

Supporting Information for

***In-situ* Studies of Copper-based CO₂ Reduction Electrocatalysts by Scanning Transmission Soft X-ray Microscopy**

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Section S-1 Comparison of *in-situ* and reactor CV: calibration of V_{Au} versus V_{RHE}

Fig. S-1a,b displays the cyclic voltammetry (CV) in CO_2 saturated 0.1M $KHCO_3$ in a 2-compartment electrolyte membrane separated cell. The working electrode is Cu particles electro-deposited on a Au-coated graphite foil prepared by physical vapor deposition. The details for the preparation of Cu electrode are provided in **section 5.1**. A Pt foil was used as the counter electrode. A Ag/AgCl electrode was used as the reference electrode. The Ag/AgCl reference electrode was calibrated versus a home-made reversible hydrogen electrode (RHE), and the potentials are reported versus RHE. The catholyte and anolyte chambers were separated by an ion exchange membrane (Selemion AMV, AGC Inc). The potential range is +0.1 to +0.8 V_{RHE} and scan rate is 20 mV/s.

Fig. S-1c,d displays the CV in CO_2 saturated 0.1M $KHCO_3$ in a 3-electrode (beaker) cell. The working electrode (WE) is the electrodeposited Cu on the Au foil. The method for preparing the Cu electrode is the same Cu electrodeposition on the Au-coating graphite foil, shown in **section 5.1**. A Pt foil was used as the counter electrode (CE) and a Ag/AgCl electrode was used as the reference electrode (RE). The potential range is +0.25 to +0.7 V_{RHE} and scan rate is 20 mV/s.

Fig. S-1e,f displays the CV in CO_2 saturated 0.1M $KHCO_3$ in an *in-situ* cell. The working electrode is the electrodeposited Cu on the micro-working electrode of the *in-situ* cell. Details for the preparation of Cu electrode are in **section 5.4**. Au micro-electrodes are used as the counter electrode and the reference electrode. The potential range is -0.4 to +0.2 V_{Au} and scan rate is 20 mV/s. The CV measured under *in-situ* conditions (**Fig. S1f**) was stopped at +0.2 V_{RH} , resulting in a narrow anodic peak compared to the other two CV curves, in order to avoid oxidizing the Cu particles all the way to Cu(II) ions which readily dissolve into the electrolyte. The current density was estimated by dividing the measured current by the estimated electrode area of 2200 μm^2 (the geometrical area of the Au working electrode including all of the round region and a rectangle region at the top of the WE).^[S1] **[Figure S-2]**. All other areas of the working electrode are coated with an insulating layer.^[S1] Compared to the current densities measured by CV in a beaker cell and in the 2-compartment membrane cell, the *in-situ* CV current density is ~4 times larger. This could be due to the actual surface area being larger than the estimated area. It may also reflect additional active surface area at the sides or interior of the particles.

Fig. S-1g displays the potential (V_{Au}) versus time (s) under the *in-situ* condition when no potential is applied, which is the open circuit potential (OCP) between the working electrode and reference electrode. The OCP was $-48 mV_{Au} \pm 4 mV_{Au}$. This shows that the Au pseudo reference electrode under *in-situ* conditions provides a stable potential reference.

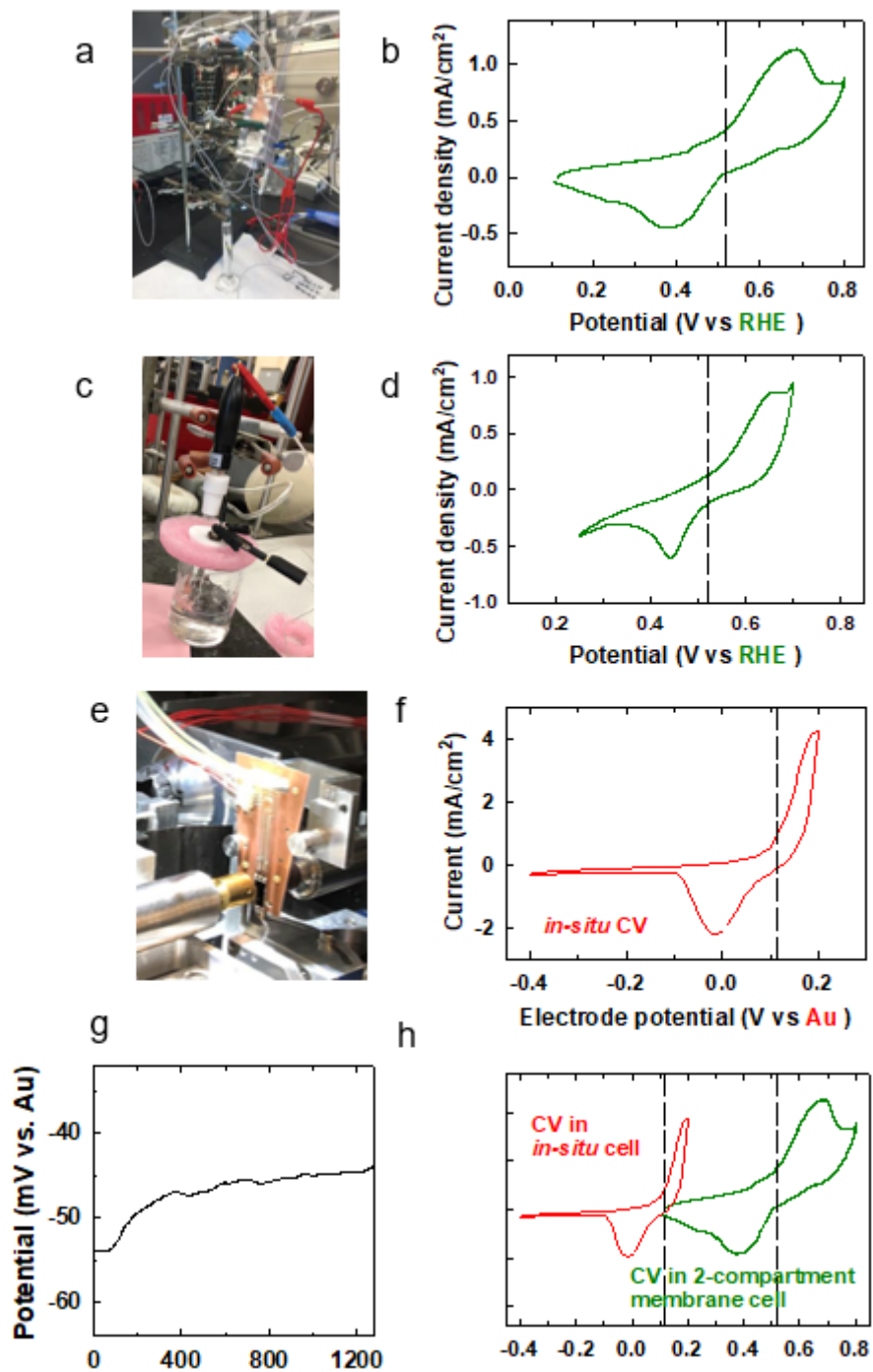


Figure S-1 CV of electrodeposited Cu in: **a)** photo of 2-compartment membrane cell. **b)** CV measured in 2-compartment cell. 20 mV/s scan rate. **c)** photo of 3-electrode (beaker) cell. **d)** CV in beaker cell. **e)** photo of *in-situ* cell. **f)** CV measured in *in-situ* cell. **g)** potential (mV_{Au}) vs time (s) under *in-situ* open circuit potential (OCP) conditions. **h)** CV used to derive the relationship of the potential relative to Au (V_{Au}) to that relative to the reversible hydrogen electrode (V_{RHE}) in CO₂ saturated 0.1M KHCO₃.

Due to the use of a Au pseudo reference in the *in-situ* STXM experiments, the potentials vs Au were converted to the RHE scale for convenience in comparing to literature. In order to relate the two reference scales, the CV with potentials vs RHE (**Fig. S-1b**) can be compared with the *in-situ* CV potentials vs Au (**Fig. S-1d**) to relate the two scales. (**Fig. S-1h**) This results in a conversion equation in this work:

$$E_{(\text{RHE})} = E_{\text{Au}} - 0.40 \text{ V} \quad (\text{Eqn. S1})$$

The accuracy and reproducibility of Au pseudo reference electrode was checked multiple times by comparing CV curves for Cu redox in CO₂ saturated 0.1 M KHCO₃ or NaHCO₃. The difference between the Au pseudo reference electrode and RHE observed via CVs was -0.43 ± 0.07 V. In addition, we have checked this result by measuring Au and RHE reference CVs for 0.1 M Fe(II) / Fe(III) cyanides solutions, which showed a shift of 0.5 ± 0.1 V.

All potentials shown in the manuscript and Supporting Information (SI) are converted to RHE using Eqn. S1, unless stated otherwise.

Section S-2 The electrolyte filling process under optical microscopy

Figure S-2 displays the process of filling the electrochemical cell used for *in-situ* STXM measurements with the electrolyte, as observed by optical microscopy.

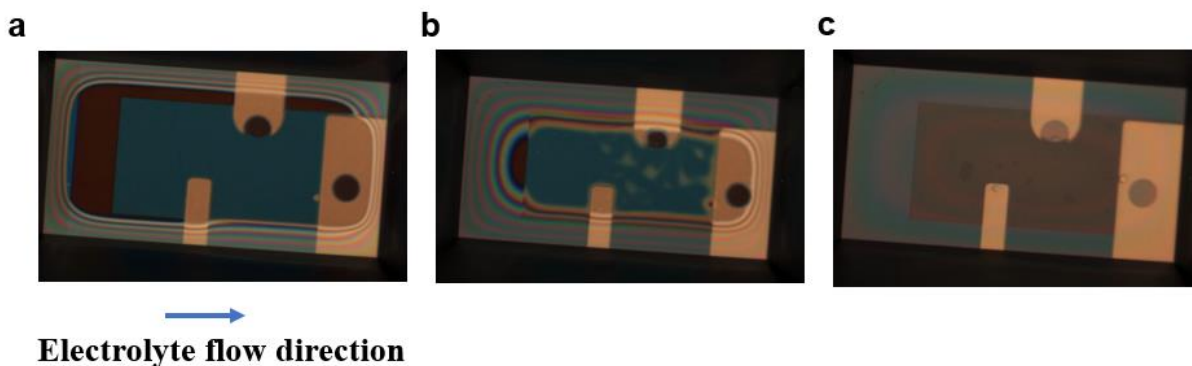


Figure S-2 Filling the *in-situ* cell with a solution of 5mM CuSO₄ and 5mM KCl under an optical microscope. (a), (b), (c) are reflection images ~5 minute (m) apart (magnification 20x). The direction for the electrolyte flow is shown as the arrow in (a)

Section S-3 Details of *in-situ* electrodeposition of Cu particles

Figure S.3 displays details of the *in-situ* deposition of Cu particles on the Au working electrode (WE) in the *in-situ* cell. **Fig. S-3a** shows the 3 cycle cyclic voltammetry curves for Cu deposition. The STXM

images before and after the Cu deposition on Au working electrode are shown in **Fig. S-3b** and **Fig. S-3c**.

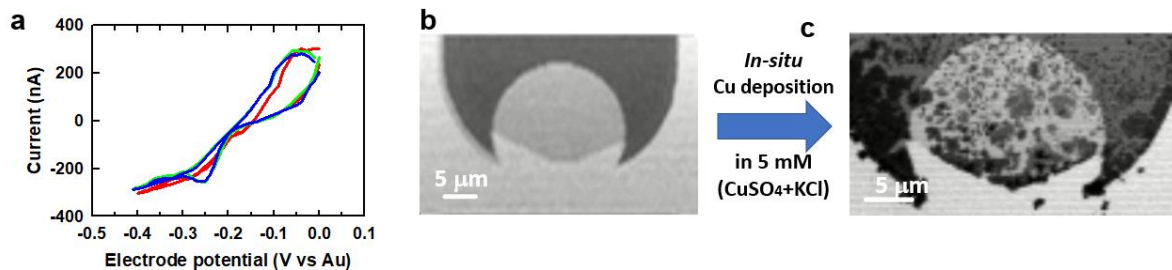


Figure S-3 *in-situ* electrodeposition of Cu particles from a 5 mM CuSO₄, 5 mM KCl solution. (a) Cyclic voltammetry (3 cycles) (b) STXM images at 960 eV before the Cu deposition (c) STXM images at 933.5 eV after the deposition of Cu particles. The horizontal bands in the STXM images (**Fig. S-3b, S-3c**) are an artifact arising from slow (period ~ 1 s) oscillations of the incident X-ray intensity due to shifts in the position of the electron beam in the CLS ring, which sometimes occur.

Section S-4 Chronoamperometry (CA) current-time plots at indicated potentials.

Figure S-4 plots the currents measured as a function of time during the chronoamperometry scans at increasingly negative potentials. There is a current transient at the beginning of each scan which is associated with the transition from the 30 second open circuit hold prior to each measurement.

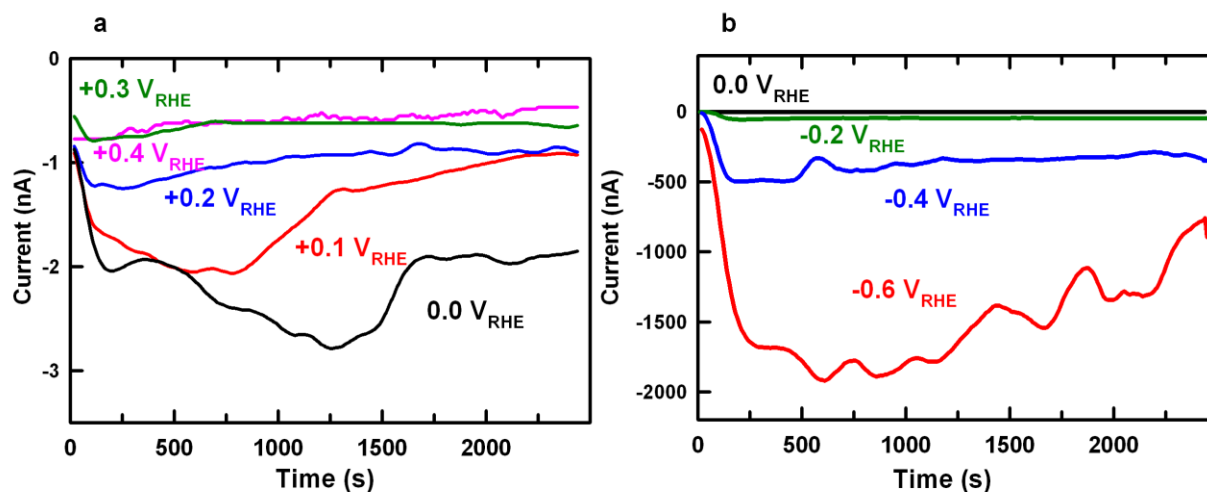


Figure S-4 Current vs time curve at each potential. (a) +0.4 to 0 V_{RHE}. (b) -0.2 to -0.6 V_{RHE}. Note the change in the current scale between (a) and (b).

Section S-5 Calculating the electrolyte thickness.

Figure S-5 shows how the electrolyte thickness is calculated. The positions for measuring the X-ray signal through the cell (electrolyte and SiNx windows) and through an empty hole in the *in-situ* device are shown in **Fig. S-5a** and **Fig. S-5b**. **Fig. S-5c** compares the X-ray signal of the incident X-ray with that from the SiNx windows. **Fig. S-5d** plots the OD spectrum of the electrolyte, indicating the contributions from 150 nm of SiNx windows and ~1.6 μ m of the electrolyte, which is dominated by the absorbance by water.

Section S-6 Details of STXM measurements and analysis

Figure S-6 displays the details for the comparison between the full energy spectra and 4-energy spectra. The comparison of full (53 energy) spectra vs 4-energy spectra for Cu(0) (**Fig. S-6a**) and Cu(I) (**Fig. S-6b**) shows that the 4-energy spectra provides the same chemical information as full energy spectra. Therefore, 4-E stack was used to obtain the same information as a full energy stack to save time.

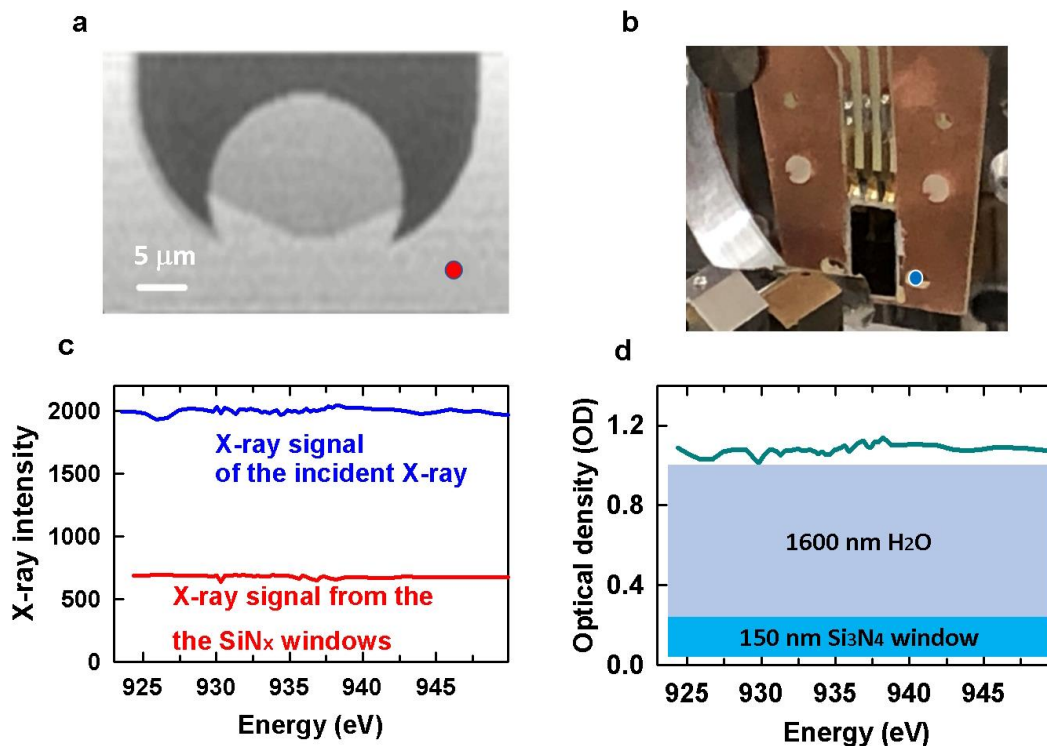


Figure S-5 Estimating the thickness of the electrolyte layer. (a) STXM transmission image at 960 eV. The red dot indicates where the electrolyte spectrum was measured. (b) Photo of the in situ cell in the STXM. The blue dot indicates the hole through the *in-situ* device where the incident flux was measured. (c) comparison between the X-ray signal of the incident X-ray beam (blue) and that from the X-ray beam passing through the electrolyte region of the cell (red), which includes 150 nm of SiN_x windows. (d) The OD spectrum of the electrolyte and the windows. The OD signal from 1600 nm of water and 150 nm of SiN_x are indicated, consistent with an electrolyte thickness of ~1.6 μm.

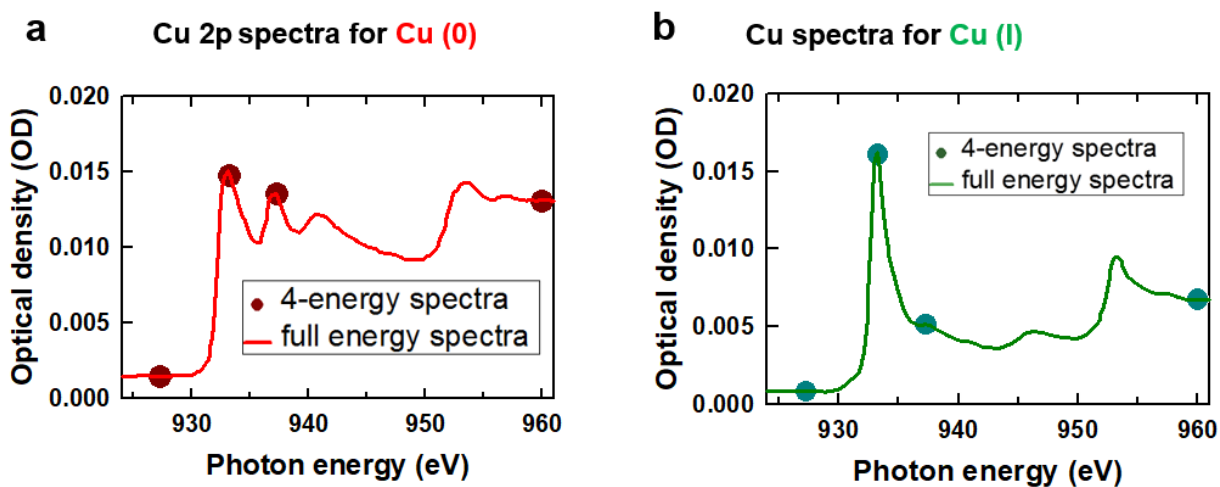


Figure S-6 Full energy spectra vs 4-energy spectra for (a) Cu(0), and (b) Cu(I)

Table S.1 Summary of main STXM measurements reported in this paper. A dwell of 3 ms/pixel and a flow rate of 25 $\mu\text{L/h}$ was used for all measurements.

Sample/Region	Fig #	Type	File	Size (μm)	Size (pixels)	Energy (eV)	#E	V_{RHE}
SiN _x window	Fig. S-5	Point scan	A210919005	0.04	1	924-950	50	OCP
Empty hole on device	Fig. S-5	Point scan	A210919008	0.04	1	920-965	53	OCP
Whole WE (before Cu deposition)	Fig. S-3	image	A210919020	40 x 30	80*60	960	1	OCP
Whole WE (after Cu deposition)	Fig. S-3, Fig. 3a	image	A210919059	30 x 15	120*60	960	1	OCP
Region of particles	Fig. 3a	image	A210915066	2.9 x 3.7	87*110	933.5	1	OCP
Region of particles	Fig. 3b, 3c	4-E stack	A210915065	2.9 x 3.7	87*110	920-960	4	OCP
Region of particles	Fig. 5	image	A210915067	2.8 x 3.6	84*96	933.5	1	+0.4
Region of particles	Fig. 5	4-E stack	A210915068	2.8 x 3.6	56*72	920-960	4	+0.4
-	Fig. 5	Full stack	A210915069	2.8 x 3.6	56*72	920-965	53	+0.4
-	Fig. 5	image	A210915070	2.8 x 3.6	56*72	933.5	1	+0.4
-	Fig. 5	4-E stack	A210915073	2.8 x 3.6	56*72	920-960	4	+0.3
-	Fig. 5	Full stack	A210915074	2.8 x 3.6	56*72	920-965	53	+0.3
-	Fig. 5	4-E stack	A210915078	2.8 x 3.6	56*72	920-960	4	+0.2
-	Fig. 5	Full stack	A210915079	2.8 x 3.6	56*72	920-965	53	+0.2
-	Fig. 5	4-E stack	A210915082	2.8 x 3.6	56*72	920-960	4	+0.1
-	Fig. 5	Full stack	A210915083	2.8 x 3.6	56*72	920-965	53	+0.1
-	Fig. 5	4-E stack	A210915086	2.8 x 3.6	56*72	920-960	4	0
-	Fig. 5	Full stack	A210915087	2.8 x 3.6	56*72	920-965	53	0
-	Fig. S-9	4-E stack	A210915090	2.8 x 3.6	56*72	920-960	4	-0.2
-	Fig. S-9	Full stack	A210915091	2.8 x 3.6	56*72	920-965	53	-0.2
-	Fig. S-9	4-E stack	A210915094	2.8 x 3.6	56*72	920-960	4	-0.4
-	Fig. S-9	Full stack	A210915095	2.8 x 3.6	56*72	920-965	53	-0.4
-	Fig. 5	4-E stack	A210915098	2.8 x 3.6	56*72	920-960	4	-0.6
Region of particles	Fig. 5	Full stack	A210915099	2.8 x 3.6	56*72	5920-965	53	-0.6

Section S-7 STXM analysis of electrodeposited Cu particles

Figure S-7 displays the details for SVD fitting analysis of the 4-energy stack of deposited Cu particles.

The component maps of Cu(0) (**Fig. S-7a**) and Cu(I) (**Fig. S-7b**) show the distribution of Cu(0) and Cu(I), with the gray scale bar showing the thickness. The residual map (**Fig. S-7c**) shows the residual signal (averaged over all energies) of the fit. The small and unstructured residual (maximum OD is 0.15, <10% of the total OD signal) indicates a high quality SVD fit. **Fig. S-7d** is the colour-coded composite map showing Cu(0) in red and Cu(I) in green. **Figure S-8** displays the spectra of Cu(0)-rich and Cu(I)-rich regions extracted from the 4-E stack. **Figure S-8a** shows the regions to collect the spectra, generated from **Fig. S-7d**. **Figure S-8b** and **Fig. S-8c** show the spectra of the Cu(0)-rich region and Cu(I)-rich region, compared to the Cu(0) and Cu(I) reference spectra.

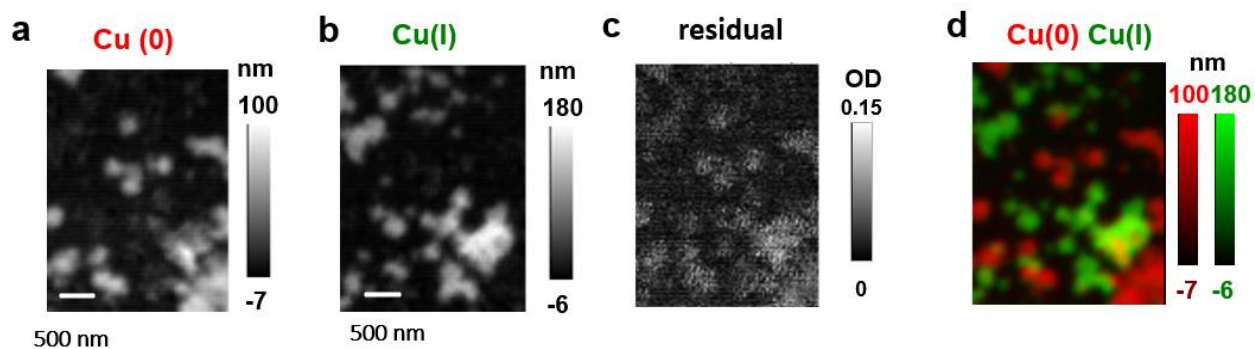


Figure S-7 Analysis of the 4-energy stack of deposited Cu particles. Component maps of (a) Cu(0), (b) Cu(I), (c) residual, and (d) colour-coded composite map.

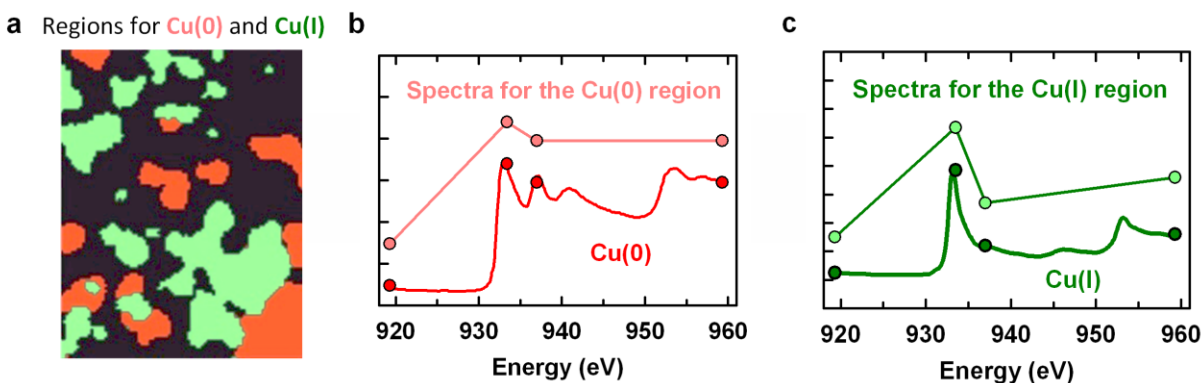
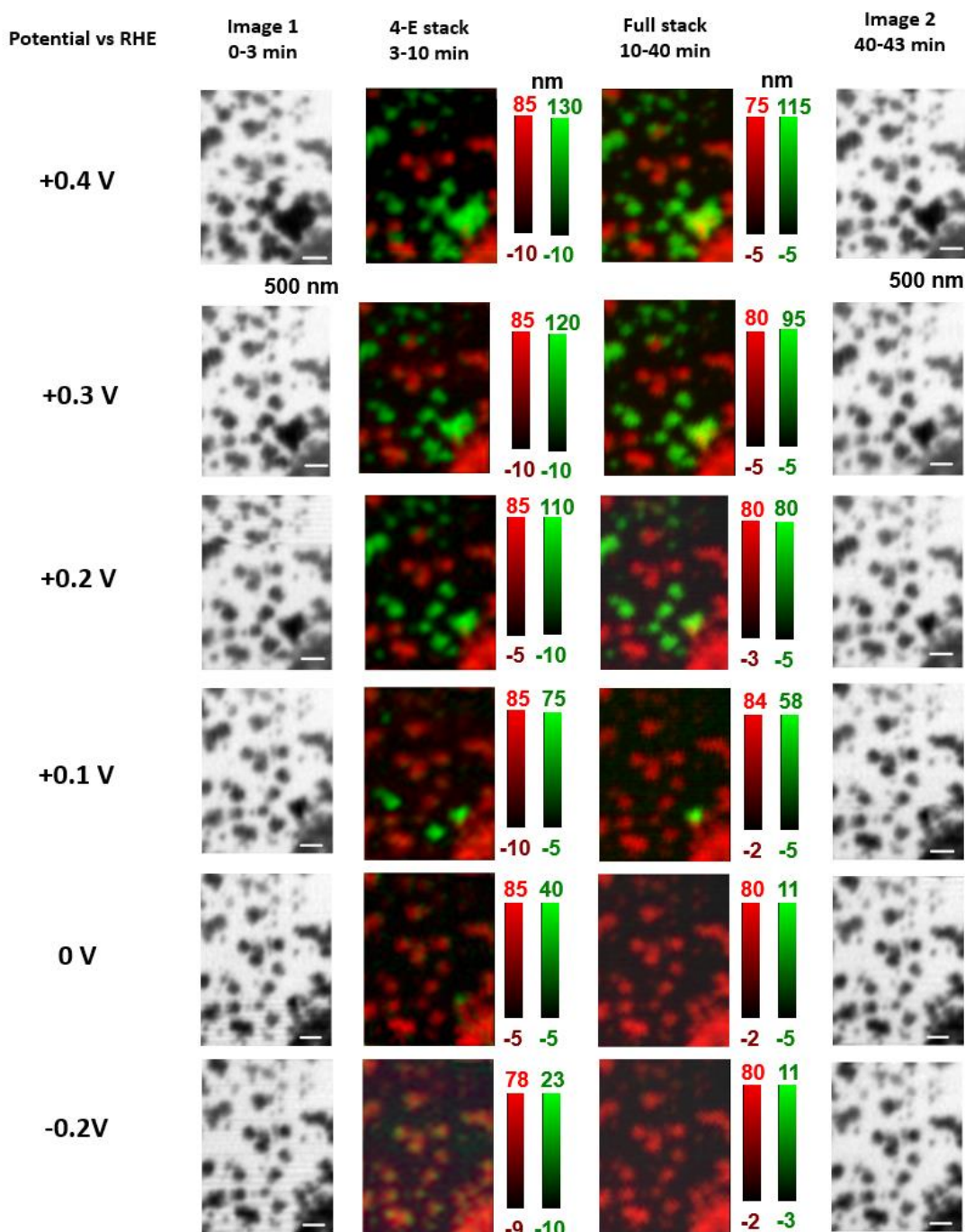


Figure S-8. Verification of the analysis of 4-energy stack of deposited Cu particles. (a) Regions for the Cu(I) and Cu(0) areas derived by component maps (b) extracted spectra from the Cu(0) region compared with Cu(0) reference spectra. (c) extracted spectra from the Cu(I) region compared with Cu(I) reference spectra.

Section S-8 STXM results at applied potentials from +0.4 to -0.6V_{RHE}

Figure S-9 displays the details for the various STXM results: 2 STXM images (image 1 and 2, 933.5 eV, ~ 3 mins for each), a fast 4-energy STXM stack (4-E: 920, 933.5, 937 and 960 eV, ~7 mins) and a complete Cu 2p STXM stack (full stack, 53 energies from 920 to 965 eV, ~30 min) at potentials from +0.4 to -0.6 V_{RHE}.



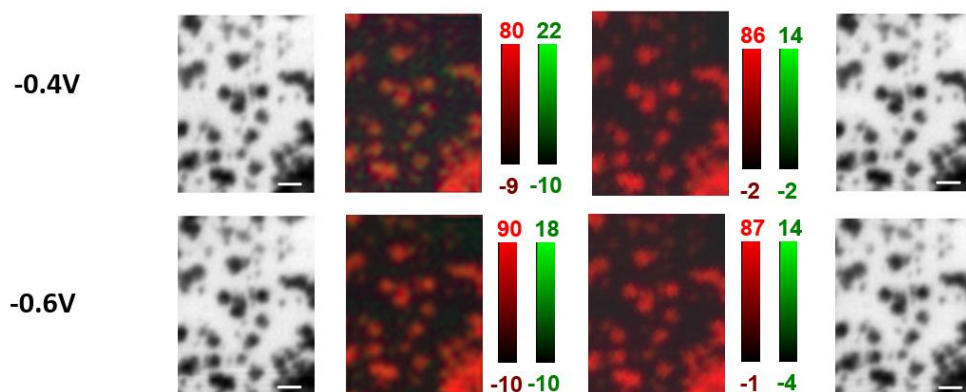


Figure S-9 Cu particle morphology and chemistry under various potentials. (Left 1) image 1 at 0-3 min under applied potentials. **(Left 2)** Color coded composites at the indicated potentials (vs RHE) derived from 4 energy stacks (3-10 min). **(Right 2)** Color coded composites at the indicated potentials (vs RHE) derived from 54 energy full stacks (10-40 min). **(Right 1)** image 1 at 40-43 min under applied potentials.

Section S-9 Sample calculation of volume of Cu(0) and Cu(I) at +0.4 V_{RHE} .

Figure S-10 displays the details for the calculation of the volume of Cu(0) and Cu(I) from the full stack at +0.4 V_{RHE} . First, the region to collect spectra (**Fig. S-10a**) was identified by threshold masking the component maps. Then the average spectra of Cu(0) region and Cu(I) region were extracted from the full stack at +0.4 V_{RHE} and shown in **Fig. S-10b**. The average spectra of Cu(0) and Cu(I) regions were analyzed using SVD curve-fitting to calculate the composition in terms of an average thickness; the results are shown **Fig. S-10c** and **Fig. S-10d**. These values were combined with the area of the Cu(0) and Cu(I) regions to determine a total volume, and volume ratio, of Cu(0) and Cu(I) as a function of the potential. The results for +0.4 V_{RHE} are summarized in **Table S.2**. A similar compositional analysis was carried out from the STXM results at all potentials, as further described in **section S-10**.

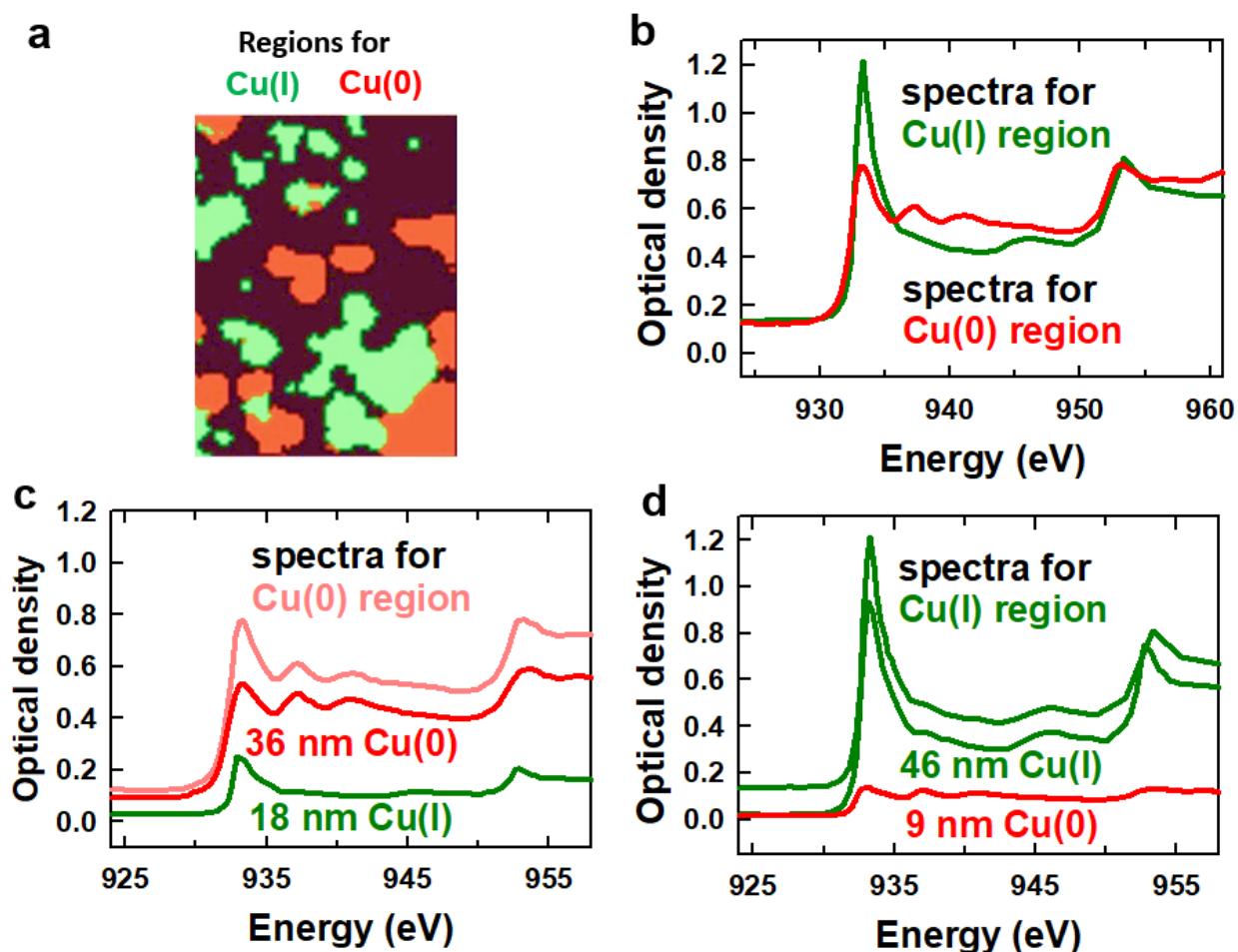


Figure S-10 Analysis of the STXM full stack of particles at +0.4 V_{RHE} . (a) regions for Cu(I) and Cu(II) from the component maps. (b) the average spectra of region Cu(0) and Cu(I). (c) Composition of average spectra from Cu(0) region using SVD curve-fitting. (d) Composition of average spectra from Cu(I) region using SVD curve-fitting.

Table S.2 Volume compositional analysis for the full stack at +0.4 V_{RHE} .

Regions	Area	Average thickness	Volume of Cu(0) (μm^3)	Volume of Cu(I) (μm^3)
Cu(0) region	2.1 μm^2	36 nm Cu(0) 18 nm Cu(I) Residual 0.035(OD)	76*10 ⁻³	38*10 ⁻³
Cu(I) region	2.3 μm^2	9 nm Cu(0) 46 nm Cu(I) Residual 0.053(OD)	21*10 ⁻³	106*10 ⁻³
			Cu(0)	Cu(I)
Total volume (μm^3)			96 *10 ⁻³	144*10 ⁻³
Volume Ratio			40%	60 %

a. The uncertainty of $\pm 10\%$ is estimated from a combination of statistical and systematic uncertainties.

Section S-10 Volume composition of Cu(0) and Cu(I) at various potentials

First, Cu(I)-rich and Cu(0)-rich regions were identified by threshold masking the component maps from STXM full stack at +0.4 V_{RHE} shown in **Fig. 5**, as shown in **Fig. S-10a**. The average spectra of Cu(I)-rich and Cu(0)-rich regions from STXM full stack at +0.4 V_{RHE} were then extracted and compared in **Fig. S-10b**. The average thickness of Cu(I) and Cu(0) in each region was determined by SVD curve fitting the average spectra to the quantitative OD1 reference spectra (**Fig. 3b**), as shown in **Fig. S-10c** and **Fig. S-10d**. Subsequently the volumes of each Cu species were calculated from the average thickness and the geometric cross-sectional area of the catalyst regions. These results are summarized in **Table S-3**.

Table S.3 Volumes of Cu(0) and Cu(I) at various potentials.

Potentials (V _{RHE})	STXM measurements	Total volume of Cu(0) (10 ⁻³ *μm ³)	Total volume of Cu(I) (10 ⁻³ μm ³)	Volume Ratio of Cu(0)	Volume Ratio of Cu(I)
+0.4	4-E stack	112	150	43%	57%
	Full stack	96	144	40%	60%
+0.3	4-E stack	111	123	48%	52%
	Full stack	107	88	55%	45%
+0.2	4-E stack	102	67	60%	40%
	Full stack	106	44	71%	29%
+0.1	4-E stack	96	22	82%	18%
	Full stack	115	6	94%	6%
0	4-E stack	123	9	93%	7%
	Full stack	119	0.1	99.9%	0.1%
-0.2	Full stack	120	1	99.1%	0.9%
-0.4	Full stack	128	0.6	99.5%	0.5%
-0.6	Full stack	123	1.2	99.0%	1%

a. The uncertainty of ± 10 % is estimated from a combination of statistical and systematic uncertainties.

Section S-11 Evaluating radiation dose and possible radiation damage.

S-11.1 Evaluating radiation dose

Methods to evaluate the dose delivered in a STXM measurement have been reported elsewhere^{S2 S3, S4} and have been used to estimate the dose delivered in the measurements reported in this work. Briefly, the dose delivered by STXM in units of MGy (a) is given by^[S2]

$$a(STXM) = \frac{I_0(1 - e^{-OD})Et}{\varepsilon V \rho} \times 1.60 \times 10^2 \quad (\text{Eqn. S2})$$

where I₀ is the incident flux (number of photons per second), E is the exposure energy in eV, t is the

exposure time in milliseconds (ms), ϵ is the detector efficiency (measured to be 80% at the Cu 2p edge)^[S5], V is the volume of the exposed region, ρ is the sample density (g/cm³), and OD is the optical density of the exposed region at the energy of irradiation. Based on eqn. S2 and the experimental parameters summarized in **Table S.4**, the dose for the 54E in-situ STXM full stacks is ~110 MGy. The average dose for 4E STXM stacks is ~10 MGy.

Table S4 Estimating dose for *in-situ* full 54- E STXM stack

symbol	A210915069- mostly Cu(I)	A210915099- mostly Cu metal	comments
I ₀	6 MHz	11 MHz	-
OD	0.55	0.45	OD average over energy range measured
E	933 eV	933 eV	
t	162 ms	162 ms	Although the measurements took a long elapsed time (~30 min), the actual time the beam was on any given ~40 nm spot of the sample was quite small, (3 ms dwell/pixel ; 54 images = 162 ms total)
ϵ	0.8	0.8	[S5]
V	100000 nm ³	110000 nm ³	Different density and thickness
ρ	7 g/cm ³	9 g/cm ³	
Dose	108 MGy	120 MGy	Average is ~110 MGy

2. Evidence that there is no damage from *in-situ* STXM

Before the STXM measurements reported in this paper, several STXM 4E-stack and full stack measurements were made on a different region in the same cell, with results shown in **Figure S-11**. No significant change in morphology or oxidation state distributions were detected by 4E stack analysis before and after a 54-E stack. The subsequent *in-situ* STXM experiments were not performed in this region because some Cu particles dissolved after applying high positive potentials. The Cu particles were re-deposited on the working electrode and the study was performed in the region shown in the paper.

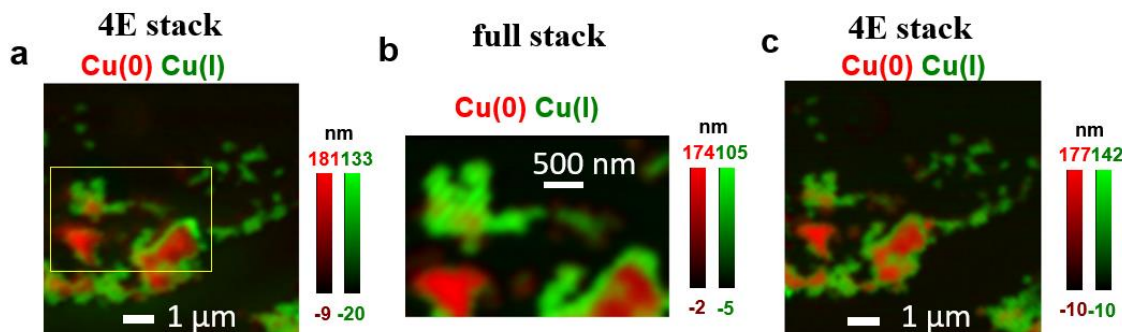


Figure S-11 Chemical maps measured in sequence on a different region in the same cell under *in-situ* conditions, prior to the studies reported in the manuscript. (a) 4-E stack, A210919045. The yellow frame is the region for full stack (b) Full stack, 210919046. (c) 4-E stack, 210919048.

In addition, after all the *in-situ* STXM measurements shown in the paper (**Fig. 5**), a 4-E stack was measured on a larger region of the electrode, which included adjacent areas which had never been exposed to the X-ray beam (**Figure S-11**). The same morphology and similar oxidation state distributions were found between the area that had been illuminated by STXM measurements and the particles in the un-exposed surrounding area, suggesting there was negligible beam damage on Cu electrocatalysts during *in-situ* STXM measurements.

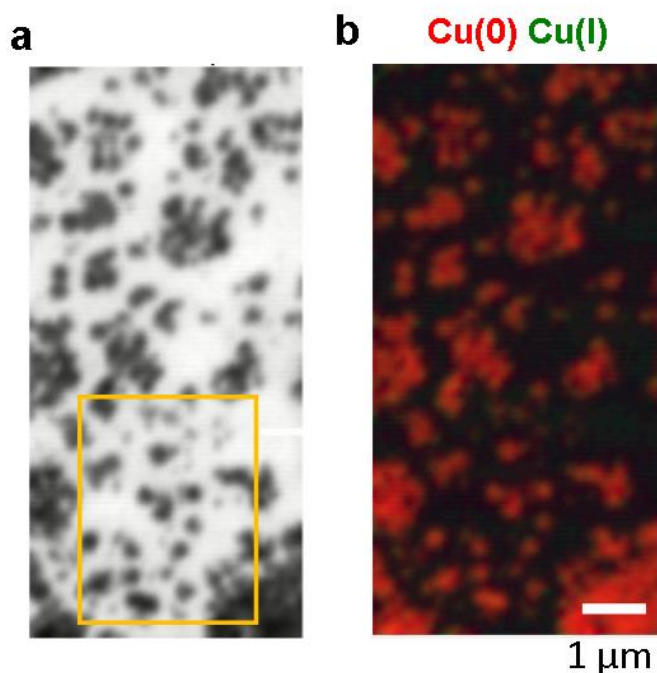


Figure S-12 Chemical maps from a larger region after all the *in-situ* STXM measurements were made in the area indicated by the yellow box. (a) STXM image at 933.5 eV. The yellow frame is the region of all in-situ STXM measurements. (b) color-coded components map for the larger region.

3. Evaluation of possible damage at higher STXM doses (ex-situ, dry)

To further address the radiation damage issue, we intentionally exposed a square region of Cu metal, Cu₂O and CuO to much larger doses. If damage occurred, changes would be visible at specific energies and/or in the derived chemical maps in the region heavily dosed. Despite intentional doses greater than 5000 MGy (more than 7 times larger dose than the total beam dose used for the measurements reported in **Fig. 5** and **6**, no changes beyond statistical variations were observed – see **Figs. S-13** and **S-14**.

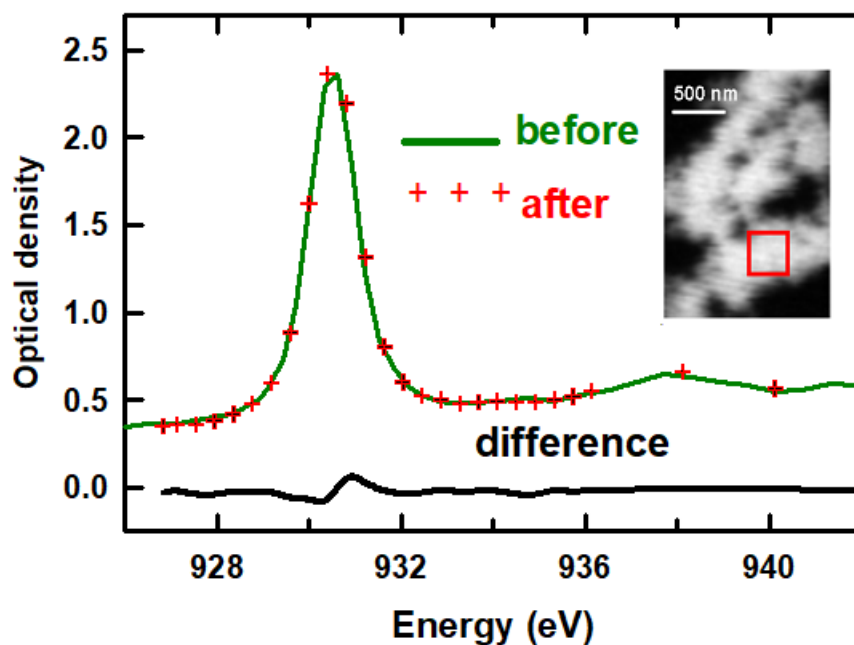
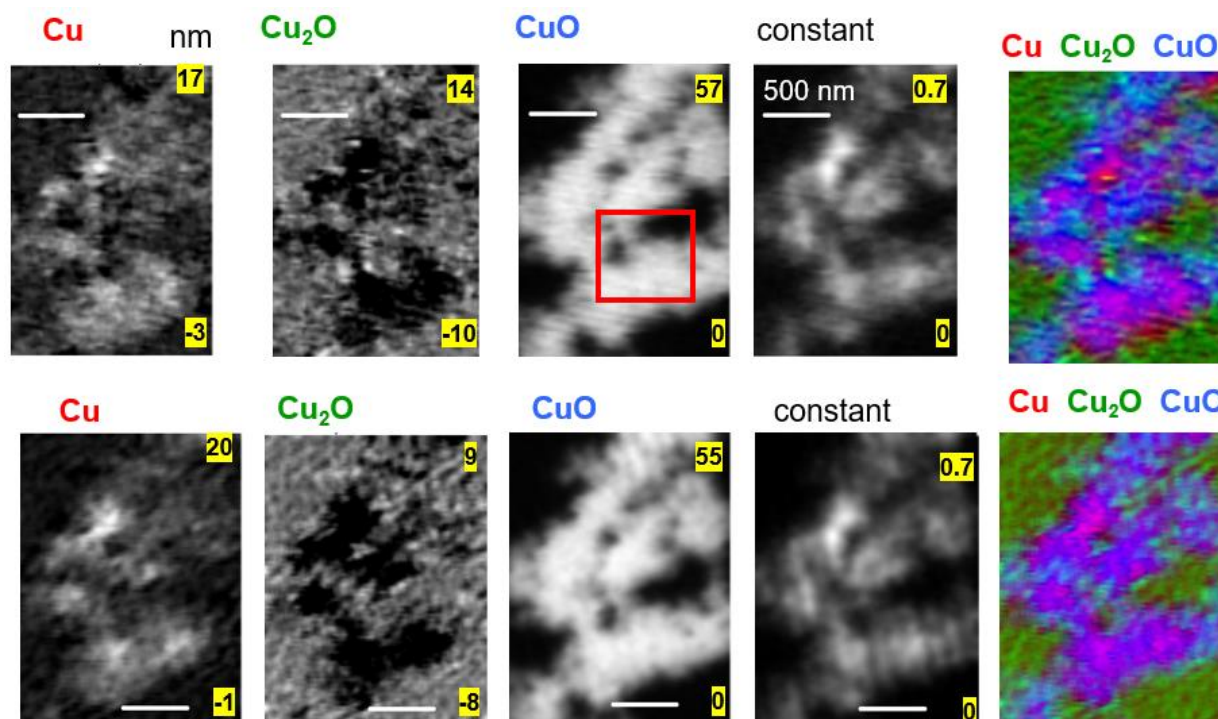


Figure S-14. Comparison of Cu L_3 spectra of the area of added dose before and after the ~ 5000 MGy dose.

References:

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