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

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Figure S1 - 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 Cu⁰. No satellite peaks typically seen with Cu²⁺ were observed, confirming the presence of Cu⁰ on glassy carbon after electrolysis.
Figure S 4 - $^1\text{H}$ 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$_2$SO$_4$ 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
<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_{mt}$ (Ω)</th>
</tr>
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<tbody>
<tr>
<td>CL10</td>
<td>16.9</td>
<td>Negligible</td>
</tr>
<tr>
<td>CL25</td>
<td>14.1</td>
<td>1.1</td>
</tr>
<tr>
<td>CL66</td>
<td>63.9</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Table S 1 - Simulated data values for model in Fig S7 showing $R_{ct}$ and $R_{mt}$ values for CL10, CL25 and CL66 at -1.4 V