Supporting Information for

Electrochemical Water Oxidation Using a Copper Complex

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Instrumentation

A combined glass electrode (*Metrohm 6.0224.100*) filled with 3 M KCl in water was used for pH determination (daily calibration).

For the electrochemical investigations a Gamry Instruments Reference 600 or Reference 600+. All electrochemical measurements were performed with iR compensation using the positive feedback method which is implemented in the PH200 software of Gamry.

The UV/vis spectra were recorded with an Agilent Cary 5000 UV-VIS-NIR spectrometer or Analytic Jena SPECORD® 50 PLUS spectrometer.

GC experiments of the headspace were carried out with a Shimadzu GC-2014 equipped with a TCD detector and a molecular sieve column (5 Å, 80/100, 2 m length, 2 mm ID). Methane was used as internal standard and injected into the headspace before each CPE. To calculate n_{O2}, a calibration curve by measuring known quantities of n_{O2}/n_{CH4} mixtures was done.

The SEM and EDX analysis was carried out with a Nova NanoSem 650 in-situ SEM from FEI. A "through the lens" (TL) and an "Everhart-Thornley (ET) detector was used to take images at an acceleration voltage of 10 kV. For the energy-dispersive X-ray spectroscopy (EDX) an Oxford Instrument X-max detector was deployed. The EDX measurements were carried out at an acceleration voltage of 20 kV and a live time of 90 s for every measuring point.

Molecular Copper Oxygen Evolution Catalysts

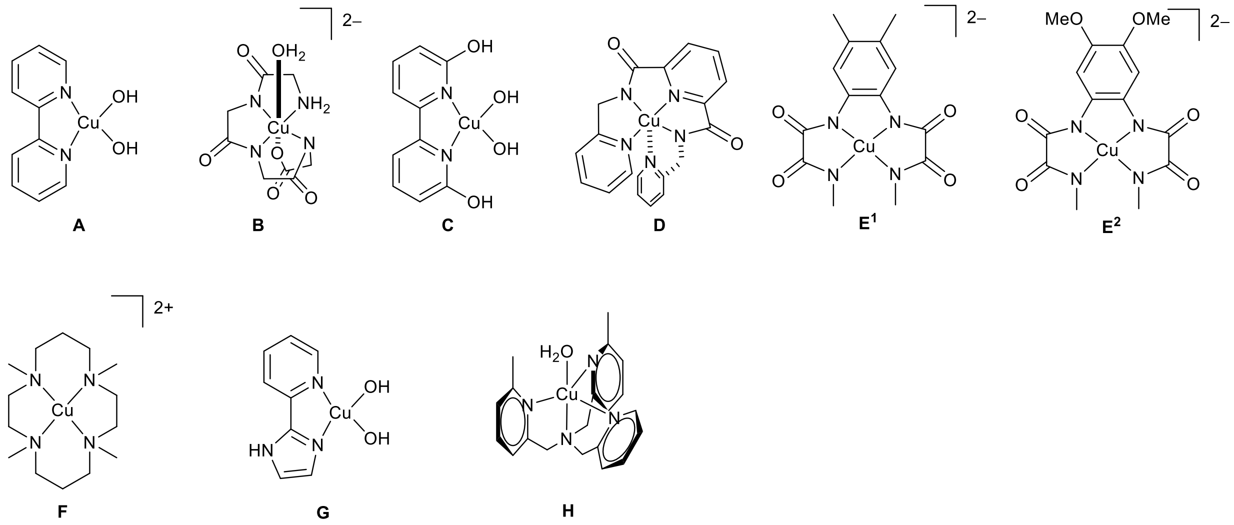

Figure S 1. Overview of selected mononuclear copper oxygen evolution catalysts, ref. see main text.

Electrochemical Measurements

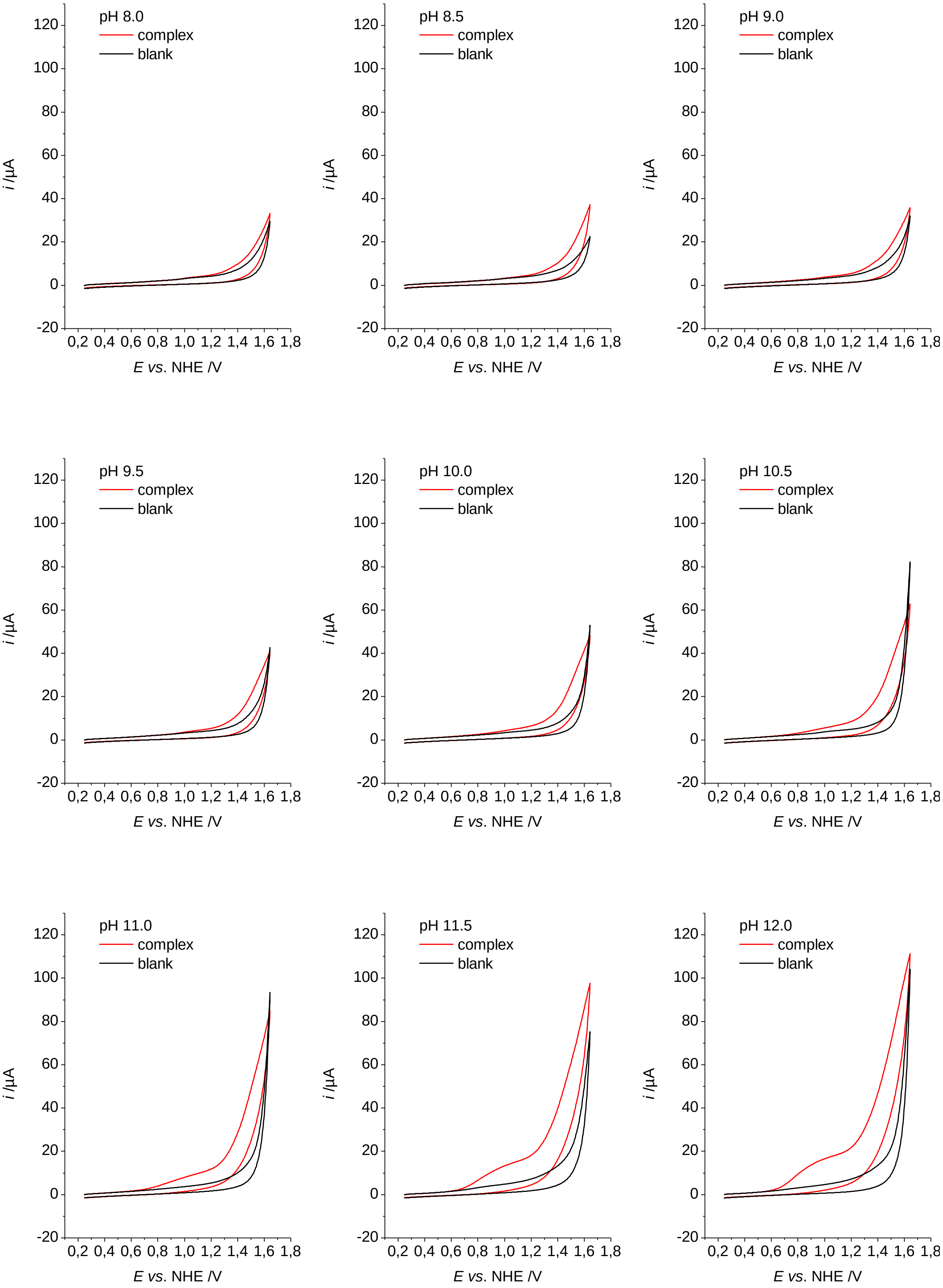

Figure S 2. pH dependent CV data of ***1*** *in Millipore water ([**1**] ≈ 1 mM, I= 0.1 M* PO_4^{3-}*, without Chelex®,* v *= 0.1 Vs*$^{-1}$*).*

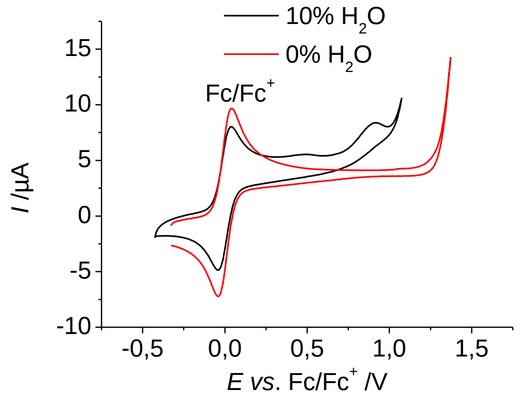

Figure S 3. CV data of ***1*** *in acetonitrile with 0 % (red) and 10 % (black) water ([****1****] ≈ 1 mM, I = 0.1* M *$^{n}Bu_4NPF_6$, pH = 8, v = 0.1 Vs^{-1}).*

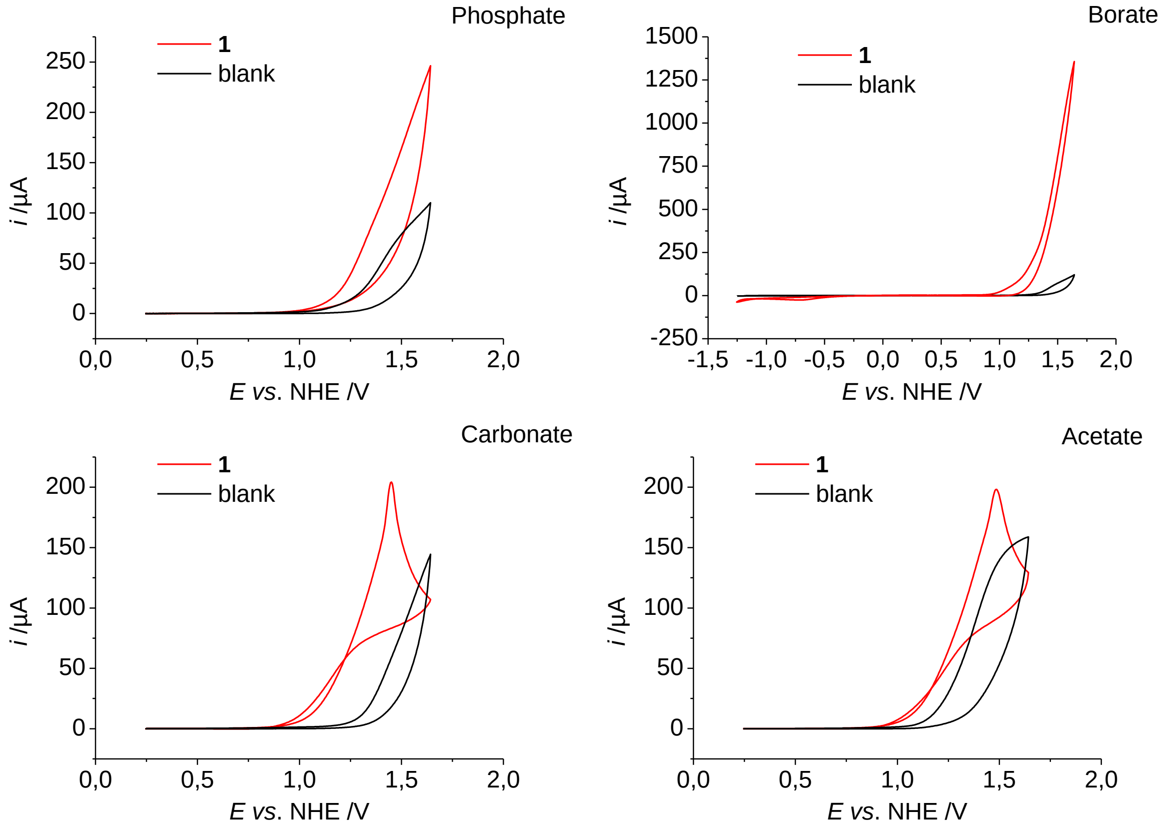

Figure S 4. CV data of ***1*** *in Millipore water employing a BDD electrode and various buffer salts ([****1****] ≈ 1 m*M*, I = 0.1* M *buffer, pH = 12). Borate, carbonate and acetate buffer solutions were adjusted to pH 12 with NaOH and used without Chelex®.*

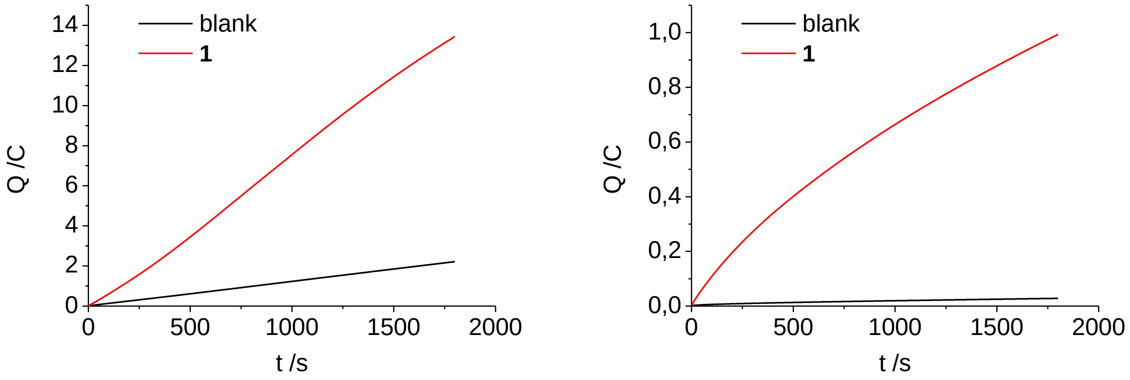

Figure S 5. Bulk electrolysis experiments in Millipore water with ***1*** *and a 7 mm GC rod in a two-compartment cell. The GC rod was polished and conditioned by 30 CV cycles between 1.6 V and −1.0 V in electrolyte solution prior CPE. Left:* E^{appl} *= 1.494 V, right:* E^{appl} *= 0.944 V; ([****1****] ≈ 1 mM, I = 0.1 M* PO_4^{3-}*, pH = 12).*

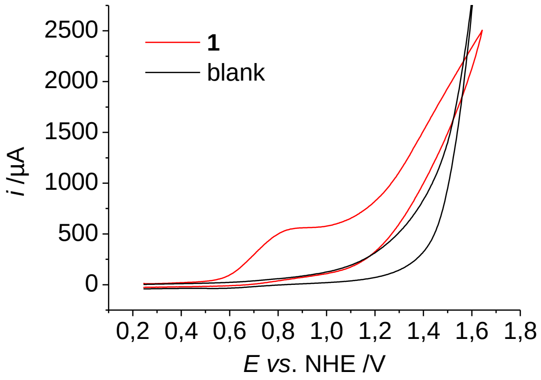

Figure S 6. CV data of ***1*** *using the GC plates ([****1****] ≈ 1 mM, I= 0.1 M* PO_4^{3-}*, v = 0.1* Vs^{-1}*, pH = 12) after conditioning and before CPE. The red curve represents the CV of* ***1*** *in electrolyte solution and the black curve pure electrolyte solution.*

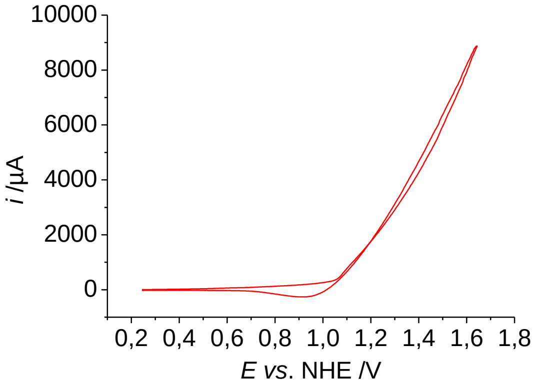

Figure S 7. CV data of 3 M $CuSO_4$ *in 1.0 M* Na_2CO_3 *using the GC plates (I= 0.1 M, v = 0.1* Vs^{-1}*, pH ≈ 10.8) after conditioning and before CPE, (without Chelex®).*

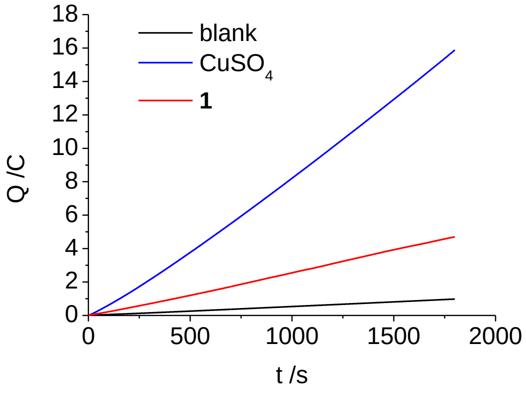

*Figure S 8. Charge vs. time plot during CPE using GC plates. Blue: 3 mM $CuSO_4$ in 1.0 M Na_2CO_3 solution, $E^{appl} = 1.30$ V; red: **1**, $E^{appl} = 1.494$ V ([**1**] ≈ 1 mM, I= 0.1 M PO_4^{3-}, pH 12); black: pure electrolyte solution, $E^{appl} = 1.494$ V (I= 0.1 M PO_4^{3-}, pH = 12).*

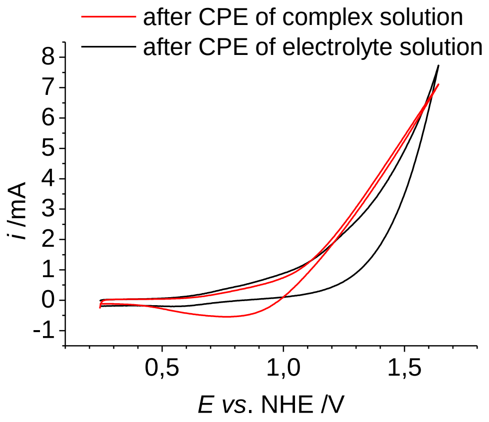

*Figure S 9. CV data of the reused electrode in new electrolyte solution after 30 min CPE at $E^{appl} = 1.494$ V ([**1**] ≈ 1 mM, I = 0.1 M PO_4^{3-}, ν = 0.1 Vs^{-1}, pH = 12). The GC-electrode was rinsed off but not polished between the experiments.*

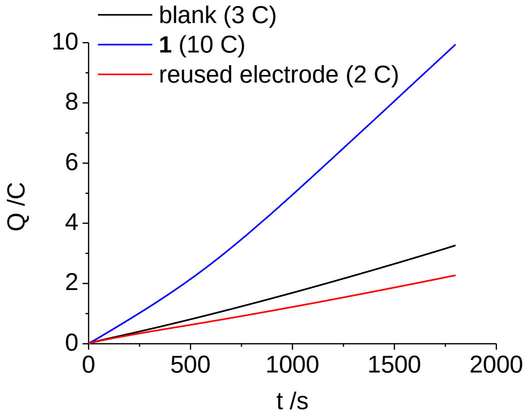

Figure S 10. Plot of the electric charge vs. time during CPE with the reused electrode in new electrolyte solution (red), polished and conditioned electrode in electrolyte solution (black), polished and conditioned electrode in complex solution (blue).

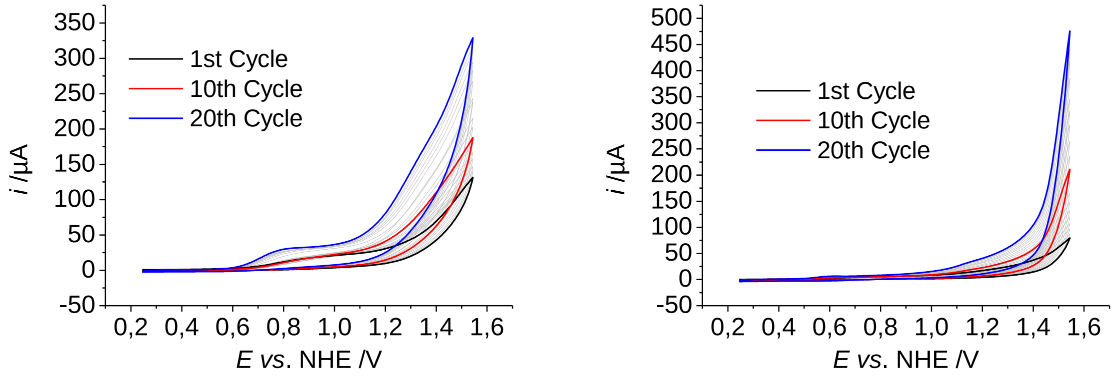

Figure S 11. Left: 20 successive scans of ***1*** *([**1**] ≈ 1 mM) in Millipore water; right: 20 successive scans of complex free solution. (I = 0.1 M PO$_4^{3-}$, ν = 0.1 Vs^{-1}, pH = 12).*

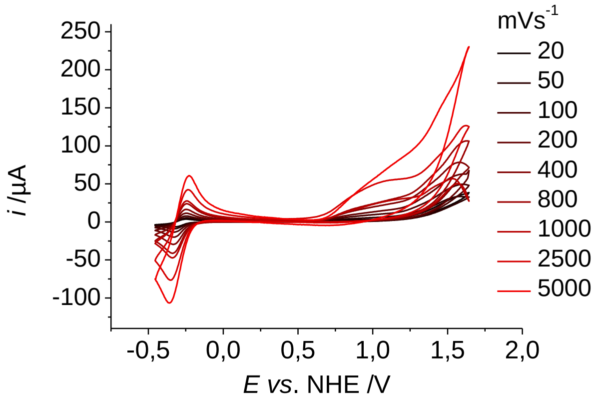

Figure S 12. Scan rate dependent CV data of ***1*** *in Millipore water ([**1**] ≈ 1 mm, I = 0.1 M PO$_4^{3-}$, pH = 12), background subtracted.*

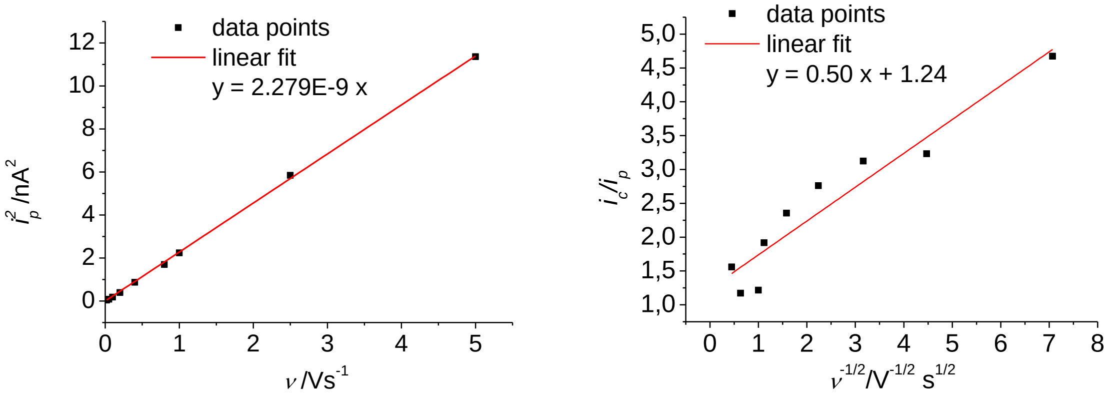

Figure S 13. Left: Plot of the square of the peak current for the Cu(II) reduction in dependence of the scan rate. Right: Plot of the ratio of the catalytic current (E = 1.494 V) over the current of the Cu(II) reduction vs. the square root of the scan rate.

$$i_p = 0.4463 \cdot n_p \cdot F \cdot A \cdot \left(\frac{n_p \cdot F \cdot v \cdot D}{R \cdot T}\right)^{\frac{1}{2}} \quad \text{(S1)}$$

$$D = \frac{R \cdot T \cdot m}{F^3 \cdot A^2 \cdot c^2 \cdot 0.1192} = 1.24 \cdot 10^{-5}\,\frac{cm^2}{s} \quad \text{(S2)}$$

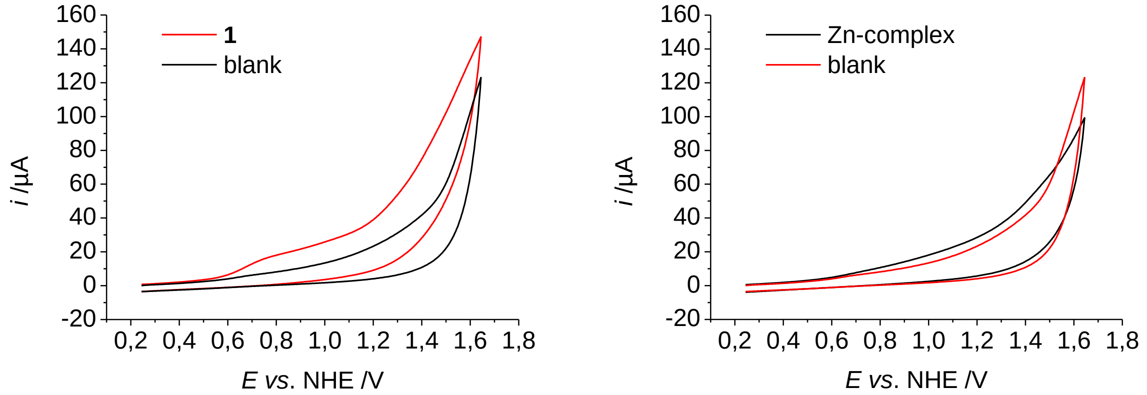

Figure S 14. CV data of ***1*** *(left)) and the equivalent zinc complex (right) in Millipore water ([****complex****] ≈ 1 mM, I = 0.1 M* PO_4^{3-}*,* $\nu = 0.1$ *Vs*$^{-1}$*, pH = 12).*

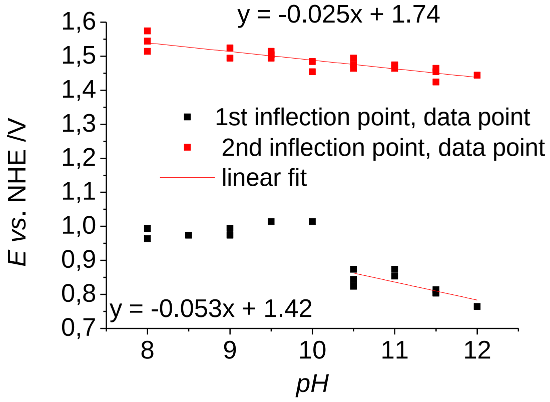

Figure S 15. Plot of the potential of the inflection points of the CV data at different pH, black: 1st inflection point, red: 2nd inflection point.

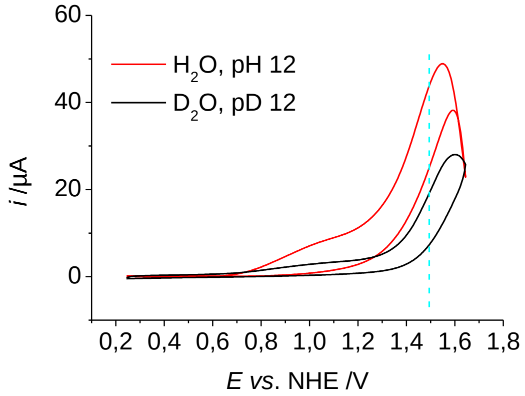

Figure S 16. CV data of ***1*** *in Millipore water ([****1****] ≈ 1 mM, I = 0.1 M* PO_4^{3-}*,* $\nu = 0.1$ *Vs*$^{-1}$*,). Red:* H_2O *(pH = 12), black:* D_2O *(pD = 12).* K_2HPO_4 *was used for the* D_2O *solution and the pD was adjusted with NaOD. The pH* was measured with a glass electrode and converted to pD by adding 0.45.*[1]

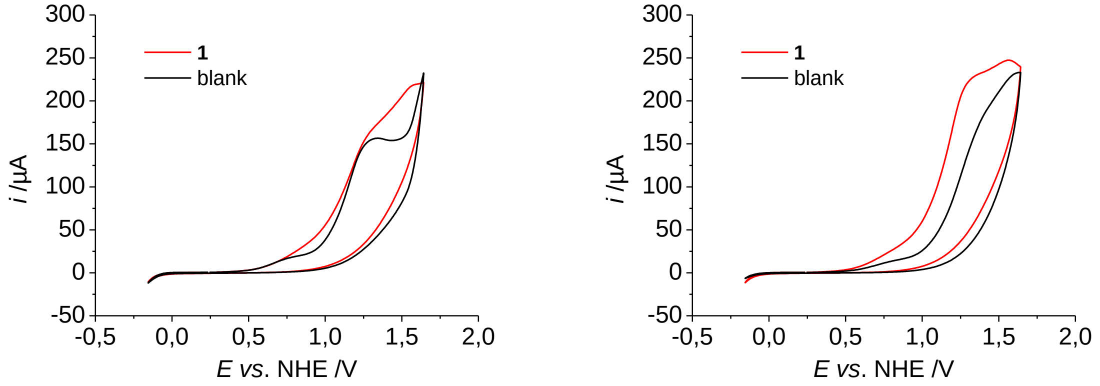

*Figure S 17. CV data of **1** and 1 eq. (left) and 10 eq. (right) of H_2O_2 ([**1**] ≈ 1 mM, I = 0.1 M PO_4^{3-}, pH = 12).*

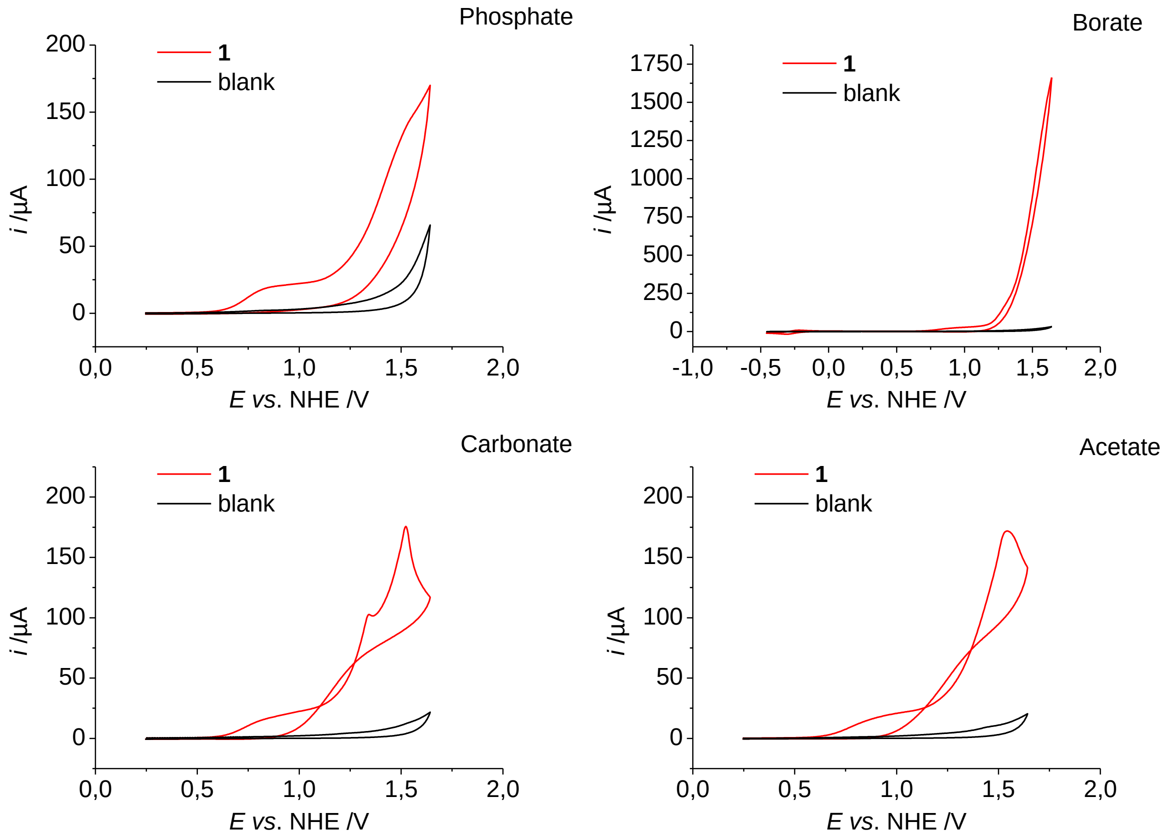

*Figure S 18. CV data of **1** in Millipore water with various buffer salts ([**1**] ≈ 1 mM, I = 0.1 M buffer, pH = 12). Borate, carbonate and acetate buffer solutions were adjusted to pH 12 with NaOH and used without Chelex®.*

GC-TCD Traces

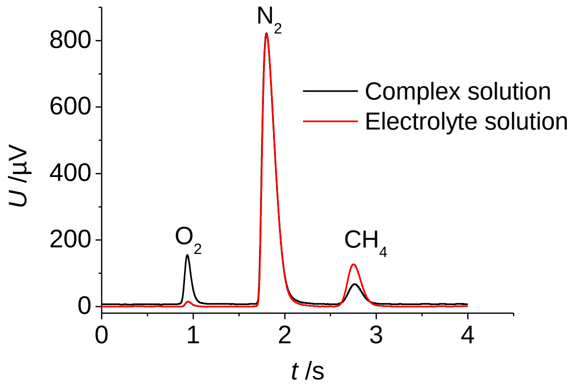

*Figure S 19. GC-TCD traces of the headspace after 30 min CPE (E^{appl} = 1.494 V, I = 0.1 M PO_4^{3-}, pH = 12). Red: trace after CPE of electrolyte solution; black: trace after CPE of complex solution ([**1**] ≈ 1 mM).*

Vis Spectroscopy

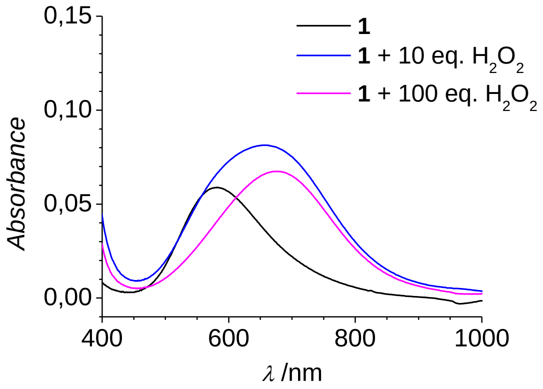

*Figure S 20. Vis spectra of the complex solution in the presence of various amounts of H_2O_2 ([**1**] ≈ 1 mM, I = 0.1 M, pH 12).*

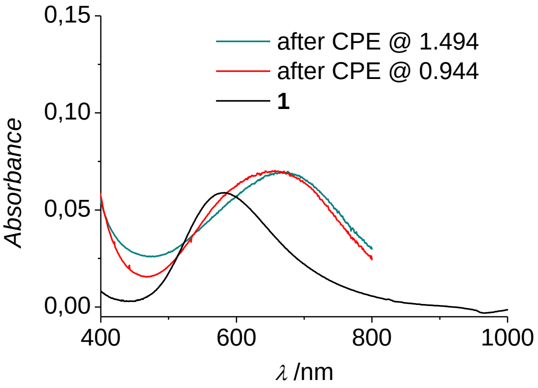

*Figure S 21. Vis spectra of the complex solution before CPE (black), after CPE at 1.494 V (green), and after CPE at 0.944 V (red), ([**1**] ≈ 1 mM, I = 0.1 M PO_4^{3-}, pH = 12).*

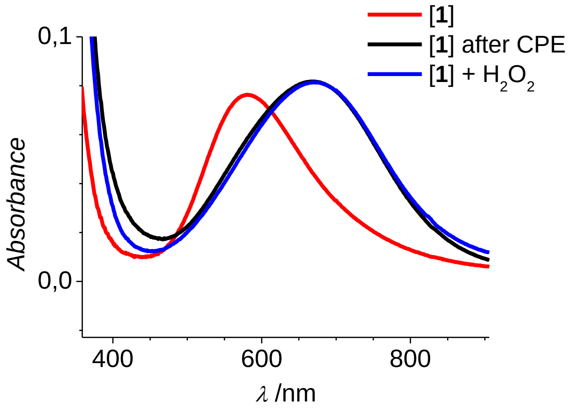

*Figure S 22. Vis spectra of the complex solution before CPE (red), after CPE at 1.494 V (black), and with ex. H_2O_2 (blue), ([**1**] ≈ 1 mm, I = 0.1 m PO_4^{3-}, pH = 12).*

Surface Analysis

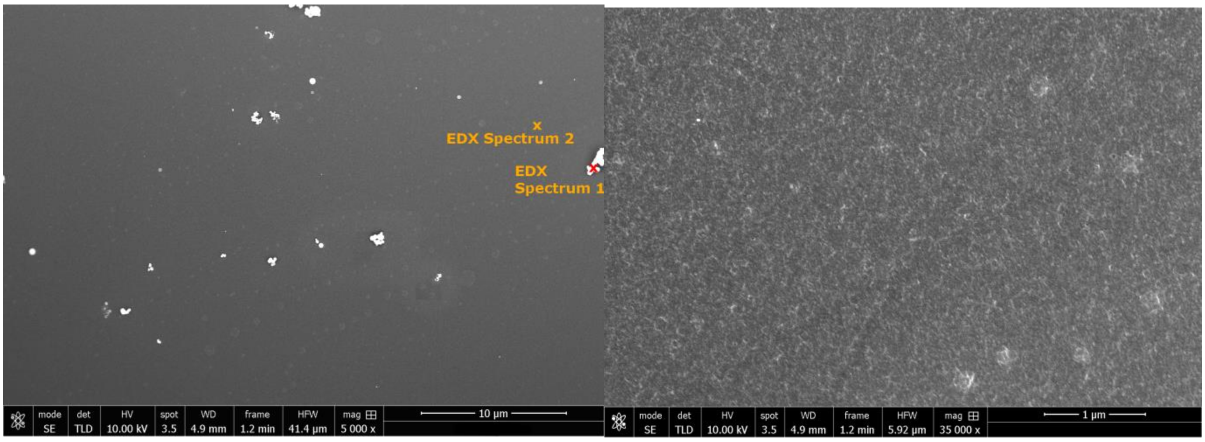

*Figure S 23. SEM pictures of the GC electrode after CPE employing 1mM solution of **1** at pH = 12, applied potential of 1.49 V.*

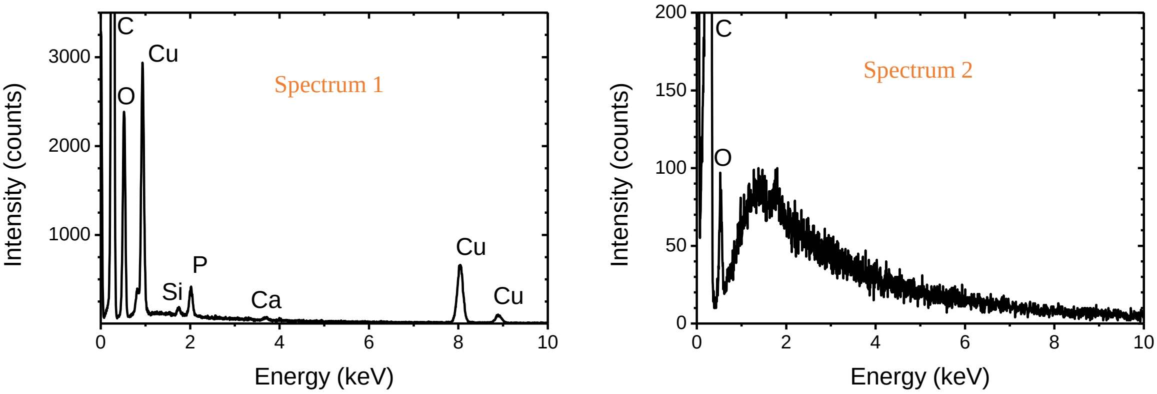

*Figure S 24. EDX spectra of the GC electrode after CPE employing 1mM solution of **1** at pH = 12, applied potential of 1.49 V; left picture: EDX spectrum 1, position see Figure S 22; Right: EDX spectrum 2, position see Figure S 22.*

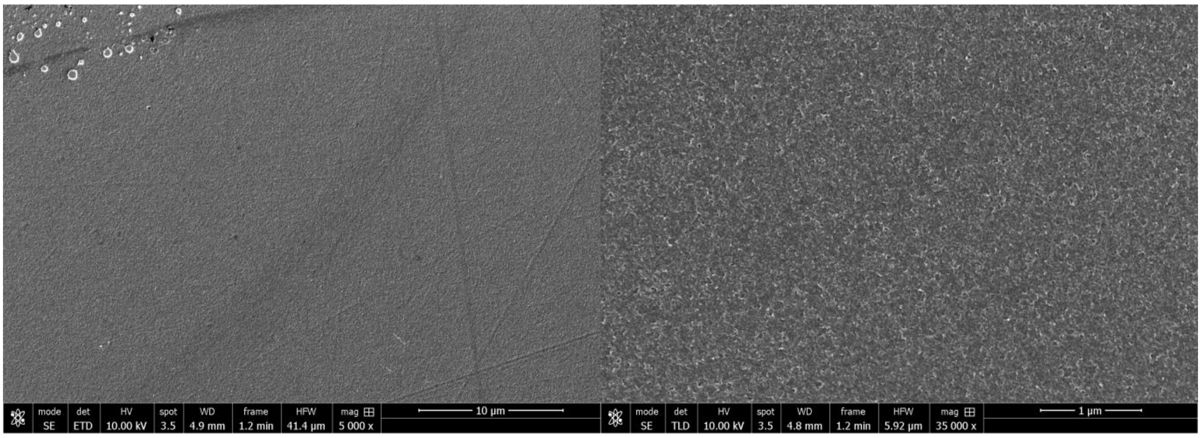

Figure S 25. SEM pictures of the GC electrode after CPE without the complex at pH = 12, applied potential of 1.49 V.

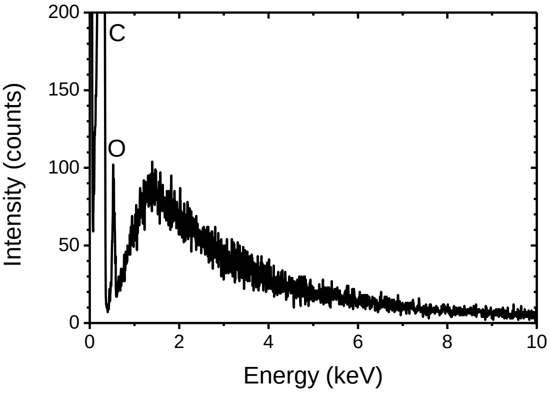

Figure S 26. EXD spectra of the GC electrode after CPE without the complex at pH = 12, applied potential of 1.49 V.

CPE with Cu(II)SO_4 was used as reference system for copper deposition, which was reported by *Meyer* and co-worker.[2] A 3 mM Cu(II)SO_4 solution (in 1.0 M Na_2CO_3) was electrolysed 30 minutes at 1.30 V (Figure S 8).

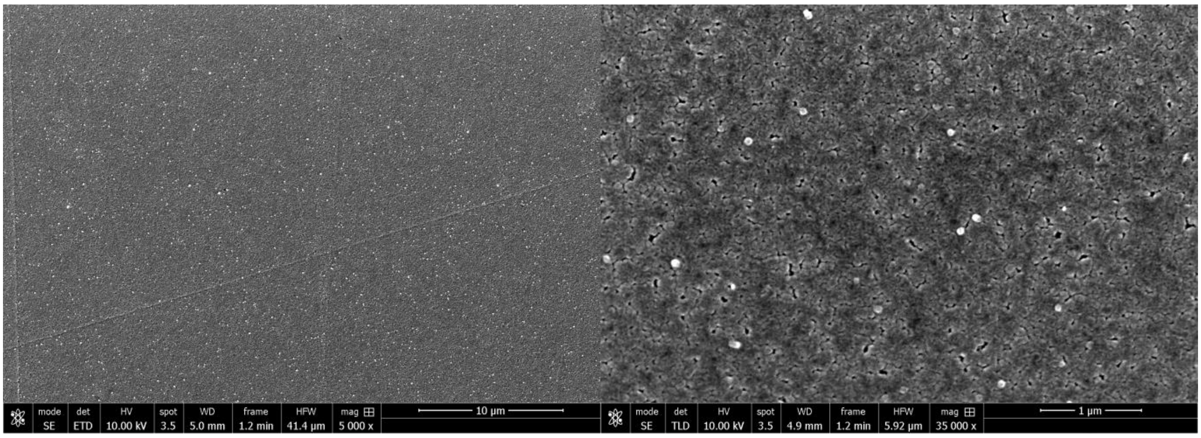

Figure S 27. SEM pictures of the GC electrode after CPE employing 3 mM solution of $CuSO_4$ at pH ≈ 10.8, applied potential of 1.30 V.

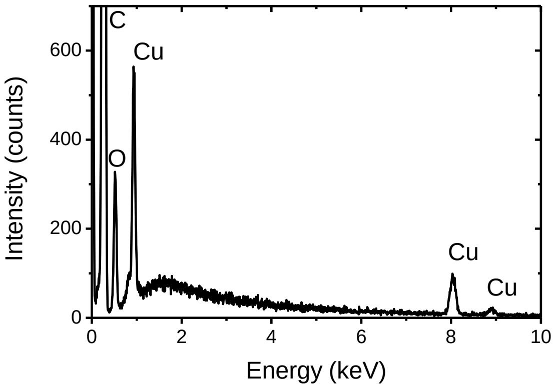

Figure S 28. EDX spectra of the GC electrode after CPE employing 3 mM solution of $CuSO_4$ at pH ≈ 10.8, applied potential of 1.30 V.

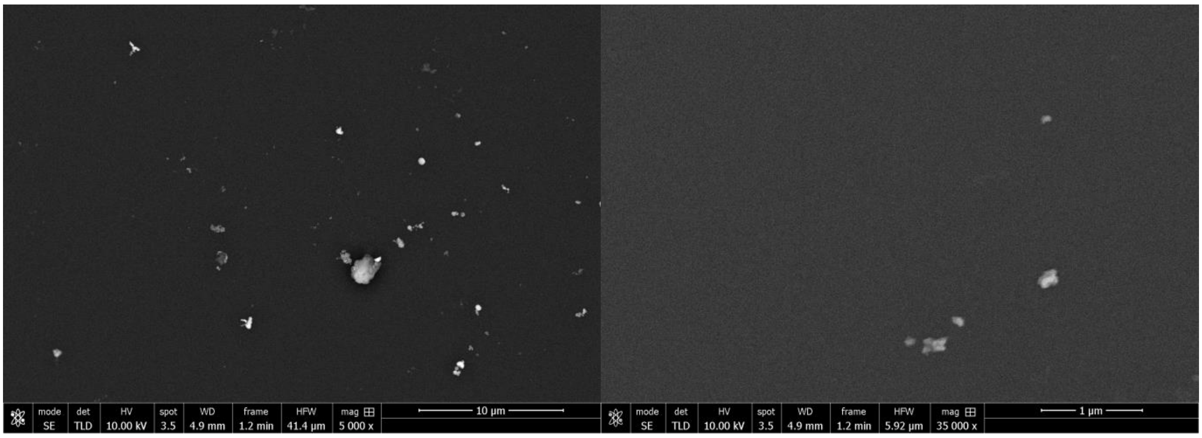

Figure S 29. SEM pictures of a bare GC electrode.

References

[1] A. Krężel, W. Bal, *J. Inorg. Biochem.* **2004**, 98, 161 – 166.
[2] Z. Chen, T. J. Meyer, *Angew. Chem. Int. Ed.* **2013**, 52, 700 –703; *Angew. Chem.* **2013**, *125*, 728 –731.