Supporting Information

for

Electrochemical CO₂ Reduction Reaction over Cu Nanoparticles with Tunable Activity and Selectivity Mediated by Functional Groups in Polymeric Binder

Qiaowan Chang,¹,+ Ji Hoon Lee,¹,2,+ Yumeng Liu,¹,+ Zhenhua Xie,³ Sooyeon Hwang,⁴ Nebojsa S. Marinkovic,¹ Ah-Hyung Alissa Park,¹,5,6* Shyam Kattel,⁷,* and Jingguang G. Chen¹,3,6*

¹ Department of Chemical Engineering, Columbia University, New York, NY 10027, USA
² School of Materials Science and Engineering, Kyungpook National University, Daegu 41566, Republic of Korea
³ Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA
⁴ Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA
⁵ Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA
⁶ Lenfest Center for Sustainable Energy, The Earth Institute, Columbia University, New York, NY 10027, USA
⁷ Department of Physics, Florida A&M University, Tallahassee, FL 32307, USA

*Corresponding authors: ap2622@columbia.edu, shyam.kattel@famu.edu, jgchen@columbia.edu

+These authors contributed equally to this work.
A. Supporting Methods

Chemicals

Potassium carbonate (K$_2$CO$_3$), potassium hydroxide (KOH), Nafion solution (10 wt%), powder binders (polyacrylic acid (PAA), polyvinylidene difluoride (PVDF), N-methyl-2-pyrrolidone (NMP), Nafion 117 membrane, and isopropanol were purchased from Sigma Aldrich. Carbon paper (10 wt% water proofed) was purchased from Fuel Cell Store. Commercial 20wt% copper nanoparticles (Cu NPs) on carbon (Cu/C, particle size=50 nm) was purchased from E-TEK. All reagents were used without purification.

Electrolyte and electrode preparations

All the chemicals in this work were purchased from Sigma Aldrich unless otherwise noticed. All reagents were used without purification. 0.1M potassium bicarbonate (KHCO$_3$) in deionized (DI) water was prepared by bubbling CO$_2$ gas for 12 h into 0.05 M K$_2$CO$_3$ in DI water. The pH values of these solutions were ~6.8 after the full saturation of CO$_2$.

The commercial carbon-supported copper catalyst (Cu/C, 20 wt%, 50 nm, E-TEK) was dispersed in the mixture of deionized water and isopropanol solution (v:v=1:1) containing 0.5 wt% binder (Nafion, PAA, and PVDF) with a concentration of 2 mg mL$^{-1}$. After sonication for 20 min, 50 µl of homogeneous freshly made catalyst ink was dropped on the Toray carbon paper (0.25 cm$^2$). It should be noticed that NMP was chosen as the solvent in using PVDF because PVDF is well-known to be dissolved in NMP. Each Cu/C electrode with different binders was referred to as Cu-X with X being the binder (i.e., Cu-Nafion, Cu-PAA, and Cu-PVDF).
Electrochemical measurement and product analysis

Saturated calomel electrode (SCE) and graphite rod were used as reference and counter electrodes, respectively. The CO$_2$-saturated 0.1M KHCO$_3$ was utilized as an electrolyte. The reference electrode was calibrated before each electrolysis experiment by using a reversible hydrogen electrode (HydroFlex, ET-070, EDAQ).

A typical air-tight two-compartment cell was filled with CO$_2$-saturated solution. In each compartment, 17 mL of the electrolyte was filled, leaving 12 mL of empty head space. A Nafion 117 membrane was used to separate catholyte and anolyte. The working electrode was placed together with reference electrode in the air-tight cathodic compartment. The counter electrode was located in the anodic compartment.

The electrochemical measurements were carried out using a Biologic potentiostat (SP-300). The applied potential (V) was controlled by iR-compensation (80%) and converted to the reversible hydrogen electrode by using the following Equation (1):

$$V = V_{SCE} + 0.248 + 0.059 \times \text{pH} \quad (1)$$

Thus, all of the potentials in this study are written based on the reversible hydrogen electrode potential.

In order to achieve stable electrochemical CO$_2$ reduction data, the linear scanning voltammetry (LSV) technique were first performed with a scan rate of 100 mV s$^{-1}$ from 0 to –1.2 V to reduce CuO to metallic Cu. After that, cyclic voltammetry (CV) scan from 0.1 to 1.1 V was scanned to get rid of the products from the previous LSV step under CO$_2$ purging. The same pretreatment was repeated twice to get the steady LSV curves. After the additional CO$_2$ bubbling for 10 min, the electrochemical CO$_2$RR performance was evaluated by using the chronoamperometry (CA) method at each constant potential. The vigorous magnetic stirring was applied during the
electrolysis to help mitigate the mass transport limitation of dissolved CO\textsubscript{2} in the electrolyte.

The gaseous product distribution was analyzed by using gas chromatography (GC, Agilent, Agilent 7890B). Once each CA was completed for CO\textsubscript{2}RR, 100 \( \mu \text{L} \) of gas in the empty head space at the cathodic compartment was collected and injected into GC to quantify the gaseous products (H\textsubscript{2}, CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4}). The liquid product was analyzed by using high performance liquid chromatography (HPLC, Agilent, 1260 Infinity II equipped with Hi-Plex H columns).

**Faradaic Efficiency (FE) and Partial Current Density Calculations**

The FE of the product was calculated by using the following equation (1):

\[
\text{FE} \ [\%] = \left( \frac{n \times 96485 \ (\text{C mol}^{-1}) \times N_X}{\int_{0}^{t} i \, dt} \right) \times 100 (1)
\]

, where \( N_X \) is the amount of product X (X=H\textsubscript{2}, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, and HCOOH) determined by GC and HPLC. For FE calculations, Faradaic constant (96485 C mol\textsuperscript{-1}) and the number of electron (n) for each product were used. \( i \) and \( t \) refer to the current (Ampere, A) and electrolysis time (seconds) measured by the Potentiostat, respectively.

The partial current density of product X (\( J(X) \), X= H\textsubscript{2}, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, and HCOOH) and total current density (\( J(\text{total}) \)) were calculated based on the following equations (2-3):

\[
J(X) \ [\text{mA cm}^{-2}] = \text{FE}(X) \times \left( \frac{\int_{0}^{t} i \, dt}{A \times t} \right) \times 100 \quad (2)
\]

\[
J(\text{total}) \ [\text{mA cm}^{-2}] = \left( \frac{\int_{0}^{t} i \, dt}{A \times t} \right) \times 100 \quad (3)
\]

\( A \) is the geometrical area of the working electrode. The error bars in FE and J calculations were obtained from repeated experiments using GC and HPLC.
**In-situ X-ray absorption fine structure (XAFS)**

The lab-made acryl kit was used for the *in-situ* X-ray measurements. The areal mass loading of working electrode was ~4 mg cm\(^{-2}\) in order to achieve sufficient XAFS signal. During the measurements, CO\(_2\) gas was continuously bubbled into the electrolyte. The other conditions were the same as in the electrochemical measurements.

*In-situ* XAFS measurements were conducted on the 1D beamline (KIST-PAL) at Pohang Light Sources (PLS) in Pohang Accelerating Laboratory (PAL). Both transmission and fluorescent signals were detected. Each potential was held for 12 min using CA technique during XAFS measurement. The typical duration for a single spectrum was around 3 min and four spectra were merged to get high signal-to-noise spectrum at each potential. During all of the XAFS measurements, the spectrum of reference Cu foil was simultaneously recorded, and was further used for calibrating the edge energy (E\(_0\)) of the sample under analysis.

The obtained spectra were processed using the ATHENA and ARTEMIS software in IFFEFIT package. The procedure which was described in B. Ravel *et al.*, was followed during the data process. EXAFS analyses were conducted by using the ARTEMIS software. The EXAFS spectrum (\(\chi(k)\)) was weighted with \(k^3\) value to intensify the signal at high k-regime. The Hanning window was utilized for the Fourier-transform. All of the EXAFS fitting were done in the R-space. The goodness of fitting was evaluated based on the reliable factor (R-factor) and reduced chi square (reduced \(\chi^2\)). The representative fitted EXAFS spectra are shown in Figure S9. The fitting parameters are tabulated in Table S3.

**Computational Methods**

The binding energy (BE) of adsorbate was calculated based on the equation (4):
\[ \text{BE(adsorbate)} = \text{E(slab + adsorbate)} - \text{E(slab)} - \text{E(adsorbate)} \quad (4) \]

where \( \text{E(slab + adsorbate)} \), \( \text{E(slab)} \), and \( \text{E(adsorbate)} \) are the total energies of the slab with adsorbate, clean slab, and adsorbate species in the gas phase, respectively.

The Gibbs free energy (\( G \)) is calculated based on the equation (5):

\[ G = E + \text{ZPE} - \text{TS} \quad (5) \]

Here, \( E \) is the total energy obtained from DFT calculations, \( \text{ZPE} \) and \( S \) are the zero-point energy and entropy respectively, and \( T = 298.15 \text{ K} \).

The transition state of a chemical reaction was located using the climbing image nudged elastic band (CI-NEB) method implemented in VASP.

The free energy diagrams of CO\(_2\)RR to CO (See the equations (6)-(8)), HCOOH (see the equations (9)-(12)) and CH\(_4\) (See the equations (6), (7), (9)-(14), and equations (11)-(16), (18), (19)) were calculated by considering the following sequential steps:

\[
\begin{align*}
\text{CO}_2(g) + (\text{H}^+ + \text{e}^-) + * &\rightarrow *\text{COOH} \quad (6) \\
*\text{COOH} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{CO} + \text{H}_2\text{O}(g) \quad (7) \\
*\text{CO} &\rightarrow \text{CO}(g) + * \quad (8) \\
*\text{CO} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{HCO} \quad (9) \\
*\text{HCO} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{H}_2\text{CO} \quad (10) \\
*\text{H}_2\text{CO} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{H}_3\text{CO} \quad (11) \\
*\text{H}_3\text{CO} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{CH}_3 + *\text{OH} \quad (12) \\
*\text{CH}_3 + *\text{OH} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{CH}_3 + \text{H}_2\text{O}(g) \quad (13) \\
*\text{CH}_3 + (\text{H}^+ + \text{e}^-) &\rightarrow \text{CH}_4(g) + * \quad (14) \\
\text{CO}_2(g) + (\text{H}^+ + \text{e}^-) + * &\rightarrow *\text{HCOO} \quad (15) \\
*\text{HCOO} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{HCOOH} \quad (16) \\
*\text{HCOOH} &\rightarrow \text{HCOOH}(g) + * \quad (17) \\
*\text{HCOOH} + (\text{H}^+ + \text{e}^-) &\rightarrow *\text{H}_2\text{COOH} \quad (18)
\end{align*}
\]
\[ \text{H}_2\text{COOH} + (\text{H}^+ + \text{e}^-) \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}(\text{g}) \]  

(19)

In aqueous electrolytes, the HER inevitably takes place via the following sequential steps\(^7\) (See the equation (20) and (21), and competes with the CO\(_2\)RR:)

\[ \text{H}^+ + \text{e}^- + * \rightarrow \text{H} \text{ (Volmer step)} \]  

(20)

\[ *\text{H} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2 + * \text{ (Heyrovsky step)} \]  

(21)
B. Supporting Figures and Table

Figure S1. A picture of the working electrodes with different binders.
**Figure S2.** CO$_2$RR performance at $-1.4$ V with different Nafion binder loading. (A) Faradaic efficiency and (B) partial current density.
Figure S3. (A-B) High resolution transmission electron microscopy (HR-TEM) and (C-E) scanning TEM (STEM) images of the commercial Cu/C used in this study.
Figure S4. Chronoamperometry curves at different potentials. (A) Cu-Nafion, (B) Cu-PAA, and (C) Cu-PVDF.
Figure S5. Partial current densities of (A) CO, (B) C\textsubscript{2}H\textsubscript{4}, and (C) H\textsubscript{2}.
Figure S6. Partial current density profiles measured at –1.4 V for 2 h. (A) Cu-Nafion, (B) Cu-PAA, and (C) Cu-PVDF.
Figure S7. TEM images taken after CO$_2$RR at -0.9 V for 2 h. (A) Cu-Nafion, (B) Cu-PAA, and (C) Cu-PVDF.
Figure S8. A digital picture of the working electrodes with different binders used in this study before (top) and after (bottom) stability tests for 2 h. The different contrast in pictures mainly originates from the wetting of electrodes.
Figure S9. *In-situ* EXAFS fitting results at 0 V, –1.2 V, and –1.3 V. (A-C) Cu-Nafion, (D-F) Cu-PAA, and (G-I) Cu-PVDF.
Figure S10. DFT calculated free energy diagram of CO$_2$RR at a potential of 0 V on CF$_2$-Cu(111) and SO$_3$H-Cu(111) surfaces.
Figure S11. DFT calculated free energy diagram of HER at a potential \( (U) = 0 \text{ V} \).
Table S1. Faradaic efficiency (%) values of Cu/C catalysts with different binders measured at various potentials.

| Cu-Nafion | Product     |     |     |     |     |
|-----------|-------------|-----|-----|-----|-----|
| Potential | H₂          | CO  | CH₄ | C₂H₄| HCOOH |
| –0.6 V    | 50.5        | 12.6| 6.4 | 2.88| 19.8  |
| –0.9 V    | 34.5        | 28.7| 1.5 | 0.8 | 32.8  |
| –1.2 V    | 28.3        | 24.4| 3.7 | 5.5 | 30.9  |
| –1.4 V    | 26.1        | 21.5| 12.2| 10.6| 17.4  |

| Cu-PAA    | Product     |     |     |     |     |
|-----------|-------------|-----|-----|-----|-----|
| Potential | H₂          | CO  | CH₄ | C₂H₄| HCOOH |
| –0.6 V    | 61          | 11.2| 3.9 | 1.6 | 13.5  |
| –0.9 V    | 30.1        | 29.3| 1.5 | 0.8 | 36.1  |
| –1.2 V    | 24.5        | 32.2| 2.2 | 1.9 | 37.6  |
| –1.4 V    | 25.5        | 19.2| 7.6 | 6.1 | 29.8  |

| Cu-PVDF   | Product     |     |     |     |     |
|-----------|-------------|-----|-----|-----|-----|
| Potential | H₂          | CO  | CH₄ | C₂H₄| HCOOH |
| –0.6 V    | 63          | 9.6 | 5   | 2.2 | 9.5   |
| –0.9 V    | 20.1        | 37.4| 2.2 | 1.1 | 36.4  |
| –1.2 V    | 23          | 33.1| 3.2 | 6.1 | 21.1  |
| –1.4 V    | 25.2        | 20.1| 12.0| 5.7 | 21.0  |
Table S2. Faradaic efficiency (%) and partial current density (J, mA cm\(^{-2}\)) values of Cu/C catalysts measured at –0.6 V for 2 h.

| Cu-Nafion | H\(_2\) | CO | CH\(_4\) | C\(_2\)H\(_4\) | HCOOH |
|-----------|--------|----|---------|--------------|-------|
| Time (min)| FE     | J  | FE      | J            | FE    |
| 60        | 50.5   | 0.87 | 12.6    | 6.4          | 0.11  |
| 120       | 57.6   | 0.95 | 9.5     | 7.6          | 0.13  |

| Cu-PAA    | H\(_2\) | CO | CH\(_4\) | C\(_2\)H\(_4\) | HCOOH |
|-----------|--------|----|---------|--------------|-------|
| Time (min)| FE     | J  | FE      | J            | FE    |
| 60        | 61.1   | 1.70 | 11.2    | 3.9          | 0.11  |
| 120       | 67.7   | 1.82 | 9.8     | 4.3          | 0.12  |

| Cu-PVDF   | H\(_2\) | CO | CH\(_4\) | C\(_2\)H\(_4\) | HCOOH |
|-----------|--------|----|---------|--------------|-------|
| Time (min)| FE     | J  | FE      | J            | FE    |
| 60        | 63     | 1.28 | 9.6     | 5            | 0.10  |
| 120       | 70.2   | 1.43 | 7.8     | 6            | 0.12  |
## Table S3. *In-situ* EXAFS fitting results.

| Parameter                  | Cu-Nafion | Cu-PAA  | Cu-PVDF             |
|----------------------------|-----------|---------|---------------------|
| Independent Points         | 83.5      | 83.4375 | 74.2558594          |
| Number of Variables        | 45        | 45      | 39                  |
| Chi-square                 | 1063.7622755 | 1212.1074729 | 2608.4657048     |
| Reduced Chi-square         | 27.6301890 | 31.5345034 | 73.9867288         |
| R-factor                   | 0.0164860 | 0.0146518 | 0.0165359          |
| k-range                    | 3.000 – 11.432 | 3.000 – 11.441 | 3.000 – 11.432 |
| R-range                    | 1 – 3     | 1 – 3   | 1.2 – 3             |
| Number of Data Set         | 8         | 8       | 8                   |

### Structure Model

| Chemical Formula  | Cu   | Cu$_2$O |
|-------------------|------|---------|
| Space Group       | Fm-3m (a=3.62126 Å) | R-3m (a=2.82 Å, C=12.7 Å) |
| Atomic Position   | Cu (0, 0, 0) | Cu(0, 0, 0.25), O (0, 0, 0) |
Table S4. DFT calculated binding energies (in eV).

| Adsorbate | Cu(111) | SO$_2$H-Cu(111) [Cu-Nafion] | COOH-Cu(111) [Cu-PAA] | CF$_2$-Cu(111) [Cu-PVDF] |
|-----------|---------|-----------------------------|------------------------|--------------------------|
| *H        | -0.30   | -0.21                       | -0.22                  | -0.14                    |
| *CO       | -0.94   | -0.84                       | -0.95                  | -0.89                    |
| *HOOC     | -1.82   | -1.76                       | -2.46                  | -1.83                    |
| *OH       | -3.20   | -3.09                       | -3.55                  | -3.11                    |
| *HCO      | -1.49   | -1.36                       | -1.80                  | -1.50                    |
| *H$_2$CO  | -0.29   | -0.29                       | -0.69                  | -0.33                    |
| *H$_3$CO  | -2.47   | -2.06                       | -2.65                  | -2.57                    |
| *HCOO     | -3.09   | -2.98                       | -3.28                  | -3.17                    |
| *HCOOH    | -0.35   | -0.55                       | -1.14                  | -0.45                    |
| *H$_2$COOH| -2.35   | -2.02                       | -2.55                  | -2.38                    |
C. Supporting References

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