Supporting Information

Tandem Electroreduction of Nitrate to Green Ammonia on Recycled Copper Sheets from Spent Batteries: Splicing the Surface Roughness Achieves High Yield Rate

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Reagents.

Sodium hydroxide (NaOH, 96%), potassium hydroxide (KOH, ≥85%) and Hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich. Urea and Absolute ethanol were purchased from Merck. Ferric nitrate nonahydrate ($FeN_3O_{9.9}H_2O{\cdot}4H_2O$, ≥98.0%), were purchased from Alfa Aesar. Ammonium chloride (NH_4Cl, ≥98%) was purchased from Fischer. Trisodium citrate, Citric acid ($C_8H_8O_7$, 99.5%), and Salicylic acid ($C_7H_6O_3$, 99%) were purchased from Loba Chemie. Sodium nitroferricyanide ($Na_2[Fe(CN)_5NO]$. $2H_2O$, 99%) was purchased from Alpha Chemika. Sodium hypochlorite (NaOCl, approx. 4%w/v) was purchased from SDDFCL. P Dimethyl Amino Benzaldehyde (C9H11NO, 98%) was purchased from Qualikems.

Characterization.

XRD patterns of the obtained powders were performed using a D8 Discover (Bruker). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometer (EDS) elemental mapping were conducted using a Thermo Fisher (USA) Quattro S Felid Emission Gun, Environmental SEM "FEG ESEM" and energy-dispersive X-ray spectrometer (EDS) elemental mapping were conducted on a JEM-ARM 200F. Ultraviolet−visible (UV−vis) spectra were carried out on a SHIMADZU UV-2700 UV−vis spectrophotometer. FTIR spectroscopy on a Nicolet 380 spectrometer (Thermo Scientific Nicolet, Waltham, MA, USA).

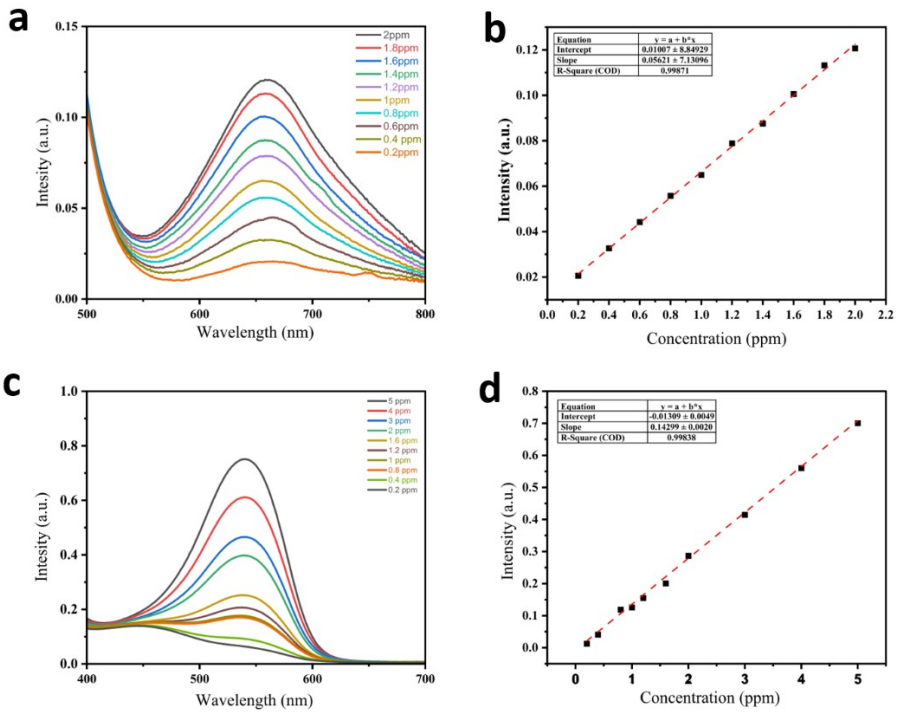

Figure S1. (a) UV-Vis spectrum of NH_4OH with different concentrations with the as-prepared indicator, (b) the corresponding calibration curve, (c) the UV-Vis spectrum of potassium nitrite with the as-prepared indicator, and (d) the corresponding calibration curve.

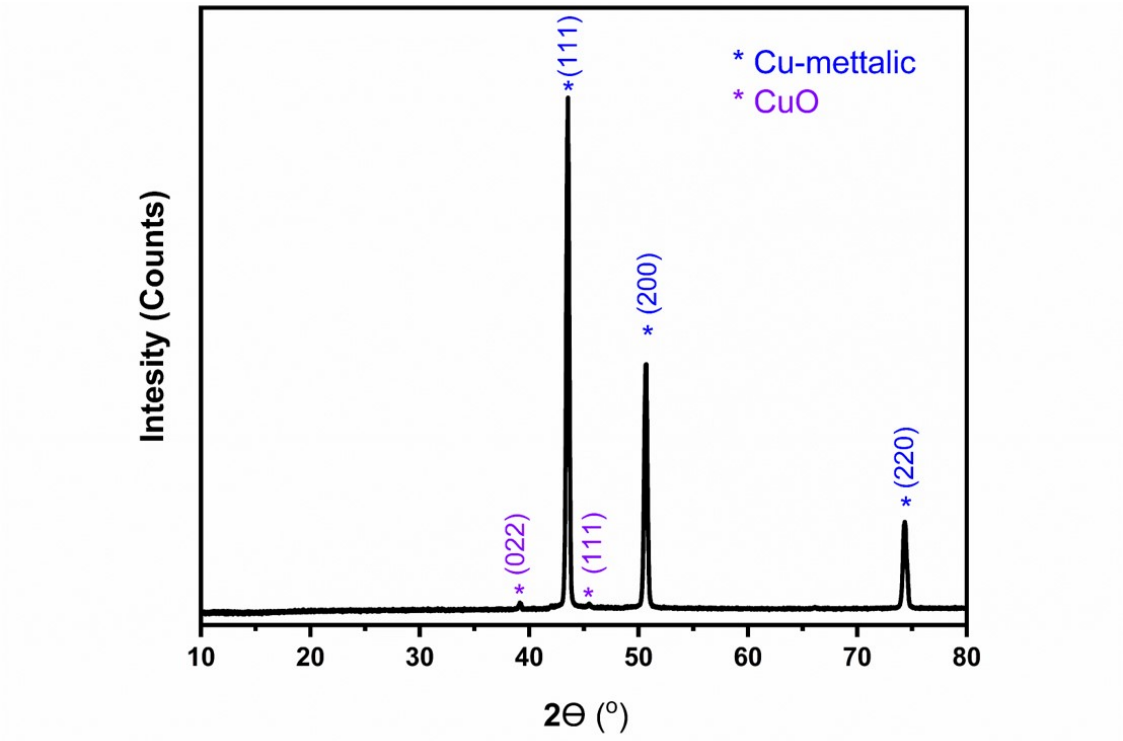

Figure S2. XRD pattern of the bare Cu-foil

Table S1. Elemental composition of the bare Cu-foil as revealed from the XRF analysis

Element	Cu (%)	Na (%)	Mg (%)	Al (%)
Percent	98.41	0.94	0.17	0.014

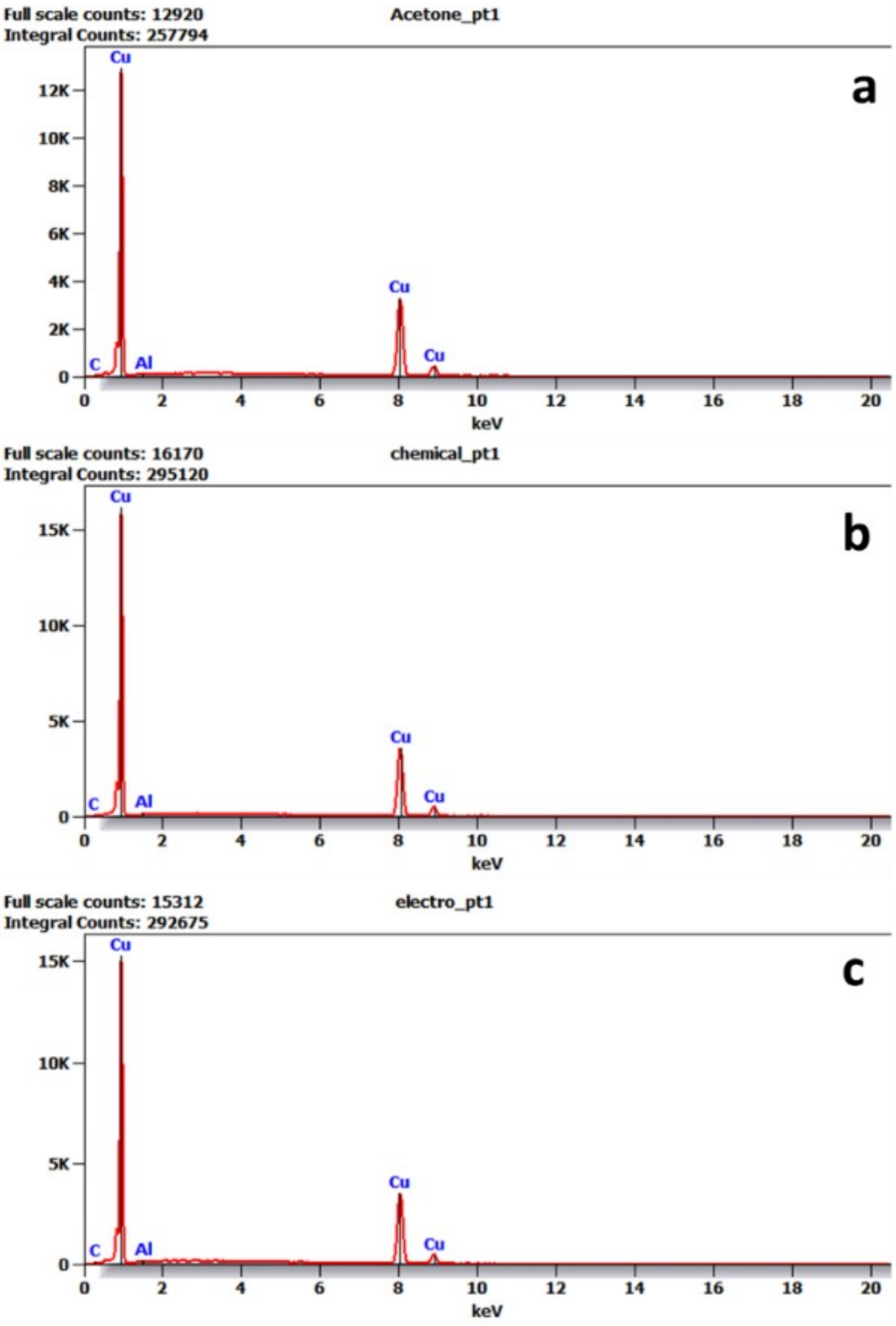

Figure S3 EDX spectra of the (a) acetone-treated, (b) acid-treated, and (c) electropolished Cu-foil samples.

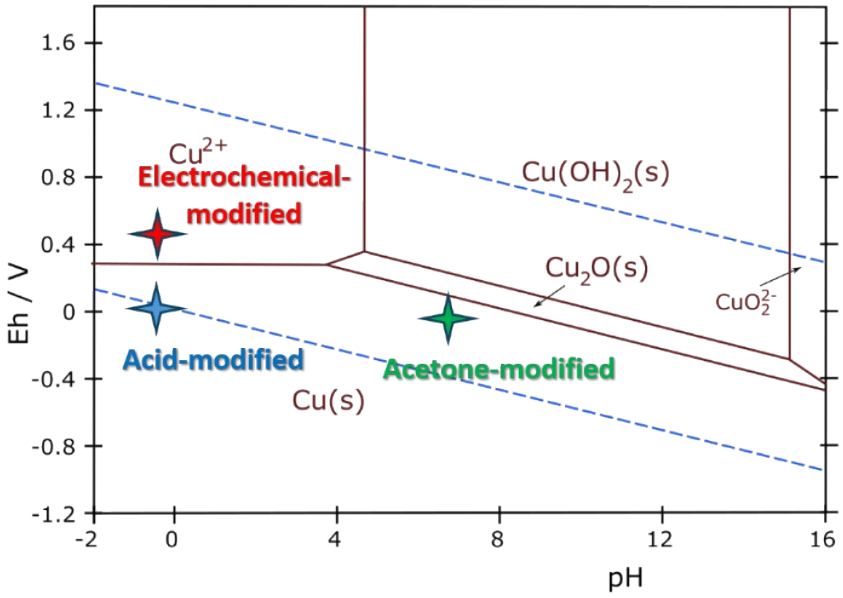

Figure S4. Pourbaix diagram of Cu.

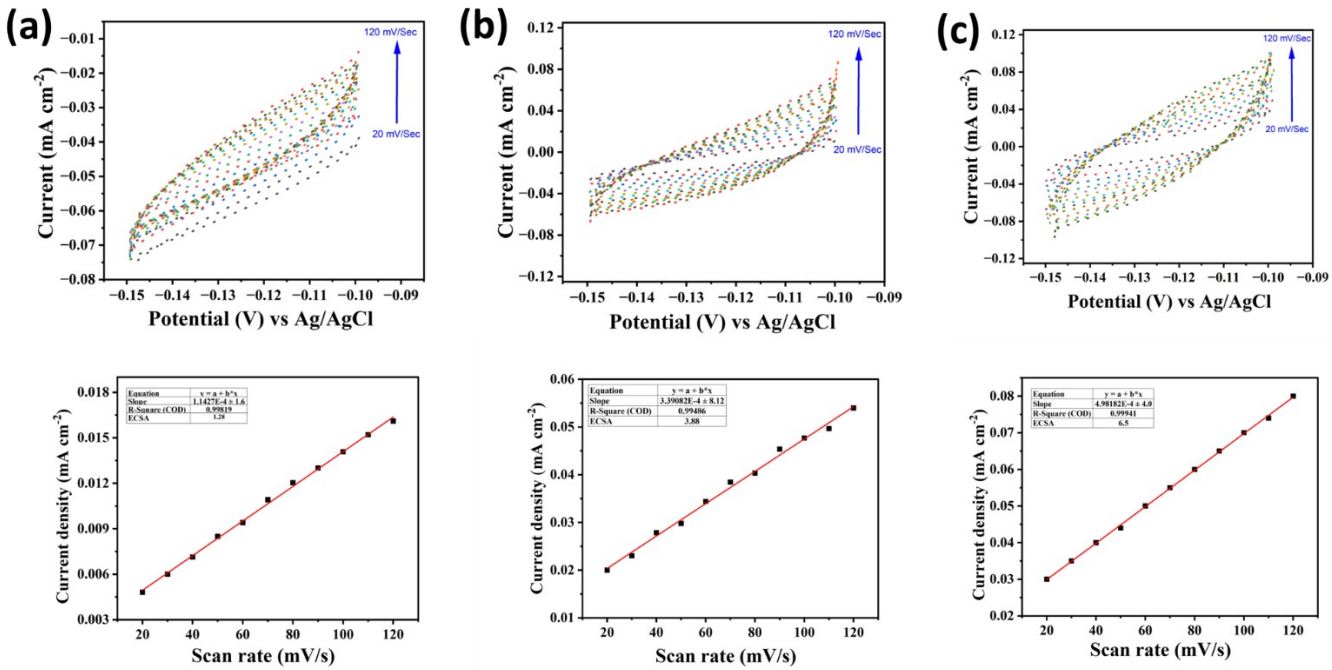

Figure S5. Cyclic voltammograms of Cu-foil measured at different scan rates from 20 to 120 mV/s. a) The CVs for acetone treated sample (top) and the linear best-fit line of C_{dl} (bottom) b) CVs (top) and best linear fit (bottom) for acid-treated sample c) CVs (top) and best linear fit (bottom) for electropolished sample

Computational details:

The equations applied for NO_3^- conversion to NH_3 are as follows:

$$* + NO_3^- \rightarrow *NO_3 + e^-$$

$$*NO_3 + 2H^+ + 2e^- \rightarrow *NO_2 + H_2O$$

$$*NO_2 + 2H^+ + 2e^- \rightarrow *NO + H_2O$$

$$*NO + H^+ + e^- \rightarrow *NOH$$

$$*HNO + 2H^+ + 2e^- \rightarrow *NH_2OH$$

$$*NH_2OH + 2H^+ + 2e^- \rightarrow *NH_3 + H_2O$$

$$*NH_3 \rightarrow *NH_3 + *$$

where * represents the surface. Then, the reaction Gibbs free energy change can be calculated by the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the total energy difference before and after intermediate adsorbed, ΔE_{ZPE} and ΔS are the differences of zero-point energy and entropy, respectively. The vibrational frequency calculations were applied to calculate the zero-point energy and entropy of free molecules and adsorbents. To avoid directly computing the energy of charged NO_3^-, gaseous HNO_3 is used as a reference in the following steps. Correspondingly, the adsorption energy of NO_3^-

(ΔG^*_{NO3}) can be approximately calculated as

$$\Delta G^*NO_3 = G^*NO_3 - G^* - GHNO_{3(g)} + 0.5GH_{2(g)}$$

where G^*_{NO3}, G*, $G_{HNO3(g)}$ and G_{H2} are the Gibbs free energy of NO_3^- adsorbed, HNO_3 and H_2 molecules in the gas phase, respectively. The HER catalytic activity of catalysts can be evaluated by ΔG_H, which is defined as were calculated based on.

$$\Delta E = E_{surf+H} - E_{surf} - {}^1/_2E(H_2)$$

The Gibbs free energy of Hydrogen is calculated using:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

ΔZPE is the difference in zero-point energy and ΔS is the difference in entropy between the adsorbed state and gas phase. Since ΔZPE - TΔS ≈ 0.24 eV, thus ΔG = ΔE + 0.24 eV.

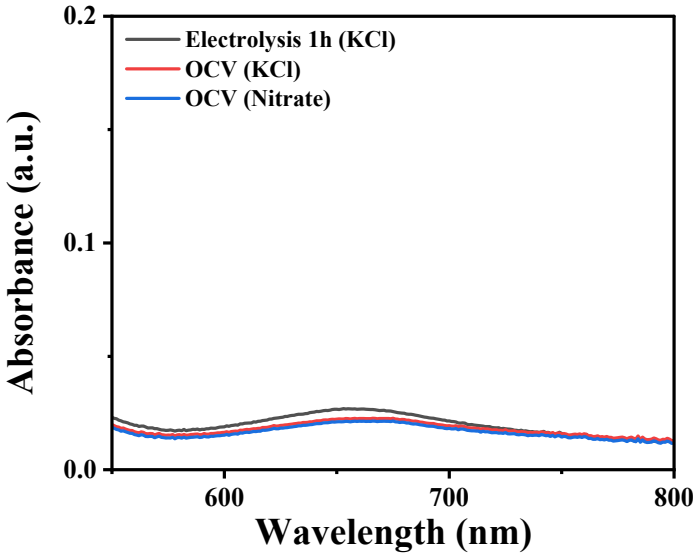

Figure S6. Control experiment

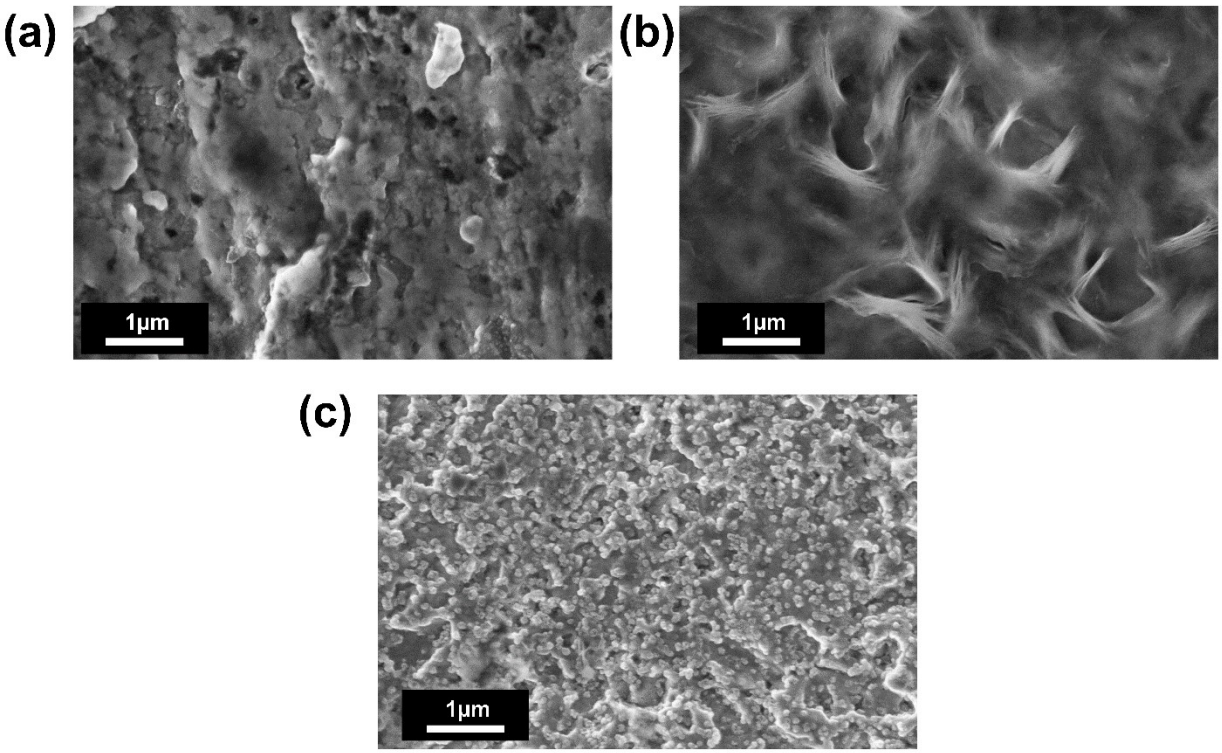

Figure S7. SEM images of a) acetone treated b) acid treated and c) electropolished Cu sheets after a complete electrochemical run under -0.8V vs RHE

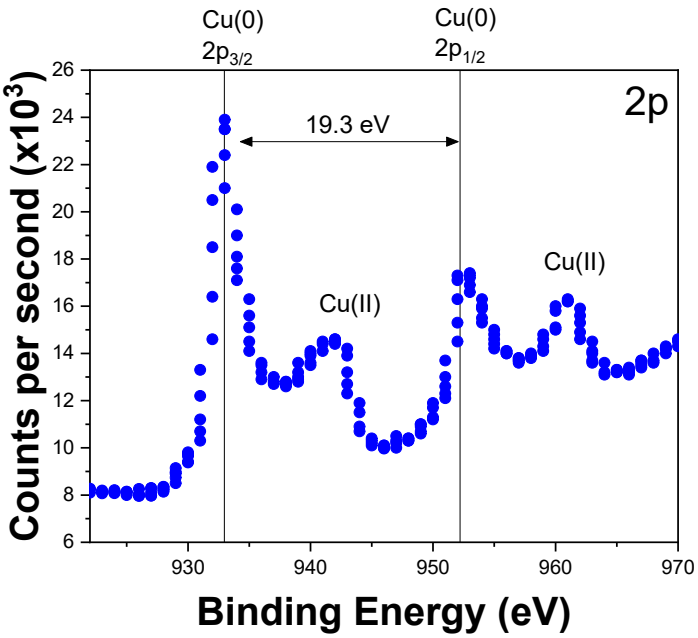

Figure S8. XPS spectra of the electropolished Cu sheet