Supporting information

Cu,S,N Heteroatom-Tailored Carbon Quantum Dots Enabling Efficient Electrochemical CO_2 Reduction to Acetate and Formate

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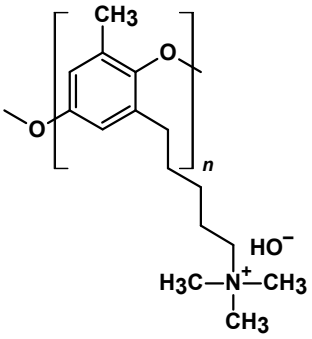
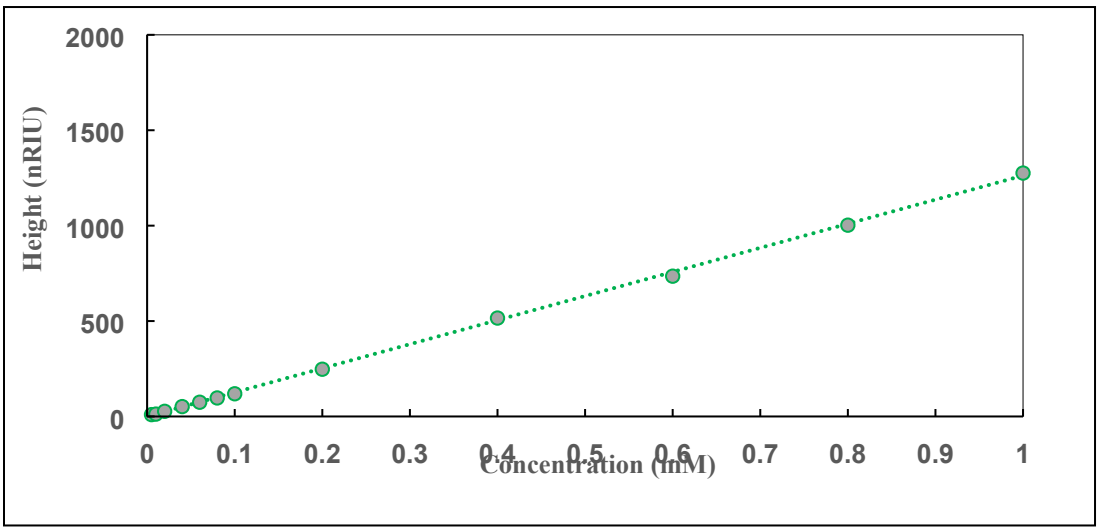


Figure S1. Chemical formula of PPO-LC.

HPLC analysis

a)



b)

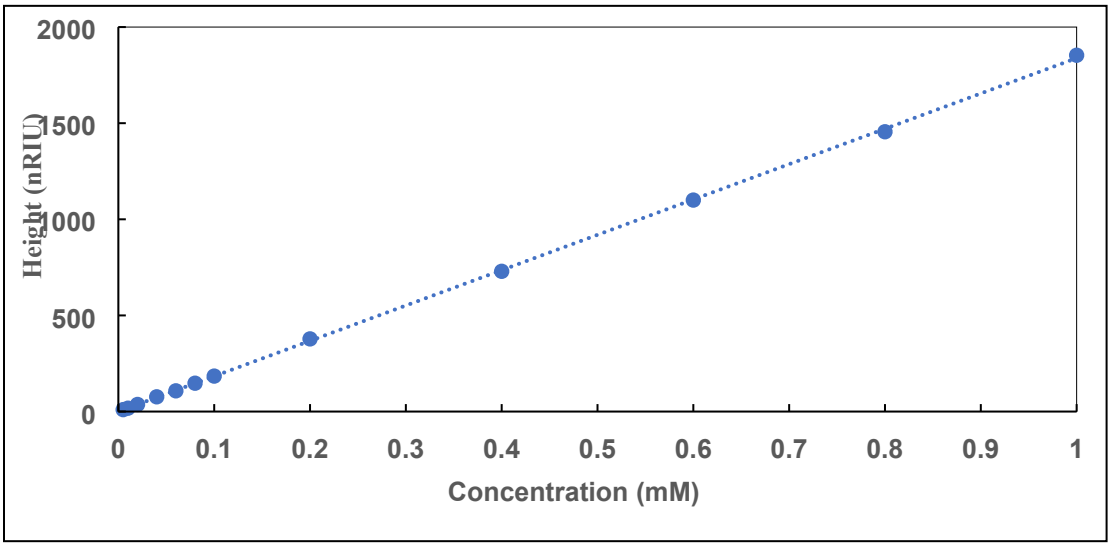


Figure S2. Calibration curves of a) formic acid and b) acetic acid

^{1}H NMR analysis

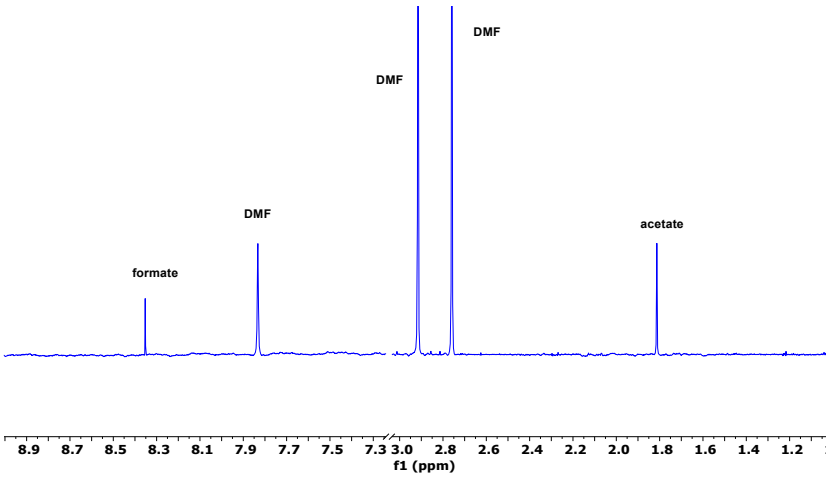


Figure S3. ^{1}H NMR spectrum of the catholyte (Cu,S,N-CQD-GAH) at -0.4 V vs RHE with D_2O as internal lock.

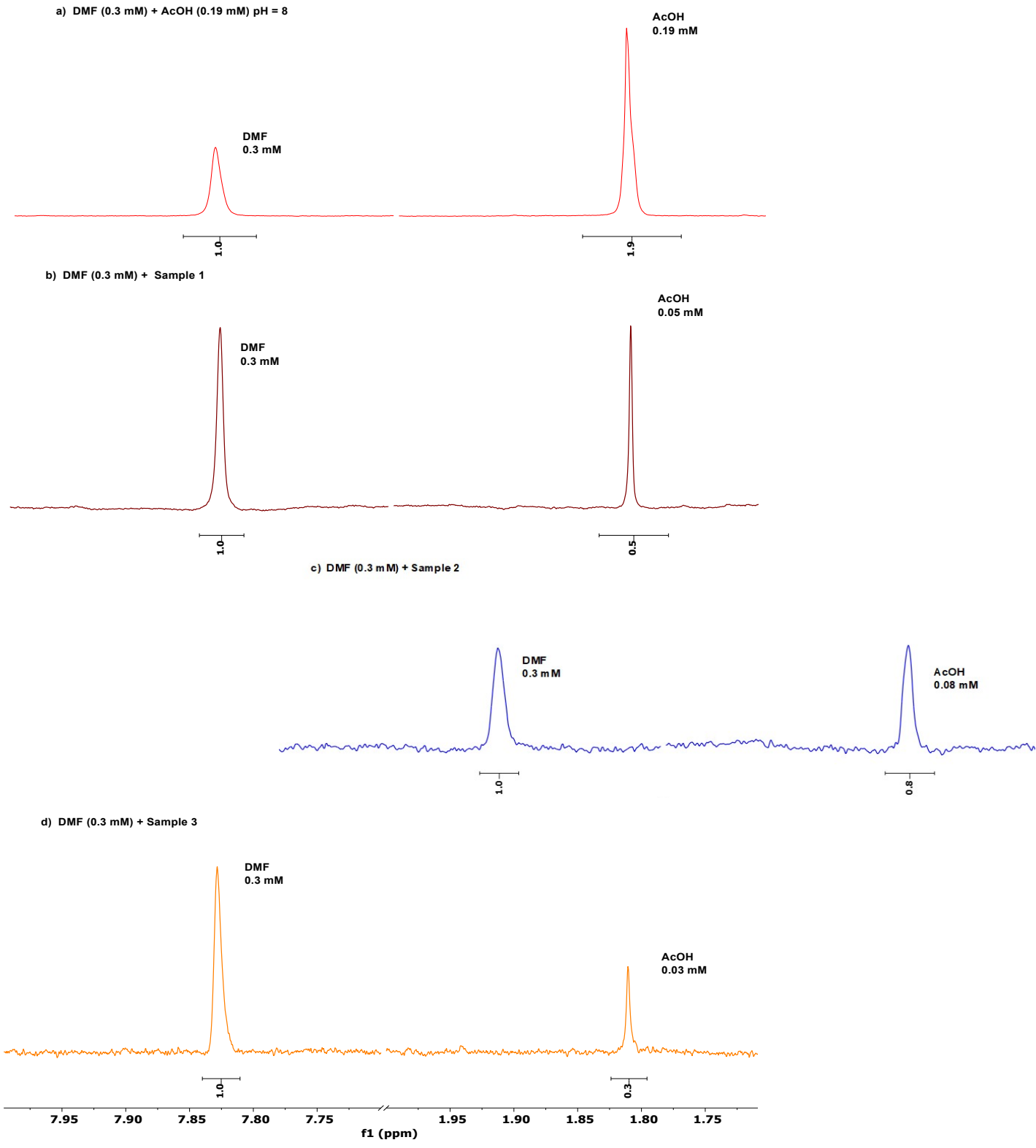


Figure S4. ^{1}H NMR of the catholyte samples with D_2O as internal lock.

The concentrations were detected with an internal standard dimethylformamide (DMF) and the analysis was confirmed by calibration with known concentrations of acetate (spectrum a).

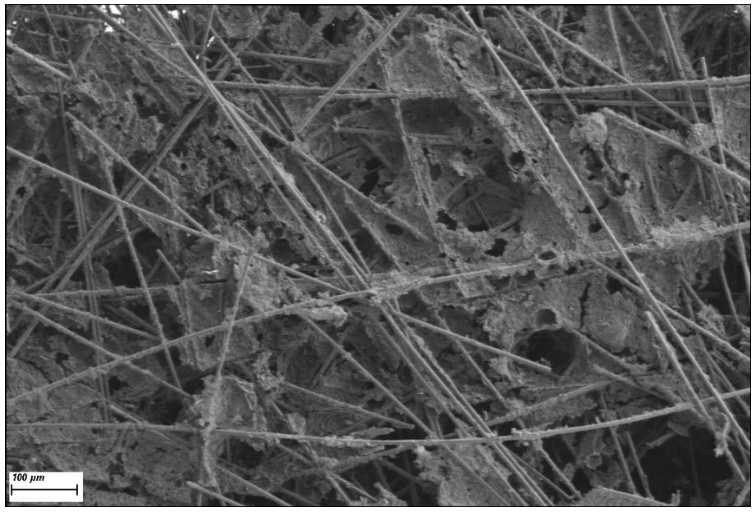
To perform the NMR measurements the catholytes were initially concentrated by a factor of 5, the actual acetate concentrations reported in Table S2 take this factor into account.

Table S1. Comparison of acetate concentrations detected by NMR and HPLC for the three samples at -0.4 V vs RHE.

Sample	**c (mM) by NMR**	**c (mM) by HPLC**
Cu,S,N-CQD-CA	0.010	0.009
Cu,S,N-CQD-GAH	0.016	0.016
Cu,N-CQD-GAH	0.006	0.008

Scanning Electron and Optical Microscopies

a)



b)

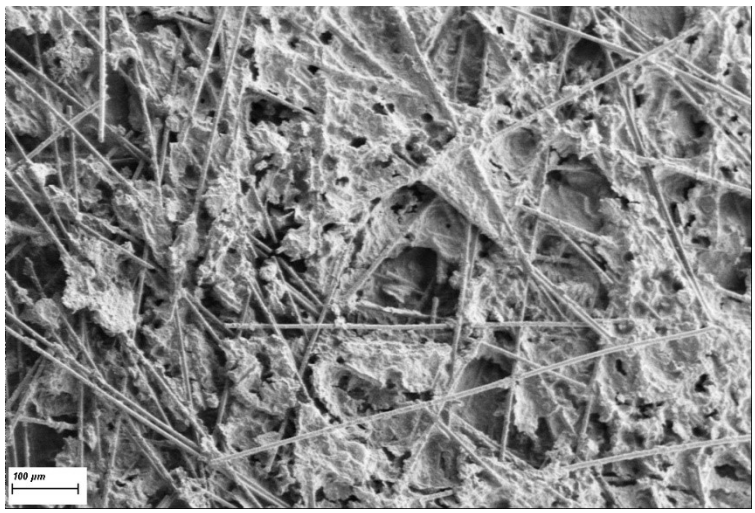


Figure S5. Scanning Electron Micrographs of electrodes with a) Cu,S,N-CQD-CA, b) Cu,N-CQD-GAH.

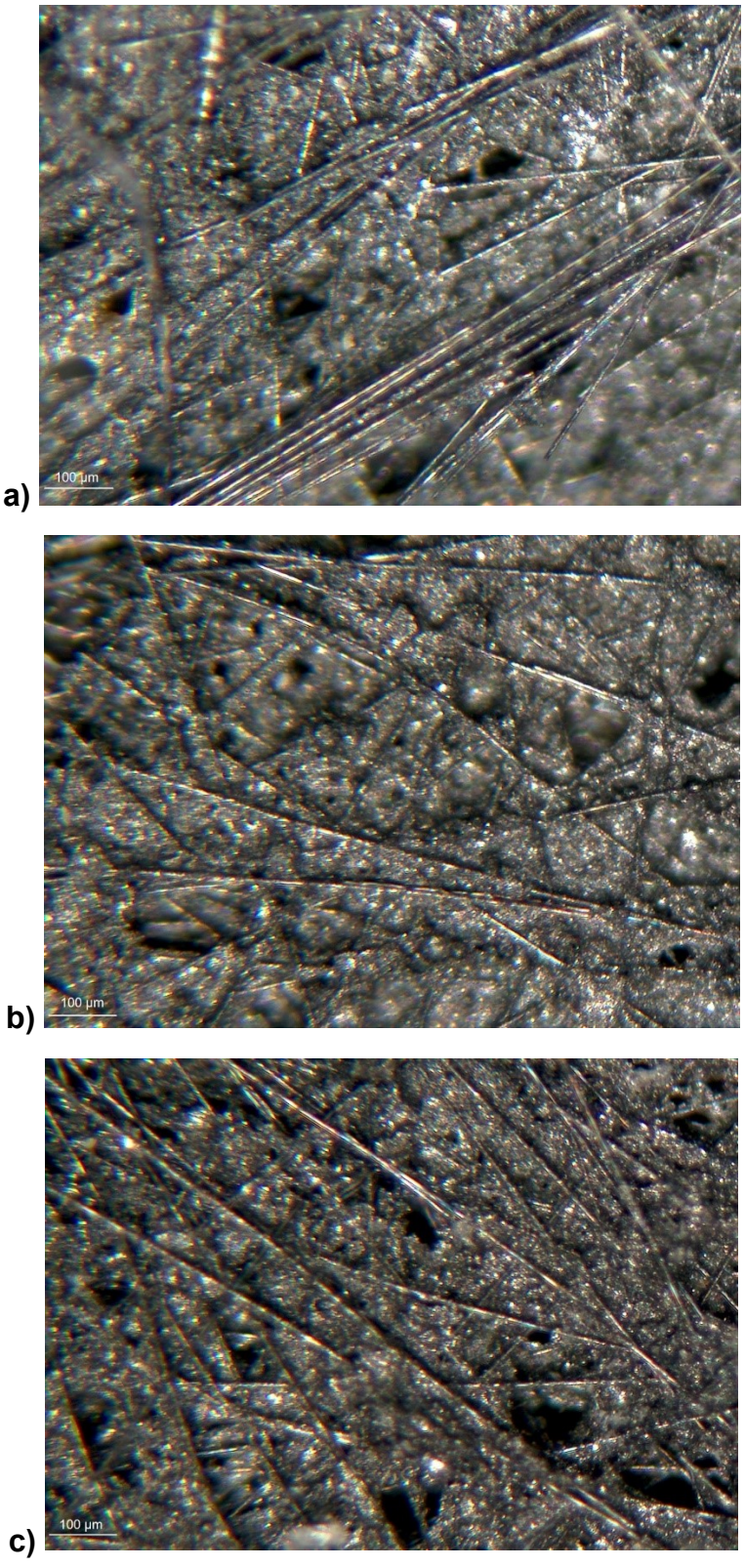
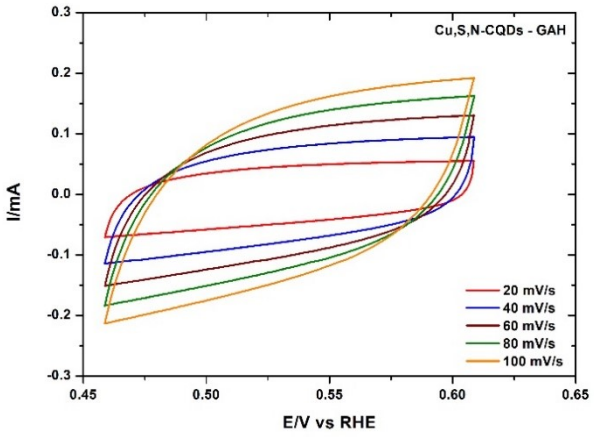


Figure S6. Optical micrographs of electrodes with a) Cu,S,N-CQD-CA, b) Cu,S,N-CQD-GAH, c) Cu,N-CQD-GAH.

Cyclovoltammetry

a)



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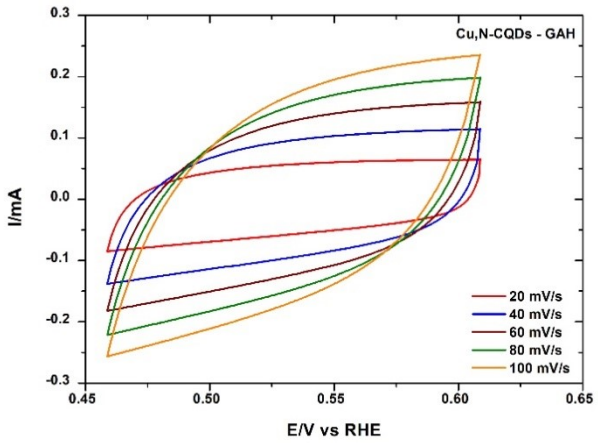

Figure S7. Cyclovoltammograms at various scan rates.

Impedance spectroscopy

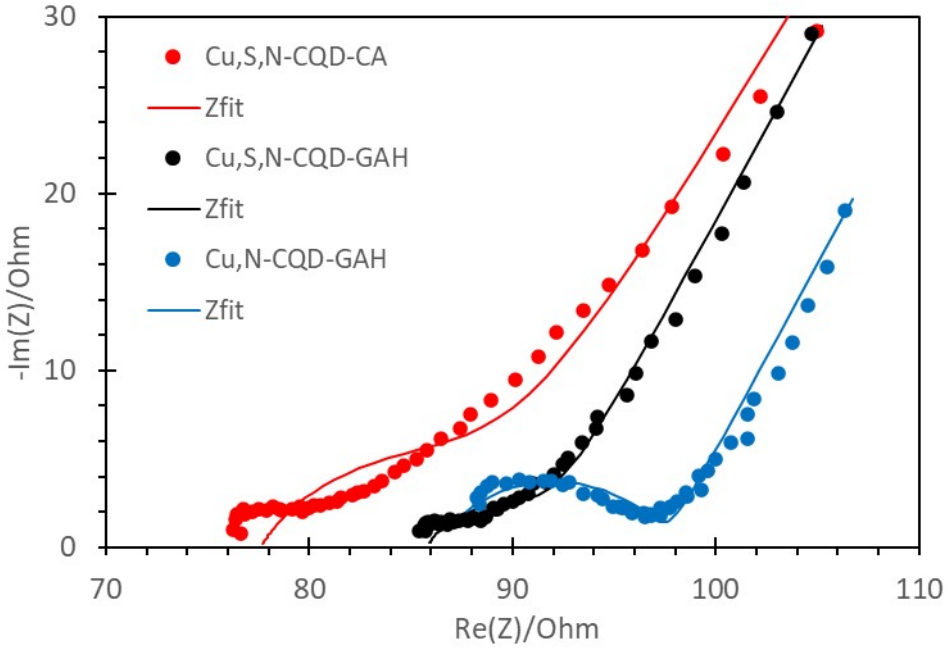

Figure S8. Impedance spectra of electrodes in 0.1 M $KHCO_3$.

The impedance spectra can be fitted using an equivalent circuit, where a resistance R1 is in series with a parallel circuit of a resistance R2 and constant phase element (CPE) Q2 and with a constant phase element Q3. R1 can be attributed to the resistance electrolyte solution and the electrode. R2 and Q2 are the charge transfer resistance and interfacial CPE, whereas Q3 can be compared to the capacitance of the electrodes. The impedance of a constant-phase element can be written:

$$Z(Q) = (\frac{1}{Q})\,(i\omega)^{-n} \qquad (1)$$

where i is the imaginary unit, ω the angular frequency, Q the CPE value, and n the CPE exponent, which is characteristic of the physical nature of the element. The non-linear least square best-fit parameters are shown in Table S1.

Table S2. Best-fit data from impedance spectra (R1, R2, Q2 and Q3, n2 and n3) and d.c. capacity (C) measurements.

	Cu,S,N-CQD-CA	Cu,S,N-CQD-GAH	Cu,N-CQD-GAH
R1/Ohm	77.6	85.8	86.3
Q2/µF $s^{(n-1)}$	277.4	249.9	12.7
n2	0.70	0.72	0.74
R2/Ohm	11.2	5.7	11.1
Q3/µF $s^{(n-1)}$	1696	2177	2760
n3	0.70	0.72	0.72
C / µF	1250	1450	1850

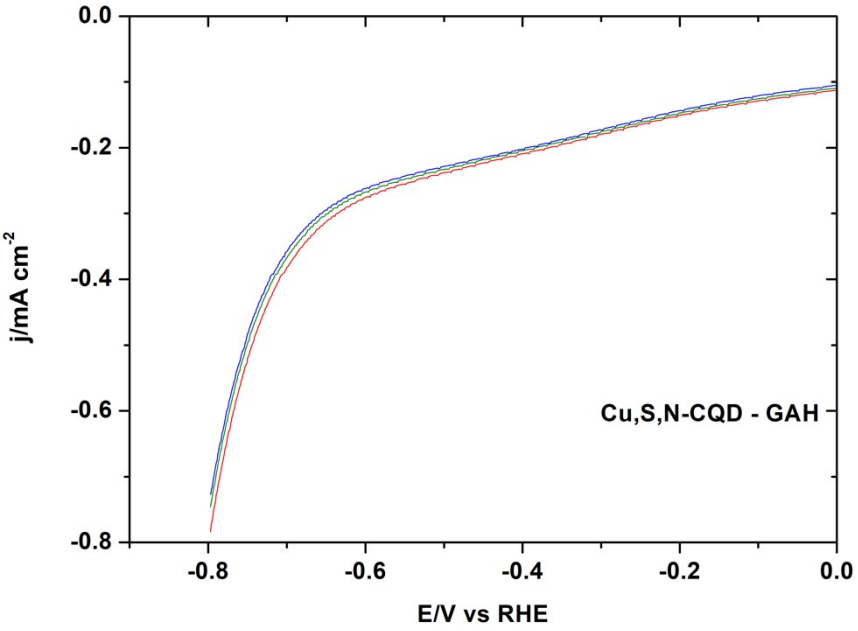

Figure S9. Repeatability of linear sweep voltammograms.

Water contact angle

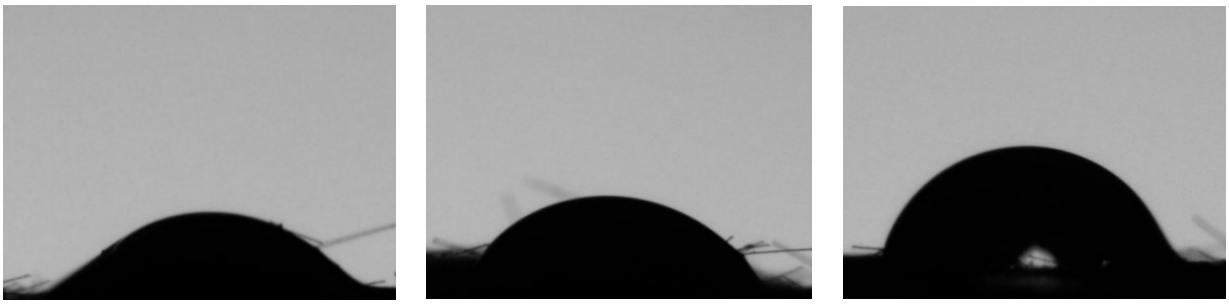

Figure S10. Water contact angle measurements. a) Cu,S,N-CQD-CA, b) Cu,S,N-CQD-GAH, c) Cu,N-CQD-GAH.