Peripherally and non-peripherally carboxylic acid substituted Cu(II) phthalocyanines/reduced graphene oxide nanohybrids for hydrogen evolution reaction catalyst

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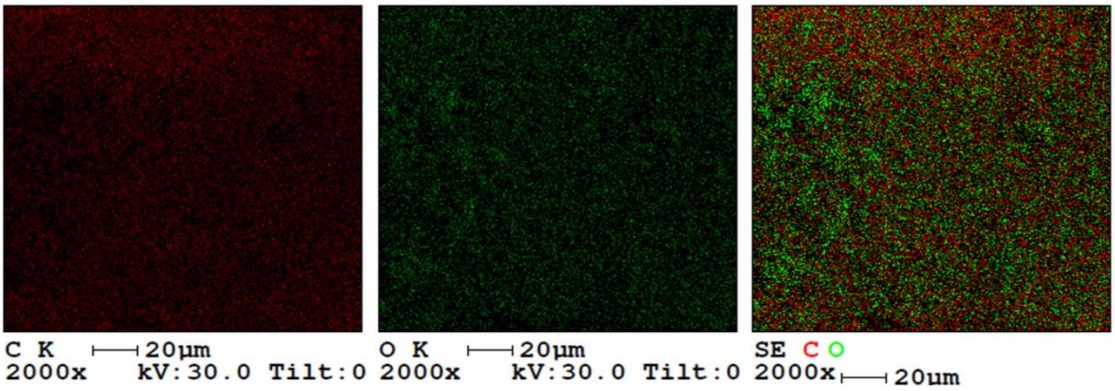

Figure S1: rGO EDS Mapping

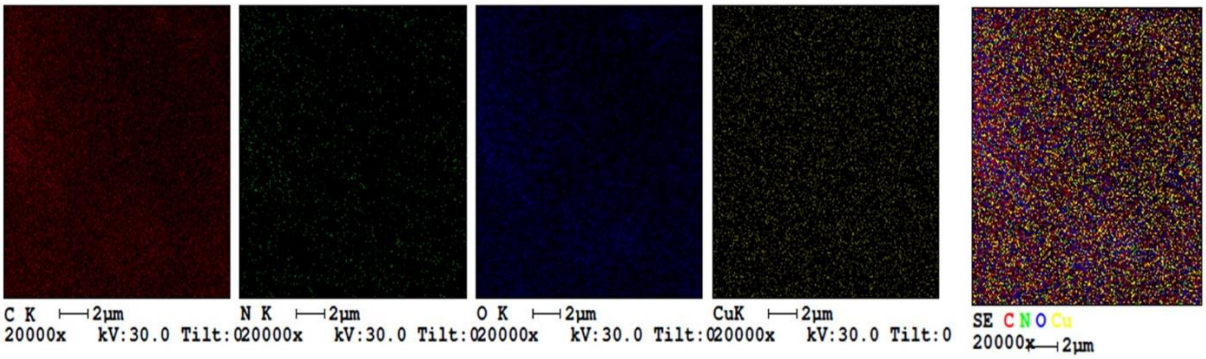

Figure S2: rGO/CuPc(**1**) EDS Mapping

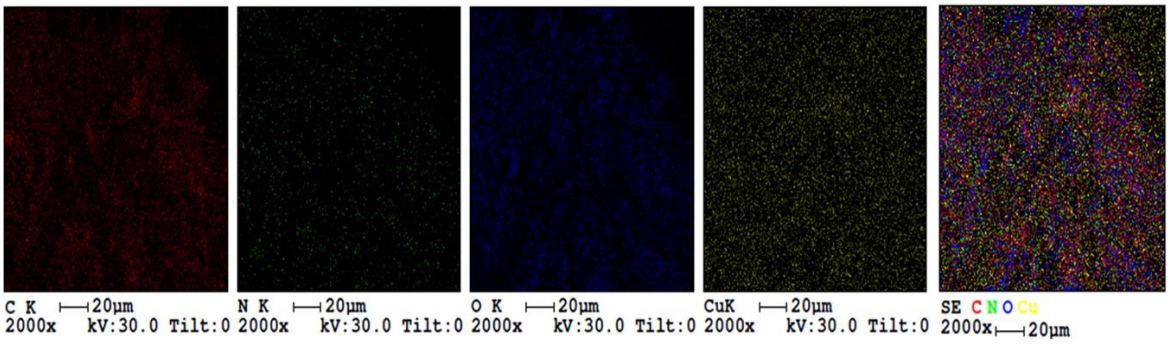

Figure S3: rGO/CuPc(**2**) EDS spectrum

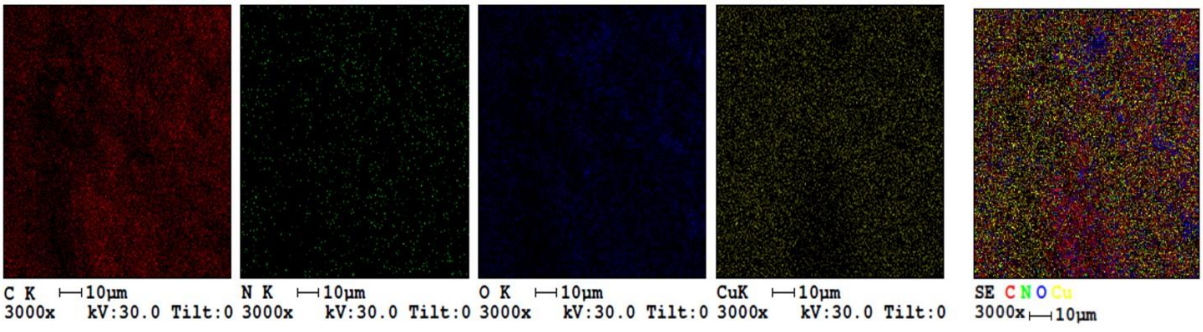

Figure S4: rGO/CuPc(**3**) EDS spectrum

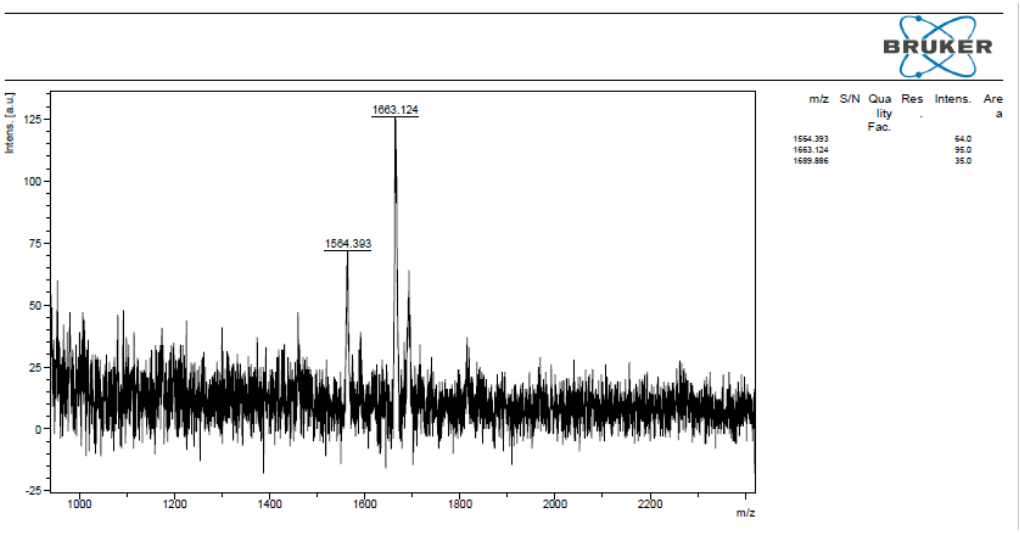

Figure S5: MALDI-TOF spectrum of CuPc(**3**)

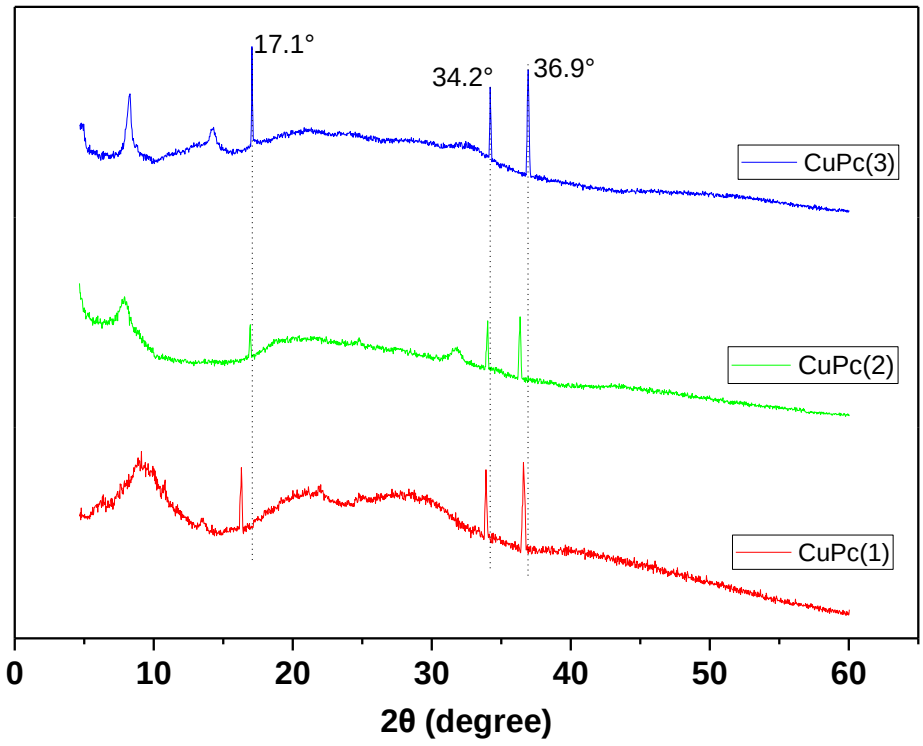

Figure S6: XRD analysis of the CuPc samples without rGO

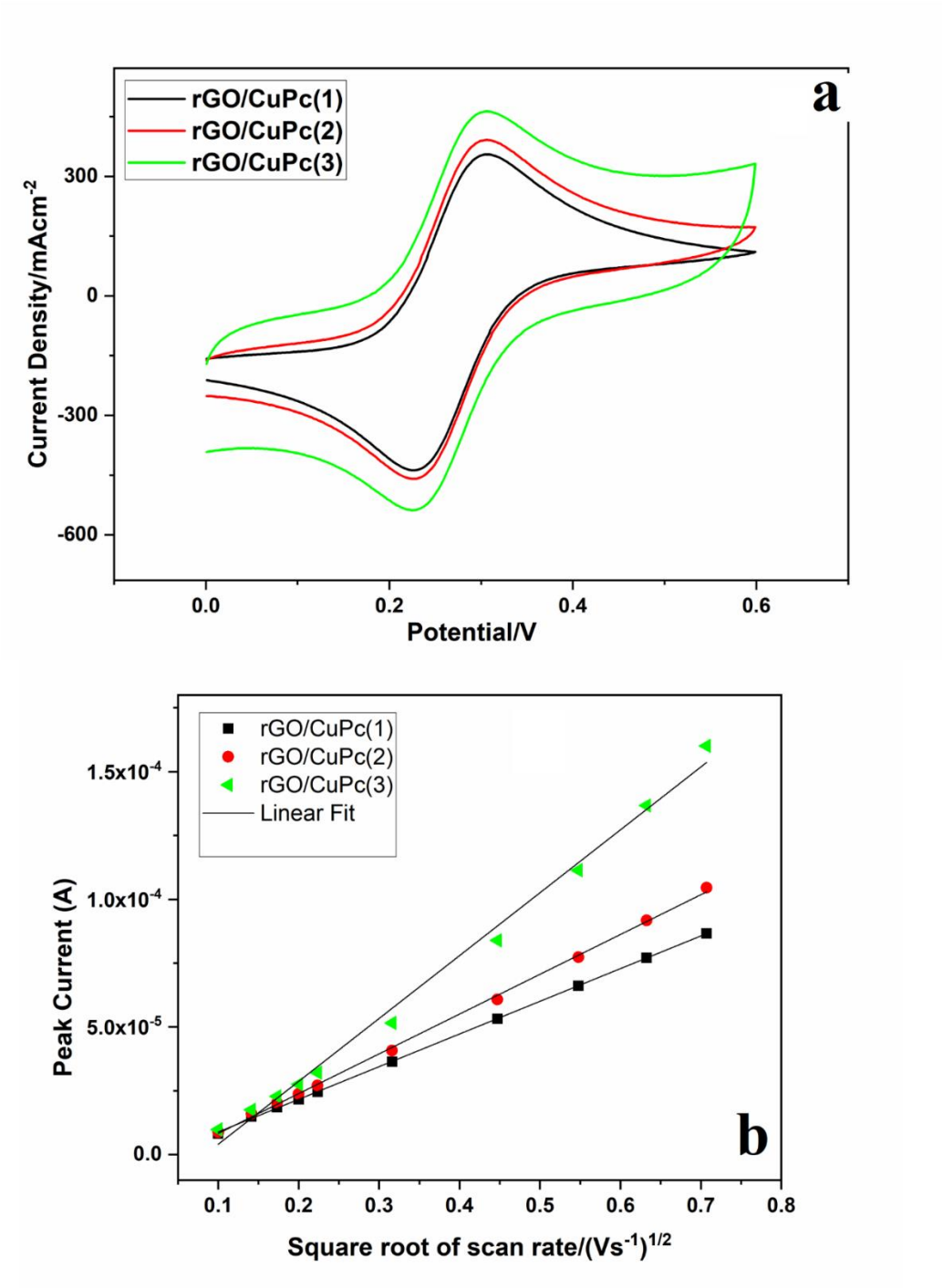

Figure S7: (a) Cyclic voltammogram of RGO/CuPc(1), RGO/CuPc(2), RGO/CuPc(3) in 1 mM K3Fe(CN)6 containing 0.1 M KCl solution at a scan rate of 50 mVs^{-1}, and (b) ip vs $v^{1/2}$ plots for determination of effective surface area of RGO/CuPc electrodes (R^2 = 0.9998, slope = 1.28×10^{-4} for RGO/CuPc(1), R^2 = 0.9990, slope = 1.56×10^{-4} for RGO/CuPc(2) and (R^2 = 0.9935, slope = 2.46×10^{-4} for RGO/CuPc(3)).

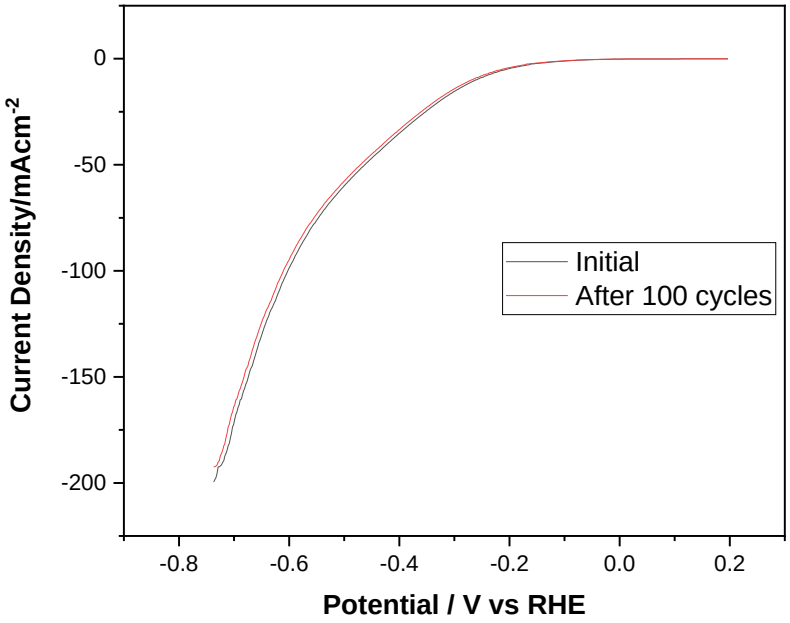

Figure S8: LSV curves of rGO/CuPc(**3**) electrode before and after 100 cycles.

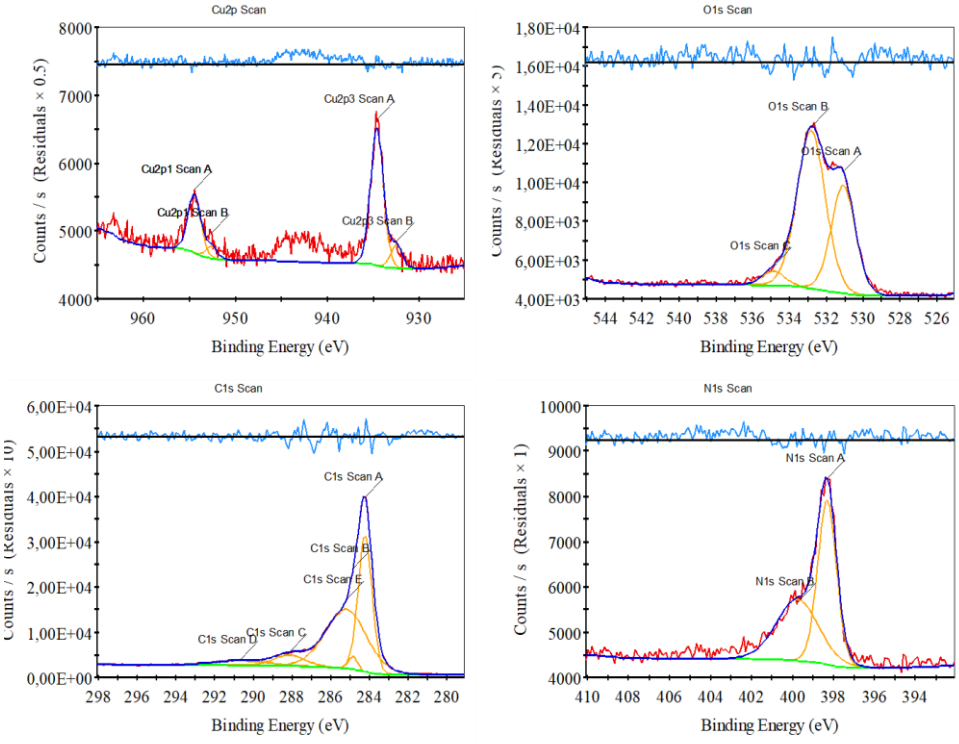

Figure S9: XPS of rGO/CuPc(1) showing (a) Cu2p, (b) O1s, (c) C1s, and (d) N1s scans.

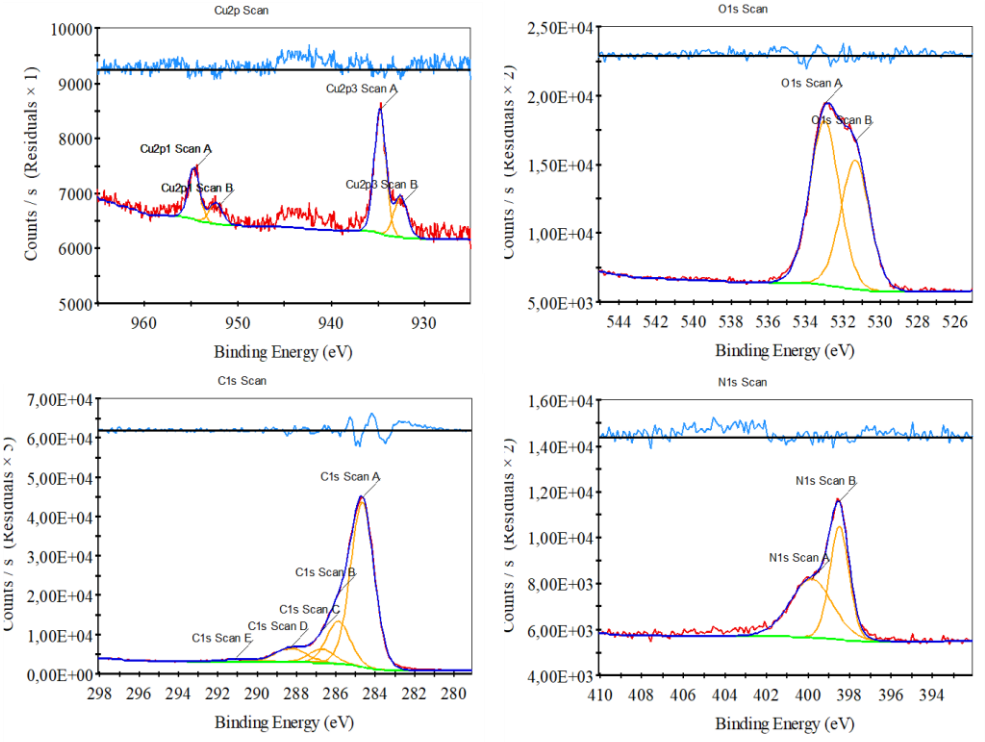

Figure S10: XPS of rGO/CuPc(2) showing (a) Cu2p, (b) O1s, (c) C1s, and (d) N1s scans.

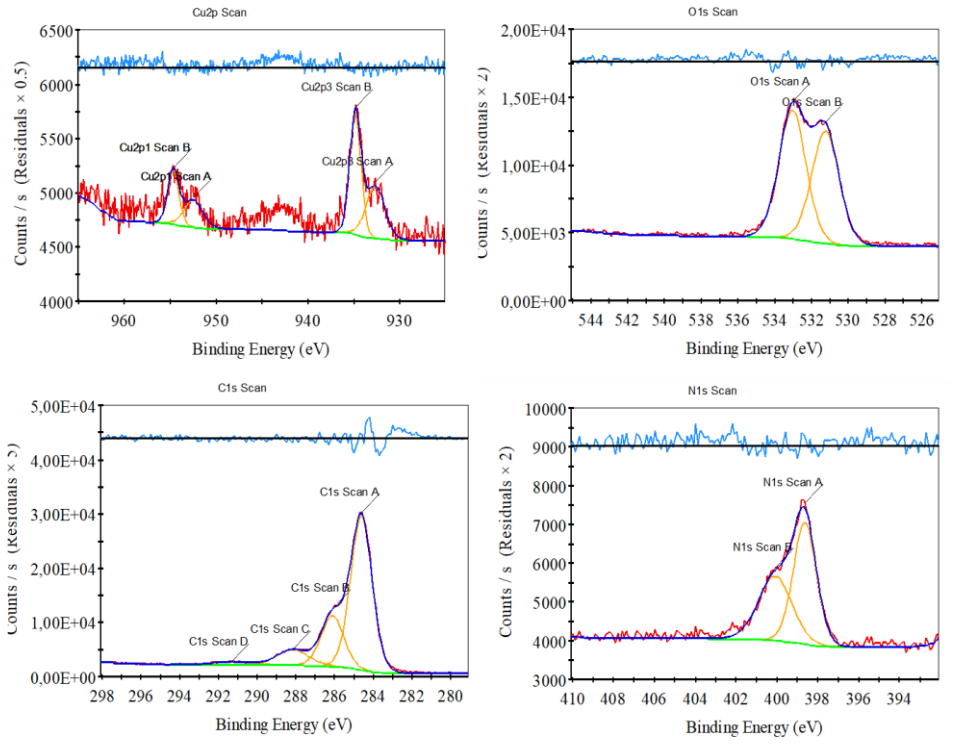

Figure S11: XPS of rGO/CuPc(3) showing (a) Cu2p, (b) O1s, (c) C1s, and (d) N1s scans.

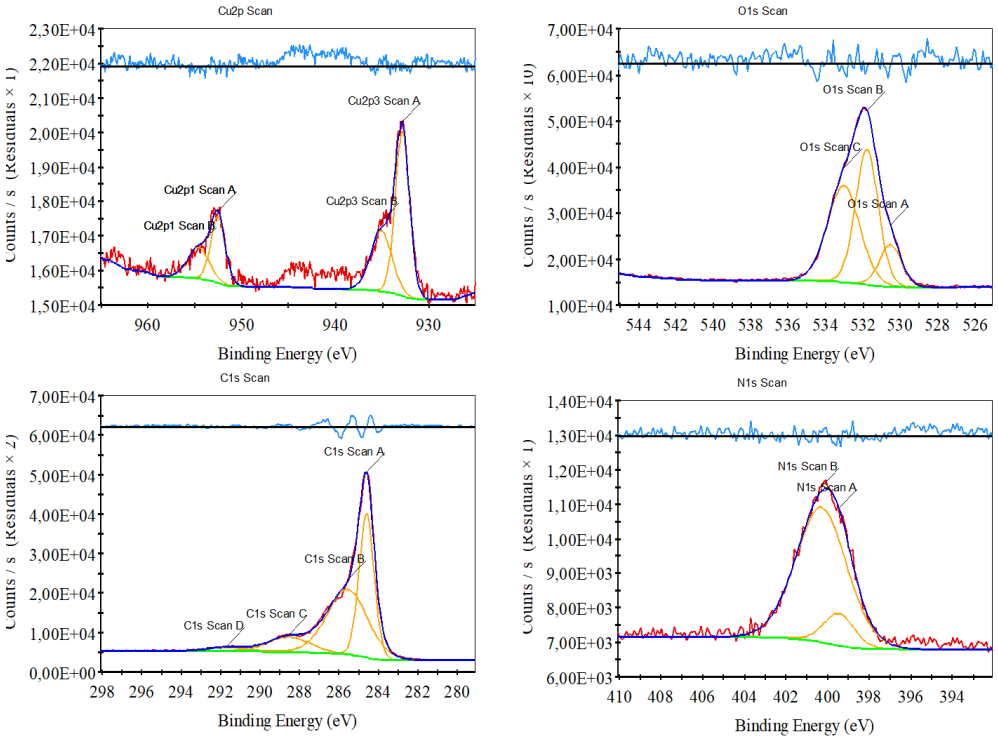

Figure S12: XPS of rGO/CuPc(3) as-coated on ITO showing (a) Cu2p, (b) O1s, (c) C1s, and (d) N1s scans.

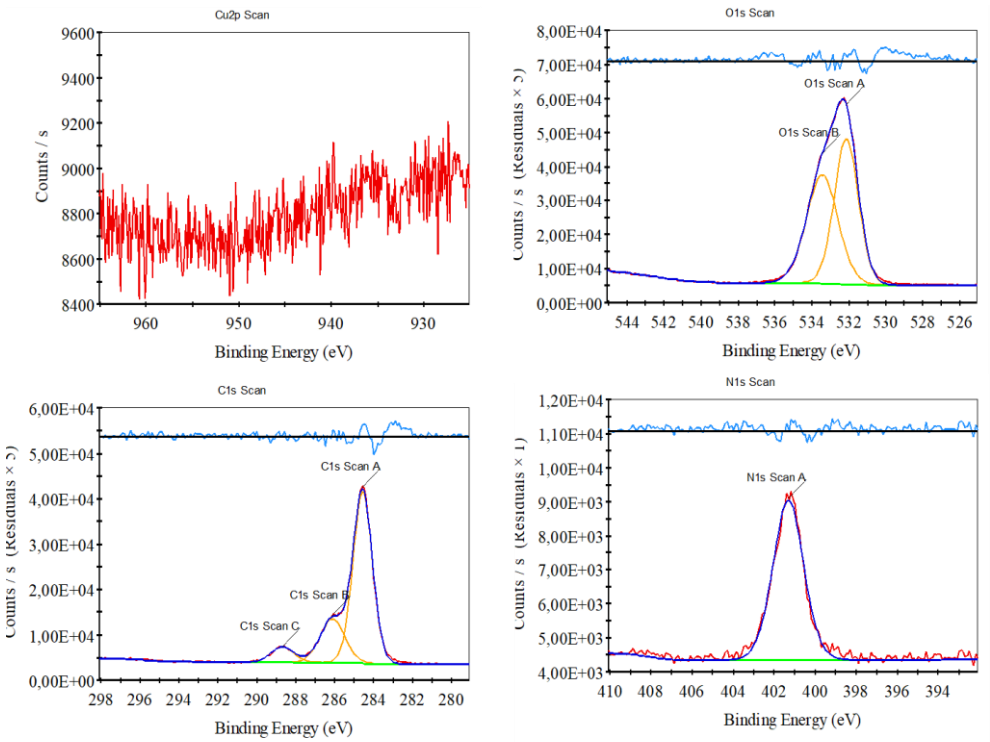

Figure S13: XPS of rGO/CuPc(3) on ITO after electrochemistry showing (a) Cu2p, (b) O1s, (c) C1s, and (d) N1s scans.

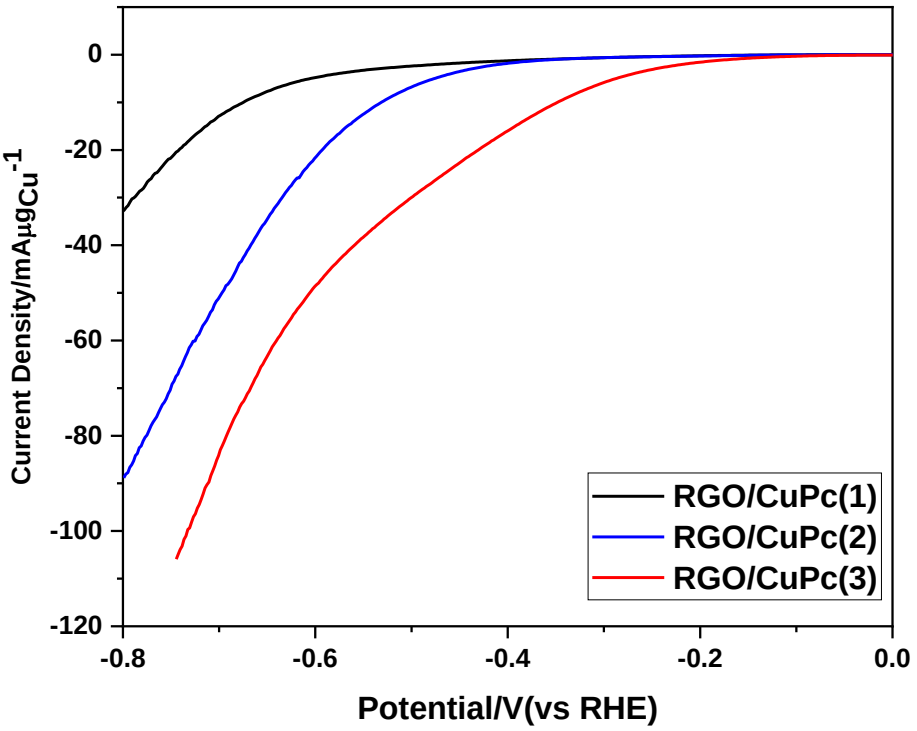

Figure S14: LSV curves of rGO/CuPc(1), rGO/CuPc(2) and rGO/CuPc(3) coatings in 0.5 M H_2SO_4 solution, the peak current value is normalized by mass of Cu loaded on rGO.

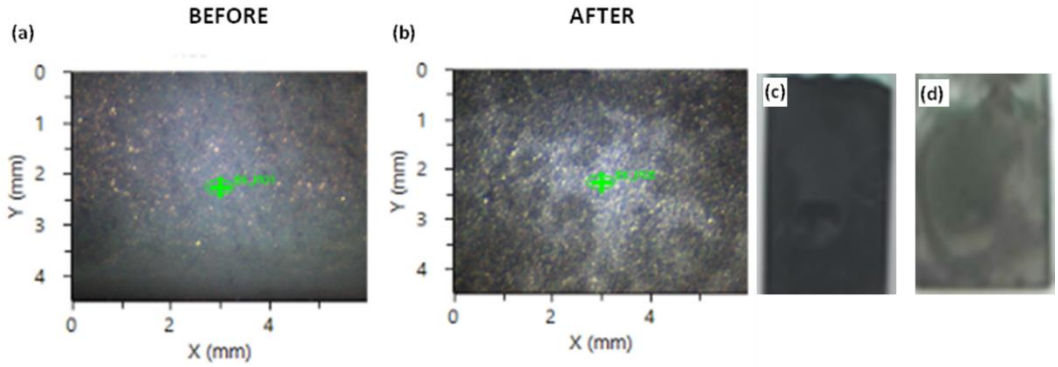

Figure S15: The microscopic images analyzed by XPS (a) before and (b) after HER. The digital imaging of the overall coating (c) before and (d) after HER.

Table S1: Composition and analysis of the rGO/CuPc samples and rGO/CuPc(3) coated ITO Glass (before and after electrochemical measurement). (The rest of the elements are disregarded owing to their small content or since they come from the electrolyte.) Due to instability of rGO/CuPc on ITO in acidic solution during cathodic polarization and low content of Cu, the determination of the Cu signal is not accurate.

	rGO/CuPc(1)	rGO/CuPc(2)	rGO/CuPc(3)	rGO/CuPc(3) coated ITO Glass (before electrochemical measurement)	rGO/CuPc(3) coated ITO Glass (after electrochemical measurement)
C	81.83	77.21	75.47	60.26	55.15
N	5.58	6.78	6.88	5.82	4.54
O	12.13	14.28	16.32	27.59	40.19
Cu	0.45	0.31	0.39	0.84	-
In				2.07	0.12
Sn				0.29	-

*Due to instability of rGO/CuPc on ITO in acidic solution during cathodic polarization and low content of Cu, the determination of the Cu signal is not accurate [1].

References

1 M. Senthilkumar, J. Mathiyarasu, J. Joseph, K. L. N. Phani and V. Yegnaraman, *Mater. Chem. Phys.*, 2008, **108**, 403–407.