Supplementary Information

Highly efficient electro-reduction of CO$_2$ to formic acid by nano-copper

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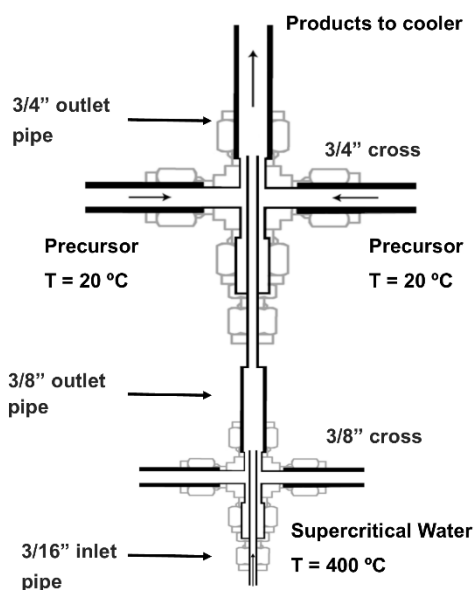*Corresponding author: Professor Jawwad A. Darr
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Figure S 1 - Schematic of the confined jet mixers with pipework and mixer sizes used to synthesise ultrafine CuO via continuous hydrothermal flow synthesis
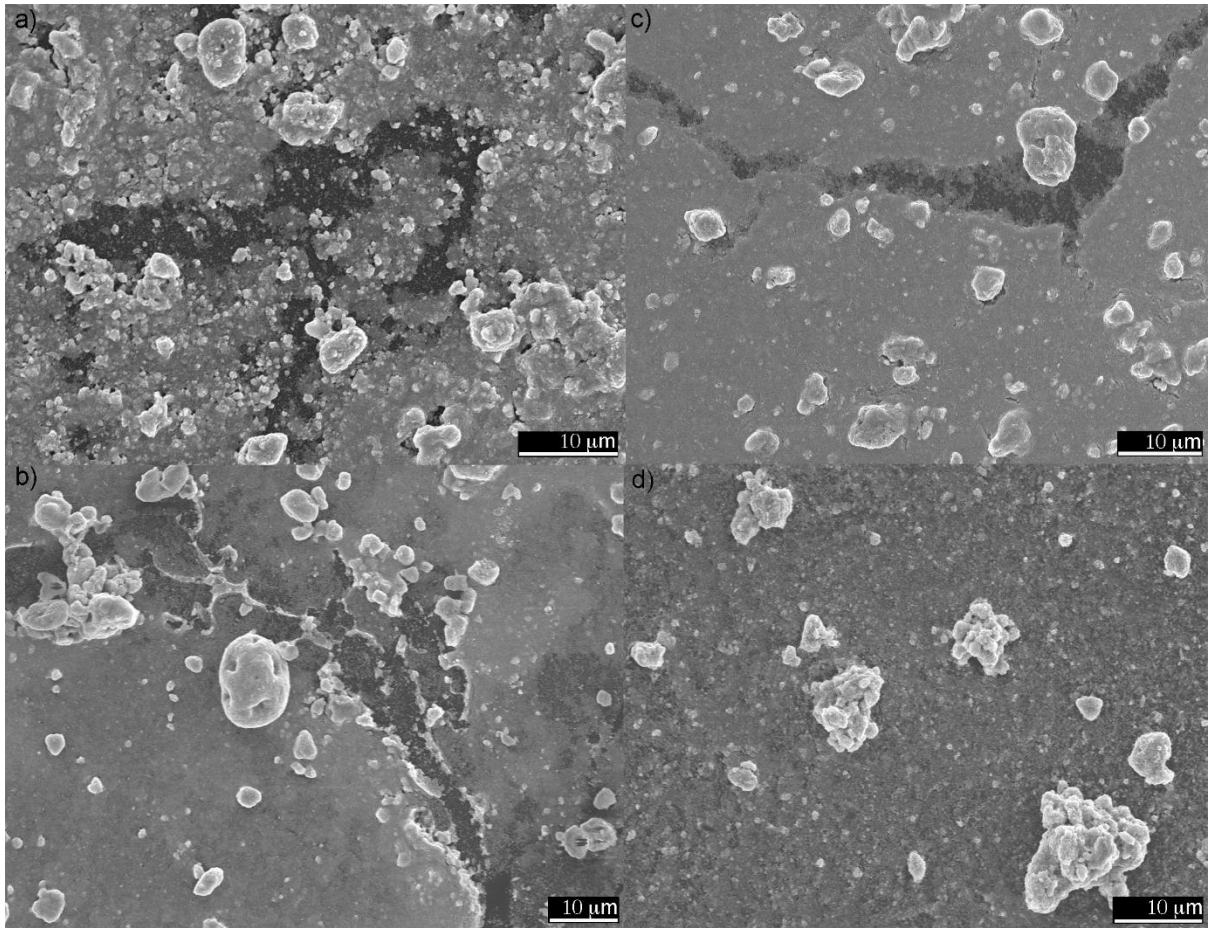
Figure S 2 - SEM of CuO deposited on glassy carbon electrode with a) 1 wt.%, b) 10 wt.%, c) 25 wt.% and d) 66 wt.% Nafion fraction before electrolysis
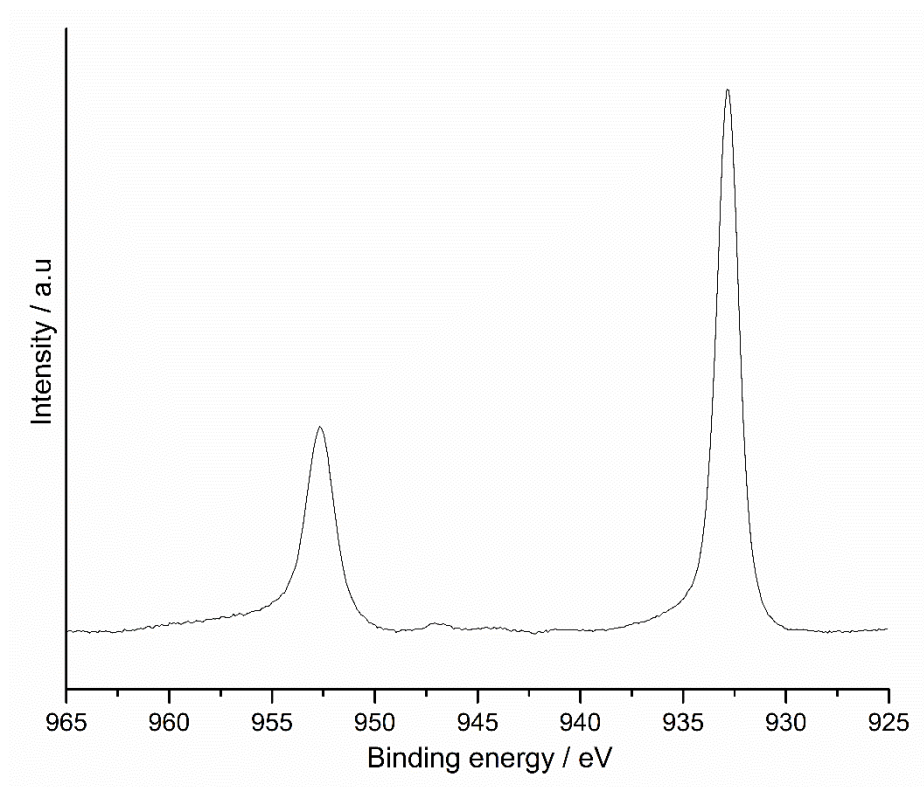
Figure S 3 - XPS spectra of CL1 post electrolysis (-1 V vs. Ag/AgCl for 3 hrs) showing Cu 2p 3/2 932.4 eV and Cu 2p 1/2 952.6 eV for Cu[0]. No satellite peaks typically seen with Cu[II] were observed, confirming the presence of Cu[0] on glassy carbon after electrolysis
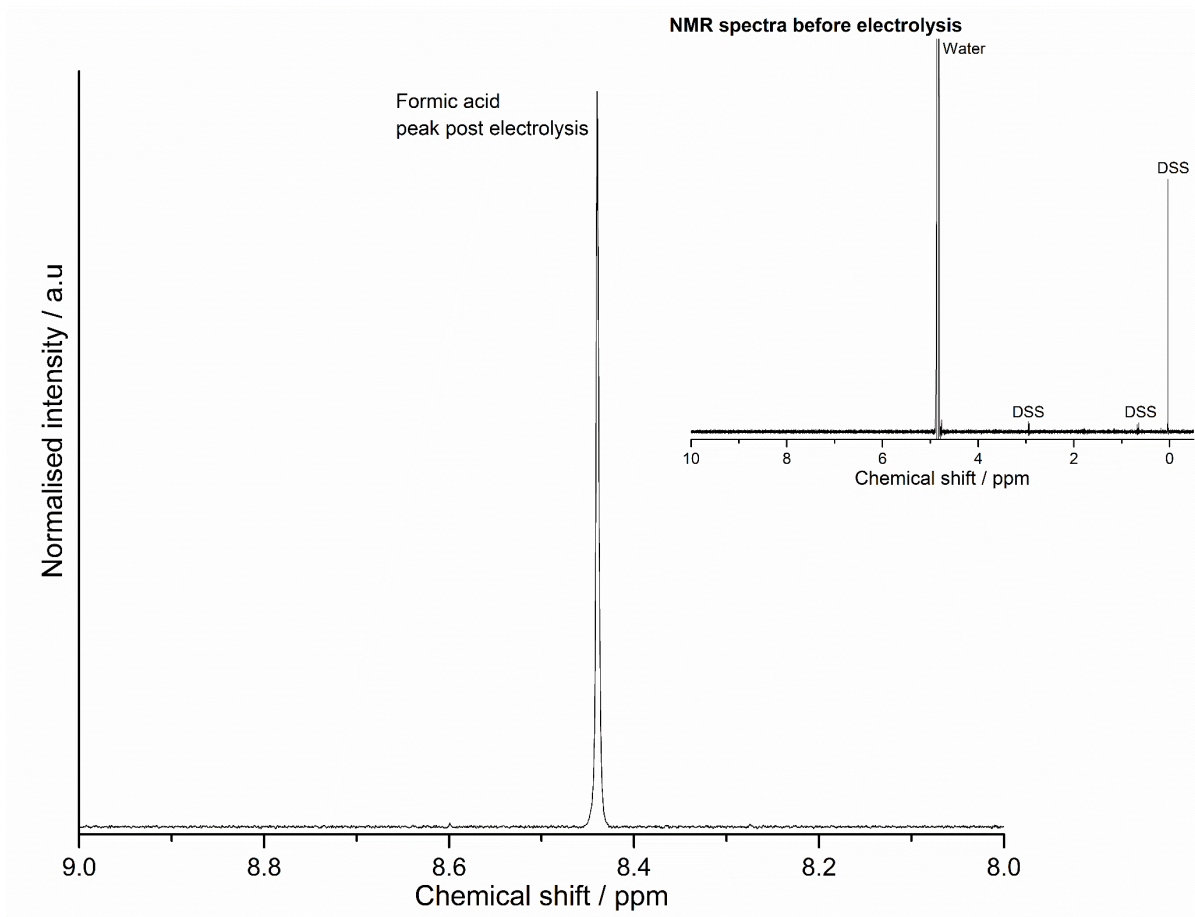
Figure S 4 - [1]**H NMR of formic acid formed during electrolysis using CL25 at -1.4 V vs. Ag/AgCl. Inset shows NMR spectra before electrolysis, DSS peaks are highlighted, where DSS was used as a reference control and strong water signal is observed at 4.75 ppm.**
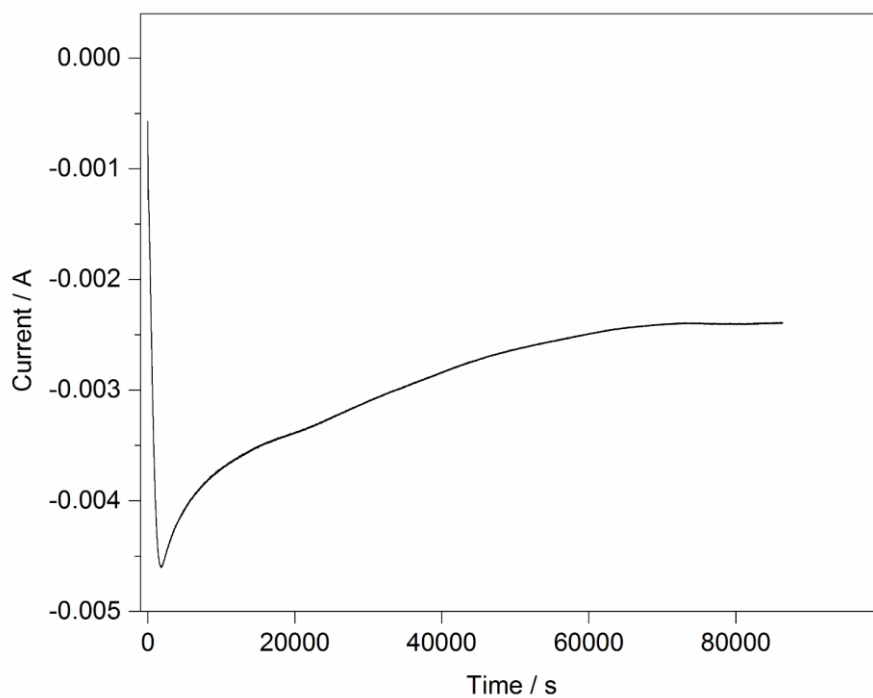

Figure S 5 – Long term stability test of sample CL25 held at -1.4 V vs. Ag/AgCl for 24 hours in CO_2 saturated 0.5 M $KHCO_3$ solution
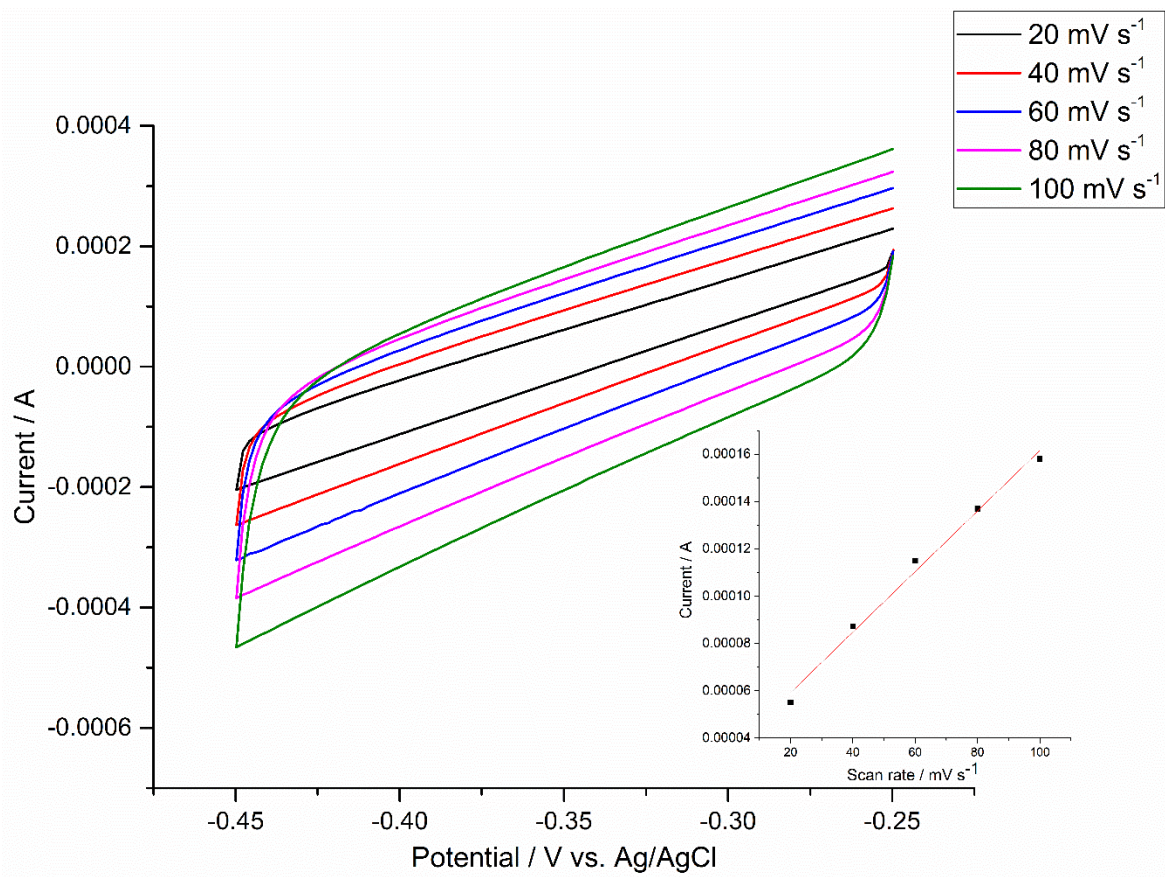
Figure S 6 - Plot of current vs potential of CL10 in 0.1 M H_2SO_4 cycled between -0.25 and -0.45 V vs. Ag/AgCl at scan rates in the range of 20 – 100 mV s^{-1}. Inset shows plot of current vs scan rate where the linear regression gives capacitance information
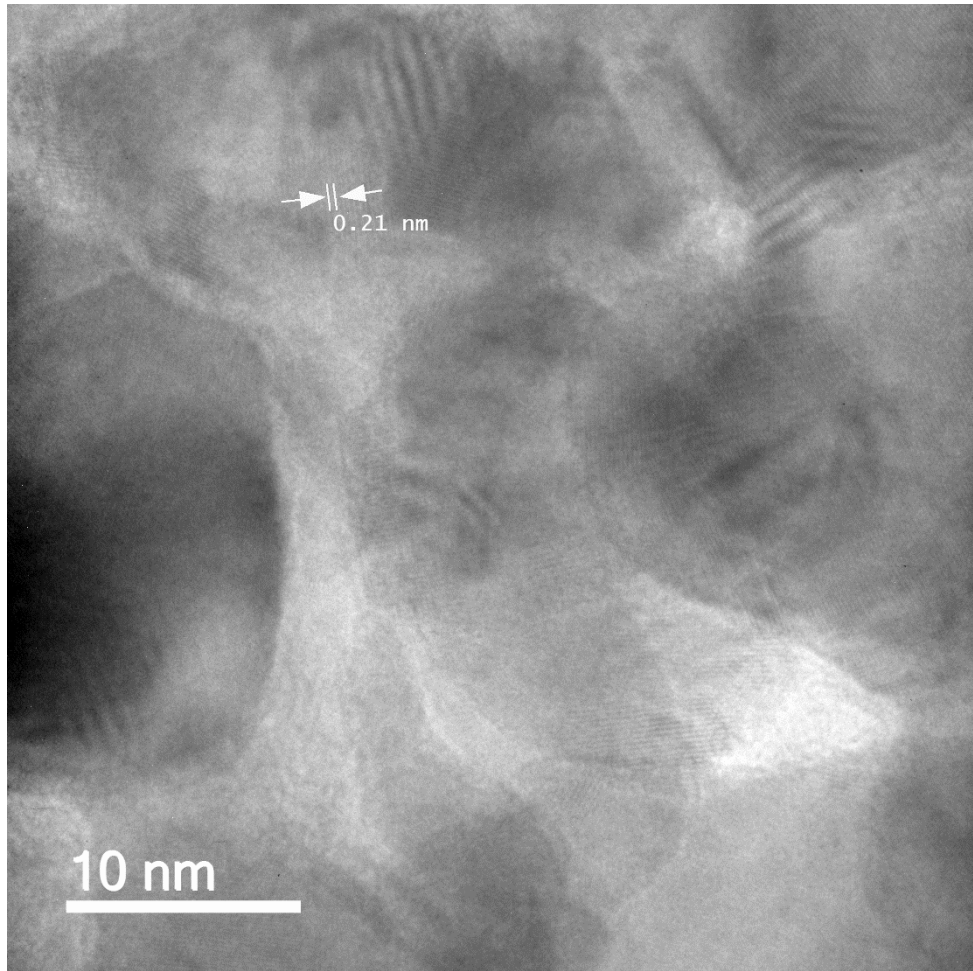
Figure S 7 - TEM of CL25 post electrolysis at -1 V for 3 hrs showing 111 surface plane with a d-spacing of 0.21 nm consistent with Cu d_{111}
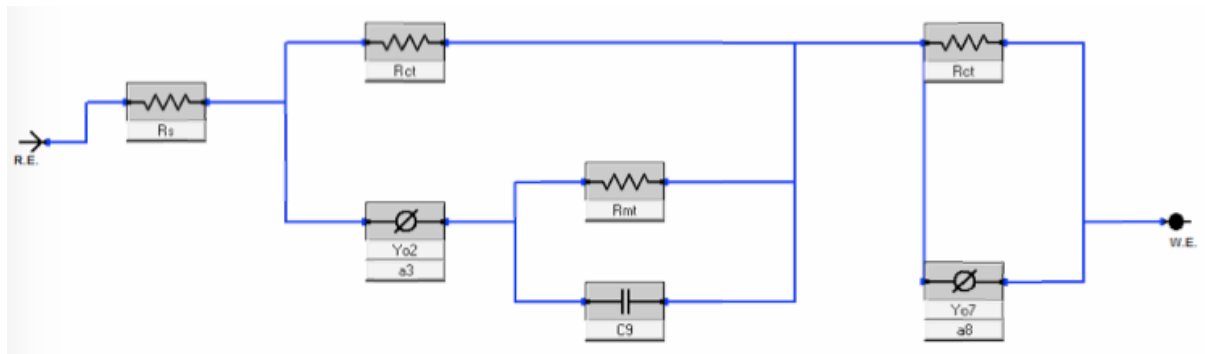

Figure S 8 - Equivalent circuit model of three electrode set up with nafion thin film coating on the glassy carbon electrode

Sample	R_{ct} (Ω)	R_{mt} (Ω)
CL10	16.9	Negligible
CL25	14.1	1.1
CL66	63.9	9.6

Table S 1 - Simulated data values for model in Fig S7 showing R_{ct} and R_{mt} values for CL_{10}, CL_{25} and CL_{66} at -1.4 V