beyond CO, with no less than 16 kinds of products. Different types of Cu aggregates, from single atoms (SAs) to nanoclusters (NCs) to nanoparticles, catalyze CO₂RR to generate different carbon products. However, the synthesis of finely tunable aggregation of Cu atoms is still challenging. For instance, the pyrolysis method usually needs complex and energy-intensive procedures. In addition, the dispersed metal atoms are inclined to aggregate into larger clusters or particles during the synthesis. Thus, exploring a facile, controllable, and low-cost method to tune the aggregates of Cu atoms is of high significance.

Recently, the cofacial packed two-dimensional (2D) covalent organic frameworks (COFs) have attracted considerable attention in the electrochemical energy storage and conversion system, due to the efficient electron transfer by the conjugated molecular building blocks linked via the in-plane covalent bonds and interlayer π–π interactions. The rich porosity in the COF network can be utilized to confine the growth of Cu aggregates, the dimension of which can be tuned by selecting COFs with tunable nanoscale pore sizes. In addition, the pores of the COF network with N-containing functional groups have been proven to be beneficial for CO₂ capture and fixation, which may promote the CO₂RR. Furthermore, the functional groups of the COFs can not only serve as possible anchor sites for Cu atoms, but also act as stabilization sites for CO₂RR intermediates. Thus, incorporating Cu aggregates into COFs with tunable pore size and functional groups can be a feasible approach to form different Cu aggregates to produce designated products for CO₂RR.

Since the electrochemical conversion of CO₂ into various carbon products usually requires multiple proton-coupled electron transfer steps through different pathways depending on the kinetics of the electron transfer process, the dissociated protons and key intermediates are essential to determine the final products. As one of the highly reduced carbon products, CH₄ is the main component of conventional fuels with the cleanest burning emission in modern energetics. Nevertheless, the production of CH₄ involves an eight-electron reduction process together with proton transfers. The activation of H₂O, the proton source for producing hydrocarbons in CO₂RR, plays a significant role. Due to the lack of dissociated protons in neutral and basic electrolytes, such a protonation process usually entails sluggish reaction kinetics of CO₂RR. Meanwhile, a strong hydrogen evolution reaction (HER) occurs as an unavoidable competitive reaction. Due to the substantial excess of H₂O and much lower overpotential, the reduction to hydrogen by-product is usually more facile to happen. Thus, improving the selectivity of CH₄ through the activation of H₂O while suppressing the HER is exceptionally challenging in the production of CH₄.

Herein, we have rationally developed a tandem electrocatalyst consisting of Cu SAs and NCs to produce CH₄. A redox-active robust COF (DAAQ-TFP, synthesized by 2,6-diaminoanthraquinone [DAAQ] and 2,4,6-triformylphloroglucinol [TFP]), is used as the network for anchoring and confining different types of Cu aggregates by a simple electrodeposition method. The aggregation of Cu dispersed in the COF network can be tuned from SAs to NCs by controlling the electrodeposition duration time. The carbonyl groups (C=O) of DAAQ-TFP become potassium-ion coordinated groups (C–O–K) under the reduction potential, which is found to benefit the activation of CO₂ and the H₂O dissociation. By activating CO₂ and stabilizing the key protonated intermediates by the COF network, Cu-integrated COFs are tuned to facilitate the production of CH₄ while suppressing the HER.
2 | EXPERIMENTAL DETAILS

2.1 | Synthesis of COF

The COF was synthesized according to a modified method in the previous report. In a typical synthesis, 17.62 mg of DAAQ was dissolved in 9.6 ml N,N-dimethylformamide (DMF). A precleaned glassy carbon electrode with a diameter of 10 mm was submerged in the solution, followed by heating to 90°C. 10.39 mg of TFP in 3 ml DMF was added dropwise into the above solution. Subsequently, the reaction continued to proceed at 90°C for 3 h. Finally, the electrode covered with the DAAQ-TPF COF film was rinsed with DMF and acetone, followed by drying in air.

2.2 | Electrodeposition of Cu

The COF film-covered or bare glassy carbon electrode was soaked in Ar-saturated 0.1 mol/L CuSO4/0.5 mol/L H2SO4 solution. A potential versus 0.12 VAg/AgCl was applied to the electrode for 100 and 500 s to deposit Cu on the COF film-covered electrode to obtain SA Cu/COF and NC-SA Cu/COF, respectively. A bare glassy carbon electrode was also undergoing Cu deposition for 500 s to obtain a Cu thin film for comparison.

2.3 | Electrochemical measurements and product analyses

A gas-tight H-type cell was used for the CO2RR measurements, with a Nafion 117 membrane (Sigma-Aldrich) as the separator, an Ag/AgCl electrode (Gaossunion) as the reference electrode and a 2 cm × 2 cm Pt mesh as the counter electrode. Cathodic compartment was filled with 40 ml of 0.5 mol/L KHCO3 electrolyte (pH 6.8), and the anodic compartment was filled with 40 ml of 0.5 mol/L KHCO3 electrolyte. A flow rate of 30 sccm CO2 (99.999%; Asia Pacific Gas Enterprise Co., Ltd.) was purged into the KHCO3 electrolyte for 1 h before the experiments and continued during the entire measurement. The electrolyte was magnetically stirred at a rate of 800–1000 r/min to release the bubbles generated on the surface of the working electrode. Eighty percent of IR compensation was automatically conducted by the electrochemical workstation, with the remaining 20% manually compensated.

The potentials were converted to the RHE reference scale according to the equation of $E$(vs. RHE) = $E$(vs. Ag/AgCl) + $E_{Ag/AgCl} + 0.0591 \times (6.8 - 1.1)$, where $E_{Ag/AgCl}$ is the potential of the Ag/AgCl reference electrode measured in 0.1 mol/L HClO4 solution (pH 1.1) against RHE. The gas products were analyzed by an online gas chromatography (GC2060; Ramiin). Sampling was conducted at the 15th, 28th, 41st, and 54th min, sequentially. The current density was calculated according to the total charges collected in the 30 s before each sampling. Three independent measurements were carried out to assure the accuracy of CO2RR measurements for each catalyst, from which the standard errors were derived.

2.4 | Physical characterization

Scanning electron microscopy images were collected by a JEOL-6700F microscope. Transmission electron microscopy images were taken on a JEOL-2010F microscope. Aberration-corrected scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) were recorded on an FEI Themis G2 60-300 microscope with double spherical aberration-correctors. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra DLD multitechnique surface analysis system. X-ray diffraction (XRD) pattern was obtained on an X’pert Pro (PANalytical) diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

2.5 | In situ attenuated total reflection-Fourier transform infrared spectroscopy measurements

In situ ATR-FTIR measurements were conducted according to our previous report. Real-time ATR-FTIR spectra were collected during a linear sweep of the catalyst-loaded Au/Si prism working electrode from 0.6 to $-1.4 \text{V}_{RHE}$ at a scanning rate of 5 mV/s in a CO2-saturated 0.1 mol/L KHCO3 electrolyte. The first spectrum was used as the IR background.

2.6 | Computational details

Spin-polarized density functional theory (DFT) calculations were conducted using Vienna Ab initio Simulation Package, according to the generalized gradient approximation of the Perdew–Burke–Ernzerhof functional. The interactions between core and valence electrons were described by using the projector-augmented wave method, the plane wave energy cutoff of which was 500 eV. The total energy tolerance was $10^{-4}$ eV. The force tolerance was 0.05 eV/Å. The electronic occupancies were calculated by Gaussian smearing, the smearing width of which was 0.10 eV. The zero-damping DFT-D3 method of Grimme was employed to calculate van der Waals corrections.
1 × 1 × 1 Monkhorst–Pack k-point sampling was used for structural optimization.

On the basis of the XRD pattern of the COF (Figure S3), the peak at ∼26° may be due to the reflection of (001) plane caused by the π–π stacking between layers of the COF.31 Thus, in this study, the structure of COF was modeled with an interlayer spacing of 3.45 Å. The optimized unit cell and the 2 × 2 supercells of COF were illustrated in Figure S10A,B. It was found that the single Cu atom of SA Cu/COF was stabilized by two layers of COF by binding to two O atoms on neighboring layers, as shown in Figure S2. Thus, the optimized two-layer COF configuration was used as the substrate for deposition of the single Cu atoms and the Cu NCs. In addition, K+ ions were included to simulate the model under experimental conditions, as illustrated in Figure S7. A vacuum layer of 15 Å was added above the two-layer COF to prohibit periodic interactions of the model.

According to the computational hydrogen electrode model, the Gibbs free energy change (ΔG) was calculated using32:

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S, \quad (1)
\]

where \( E \) is the total energy resulting from DFT calculations; \( ZPE \) is the zero-point energy calculated from vibrational frequencies; \( T \) is the temperature at 298 K; and \( S \) is the entropy, which can be obtained from standard thermodynamics tables for gaseous species33 or from vibrational frequencies for adsorbed species.

**FIGURE 1** (A) Schematic synthesis of SA Cu/COF and NC-SA Cu/COF, (B) SEM image, (C) HAADF-scanning transmission electron microscopy (STEM) image, (D) enlarged HAADF-STEM image, (E) aberration-corrected-STEM image, and (F) EDX elemental mappings of NC-SA Cu/COF. COF, covalent organic framework; EDX, energy-dispersive X-ray spectroscopy; HAADF, high-angle annular dark-field; NC, nanocluster; SA, single atom; SEM, scanning electron microscopy.
3 | RESULTS AND DISCUSSION

The schematic controllable synthesis of the COF confined Cu aggregates is shown in Figure 1A. The 2D-COF grew on the glassy carbon electrode by in situ polymerization, which is supposed to have good conductivity. Cu was deposited onto the electrode to form atomically distributed Cu aggregates from SAs to NCs by controlling the electrodeposition time. At an electrochemical reduction potential of $0.12 \text{ V}_{\text{Ag}/\text{AgCl}}$ for 100 s, SA Cu was formed in the COF network (denoted as SA Cu/COF, Figure S1A), which may prefer to be anchored by two O atoms on neighboring layers according to the DFT calculation due to the lowest energy (Figure S2A). When the electrodeposition time was extended to 500 s, Cu NCs were formed through the aggregation of more Cu atoms (denoted as NC-SA Cu/COF). The NC-SA Cu/COF presents a 3D interconnected network as shown in Figure 1B, which inherited the original morphology of the pure COF (Figure S1B). The high-angle annular dark-field-STEM image of NC-SA Cu/COF (Figure 1C) further shows an intrinsic microporous structure in the interconnected COF network. Such accessible micropores are favorable to expose active sites and promote mass transport during electrocatalysis. As shown in Figure 1D,E, the electrodeposited Cu NCs (marked with blue circles) were distributed around SAs (marked with red circles) in a diameter of 1–2 nm, which matched the pore size (1.9–2.3 nm) of the DAAQ-TFP COF. Nevertheless, the electrodeposition of Cu without a COF network resulted in Cu particles in micrometer size (Figure S1C), indicating that the micro-/mesopores of COFs effectively confined the growth of Cu clusters. In addition, all samples displayed a broad peak at $2\theta$ of $\sim26^\circ$ belonging to the (001) plane of the stacked COFs (Figure S3). The peak assigned to (001) plane of both XRD patterns of SA Cu/COF and NC-SA Cu/COF shifted to lower degrees. The slightly expanded layer spacing of the COFs in SA Cu/COF and NC-SA Cu/COF may result from the anchoring of Cu atoms between neighboring COF layers. SA Cu/COF exhibited a broad peak at $2\theta$ of 43.4°, which may be caused by the anchored Cu SAs. Similar to the previously published result, NC-SA Cu/COF showed a slightly sharp peak resulting from the Cu NCs. The uniform atomic distribution of Cu in the COF network in the NC-SA Cu/COF sample was also confirmed by the EDX elemental mappings, as evidenced by Figure 1F.

**Figure 2** Gas product distribution of (A) NC-SA Cu/COF, (B) SA Cu/COF, and (C) pure COF under different potentials; (D) comparison of CO$_2$ reduction current densities among NC-SA Cu/COF, SA Cu/COF, and pure COF; (E) comparison of CH$_4$ partial current densities between NC-SA Cu/COF and bare Cu; and (F) stability test of NC-SA Cu/COF at a potential of $-1.30 \text{ V}_{\text{RHE}}$. COF, covalent organic framework; NC, nanocluster; SA, single atom.
Figure 2A–C exhibits the faradaic efficiencies (FEs) of gas products for NC-SA Cu/COF, SA Cu/COF, and pure COF at different potentials. The NC-SA Cu/COF achieved the lowest FE$_{\text{H}_2}$ among all samples throughout all potentials and the highest FE$_{\text{CH}_4}$ of (56.2% ± 5%) at −1.26 V relative to the reversible hydrogen electrode (V$_{\text{RHE}}$) after ohmic loss correction (Figure 2A). In comparison, the SA Cu-COF without Cu NCs catalyzed half-half CO generation and H$_2$ evolution (Figure 2B), providing the possibilities for sufficient key intermediates and proton sources in the CH$_4$ pathway. In addition, the pure COF displayed a major H$_2$ production with FEs close to 80% (Figure 2C) and negligible CO$_2$ reduction current densities (Figure 2D), suggesting that the catalytic active sites of NC-SA Cu/COF and SA Cu/COF are Cu atoms rather than the COF framework. After 1 h catalysis, the morphology of the COF still remained the same (Figure S4), and there were no other products detected in the electrolyte after reaction (Figure S5). This indicated that the COF framework was stable and robust under the reduction condition.

Interestingly, NC-SA Cu/COF and SA Cu/COF showed a big difference in the product distribution, whereas they shared similar CO$_2$ reduction current densities as shown in Figure 2D. It indicated that the Cu NCs of NC-SA Cu/COF played an important role in the reduction of CO$_2$, which changed the CO$_2$RR pathway toward CH$_4$. The significant enhancement of deep reduction products may be enabled by the tandem catalysis of the SA Cu/COF and Cu NCs, that is, the CO generated on SA Cu/COF was quickly transferred to the nearby Cu NCs for subsequent reduction to CH$_4$, as similarly reported recently.$^{16,35}$

Compared with the bare Cu (Figure S6), the NC-SA Cu/COF achieved much higher FE$_{\text{CH}_4}$ with suppressed HER (Figure 2E). The results manifested that the COF framework of NC-SA Cu/COF promoted the CO$_2$RR toward CH$_4$. In addition, the steady current density and a stable FE$_{\text{CH}_4}$ over 10 h continuous operation suggested good stability for the NC-SA Cu/COF (Figure 2F). The enhanced CO$_2$ activity and improved selectivity of CH$_4$ on NC-SA Cu/COF may be due to the higher local concentration of CO generated on SA Cu/COF and the facilitated process of protonated intermediates toward CH$_4$ production.

It is well known that redox-active carbonyl groups (C=O) can be used for the reversible storage of metal ions in metal-ion batteries due to their coordination with...
metal ions (C–O–M). The cyclic voltammetry curves of COF exhibited broad redox peaks between −0.6 and 0.6 V<sub>RHE</sub> as shown in Figure 3A, which may be attributed to the reversible coordination between the carbonyl groups of COF and K⁺ ions. The in situ ATR-FTIR spectra (Figure 3B) scanned from 0.6 V<sub>RHE</sub> to −1.4 V<sub>RHE</sub> displayed a gradual increase at the peak of 1160 cm<sup>−1</sup>, which can be assigned to the formation of C–O–K bonds. This was also supported by the C1s and O1s spectra of the COF before and after the reduction reaction. As shown in Figure 3C, the split C1s spectrum of the COF at −1.4 V<sub>RHE</sub> showed the decreased peak density of C=O (286.9 eV) and the occurrence of another peak belonging to C–O bonds (286.1 eV). At the same time, a new peak centered at 532.5 eV appeared in the O1s spectrum at −1.4 V<sub>RHE</sub>, further confirming the opening of C=O bonds and the formation of C–O bonds. The formed C–O bonds were coordinated with K⁺ ions, as previously reported. The coordinated K⁺ ions led to the increase of the HCO⁻<sub>3</sub>⁻ counterions, pushing the equilibrium balance to generate more CO<sub>2</sub> and thus the increased local CO<sub>2</sub> concentration around the Cu active sites. Meanwhile, the coordinated K⁺ ions may also benefit the CO<sub>2</sub> activation and stabilization of reaction intermediates, thus promoting the subsequent CO<sub>2</sub> conversion.

Furthermore, DFT simulations were performed to investigate the CO<sub>2</sub>RR performance of NC-SA Cu/COF. Using the optimized two-layer K⁺-coordinated COF configuration (Figure S7) as the substrate, a single...
Cu atom and a Cu\textsubscript{50} cluster with a diameter of \textasciitilde{}1 nm were deposited into the pores of COF, as demonstrated in Figure 4A. When Cu NC was present, it preoccupied the previous anchoring site of single-atom Cu, driving the SA Cu to another site (Figure S8). The system energy was dependent upon the anchoring site for SA Cu, which was found to be the lowest when the single-atom Cu was anchored by an O atom and a C atom on neighboring COF layers. Figure 4B shows that \*CO\textsubscript{2} was adsorbed most strongly on the single Cu atom by binding via the C atom, whose O atoms were stabilized by the K\textsuperscript{+} ions (Figure S9). As \*CO\textsubscript{2} was reduced to \*COOH, the intermediate moved closer to the Cu cluster, which further stabilized \*COOH by binding to one of its O atoms. After the reduction of \*COOH, \*CO was found to adsorb most strongly on the Cu cluster, with the C atom binding to the Cu cluster and the O atom binding to the K\textsuperscript{+} ion. Thus, the active site changed from the single Cu atom to the Cu cluster, confirming the tandem catalysis of NC-SA Cu/COF for CO\textsubscript{2}RR. In addition, the coordinated K\textsuperscript{+} ions can promote the adsorption and activation of reaction intermediates by stabilizing the more electronegative O atoms in the adsorbed species. Figure 4C shows the Gibbs free energy diagram of CO\textsubscript{2}RR on NC-SA Cu/COF, where all electrochemical reduction steps were exothermic except the reduction of *CO to *CHO. The adsorption free energy of \*CO\textsubscript{2} was \textasciitilde{}0.38 eV, indicating that the adsorption of CO\textsubscript{2} was spontaneous on NC-SA Cu/COF. The potential-determining step, that is, the electrochemical step with the maximum \(\Delta G\) was the reduction of *CO to *CHO, whose \(\Delta G\) was 0.44 eV. It is worth noting that the \(\Delta G\) for the desorption of *CO was higher than that for the reduction of *CO, making it less favorable to release CO and thus favoring the pathway toward CH\textsubscript{4} production. As illustrated in Figure 4D, The adsorption of H\textsubscript{2}O was also assisted by the presence of K\textsuperscript{+} ions, which stabilized *H\textsubscript{2}O via its O atoms. The dissociation of *H\textsubscript{2}O to *H and *OH was found to be thermodynamically favorable, which had a \(\Delta G\) of \textasciitilde{}0.05 eV. The resulting *OH was adsorbed on the single Cu atom and stabilized by the nearby K\textsuperscript{+} ions, while the resulting *H was adsorbed on the Cu cluster, serving as a proton source for CO\textsubscript{2}RR.

4 Conclusion

In conclusion, we have proposed a strategy of employing redox-active COFs to prepare Cu SAs and NCs for CO\textsubscript{2}RR. The potassium-coordinated DAAQ-TFP COF under the reduction condition can promote the CO\textsubscript{2} activation and H\textsubscript{2}O dissociation, enhancing the CO\textsubscript{2}RR toward CH\textsubscript{4} production while suppressing the HER. The selective CH\textsubscript{4} production was realized through the tandem catalysis on Cu NCs and SAs immobilized on the DAAQ-TFP COF. The CO was generated on SA Cu/COF and then transferred quickly to the nearby Cu NCs for the subsequent reduction to CH\textsubscript{4}. This study can not only expand the application of redox-active COFs, but also offer a platform for the confined synthesis of different Cu aggregates from SAs to NCs. Furthermore, the diversity of redox-active COFs provides great space for development and paves the way for novel catalysts for CO\textsubscript{2}RR into other value-added chemicals.

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Conflicts of Interest

The authors declare no conflicts of interest.

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**SUPPORTING INFORMATION**

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