From batch to flow: the effect of pH, current, and crystal facets of Cu_2O on the electrochemical CO_2 reduction

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Supporting Information

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Keywords

CO_2 to C_{2+} products, flow electrolyzer, crystal facets, Cu_2O nanocrystals, pH and current effect, electrode stability

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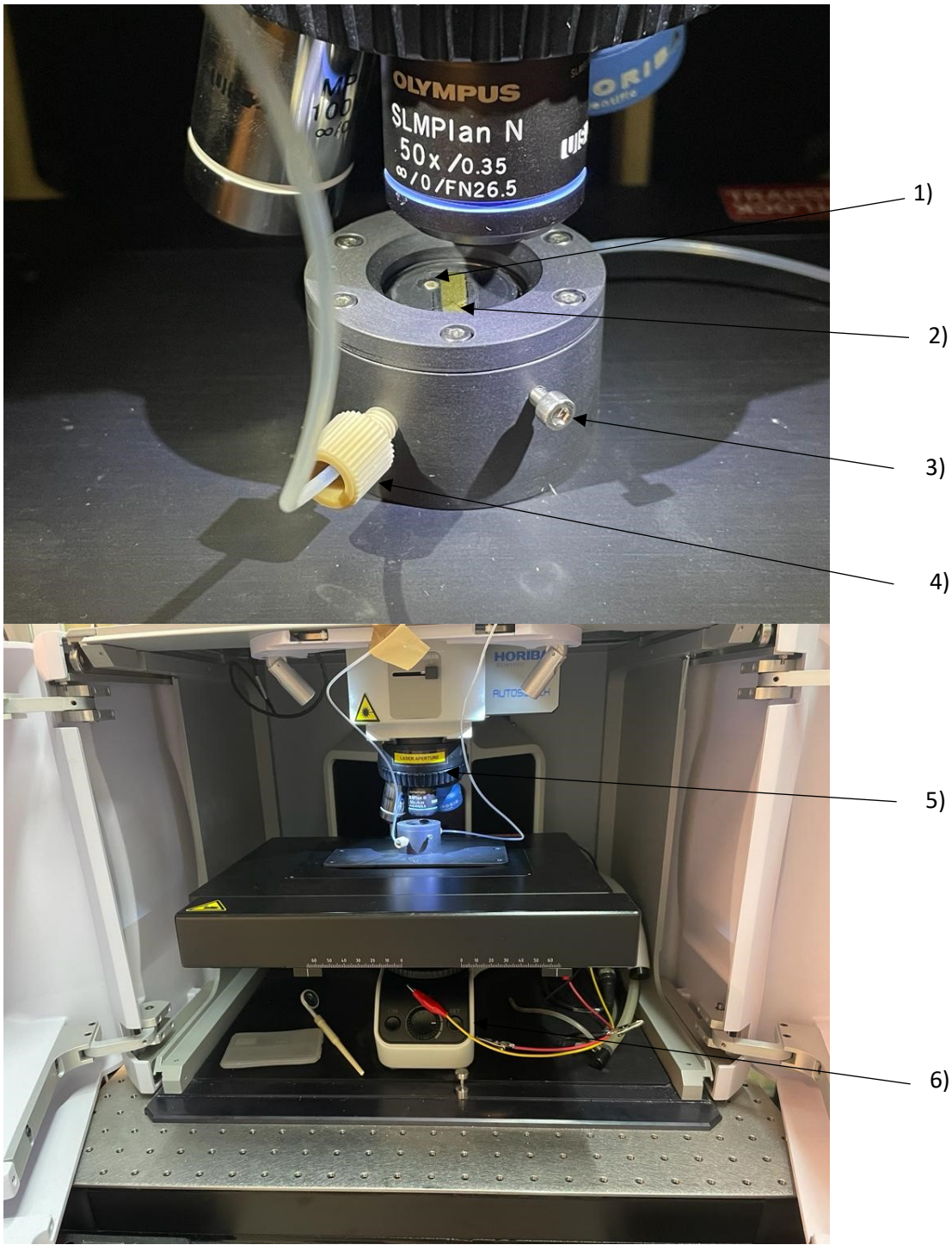


Figure S1. In situ Raman flow setup. 1) reference electrode Ag/AgCl, 2) GDE as working electrode with gold finger, 3) connection to working electrode, 4) flow channels for electrolyte, 5) Raman laser, and 6) electrical connections to reference- and counter electrode.

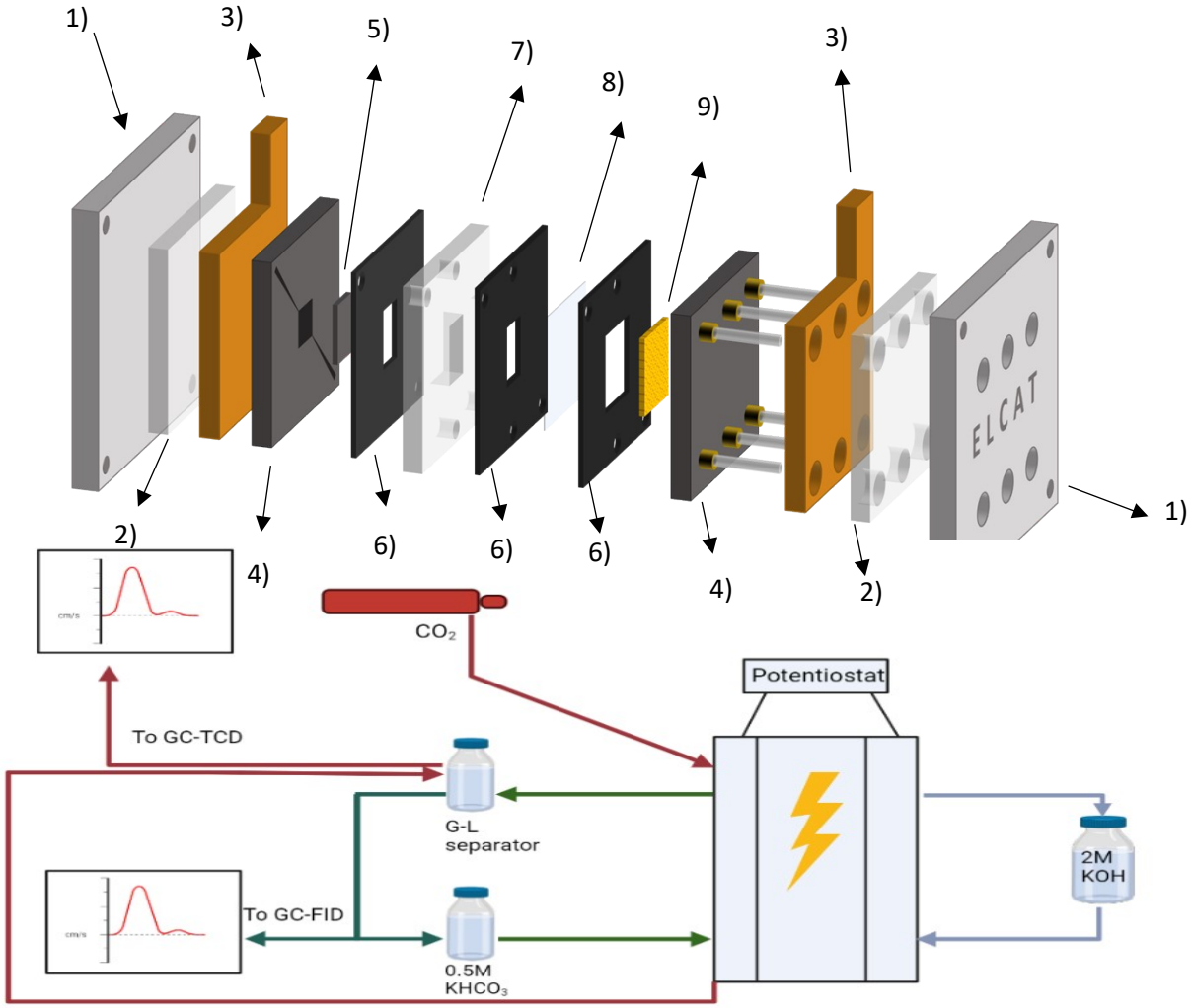


Figure S2. A schematic view of the electrochemical CO_2 reduction, along with an in depth depiction of the flow cell. 1) Aluminum plates, 2) PMMA isolation plates, 3) Conductive copper plates, 4) Flat designed graphite substrate plates without vortex generators, 5) Catalyst coated GDE, 6) Rubber gaskets, 7) Reference electrode holder, 8) Nafion 117 membrane, and 9) Nickel foam anode

Liquid samples for the detection of alcohols were prepared as follows: 1 mL of sample was added to a vial with 100 µL 1% Butanol as Internal standard (IS), which was uniformly mixed. Another vial was prepared which contained 100 µL of IS, 1% ethanol, and 1% 1-propanol, diluted with water to a total volume of 1.1 mL. The areas of the standard mixture were used to calculate the amount of ppm of product present in the sample, the internal standard was used for the correction. Based on the ppm, the faradaic efficiency was calculated. For the detection of formic acid, 1 mL of sample was combined with 1 mL of 1.2 M of $HClO_4$ to precipitate the salts. Then, 1 mL of this mixture was analyzed with HPLC (Diluted x2) and compared with a standard of 100 ppm formic acid.

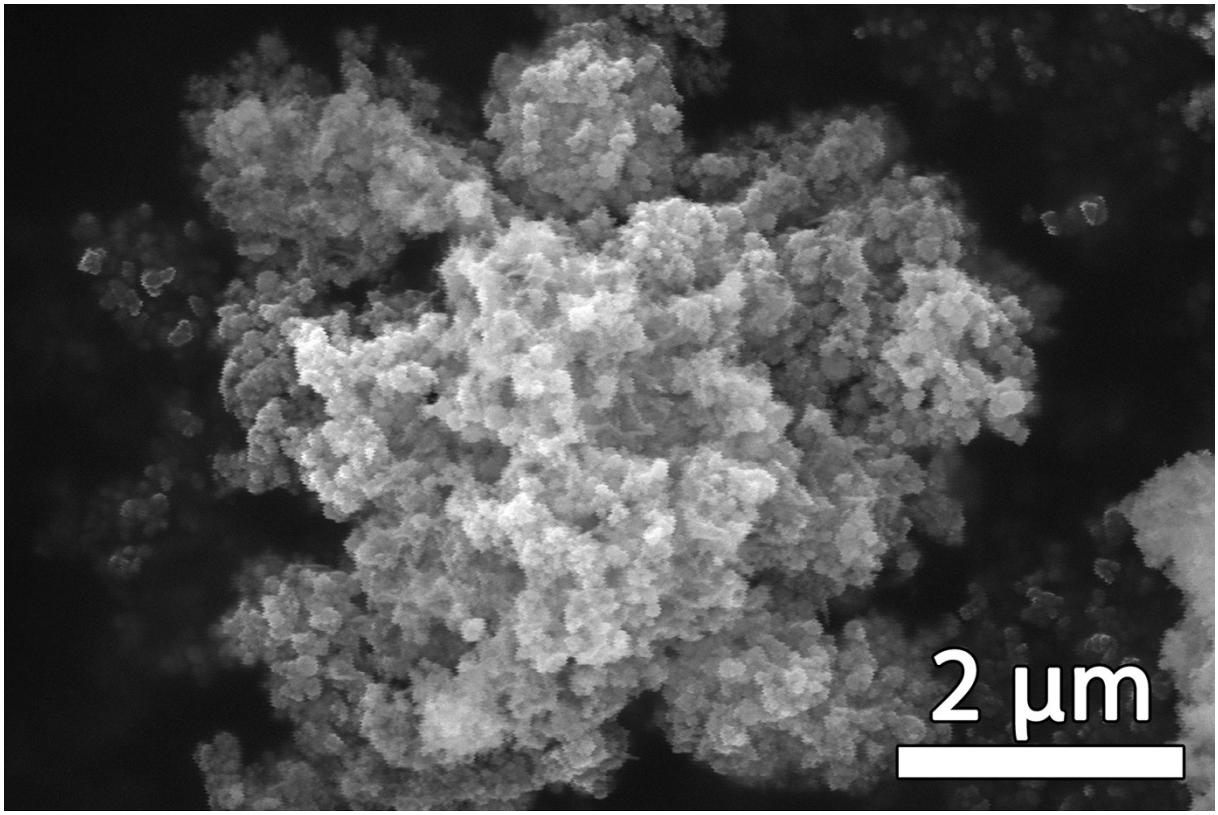
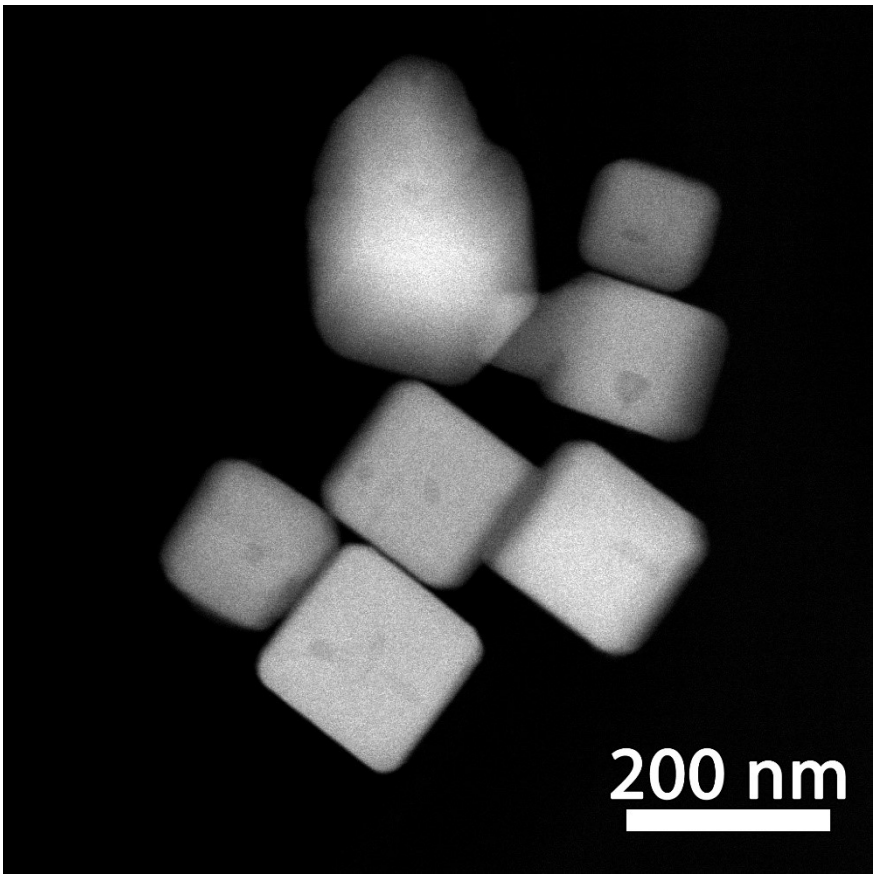


Figure S3. SEM image of Cu_2O-NF

a)



b)

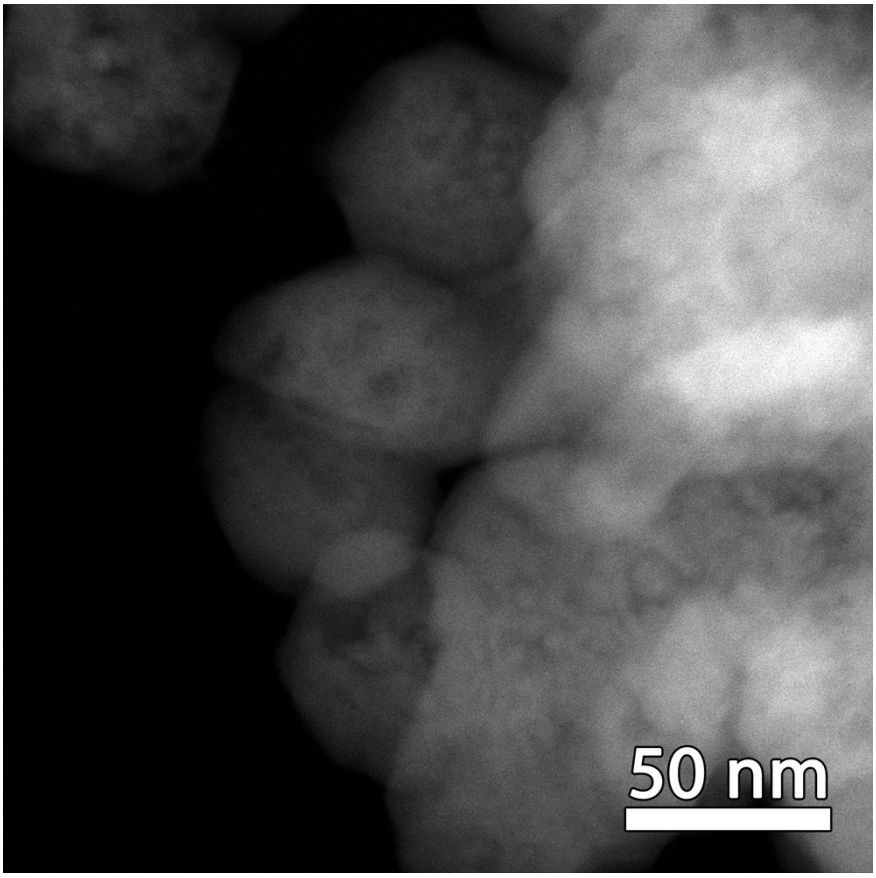


Figure S4. TEM images of a) Cu_2O-NC, and b) Cu_2O-NF

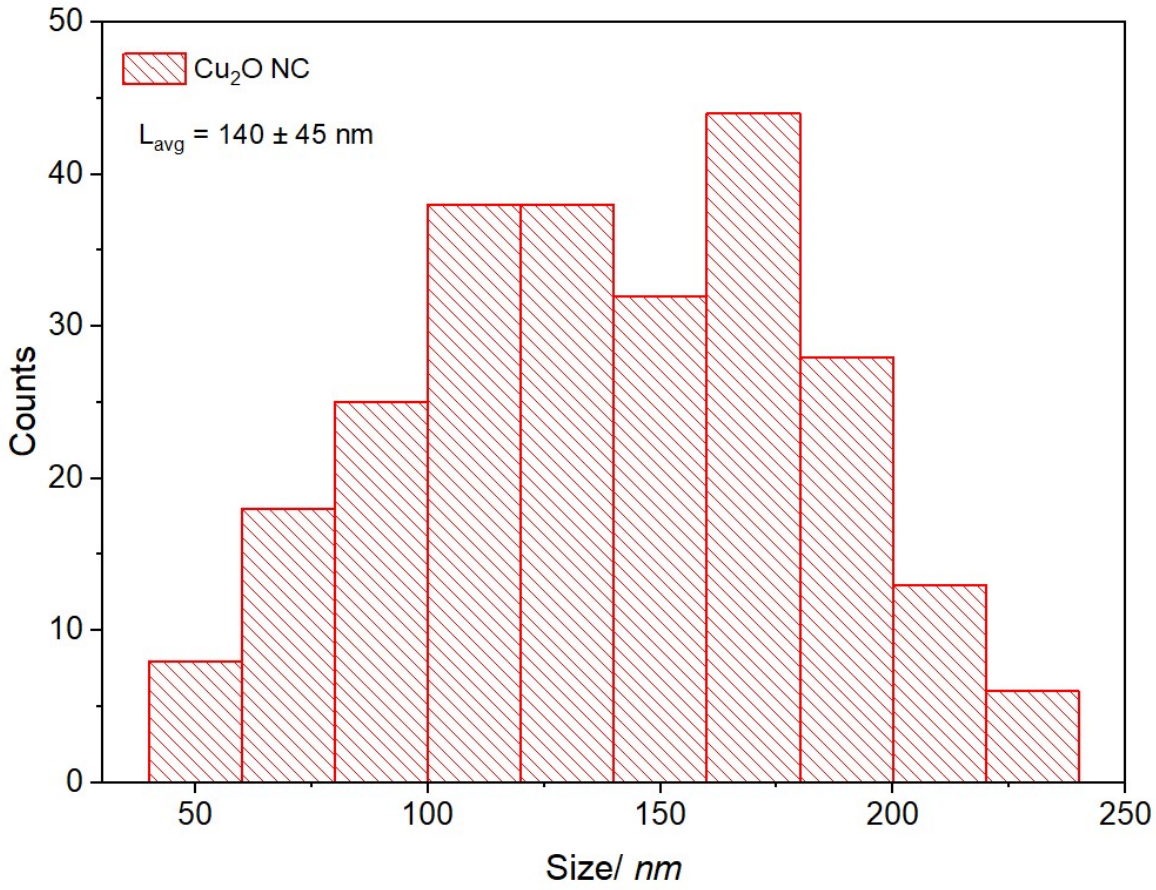


Figure S5. Particle size distribution histogram of Cu_2O-NC, 300 particles were used for the calculations, with the edge length as the value that was used for calculating the size.

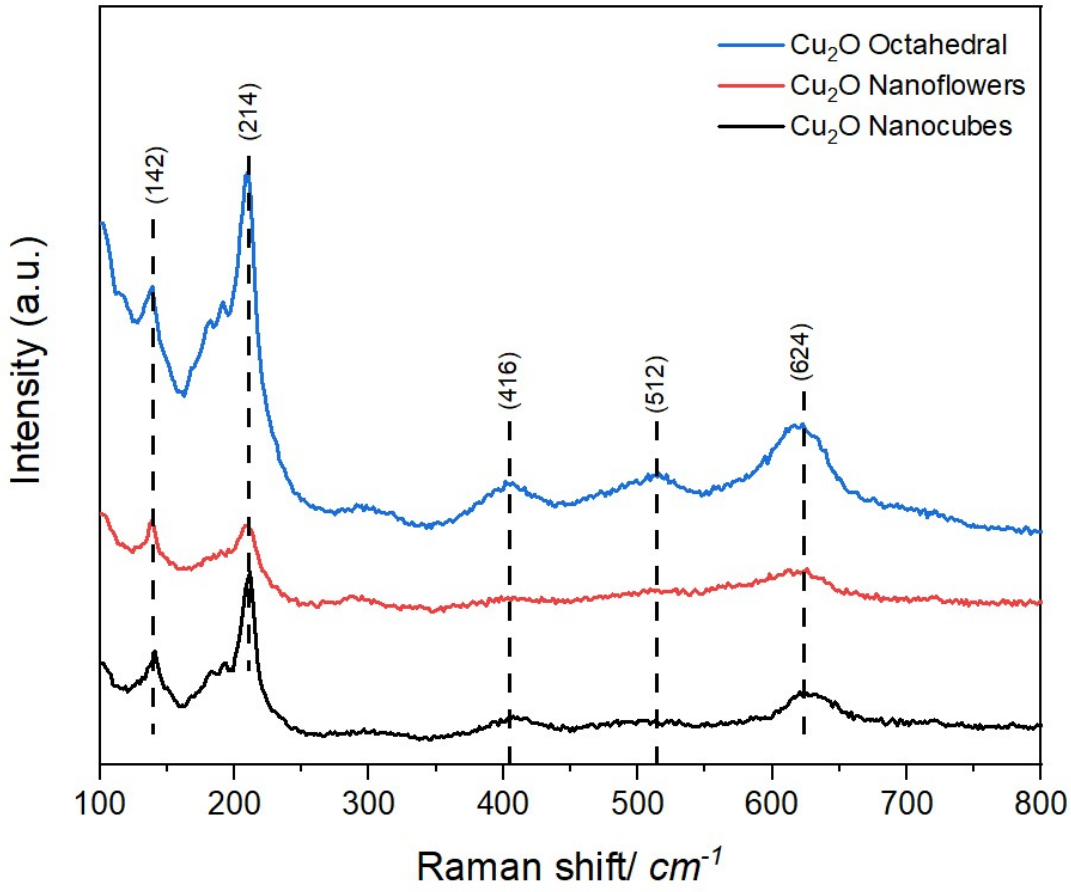


Figure S6. Raman spectrums of Cu2O-Octahedral, nanoflowers, and nanocubes respectively

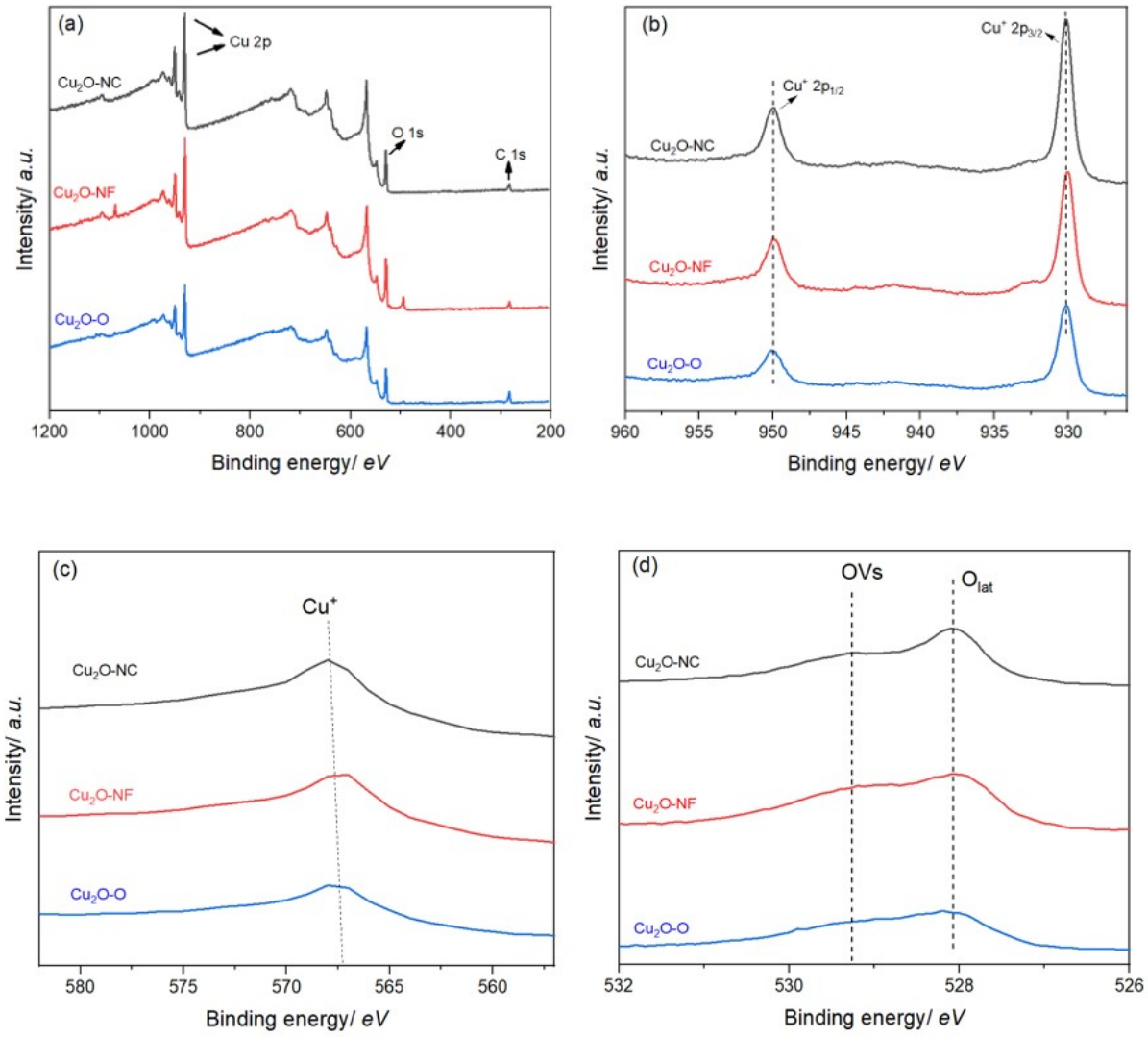
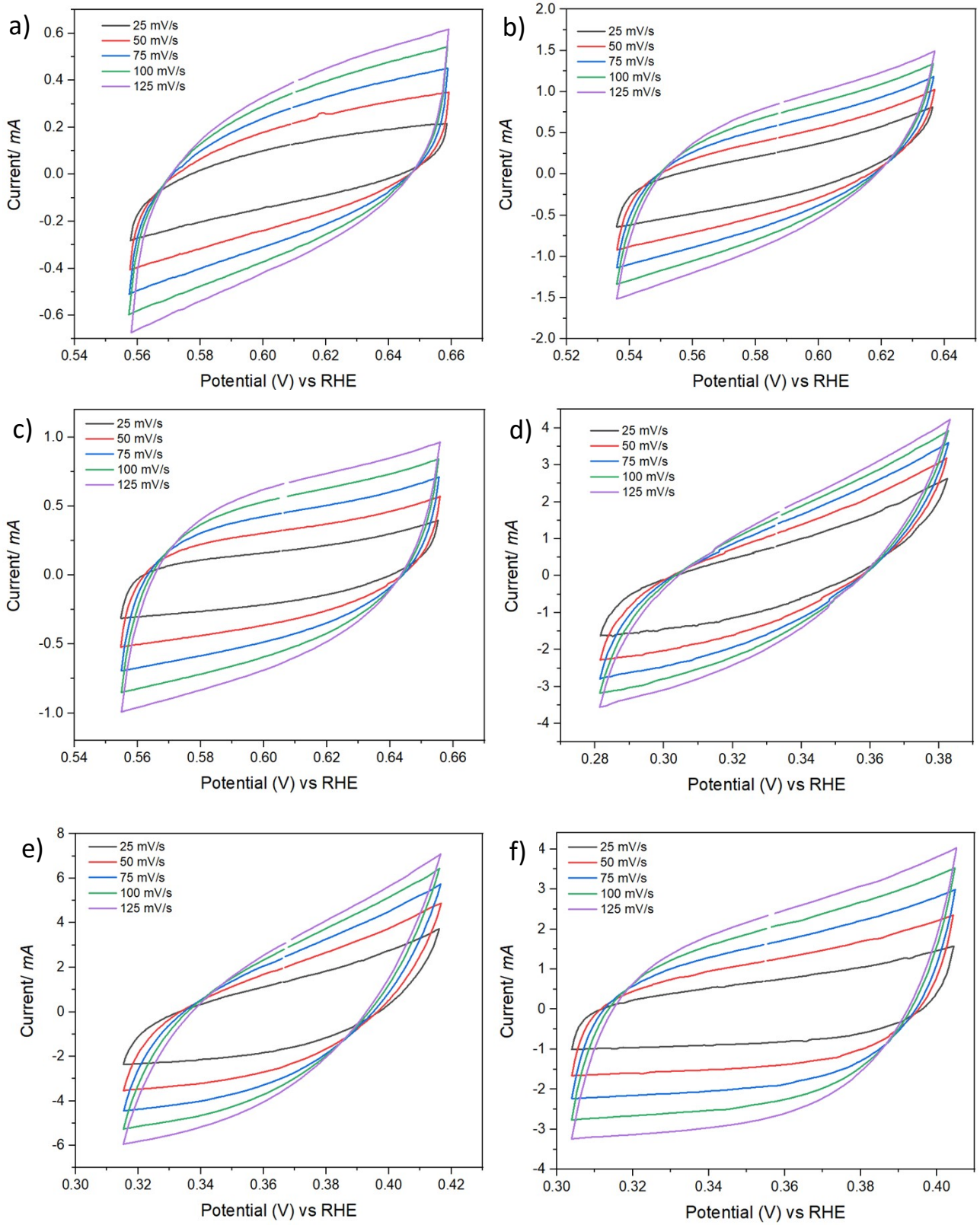


Figure S7. XPS images of the different Cu2O catalysts: (a) Survey profiles, (b) Cu 2p spectra, (c) Cu LM2 spectra, and (d) O 1s spectra.


a)
b)
c)
d)
e)
f)
25 mV/s
50 mV/s
75 mV/s
100 mV/s
125 mV/s
Current/ mA
Potential (V) vs RHE

g)

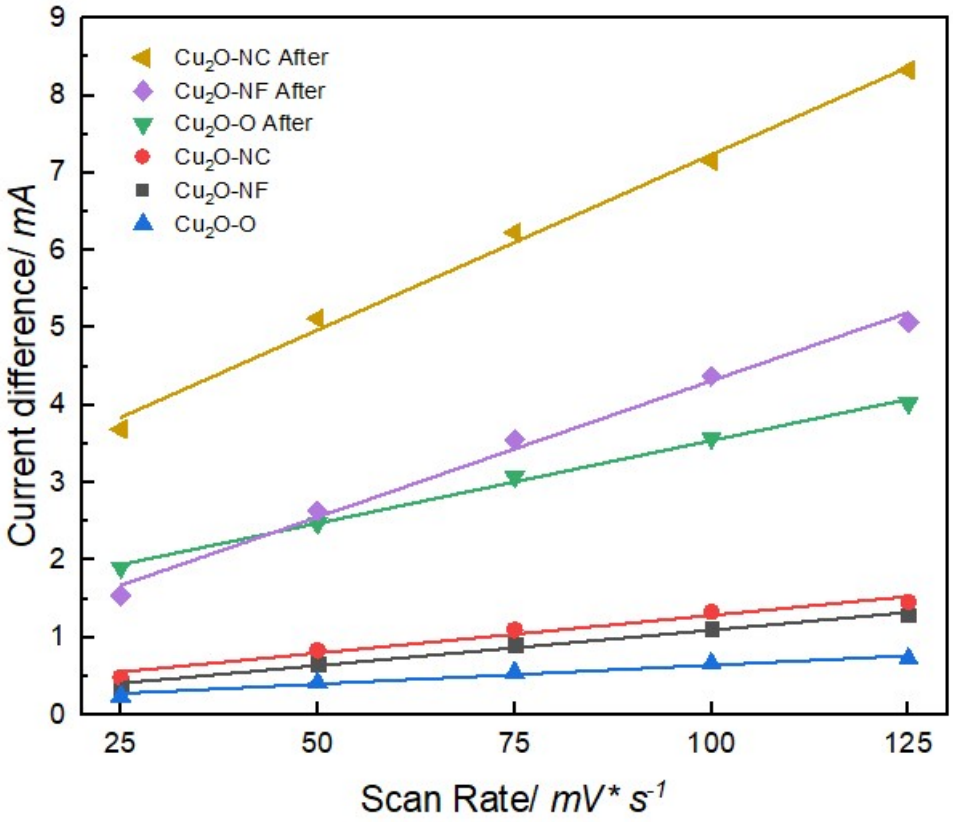


Figure S8. All of the following CVs were measured ± 50 mV from OCP with scan rates of 25-50-75-100-125 mV s^{-1}. a) Cu_2O-O, b) Cu_2O-NF, c) Cu_2O-NC, d) Cu_2O-O After, e) Cu_2O-NF after, f) Cu_2O-NC After, and g) Linear fit of calculated ECSA, Starting bottom to top, The ECSA of Cu2O-O (5.21 mF), Cu2O-NF (9.7 mF), Cu2O-NC (11.29 mF), Cu_2O-O After (21.38 mF), Cu_2O-NF (35.23 mF), and Cu_2O-NC (45.25 mF)

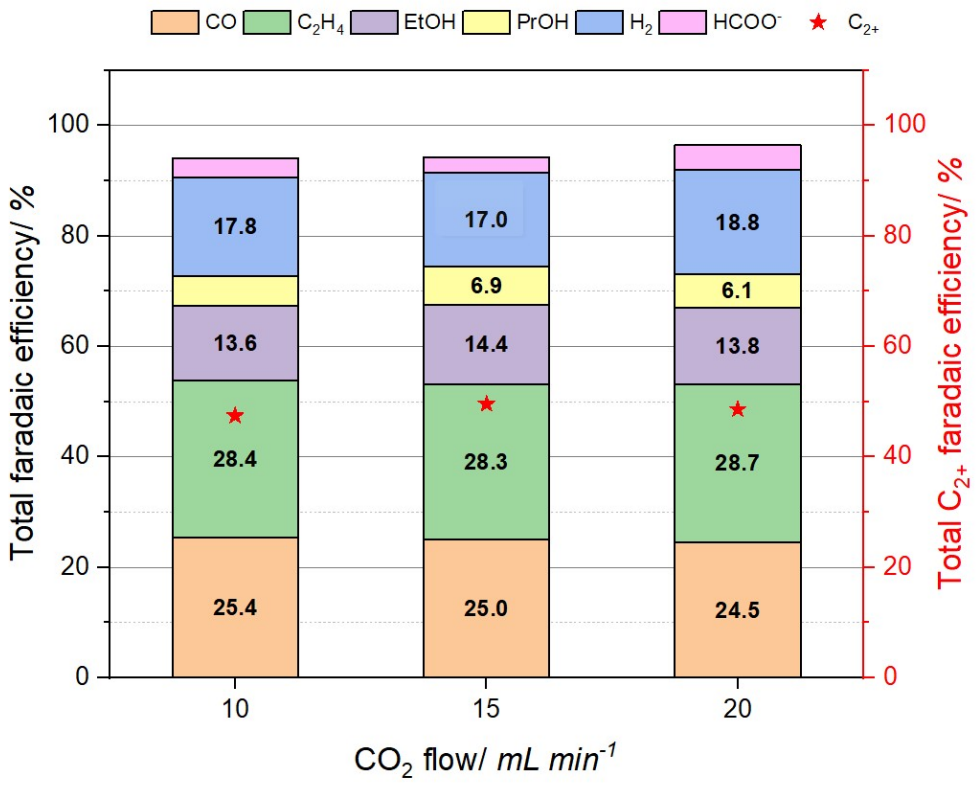


Figure S9. CO_2RR at 150 mA cm^{-2} with Cu_2O-NC for different flow rates at pH 11

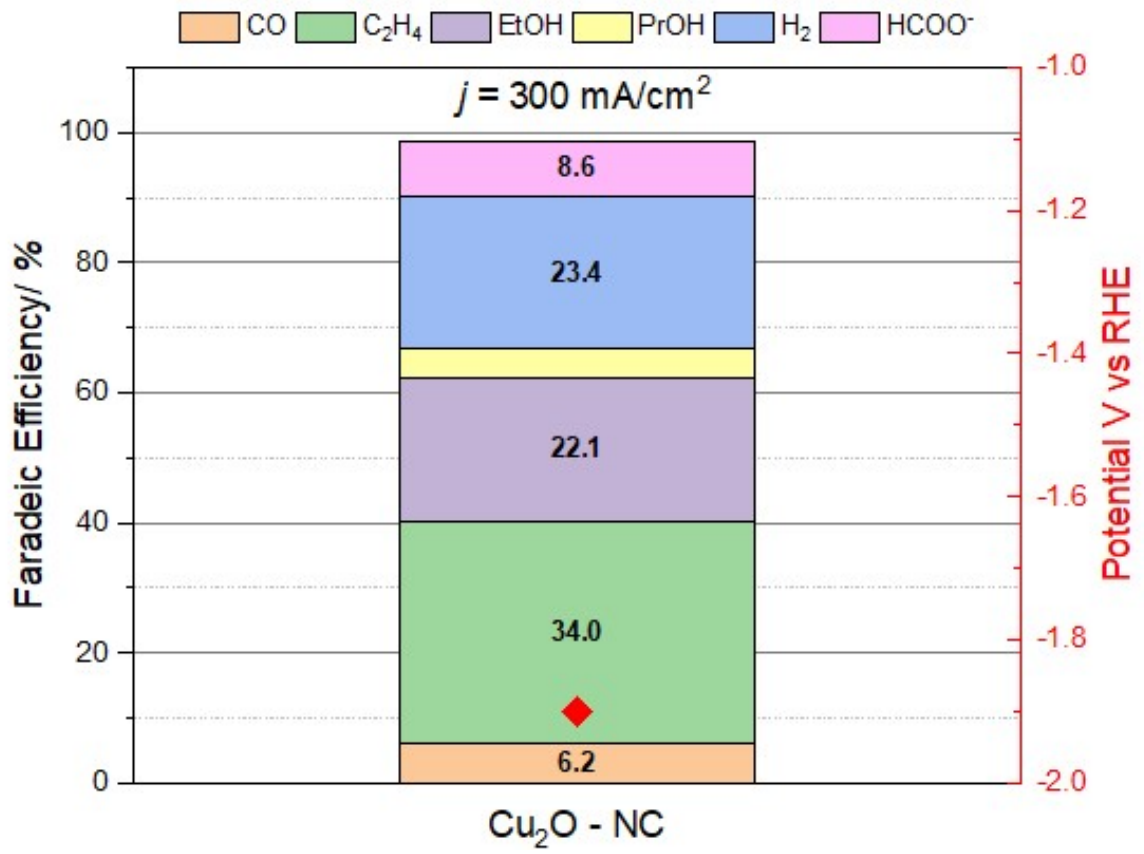


Figure S10. CO_2RR at 300 mA cm^{-2} with Cu_2O-NC for 1 hour at pH 8.5

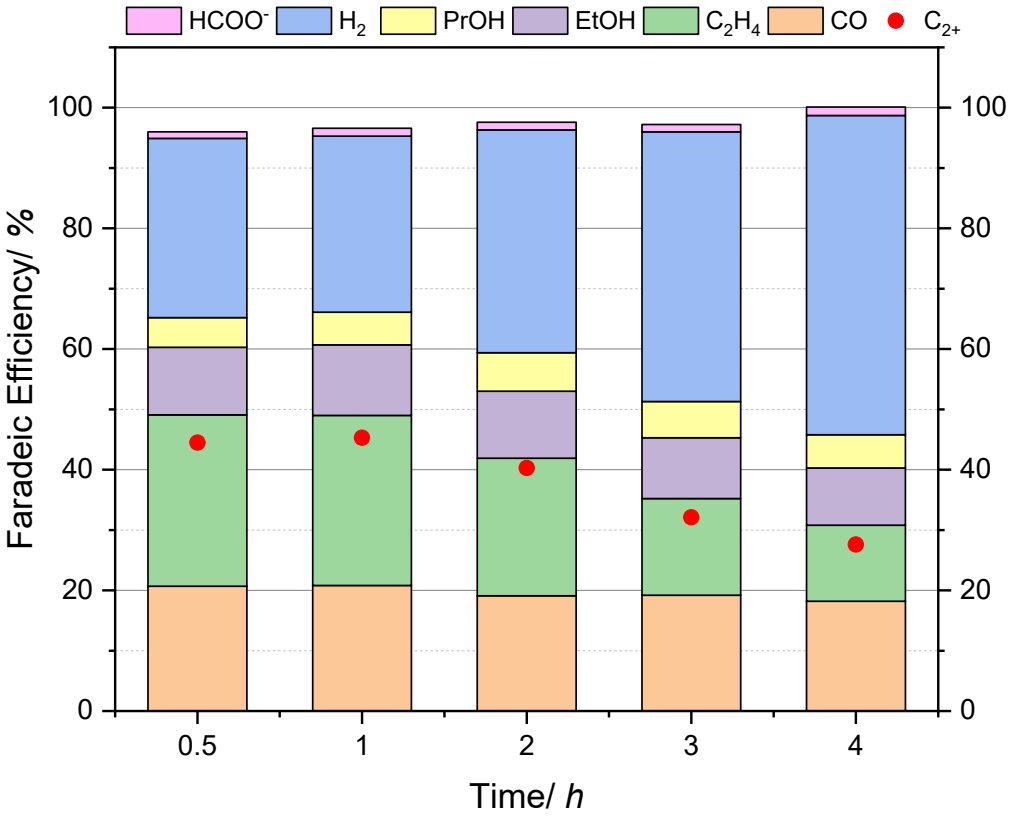


Figure S11. Long term stability test of Cu_2O-NF, performed at 150 mA cm^{-2} and pH 8.5. The different products are represented at each time interval along with total C_{2+} FE.

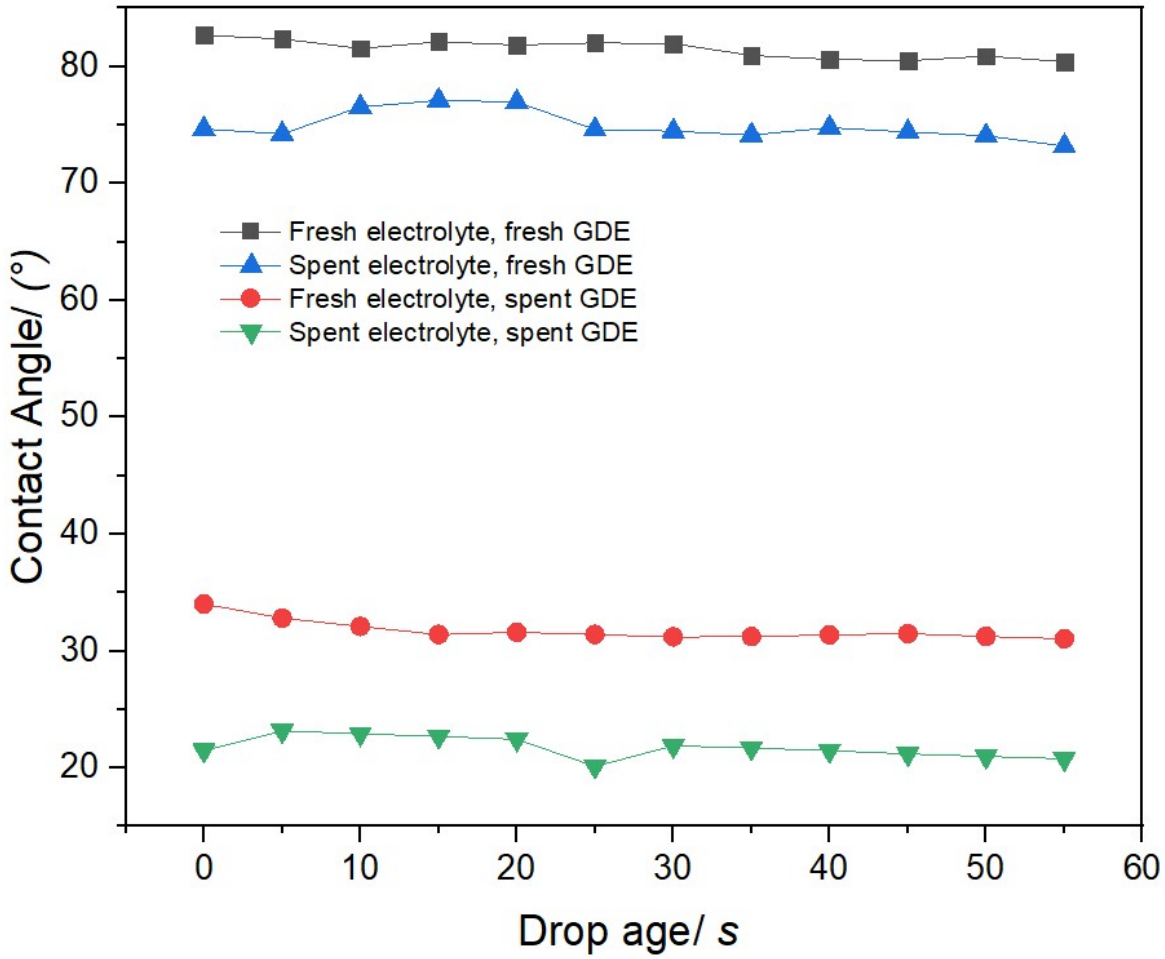


Figure S12. Contact angle measurements, off fresh and spent electrolyte on fresh and spent GDE

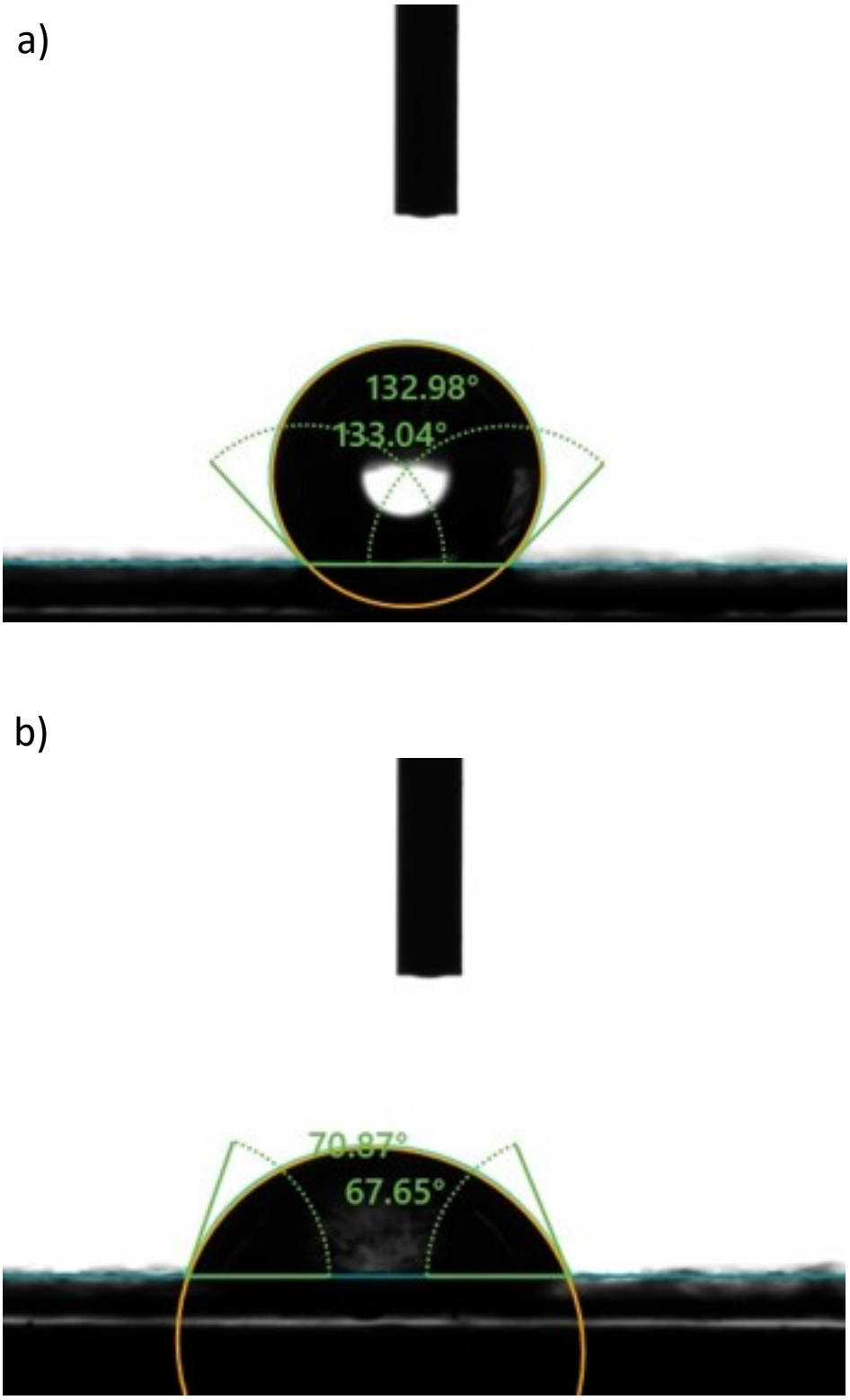


Figure S13. Contact angle measurements, on a) GDE coated Cu_2O-NC before electrolysis, and b) GDE coated Cu_2O-NC after electrolysis at 150 mA cm^{-2}. Both were measured after 5 seconds of droplet aging

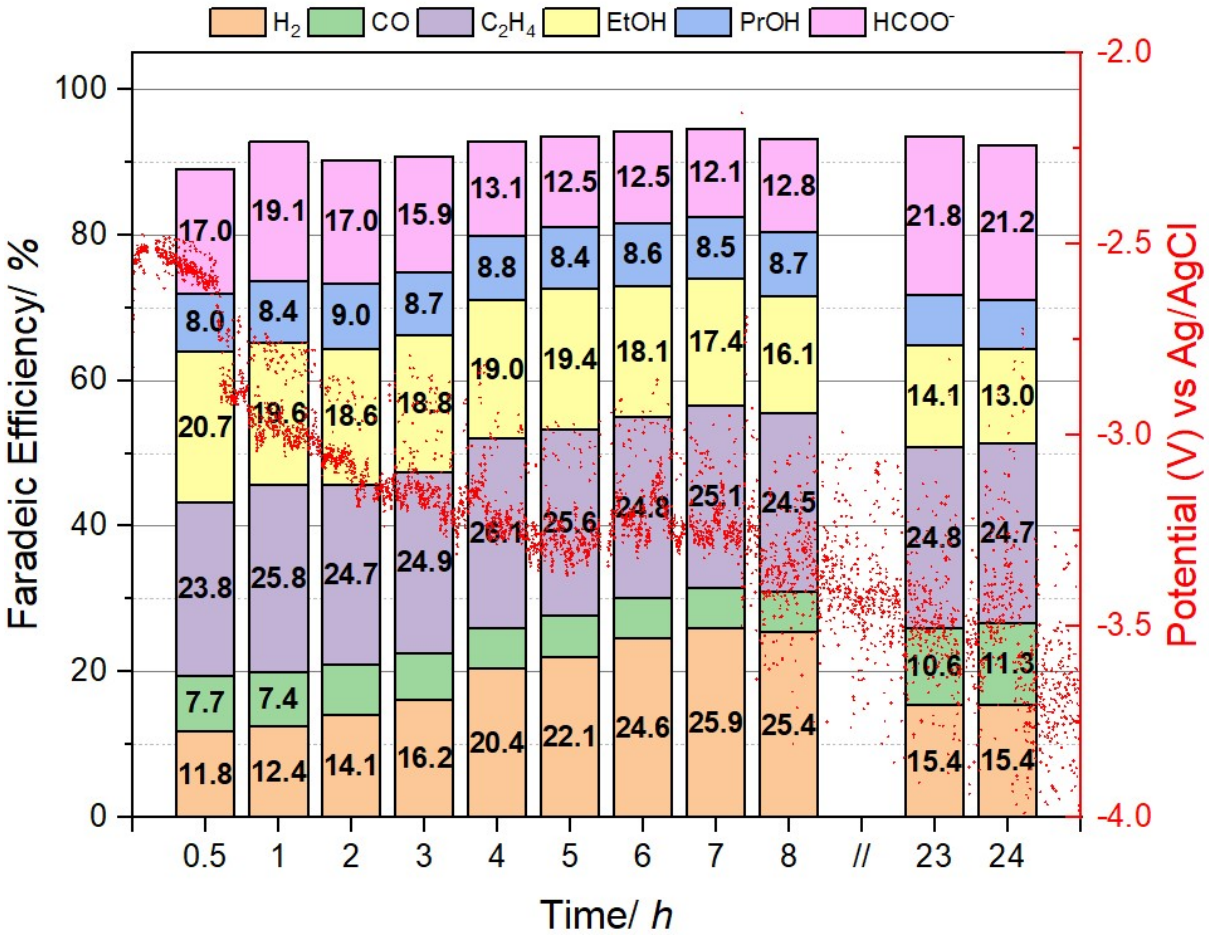


Figure S14. Long-term stability measurement with single pass 0.5 M $KHCO_3$ catholyte

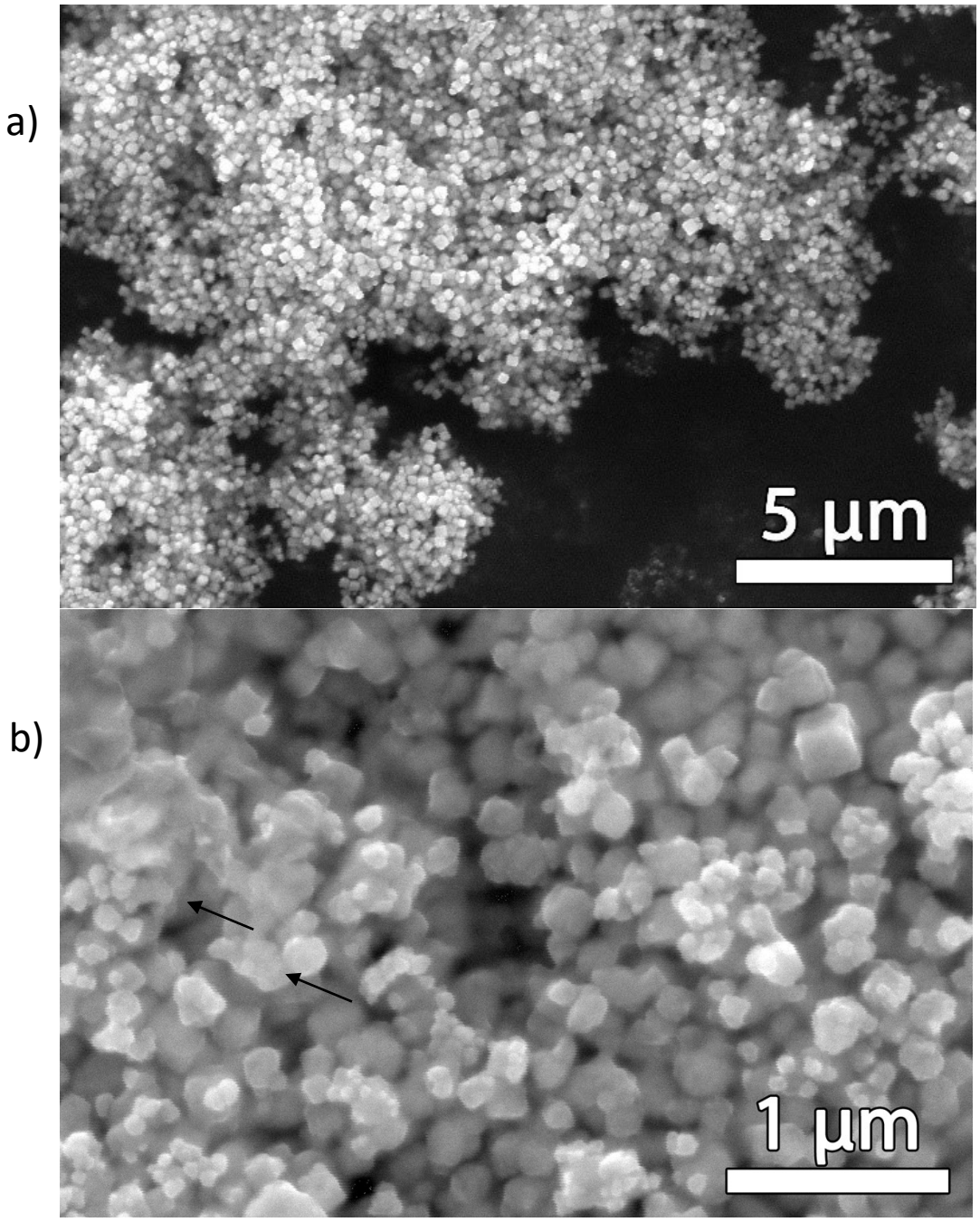


Figure S15. SEM measurements for Cu_2O-NC, a) before electrolysis, and b) after electrolysis, with arrows indicating the roughening

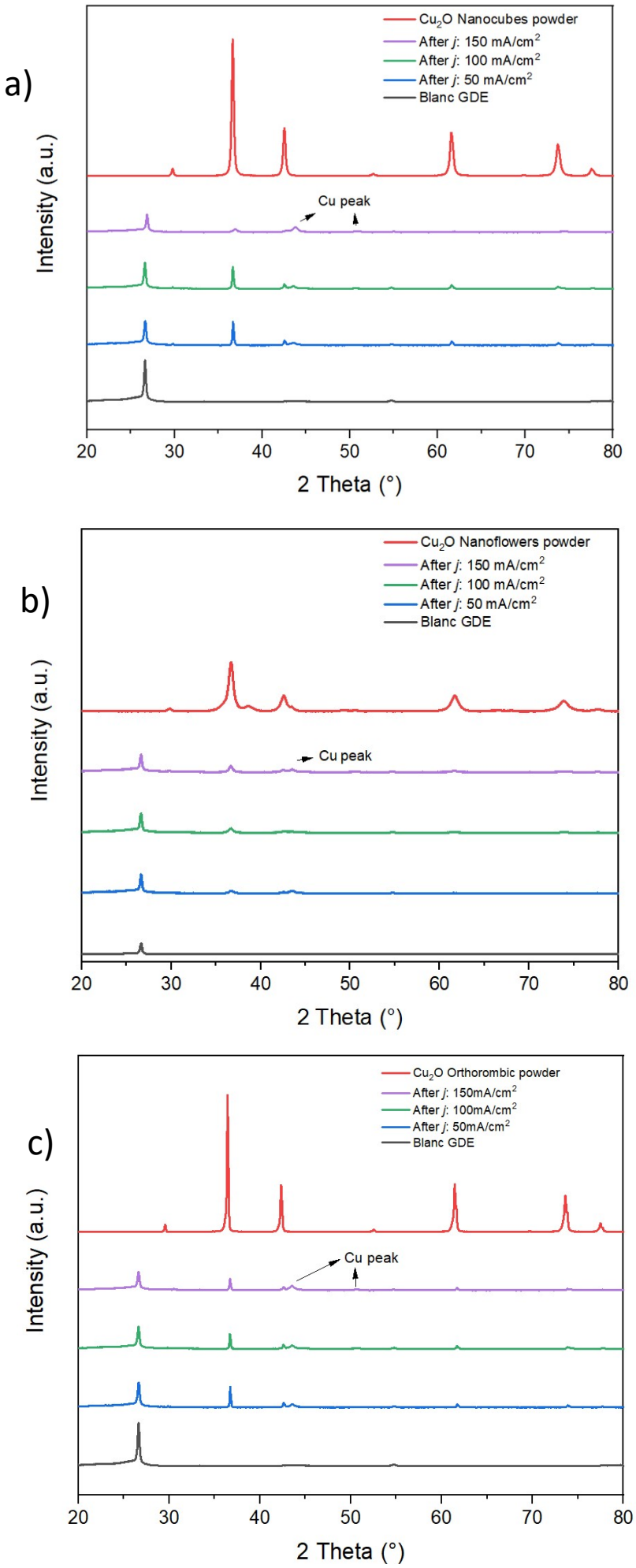


Figure S16. XRD spectra taken after electrolysis on GDE compared to the original powder. Spectra given after electrolysis of the different current densities. a) Cu_2O-NC, b) Cu_2O-NF, and Cu_2O-O