

Cell Reports Physical Science, Volume 4

Supplemental information

Copper carbon dioxide reduction electrocatalysts

studied by *in situ* soft X-ray spectro-ptychography

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Note S1. X-ray refraction, CDI, and basic concepts of ptychographic reconstruction

A number of reviews of X-ray ptychography have been published. [S1 – S6]. The following is a distillation of these. Ptychography is a scanned coherent diffraction imaging (CDI) method which consists of measuring diffraction images (DI) generated when a beam of partially or fully coherent X-rays passes through an optically thin sample ($OD < 2$). The DI are typically measured using a high performance camera with single X-ray photon/pixel sensitivity, placed downstream from the sample (**Fig. S1**).

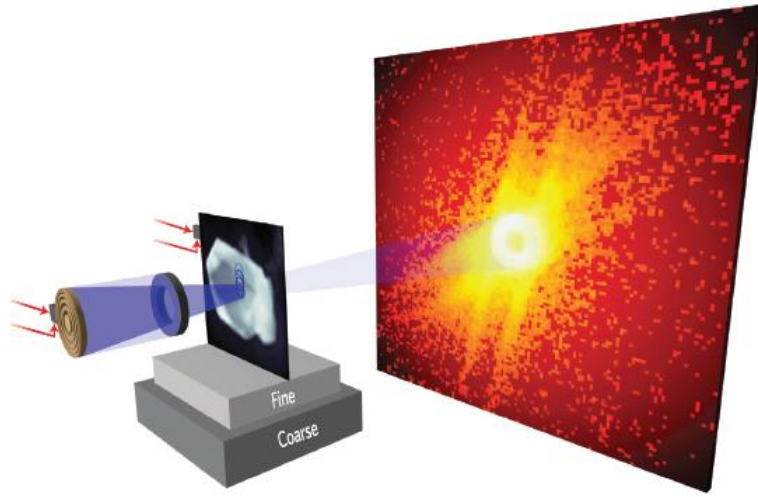


Figure S1. Schematic of measurement of coherent diffraction image (DI) from one point on a sample. Sets of these DI measured with overlap of the sampled points constitutes a scanned CDI or ptychographic measurement. Reproduced with permission from *Nature Photonics* **8**, 765-769 (2014).

The interaction of X-rays with an optically thin sample depends on the refractive index of the material(s), η , which is a complex, photon energy dependent quantity

$$\eta = (1 - \delta) - i\beta \quad \text{Eqn SI-1.1}$$

where the real part ($1 - \delta$) is the phase and the complex part (β) is the amplitude response of the X-ray interacting with the material. The propagation of an X-ray through a material is a spatial, temporal and photon energy dependent quantity that can be described by

$$U = Ae^{i\varphi} \quad \text{Eqn SI-1.2}$$

where A is the amplitude at a given position and time, and φ is a complex propagation/loss function, which contains η . Upon interaction with a sample, the complex wavefield of the coherent scattered light (SC), $U^{SC}(\mathbf{r}, \omega)$, is related to the wavefield of the light impinging on the sample (inc), $U^{inc}(\mathbf{r}', \omega)$, by

$$U^{SC}(\mathbf{r}, \omega) = \int_V F(\mathbf{r}', \omega) U^{inc}(\mathbf{r}', \omega) \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad \text{Eqn SI-1.3}$$

where $\mathbf{r}$ and $\mathbf{r}'$ are time dependent position vectors of the X-ray after and before the sample, ω is the angular frequency of the light ($= \omega 2\pi$; the photon energy (E) is given by $E=h\nu$) and $e^{ik|\mathbf{r}-\mathbf{r}'|}/|\mathbf{r}-\mathbf{r}'|$ is a plane wave description of the light wave. The DI measured in ptychography only measure the amplitude of the scattered X-rays, U^{SC} . The challenge of ptychographic reconstructions is to solve the phase inversion problem [S4, S6].

Amplitude and phase images of the sample (object) and the incident X-ray beam (probe) can be derived from sets of DI using an iterative algorithm. For a single DI the reconstruction can be described conceptually by (**Fig. S2a**), while this approach uses Fourier transforms ($F\{\rho(x)\}$ and $F^{-1}\{\rho(x)\}$) as propagators, other mathematical functions can be used.

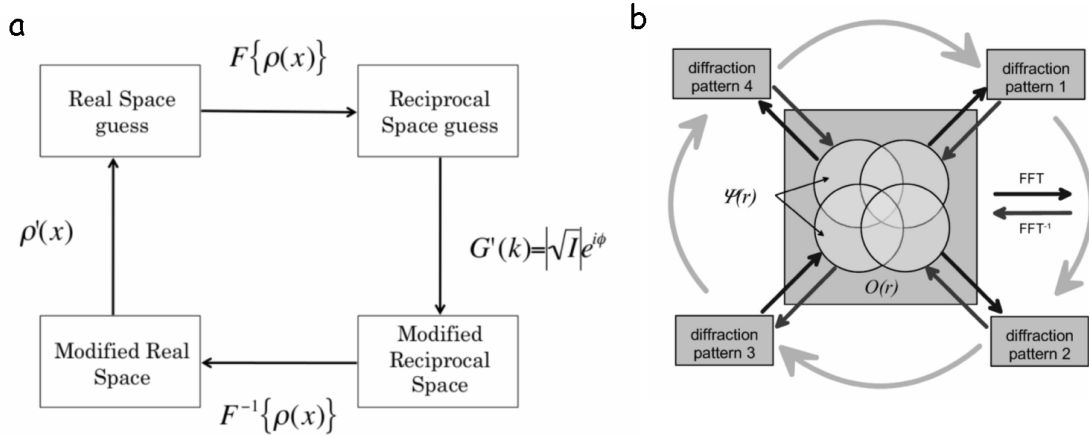


Figure S2. Descriptions of the reconstruction process. (a) Schematic outline of an iterative procedure to generate the phase and amplitude of an object from a single coherent diffraction image. (b) Outline of iterative procedure to generate the phase and amplitude of an object from sets of diffraction images measured with spatial overlap. (Figure reprinted with permission from *Phys. Rev. Lett.* 98, 034801 (2007) [S3], copyright 2007 by the American Physical Society).

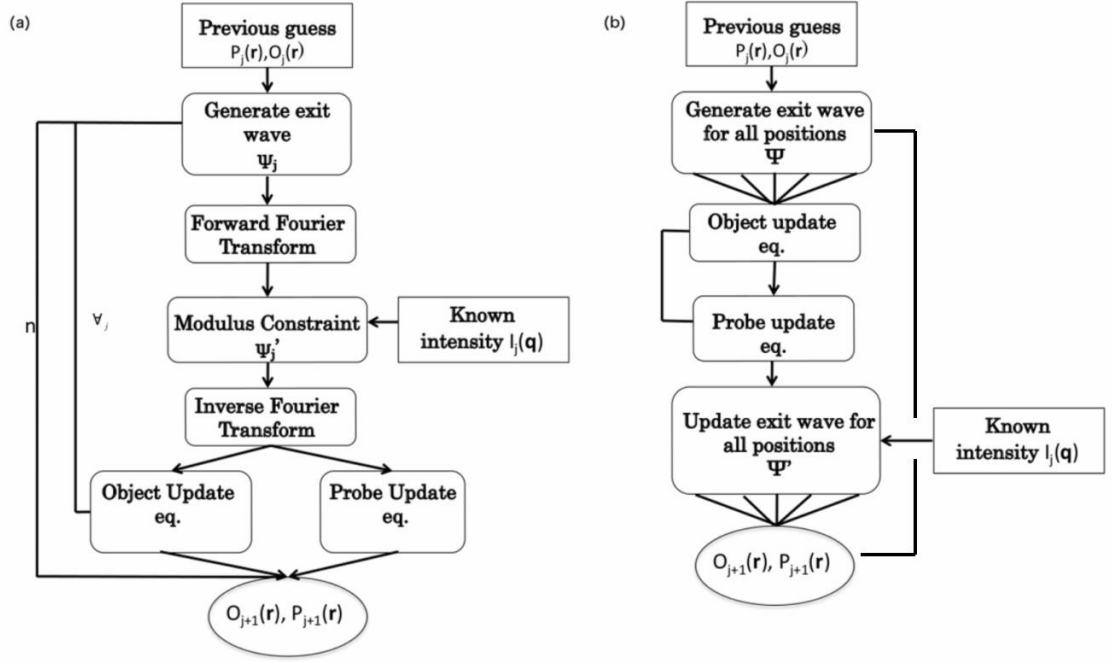


Figure S3. Descriptions of the reconstruction methods. Flow diagrams for, (left) the extended Ptychographic Iterative Engine (ePIE), and (right) Difference Method (DM) algorithms for reconstruction of sets of diffraction images recorded over a set of overlapping positions on a sample. The ePIE method works through the set of DI images in a quasi-serial pattern, whereas the DM method carries out the algorithm in a more parallel fashion. In each case a guess is made of the starting probe properties, while the initial phase of the object is set to a constant. On each iteration, the updated (n^{th}) amplitude prediction of the object is compared with the measured diffraction images, with further constraints in the overlapping spatial regions. The difference is then used to refine the phase and amplitude predictions for the $(n+1)^{\text{th}}$ iteration. Typically a pre-set number of iterations is used, rather than a self consistent approach (iteration until the difference falls below a user-defined magnitude). Adapted from Figure 2.6 of S5, with permission from the author.

In the case of ptychography where multiple diffraction images are measured with spatial overlap, a more extended reconstruction process is required (**Fig. S2b**). Additional steps are used to constrain the functions describing the sample and the probe in the spatially overlapping regions. Two methods used for such iterative ptychographic reconstruction are (i) the extended Ptychographic iterative engine (ePIE) developed by Maiden et al. [S4] and (ii) the Difference Map (DM) algorithm, developed by Thibault et al. [S2]. **Figure S3**, taken from the PhD thesis of Shemilt [S5], outlines these two approaches. In this work an alternating projection (AP)

reconstruction method implemented in PyNX [S7] was used, since it was found to be more stable and provide more rapid convergence than DM method implemented in PyNX.

Note S2. Estimation of spatial resolution of STXM and ptychography

Figure S4 presents results of spatial resolution evaluation using the Fourier ring correlation (FRC) method [S8]. Ptychographic reconstructions using large degrees of overlap introduce a large degree of correlation among the signal at adjacent spatial points. Thus inaccuracies could be introduced by using the even / odd pixel index method of using FRC to evaluate spatial resolution from a single ptychographic reconstructed image. In order to avoid such artifacts, we have used 2 independently measured ptychographic data sets from the same spatial region. These images are displayed as **Fig. S5a** and **S5b**. The pixel size in these images is 5.5 nm. The FRC applied to these two images is presented in **Fig. S5c**. Using the half-bit criterion, probably the most common metric used in soft X-ray ptychography, a spatial resolution of 7 nm (half-pitch) or 14 nm (full pitch) is estimated. The more conservative half-height criterion results in a spatial resolution of 16 nm (half-pitch) or 32 nm (full pitch). Thus, we conservatively estimate the spatial resolution of the *in situ* spectro-ptychography as 25 ± 5 nm.

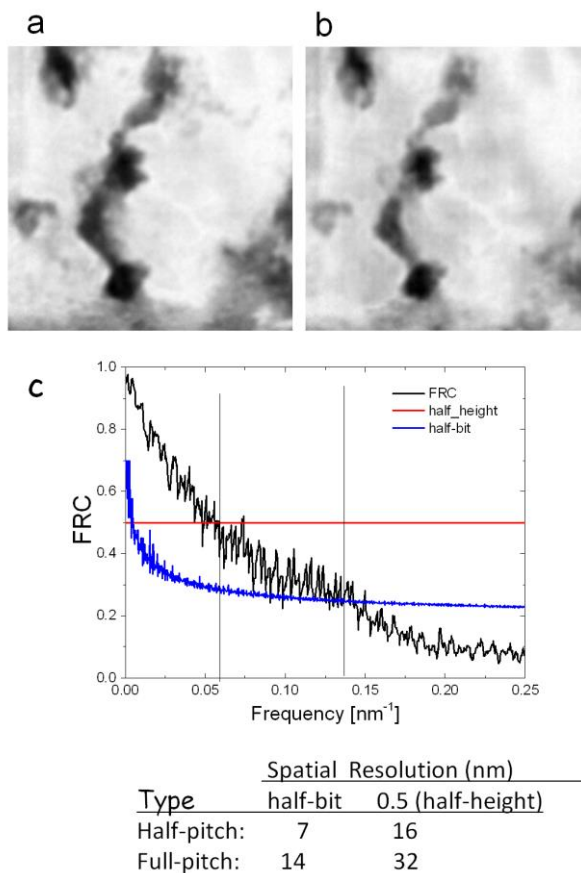


Figure S4. Fourier ring correlation (FRC) analysis of the spatial resolution of the cubic particle in area C. (a) first image. (b) second image (from same area). (c) FRC plot.

Figure S5 plots line profiles across abrupt features in the ptychography and STXM images of **area C**. The abruptness of the profile across the STXM image (**Fig. S5a**) is 80 ± 10 nm, while that for the profile across the ptychography image (**Fig. S5c**) is 37 ± 4 nm, as measured from the 20 % to 80 % intensity levels.

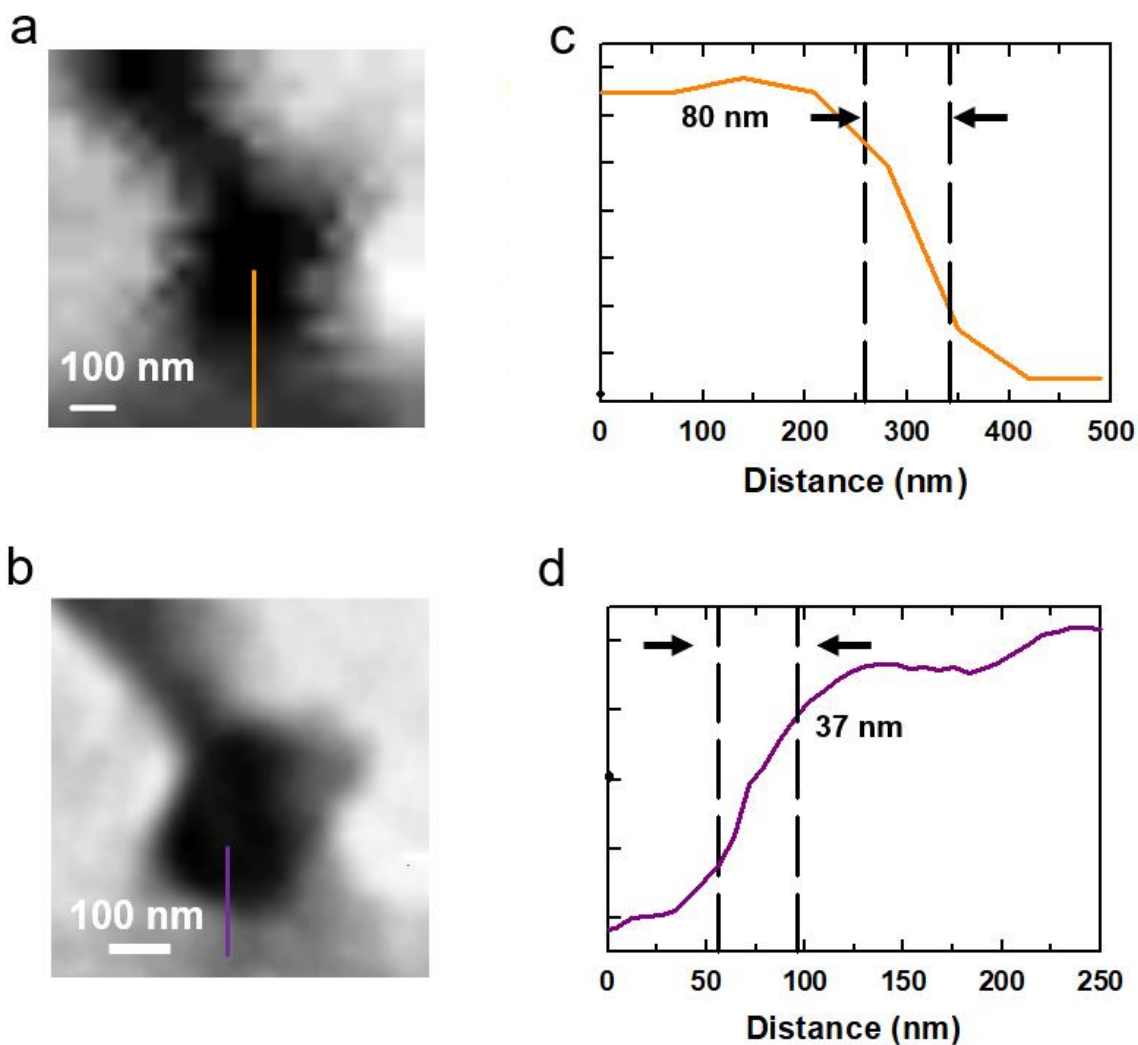


Figure S5. Estimation of spatial resolution from a knife-edge measurement (line profile across a high contrast boundary) in area C. (a) *In situ* STXM image at 933.3 eV. (b) *In situ* ptychography amplitude image at 933.3 eV. (c) Line profile across the orange line. The abruptness of the rise in optical density (20% – 80 %) is 80 ± 10 nm. (d). Line profile across the purple line. The abruptness of the rise in optical density (20% – 80 %) is 37 ± 4 nm.

Note S3. Cu L₃ (2p_{3/2}) reference spectra

Figure S6 presents the Cu L₃ reference spectra of Cu metal, Cu₂O and CuO used for generating quantitative component maps from the absorption stacks and spectra derived from spectroptychography amplitude image sequences. These spectra were digitized carefully from the paper by Jiang et al. [S9]. The dots indicate the 4 energies used to produce chemical mapping from the 4-E stack measurements. By carefully selecting energies which best differentiate the 3 oxidation states, we found that the 4-E stack can provide similar chemical information and mapping of the Cu(0), Cu(I) and Cu(II) species as achieved with 40-energy stack measurements.

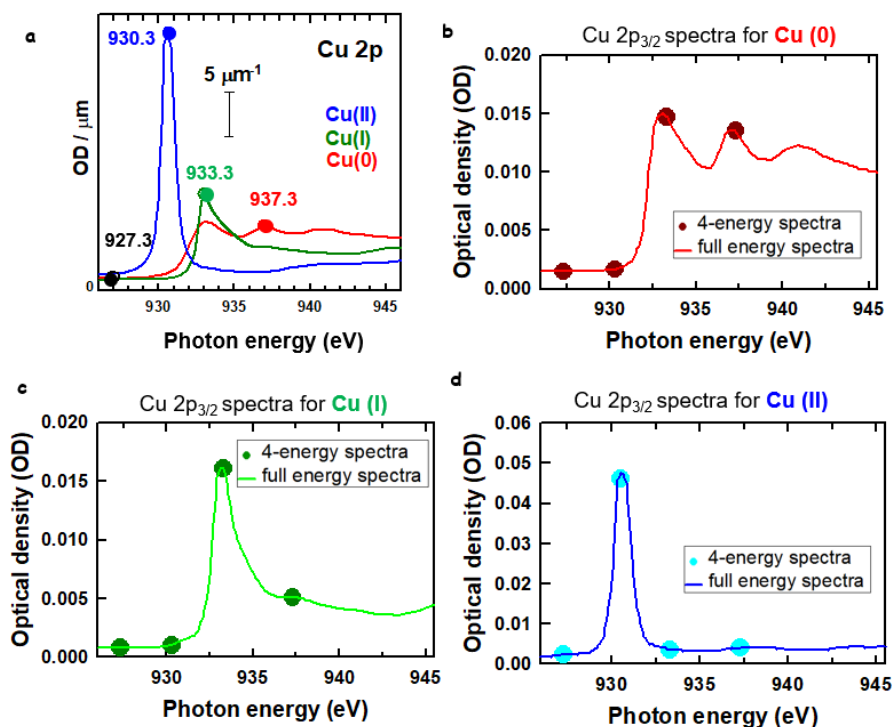


Figure S6. Cu L₃ (2p_{3/2}) reference spectra. Spectra of Cu metal, Cu₂O and CuO digitized from Jiang et al. [S9]. The intensity has been placed on an absolute scale (optical density per nm at standard density) [S10]. (a) 4 energies location on the 3 Cu reference spectra plotted on the same scale. (b) Cu(0). (c) Cu(I). (d) Cu(II). The energies used in the 4-E stack approach are indicated.

Note S4. STXM and spectro-ptychography 4-E stacks of area A

Figure S7 presents the 4 energy (4-E) STXM transmission images (**Fig. S7a**) and the 4-E spectro-ptychography amplitude transmission images (**Fig. S7b**) of **area A**. The spectral signals averaged over all particles in **area A** are displayed in **Fig. S7c** and **Fig. S.d**. Comparison to the reference spectra indicate these particles are a combination of Cu(I) and Cu(II). **Figure S8** displays the component maps for Cu(I) and Cu(II) derived by singular value decomposition (SVD) of the STXM (**Fig. S8a-c**) and spectro-ptychography (**Fig. S8d-f**). **Figure S7** presents the average STXM 4-E spectra and average spectra-ptychography 4-E spectra of the particles in **area A** to show the existence of Cu₂O and CuO.

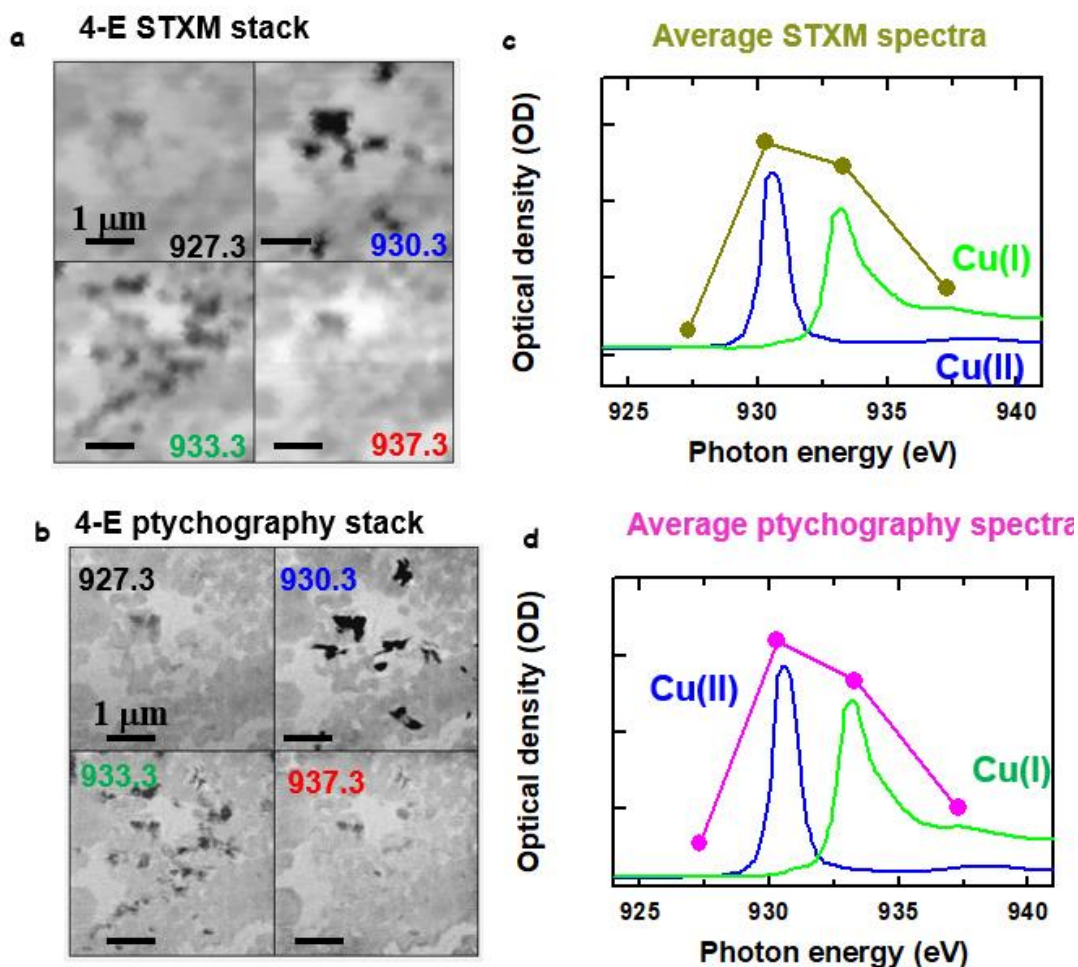


Figure S7. 4-E STXM and spectro-ptychography stacks of area A. (a) STXM transmission images at 4 E. (b) Spectro-ptychography amplitude images at 4 E. (c) average STXM 4-E spectra of the Cu particles in **area A** compared to Cu(I) and Cu(II) spectra. (d) average spectra-ptychography 4-E spectra of the particles in **area A** compared to Cu(I) and Cu(II) spectra.

Note S5. Analysis of the STXM and spectro-ptychography 4-E stacks of area A

Figure S8 presents an SVD fit analysis of the STXM and ptychography 4-E stack of **area A**. Using suitable, quantitative reference spectra (**Fig. S6**), OD (STXM) or absorption images derived from reconstructed amplitude images are reduced to a set of chemical component maps by the singular valued decomposition (SVD) procedure, which is described in detail in **Note S13**.

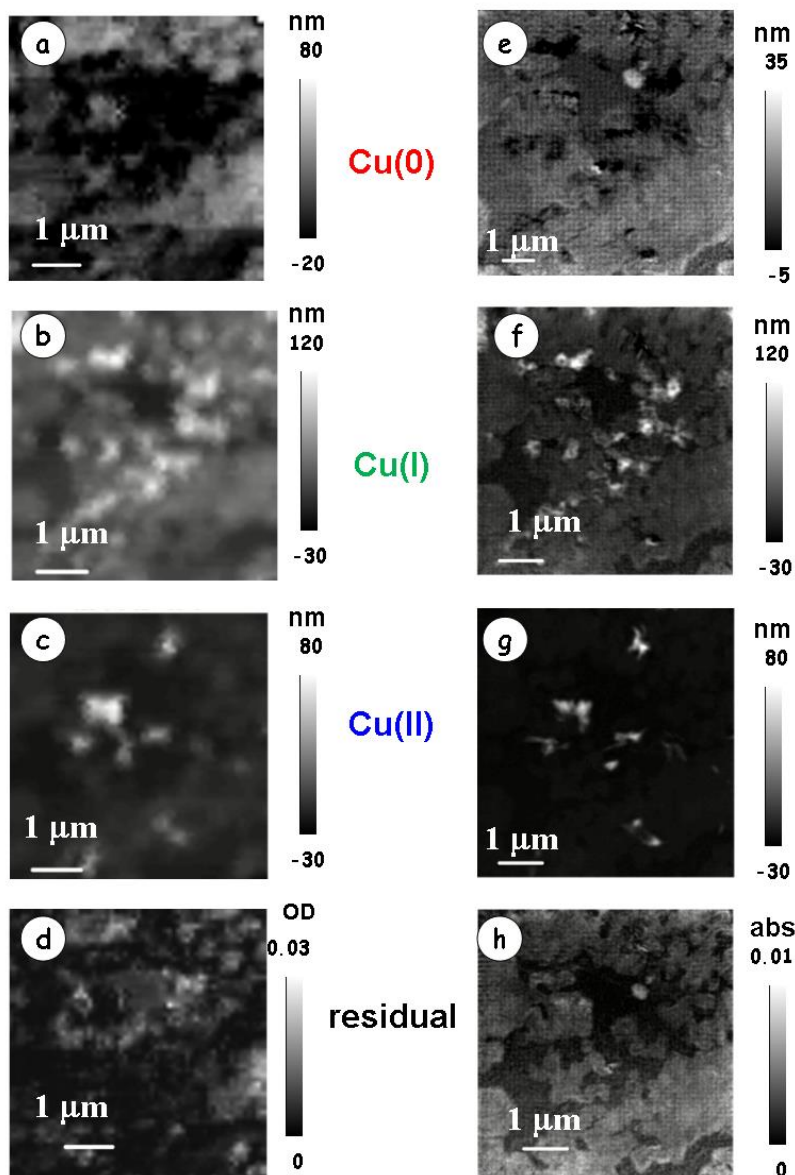


Figure S8. SVD fitting analysis of 4-E STXM and 4E spectro-ptychography stacks for **area A** (a) Cu(0), (b) Cu(I), (c) Cu(II) component maps and (d) residual map from SVD analysis of the 4-E STXM stack. (e) Cu(0), (f) Cu(I), (g) Cu(II) component maps and (h) residual map from SVD analysis of the 4-E spectro-ptychography stack.

Note S6. Analysis of spectro-ptychography full (40-E) stacks of area B

Figure S9 presents details of the analysis of the ptychography full stack of **area B**. **Figure S9a** plots the chronoamperometry (current vs time) graph when $+0.7 V_{\text{RHE}}$ was applied. There is a pulse-like structure superimposed on the current versus time chronoamperometry signal. This is due to a combination of a small X-ray induced current (XBIC) and the use of a shutter to block the X-ray beam while the photon energy is changed, which takes ~ 15 s. During the time the X-ray beam is off the current changes by the amount induced by the X-ray beam. Once the shutter is re-opened and the ptychography measurements start, the XBIC signal is again observed. The ~ 85 s taken to measure the ptychography image at each energy matches the scan parameters used (900 diffraction images (DI), 60 ms dwell/DI plus ~ 30 ms to readout each DI image). This type of XBIC signal has been reported in other X-ray measurements, and in fact has been used as an imaging signal [S11].

Figure S9b shows the regions from which Cu(I)-rich and Cu(0)-rich spectra (**Fig. S9c**) were extracted. **Figure S9d** shows the spectral decomposition of the spectrum of the Cu(0)-rich selected area. **Figure S9e** shows the spectral decomposition of the spectrum of the Cu(I)-rich selected area, suggesting a higher amount of Cu(I) in this region.

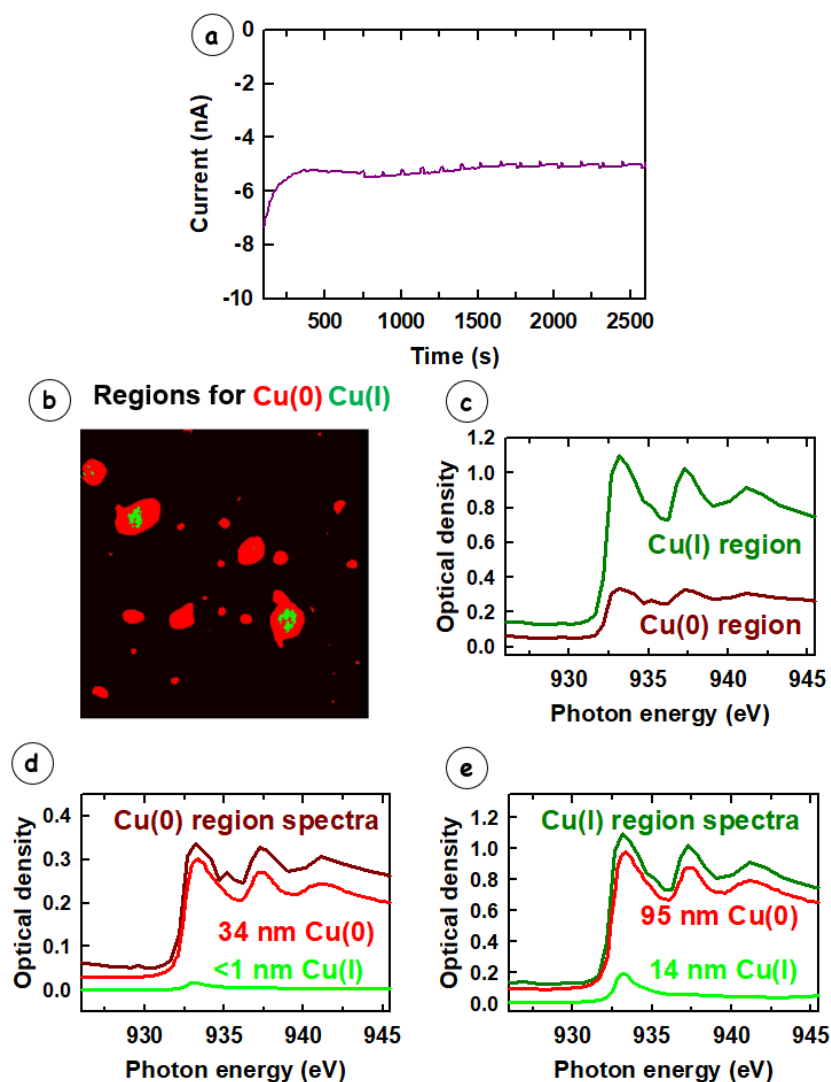


Figure S9. Analysis of the ptychography amplitude full stack of area B. (a) current vs time graph at the +0.1V vs RHE (b) regions for Cu(I) and Cu(II) from the component maps. (c) the average spectra of masked Cu(0)-rich and Cu(I)-rich regions. (d) decomposition of average spectra from the masked Cu(0)-rich region using SVD curve-fitting. (e) decomposition of average spectra from Cu(I) region using SVD curve-fitting.

Note S7. Physical basis of ptychography amplitude and ptychography phase signals

Figure S10 sketches the physical origin of the X-ray absorption, ptychography amplitude and ptychography phase signals. Absorption spectra derived from ptychographic amplitude and integrated X-ray transmission signals are similar, but not the same. Phase spectra derived from ptychographic reconstructions are quite different than absorption or amplitude-derived spectra. An interesting question, still incompletely answered in the literature, is, “*Is there additional, independent information from the object phase signals provided by ptychographic reconstruction ?*”.

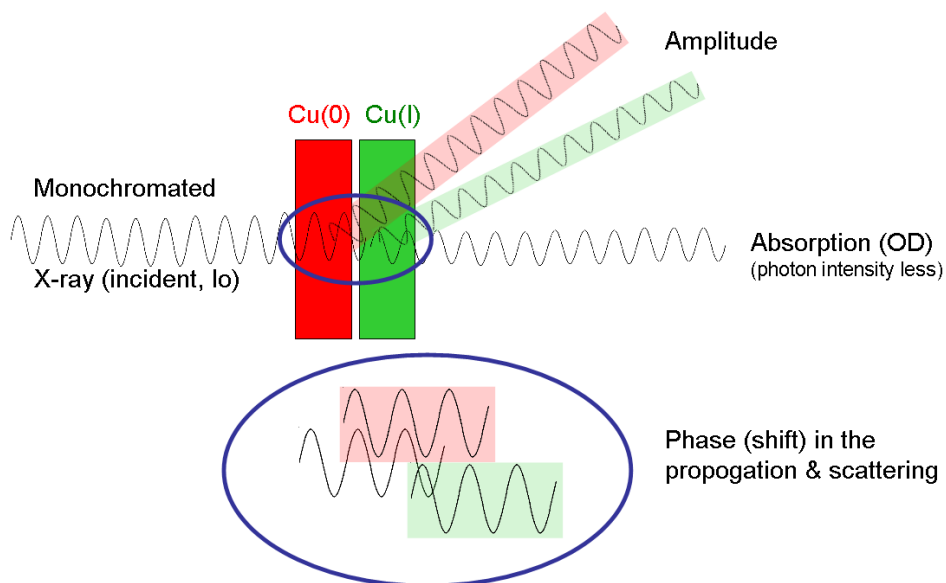


Figure S10. Schematic of the physical origin of the X-ray absorption, ptychography amplitude, and ptychography phase signals.

Note S8. Chronoamperometry at potentials from +0.1 to -0.85 V_{RHE}

Fig. S11 shows the chronoamperometry current curve at five potentials from +0.1 to -0.85 V_{RHE}. Only the parts of the current response after it became stable are plotted.

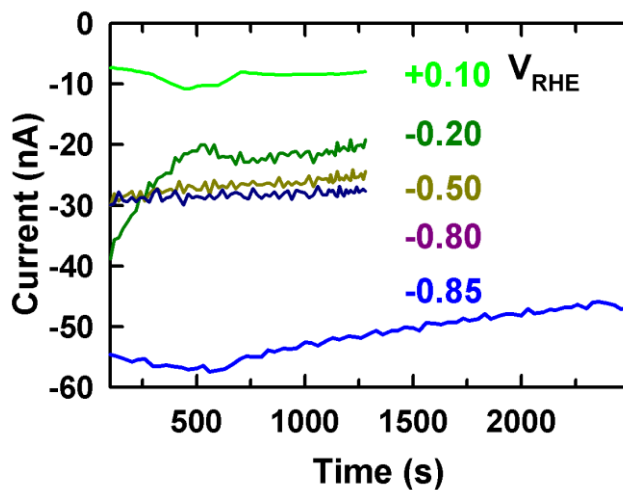


Figure S11. Current versus time curve at each potential. +0.1 to -0.85 V_{RHE}

Note S9. Spectro-ptychography 4-E stacks of area C at 5 potentials

Figure S12 displays the Cu(0), Cu(I) and Cu(II) component maps of **area C** at 5 potentials [OCP, +0.1, -0.2, -0.5 and -0.8 V_{RHE}] derived from SVD fitting of the absorption images at 4 energies, derived from the 4-E ptychography amplitude stacks, analyzed through SVD-fitting using the OD1 reference spectra of Cu(0), Cu(I) and Cu(II) under various indicated potentials.

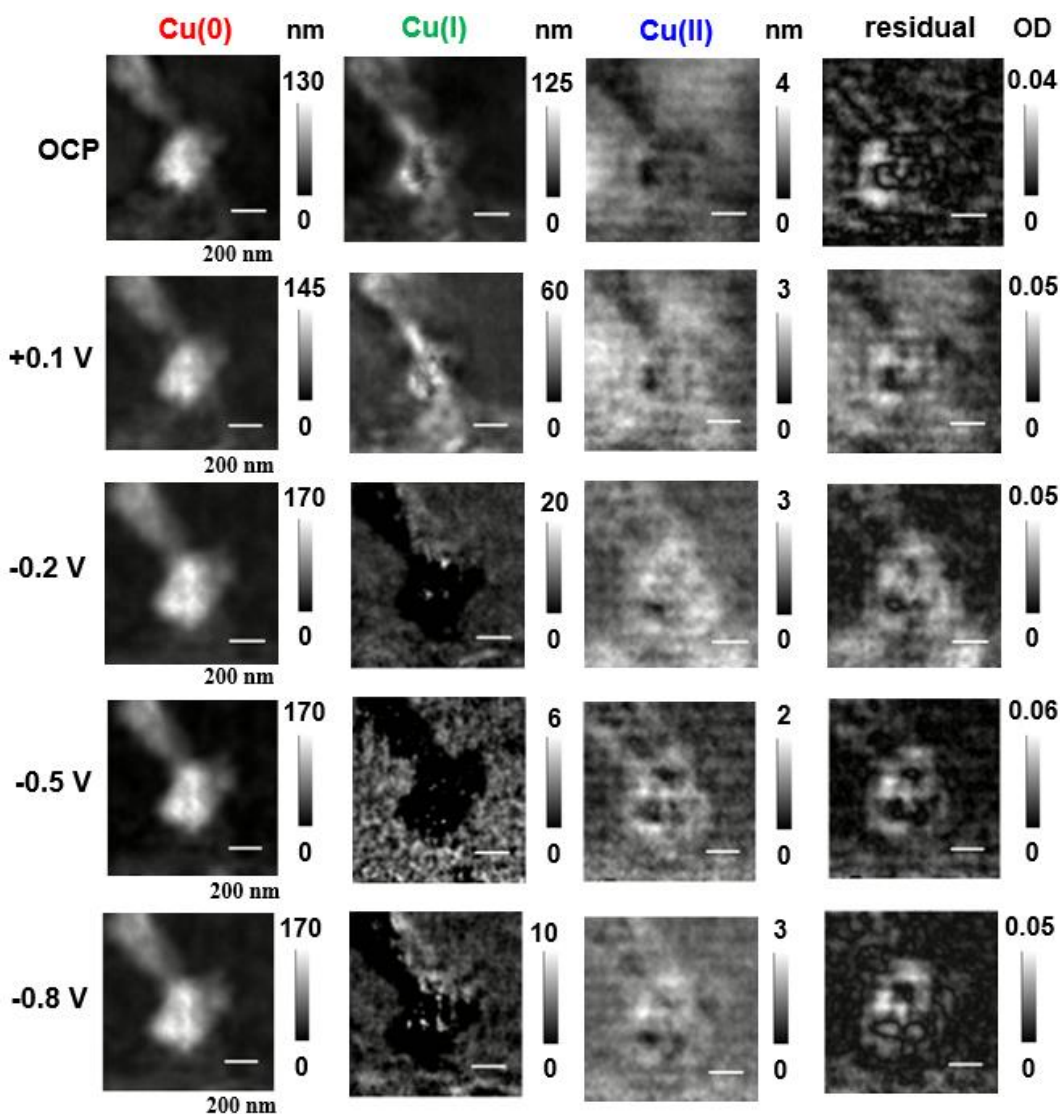


Figure S12. Results for 4-energy ptychography amplitude stacks of area C analyzed through SVD-fitting using the OD1 reference spectra of Cu(0), Cu(I) and Cu(II) at the indicated potentials.

Figure S13 plots the 4E spectra for the 5 potentials (averaged of the particle regions), along with the spectrum extracted from the full 34 energy stack with an applied potential of $-0.85\text{ V}_{\text{RHE}}$. The change in slope between 933 and 937 eV between -0.2 V and -0.5 V indicates the reduction of the Cu(I) between these 2 potentials. This figure shows the changes of the 4E spectra due to the conversion of Cu_2O to Cu metal.

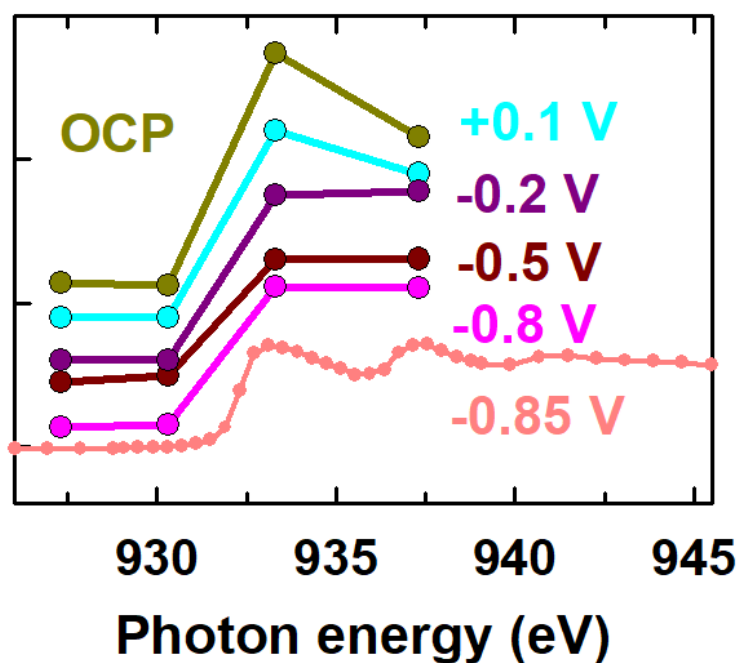


Figure S13. Extracted average spectra from 4-E and 34-E stack ptychography amplitude from the Cu cubic particle at each potential.

Note S10. Multivariate statistical analysis of ptychography stack at +0.1 V_{RHE}

In addition to forward fitting (least squares analysis), multivariate statistical methods [S12 – S14] were applied to the spectro-ptychography stack measured in **area B**. **Figure S14** presents the eigenvalue analysis of the absorption stack derived from the reconstructed ptycho amplitude stack, measured at +0.1 V_{RHE} and an average current of 5 nA. This suggests there could be 4 statistically significant spectral components. In order to check this and to get a rotation of the PCs into a “cluster space” where the spectra are more clearly XAS, a PCA_GUI cluster analysis was performed. The results of this analysis are presented in **Fig. S15**. The statistical evaluation reports that there are only 3 statistically significant spectral components, despite using the first four PCs in the cluster analysis. Further the first component is representative of 97 % of all pixels, while the second cluster component, which is a spectrum of Cu metal with a small amount of Cu(I) at the center of the thickest particles, is only ~3 % of the pixels. The 3rd component (<1% of the pixels) is clearly noise. Thus the statistical analysis unequivocally supports the conclusion drawn from the forward fitting analysis presented in the manuscript, namely, that even at +0.1V_{RHE}, higher potential than the onset of CO₂R, the particles are mostly Cu metal.

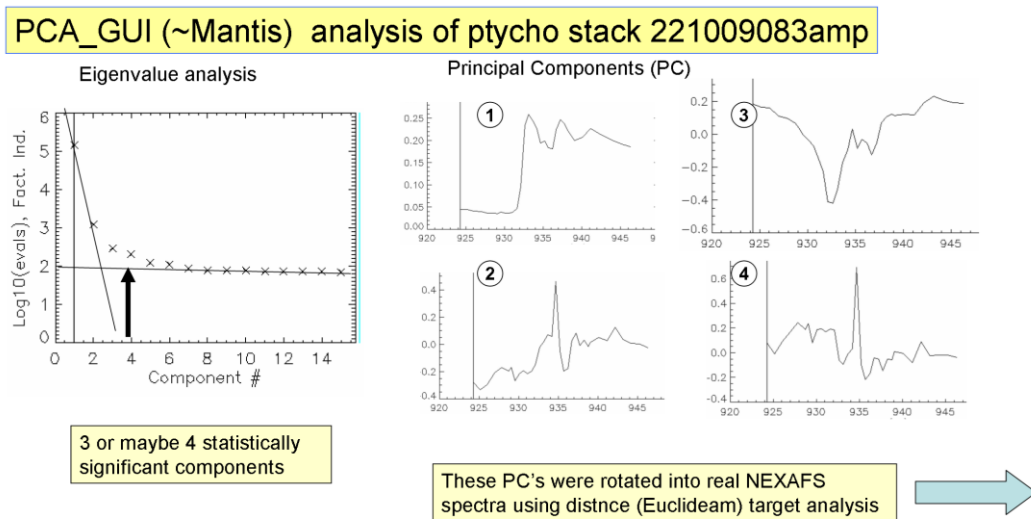


Figure S14. The eigenvalue analysis of the absorption stack derived from the reconstructed ptycho amplitude stack shown in Figure 2. (left) logarithmic display of the eigenvalues (orthogonalized contributions). Typically the statistically significant PCs are those above the extrapolation of the trend at large PC# (low contributions which are patterns of noise). PC components 1, 2, 3, 4 are candidates for statistically significant signals. (right) the first 4 PC spectra (eigenfunctions). Only the first one is “NEXAFS-like”, and is clearly identified as the Cu L₃ spectrum of Cu metal. The second (largest deviation of average spectrum from PC1 looks like a damped inverted Cu metal spectrum.

Rotated (NEXAFS) components

Ptychography stack is 42 mages, each with 579x596 pixels ~ ¼ Megapixel)

The first four eigenspectra (PC components) were used to seek for 4 statistically significant components. Only 3 were found,

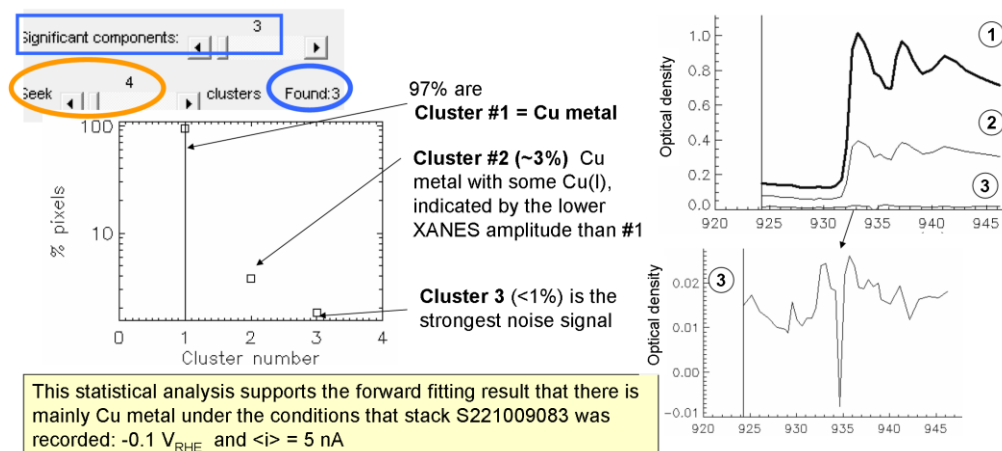


Figure S15. The PCA_GUI cluster analysis of the absorption stack derived from the reconstructed ptycho amplitude stack shown in Fig. 2 (upper left) report of the cluster analysis. (lower left) plot of %-pixels corresponding to the three statistically significant cluster components. (upper right) Plot of the first 3 component spectra on the same OD scale. (lower right) expanded scale plot of the 3rd cluster component.

Note S11. Bubble formation during Cu L₃ spectro-ptychography stack of area C with -0.8 V_{RHE} applied

Figure S16 presents images taken from the full spectro-ptychography stack measured with -0.85 V_{RHE} applied. A bubble formed during the measurements. Despite the continuous change of electrolyte level during the measurement (see supplementary movie, **SI-video.gif**), the ptychography data reconstructed very well. At this potential there is possibility of water splitting, generating H₂. Alternatively the bubble could have been CO, generated by CO₂ reduction. If C 1s measurements could be made from the bubble, these two alternatives could be distinguished.

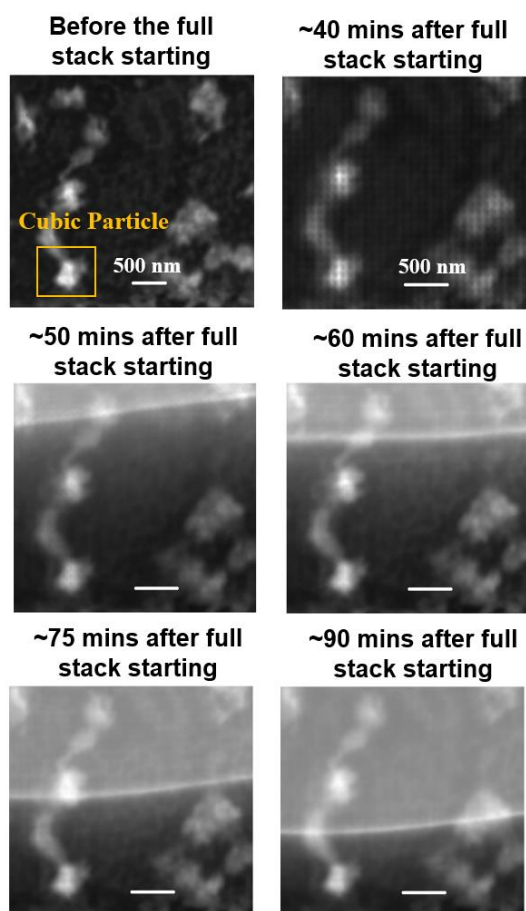


Figure S16. Absorption images from amplitude images reconstructed from spectro-ptycho stack S221008048, with potential fixed at -0.85 V_{RHE}. Interpretation is bubble generation either water splitting (H₂) or CO₂ reduction (CO or other product gases).

Note S12. Chemical maps derived from full spectro-ptychography stack of area C

Figure S17 shows the SVD fitting analysis of ptychography amplitude full stack for the Cu cubic particle measured at -0.85V RHE .

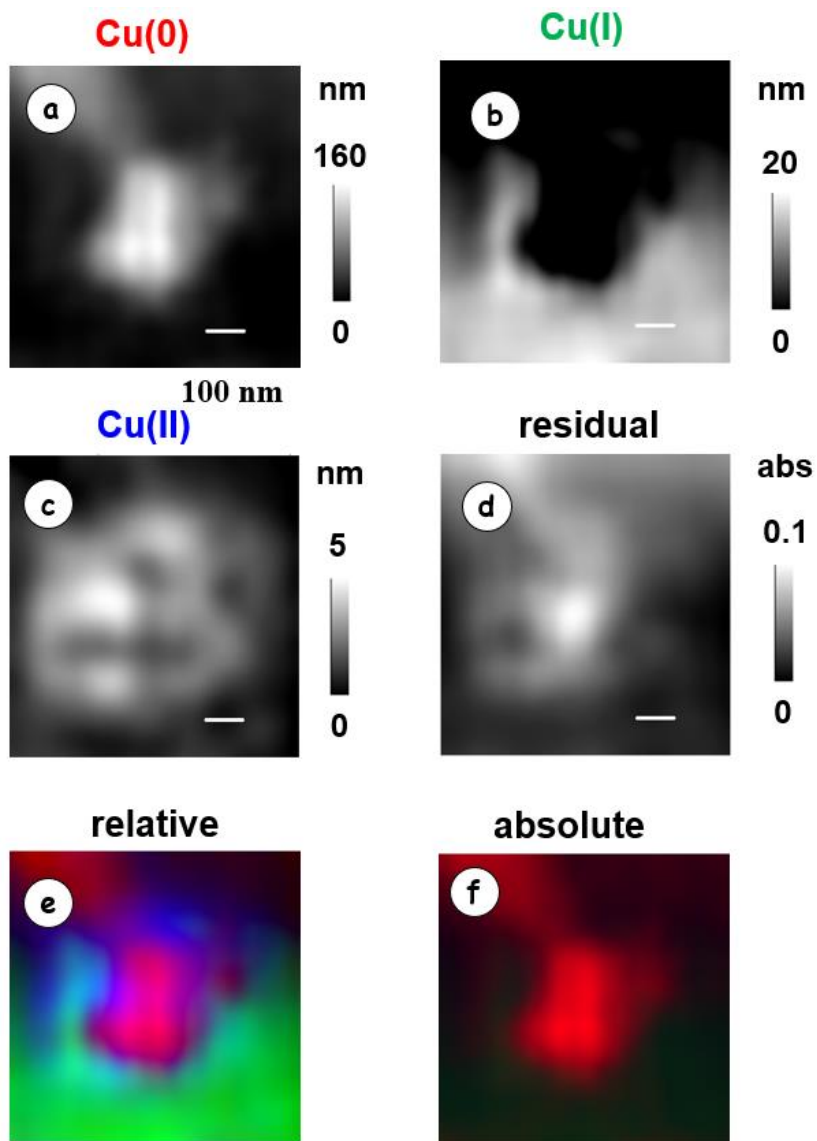


Figure S17. SVD analysis of ptychography amplitude full stack for Cu cubic particle (area C) under $-0.85\text{V}_{\text{RHE}}$. Component maps of (a) Cu(0), (b) Cu(I), (c) Cu(II), (d) residual. Colour-coded component map using (e) relative scaling and (f) absolute scaling. The data has been subjected to a 9-point Savitsky-Golay 2D smooth to remove raster-scan artefacts (original pixel size is 5 nm).

Note S13. Details of the *in situ* flow electrochemical device

Figure S18 displays the microfluidic-based flow electrochemical device for *in situ* STXM and ptychography experiments. The *in situ* device consists of a machined printed circuit board frame (PCB, **Fig. S18a**), a poly(methyl methacrylate) (PMMA) backplate (**Fig. S18b**), a polydimethylsiloxane (PDMS)/glass cell (**Fig. S18c**), and a set of custom electrode-equipped Si / SiN_x / Au chips (Norcada Inc) (**Fig. S18d**). The PCB frame is machined at the Chemical Engineering department in McMaster University. The PMMA backplate and PDMS/glass cell are prepared in the Hitchcock laboratory (Chemistry & Chemical Biology, McMaster University). The PCB frame provides mechanical support for the PDMS/glass/electrode assembly, and electrical connections. Au coated Cu spring clips soldered to the PCB traces are used to electrically connect the 3 Au electrodes - (working/ counter/ reference electrodes (WE/CE/RE) - on the *in situ* chip to a potentiostat via a 4-pin connector and cable. The PCB frame is attached to the PMMA backplate by 8 nylon screws. The PDMS /glass cell is sandwiched between the assembled PCB frame and the PMMA backplate. The PDMS layer contains 4 channels (dotted lines, **Fig. S18c**) which connect flow channels in the *in situ* chips to 4 flow tubes (2 inlet, 2 outlet). The flow tubes can be connected to one or more fluid circulation devices, such as syringe or pressure pumps, to establish a stable flow of electrolytic fluid into the *in situ* chips. The *in situ* chips are purchased from Norcada Inc (Edmonton, Canada, <https://www.norcada.com>) There are 3 Au electrodes on **base chip E (Fig. S18e)**. **Spacer chip F** has a spacer layer (500 nm, 1 μ m or 1.5 μ m thick) defining the height of the flow channel. In this work we used a 1 μ m spacer layer. The SiN_x window area is 240 μ m wide and 100 μ m high. The SiN_x windows have a thickness of 100 nm (base chip E) and 50 nm (spacer chip F). The areas typically used for electrocatalysis studies (dark circles on WE and CE, **Fig. S18e**) are 20 μ m diameter and have a coating consisting of 5 nm Cr and 15 nm Au.

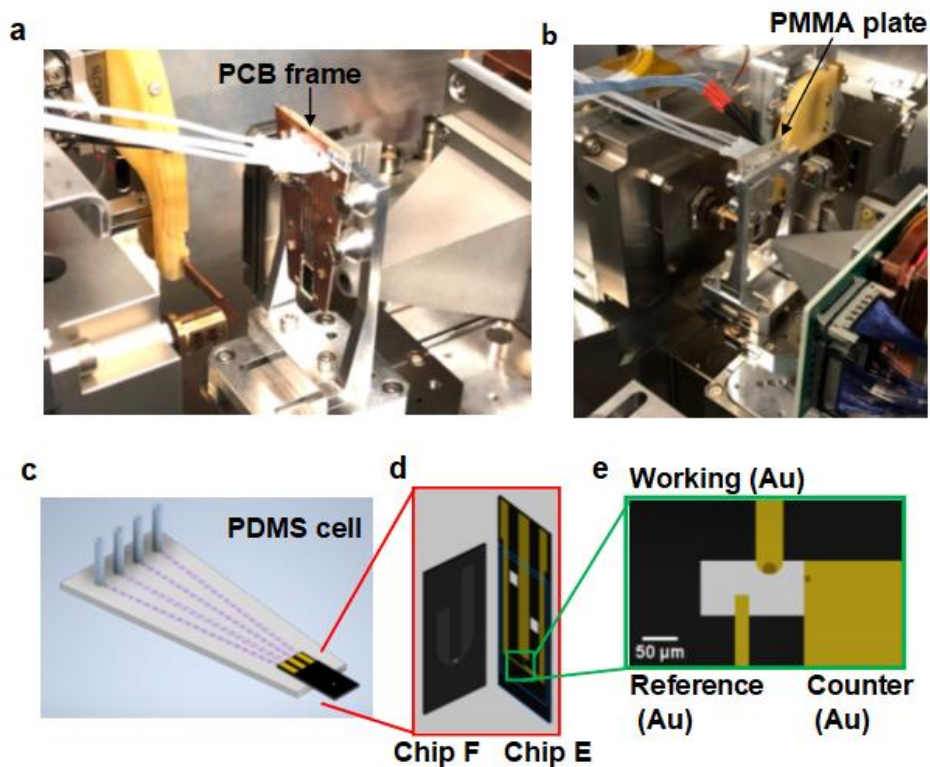


Figure S18. *in situ* flow electrochemical device for soft X-ray STXM and ptychography. Photograph of the assembled device inside the HERMES' STXM chamber: (a) front side; (b) back side. Schematics of (c) PDMS/glass cell; (d) in situ chips; (e) the 3-electrodes region on in situ chip E.

Note S14. Detailed *in situ* procedures and summary of measurements.

Cu nanoparticle electrodeposition: The 4 electrolyte tubes were pre-filled with a solution of 10 mM CuSO₄ and 10 mM KCl and then connected to the 4 channels of the assembled *in situ* device. A syringe pump (New Era N1000) was used in push mode with a flow rate 25 μ l/hr for 10 mins to fill the *in situ* device with electrolyte from the inlet channels. The filling process was monitored under an optical microscope (20x objective) to confirm that the electrolyte completely filled the window region and the cell was free of bubbles.

Figure S19a is a reflection optical image of the window area of the device after filling the CuSO₄/KCl electrolyte. Once the 3-electrode region was filled with the electrolyte, a potentiostat (either an Ivium pocketstat or an Emstat 4s) was connected to the *in situ* device via the 4-pin connector. The open circuit potential (OCP) was stable and around -0.045 V_{Au} (equivalent to +0.355 V_{RHE}). Then 3 cycles of cyclic voltammetry (CV) in the potential range -0.5 to 0 V_{Au} (-0.1 to +0.4 V_{RHE}) with a scan rate of 20 mV/s were performed. **Fig. S.19b** is a reflection optical image of the window area after the electrodeposition. The Cu particles in **area A** and **area B** were electrodeposited in two different *in situ* cells using this procedure.

Changing the electrolyte to CO₂ saturated 0.1M KHCO₃: Millipore filtered, deionized water was first used to flush the CuSO₄/KCl out of the *in situ* device using the syringe pump with a flow rate 25 μ l/hr for 5 min. Then the water in the cell was replaced with CO₂ saturated 0.1M KHCO₃ electrolyte using the syringe pump with 25 μ l/hr flow for 15 min. This process was also conducted under the optical microscopy to ensure the window region was free of bubbles and the Cu deposit was largely unchanged. Note that, although the process above was followed for these *in situ* ptychography measurements, we have also loaded an empty cell into the STXM and performed the electrodeposition and exchange of electrolytes inside the STXM (with the sample retracted in case of leaks).

Loading the *in situ* device into the STXM: First, the potentiostat and syringe pumps were disconnected to simplify device insertion into the STXM. The *in situ* device, connected only to the 4 electrolyte silicone tubes, was moved carefully from the optical microscope into the STXM chamber. In the chamber, the edges of the *in situ* device were engaged with the 3-pins of the trapezoidal kinematic holder. Once the device was firmly in position, the potentiostat cables were re-connected. A 2-sided 9 pin D-subminiature (“DB9”) connector welded into a 2-3/4” (70 mm

OD) conflat flange was used for electrical connection through the STXM vacuum chamber wall. The fluid lines were passed through 4 holes in the same flange and sealed with epoxy. After loading the device, the syringe pump was connected and operated at a flow rate of 25 $\mu\text{l/hr}$ to keep a stable electrolyte flow. The electrolyte tubes and potentiostat cables were organized in the STXM chamber and stabilized using Kapton tape to attach them to a suitable position in the chamber to avoid interfering with STXM operations such as sample scanning. After the *in situ* device was loaded in the STXM, the air in the tank was changed from air to He gas by displacing the air at a slow rate (~ 10 min), maintaining the chamber pressure slightly above 1 bar. Replacing air with He was directly monitored using the intensity of transmitted X-rays. After achieving a plateau in X-ray transmission, the He gas flow was stopped and the STXM chamber was sealed.

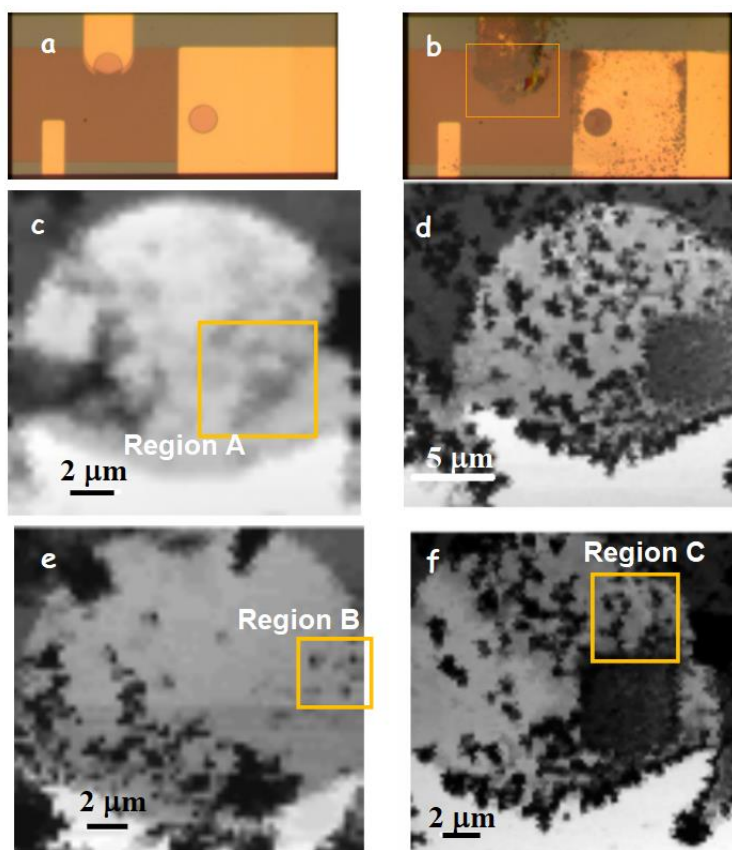


Figure S19. Images of the areas for testing. (a) Reflection optical image after filling with 10 mM CuSO_4 / 10 mM KCl electrolyte. (b) Reflection optical image after Cu electrodeposition. (c) STXM image at 933.3 eV prior to study of **area A**. (d) STXM image at 933.3 eV after STXM and ptychography study of **area A**. (e) STXM image at 933.3 eV prior to study of **area B**. (f) STXM image at 933.3 eV prior to study of **area C**.

Performing *in situ* flow electrochemical measurements by spectro-ptychography:

STXM images were used to find a region consisting of Cu particles. Region A was found and studied. A four energy (4-E) STXM stack and a 4-E ptychography stack were conducted at **area A** with applied potentials (OCP). Then a full ptychography stack was measured on region A using an elevated flux (slits of 15 μm x 15 μm) in an attempt to get stronger ptychography signals. This ptychography stack on **area A** took ~90 min with X-ray intensity of much more than 50 MHz/s (that was the intensity observed by the phosphor/PMT STXM detector, but that detector is known to be saturated at 50 MHz). The high dose caused radiation damage in the form of X-ray induced reduction, as observed by the square in image **Fig. S19d**. After this was observed, the X-ray beam intensity was reduced to ~20 MHz/s by closing the exit slits to 5 μm x 5 μm . Analyzable ptychography diffraction images were still obtained. All subsequent experiments were performed with 20 MHz flux, without observable radiation damage, as is discussed in **Note. S19**, and **Figs S20** and **S21**.

Since **area A** was damaged, the Cu particles were deposited again according to the above Cu nanoparticle electrodeposition process. **Area C** was found, showing well-defined Cu particles. 4E stack or full stack at Cu 2p_{3/2} edge were measured from **area C** while chronoamperometry scans at various potentials [OCP, +0.1, -0.2, -0.5, -0.8 and -0.85 V_{RHE}] were sequentially applied. The potential was returned to OCP (+0.355 V_{SHE}) between measurements. After the tests on **area A** and **area C**, another *in situ* cell (cell 2) was used. First the Cu deposition were conducted according to the above Cu nanoparticle electrodeposition process. **Area B**, consisting of many well defined Cu particles, was found. Chronoamperometry was performed under reducing conditions (-0.3 V_{Au}, +0.1 V_{RHE}) while recording a full Cu 2p_{3/2} ptychography stack on **area B**.

The *in situ* conditions for Cu particles: The electrodeposited Cu particles are not stable under *in situ* conditions and the oxidation states of Cu could change with different local electrochemical conditions. First, Cu metal and Cu₂O are not thermodynamically stable relative to CuO at potentials above +0.2 V_{SHE} (vs Standard Hydrogen Electrode, SHE) according to the Pourbaix diagram for Cu in aqueous solution at 25 °C [S15]. Thus the Cu(0) and Cu(I) species generated by electro-reduction should ultimately become CuO, which is water-insoluble. The fact that particles with large Cu(0) and Cu(I) content are observed after completing electrodeposition, is related to slow kinetics for oxidation.

Second, with different electrochemical histories, the Cu particles are shown in different chemical conditions. Although the Cu particles are electrodeposited on **areas A, B, C** by the same method shown in **Note S14**, the different conditions when STXM and ptychography measurements were conducted and different electrochemical environments can change the Cu particles. For **area A**, the time from electrodeposition to the measurement was quite long (~8 hours) due to various technical issues. During this period the cell was filled with a 0.1 M KHCO₃ solution with an open circuit potential of +0.4 V_{RHE}. This gave time for the oxidation to occur, resulting in the observation of more Cu(I) and Cu(II) particles (see **Fig. 1**). The STXM and ptychography measurements on **area B** were made immediately after changing the electrolyte to KHCO₃ so there was insufficient time for the as-deposited particles to be oxidized. When ptychography measurements were tested on **area B**, an +0.1 V_{RHE} was applied, and most Cu particles were electrochemically reduced to metallic Cu (see **Fig. 2**). **Area C** is in the same in situ device as **Area A**, but under different conditions. After *in situ* STXM/ptychography measurements on **Area A** which caused radiation damage, **Area C** was then found and measured in **Fig. 5**.

Note S15. Evaluating radiation dose and possibility of radiation damage

Although radiation damage was observed in **area A (Fig. S.19d)** due to a long measurement and too high an X-ray intensity, this was caused by a stack measured **after** the 4E ptychography stacks shown in **Fig. 1** were measured. After the image in Fig. 19.d was measured, the slits were reduced until the incident flux was 20 MHz, the value that was used for all subsequent measurements. Here we evaluate the dose and present evidence that no further damage was observed.

S15.1 Evaluating radiation dose for ptychography measurements.

The dose delivered in a spectro-ptychography measurement depends on the rate of X-ray absorption per unit area and the length of time the beam is on a given area. [S.16, S.17] Briefly, the dose in units of MGy is given by [S.16]

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

where I_0 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, V is the volume of the exposed region, ρ is the sample density (g/cm^3), and OD is the optical density of the exposed region at the energy of irradiation.

The estimated dose for 4E in situ ptychography stacks is 70 MGy and for 34E ptychography stacks is 1020 MGy using the parameters listed in **Table S.1**. For comparison, if the same area was measured by conventional STXM with the fully focused 50 nm spot size, 20 nm step size and 20 ms/point, the estimated doses would be 450 MGy for a 4E stack and 6,500 MGy for a 42-E stack. Thus spectro-ptychography using a 1 μm defocused spot size delivers about 6 times lower dose than STXM, while at the same time giving better statistical precision and much better spatial resolution.

Table S1. Parameters for estimating dose for in situ spectro-ptychography stacks

symbol	4E stack	34E stack	comments
I_0	20 MHz	20 MHz	-
OD	0.23	0.3	average over E/s measured
E	933 eV	933 eV	-
t	320 ms	3.2s	Although the measurements took a long elapsed time (~90 min for full stack and ~20 min for 4E stack), the actual time the beam was on any given spot of the sample was quite small (60 ms dwell/pixel)
ϵ	0.8	0.8	-
diameter (μm)	1	1	-
Thickness (nm)	75	35	-
V	$7.5 \times 10^6 \text{ nm}^3$	$3.5 \times 10^6 \text{ nm}^3$	From Table 1 and Fig. 5. Different density and thickness
ρ	7 g/cm ³	9 g/cm ³	
Overlap factor	100	100	1 μm spot stepped 0.1 μm , in 2-D
Calculated dose	70 MGy	1020 MGy	

4E-stack : 221008037 (mostly CuO) 34-E stack: 221008048 (mostly Cu)

S15.2. Evidence that there is negligible damage from *in situ* spectro-ptychography

Color coded composites of component maps derived from 4E spectro-ptychography stacks measured before and after a full ptychography stack (**area B, Fig. 2**) are shown in **Figure S20**. No significant change in morphology or oxidation state distributions were detected.

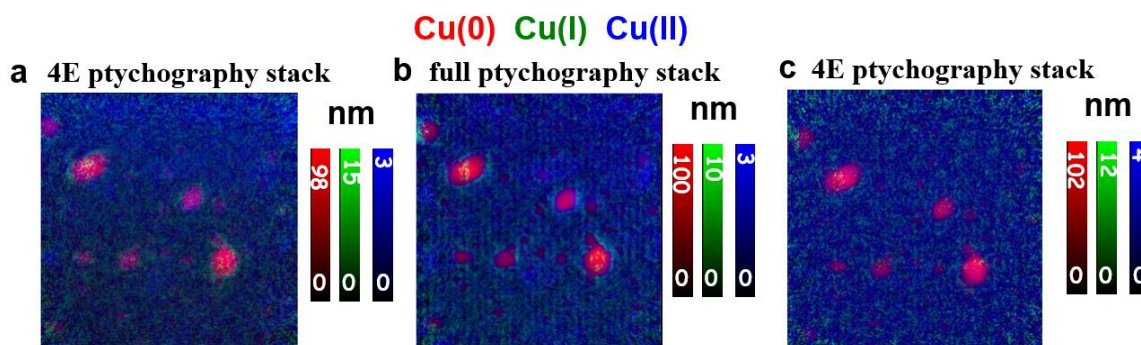


Figure S20. Check for radiation damage, by measuring 4E stacks before and after a 42E stack under *in situ* condition (+0.1 V_{RHE}, 5 nA). Color coded composites of component maps derived from (a) 4-E ptychography, 2022109082. (b) Full stack, 2022109083. (c) 4-E stack, 2022109086.

In addition, after completing all the *in situ* ptychography measurements on **area C** (**Fig. 5**), a 4-E stack was measured on a larger region which included adjacent areas which had never been exposed to the X-ray beam (**Figure S.21**). The same morphology and similar oxidation state distributions were found between the area that had been illuminated by ptychography measurements and the particles in the un-exposed surrounding area, indicating there was negligible beam damage on Cu electrocatalysts during *in situ* ptychography measurements.

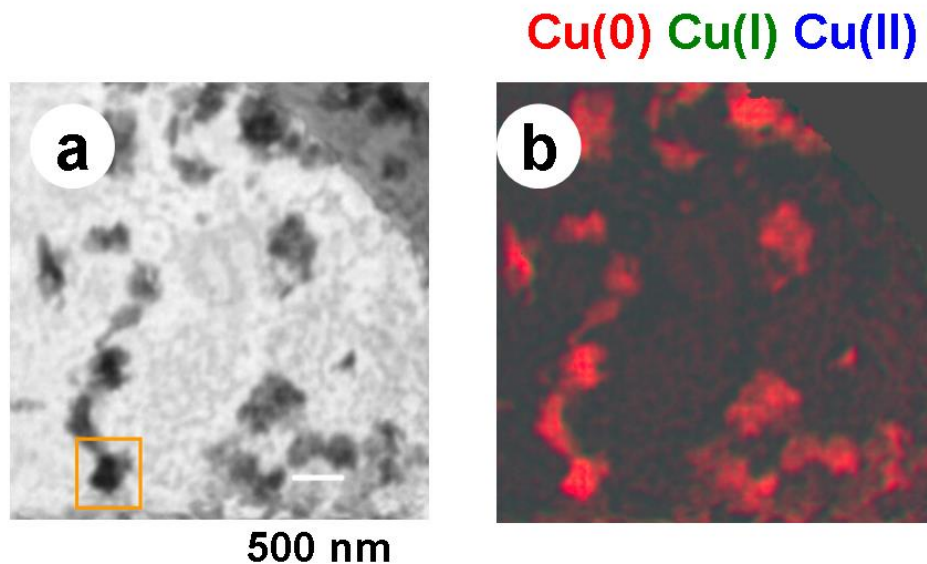


Figure S21. Check for damage after measurements in area C. (a) STXM image at 933.5 eV. The yellow frame is the region of the *in situ* ptychography measurements on **area C** (**Fig. 5**). **(b)** color-coded composite of the component maps derived from 4E spectro-ptychography stack measured over a larger region after all the chronoamperometry and stacks were completed.

Table S2. Summary of ptychography measurements reported in this paper

Note: **Area A** and **area C** are different areas on the same *in situ* device, but with a different electrochemical history.

Area B is from a different *in situ* device, but using a similar deposition protocol as used for **Area A**.

Area	Fig #	Type	File (202210xxx) (day)###	Size (μm, pixel)	Flow (μL/h)	V vs RHE @	algorithm [#]	Maxsize ^{\$}	Thresh ^{&}	Det. Dist [^] (mm)	Defocus [!] (μm)	Acquisition time (min)
A	Fig. 1	STXM	7-024	6 *6; 60*60	20	OCP	NA					25
A	Fig. 1	ptycho	7-029	5 *5 ; 50*50	20	OCP	AP**800	1100	10	52.25	-25	30
B	Fig. 2,3	ptycho	9-083	3 *3, 30*30	20	+0.10	AP**200	1100	10	54.9	-26	90
C	Fig. 5	STXM	8-036	5 *5 , 100*100	20	OCP	NA					20
C	Fig. 5	ptycho	8-037	0.5*0.5 ,10*10	20	OCP	AP**500	1100	5	52.07	-18	20
C	Fig. 5	ptycho	8-038	0.5*0.5 ,10*10	20	+0.10	AP**500	1100	5	52.07	-18	20
C	Fig. 5	ptycho	8-040	0.5*0.5 ,10*10	20	-0.20	AP**500	1100	5	52.07	-18	20
C	Fig. 5	ptycho	8-041	0.5*0.5 ,10*10	50	-0.50	AP**500	1100	5	52.07	-18	20
C	Fig. 5	ptycho	8-042	0.5*0.5 ,10*10	50	-0.80	AP**500	1100	5	52.07	-18	20
C	Fig. 5	ptycho	8-048	0.5*0.5 ,10*10	50	-0.85	AP**500	1100	5	52.07	-18	100

adaptq = hard was used for all reconstruction. This means the camera is moved at each photon energy so the Q-range of the diffraction image (DI) was the same at all energies of a stack. (There is a software correction, but moving the camera is better)

bin = 1 for all reconstructions.

@ **nc** = not connected

AP – alternate projection mode of PyNX, # after ****** is # of iterations.

Note there is no test for convergence, as typically done in self-consistent field quantum chemical calculations.

\$ maxsize: camera images are 2000 x 2000 (11 μm pixels). Maxsize = 1300 gives good reconstruction for strong scatterers like Siemen's stars (Au), but maxsize=1100 was better for these reconstructions.

& threshold is applied AFTER background subtraction.

^ Detector distance Physical distance from the sample to the sensor in the camera

! Defocus This is the change in the ZP-z position used to get the desired spot size. Sign is important

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