

## Supporting Information

### **Plasma-modified dendritic Cu catalyst for CO<sub>2</sub> electroreduction**

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### Faradaic efficiency calculation of gas products:

$$F_{gas,i} = \frac{5}{3} \frac{f_{flow} * c_{gas} * n_i * F}{V_m * I}$$

### Faradaic efficiency calculation of liquid products:

$$F_{liquid} = \frac{c_{liquid} * V * n * F}{Q_{total}}$$

### Production rate calculation of gas products:

$$J_{partial,j} = \frac{F_j * I}{100 * A}$$

where:

$f_{flow}$  is the flow rate of CO<sub>2</sub> in mL\*min<sup>-1</sup>;

I is the average electrolysis current over 60 min; [I]=1A,

$c_{gas}$  is the volume ratio of the gas product, as determined by the online GC

$V_m$  is the molar volume of an ideal gas; [ $V_m$ ]=1 mL\*mol<sup>-1</sup>

$c_{liquid}$  is the concentration of liquid product after 1 hour of CO<sub>2</sub>RR, as determined by the HPLC and/or liquid GC; [ $c_{liquid}$ ]= 1 mol\*L<sup>-1</sup>

V is the volume of the electrolyte within the used cell, here V=55 ml

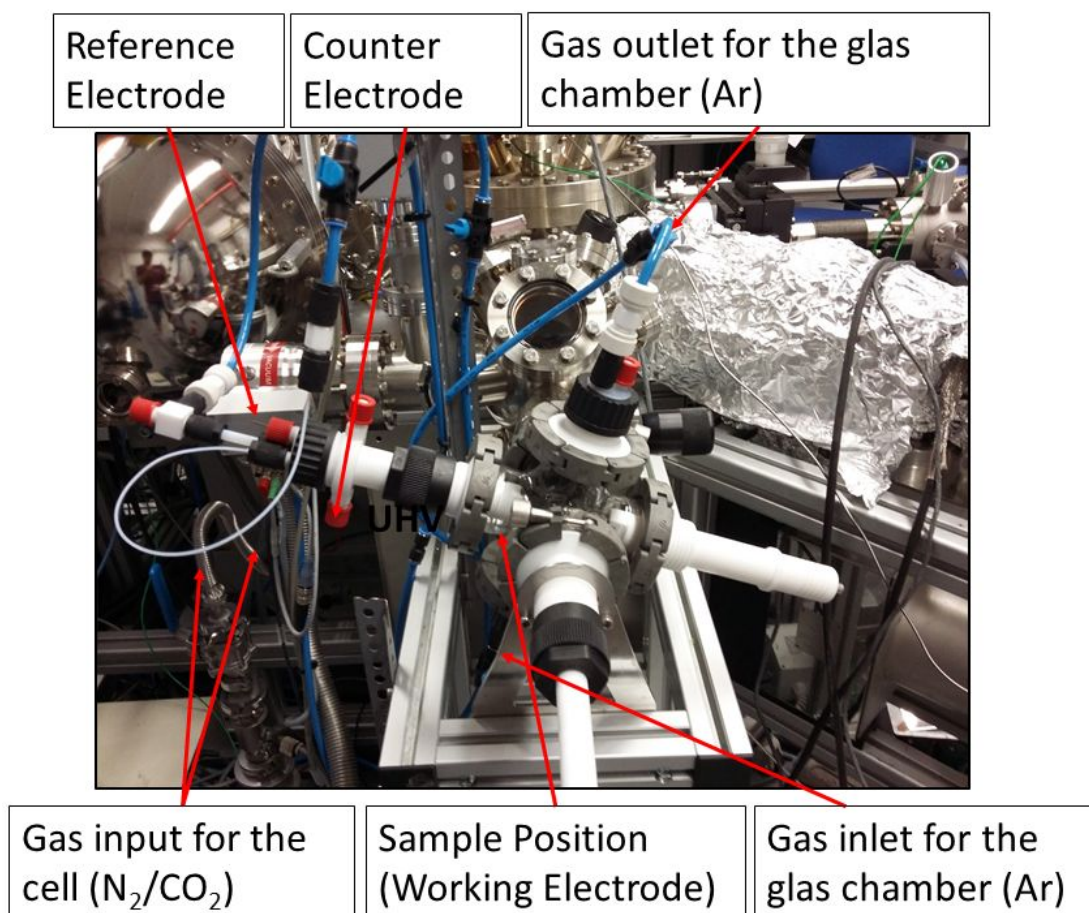
$Q_{total}$  is the total charge consumed during electrolysis; [ $Q_{total}$ ]= 1C

$n_i$  is the number of electrons transferred for a certain product i

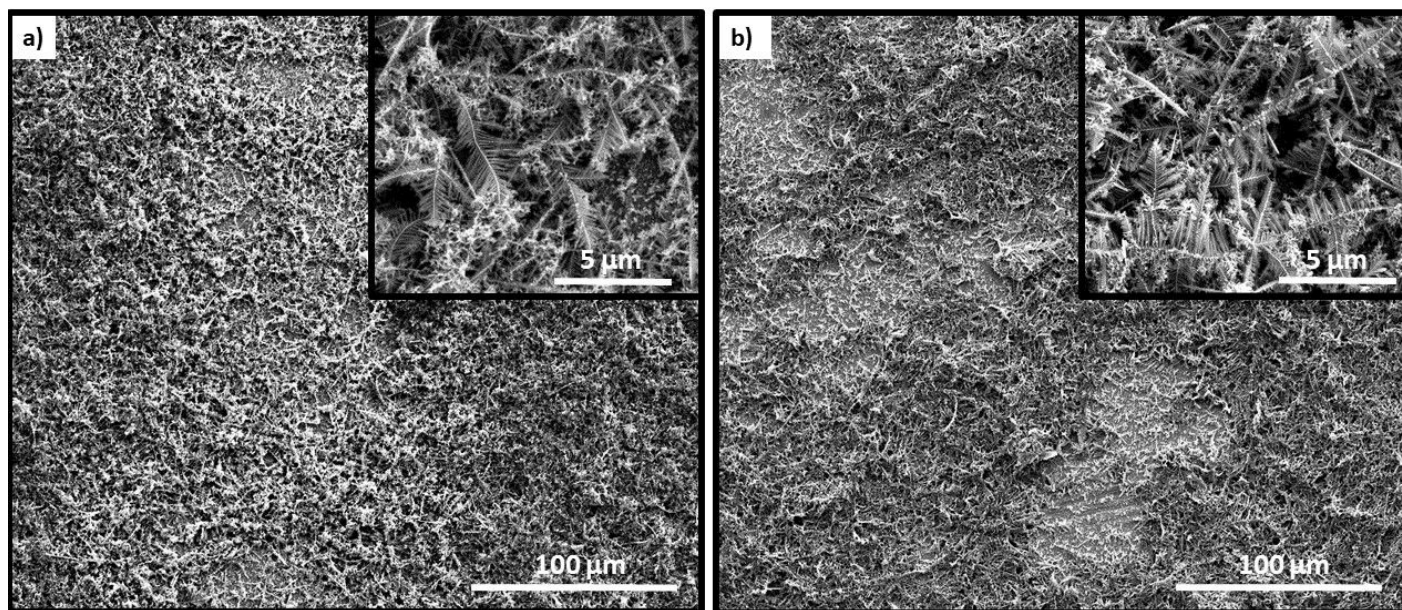
F is the faradaic constant F = 96485 C \*mol<sup>-1</sup>

$F_j$  is the faradaic efficiency of a given species

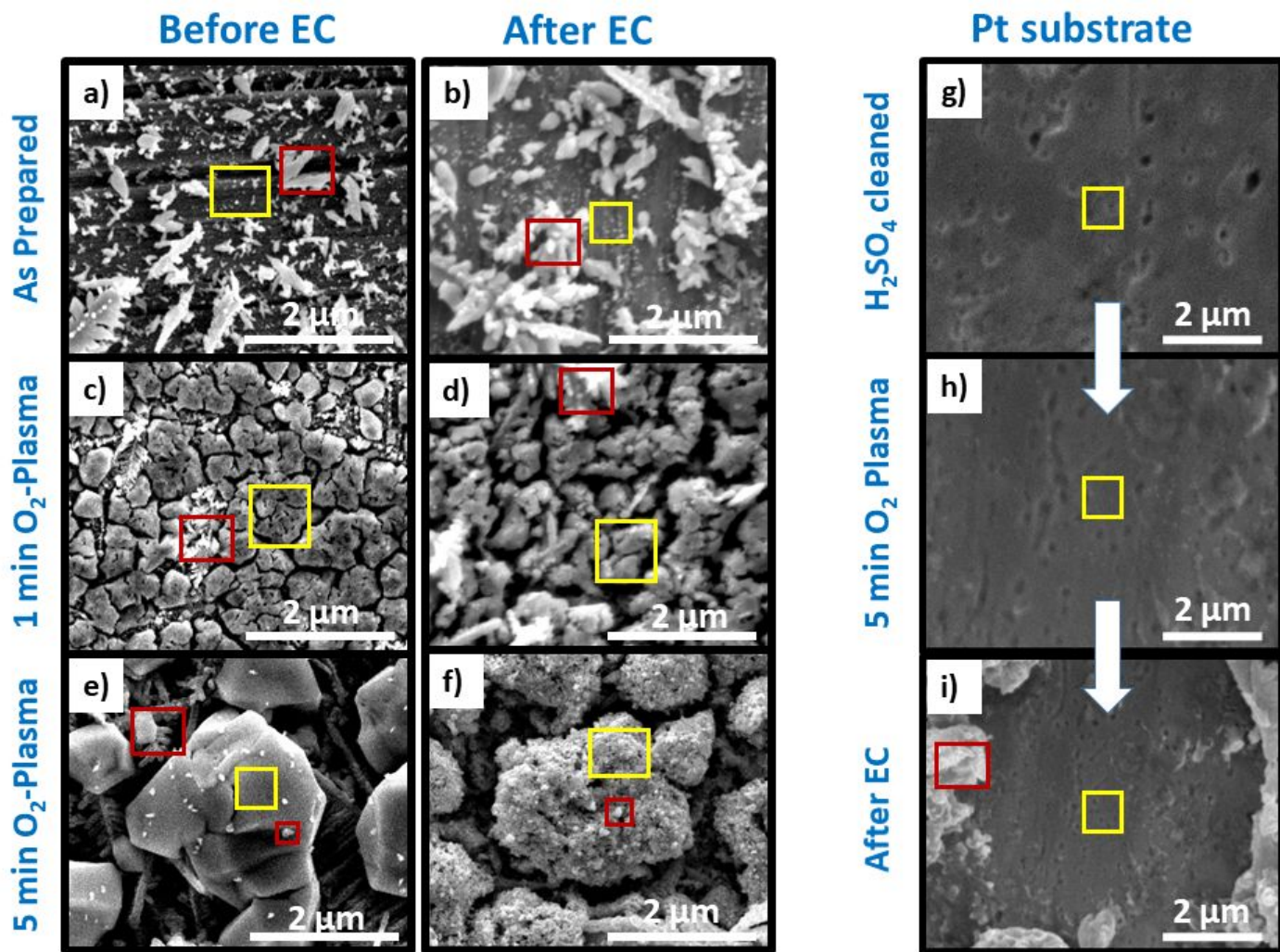
$A_k$  is the used surface area; [ $A_k$ ]=1 cm<sup>2</sup>



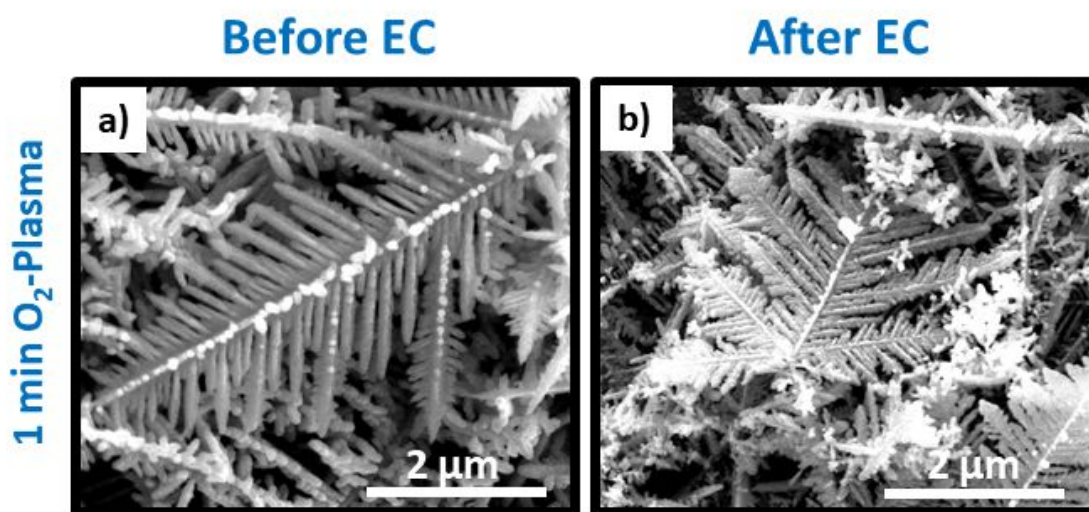
**Figure S1:** Electrochemical cell directly attached to an UHV system containing the XPS analysis setup. The glass part through which the sample is transferred after electrochemistry into vacuum is constantly filled with a pressurized argon flow ( $p_{\text{Ar}}=1.1\text{bar}$ ).



**Figure S2:** SEM images of as prepared samples (a) on Ag and (b) on Pt acquired directly after electrodeposition and a short transfer in air to the SEM. Bright spots corresponding to lower dendrite coverages on the substrate are easier to be seen on Pt due to the good elemental contrast. Insets show higher resolution images.



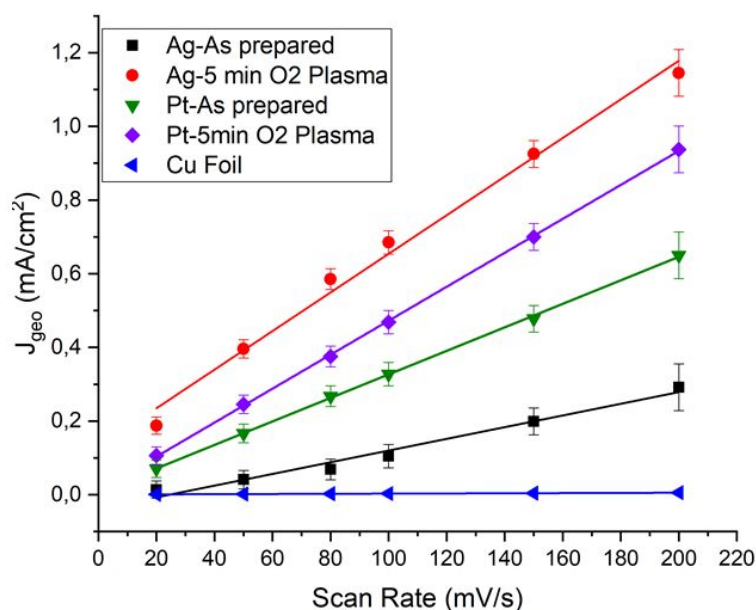
**Figure S3:** SEM images of the Ag (a-f) and Pt (g-i) substrates with deposited dendrites after different treatments. Yellow rectangles mark the representative regions for the Ag (a-f) and Pt (g-i) substrate while the red ones correspond to areas containing Cu. The Ag substrate shows a significant change in morphology even after short plasma treatments. Upon applying a potential of  $-0.9\text{V}$  vs RHE (b,d,f) the Ag substrate displayed an increased roughness, as extracted also from the electrochemical surface area (ESCA) data (Fig. S8). The Pt substrate is much less sensitive to the O<sub>2</sub>-plasma treatment as well as to the exposure to the electrochemical CO<sub>2</sub>RR conditions ( $-0.9\text{V}$  vs RHE).



**Figure S4:** SEM images and EDX data acquired on Cu dendrite samples electrochemically grown on Ag before (a) and after (b) 1h of CO<sub>2</sub>RR at -0.9V vs RHE.

**Table S1:** Relative content of Cu, O, Ag and Pt in different Cu dendrite samples supported on Ag and Pt foils as extracted from EDX analysis

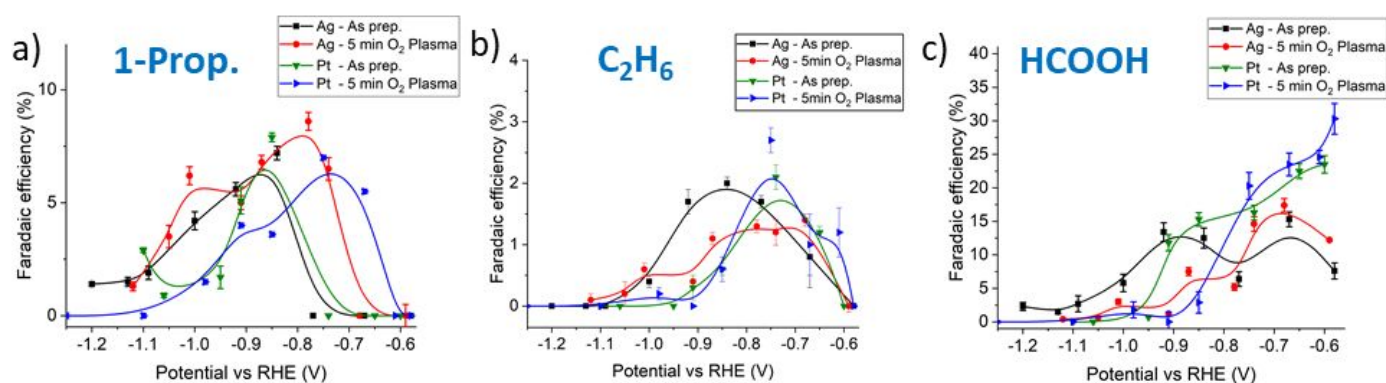
Sample	Before EC		After EC	
	Dendrites	Substrate	Dendrites	Substrate
Ag - As prep.	87% Cu	79% Ag	95% Cu	86% Ag
	13 % O	16% Cu 5% O	5% O	12% Cu 2% O
Ag - 5 min O <sub>2</sub> Plasma	51% Cu	55% Ag	93% Cu	67% Ag
	49% O	40% O 5 % Cu	7% O	21% Cu 12% O
Pt - As prep.	86% Cu	61% Pt	95% Cu	59% Pt
	14% O	39% Cu	5% O	41% Cu
Pt - 5 min O <sub>2</sub> Plasma	54% Cu	48% O	83% Cu	64% Pt
	46% O	28% Pt 24% Cu	17% O	35% Cu



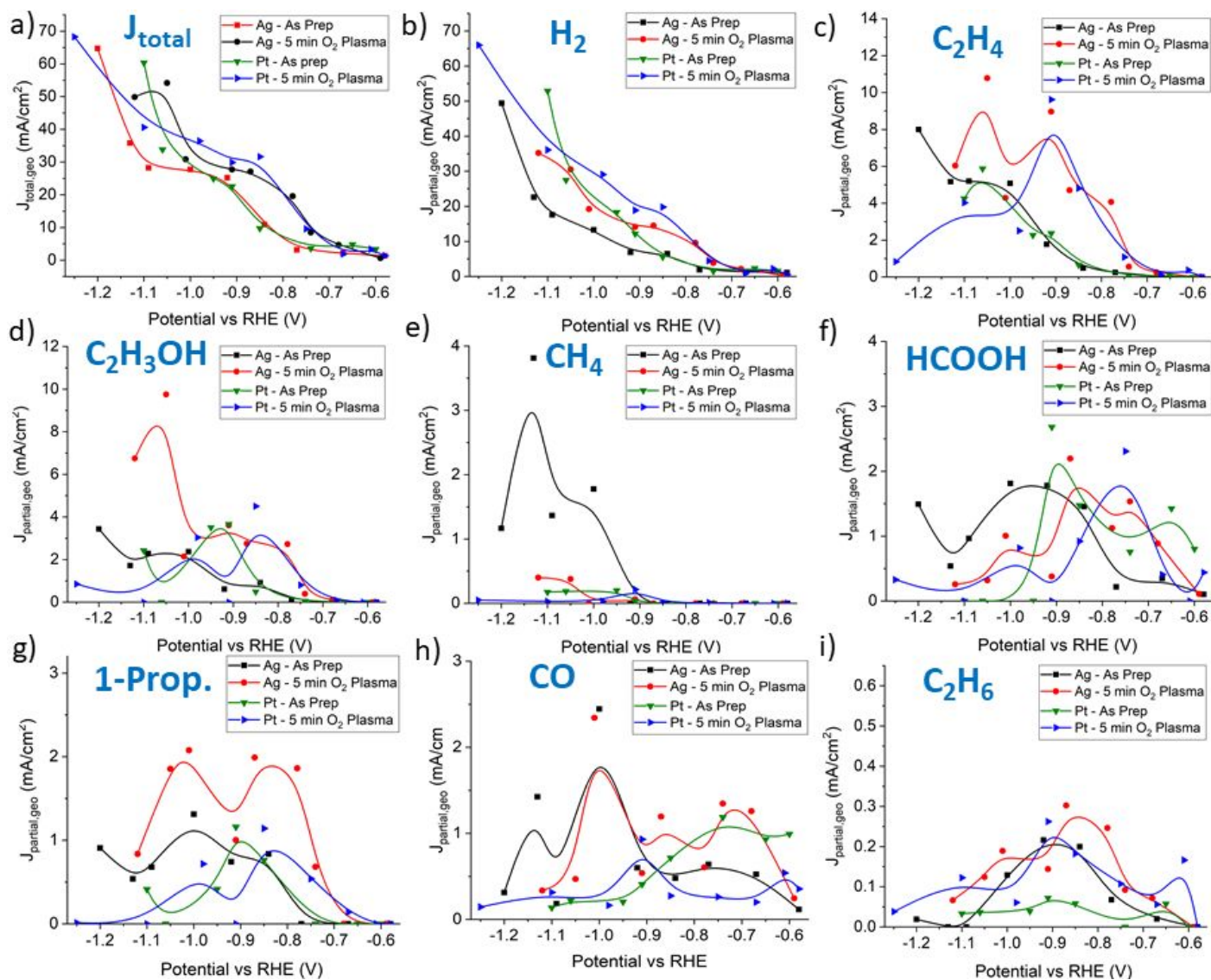
Sample	Slope (mF/cm <sup>2</sup> )	R
Cu Foil	0,026	1
Ag – As prepared	1,59	62
Ag – 5 min O <sub>2</sub> Plasma	5,24	203
Pt – As prepared	3,19	123
Pt – 5 min O <sub>2</sub> Plasma	4,61	178

**Figure S5:** Capacitance per cm<sup>2</sup> of the untreated and plasma-treated samples on Ag and Pt measured directly after 1 h of CO<sub>2</sub>RR at -0.9V vs RHE in 0.1M KHCO<sub>3</sub> and the corresponding roughness factors. The roughness factor of an electropolished Cu foil is used as reference and defined to be 1.

Electrochemical capacitance measurements (Fig. S5) have been carried out after 1.5 h of CO<sub>2</sub>RR in order to gain information about the surface roughness. On both substrates, the O<sub>2</sub>-plasma treated samples display higher roughness, with the largest increase being observed for the Ag-supported Cu dendrites. The latter is assigned to the stronger effect of the O<sub>2</sub>-plasma on the morphology of the Ag substrate as compared to Pt (Fig. S3). Therefore, any changes in the reactivity observed after the plasma treatment in the Pt-supported Cu dendrites are mainly assigned to the roughness and defects created on the Cu dendrites themselves, while for the Cu/Ag system the rough Ag surface will also play a role.

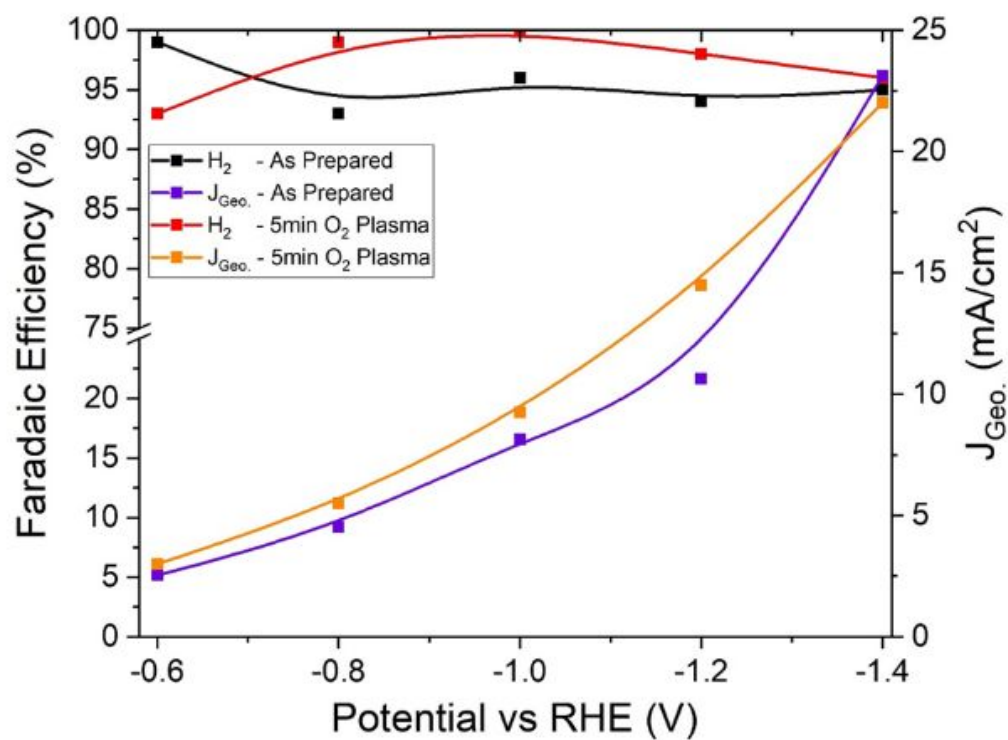


**Figure S6:** (a-c) Faradaic efficiency as a function of applied potential for the as prepared and 5 min O<sub>2</sub> plasma-treated Cu dendrites on Ag and Pt substrates for the measured CO<sub>2</sub>RR products not shown in the main text. All measurements carried out in 0.1M KHCO<sub>3</sub>.

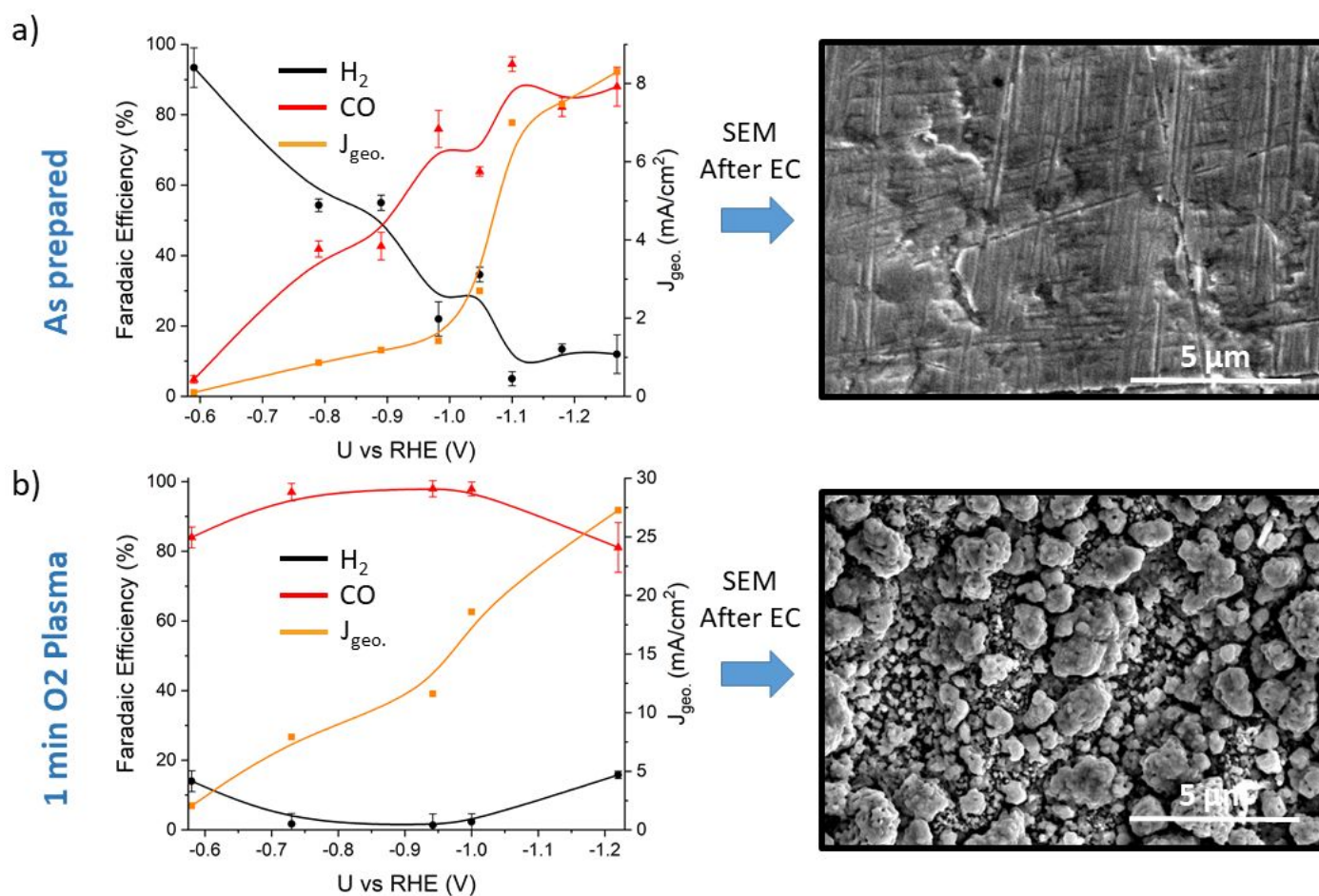


**Figure S7:** (a) Current density normalized to the geometric surface area and (b-i) corresponding partial current densities as function of applied potential for the as prepared and 5 min  $\text{O}_2$  plasma-treated Cu dendrites on Ag and Pt substrates for all measured  $\text{CO}_2\text{RR}$  products in 0.1M  $\text{KHCO}_3$ .

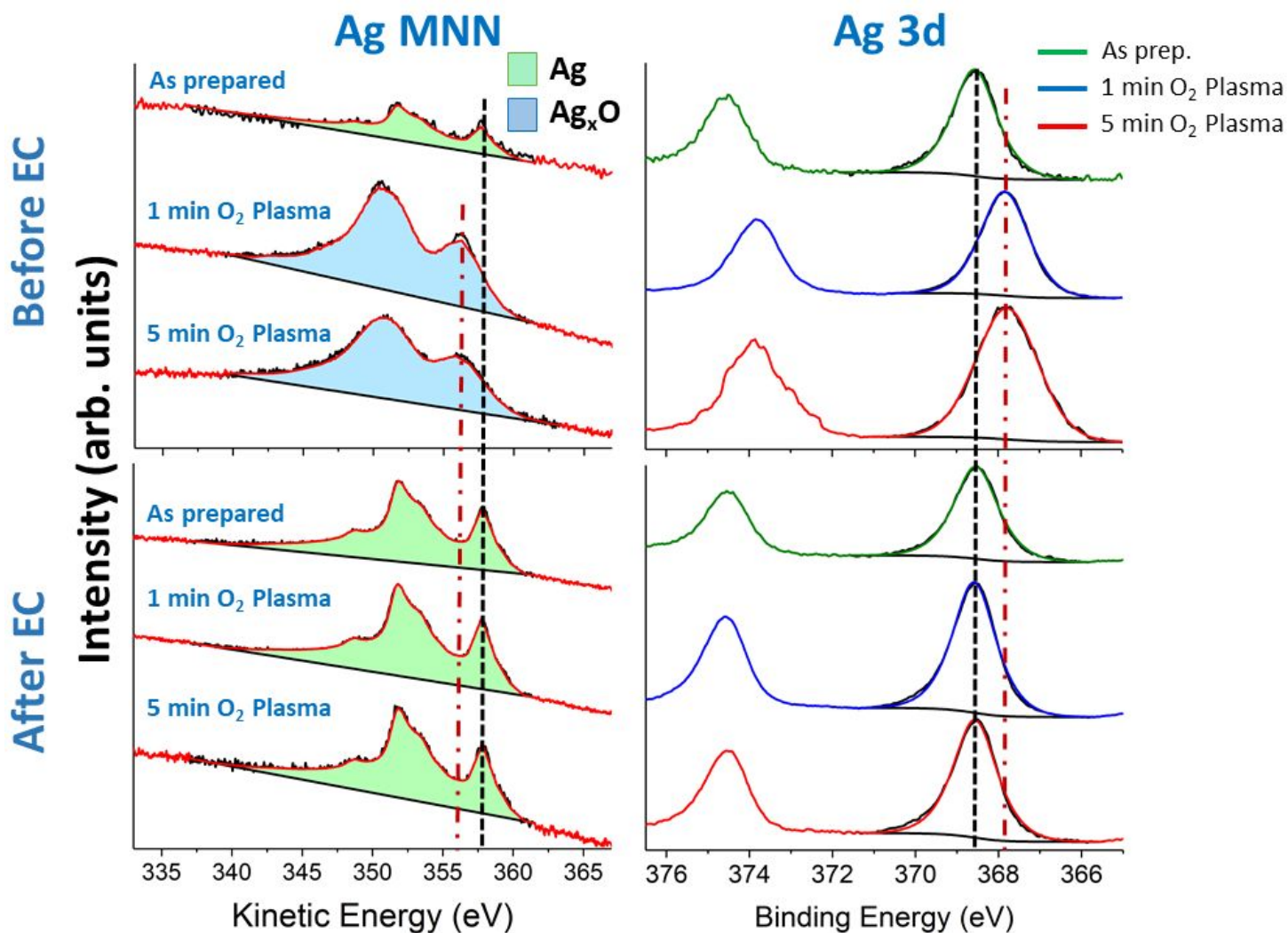




**Figure S8:** Faradaic efficiency for the gas products and the geometric current density obtained for the untreated and 5 min  $\text{O}_2$  plasma treated Cu-free Pt substrate as a function of the applied potential.



**Figure S9:** Faradaic efficiency for the Cu-free Ag substrate as a function of the applied potential (a) untreated and (b) after 1 min O<sub>2</sub> plasma treatment together with the corresponding SEM images. The change in selectivity upon plasma treatment is accompanied by a significant change in morphology, i.e. an increase of the surface roughness.



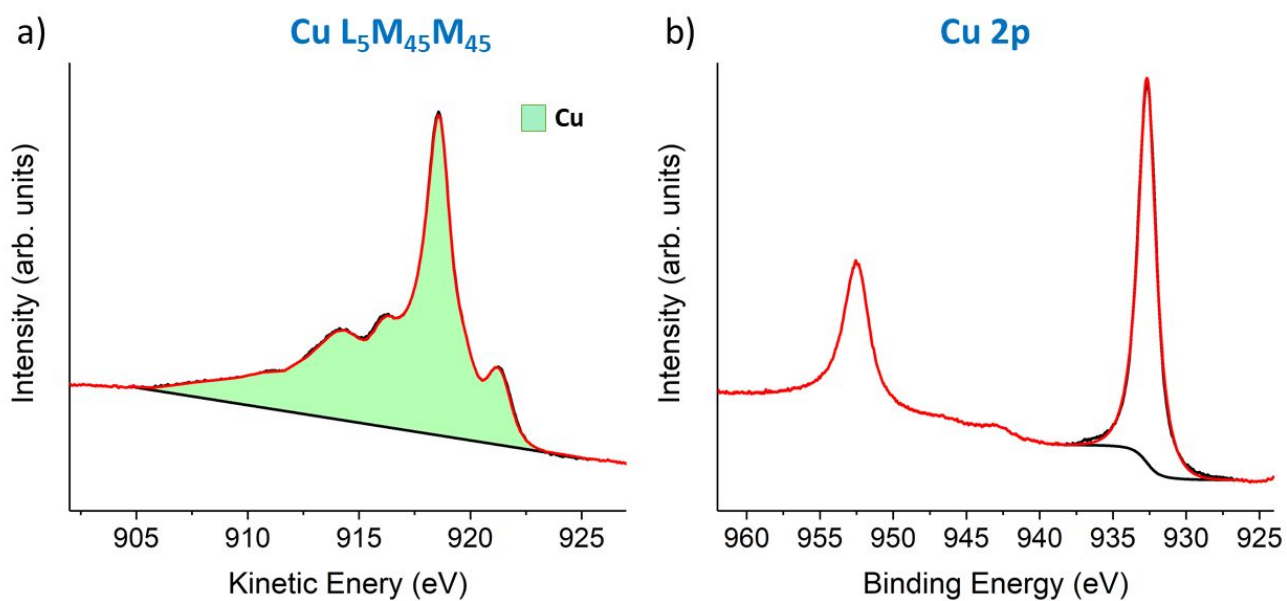
**Figure S10:** *Quasi in situ* XPS spectra of the Ag MNN AES and Ag-3d core level regions acquired on plasma-treated Cu dendrites supported on Ag for different O<sub>2</sub>-plasma treatment times. Red and black dashed line are a guide for the eye and mark the corresponding binding energies of the oxidized and metallic Ag species.

**Table S2:** Modified Auger parameter and XPS binding energies of the Ag 3d region for the data shown in Fig. S9 and for comparison also values taken from the literature.

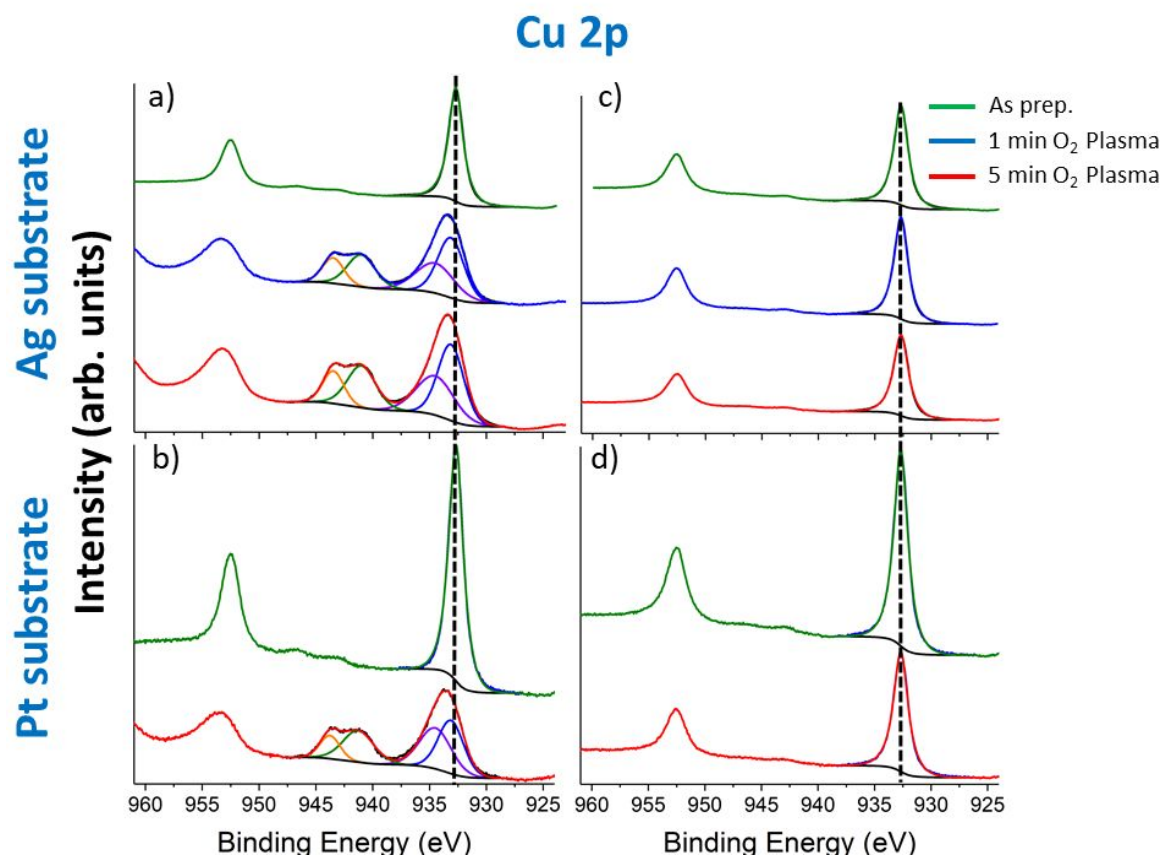
Region/Species	This Work/ eV	Literature [1]/ eV	Literature [2]/ eV
Ag M <sub>5</sub> N <sub>45</sub> N <sub>45</sub> Mod. Auger Parameter	720.2	—	720.5
AgO M <sub>5</sub> N <sub>45</sub> N <sub>45</sub> Mod. Auger Parameter	718.3	—	718.3
Ag 3d	368.4	368.3	368.2
AgO 3d	367.8	367.8	367.6

[1] Ferrara, A.M.; Carapeto, A.P.; Botelho do Rego, A.M X-ray photoelectron spectroscopy: Silver salts revisited, *Vacuum*, 86 (2012) 1988-1991

[2] Wagner, D.; Naumkin, A.V.; Kraut-Vass, A.; Allison, J.W.; Powell, C.J.; Rumble, J.R. NIST Standard Reference Database 20, Version 3.4 (web version) (<https://srdata.nist.gov/xps/>) 2003, accessed 04-25-2019.



**Figure S11:** Quasi *in situ* LMM Auger spectrum (a) and Cu-2p XPS spectra acquired on a gas diffusion electrode (GDE) as used by Reller et. al.<sup>1</sup> after quasi *in situ* electrodeposition of copper dendrites with the same parameters mentioned in the experimental part. Only metallic Cu was detected.



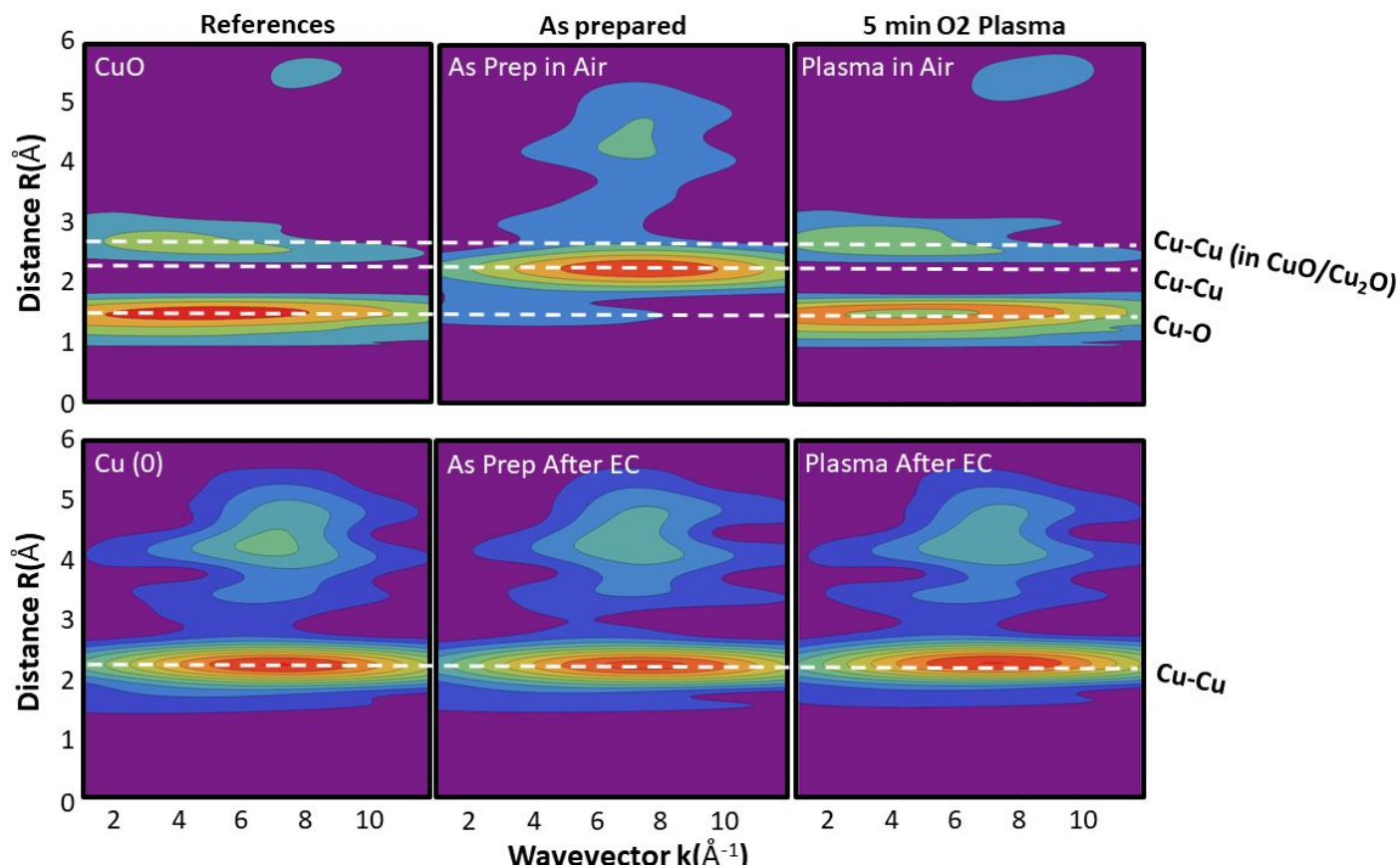
**Figure S12:** *Quasi in situ* XPS spectra of the Cu 2p region of Cu dendrites supported on Ag (a,c) and Pt (b,d) obtained before (a,b) and after (c,d) CO<sub>2</sub>RR for 1h at -0.9V vs RHE in 0.1M KHCO<sub>3</sub>.

**Table S3:** Results of linear combination fitting of our XANES spectra of Cu dendrites supported on Ag and Pt substrates with the measured references. Before EC denotes the measurement in air prior to any electrolyte contact. Samples during EC are measured under operando conditions in 0.1M KHCO<sub>3</sub> while being held at a potential of -0.9V vs RHE during CO<sub>2</sub>RR.

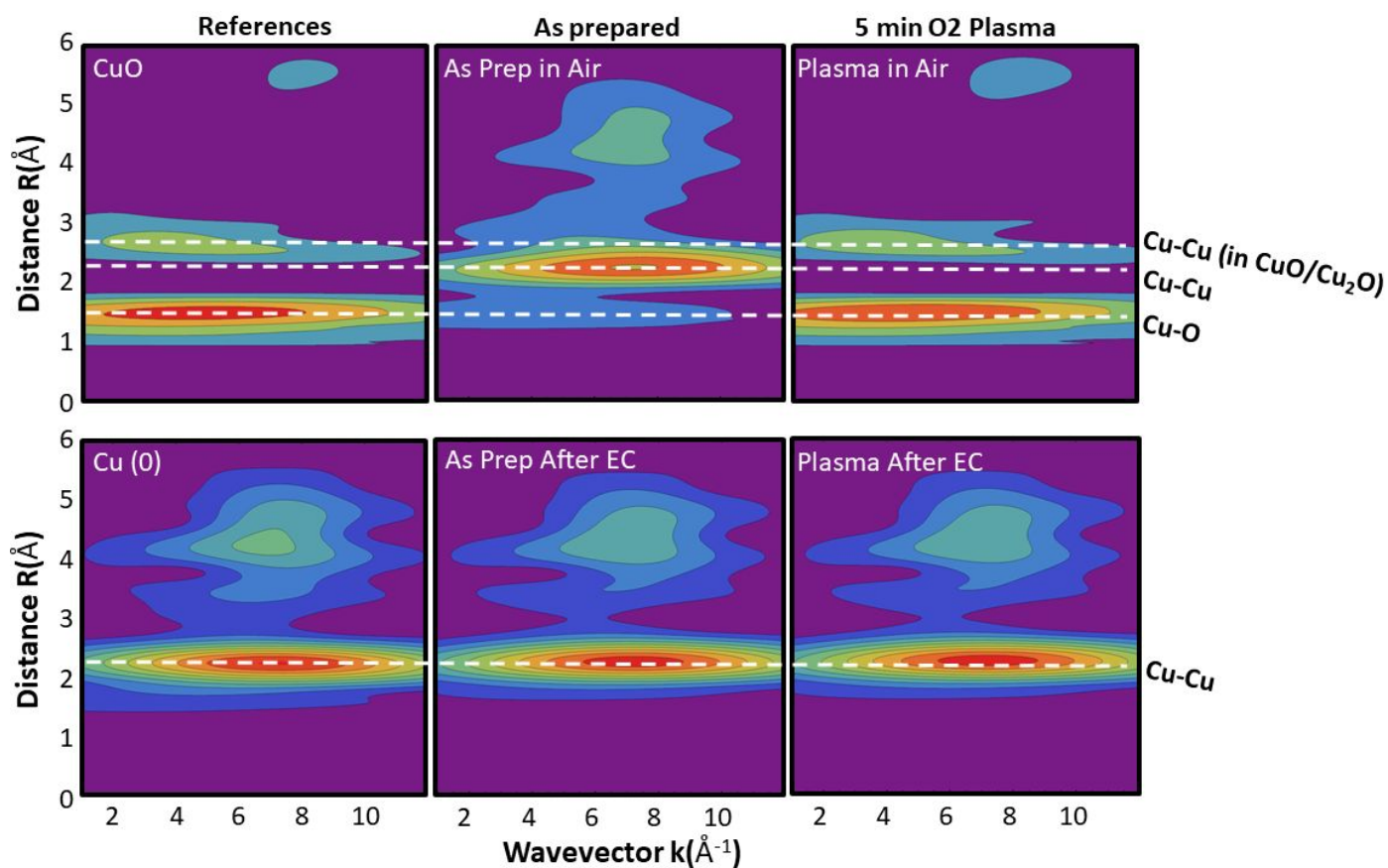
Sample	Cu (%)	Cu <sub>2</sub> O (%)	CuO (%)
Before EC As prep. on Pt	53	46	1
During EC As prep. on Pt	100	—	—
Before EC 5 min O <sub>2</sub> Plasma on Pt	—	5	95
During EC 5 min O <sub>2</sub> Plasma on Pt	100	—	—
Before EC As prep. on Ag	7	86	7
During EC As prep. on Ag	100	—	—
Before EC 5 min O <sub>2</sub> Plasma on Ag	—	3	97
During EC 5 min O <sub>2</sub> Plasma on Ag	100	—	—

**Table S4:** EXAFS fit parameters for the coordination numbers (N), interatomic distances (r) and variance ( $\sigma^2$ ) for the plasma and pristine Cu dendrites grown on Ag and Pt foils. Before EC denotes the measurement in air prior to any electrolyte contact. Samples during EC are measured in 0.1M KHCO<sub>3</sub> while a potential of -0.9V vs RHE is applied.

Sample	Path	N	r (Å)	$\sigma^2(\text{Å}^2)$
<b>Before EC</b> As prep. <b>on Pt</b>	Cu-Cu (Cu <sup>0</sup> )	6.8 ± 1.2	2.55 ± 0.01	0.01 ± 0.001
	Cu-O (Cu <sub>2</sub> O)	1.5 ± 0.5	1.84 ± 0.04	0.001 ± 0.001
<b>During EC</b> As prep. <b>on Pt</b>	Cu-Cu (Cu <sup>0</sup> )	10.6 ± 1.0	2.55 ± 0.01	0.01 ± 0.001
<b>Before EC</b> 5 min O <sub>2</sub> Plasma <b>on Pt</b>	Cu-O (CuO)	3.7 ± 0.6	1.95 ± 0.02	0.0029 ± 0.001
<b>During EC</b> 5 min O <sub>2</sub> Plasma <b>on Pt</b>	Cu-Cu (Cu <sup>0</sup> )	11.3 ± 1.0	2.55 ± 0.004	0.008 ± 0.001
<b>Before EC</b> As prep. <b>on Ag</b>	Cu-O (Cu <sub>2</sub> O)	3.7 ± 0.9	1.84 ± 0.02	0.0019 ± 0.0003
<b>During EC</b> As prep. <b>on Ag</b>	Cu-Cu (Cu <sup>0</sup> )	11.8 ± 1.5	2.55 ± 0.02	0.01 ± 0.001
<b>Before EC</b> 5 min O <sub>2</sub> Plasma <b>on Ag</b>	Cu-O (CuO)	4.0 ± 0.7	1.95 ± 0.10	0.004 ± 0.002
<b>During EC</b> 5 min O <sub>2</sub> Plasma <b>on Ag</b>	Cu-Cu (Cu <sup>0</sup> )	11.8 ± 1.5	2.55 ± 0.12	0.008 ± 0.001



**Figure S13:** Wavelet-transformed spectra of the EXAFS data acquired on the Ag-supported Cu dendrites before and during electrochemistry (-0.9V vs RHE, 0.1M KHCO<sub>3</sub>).



**Figure S13:** Wavelet-Transformed spectra of the EXAFS data acquired on the Pt-supported Cu dendrites before and during electrochemistry (-0.9V vs RHE, 0.1M KHCO<sub>3</sub>).