Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information for:

Copper and silver gas diffusion electrodes performing CO_2 reduction studied through operando X-ray absorption spectroscopy

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Data analysis The raw data obtained in an XAS experiment is often averaged when multiple scans are taken consecutively under the same reaction conditions on one sample. The averaged spectra are then normalised, sometimes smoothed and plotted to show the normalised absorption coefficient $\mu(E)$. Often only the 30 - 100 eV after the absorption edge are shown, this is the XANES spectrum. The $\mu(E)$ can be converted to give the EXAFS $\chi(k)$ as explained in great detail by many other books and papers.[1,2,3] The Fourier Transform (FT) of $\chi(k)$ gives a spectrum that is easier to interpret by eye compared to the $\chi(k)$ spectrum. The x-axis now displays the distance between the absorber atom and the neighbouring shells, the y-axis is a measure of the intensity. The EXAFS can be fit to the EXAFS equation using different software tools, including GNXAS, Athena and Viper.[4–6,7] The different contributions to $\chi(k)$ are frequencies of different types of oscillators. For example, in a silver oxide, the Ag-O frequency is different than the Ag-Ag frequency. The EXAFS equation (equation S1) can be fitted to $\chi(k)$ and is in fact a summation of these different frequencies that all have their own interatomic distance (R), coordination number (N) (a measure of the amount) and Debye-Waller factor (σ^2) (the disorder).

$$\chi(k) = \sum_i \frac{N_i f_i(k) e^{-2k^2\sigma_i^2}}{k R_i^2} \sin[2kR_i + \delta_i(k)] \qquad \text{S1}$$

The scattering amplitude f and the phase-shift δ are known values for standard components and can be entered into the fitting equation to generate values for R, N and σ^2. Since the oscillations diminish quickly at larger distances from the absorber atom, $\chi(k)$ can be multiplied with a factor k^2 or k^3. For a pure metal, the different oscillations are different shells around the absorber atom: metal atoms at various distances within the same unit cell. For an oxide, some shells are M-O contributions and others are M-M.

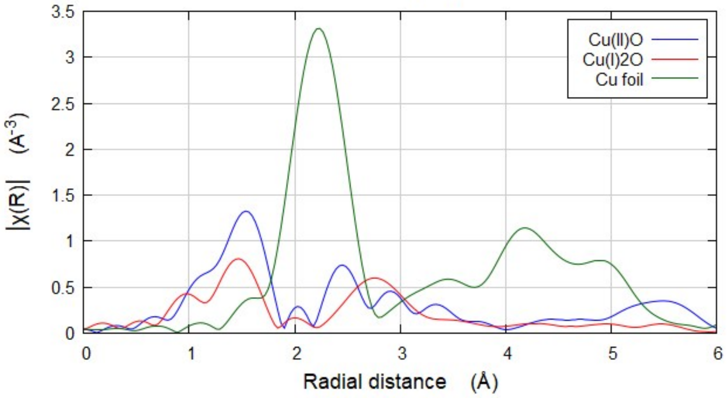

Figure S1. k^2-weighted FT EXAFS spectra of copper foil, CuO and Cu$_2$O reference samples, measured in transmission mode.

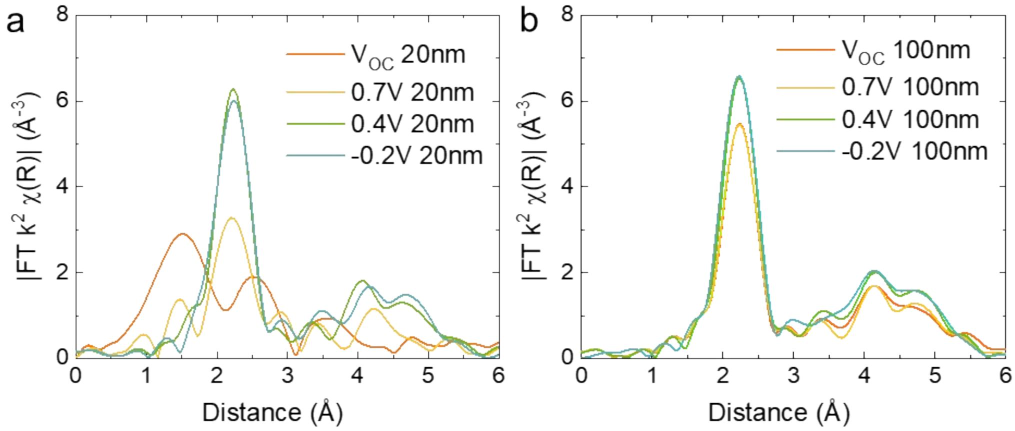

Figure S2. k^2-weighted FT EXAFS spectra of (a) 20 and (b) 100 nm Cu GDE samples in 1 M KOH at open circuit conditions and various applied positive and negative potentials.

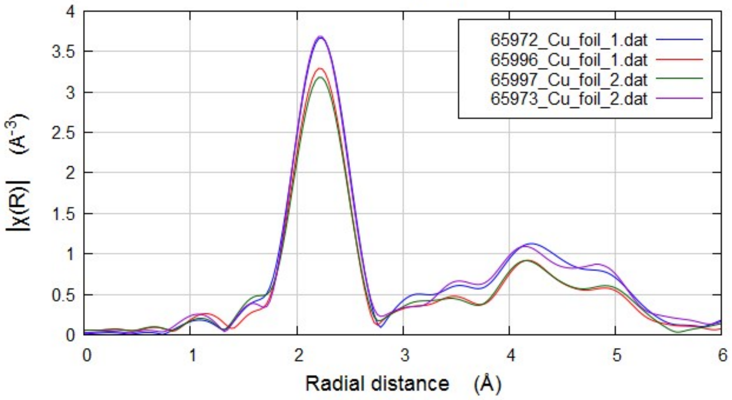

Figure S3. k^2-weighted FT EXAFS spectra of copper GDE samples. Blue and purple are scan 1 and 2 of the 100 nm Cu GDE 100mA/cm^2 in KOH, red and green are scan 1 and 2 for the 20 nm Cu GDE at 100 mA/cm^2 in KOH.

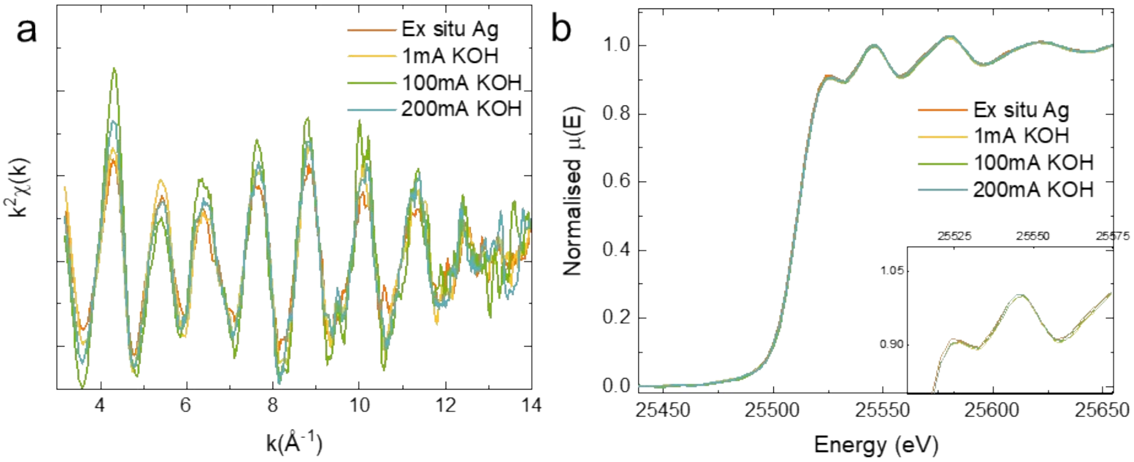

Figure S4. (a) EXAFS data in $k^2\chi(k)$ and (b) XANES spectra for 100 nm Ag GDEs measured under various experimental conditions, the matching FT spectra are shown in Figure 5a. Note that the 1mA and 100mA labels in the figures correspond to 1 and 100 mA/cm² current density.

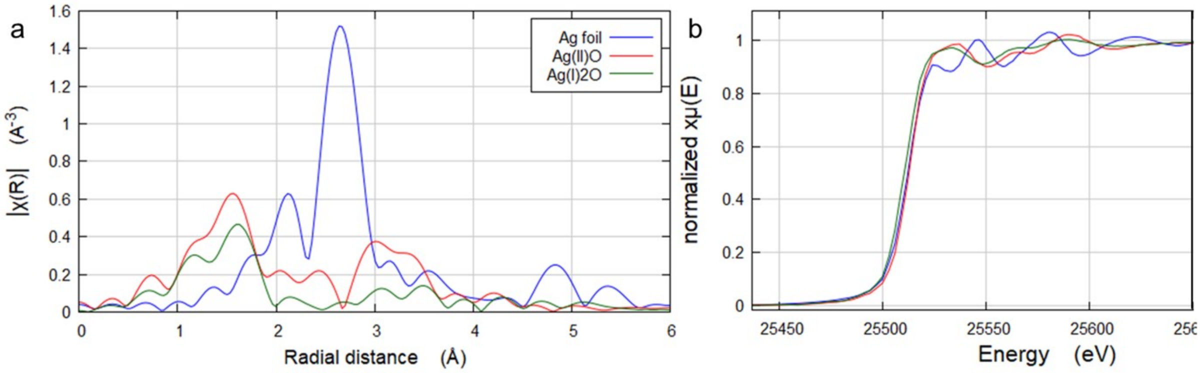

Figure S5. (a) k^2-weighted FT EXAFS spectra and (b) corresponding XANES spectra of silver foil, AgO and Ag_2O reference samples, measured in transmission mode.

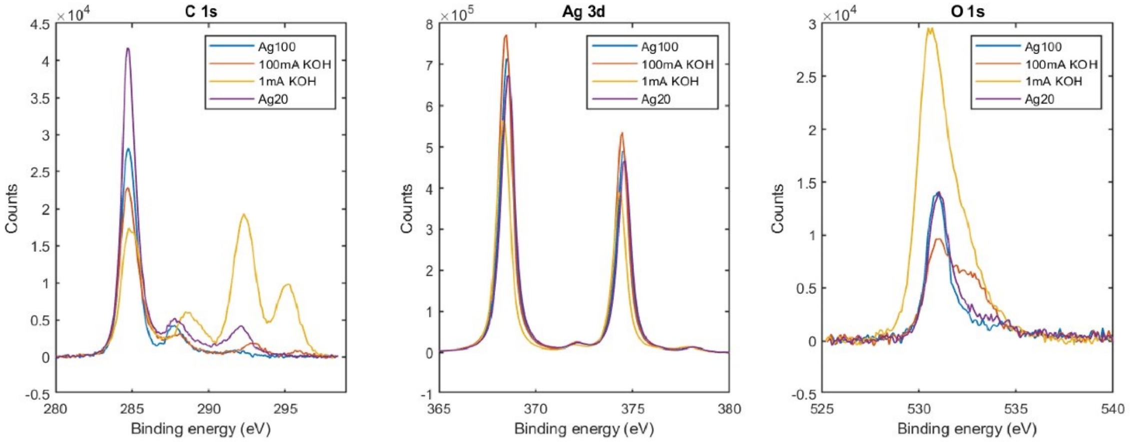

Figure S6. XPS C 1s, Ag 3d and O 1s spectra of a fresh 100 nm Ag on GDE, samples after 1h at 100 mA/cm² and 1 mA/cm² in KOH on a 100 nm Ag GDE and a fresh 20 nm Ag GDE sample. The C 1s graph includes the K 2p signal at 292 and 295 eV. Note that the 1mA and 100mA labels in the graphs correspond to 1 and 100 mA/cm² current density.

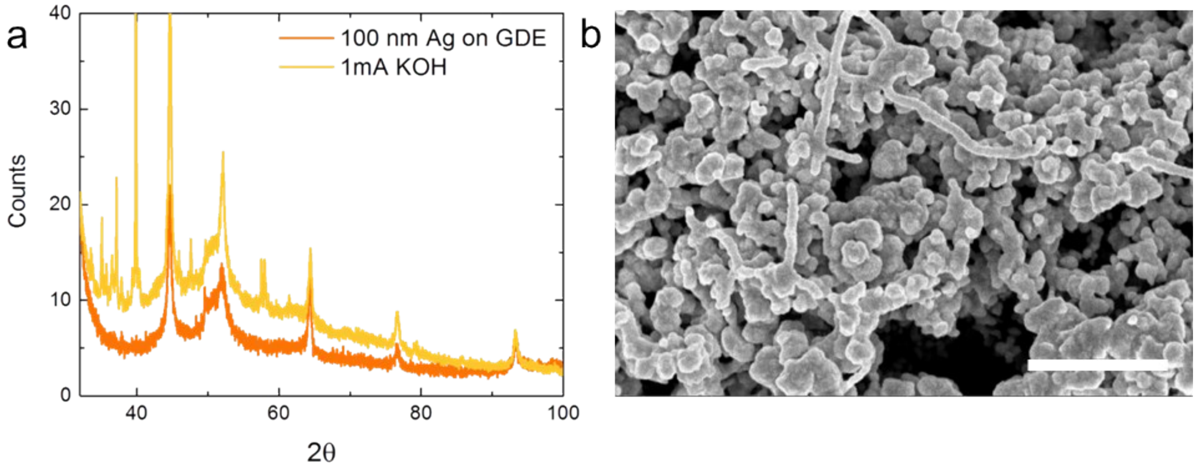

Figure S7. (a) XRD of a fresh 100 nm Ag GDE and a 100 nm Ag GDE after 1h at 1 mA/cm^2 in KOH sample. Besides the silver and GDE diffraction peaks, the 1 mA KOH sample also gives diffraction peaks of monoclinic kalicinite, or $KHCO_3$ crystals. (b) HR-SEM image of the 1mA KOH sample showing thread-like kalicinite structures on top of the Ag thin film. Scale bar is 1 µm. Note that the 1mA label in the figure corresponds to 1 mA/cm^2 current density.

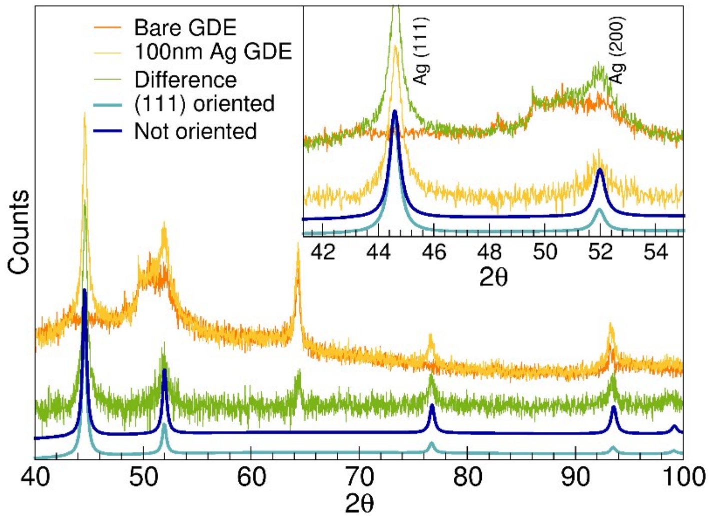

Figure S8. Rietveld analysis of 100 nm Ag GDE, indicating a preferred orientation of the (111) facet.

References

(1) Vlaic, G.; Olivi, L. EXAFS Spectroscopy : A Brief Introduction. *Croat. Chem. Acta* **2004**, *77* (3), 427–433.

(2) Newville, M. Fundamentals of XAFS. *Rev. Mineral. Geochemistry* **2014**, *78* (1), 33–74. https://doi.org/10.2138/rmg.2014.78.2.

(3) Calvin, S. *XAFS for Everyone*; CRC Press, 2013.

(4) Filipponi, A.; Di Cicco, A.; Renzo Natoli, C. X-Ray-Absorption Spectroscopy and n-Body Distribution Functions in Condensed Matter. I. Theory. *Phys. Rev. B* **1995**, *52*, 15122–15134.

(5) Filipponi, A.; Cicco, A. Di. X-Ray-Absorption Spectroscopy and n-Body Distribution Functions in Condensed Matter. II. Data Analysis and Applications. *Phys. Rev. B* **1995**, *52*, 15135–15149.

(6) Ravel, B.; Newville, M.; Calvin, S. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.

(7) Klementev, K. V. Deconvolution Problems in X-Ray Absorption Fine Structure Spectroscopy. *J. Phys. D. Appl. Phys.* **2001**, *34*, 209–217. https://doi.org/10.1088/0022-3727/34/15/301.