Supporting Information for

A Direct Grain-Boundary-Activity Correlation for CO Electroreduction on Cu Nanoparticles

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Experimental Methods

(1) Materials:
Copper (Cu) evaporation pellets (99.999%) were purchased from Kurt J. Lesker Company; Cu wire (0.50 mm diameter, 99.9999%) was purchased from Alfa Aesar; potassium hydroxide (99.99%), perchloric acid (~70% solution in water), platinum gauze (99.9%) and platinum wire (99.9%) were purchased from Sigma-Aldrich; carbon monoxide (99.99%) and nitrogen gases (99.99%) were purchased from Praxair. All chemicals were used without further purification. Electrolyte solutions were prepared with deionized water (Ricca Chemical, ASTM Type I).

(2) Preparation of Cu/CNT electrodes:
A carbon nanotube (CNT) film was first drawn from a super-aligned CNT array grown on a Si substrate (Figure S1). Two layers of CNT films were cross-stacked onto a stainless steel frame with an open area of 5 cm × 5 cm. Cu was deposited onto the CNT films using a Kurt J. Lesker e-beam evaporator with a nominal thickness of 10 nm (at a deposition rate of 2 Å s⁻¹ for 50 s). The Cu/CNT films were twisted into a yarn and connected to a Cu wire as an electrode. The typical Cu loading of an electrode is ~0.30 mg. Thermally annealed Cu/CNT samples were prepared by heating the as-deposited samples at the indicated temperature (200–500 °C) in a tube furnace (Thermo Scientific) under flowing N₂ (200 cm³ min⁻¹) for 1 h using a ramp rate of ~30 K min⁻¹. The samples cooled to ambient temperature in 1 h. The electrodes were stored in flowing N₂ when not in use.

(3) Electrochemical measurements and product analysis:
A CH Instruments 760D or 660D Potentiostat was used for all CO reduction experiments. A piece of Pt gauze was used as the counter electrode. Unless otherwise stated, the electrolyte used for all CO reduction experiments was 0.1 M KOH saturated with CO with a pH of 13. Potentials E were measured against an Hg/HgO reference (0.1 M KOH, Koslow Scientific) or an Ag/AgCl reference electrode (3.0 M KCl, World Precision Instruments) and converted to the RHE reference scale using:

\[ E_{\text{vs RHE}} = E_{\text{vs Hg/HgO}} + 0.140 \text{V} + 0.0591 \text{V} \times \text{pH} \]

\[ E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + 0.210 \text{V} + 0.0591 \text{V} \times \text{pH} \]

Electrolyses were performed in a two-compartment electrochemical cell sealed to be gastight with silicone stoppers. A piece of Selmemion anion exchange membrane was used as the separator. Each compartment contained 20 mL of 0.1 M KOH electrolyte. The solution in the cathodic compartment was purged with CO for 15 min before the electrolysis. The headspace of the cathodic compartment was approximately 5 mL. CO gas was delivered into the cathodic compartment at a rate of 5.00 cm³ min⁻¹ and vented directly into the gas-sampling loop of a gas chromatograph (GC, SRI Instruments). The electrolyte in the cathodic compartment was stirred at a rate of 800 rpm during electrolysis.

A GC run was initiated every 30 min. The GC was equipped with a packed MolSieve 13X column and a packed HaySep D column. Ar (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector with methanizer was used to quantify C₂H₄ and C₂H₆ concentration and a thermal conductivity detector was used to quantify H₂ concentration. The products were quantified by comparison of the peak integrals to standard gases and the molar quantities were converted to Coulombs (C) by multiplying by \( nF \), where \( F \) is Faraday’s constant and \( n = 8, 10, \ldots \).
and 2 for C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and H\textsubscript{2}, respectively. The charges corresponding to each product were then compared to the integrated electrolysis charge to determine the Faradaic efficiency.

Solution-phase products, ethanol (EtOH), acetate (AcO\textsuperscript{−}), and n-propanol (n-PrOH), were quantified at the end of each experiment using a Varian Inova 600-MHz NMR spectrometer. A 0.5-mL sample of the electrolyte was mixed with 0.1 mL D\textsubscript{2}O containing 100 parts per million (by mass fraction) dimethyl sulphoxide (Sigma-Aldrich, 99.99%) as an internal standard. The one-dimensional \textsuperscript{1}H spectrum was measured with water suppression using a presaturation method. The sum of the Faradaic efficiencies for all the products determined in this way shows minor fluctuations around 100% (± 5%).

Specific (surface area–normalized) current densities for CO reduction and H\textsubscript{2} evolution were calculated from the total current, the Faradaic efficiencies as determined above, and Cu surface area (see below), using the following equations:

\[
\text{Specific } j_{\text{COredn}} = \frac{\text{Total current } \times \text{COredn Faradaic efficiency}}{\text{Cu surface area}}
\]

\[
\text{Specific } j_{\text{H2}} = \frac{\text{Total current } \times \text{H2 Faradaic efficiency}}{\text{Cu surface area}}
\]

Typically, more than 30 C charge was passed through an electrode for product analysis. Error bars for specific current densities were determined by measurements on 3 independently prepared samples under the same electrolysis conditions. They exhibited <10% variation in the mass activities and <5 percentage point variation in the Faradaic efficiency for CO reduction.

(4) Electrochemical surface area measurement:

The electrochemical surface areas of Cu electrodes relative to polycrystalline Cu foil were determined by measuring the double layer capacitances. Cyclic voltammetry was performed in the same electrochemical cell as in bulk electrolyses with a Nafion proton exchange membrane and 0.1 M HClO\textsubscript{4} electrolyte. Only double-layer charging and discharging occurs (no Faradaic process) in the potential window of 0 – 0.2 V vs RHE. The current in the potential window was plotted against the scan rate of the cyclic voltammetry. The slope of the linear regression gives the capacitance. A representative set of the cyclic voltammometries is shown in Figure S11.

(5) Characterization of Cu/CNT electrodes:

Transmission electron microscopy (TEM) images were acquired using a FEI Tecnai G2 F20 X-TWIN transmission electron microscope operated at 200 kV in bright-field TEM mode and high-resolution TEM mode. In situ TEM videos and post-electrolysis characterization were acquired using a FEI Titan 80-300 environmental transmission electron microscope at 300 kV (with a DENSsolutions heating holder). X-ray photoelectron spectra were obtained with a PHI VersaProbe II scanning X-ray photoelectron spectroscopy Microprobe. Grazing-incidence X-ray diffraction patterns were acquired at beamline 2-1 of the Stanford Synchrotron Radiation Lightsource using an 11.5 keV synchrotron X-ray beam with Soller slits and a photomultiplier tube detector. All patterns were acquired at an incidence angle of 4°.

(6) Measurement of grain boundary (GB) surface density from TEM images:

The method described below was used to provide an accurate measurement of the relative GB surface density between Cu/CNT samples. For each type of Cu/CNT sample (Cu/CNT_as-
dep, Cu/CNT_200, Cu/CNT_300, Cu/CNT_400, Cu/CNT_500), high-resolution TEM images were obtained for around 200 Cu nanoparticles. For each of the nanoparticle images, the length of the GBs (if present) and the particle area were measured:

\[ L_i = \text{GB length in TEM image for particle } i \text{ (with uncertainty } \delta L_i) \]

\[ A_i = \text{particle area in TEM image for particle } i \text{ (with uncertainty } \delta A_i) \]

\( L_i \) was determined by measuring the length of a line traced over the GB image. In most nanoparticles that have GBs, the GBs are readily identified. \( \delta L_i \) arises from the blurring of the nanoparticle image at the edges and from GB curvature and it is typically ~1–2 nm. For a small fraction of particles, in addition to GBs that are readily identified, there are other lines in the particle image that cannot be conclusively identified as GBs. These inconclusive GBs make an additional contribution to \( \delta L_i \). To measure \( A_i \), each particle image was approximated either as a circle, a rod with semi-circular caps, or a combination of these shapes (see below). The image was fit to two shapes, one slightly smaller than the image and one slightly larger. \( A_i \) was taken to be the average of the areas of these two fits and \( \delta A_i \) was the standard deviation. This method of measuring the particle area in the TEM image was chosen because the values could readily be converted into 3D particle surface areas.

The measured values \( L_i \) and \( A_i \) were converted to the 3D GB surface lengths and the 3D particle surface areas using conversion factors derived from the assumption that the particles have round morphologies:

\[ C_L = \text{conversion factor from measured GB length } L_i \text{ to 3D GB surface length} \]

\[ C_A = \text{conversion factor from measured particle area } A_i \text{ to 3D particle surface area} \]

The 3D GB surface length was approximated as the circumference of a circle with diameter \( L_i \).

\[ 3D \text{ GB surface length} = \pi L_i \]

3D GB surface length = \( \pi L_i \), so conversion factor \( C_L = \pi \).

The value for \( C_A \) depends on the particle shape as illustrated in the following examples:

(1) Spherical shape, with radius \( R \) and measured GB length \( L \)

3D GB surface length = \( \pi L \)

3D particle surface area = \( 4\pi R^2 \), so conversion factor \( C_A = 4 \) for this model.

(2) Cylindrical shape with length \( H \), hemispherical ends of radius \( R \), and GB length \( L \)

3D GB surface length = \( \pi L \)
3D particle surface area = $4\pi R^2 + 2\pi RH$, so \( C_A = \frac{4\pi R^2 + 2\pi R}{\pi R^2 + 2R} \) for this model.

(3) Other complicated geometries (a small fraction) could be divided into parts that fit simple models such as sphere, hemisphere, and cylinder.

Using all of the measured values for \( L_i \) and \( A_i \) for all of the nanoparticles imaged, and the appropriate conversion factors, the 3D GB surface densities were calculated as follows:

\[
\text{3D GB surface density} = \frac{\sum_{\text{All particles}} \text{GB surface length}}{\sum_{\text{All particles}} \text{surface area}} = \frac{\sum_i \pi \cdot L_i}{\sum_i C_A \cdot A_i}
\]

The uncertainties of the GB surface density were calculated as follows:

\[
\text{Uncertainty of the total GB surface length} = \frac{\sum_i \delta L_i}{\sum_i L_i}
\]

\[
\text{Uncertainty of the total surface area} = \frac{\sum_i \delta A_i}{\sum_i A_i}
\]

\[
\text{Uncertainty of the GB surface density} = \left( \frac{\sum_i \delta L_i}{\sum_i L_i} \right)^2 + \left( \frac{\sum_i \delta A_i}{\sum_i A_i} \right)^2
\]

The percentage uncertainties for the GB lengths, particle areas and GB surface densities for the five samples are:

| Sample   | \( \frac{\sum_i \delta L_i}{\sum_i L_i} \) | \( \frac{\sum_i \delta A_i}{\sum_i A_i} \) | \( \left( \frac{\sum_i \delta L_i}{\sum_i L_i} \right)^2 + \left( \frac{\sum_i \delta A_i}{\sum_i A_i} \right)^2 \) |
|----------|----------------------------------|---------------------------------|--------------------------------------------------|
| Cu/CNT   | 5.6%                             | 9.1%                            | 10.7%                                            |
| Cu/CNT_200 | 5.3%                            | 8.4%                            | 9.9%                                             |
| Cu/CNT_300 | 5.3%                            | 7.3%                            | 9.0%                                             |
| Cu/CNT_400 | 5.0%                            | 6.6%                            | 8.3%                                             |
| Cu/CNT_500 | 5.4%                            | 5.2%                            | 7.5%                                             |

The contact area between Cu and the CNTs was not considered during the calculation of GB surface density, because the contact area should have the same GB surface density as the particle surface area exposed to the electrolyte.
Figure S1. Preparation of Cu/CNT electrodes. (a) A CNT film was drawn from a super-aligned CNT array grown on Si substrate and cross-stacked onto a stainless steel frame. (b) A CNT film after vapor deposition of Cu with a nominal thickness of 10 nm. (c) The Cu/CNT film was wrapped and connected to a Cu wire as an electrode for electrochemical measurements. (d–f) TEM images of CNT film (d), an individual nanotube (e), and 10nm-Cu/CNT film (f).
Figure S2. X-ray photoelectron spectroscopy of the Cu/CNT_as-dep electrode. (a) Survey spectrum. (b) High-resolution spectrum of the Cu 2p peaks. (c) High-resolution spectrum of the Cu LMM region (vs kinetic energy).
Figure S3. Size histograms of Cu nanoparticles in the five samples as measured by TEM: (a) Cu/CNT_as-dep, (b) Cu/CNT_200, (c) Cu/CNT_300, (d) Cu/CNT_400, (e) Cu/CNT_500.
Figure S4. Additional TEM images of Cu nanoparticles in Cu/CNT as-dep. The arrows indicate the grain boundaries.
Figure S5. Additional TEM images of Cu nanoparticles in Cu/CNT_200. The arrows indicate the grain boundaries.
Figure S6. Additional TEM images of Cu nanoparticles in Cu/CNT_300. The arrows indicate the grain boundaries.
Figure S7. Additional TEM images of Cu nanoparticles in Cu/CNT_400. The arrows indicate the grain boundaries.
Figure S8. Additional TEM images of Cu nanoparticles in Cu/CNT_500. The arrows indicate the grain boundaries.
Figure S9. TEM images extracted from video S1 at indicated times showing the structural evolution of a polycrystalline Cu particle at 500 °C. The arrows indicate the grain boundaries. The upper boundary was lost via migration, while the lower one persisted. Apart from grain boundary loss, the overall structure of the particle remains relatively unaffected.
Figure S10. Williamson–Hall plots derived from grazing-incidence X-ray diffraction patterns of the samples: (a) Cu/CNT_as-dep, (b) Cu/CNT_200, (c) Cu/CNT_300, (d) Cu/CNT_400, (e) Cu/CNT_500, where $B$ is the integral breadth of peaks, and the points highlighted in red have been excluded. To calculate the crystallite size and strain, the following equation was used: $B = K\lambda/<D>\cos\theta + 4\varepsilon\cdot\tan\theta$, where $<D>$ is the average crystallite size, $\lambda$ is the wavelength, $\varepsilon$ is the non-uniform strain (microstrain), and the Scherrer constant $K \approx 1$. 
Figure S11. Electrochemical surface area measurement for Cu/CNT_as-dep electrode with 0.3 mg Cu loading. (a) A cyclic voltammetry scan taken at 50 mV s$^{-1}$ in 0.1 M HClO$_4$ electrolyte, showing that only double-layer charging and discharging occurs in the potential window of 0 – 0.20 V vs RHE. (b) Cyclic voltammograms taken over a range of scan rates in the potential window. (c) Double-layer charging current vs the cyclic voltammetry scan rate. The slope of the linear fit is the double-layer capacitance. The capacitance for CNT film without Cu loading was <2% of that for the Cu/CNT electrode. The capacitance was converted to surface area with polycrystalline Cu foil as a reference (29 μF cm$^{-2}$).
Figure S12. Representative bulk-electrolysis data for CO reduction on the Cu/CNT_as-dep electrode at –0.4 V vs RHE in 0.1 M KOH electrolyte. Total mass activity over time (left), and Faradaic efficiencies over time (right) for H₂ (red), C₂H₄ (green), and C₂H₆ (blue). Efficiencies for EtOH, AcO⁻, and n-PrOH were obtained at the end of the electrolysis by NMR analysis of the electrolyte.
Figure S13. Representative NMR spectra for the liquid products of CO reduction at –0.35 V (a) and –0.45 V (b) vs RHE in 0.1 M KOH electrolyte. Dimethyl sulfoxide (DMSO) was used as the standard.
**Figure S14.** Specific activity for H₂ evolution on the Cu/CNT electrodes in N₂-saturated or CO-saturated 0.1 M KOH electrolyte.
Figure S15. Dependence of the geometric current density for CO reduction with Cu/CNT on the catalyst loading. (a) Cu/CNT yarn and (b, c) Cu/CNT films stretched over a flat Cu foil. The Cu loading per electrode is about 0.3 mg for (a, b) and 0.6 mg for (c). The geometrical area is not well-defined in (a); in (b) and (c), the geometrical area is 2 cm². The total current and Faradaic efficiencies for CO reduction at –0.30 V vs RHE in 0.1 M KOH electrolyte are listed below each sample.
Figure S16. Additional TEM images of Cu nanoparticles in Cu/CNT_as-dep after electrolysis at –0.30 V vs RHE in 0.1 M KOH electrolyte for 14 hours. The images were taken using Titan TEM, and the arrows indicate the grain boundaries.
Figure S17. Faradaic efficiencies for CO reduction products at selected potentials in 1 M KOH electrolyte with Cu/CNT_as-dep. The remaining efficiency corresponds to H$_2$ evolution.
Figure S18. (a) Faradaic efficiencies for CO reduction on as-deposited Cu/CNT samples with different Cu deposition thicknesses at –0.30 V vs RHE in 0.1 M KOH electrolyte. (b–d) TEM images of the samples with a nominal deposition thickness of 30 nm (b), 50 nm (c), and 70 nm (d). For the Cu/CNT sample with 50-nm Cu deposition, the CNTs are fully coated with Cu so that no Cu/C sites are exposed. This sample still shows very high activity, although it is a little lower than 10nm-Cu/CNT_as-dep because the Cu nanoparticles sintered to form larger grains (thus lower grain boundary density) during the longer deposition process.