-Supplementary Materials-

Stabilizing copper for CO_2 reduction in low-grade electrolyte

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Experimental Methods:

Electrodeposition of copper catalyst on carbon cloth. Precursor solutions of copper(II) chloride dihydrate, were purchased from commercial vendors (Alfa Aesar) and used without further treatment. Carbon cloth was purchased from Fuel cell store. The carbon cloth pieces were prepared by sonication in acetone, 1 M hydrochloric acid and distilled water (10 mins in each solvent). Electrodeposition was conducted in a two-compartment electrochemical cell with sand core as a separator. The anodic compartment contained 25 mL of 0.1 M KCl electrolyte (pH = 1, adjusted by concentrated HCl). The cathodic compartment contained 45 mL of 0.1 M KCl electrolyte (pH = 1, adjusted by concentrated HCl) and added 1 mL of 1 M $CuCl_2$. Pt mesh (1.5 cm^2 × 2.5 cm^2) was used as the counter electrode, and Ag/AgCl was used as the reference electrode. All potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl) and converted to the RHE reference scale using E (vs RHE) = E (vs Ag/AgCl) + 0.220 V + 0.0591 V × pH. The cathodic deposition of copper on carbon cloth was operated at -0.35 V vs RHE for 10 mins with constant stirring at 200 rpm. The total loading amount of copper on 1 cm^2 carbon cloth was measure by first dissolving the sample in a known volume (20 mL) of EDTA solution (10000 mg/L) for 1 h and then testing the relative intensity of the UV-vis absorption peak characteristic for Cu^{2+}-EDTA. The complete dissolution of copper from the electrode was confirmed by XRF and the total loading amount of copper was calculated to be 0.003 mmol/cm^2.

Electrolyte preparation. Three electrolytes of varying quality were prepared from three different water sources. Low grade electrolyte was prepared from tap (**TAP**) water taken from UBC Chemistry Building (Vancouver BC, Canada) and (99%) $KHCO_3$ obtained from Alfa Aesar (product # A12429). Medium grade electrolyte was prepared from distilled (**DI**) water (0.5 MΩ

・cm) and (99%) $KHCO_3$ obtained from Alfa Aesar (product # A12429). High grade electrolyte was prepared from Milli-Q (**MQ**) water (18.2 MΩ・cm) and (99.997%) K_2CO_3 obtained from Alfa Aesar (product # 10838). All electrolytes were saturated with CO_2 gas prior to use. The pH was determined to be 6.9 for all electrolytes. The quality of the electrolyte is denoted by the type of water used in each experiment hereafter. EDTA used was brought from Sigma Aldrich (EDS), Bioultra grade, anhydrous, ≥99% (titration).

Table S1. Concentration of metallic impurities in the three electrolytes analysed by ICP-OES. The electrolytes were analyzed for Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Sb, Se, Sr, Ti, Tl, V and Zn content and any metal with concentration greater than 0.05 mM (detection limit) is listed in the table. NA = below detection limit.

	Metal concentration (mM)		
Metal	**TAP** electrolyte	**DI** electrolyte	**MQ** electrolyte
Potassium	638	604	638
Calcium	0.116	NA	NA
Magnesium	2.16	2.08	NA
Sodium	0.63	0.62	0.18
Silicon	0.19	NA	NA

Table S2. Concentration of metallic impurities in the three types of water analyzed by ICP-MS.

Metal concentration (nM)

Metal	**TAP** water	**DI** water	**MQ** water
Manganese	55.23	1.802	NA
Iron	42.89	10.05	NA
Nickel	109.3	1.278	NA
Copper	12040	113.5	1.888
Zinc	808.3	96.24	3.747
Lead	16.24	1.347	0.048

Electrochemical measurements. A CH Instruments 760D or 660D potentiostat was used for all experiments. Pt mesh (1.5 × 2.5 cm^2) was used as the counter electrode. The electrolyte used for all CO_2 reduction experiments was 0.5 M $KHCO_3$ saturated with CO_2 to a pH of 6.9. Electrolysis was performed in a gastight two-compartment electrochemical cell with a proton exchange membrane (Nafion 117; Fuel Cell Store) as a separator. Each compartment contained 50 mL of 0.5 M $KHCO_3$ electrolyte. The solution in the cathodic compartment was purged with CO_2 for 60 min prior to the start of electrolysis. The headspace of the cathodic compartment was approximately 20 mL. CO_2 gas was delivered into the cathodic compartment at a rate of 10.00 sccm and vented directly into the gas-sampling loop of a gas chromatograph (GC; Clarus 580; Perkin Elmer). A GC run was initiated every 20-25 min. The GC was equipped with a packed MolSieve 5A column and a packed HaySep D column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector (FID) with a methanizer was used to quantify CO, CH_4 and C_2H_4 while a thermal conductivity detector (TCD) was used to quantify hydrogen.

Calibration of NMR signal. ^{1}H NMR spectroscopic data were collected on a Bruker AV III HD 400 MHz spectrometer equipped with Bruker BBFO smart probe with ATMA at 25 °C. Potassium hydrogen phthalate was added to the reaction sample taken from the catholyte as an internal standard and deuterium oxide (D_2O) was added to make a H_2O:D_2O (1:9 *v*/*v*) solution for ^{1}H NMR measurements. The water signal was suppressed by using a watergate W5 pulse sequence with double gradient echoes.

Scanning electron microscopy. Imaging and energy-dispersive X-ray spectroscopy (EDX) measurements were carried out on an FEI Helios NanoLab 650 dual beam scanning electron microscope with an EDAX Pegasus system with EDS detector. For imaging, the accelerating voltage was set to 1.0 keV, and the current was set to 50 pA. For EDX measurements, the accelerating voltage was 20 keV and the current was 6.4 nA. The working distance was 4 mm for both cases.

X-ray diffraction and X-ray fluorescence. X-ray diffraction patterns were recorded on a Bruker D8-Advance X-ray diffractometer using Cu Kα radiation. The acceleration voltage was 40 kV and the current was 40 mA. Data were collected between 2θ angles of 5° and 90° with a step size of 0.04°. The step time was 0.6 s. X-ray fluorescence measurements were taken with a Thermo Fisher Scientific Niton XL3t analyzer utilizing a shielded test stand. The X-ray source was run with an accelerating voltage of 50 kV and a current of 40 μA. Scan time was 60 s for each sample.

Calibration of XRF signal. We electrodeposited copper on 2cm*3cm carbon cloth substrates with different deposition time (5 min to 30 min) under the same voltage as the copper catalysts tested in our experiment. Mass loading of copper is measure by balance and compared with XRF signal as shown in Figure S10a. The same samples are then submerged in 50 mL 0.5 M $KHCO_3$ with 1g/L EDTA for 12 h to fully dissolve copper catalyst. The concentration of EDTA-Cu is measured by UV-vis method, which is previously calibrated by standard concentration of EDTA-Cu. The result of EDTA-Cu concentration vs XRF signal are shown in Figure S10b. Both plots show good linear relationship of XRF signal vs copper mass. And a formula can be established as below:

Cu (loading μmole/cm^2)= 0.067* (XRF counts)

UV-vis absorption spectra. UV-vis absorption spectra were collected using a Cary 7000 Universal Measurement Spectrophotometer. The scanning range of all samples was 200-1100 nm and the scan rate was 10 nm/s. 0.5 M $KHCO_3$ solution was used as reference and deducted from every spectrum. For each sample, five spectra were taken and averaged for the analysis.

Copper dissolution and redeposition experiment. The XRF signal is calibrated by measuring the copper mass with an analytical balance and constructing a UV-Vis absorption titration after the copper is fully dissolved and chelated with EDTA (See in supporting information and Figure S11). In this experiment, initial copper loading on carbon cloth is controlled to be approximately 0.003 mmol/cm^2, corresponding to an XRF signal of 45 counts/s. We normalized this initial amount of copper on the carbon cloth to a relative copper level of 1.0 and marked the theoretical limited concentration of EDTA-Cu to be 0.06 mM, which is the concentration obtained if all the initial copper is fully dissolved from electrode into 50 mL of electrolyte. All XRF signals were normalized to the initial copper loading on the electrode and electrolyte copper concentrations were monitored by the characteristic absorbance peak for Cu^{2+}-EDTA at ~730 nm in the UV-Vis (Figure S12).

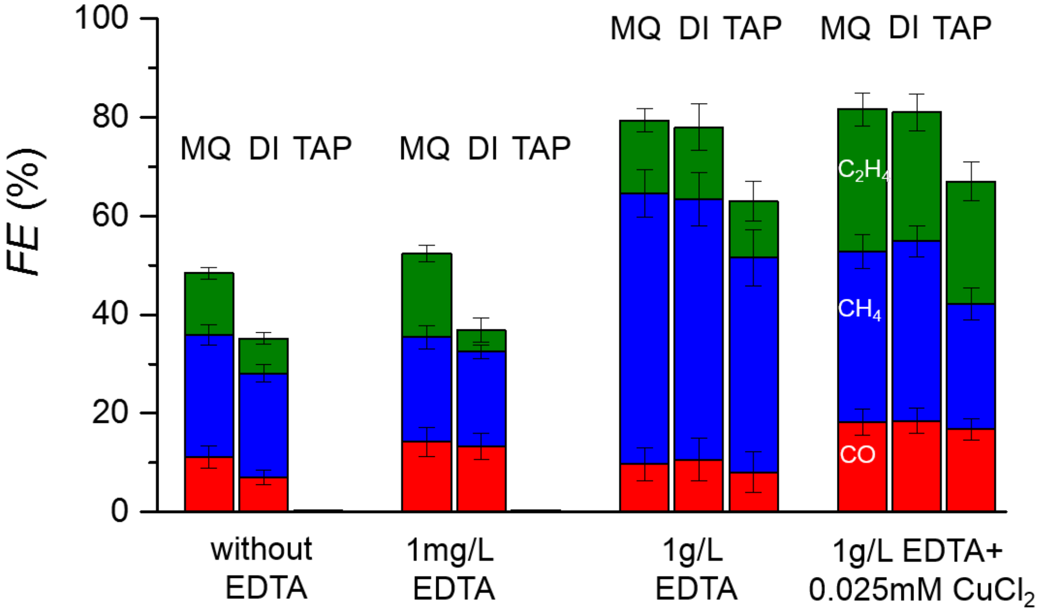

Figure S1. The Faradaic efficiencies (FEs, dots) and their error bar for CO_2 reduction products CO, CH_4 and C_2H_4 on dendritic copper catalysts supported on carbon cloth in different electrolytes. The sampling time is 3 h after operating at -1.3V vs RHE. The FE results are plotted based three individual samples tested with the same parameters.

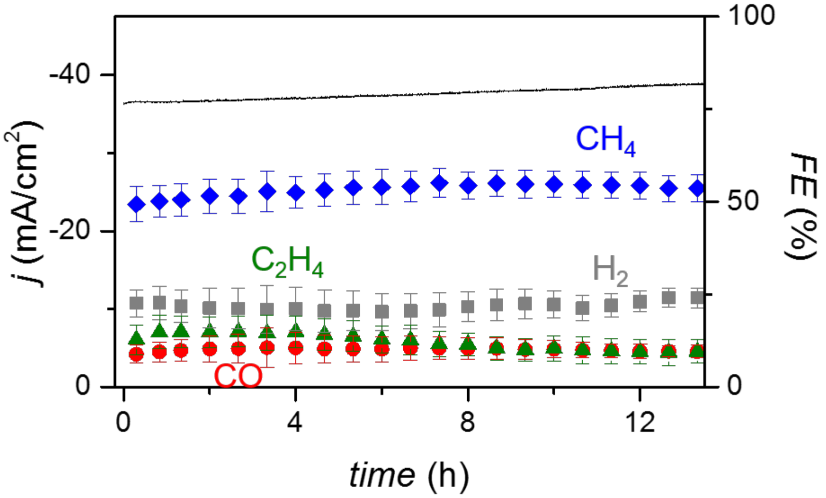

Figure S2. Time-resolved current densities (j, black line) and Faradaic efficiencies (FEs, dots) for CO_2 reduction products CO, CH_4 and C_2H_4 on dendritic copper catalysts supported on carbon cloth in a CO_2-saturated DI_{EDTA} electrolyte with error bar. The FE results are plotted based three individual samples tested with the same parameters.

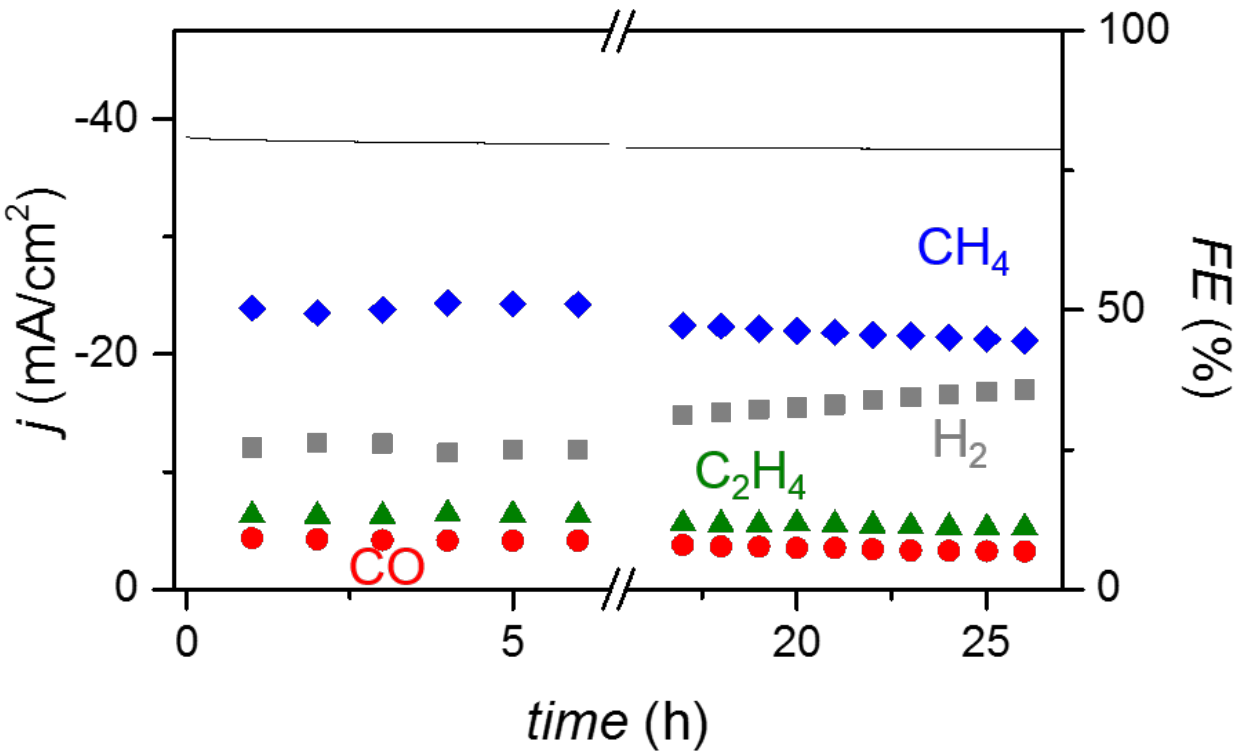

Figure S3. Time-resolved current densities (j, black line) and Faradaic efficiencies (FEs, dots) for CO_2 reduction products CO, CH_4 and C_2H_4 on dendritic copper catalysts supported on carbon cloth in a CO_2-saturated DI_{EDTA} electrolyte.

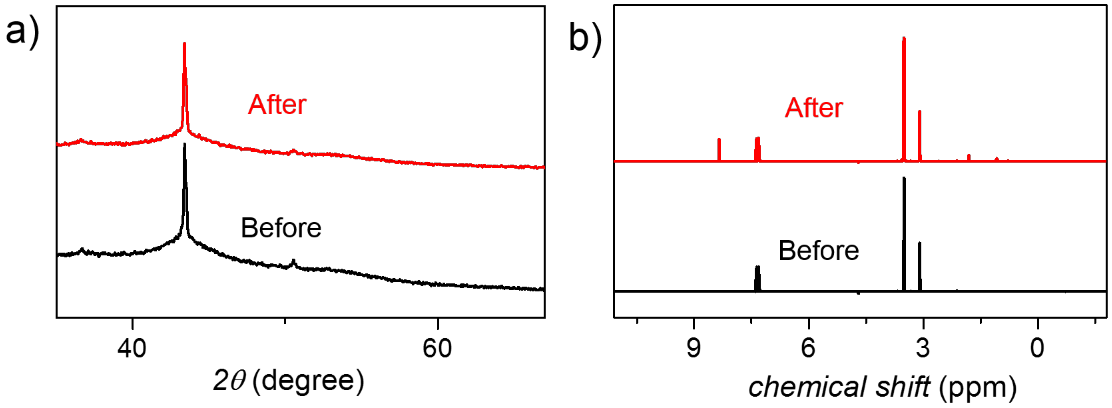

Figure S4. a) XRD of copper catalyst before and after operating in DI_{EDTA} electrolyte for 12 hours. b) ^1H NMR of the **DI_{EDTA}** electrolyte before and after operating with a copper catalyst at -1.3V vs RHE for 12 hours. Potassium hydrogen phthalate is used as internal reference (7.4 ppm). The hydrogen peaks for EDTA (3.2 and 3.6 ppm) show no change in intensity or chemical shift after 12 h continuous operation. The liquid products of formic acid, methanol and ethanol were quantified by ^1H NMR but the amounts produced were <1% and we discontinued monitoring for liquid products in subsequent tests.

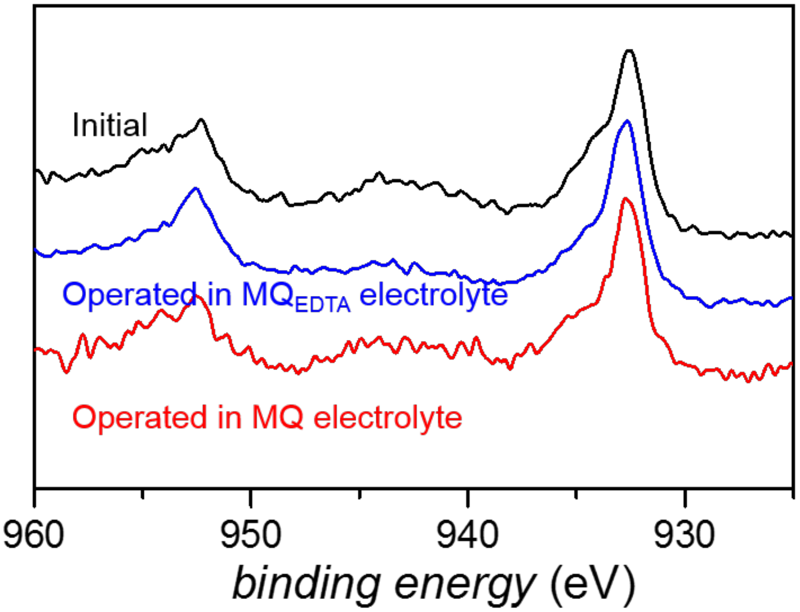

Figure S5. XPS of copper/carbon cloth electrode before and after operating for 12 h in MQ and MQ_{EDTA} electrolyte. Peaks around 933 eV and 935 eV corresponding to Cu(0)/Cu(I) and Cu(II), respectively.

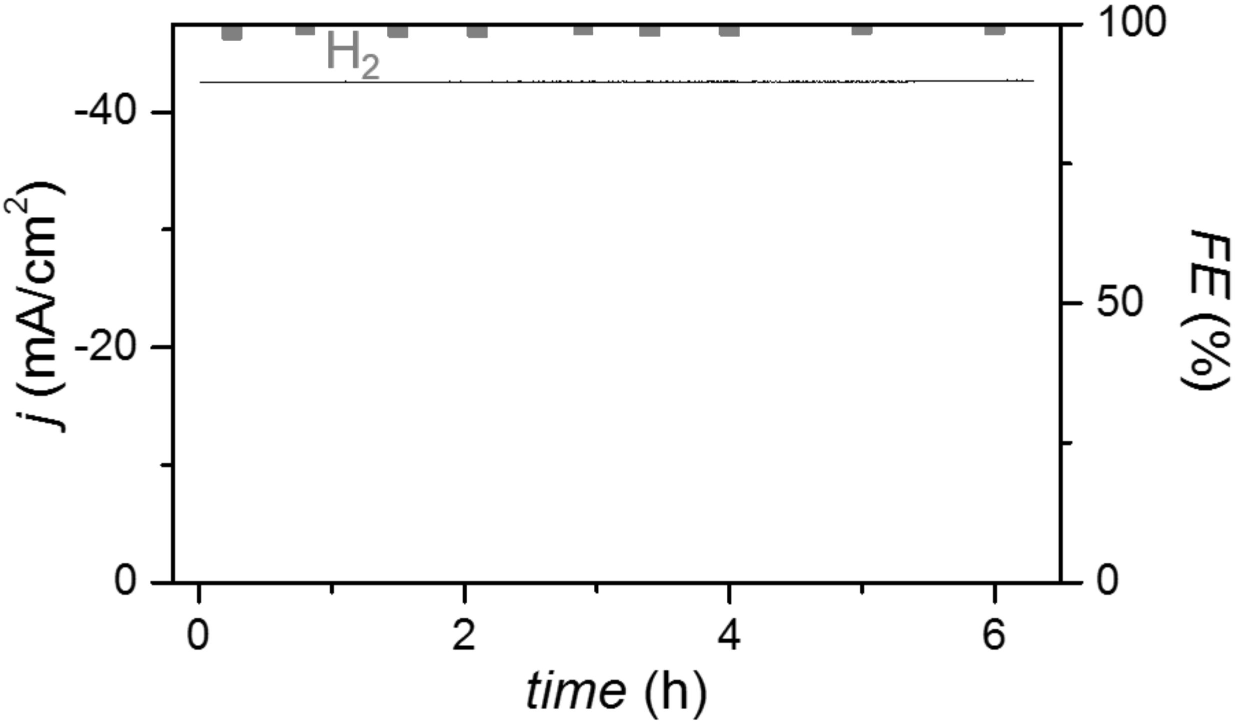

Figure S6. Time-resolved current densities (j, black line) and Faradaic efficiencies of HER (FEs, dots) for reduction of 0.5 M KCl electrolyte containing 1g/L EDTA at -1.3 V vs RHE. For the whole 6 h period, FE_{H2} maintains 100% and none other product can be detected in GC.

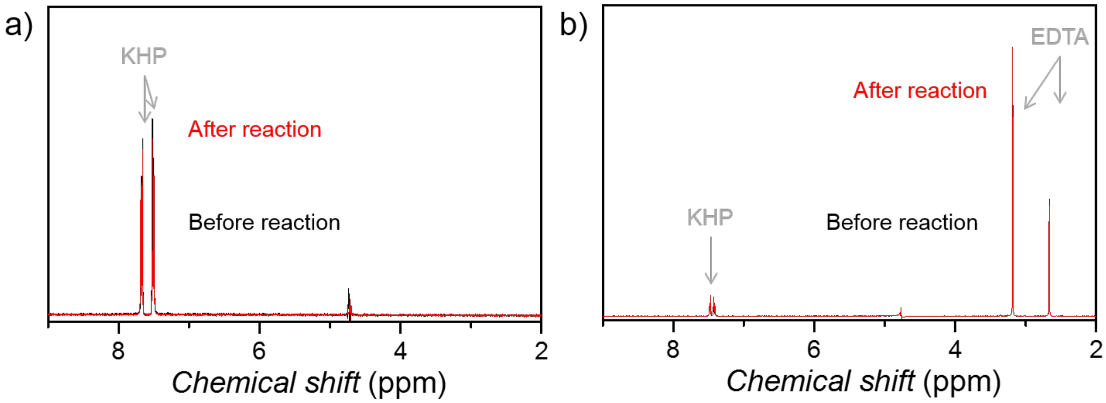

Figure S7. Figure S7. ^{1}H NMR of a) anolyte side and b) catholyte side of 50 mL 0.5 M KCl electrolyte containing 1g/L EDTA before and after operating with a copper catalyst at -1.3V vs RHE for 12 hours. The two compartments are separated by proton exchange membrane (Nafion 117; Fuel Cell Store). Potassium hydrogen phthalate is used as internal reference (7.4 ppm). Result of anode side show that no carbon contained compound can go through proton exchange membrane (Nafion 117; Fuel Cell Store) to the anolyte. The hydrogen peaks for EDTA (3.2 and 3.6 ppm) show no chemical shift and integration intensity change of 1-2% after 6 h continuous operation (3700 C). No forming of other compound such as alcohol or acid can be observed.

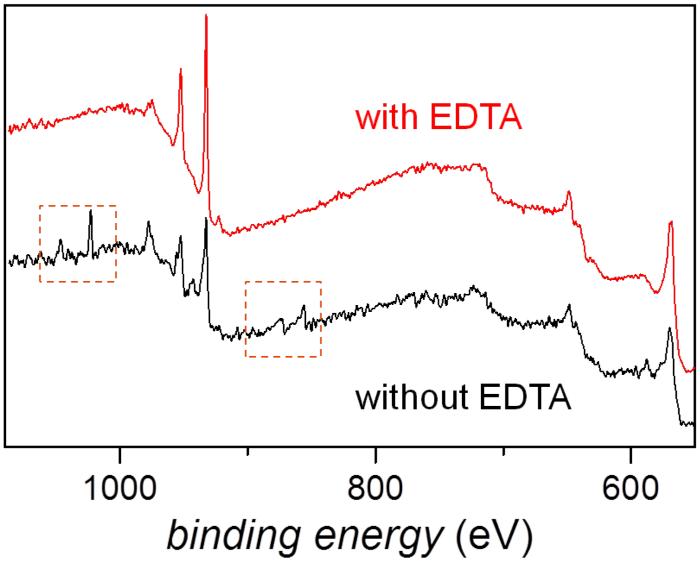

Figure S8. XPS of copper foil operating for 12 h in tap water electrolyte with or without EDTA. Peaks around 1050 eV and 860 eV highlight the Zn and Ni signatures.

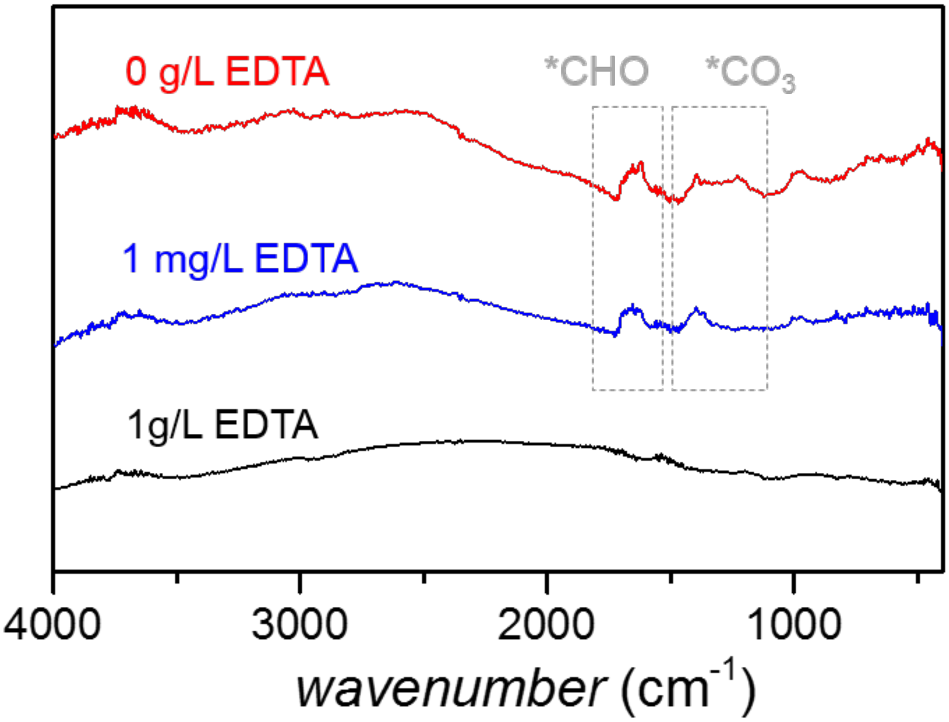

Figure S9. FTIR of copper foil operating for 12 h in tap water electrolyte without, with 1 mg/L or with 1 g/L EDTA.

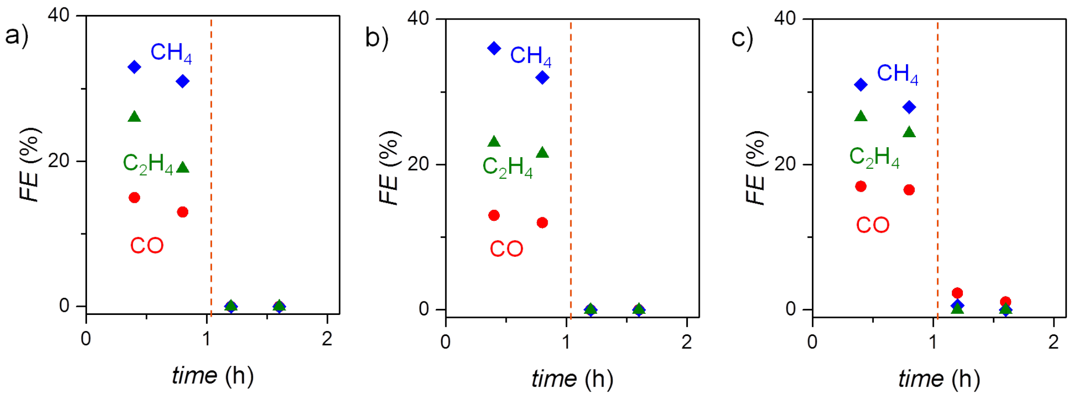

Figure S10. CO_2 reduction Faradaic efficiencies for copper catalysts operating at -1.3 V over time in **DI** electrolyte. At the dashed line, a) 0.1 M $Fe(NO_3)_3$, b) 0.1 M $Ni(NO_3)_2$, c) 0.1 M $Zn(NO_3)_2$ are added into the electrolyte. respectively, which immediately deactivates the electrocatalyst.

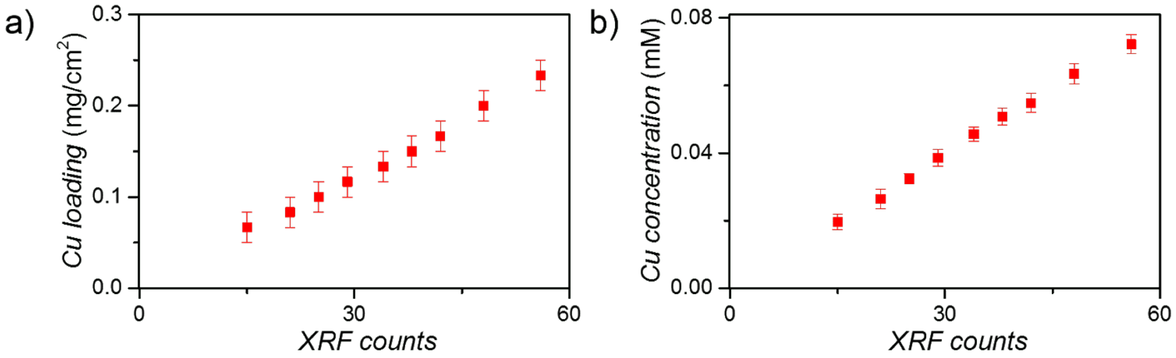

Figure S11. a) The mass loading of copper on carbon cloth as measured by balance vs. the XRF signal. b) UV-vis absorption titration after copper is fully dissolved in 50 mL 0.5 M $KHCO_3$ with 1g/L EDTA electrolyte vs. the XRF signal of copper on carbon cloth.

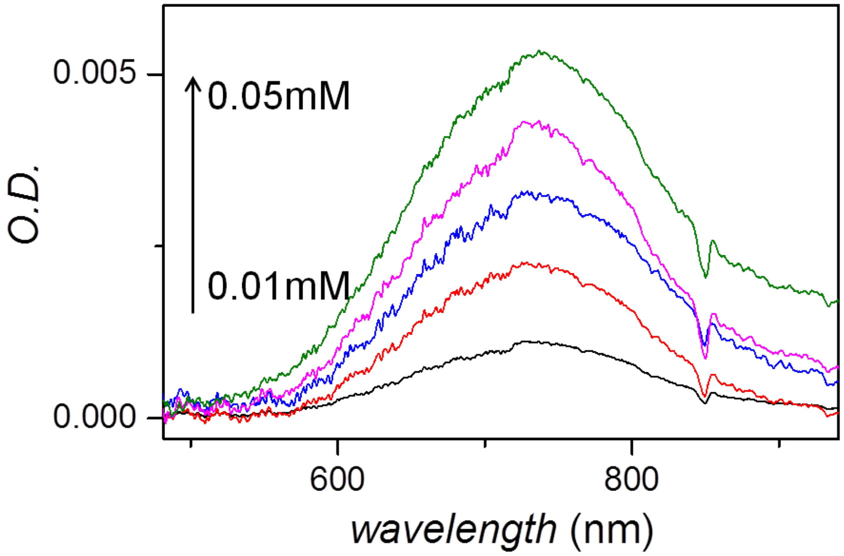

Figure S12. The UV-Vis absorption calibration test of Cu^{2+}-EDTA with concentration from 0.01 mM to 0.05 mM in 0.5 M $KHCO_3$ electrolyte.

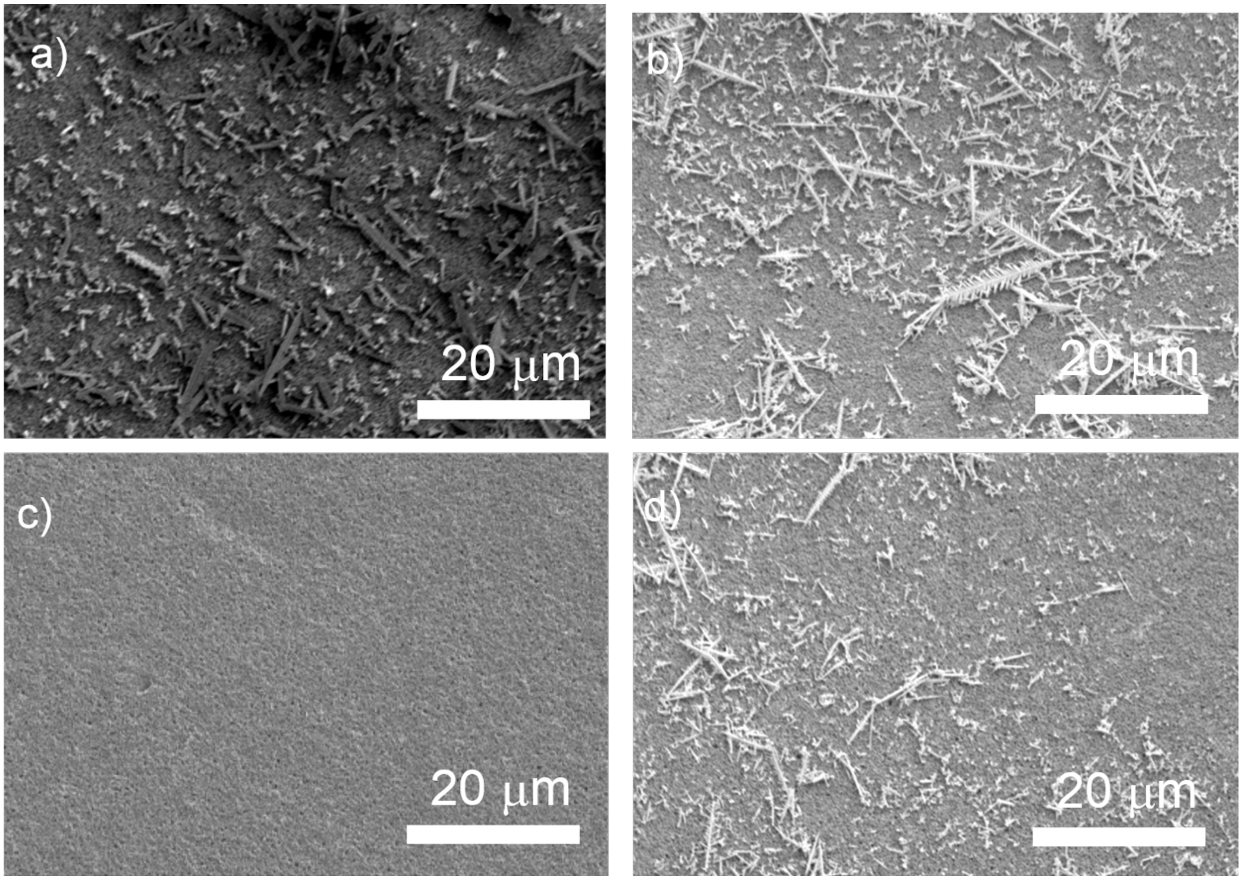

Figure S13. SEM micrographs of Cu electrocatalysts on carbon cloth: a) as-prepared; b) after operating in $\mathbf{DI_{EDTA}}$ electrolyte; c) blank carbon cloth d) after operating in DI_{EDTA} parallel to the Cu/CC electrode. The area of both blank carbon cloth electrode and working copper/carbon cloth electrode are 1 cm^2. The electrolysis is performed at -1.3V vs RHE for 6 h on both electrode.

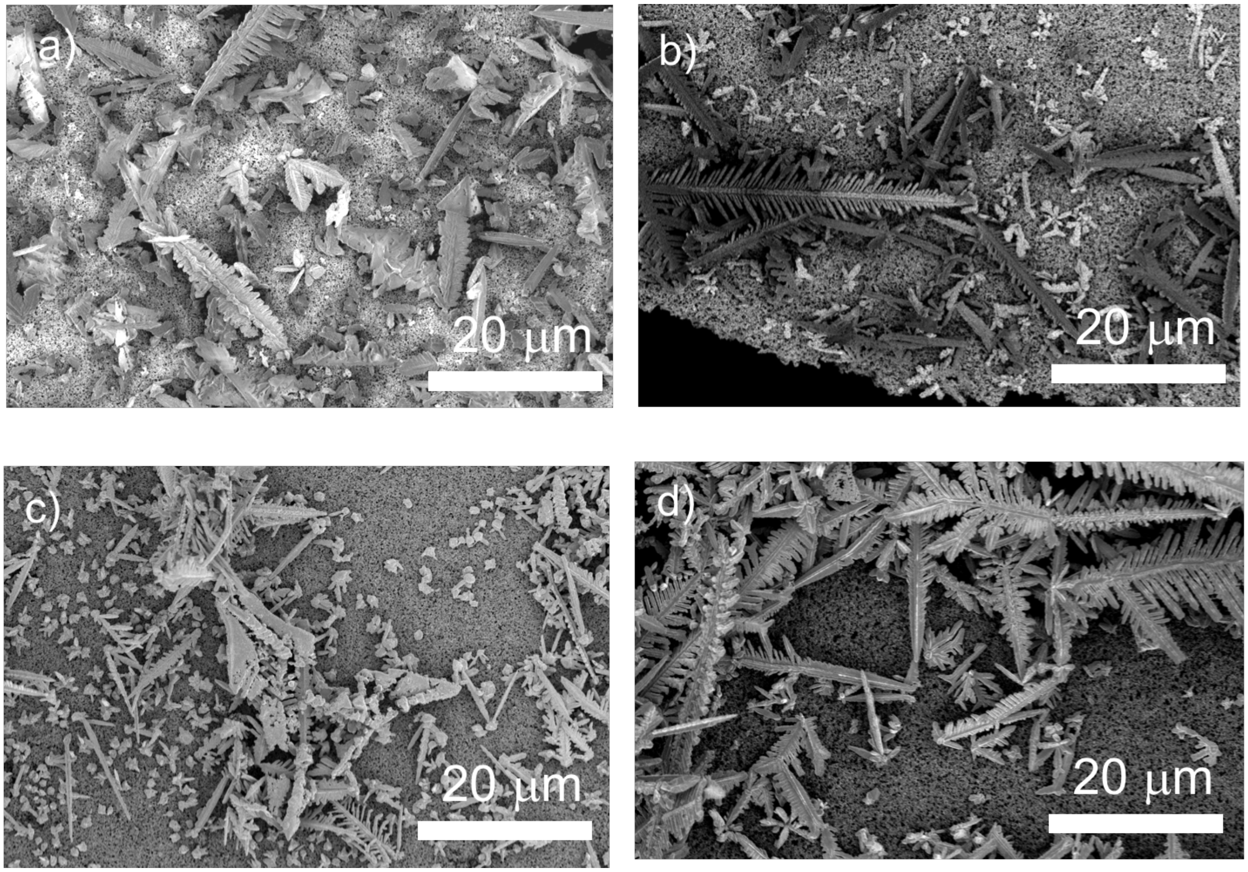

Figure S14. The SEM images of a) as-prepared copper catalysts on carbon cloth. The SEM images of copper catalysts on carbon cloth after operating in b) **DI** electrolyte c) **DI**$_{\mathbf{EDTA}}$ electrolyte and d) **DI**$_{\mathbf{EDTA}}$ electrolyte with 0.025 mM $CuCl_2$ at -1.3V vs RHE for 12 hours.

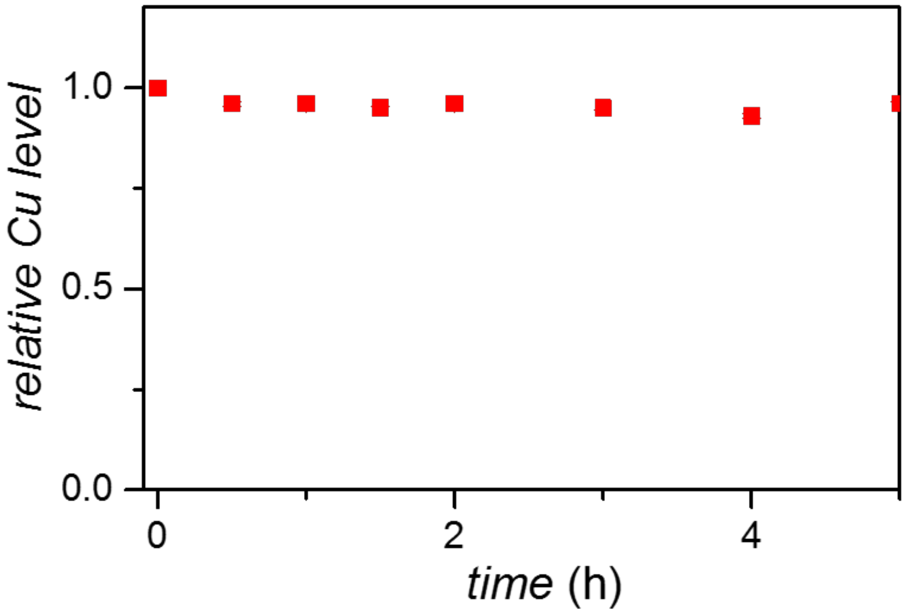

Figure S15. Normalized XRF signal for the electrode surface of copper catalyst on carbon cloth during electrolysis at -1.3 V vs RHE in DI_{EDTA} electrolyte with 0.025 mM $CuCl_2$.

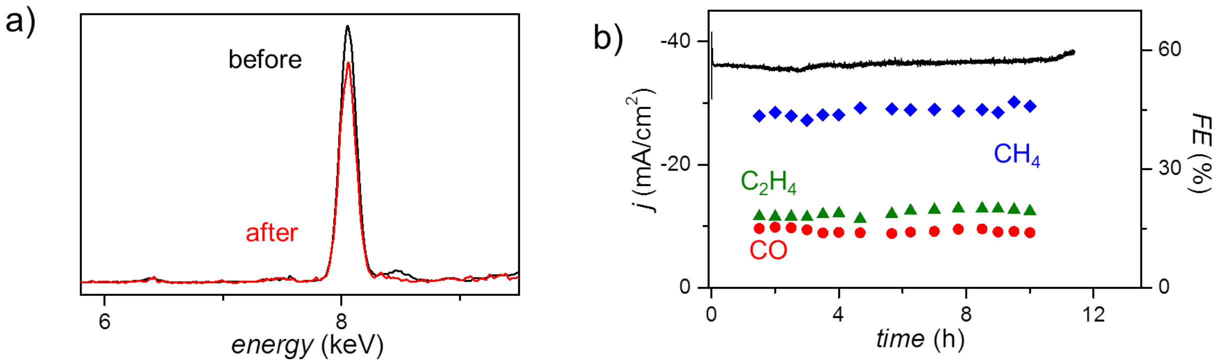

Figure S16. a) XRF spectra for the electrode surface of copper catalyst on carbon cloth before and after operating in **DI$_{\text{EDTA}}$** electrolyte with 0.01 mM $CuCl_2$ for 12 h. and b) the Faradaic efficiencies for CO_2 reduction products CO (red), CH_4 (blue) and C_2H_4 (green) during electrolysis at -1.3 V vs RHE in **DI$_{\text{EDTA}}$** electrolyte with 0.01 mM $CuCl_2$. The leaching of copper is alleviated compared with **DI$_{\text{EDTA}}$** electrolyte without $CuCl_2$ but not as effect as with **DI$_{\text{EDTA}}$** electrolyte with 0.025 mM $CuCl_2$. The C_2H_4/CH_4 producing ratio in **DI$_{\text{EDTA}}$** electrolyte with 0.01 mM $CuCl_2$ is also in between of the operating in **DI$_{\text{EDTA}}$** electrolyte without $CuCl_2$ and **DI$_{\text{EDTA}}$** electrolyte with 0.025 mM $CuCl_2$