Electronic Supplementary Material (ESI) for Analytical Methods.

Combining Cross-Reactivity of Electrode Array with the Selective Thiol Reporting Process of Redox Indicators: Targeted Sensing of Biothiols

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1. Abbreviation

AA	Ascorbic acid
Cys	Cysteine
CuPc	Copper phthalocyanine
DA	Dopamine
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMF	N,N'-dimethylformamide
DMSO	Dimethylsulfoxide
GSH	Glutathione
Hcys	Homocysteine
MnPc	Manganese phthalocyanine
MPc	Metallophthalocyanine
UA	Uric acid
GO	Graphene oxide
GCE	Glassy carbon electrode
LDA	Linear discriminant analysis
LSV	Linear sweep voltammetry
rGO	Reduced graphene oxide

2. Synthesis

2.1 Synthesis of metallophthalocyanine complexes, CuPc (1) and MnPc (2)

A mixture of anhydrous metal salts (0.35 equ), phthalonitrile (1 equ), DBU (2 equ) in pentanol was stirred at 140-160 °C for 24 h under a nitrogen atmosphere.[1] After the reaction, the mixture was allowed to cool to room temperature, and the solvent was evaporated. The crude mixture was dissolved in chloroform (10 mL) and precipitated using hexane (100 mL). Hexane was decanted, and the precipitate was dissolved in DMF (10 mL) and again re-precipitated by adding methanol (100 mL). The precipitate was washed several times with methanol using centrifugation technique. The purity of the complexes CuPc (**1**) and MnPc (**2**) was ascertained by elemental analysis as 94 % and 85% respectively. Anal. Calcd for $C_{32}H_{18}CuN_8$ (CuPc (**1**)), C, 66.4; H, 3.1; N, 19.4, Found: C, 62.8; H, 2.4; N, 18.4, Anal. Calcd for $C_{32}H_{18}MnN_8$ (MnPc (**2**)), C, 67.5; H, 3.2; N, 19.7. Found: C 58.6; H, 2.3; N 15.7.

2.2 Synthesis of graphene oxide from graphite

Graphene oxide (GO) was synthesized from graphite powder using Hummer's method.[2] To the hot (80 °C) concentrated H_2SO_4 solution (12 mL) containing $K_2S_2O_8$ (4 g) and P_2O_5 (4 g), graphite powder (2 g) was added under continuous stirring. After 6 h, the mixture was allowed to cool to room temperature. Carefully the above mixture was poured into 150 mL of MilliQ water, then filtered and dried overnight at 60 °C. The pre-oxidized graphite powder (1 g) was added to cold H_2SO_4 (46 mL) at 0 °C, and then $KMnO_4$ (6 g) was gradually added under continuous stirring in ice-bath. After 15 min, $NaNO_3$ (1 g) was slowly introduced into the above reaction mixture. The mixture was stirred at room temperature for 2 h, and it was diluted with MilliQ-water (100 mL). The reaction was quenched by adding MilliQ water (280 mL) and 30 % H_2O_2 (5 mL). The crude resultant was centrifuged, and the supernatant was discarded. The resultant colloidal material was

suspended in HCl (1 M), centrifuged and the supernatant was discarded. Finally, the material was washed with water several times using centrifugation technique.

2.3 Reduction of graphene oxide to reduced graphene oxide (rGO)

Obtained GO (20 mg) was suspended in distilled water (200 mL). To the suspension, $NaBH_4$ (2.28 g) and $CaCl_2$ (1.78 g) were added. The reaction mixture was allowed to stir at room temperature for 12 h to obtain reduced graphene oxide (rGO). Then, the rGO was filtered and washed with distilled water for several times to remove the unreacted $NaBH_4$ and $CaCl_2$.[3]

2.4 General procedure for preparation of GO-MPc-PDA (3 and 4) and rGO-MPc- PDA (5 and 6)

The general procedure for the synthesis of graphene-metallophthalocyanine-PDA materials (**3-6**) is presented in the scheme **1.** Typically 10 mg of carbon nanomaterials (GO or rGO) was suspended in 50 mL of water and DMSO (1:1 volume ratio) and sonicated for 30 min to disperse the material. To the dispersion, metallophthalocyanine **1**/or **2** (5 mg) was added and sonicated for another 15 min. Then, dopamine (5 mg) was added to the suspension and further sonicated for 3 h.[4] The suspension was washed with water followed by methanol using centrifugation method. The elemental composition of the materials was quantified using Energy Dispersive X-ray Spectroscopy (EDAX). The data are provided as follows.

GO-CuPc-PDA **3** (C-52.82 %, O-33.74 %, N-10.57%, Cu-2.87), GO-MnPc-PDA **4** (C-54.43 %, O-29.23 %, N-11.29 %, Mn-5.06 %), rGO-CuPc-PDA **5** (C-42.49 %, O-11.01 %, N-12.35 %, Ca-2.4 %, Cu-9.03 %), rGO-MnPc-PDA **6** (C-47.44 %, O-12.50, N-18.11 %, Ca-7.72, Mn-9.75 %)

3. Scanning electron microscopy (SEM)

Materials (**3**-**6**) were dispersed individually in the methanol (1 mg/1 mL) in a separate Eppendorf tube and sonicated for 30 min. The dispersion (20 μL) was drop casted over the separate SEM grid containing carbon tape and allowed it to dry at room temperature. The prepared grids were subjected to the SEM analysis. The presence of polydopamine (PDA) in materials **3-6** was evident from SEM image (Figure S4). The PDA covered the graphene sheets by forming a thin uniform layer, SEM images showing the crinkled morphology of graphene sheets, and in agreement with findings of earlier reports on similar materials.[4,5]

4. Figures

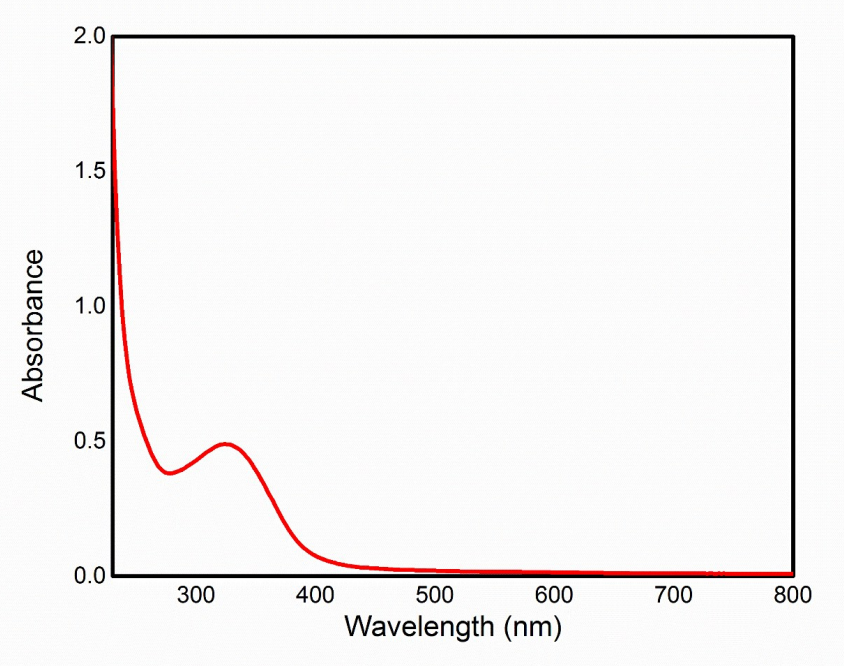
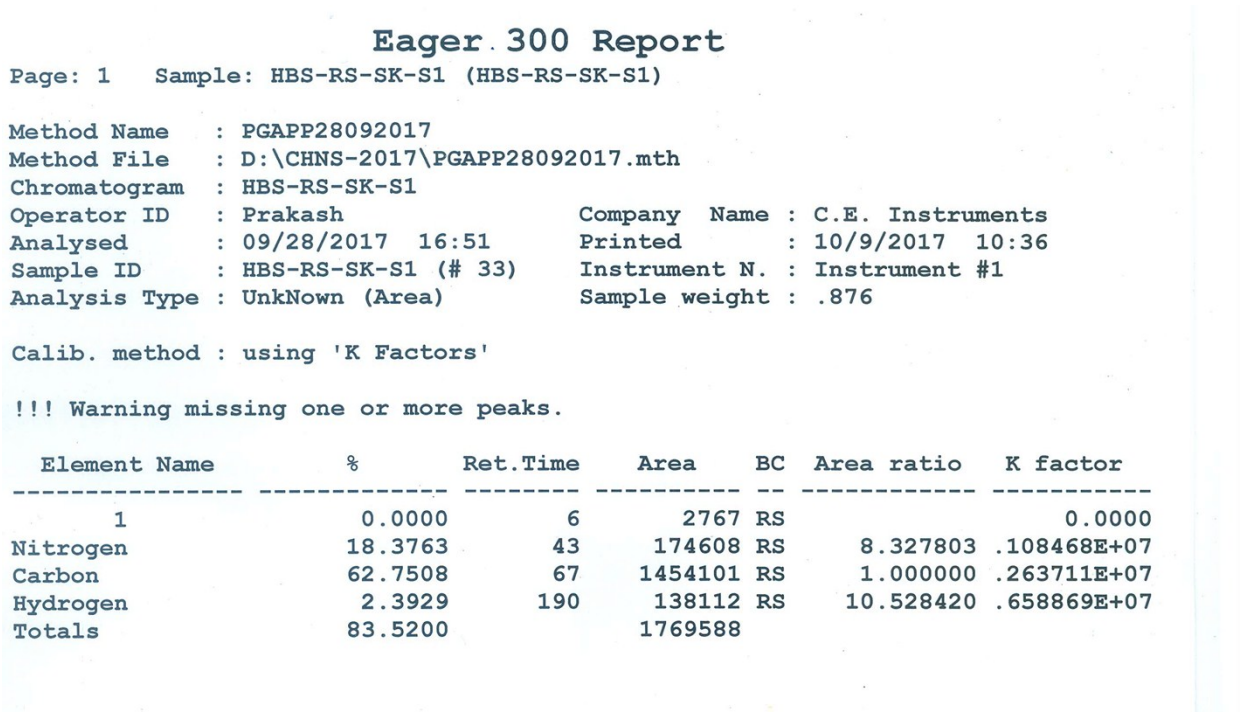


Figure S1. UV-visible spectra for the pretreated plasma (100 µL) sample spiked in the phosphate buffer (1900 µL). Concentration of the proteins = absorbance at 280 nm divided by path length[6] (1 cm).



Eager 300 Report

Page: 1 Sample: HBS-RS-SK-S1 (HBS-RS-SK-S1)

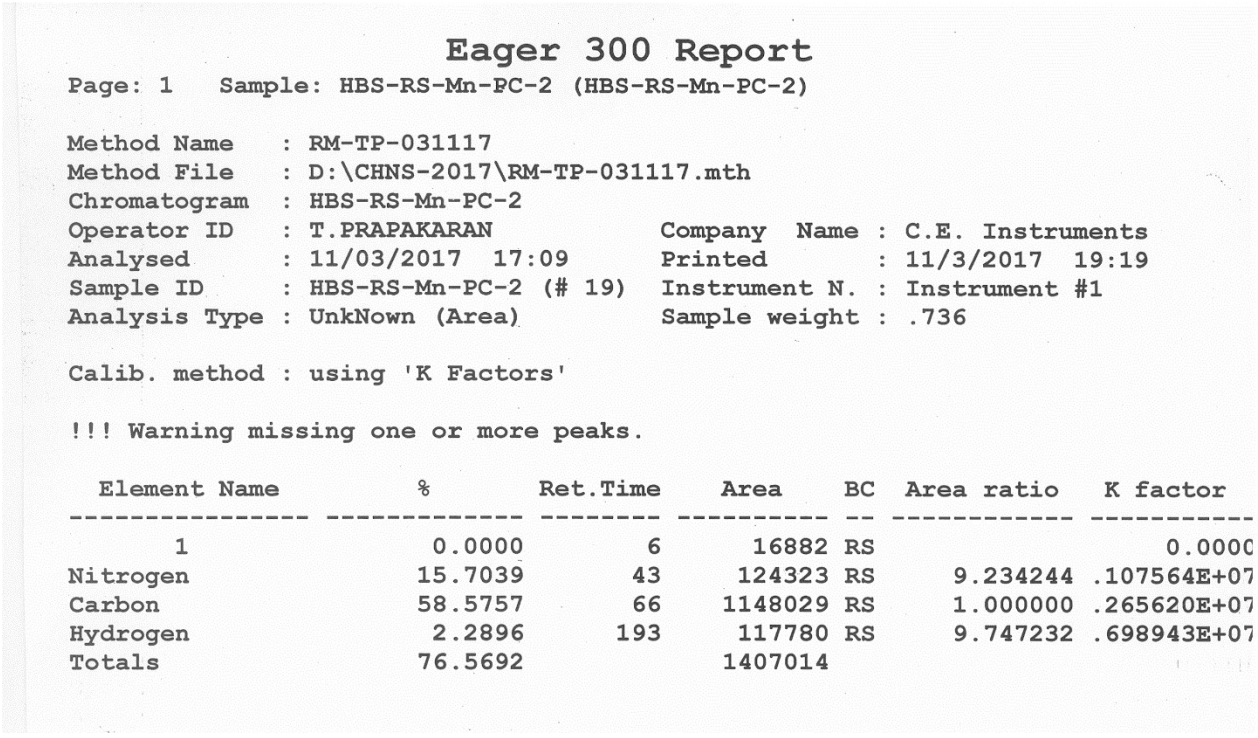
Method Name : PGAPP28092017
Method File : D:\CHNS-2017\PGAPP28092017.mth
Chromatogram : HBS-RS-SK-S1
Operator ID : Prakash Company Name : C.E. Instruments
Analysed : 09/28/2017 16:51 Printed : 10/9/2017 10:36
Sample ID : HBS-RS-SK-S1 (# 33) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : .876

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	6	2767	RS		0.0000
Nitrogen	18.3763	43	174608	RS	8.327803	.108468E+07
Carbon	62.7508	67	1454101	RS	1.000000	.263711E+07
Hydrogen	2.3929	190	138112	RS	10.528420	.658869E+07
Totals	83.5200		1769588			

Figure S2. Elemental analysis (CHN) report for CuPc (**1**).



Eager 300 Report

Page: 1 Sample: HBS-RS-Mn-PC-2 (HBS-RS-Mn-PC-2)

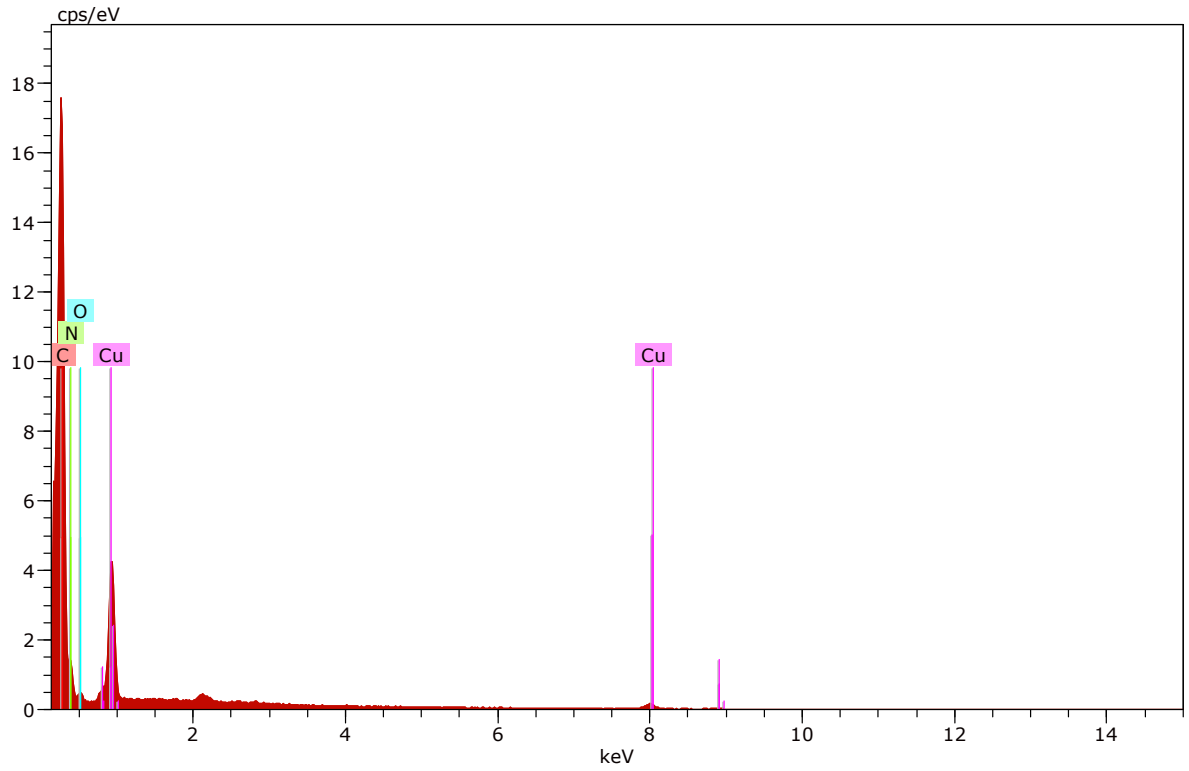
Method Name : RM-TP-031117
Method File : D:\CHNS-2017\RM-TP-031117.mth
Chromatogram : HBS-RS-Mn-PC-2
Operator ID : T.PRAPAKARAN Company Name : C.E. Instruments
Analysed : 11/03/2017 17:09 Printed : 11/3/2017 19:19
Sample ID : HBS-RS-Mn-PC-2 (# 19) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : .736

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	6	16882	RS		0.0000
Nitrogen	15.7039	43	124323	RS	9.234244	.107564E+07
Carbon	58.5757	66	1148029	RS	1.000000	.265620E+07
Hydrogen	2.2896	193	117780	RS	9.747232	.698943E+07
Totals	76.5692		1407014			

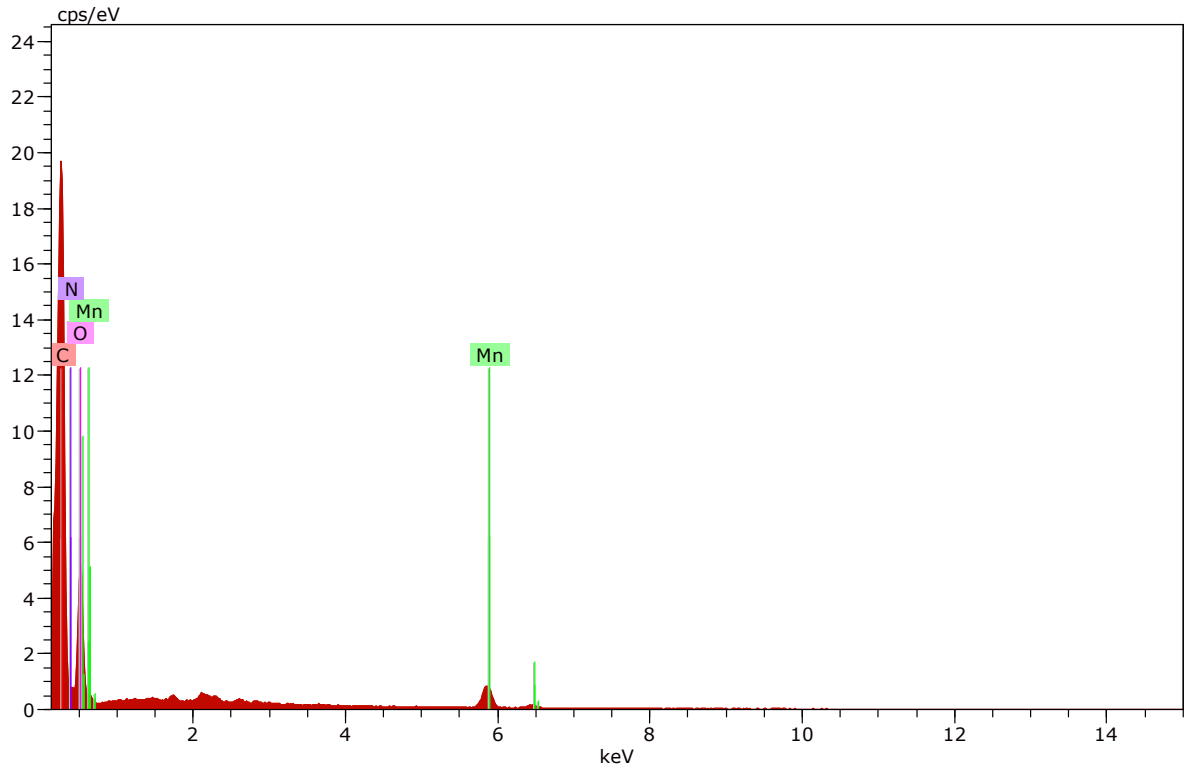
Figure S3. Elemental analysis (CHN) report for MnPc (**1**).



Spectrum: Acquisition 6677

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	61.52	61.52	67.46	7.03	0.820	0.751	1.000	1.000
N	7	K-series	28.54	28.54	26.84	4.34	0.254	1.124	1.000	1.000
O	8	K-series	5.91	5.91	4.86	1.10	0.043	1.372	1.000	1.000
Cu	29	K-series	4.04	4.04	0.84	0.21	0.012	2.861	1.000	1.181
Total:			100.00	100.00	100.00					

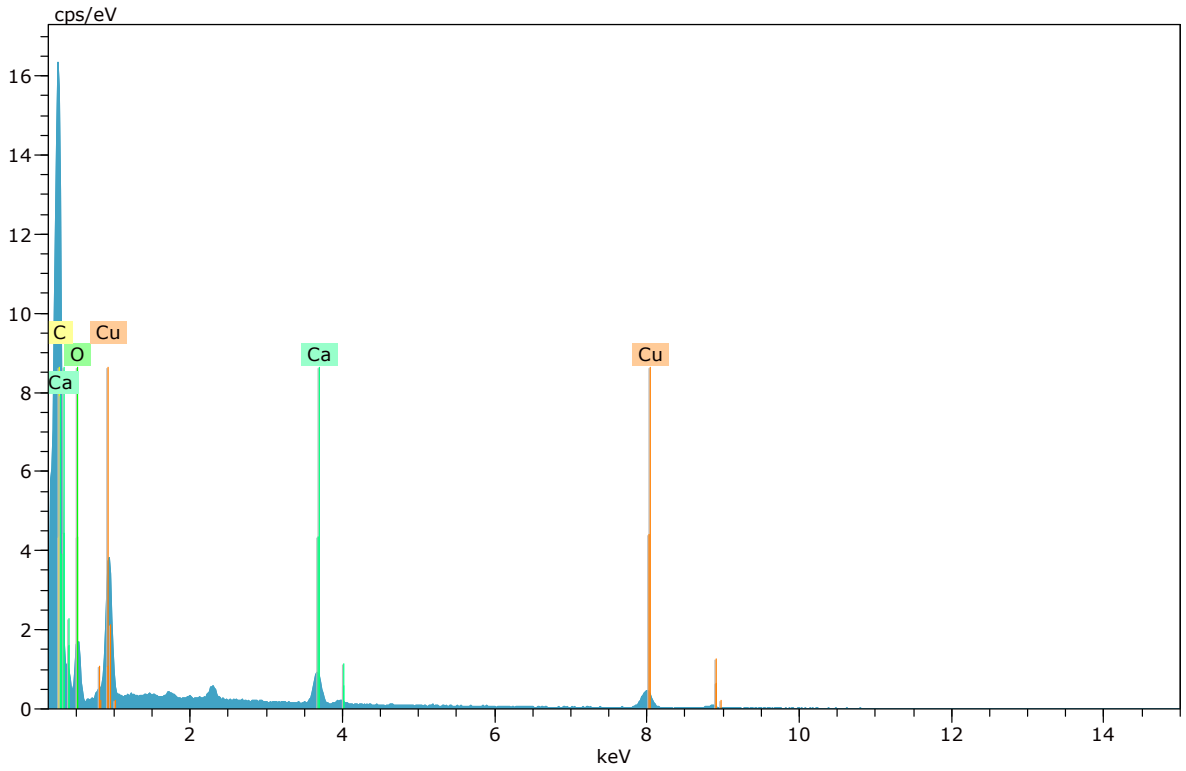
Figure S4. EDX analysis report for GO-CuPc-PDA (**3**).



Spectrum: Acquisition 6676

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	54.43	54.43	62.45	6.17	0.824	0.661	1.000	1.000
O	8	K-series	29.23	29.23	25.18	3.70	0.255	1.144	1.000	1.000
N	7	K-series	11.29	11.29	11.11	1.88	0.118	0.956	1.000	1.000
Mn	25	K-series	5.06	5.06	1.27	0.19	0.013	3.620	1.000	1.083
		Total:	100.00	100.00	100.00					

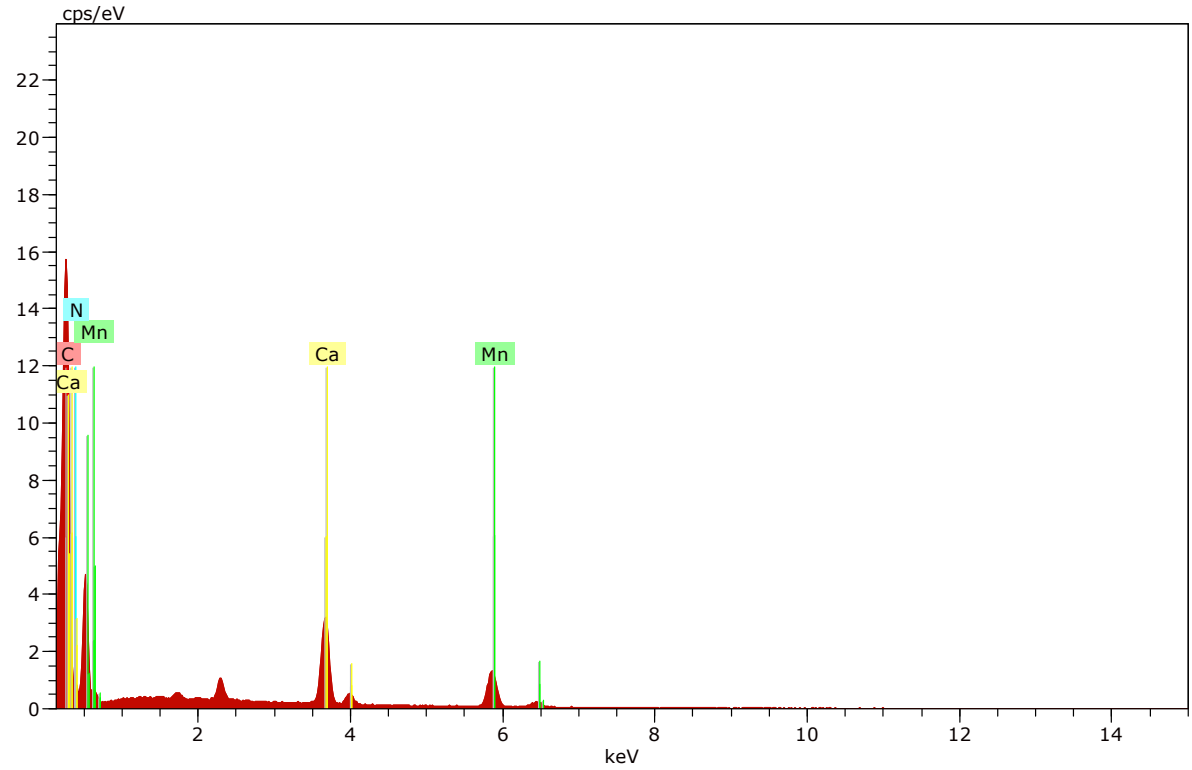
Figure S5. EDX analysis report for GO-MnPc-PDA (**4**).



Spectrum: Acquisition 6926

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	67.80	70.40	83.12	7.77	1.099	0.640	1.000	1.000
O	8	K-series	14.47	15.02	13.31	2.11	0.135	1.114	1.000	1.000
Cu	29	K-series	11.70	12.15	2.71	0.46	0.046	2.447	1.000	1.087
Ca	20	K-series	2.34	2.43	0.86	0.10	0.006	3.850	1.000	1.038
		Total:	96.31	100.00	100.00					

Figure S6. EDX analysis report for rGO-CuPc-PDA (**5**).



Spectrum: Acquisition 6674

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	47.44	57.02	70.32	5.46	0.986	0.578	1.000	1.000
N	7	K-series	18.11	21.77	23.02	2.94	0.249	0.874	1.000	1.000
Mn	25	K-series	9.75	11.72	3.16	0.33	0.038	2.926	1.000	1.041
Ca	20	K-series	7.90	9.49	3.51	0.27	0.028	3.301	1.000	1.036
		Total:	83.21	100.00	100.00					

Figure S7. EDX analysis report for rGO-MnPc-PDA (**6**).

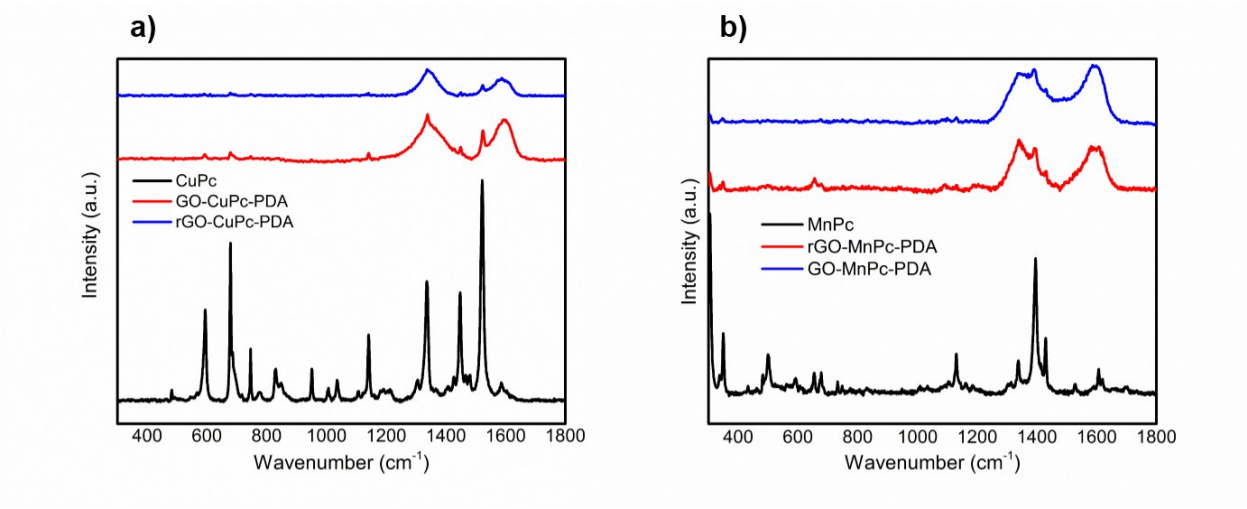


Figure S8. Raman spectra of, a) materials **1**, **3,** and **5**, and b) materials **2**, **4,** and **6**.

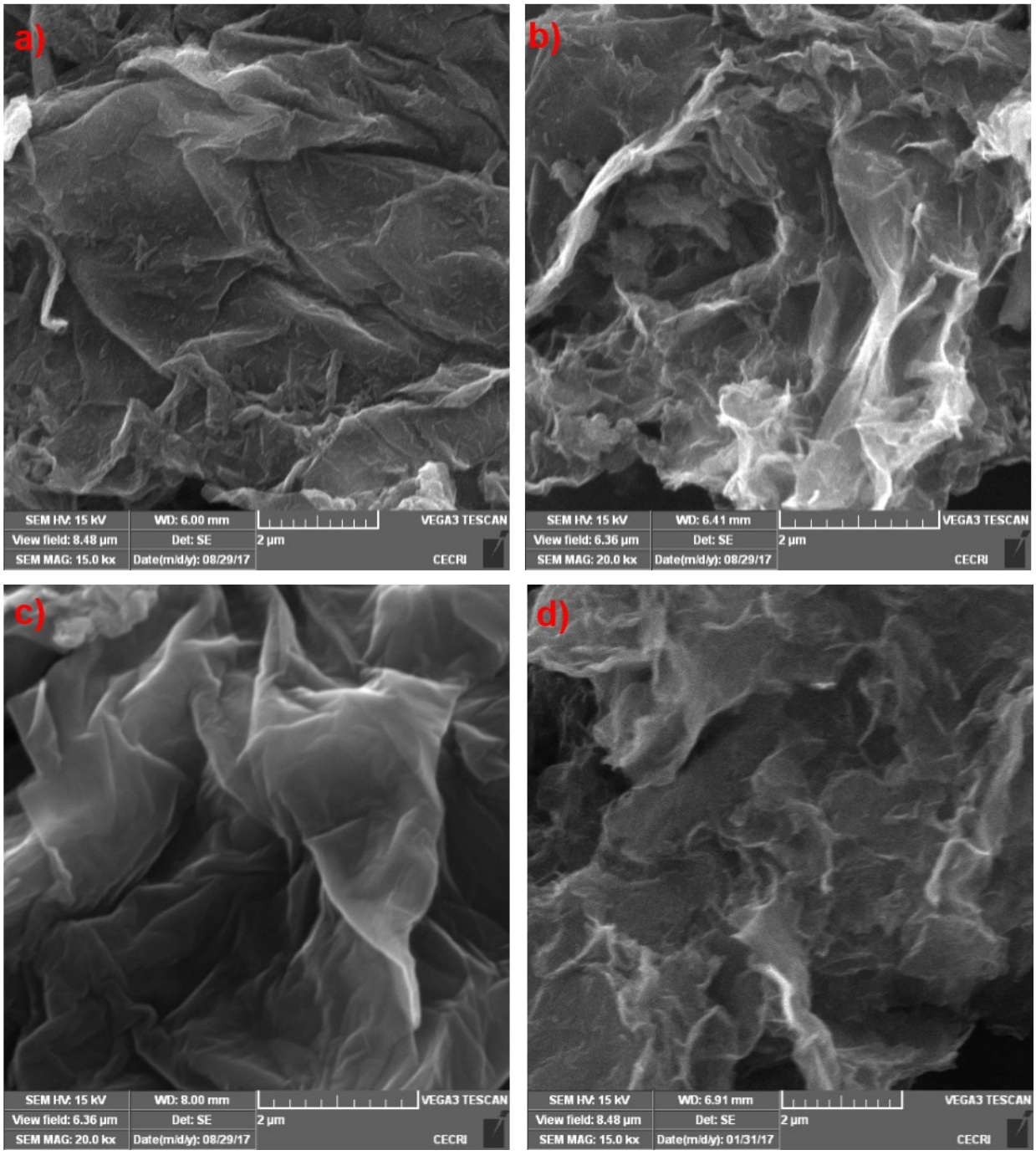


Figure S9. SEM images: a) GO-CuPc-PDA (**3**), b) rGO-CuPc-PDA (**5**), c) GO-MnPc-PDA (**4**), and d) rGO-MnPc-PDA (**6**).

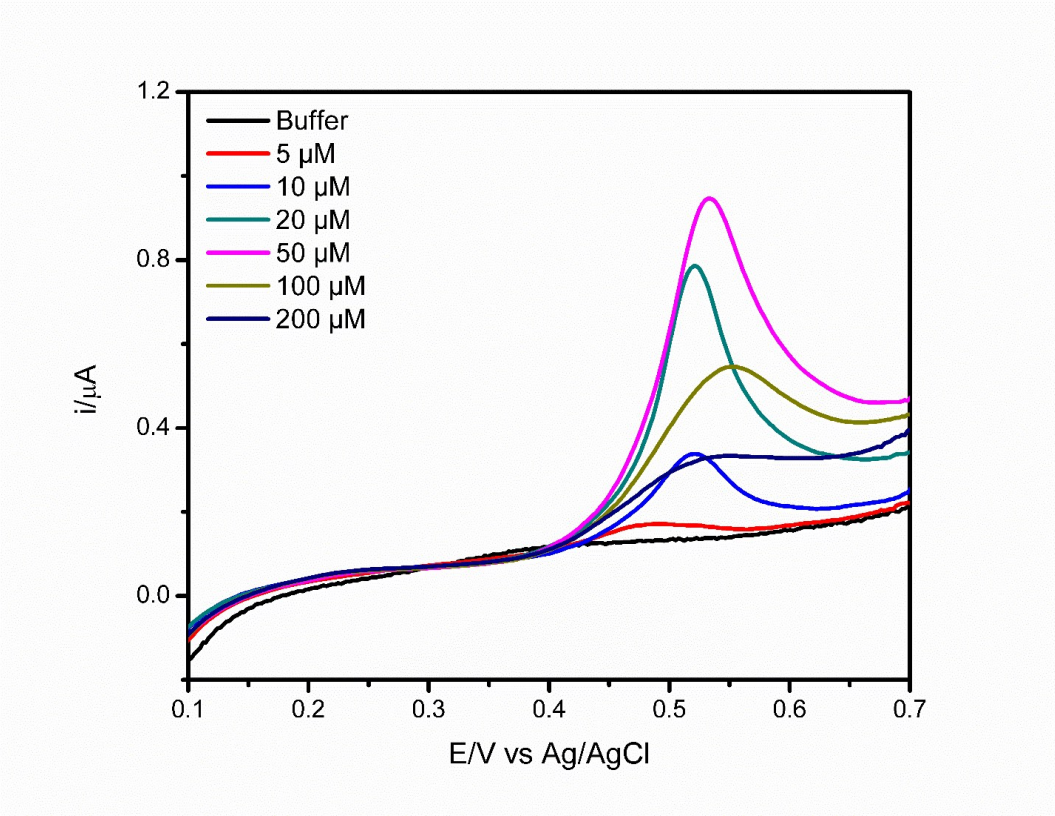


Figure S10. Linear sweep voltammogram of CuPc coated electrode (**1′**) towards GSH show the electrode fouling behavior of electrode **1′** at the concentration GSH 200 μM.

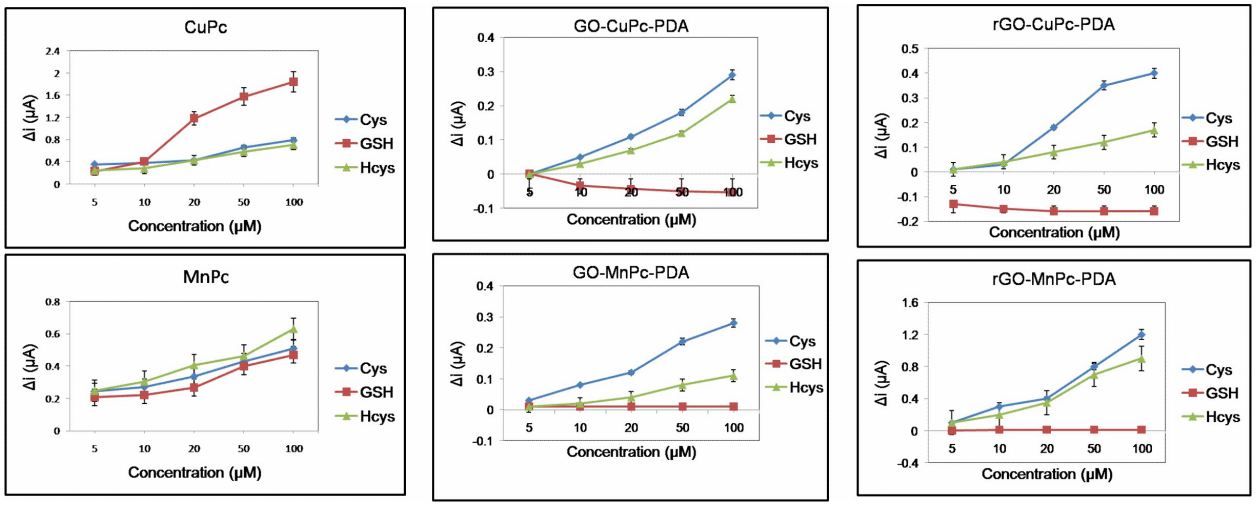


Figure S11. Current response of the modified electrodes **1′-6′** towards Cys, GSH and Hcys (50 μM).

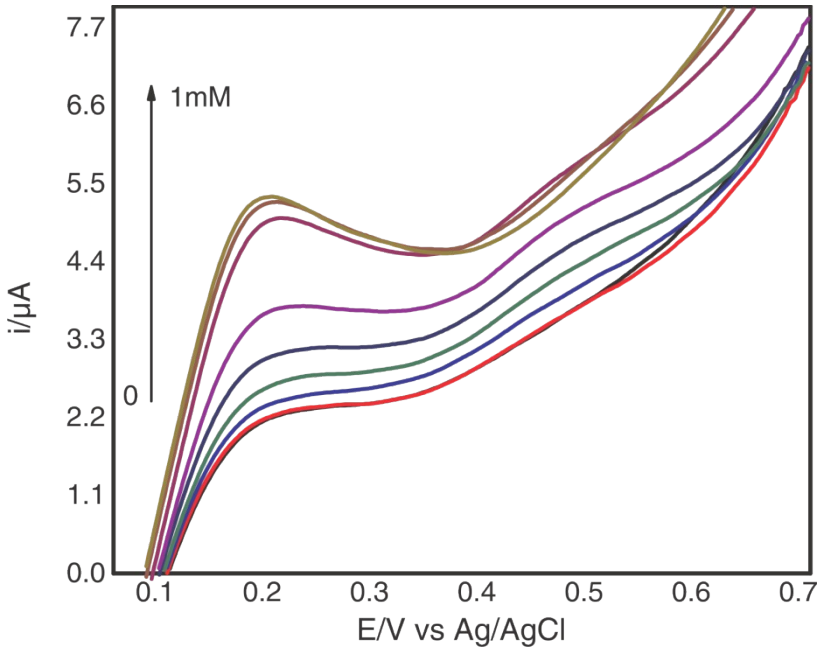


Figure S12. Linear sweep voltammogram of rGO-MnPc-PDA coated electrode (**3′**) towards Cys at various concentration (0, 5 μM, 10 μM, 50 μM, 100 μM, 200 μM, 500 μM and 1 mM).

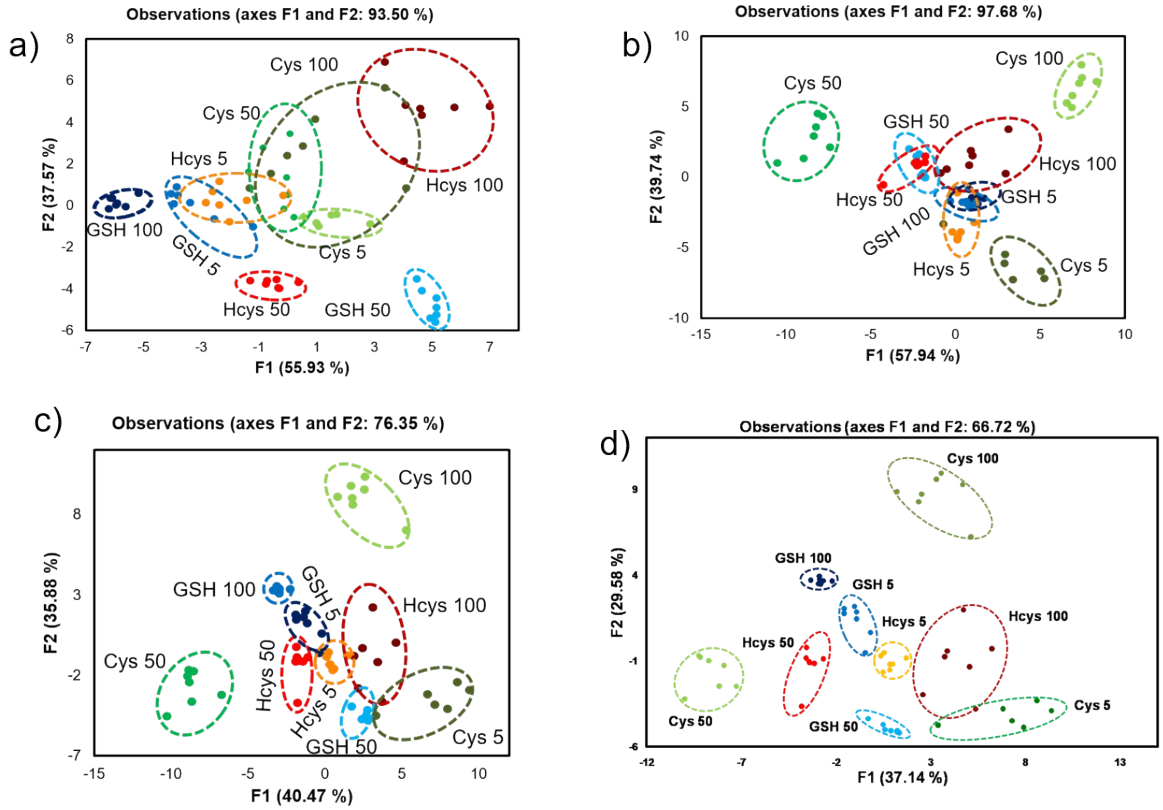


Figure S13. a) LDA score plot was generated using the difference in current data obtained using the CuPc (**1'**), GO-CuPc-PDA (**3'**) and rGO-CuPc-PDA (**5'**). b) LDA score plot was generated using the difference in current data obtained using the MnPc (**2'**), GO-MnPc-PDA (**4'**) and rGO-MnPc-PDA (**6'**). c) LDA score plot was generated using the difference in current data obtained using the GO-CuPc-PDA (**3'**) and GO-MnPc-PDA (**4'**), rGO-CuPc-PDA (**5'**) and rGO-MnPc-PDA (**6'**). d) LDA score plot was generated using the difference in current data obtained using all the array electrodes (see also figure 6b). Note: Thiol concentrations 5, 50, and 100 refers thiol concentrations, the current responses were collected at 0.45 V.

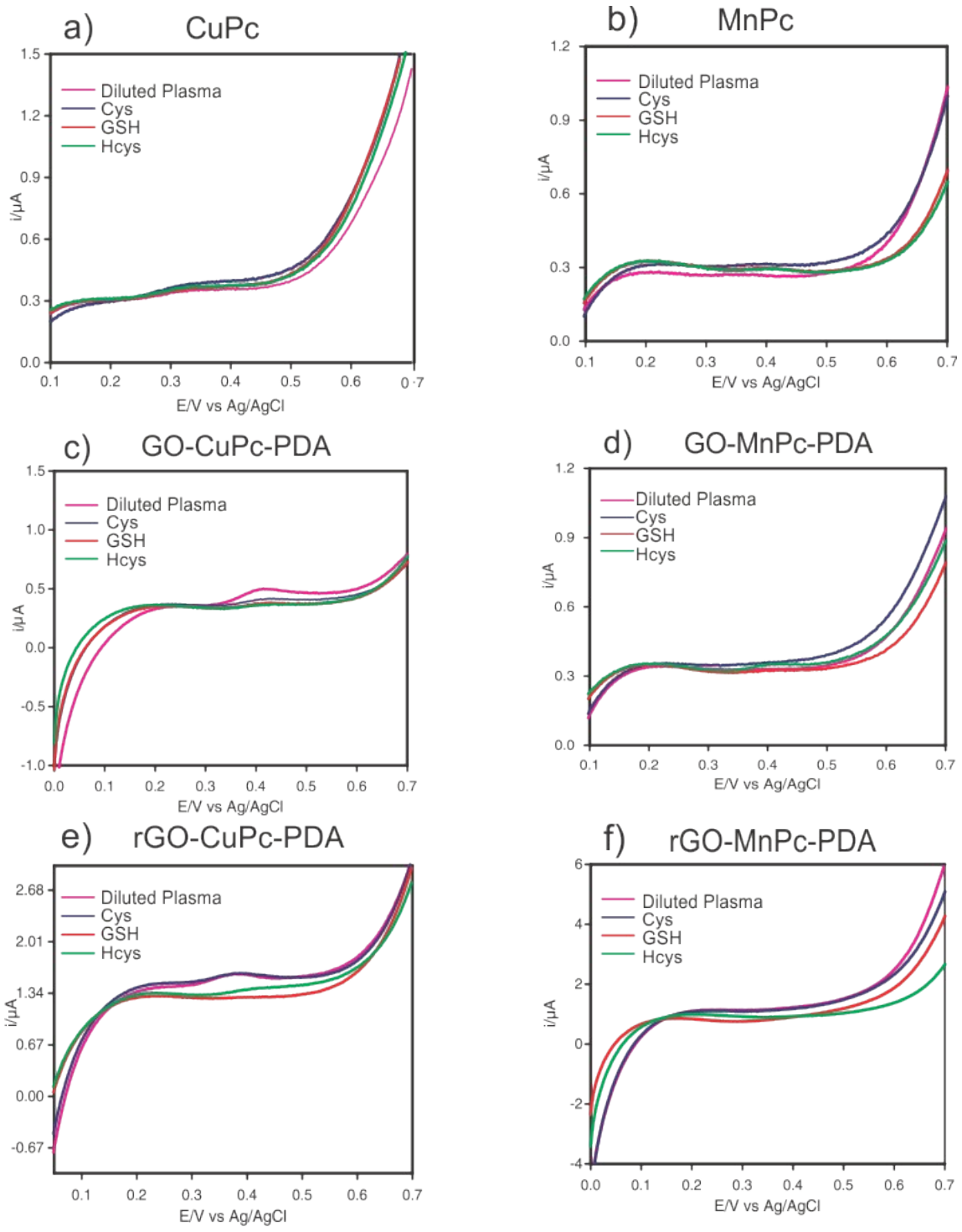


Figure S14. Linear sweep voltammograms a-f show the response of respective electrode **1′-6′** towards the thiols spiked in the diluted goat plasma; Conditions: [RSH]-50 μM, scan rate- 20mV/s.

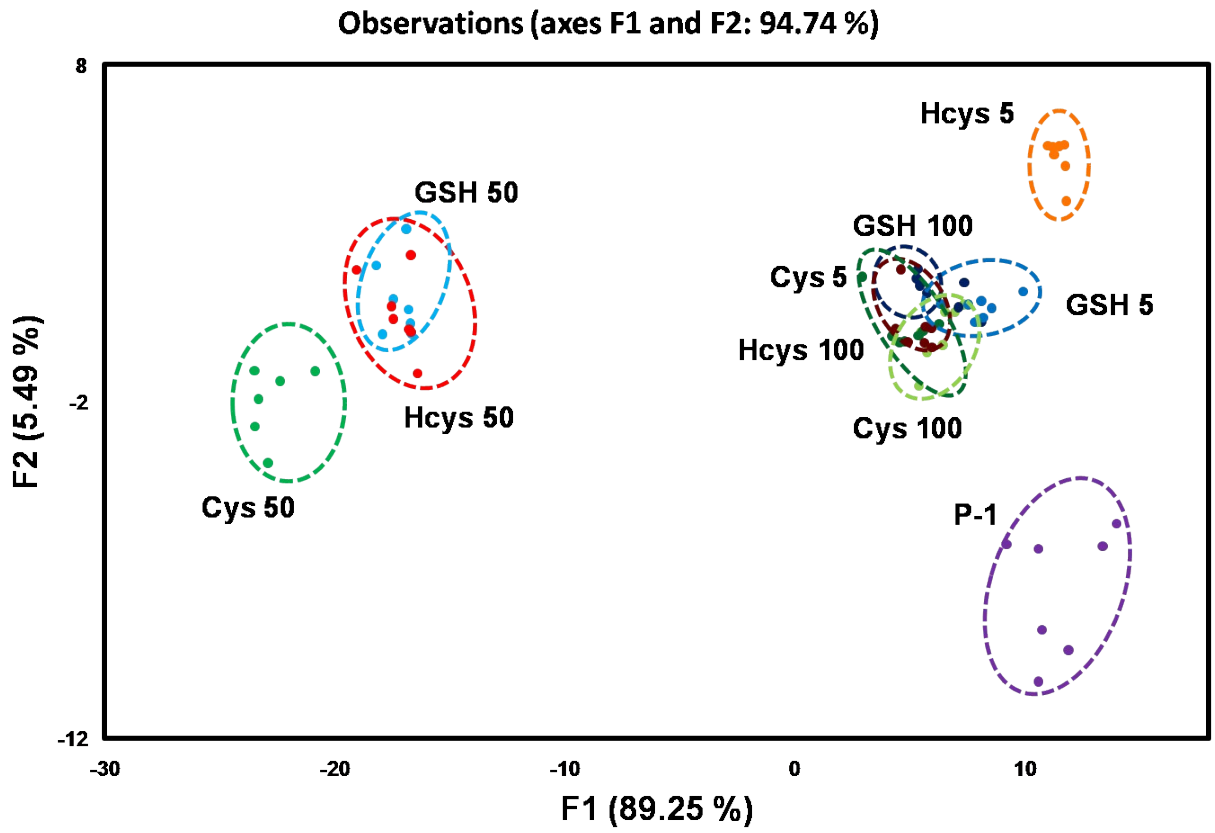


Figure S15. LDA score plot showing the poor discriminatory ability of electrode array (**1′-6′**) towards thiols spiked in diluted plasma sample that doesn't contain added redox indicator (AA, DA, and UA).

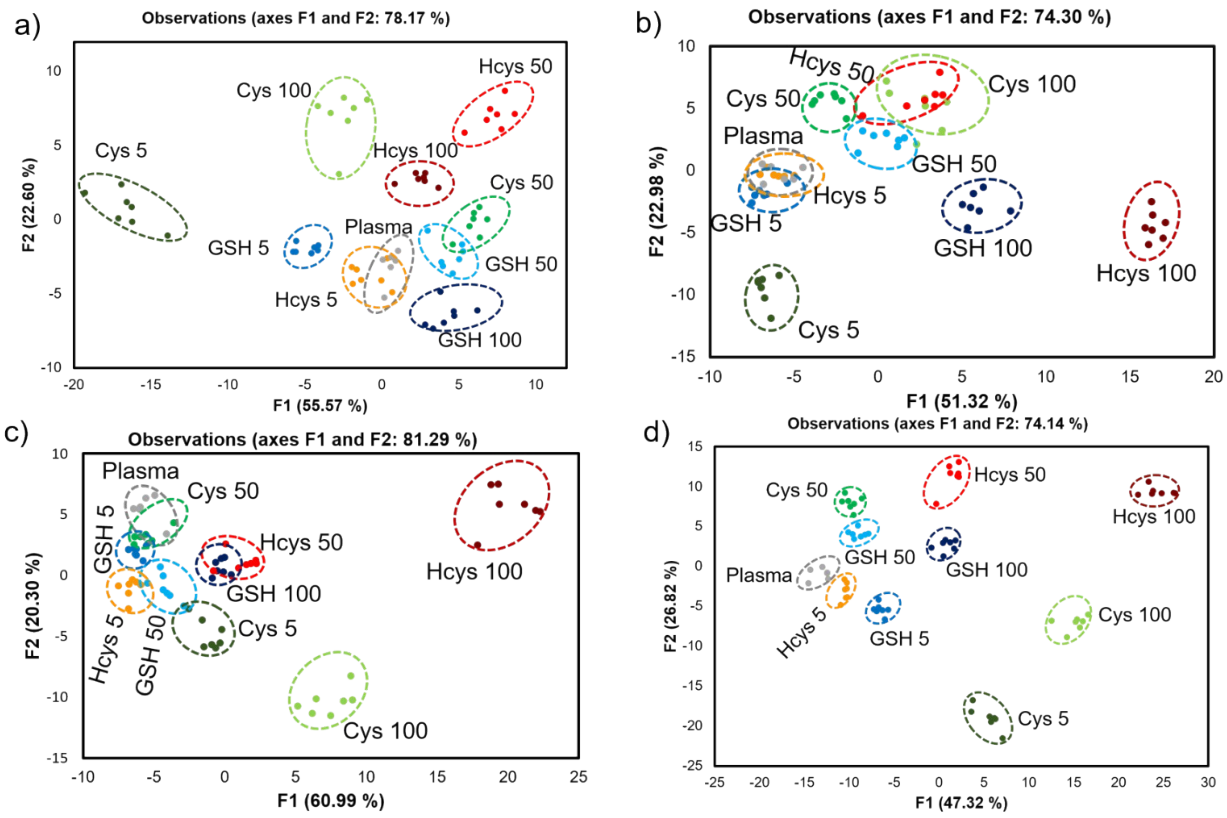


Figure S16. a) LDA score plot was generated using the difference in current data obtained using the CuPc (**1'**), GO-CuPc-PDA (**3'**) and rGO-CuPc-PDA (**5'**). b) LDA score plot was generated using the difference in current data obtained using the MnPc (**2'**), GO-MnPc-PDA (**4'**) and rGO-MnPc-PDA (**6'**). c) LDA score plot was generated using the difference in current data obtained using the GO-CuPc-PDA (**3'**) and GO-MnPc-PDA (**4'**), rGO-CuPc-PDA (**5'**) and rGO-MnPc-PDA (**6'**). d) LDA score plot was generated using the difference in current data obtained using all the array electrodes (see also figure 10). Note: Thiol concentrations 5, 50, and 100 refers thiol concentrations, the current responses were collected at 0.38, 0.48 and 0.58 V.

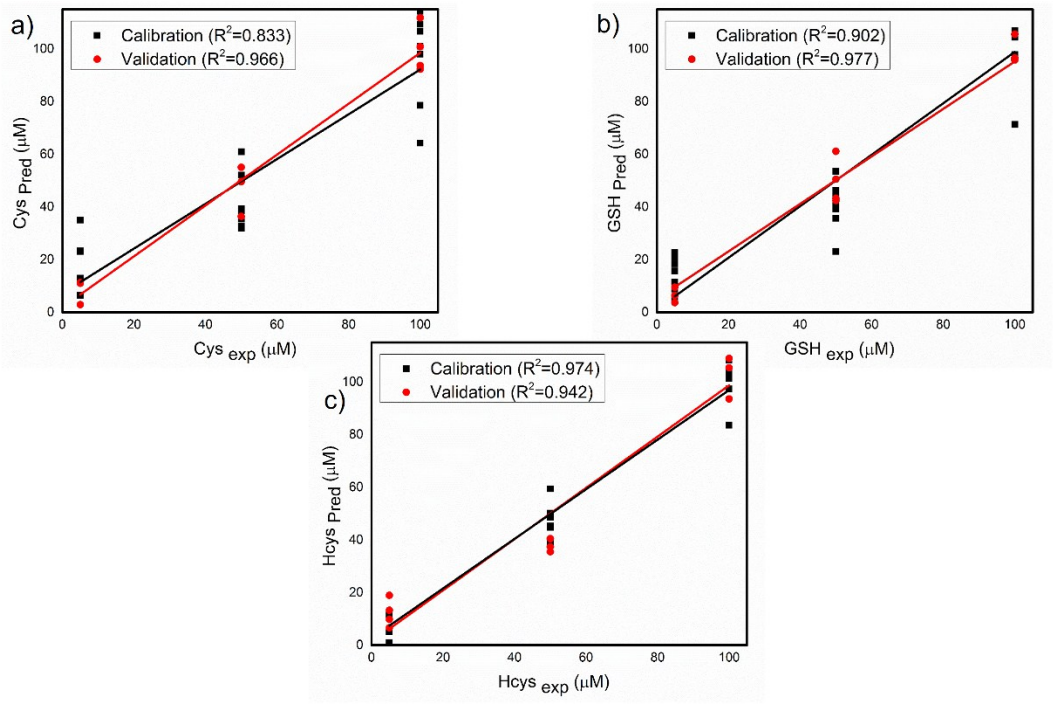


Figure S17. Predicted *vs* experimental concentration plots generated using PLS-R model for a) Cys, b) GSH, and c) Hcys. Calibration samples (Black dots) and its regression line (Black line), validation samples (Red dots) and its regression line (Red line).

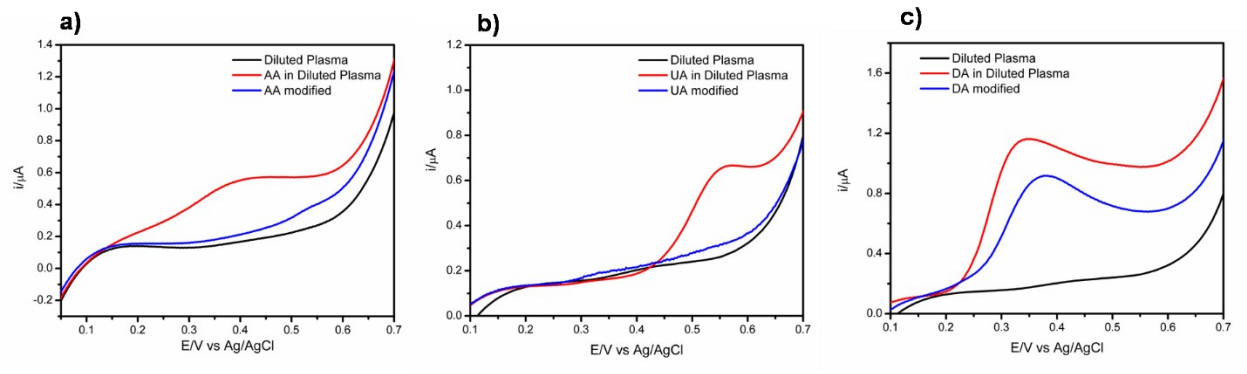


Figure S18. a) LSV of electrode **1'** in plasma spiked PBS contains AA (line red) and without AA (black line), and AA modified electrode **1'** in plasma spiked PBS (line blue), b) LSV of electrode **1'** in plasma spiked PBS contains UA (line red) and without UA (black line), and UA modified electrode **1'** in plasma spiked PBS (line blue), c) LSV of electrode **1'** in plasma spiked PBS contains DA (line red) and without DA (black line), and DA modified electrode **1'** in plasma spiked PBS (line blue).

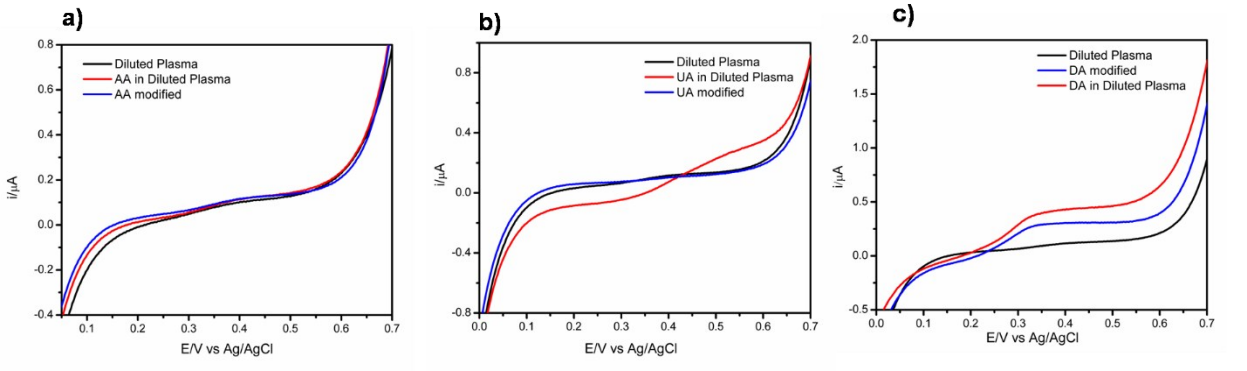


Figure S19. a) LSV of electrode **2'** in plasma spiked PBS contains AA (line red) and without AA (black line), and AA modified electrode **2'** in plasma spiked PBS (line blue), b) LSV of electrode **2'** in plasma spiked PBS contains UA (line red) and without UA (black line), and UA modified electrode **2'** in plasma spiked PBS (line blue), c) LSV of electrode **2'** in plasma spiked PBS contains DA (line red) and without DA (black line), and DA modified electrode **2'** in plasma spiked PBS (line blue)

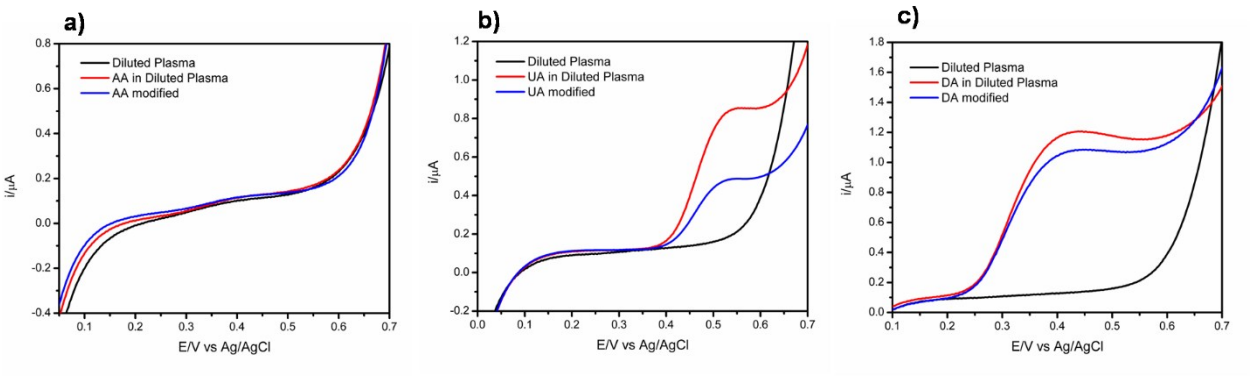


Figure S20. a) LSV of electrode **4'** in plasma spiked PBS contains AA (line red) and without AA (black line), and AA modified electrode **4'** in plasma spiked PBS (line blue), b) LSV of electrode **4'** in plasma spiked PBS contains UA (line red) and without UA (black line), and UA modified electrode **4'** in plasma spiked PBS (line blue), c) LSV of electrode **4'** in plasma spiked PBS contains DA (line red) and without DA (black line), and DA modified electrode **4'** in plasma spiked PBS (line blue)

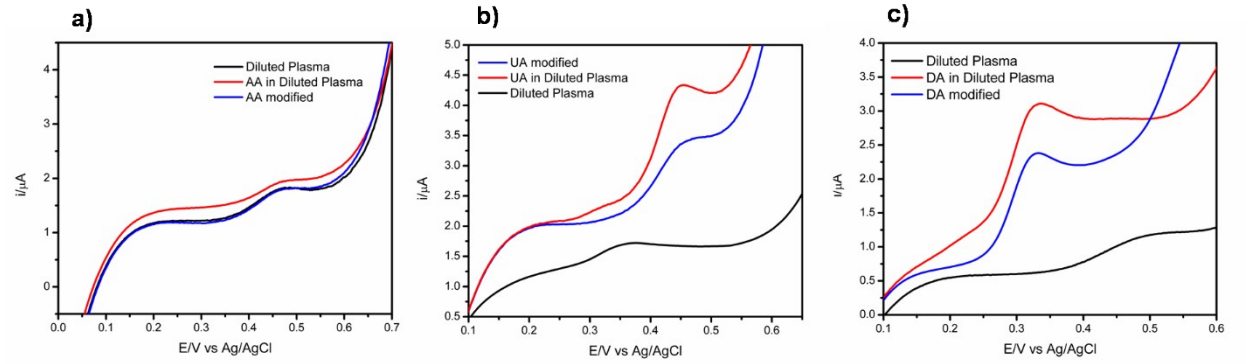


Figure S21. a) LSV of electrode **5'** in plasma spiked PBS contains AA (line red) and without AA (black line), and AA modified electrode **5'** in plasma spiked PBS (line blue), b) LSV of electrode **5'** in plasma spiked PBS contains UA (line red) and without UA (black line), and UA modified electrode **5'** in plasma spiked PBS (line blue), c) LSV of electrode **5'** in plasma spiked PBS contains DA (line red) and without DA (black line), and DA modified electrode **5'** in plasma spiked PBS (line blue)

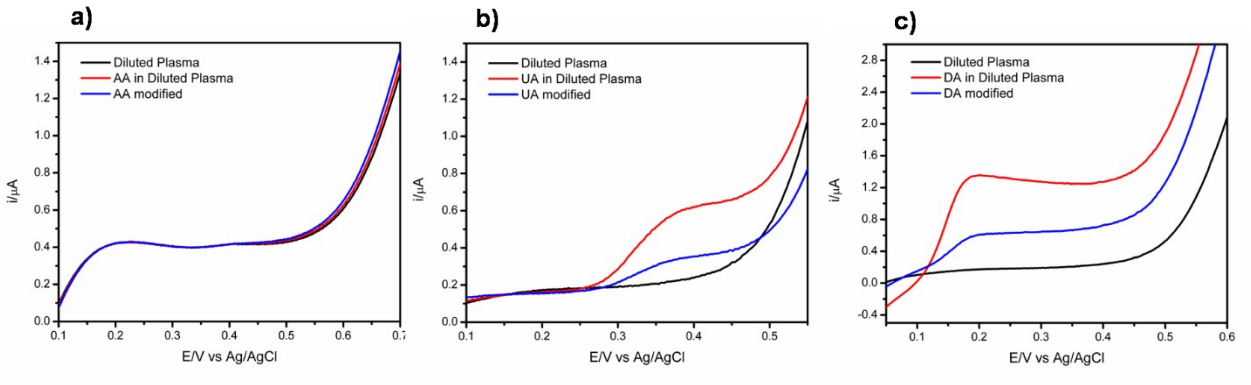


Figure S22. a) LSV of electrode **6'** in plasma spiked PBS contains AA (line red) and without AA (black line), and AA modified electrode **6'** in plasma spiked PBS (line blue), b) LSV of electrode **6'** in plasma spiked PBS contains UA (line red) and without UA (black line), and UA modified electrode **6'** in plasma spiked PBS (line blue), c) LSV of electrode **6'** in plasma spiked PBS contains DA (line red) and without DA (black line), and DA modified electrode **6'** in plasma spiked PBS (line blue).

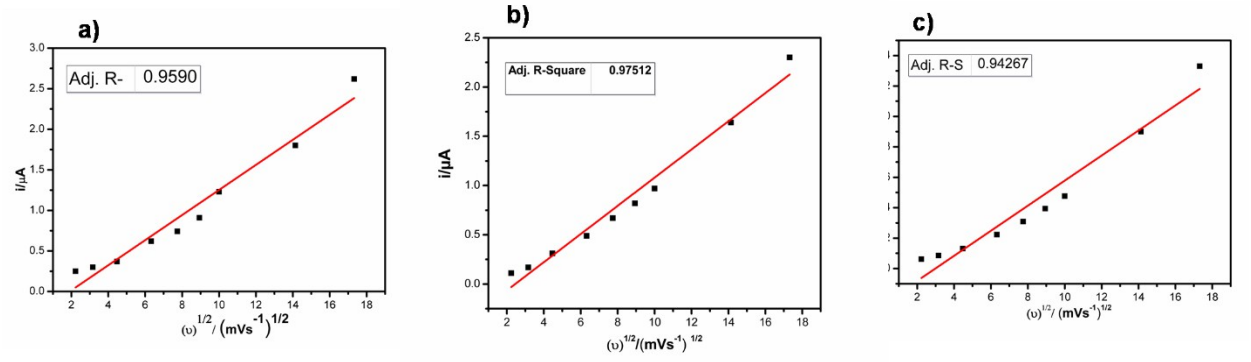


Figure S23. Shows the plot of AA oxidation current as a function of square root of scan rate for the electrodes a) **1'**, b) **3'** and c) **5'.**

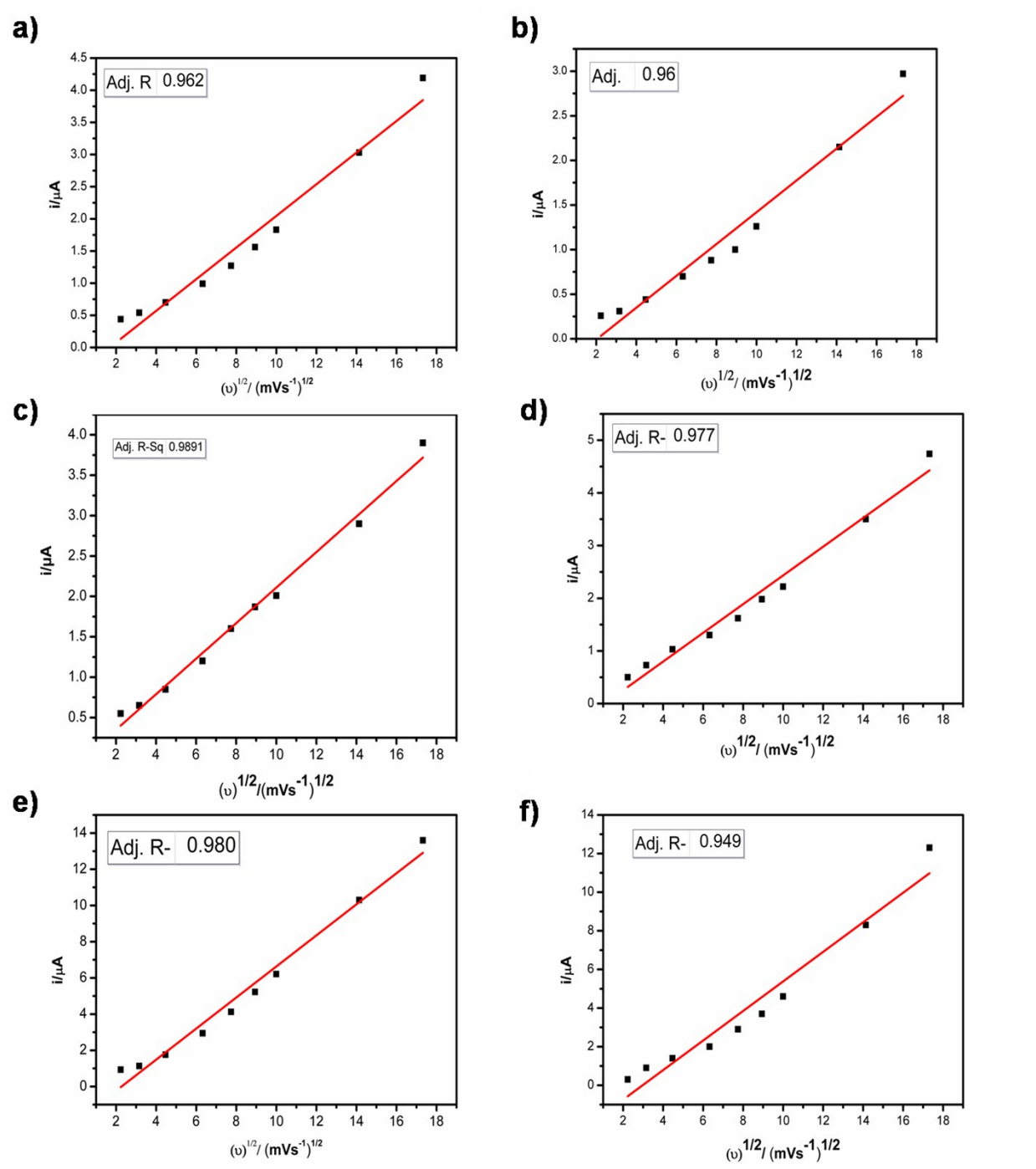


Figure S24. Shows the plot of DA oxidation current as a function of square root of scan rate for the electrodes a) **1'**, b) **2'**, c) **3',** d) **4'**, e) **5'**, f) **6'**

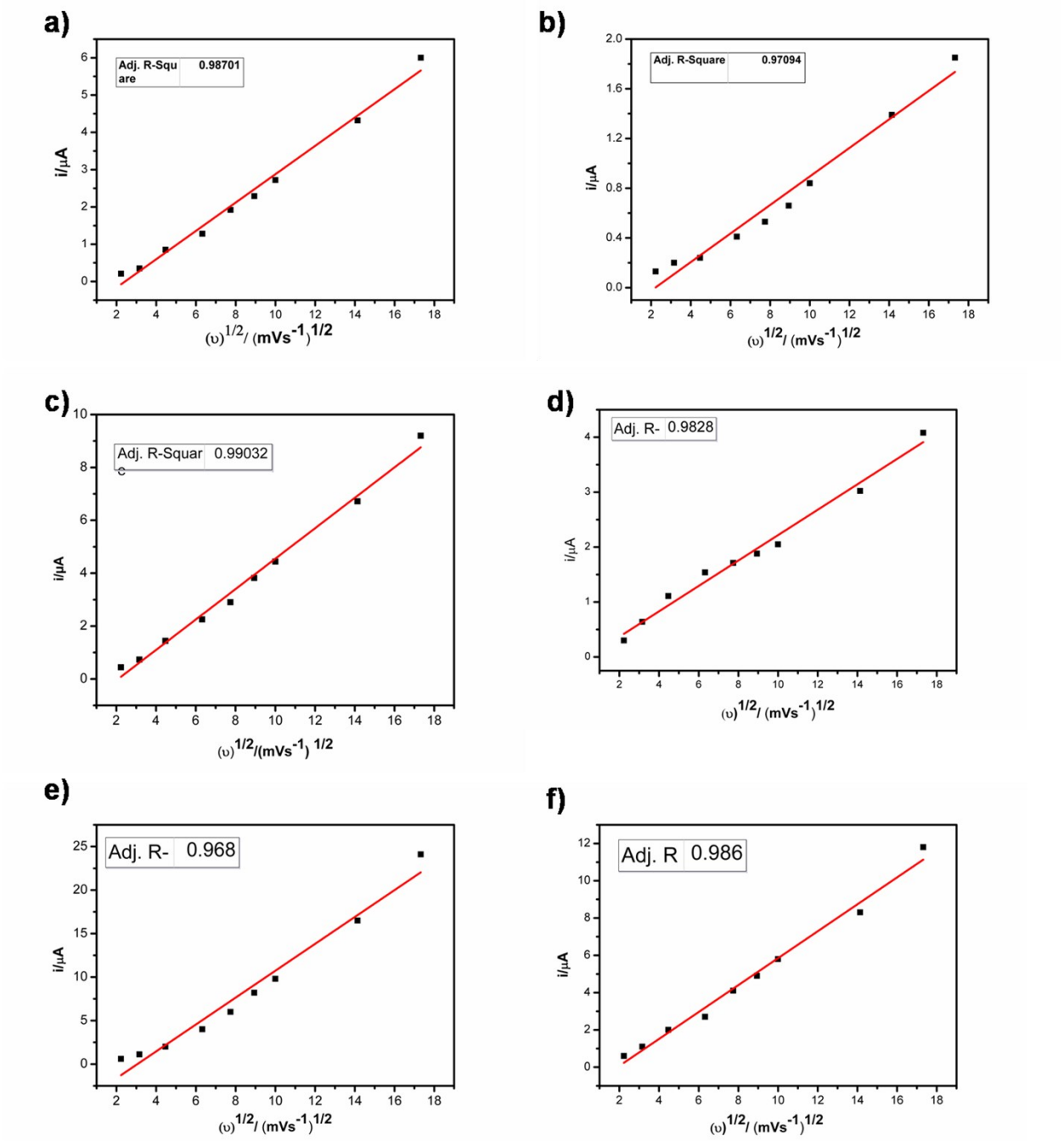


Figure S25. Shows the plot of DA oxidation current as a function of square root of scan rate for the electrodes a) **1'**, b) **2'**, c) **3',** d) **4'**, e) **5'**, f) **6'**

4. Tables

Table S1. Raw data used for generating LDA score plot shown in figure 10.

Electrodes	CuPc			MnPc			GO-CuPc-PDA			rGO-CuPc-PDA			GO-MnPc-PDA			rGO-MnPc-PDA		
Repilcates	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV
Plasma-1	6.12E-07	6.53E-07	4.61E-07	4.36E-07	8.37E-07	9.61E-07	6.36E-07	7.57E-07	8.73E-07	1.01E-06	1.13E-06	9.01E-07	9.71E-07	1.07E-06	1.72E-06	1.22E-06	1.48E-06	1.16E-06
Plasma-1	8.12E-07	7.85E-07	5.95E-07	3.9E-07	7.52E-07	1.02E-06	9.83E-07	1.18E-06	1.18E-06	1.4E-06	1.38E-06	1.13E-06	1.35E-06	1.41E-06	1.91E-06	1.72E-06	1.99E-06	1.54E-06
Plasma-1	9.04E-07	7.99E-07	6.34E-07	4.5E-07	8.38E-07	1.08E-06	1.03E-06	1.25E-06	1.2E-06	1.46E-06	1.36E-06	1.12E-06	1.51E-06	1.62E-06	2.19E-06	1.8E-06	2.09E-06	1.58E-06
Plasma-1	9.24E-07	7.94E-07	6.46E-07	3.97E-07	7.56E-07	9.78E-07	9.68E-07	1.2E-06	1.16E-06	1.45E-06	1.38E-06	1.15E-06	1.37E-06	1.48E-06	1.93E-06	1.88E-06	2.17E-06	1.63E-06
Plasma-1	9.41E-07	7.4E-07	5.02E-07	4.06E-07	7.84E-07	1.02E-06	9.99E-07	1.29E-06	1.26E-06	1.44E-06	1.43E-06	1.24E-06	1.34E-06	1.5E-06	2E-06	1.88E-06	2.21E-06	1.65E-06
Plasma-1	1.36E-06	1.44E-06	1.74E-06	6.65E-07	1.03E-06	1.29E-06	1.32E-06	1.68E-06	1.74E-06	2.25E-06	2.13E-06	2.06E-06	1.61E-06	1.77E-06	2.25E-06	3.25E-06	3.51E-06	3.61E-06
Plasma-1	8.57E-07	6.92E-07	5.08E-07	4E-07	7.98E-07	1.02E-06	9.52E-07	1.28E-06	1.22E-06	1.56E-06	1.45E-06	1.29E-06	1.38E-06	1.59E-06	2.16E-06	1.8E-06	1.79E-06	1.3E-06
Cys-50	3.91E-07	3.02E-07	2.61E-07	9.64E-08	1.9E-07	1.99E-07	4.86E-07	3.96E-07	-1.5E-08	2.04E-07	-6.4E-08	-3.6E-08	3.1E-07	1E-07	-1.8E-07	1.56E-07	-5.2E-08	-4.9E-07
Cys-50	3.78E-07	2.87E-07	1.99E-07	2.31E-07	3.26E-07	2.96E-07	8.25E-07	6.8E-07	3.01E-07	2.67E-07	3.06E-10	3.39E-08	2.93E-07	1.69E-07	9.09E-08	2.24E-07	1.59E-08	-5.8E-07
Cys-50	3.73E-07	3.16E-07	3.01E-07	1.08E-07	1.91E-07	1.79E-07	4.86E-07	3.96E-07	-1.5E-08	2.17E-07	-4.9E-08	-1.1E-08	2.15E-07	1.33E-07	1.02E-07	3.08E-07	1.11E-07	-5.8E-07
Cys-50	3.66E-07	2.98E-07	2.74E-07	8.76E-08	1.83E-07	1.65E-07	4.76E-07	4.17E-07	-4.5E-08	3.4E-07	-1E-08	2.93E-08	2.35E-07	1.34E-07	3.42E-08	3.28E-07	1.21E-07	-6E-07
Cys-50	3.29E-07	2.89E-07	2.41E-07	5.43E-08	1.14E-07	8.54E-08	4.54E-07	4.19E-07	-3E-08	1.15E-07	-1.3E-07	-7.1E-08	2.84E-07	1.39E-07	-4.8E-08	3.23E-07	7.08E-08	-6.9E-07
Cys-50	1.64E-06	1.75E-06	2.04E-06	5.17E-07	8.25E-07	9.95E-07	1.53E-06	1.79E-06	1.99E-06	3.17E-06	2.71E-06	2.56E-06	1.72E-06	1.66E-06	2.19E-06	2.23E-06	2.49E-06	2.63E-06
Cys-50	2.73E-07	2.87E-07	3.25E-07	5.25E-08	1.43E-07	1.68E-07	5.26E-07	5.35E-07	1.08E-07	1.97E-07	-6.2E-08	-6.1E-10	3.03E-07	1.79E-07	3.2E-08	3.13E-07	3.31E-07	-5E-07

GSH-50	3.57E-07	3.34E-07	3.4E-07	4.91E-08	1.19E-07	2.56E-07	5.84E-07	7.06E-07	5.15E-07	1.25E-06	6.35E-07	5.15E-07	7.88E-07	6.21E-07	3.58E-07	8.38E-07	3.81E-07	2.21E-07
GSH-50	4.39E-07	4.48E-07	4.48E-07	7.6E-08	1.66E-07	3.12E-07	4.52E-07	6.57E-07	4.24E-07	7.41E-07	1.94E-07	1.73E-07	7.44E-07	6.56E-07	3.77E-07	8.02E-07	2.89E-07	9.64E-08
GSH-50	3.75E-07	4.04E-07	4.27E-07	5.34E-08	1.21E-07	2.55E-07	3.2E-07	5.96E-07	2.89E-07	6.56E-07	9.22E-08	8.48E-08	6.86E-07	6.45E-07	3.29E-07	8.53E-07	4.4E-07	1.96E-07
GSH-50	3.01E-07	3.5E-07	4.09E-07	5E-08	1.15E-07	2.63E-07	2.3E-07	6E-07	2.94E-07	6.45E-07	1.52E-09	-9.5E-09	7.13E-07	7.03E-07	2.86E-07	7.94E-07	4.55E-07	1.83E-07
GSH-50	3.88E-07	4.01E-07	4.29E-07	5.71E-08	1.41E-07	3.11E-07	3.35E-07	7.11E-07	4.14E-07	5.77E-07	-9.1E-08	-7.4E-08	6.65E-07	7.06E-07	4.97E-07	8.15E-07	4.62E-07	1.71E-07
GSH-50	1.74E-06	1.79E-06	2.06E-06	4.7E-07	8.15E-07	1.22E-06	1.48E-06	1.97E-06	1.97E-06	3.54E-06	3.11E-06	2.87E-06	2.04E-06	2.19E-06	2.67E-06	2.74E-06	2.87E-06	2.97E-06
GSH-50	3.23E-07	3.32E-07	3.36E-07	4.64E-08	9.4E-08	2.13E-07	3.32E-07	8.53E-07	4.95E-07	9.35E-07	1.48E-07	1.21E-07	6.35E-07	7.33E-07	3.88E-07	7.18E-07	3.37E-07	5.68E-08
Hcys-50	7.5E-07	5.29E-07	5.57E-07	3.31E-07	3.16E-07	2.61E-07	4.93E-07	3.16E-07	1.94E-07	8.27E-07	4.86E-07	4.63E-07	3.38E-07	2.4E-07	1.26E-07	2.84E-07	5.89E-08	-1.4E-07
Hcys-50	9.31E-07	6.7E-07	7.54E-07	4.01E-07	3.73E-07	2.33E-07	4.83E-07	3.23E-07	1.84E-07	1E-06	6.29E-07	6.56E-07	3.02E-07	2.97E-07	1.66E-07	4.28E-07	1.61E-07	-9.6E-08
Hcys-50	7.25E-07	5.31E-07	6.11E-07	4.14E-07	4.04E-07	2.61E-07	7.18E-07	4.78E-07	3.2E-07	8.91E-07	5.18E-07	5.73E-07	2.76E-07	3.56E-07	1.75E-07	3.67E-07	1.1E-07	-2E-07
Hcys-50	8.04E-07	5.98E-07	6.56E-07	4.08E-07	4.17E-07	2.64E-07	3.89E-07	2.8E-07	1.61E-07	9.08E-07	4.82E-07	5.44E-07	1.63E-07	3.69E-07	2.95E-07	2.55E-07	3.66E-09	-3.4E-07
Hcys-50	8.45E-07	6.11E-07	6.88E-07	4.1E-07	4.35E-07	2.62E-07	3.23E-07	2.45E-07	1.48E-07	8.5E-07	3.67E-07	4.21E-07	3.02E-07	2.97E-07	1.66E-07	4.05E-07	2.4E-07	-1.3E-07
Hcys-50	1.71E-06	1.58E-06	1.93E-06	7.14E-07	9.66E-07	1.34E-06	2.14E-06	2.08E-06	1.95E-06	3.49E-06	2.92E-06	2.85E-06	1.46E-06	1.67E-06	1.84E-06	2.3E-06	2.41E-06	2.62E-06
Hcys-50	8.58E-07	6.11E-07	7.49E-07	3.53E-07	4E-07	2.07E-07	1E-06	7.89E-07	4.93E-07	5.86E-07	2.17E-07	3.57E-07	-5E-08	3.39E-07	1.53E-07	4.05E-07	1.13E-07	-3.4E-07
Cys 5	-2.1E-08	-2.1E-07	-1.6E-07	1.97E-07	1.85E-07	2.79E-07	2.62E-07	5.18E-07	7.23E-07	2.48E-07	4.05E-07	1.75E-07	4.27E-07	4.1E-07	3.73E-07	7.74E-07	5.7E-07	3.75E-07
Cys 5	-1.1E-08	-2.3E-07	-1.7E-07	2.11E-07	1.57E-07	2.67E-07	2.34E-07	4.4E-07	5.58E-07	4.9E-07	5.9E-07	2.58E-07	1.41E-07	1.7E-07	1.54E-07	7.46E-07	5.58E-07	2.99E-07
Cys 5	-4.3E-08	-3.2E-07	-2.4E-07	2.3E-07	1.7E-07	3.26E-07	2.87E-07	5.07E-07	6.14E-07	2.7E-07	2.98E-07	-8.5E-08	2.3E-07	3.29E-07	2.99E-07	1.12E-06	7.74E-07	5.13E-07

Cys 5	-2.6E-08	-2E-07	-9.2E-08	1.53E-07	1.62E-08	1.48E-07	2.37E-07	4.62E-07	5.71E-07	3.33E-07	1.83E-07	-1.8E-07	2.18E-07	1.56E-07	1.81E-07	7.55E-07	4.72E-07	1.8E-07
Cys 5	-2.2E-08	-8.1E-08	5.8E-08	1.93E-07	6.01E-08	2.21E-07	1.79E-07	3.32E-07	3.51E-07	3.43E-07	1.48E-07	-2.3E-07	2.32E-07	2.08E-07	2.8E-07	9.26E-07	5.39E-07	1.95E-07
Cys 5	-5.5E-08	-2E-07	-5E-08	1.71E-07	3.27E-08	1.75E-07	2.34E-07	4.4E-07	5.58E-07	2.63E-07	4.7E-08	-3.3E-07	2.86E-07	2.28E-07	3.49E-07	7.52E-07	4.14E-07	8.54E-08
Cys 5	-9.2E-08	-2.9E-07	-1.2E-07	1.49E-07	2.44E-08	2.12E-07	1.15E-07	2.78E-07	3.08E-07	2.94E-07	1.28E-08	-4E-07	2.44E-07	2.68E-07	4.48E-07	9.14E-07	4.9E-07	1.01E-07
GSH 5	7.9E-08	-3.3E-08	-9.4E-08	1.87E-07	2.67E-07	3.69E-07	2.35E-07	4.61E-07	3.93E-07	9.07E-07	7.08E-07	5.8E-07	3.97E-07	1.78E-07	1.56E-07	4.28E-07	2.6E-07	1.81E-07
GSH 5	2.28E-07	1.32E-07	1.08E-07	2.26E-07	3.4E-07	5.22E-07	2.12E-07	4.38E-07	4.04E-07	7.91E-07	6.52E-07	5.34E-07	4.18E-07	1.68E-07	1.52E-07	6.77E-07	4.16E-07	3.05E-07
GSH 5	1.94E-07	9.64E-08	8.18E-08	1.69E-07	2.48E-07	3.45E-07	1.62E-07	4.11E-07	3.98E-07	7.03E-07	5.64E-07	4.74E-07	4.43E-07	1.7E-07	1.63E-07	6.61E-07	3.64E-07	2.32E-07
GSH 5	2.38E-07	1.53E-07	1.73E-07	1.79E-07	2.56E-07	2.8E-07	1.31E-07	3.89E-07	3.79E-07	7.63E-07	5.94E-07	5.04E-07	4.04E-07	1.32E-07	1.32E-07	8.18E-07	4.61E-07	3.13E-07
GSH 5	1.45E-07	1.04E-07	1.89E-07	1.56E-07	2.37E-07	3.04E-07	1.1E-07	3.68E-07	3.65E-07	6.42E-07	5.24E-07	4.5E-07	2.55E-07	5.07E-08	1.1E-07	8.31E-07	4.41E-07	2.78E-07
GSH 5	8.55E-08	5.25E-08	1.47E-07	1.51E-07	2.29E-07	2.44E-07	6.59E-08	3.14E-07	2.9E-07	7.78E-07	5.8E-07	4.92E-07	3.04E-07	6.38E-08	1.15E-07	8.85E-07	4.83E-07	3.08E-07
GSH 5	3.6E-08	5.58E-08	2.36E-07	1.61E-07	2.58E-07	3.23E-07	-3.9E-08	1.14E-07	1.3E-07	7.64E-07	5.19E-07	4.39E-07	3.41E-07	1.58E-07	2.93E-07	9.77E-07	5.1E-07	3.16E-07
Hcys 5	1.9E-07	2.01E-07	2.05E-07	2.78E-08	4.09E-08	9.19E-08	1.35E-07	2.28E-07	1.69E-07	6.77E-07	5.48E-07	4.52E-07	5.21E-07	3.79E-07	4E-07	6.02E-07	3.54E-07	3.16E-07
Hcys 5	3.55E-07	3.14E-07	2.53E-07	1.19E-07	1.83E-07	2.84E-07	1.24E-07	2.38E-07	1.83E-07	9.83E-07	7.43E-07	6.12E-07	5.47E-07	4.1E-07	4.71E-07	7.7E-07	4.53E-07	4.16E-07
Hcys 5	1.9E-07	2.01E-07	2.05E-07	6.96E-08	1.24E-07	2.27E-07	1.05E-07	2.41E-07	1.91E-07	1.01E-06	7.64E-07	6.39E-07	4.92E-07	3.47E-07	3.86E-07	6.25E-07	4.02E-07	3.72E-07
Hcys 5	2.77E-07	2.75E-07	2.1E-07	1.21E-07	2.04E-07	3.85E-07	1.15E-07	3.16E-07	2.53E-07	1.07E-06	7.9E-07	6.59E-07	6.32E-07	4.46E-07	4.99E-07	4.82E-07	3.14E-07	2.81E-07
Hcys 5	2.67E-07	3.09E-07	2.53E-07	8.82E-08	1.66E-07	3.18E-07	1.3E-07	3.07E-07	2.18E-07	1.08E-06	8.05E-07	6.8E-07	4.69E-07	2.97E-07	2.78E-07	5.93E-07	3.2E-07	2.61E-07
Hcys 5	6.04E-08	8.18E-08	3.48E-08	9.52E-08	1.74E-07	3.13E-07	1.53E-07	2.91E-07	2.35E-07	1.09E-06	8.04E-07	6.88E-07	4.02E-07	2.66E-07	3.17E-07	3.86E-07	2.56E-07	2.43E-07
Hcys 5	4.91E-08	6.5E-08	3.63E-08	4E-08	9.03E-08	1.23E-07	1.51E-07	3.59E-07	2.83E-07	1.15E-06	8.54E-07	7.5E-07	3.92E-07	2.06E-07	1.15E-07	5.13E-07	2.88E-07	2.58E-07
Cys	2.93	5.86	1.5	5.77	3.05	4.5	6.6	9.2	7.9	8.5	6.5	7.4	5.0	5.7	2.4	9.9	9.6	5.7

100	E-07	E-08	E-07	E-07	E-07	2E-07	5E-07	4E-07	5E-07	8E-07	2E-07	7E-07	4E-07	8E-07	1E-07	2E-07	4E-07	7E-07
Cys 100	2.94E-07	-7.2E-08	1.07E-07	5.1E-07	2.43E-07	4.2E-07	7.37E-07	1.05E-06	8.33E-07	1.25E-06	9.35E-07	1.15E-06	5.61E-07	7.44E-07	3.69E-07	1.05E-06	1.12E-06	8.09E-07
Cys 100	2.33E-07	-1.4E-07	7.75E-08	3.82E-07	1.3E-07	2.92E-07	1.05E-06	1.33E-06	1.01E-06	1.16E-06	8.58E-07	1.15E-06	3.97E-07	5.53E-07	2.48E-07	1.1E-06	1.19E-06	9.31E-07
Cys 100	1.13E-07	-2.3E-07	7.94E-09	4.28E-07	1.41E-07	2.7E-07	9.63E-07	1.33E-06	1.11E-06	1.21E-06	8.11E-07	1.1E-06	3.5E-07	5.12E-07	2.57E-07	1.17E-06	1.18E-06	9.98E-07
Cys 100	1.86E-07	-2.1E-07	3.14E-08	4.58E-07	2.12E-07	3.27E-07	8.15E-07	1.2E-06	9.55E-07	9.77E-07	6.45E-07	9.97E-07	1.97E-07	5.69E-07	1.91E-07	9.89E-07	6.38E-07	5.95E-07
Cys 100	2.48E-07	-1.6E-07	7.42E-08	4E-07	1.67E-07	2.87E-07	7.13E-07	1.13E-06	8.82E-07	1E-06	7.28E-07	1.15E-06	5.77E-08	5.23E-07	1.38E-07	1.06E-06	1.01E-06	8.94E-07
Cys 100	6.87E-08	-3.1E-07	-4.3E-08	2.51E-07	6.47E-08	2.24E-07	7.19E-07	1.19E-06	9.32E-07	1.11E-06	6.13E-07	8.96E-07	-1E-07	4.03E-07	4.73E-08	6.23E-07	1.92E-07	9.16E-08
GSH 100	7.34E-07	7.6E-07	6.83E-07	2.36E-07	4.33E-07	6.96E-07	2.27E-07	5.14E-07	5.38E-07	1.31E-06	1.12E-06	1.04E-06	3.89E-07	8.21E-07	6.28E-07	7.87E-07	7.84E-07	4.33E-07
GSH 100	8.69E-07	9.47E-07	9.31E-07	2.44E-07	4.44E-07	7.52E-07	4.21E-07	8.44E-07	7.88E-07	1.44E-06	1.22E-06	1.17E-06	3.05E-07	7.89E-07	6.67E-07	1.21E-06	1.07E-06	4.7E-07
GSH 100	9.01E-07	9.8E-07	9.82E-07	1.62E-07	3.54E-07	6.45E-07	5.03E-07	9.62E-07	8.63E-07	1.2E-06	1.1E-06	1.19E-06	2.46E-07	6.99E-07	5.92E-07	2.11E-06	1.38E-06	6.29E-07
GSH 100	7.99E-07	8.98E-07	9.43E-07	2.35E-07	4.34E-07	7.26E-07	4.5E-07	9.06E-07	7.93E-07	1.23E-06	1.14E-06	1.22E-06	1.82E-07	6.21E-07	4.68E-07	1.21E-06	9.74E-07	2.87E-07
GSH 100	7.68E-07	8.9E-07	9.19E-07	1.73E-07	3.4E-07	5.65E-07	4.03E-07	8.62E-07	7.41E-07	1.05E-06	8.88E-07	8.83E-07	2.14E-07	6.75E-07	5.35E-07	1.12E-06	8.67E-07	1.22E-07
GSH 100	7.34E-07	8.3E-07	8.85E-07	1.85E-07	3.51E-07	5.66E-07	4.59E-07	9.57E-07	7.69E-07	1.02E-06	9.5E-07	9.89E-07	1.15E-07	5.76E-07	5.04E-07	1.9E-06	1.2E-06	3.57E-07
GSH 100	7.45E-07	8.47E-07	9.09E-07	1.69E-07	3.36E-07	5.89E-07	5.22E-07	1.07E-06	9.01E-07	1.08E-06	1.06E-06	1.17E-06	3.98E-07	8.8E-07	7.08E-07	1.04E-06	7.08E-07	-3.4E-08
Hcys 100	9.8E-07	8.59E-07	9.85E-07	9.82E-07	9.51E-07	1.08E-06	3.88E-07	7.19E-07	7.87E-07	1.91E-06	1.32E-06	1.24E-06	4.68E-07	9.58E-07	7.91E-07	1.43E-06	3.51E-07	-1.8E-07
Hcys 100	1.04E-06	8.87E-07	1.03E-06	1.24E-06	1.24E-06	1.31E-06	5.53E-07	1E-06	1.08E-06	1.8E-06	1.25E-06	1.22E-06	5.16E-07	1.09E-06	9.61E-07	1.89E-06	6.01E-07	7.93E-08
Hcys 100	1.07E-06	9.15E-07	1.07E-06	1.2E-06	1.21E-06	1.26E-06	5.43E-07	9.92E-07	1.09E-06	1.53E-06	9.78E-07	9.33E-07	6.02E-07	1.23E-06	1.06E-06	1.77E-06	3.66E-07	-1.3E-07
Hcys 100	1.15E-	9.74E-	1.13E-	1.16E-	1.22E-	1.27E-	6.78E-	1.23E-	1.26E-	1.6E-	1.05E-	1.02E-	4.98E-	1.22E-	1.05E-	2.18E-	7.51E-	1.68E-

	06	07	06	06	06	06	07	06	06	06	06	06	07	06	06	06	07	07
Hcys 100	1.15E-06	9.83E-07	1.14E-06	1.07E-06	1.14E-06	1.19E-06	6.14E-07	1.11E-06	1.17E-06	1.4E-06	8.89E-07	8.81E-07	4.18E-07	1.11E-06	9.41E-07	1.88E-06	5.13E-07	-6.4E-08
Hcys 100	1.18E-06	1.01E-06	1.18E-06	1.09E-06	1.19E-06	1.24E-06	6.2E-07	1.19E-06	1.24E-06	1.61E-06	1.04E-06	1.02E-06	4.93E-07	1.13E-06	1.02E-06	1.78E-06	2.62E-07	-2.6E-07
Hcys 100	1E-06	8.44E-07	1E-06	1.08E-06	1.2E-06	1.2E-06	6.34E-07	1.18E-06	1.23E-06	1.54E-06	9.47E-07	8.84E-07	3.67E-07	1.1E-06	9.67E-07	1.88E-06	5.16E-07	-7E-08

Table S2. Raw data used for generating LDA score plot shown in figure 11b.

Electrode	CuPc			MnPc			GO-CuPc-PDA			rGO-CuPc-PDA			GO-MnPc-PDA			rGO-MnPc-PDA		
Repilcates	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV
A	1.68E-07	1.43E-07	1.55E-07	1.43E-07	2.45E-07	3.62E-07	2.02E-07	3.76E-07	6.3E-07	5.14E-07	6.93E-07	3.36E-07	5.06E-07	1.73E-07	1.75E-07	8.75E-07	4.57E-07	3.05E-07
A	2.58E-07	1E-07	1.82E-07	1.79E-07	2.63E-07	4.76E-07	1.72E-07	3.79E-07	4.04E-07	7.61E-07	5.85E-07	5.43E-07	5.26E-07	1.89E-07	1.16E-07	8.32E-07	4.64E-07	3.16E-07
A	1.25E-07	9.58E-08	1.51E-07	1.2E-07	2.51E-07	5.41E-07	1.54E-06	3.57E-07	3.98E-07	7.14E-07	5.43E-07	5.19E-08	5.06E-07	1.47E-07	1.51E-07	5.7E-07	4.61E-07	3.13E-07
B	2.02E-07	-2E-07	-4.1E-07	2.97E-07	1.78E-07	3.92E-07	5.04E-07	1.25E-06	1.44E-06	8.77E-07	6.41E-07	9.97E-07	3.74E-07	5.95E-07	2.07E-07	9.89E-07	7.00E-07	5.91E-07
B	2.38E-08	-9.06E-08	3.23E-07	3.84E-07	1.97E-07	3.7E-07	5.25E-07	1.15E-06	1.47E-06	1.12E-06	6.28E-07	1.15E-06	3.77E-07	4.23E-07	1.33E-07	1.06E-06	1.02E-06	8.95E-07
B	2.51E-07	-3.6E-07	7.56E-07	2.17E-07	5.55E-07	3.27E-07	5.74E-07	1.49E-06	2.07E-06	1.23E-06	7.13E-07	8.96E-07	1.02E-07	5.54E-07	3.02E-08	6.23E-07	1.26E-07	1.00E-07
C	8.27E-07	7.4E-07	5.94E-07	4.69E-07	4.29E-07	2.51E-07	4.48E-07	3.02E-07	1.48E-07	8.08E-07	6E-07	5.00E-07	2.38E-07	2.42E-07	1.14E-07	2.77E-08	1.14E-07	-5.3E-07
C	8.01E-07	7.78E-07	5.12E-07	4.81E-07	4.73E-07	2.7E-07	3.8E-07	2.91E-07	1.8E-07	9.03E-07	5.14E-07	4.85E-07	3.24E-07	2.4E-07	2.69E-07	2.93E-07	1.2E-07	-5.8E-07
C	7.44E-07	6.22E-07	6.1E-07	4.26E-07	4.12E-07	2.27E-07	4.06E-07	4.91E-07	2.45E-07	8.61E-07	4.46E-07	4.25E-07	3.1E-07	2.75E-07	1.03E-07	3.7E-07	9.02E-08	-5.5E-07

Plasma-1	6.12E-07	6.53E-07	4.61E-07	4.36E-07	8.37E-07	9.61E-07	6.36E-07	7.57E-07	8.73E-07	1.01E-06	1.13E-06	9.01E-07	9.71E-07	1.07E-06	1.72E-06	1.22E-06	1.48E-06	1.16E-06
Plasma-1	8.12E-07	7.85E-07	5.95E-07	3.9E-07	7.52E-07	1.02E-06	9.83E-07	1.18E-06	1.18E-06	1.4E-06	1.38E-06	1.13E-06	1.35E-06	1.41E-06	1.91E-06	1.72E-06	1.99E-06	1.54E-06
Plasma-1	9.04E-07	7.99E-07	6.34E-07	4.5E-07	8.38E-07	1.08E-06	1.03E-06	1.25E-06	1.2E-06	1.46E-06	1.36E-06	1.12E-06	1.51E-06	1.62E-06	2.19E-06	1.8E-06	2.09E-06	1.58E-06
Plasma-1	9.24E-07	7.94E-07	6.46E-07	3.97E-07	7.56E-07	9.78E-07	9.68E-07	1.2E-06	1.16E-06	1.45E-06	1.38E-06	1.15E-06	1.37E-06	1.48E-06	1.93E-06	1.88E-06	2.17E-06	1.63E-06
Plasma-1	9.41E-07	7.4E-07	5.02E-07	4.06E-07	7.84E-07	1.02E-06	9.99E-07	1.29E-06	1.26E-06	1.44E-06	1.43E-06	1.24E-06	1.34E-06	1.5E-06	2E-06	1.88E-06	2.21E-06	1.65E-06
Plasma-1	1.36E-06	1.44E-06	1.74E-06	6.65E-07	1.03E-06	1.29E-06	1.32E-06	1.68E-06	1.74E-06	2.25E-06	2.13E-06	2.06E-06	1.61E-06	1.77E-06	2.25E-06	3.25E-06	3.51E-06	3.61E-06
Plasma-1	8.57E-07	6.92E-07	5.08E-07	4E-07	7.98E-07	1.02E-06	9.52E-07	1.28E-06	1.22E-06	1.56E-06	1.45E-06	1.29E-06	1.38E-06	1.59E-06	2.16E-06	1.8E-06	1.79E-06	1.3E-06
Cys-50	3.91E-07	3.02E-07	2.61E-07	9.64E-08	1.9E-07	1.99E-07	4.86E-07	3.96E-07	-1.5E-08	2.04E-07	-6.4E-08	-3.6E-08	3.1E-07	1E-07	-1.8E-07	1.56E-07	-5.2E-08	-4.9E-07
Cys-50	3.78E-07	2.87E-07	1.99E-07	2.31E-07	3.26E-07	2.96E-07	8.25E-07	6.8E-07	3.01E-07	2.67E-07	3.06E-10	3.39E-08	2.93E-07	1.69E-07	9.09E-08	2.24E-07	1.59E-08	-5.8E-07
Cys-50	3.73E-07	3.16E-07	3.01E-07	1.08E-07	1.91E-07	1.79E-07	4.86E-07	3.96E-07	-1.5E-08	2.17E-07	-4.9E-08	-1.1E-08	2.15E-07	1.33E-07	1.02E-07	3.08E-07	1.11E-07	-5.8E-07
Cys-50	3.66E-07	2.98E-07	2.74E-07	8.76E-08	1.83E-07	1.65E-07	4.76E-07	4.17E-07	-4.5E-08	3.4E-07	-1E-08	2.93E-08	2.35E-07	1.34E-07	3.42E-08	3.28E-07	1.21E-07	-6E-07
Cys-50	3.29E-07	2.89E-07	2.41E-07	5.43E-08	1.14E-07	8.54E-08	4.54E-07	4.19E-07	-3E-08	1.15E-07	-1.3E-07	-7.1E-08	2.84E-07	1.39E-07	-4.8E-08	3.23E-07	7.08E-08	-6.9E-07
Cys-50	1.64E-06	1.75E-06	2.04E-06	5.17E-07	8.25E-07	9.95E-07	1.53E-06	1.79E-06	1.99E-06	3.17E-06	2.71E-06	2.56E-06	1.72E-06	1.66E-06	2.19E-06	2.23E-06	2.49E-06	2.63E-06
Cys-50	2.73E-07	2.87E-07	3.25E-07	5.25E-08	1.43E-07	1.68E-07	5.26E-07	5.35E-07	1.08E-07	1.97E-07	-6.2E-08	-6.1E-10	3.03E-07	1.79E-07	3.2E-08	3.13E-07	3.31E-07	-5E-07
GSH-50	3.57E-07	3.34E-07	3.4E-07	4.91E-08	1.19E-07	2.56E-07	5.84E-07	7.06E-07	5.15E-07	1.25E-06	6.35E-07	5.15E-07	7.88E-07	6.21E-07	3.58E-07	8.38E-07	3.81E-07	2.21E-07
GSH-50	4.39E-07	4.48E-07	4.48E-07	7.6E-08	1.66E-07	3.12E-07	4.52E-07	6.57E-07	4.24E-07	7.41E-07	1.94E-07	1.73E-07	7.44E-07	6.56E-07	3.77E-07	8.02E-07	2.89E-07	9.64E-08
GSH-50	3.75E-07	4.04E-07	4.27E-07	5.34E-08	1.21E-07	2.55E-07	3.2E-07	5.96E-07	2.89E-07	6.56E-07	9.22E-08	8.48E-08	6.86E-07	6.45E-07	3.29E-07	8.53E-07	4.4E-07	1.96E-07
GSH-50	3.01E-07	3.5E-07	4.09E-07	5E-08	1.15E-07	2.63E-07	2.3E-07	6E-07	2.94E-07	6.45E-07	1.52E-09	-9.5E-09	7.13E-07	7.03E-07	2.86E-07	7.94E-07	4.55E-07	1.83E-07

GSH-50	3.88E-07	4.01E-07	4.29E-07	5.71E-08	1.41E-07	3.11E-07	3.35E-07	7.11E-07	4.14E-07	5.77E-07	9.1E-08	7.4E-08	6.65E-07	7.06E-07	4.97E-07	8.15E-07	4.62E-07	1.71E-07
GSH-50	1.74E-06	1.79E-06	2.06E-06	4.7E-07	8.15E-07	1.22E-06	1.48E-06	1.97E-06	1.97E-06	3.54E-06	3.11E-06	2.87E-06	2.04E-06	2.19E-06	2.67E-06	2.74E-06	2.87E-06	2.97E-06
GSH-50	3.23E-07	3.32E-07	3.36E-07	4.64E-08	9.4E-08	2.13E-07	3.32E-07	8.53E-07	4.95E-07	9.35E-07	1.48E-07	1.21E-07	6.35E-07	7.33E-07	3.88E-07	7.18E-07	3.37E-07	5.68E-08
Hcys-50	7.5E-07	5.29E-07	5.57E-07	3.31E-07	3.16E-07	2.61E-07	4.93E-07	3.16E-07	1.94E-07	8.27E-07	4.86E-07	4.63E-07	3.38E-07	2.4E-07	1.26E-07	2.84E-07	5.89E-08	-1.4E-07
Hcys-50	9.31E-07	6.7E-07	7.54E-07	4.01E-07	3.73E-07	2.33E-07	4.83E-07	3.23E-07	1.84E-07	1E-06	6.29E-07	6.56E-07	3.02E-07	2.97E-07	1.6E-07	4.28E-07	1.61E-07	-9.6E-08
Hcys-50	7.25E-07	5.31E-07	6.11E-07	4.14E-07	4.04E-07	2.61E-07	7.18E-07	4.78E-07	3.2E-07	8.91E-07	5.18E-07	5.73E-07	2.76E-07	3.56E-07	1.75E-07	3.67E-07	1.1E-07	-2E-07
Hcys-50	8.04E-07	5.98E-07	6.56E-07	4.08E-07	4.17E-07	2.64E-07	3.89E-07	2.8E-07	1.61E-07	9.08E-07	4.82E-07	5.44E-07	1.63E-07	3.69E-07	2.95E-07	2.55E-07	3.66E-09	-3.4E-07
Hcys-50	8.45E-07	6.11E-07	6.88E-07	4.1E-07	4.35E-07	2.62E-07	3.23E-07	2.45E-07	1.48E-07	8.5E-07	3.67E-07	4.21E-07	3.02E-07	2.97E-07	1.6E-07	4.05E-07	2.4E-07	-1.3E-07
Hcys-50	1.71E-06	1.58E-06	1.93E-06	7.14E-07	9.66E-07	1.34E-06	2.14E-06	2.08E-06	1.95E-06	3.49E-06	2.92E-06	2.85E-06	1.46E-06	1.67E-06	1.84E-06	2.3E-06	2.41E-06	2.62E-06
Hcys-50	8.58E-07	6.11E-07	7.49E-07	3.53E-07	4E-07	2.07E-07	1E-06	7.89E-07	4.93E-07	5.86E-07	2.17E-07	3.57E-07	-5E-08	3.39E-07	1.53E-07	4.05E-07	1.13E-07	-3.4E-07
Cys 5	-2.1E-08	-2.1E-07	-1.6E-07	1.97E-07	1.85E-07	2.79E-07	2.62E-07	5.18E-07	7.23E-07	2.48E-07	4.05E-07	1.75E-07	4.27E-07	4.1E-07	3.73E-07	7.74E-07	5.7E-07	3.75E-07
Cys 5	-1.1E-08	-2.3E-07	-1.7E-07	2.11E-07	1.57E-07	2.67E-07	2.34E-07	4.4E-07	5.58E-07	4.9E-07	5.9E-07	2.58E-07	1.41E-07	1.7E-07	1.54E-07	7.46E-07	5.58E-07	2.99E-07
Cys 5	-4.3E-08	-3.2E-07	-2.4E-07	2.3E-07	1.7E-07	3.26E-07	2.87E-07	5.07E-07	6.14E-07	2.7E-07	2.98E-07	-8.5E-08	2.3E-07	3.29E-07	2.99E-07	1.12E-06	7.74E-07	5.13E-07
Cys 5	-2.6E-08	-2E-07	-9.2E-08	1.53E-07	1.62E-08	1.48E-07	2.37E-07	4.62E-07	5.71E-07	3.33E-07	1.83E-07	-1.8E-07	2.18E-07	1.56E-07	1.81E-07	7.55E-07	4.72E-07	1.8E-07
Cys 5	-2.2E-08	-8.1E-08	5.8E-08	1.93E-07	6.01E-08	2.21E-07	1.79E-07	3.32E-07	3.51E-07	3.43E-07	1.48E-07	-2.3E-07	2.32E-07	2.08E-07	2.8E-07	9.26E-07	5.39E-07	1.95E-07
Cys 5	-5.5E-08	-2E-07	-5E-08	1.71E-07	3.27E-08	1.75E-07	2.34E-07	4.4E-07	5.58E-07	2.63E-07	4.7E-08	-3.3E-07	2.86E-07	2.28E-07	3.49E-07	7.52E-07	4.14E-07	8.54E-08
Cys 5	-9.2	-2.9	-1.2	1.49E-	2.44E-	2.12E-	1.15E-	2.78E-	3.08E-	2.94E-	1.28E-	-4E-	2.44E-	2.68E-	4.48E-	9.14E-	4.9E-	1.01E-

	E-08	E-07	E-07	07	08	07	07	07	07	07	08	07	07	07	07	07	07	07
GSH5	7.9E-08	-3.3E-08	-9.4E-08	1.87E-07	2.67E-07	3.69E-07	2.35E-07	4.61E-07	3.93E-07	9.07E-07	7.08E-07	5.8E-07	3.97E-07	1.78E-07	1.56E-07	4.28E-07	2.6E-07	1.81E-07
GSH5	2.28E-07	1.32E-07	1.08E-07	2.26E-07	3.4E-07	5.22E-07	2.12E-07	4.38E-07	4.04E-07	7.91E-07	6.52E-07	5.34E-07	4.18E-07	1.68E-07	1.52E-07	6.77E-07	4.16E-07	3.05E-07
GSH5	1.94E-07	9.64E-08	8.18E-08	1.69E-07	2.48E-07	3.45E-07	1.62E-07	4.11E-07	3.98E-07	7.03E-07	5.64E-07	4.74E-07	4.43E-07	1.7E-07	1.63E-07	6.61E-07	3.64E-07	2.32E-07
GSH5	2.38E-07	1.53E-07	1.73E-07	1.79E-07	2.56E-07	2.8E-07	1.31E-07	3.89E-07	3.79E-07	7.63E-07	5.94E-07	5.04E-07	4.04E-07	1.32E-07	1.32E-07	8.18E-07	4.61E-07	3.13E-07
GSH5	1.45E-07	1.04E-07	1.89E-07	1.56E-07	2.37E-07	3.04E-07	1.1E-07	3.68E-07	3.65E-07	6.42E-07	5.24E-07	4.5E-07	2.55E-07	5.07E-08	1.1E-07	8.31E-07	4.41E-07	2.78E-07
GSH5	8.55E-08	5.25E-08	1.47E-07	1.51E-07	2.29E-07	2.44E-07	6.59E-08	3.14E-07	2.9E-07	7.78E-07	5.8E-07	4.92E-07	3.04E-07	6.38E-08	1.15E-07	8.85E-07	4.83E-07	3.08E-07
GSH5	3.6E-08	5.58E-08	2.36E-07	1.61E-07	2.58E-07	3.23E-07	-3.9E-08	1.14E-07	1.3E-07	7.64E-07	5.19E-07	4.39E-07	3.41E-07	1.58E-07	2.93E-07	9.77E-07	5.1E-07	3.16E-07
Hcys5	1.97E-07	2.01E-07	2.05E-07	2.78E-08	4.09E-08	9.19E-08	1.35E-07	2.28E-07	1.69E-07	6.77E-07	5.48E-07	4.52E-07	5.21E-07	3.79E-07	4E-07	6.02E-07	3.54E-07	3.16E-07
Hcys5	3.55E-07	3.14E-07	2.53E-07	1.19E-07	1.83E-07	2.84E-07	1.24E-07	2.38E-07	1.83E-07	9.83E-07	7.43E-07	6.12E-07	5.47E-07	4.1E-07	4.71E-07	7.7E-07	4.53E-07	4.16E-07
Hcys5	1.97E-07	2.01E-07	2.05E-07	6.96E-08	1.24E-07	2.27E-07	1.05E-07	2.41E-07	1.91E-07	1.01E-06	7.64E-07	6.39E-07	4.92E-07	3.47E-07	3.86E-07	6.25E-07	4.02E-07	3.72E-07
Hcys5	2.77E-07	2.75E-07	2.1E-07	1.21E-07	2.04E-07	3.85E-07	1.15E-07	3.16E-07	2.53E-07	1.07E-06	7.9E-07	6.59E-07	6.32E-07	4.46E-07	4.99E-07	4.82E-07	3.14E-07	2.81E-07
Hcys5	2.67E-07	3.09E-07	2.53E-07	8.82E-08	1.66E-07	3.18E-07	1.3E-07	3.07E-07	2.18E-07	1.08E-06	8.05E-07	6.8E-07	4.69E-07	2.97E-07	2.78E-07	5.93E-07	3.2E-07	2.61E-07
Hcys5	6.04E-08	8.18E-08	3.48E-08	9.52E-08	1.74E-07	3.13E-07	1.53E-07	2.91E-07	2.35E-07	1.09E-06	8.04E-07	6.88E-07	4.02E-07	2.66E-07	3.17E-07	3.86E-07	2.56E-07	2.43E-07
Hcys5	4.91E-08	6.5E-08	3.63E-08	4E-08	9.03E-08	1.23E-07	1.51E-07	3.59E-07	2.83E-07	1.15E-06	8.54E-07	7.5E-07	3.92E-07	2.06E-07	1.15E-07	5.13E-07	2.88E-07	2.58E-07
Cys100	2.93E-07	5.86E-08	1.57E-07	5.77E-07	3.05E-07	4.52E-07	6.65E-07	9.24E-07	7.95E-07	8.58E-07	6.52E-07	7.47E-07	5.04E-07	5.78E-07	2.41E-07	9.92E-07	9.64E-07	5.77E-07
Cys100	2.94E-07	-7.2E-08	1.07E-07	5.1E-07	2.43E-07	4.2E-07	7.37E-07	1.05E-06	8.33E-07	1.25E-06	9.35E-07	1.15E-06	5.61E-07	7.44E-07	3.69E-07	1.05E-06	1.12E-06	8.09E-07
Cys100	2.33E-07	-1.4E-07	7.75E-08	3.82E-07	1.3E-07	2.92E-07	1.05E-06	1.33E-06	1.01E-06	1.16E-06	8.58E-07	1.15E-06	3.97E-07	5.53E-07	2.48E-07	1.1E-06	1.19E-06	9.31E-07
Cys100	1.13E-07	-2.3E-07	7.94E-09	4.28E-07	1.41E-07	2.7E-07	9.63E-07	1.33E-06	1.11E-06	1.21E-06	8.11E-07	1.1E-06	3.5E-07	5.12E-07	2.57E-07	1.17E-06	1.18E-06	9.98E-07

Cys 100	1.86E-07	-2.1E-07	3.14E-08	4.58E-07	2.12E-07	3.27E-07	8.15E-07	1.2E-06	9.55E-07	9.77E-07	6.45E-07	9.97E-07	1.97E-07	5.69E-07	1.91E-07	9.89E-07	6.38E-07	5.95E-07
Cys 100	2.48E-07	-1.6E-07	7.42E-08	4E-07	1.67E-07	2.87E-07	7.13E-07	1.13E-06	8.82E-07	1E-06	7.28E-07	1.15E-06	5.77E-08	5.23E-07	1.38E-07	1.06E-06	1.01E-06	8.94E-07
Cys 100	6.87E-08	-3.1E-07	-4.3E-08	2.51E-07	6.47E-08	2.24E-07	7.19E-07	1.19E-06	9.32E-07	1.11E-06	6.13E-07	8.96E-07	-1E-07	4.03E-07	4.73E-08	6.23E-07	1.92E-07	9.16E-08
GSH 100	7.34E-07	7.6E-07	6.83E-07	2.36E-07	4.33E-07	6.96E-07	2.27E-07	5.14E-07	5.38E-07	1.31E-06	1.12E-06	1.04E-06	3.89E-07	8.21E-07	6.28E-07	7.87E-07	7.84E-07	4.33E-07
GSH 100	8.69E-07	9.47E-07	9.31E-07	2.44E-07	4.44E-07	7.52E-07	4.21E-07	8.44E-07	7.88E-07	1.44E-06	1.22E-06	1.17E-06	3.05E-07	7.89E-07	6.67E-07	1.21E-06	1.07E-06	4.7E-07
GSH 100	9.01E-07	9.8E-07	9.82E-07	1.62E-07	3.54E-07	6.45E-07	5.03E-07	9.62E-07	8.63E-07	1.2E-06	1.1E-06	1.19E-06	2.46E-07	6.99E-07	5.92E-07	2.11E-06	1.38E-06	6.29E-07
GSH 100	7.99E-07	8.98E-07	9.43E-07	2.35E-07	4.34E-07	7.26E-07	4.5E-07	9.06E-07	7.93E-07	1.23E-06	1.14E-06	1.22E-06	1.82E-07	6.21E-07	4.68E-07	1.21E-06	9.74E-07	2.87E-07
GSH 100	7.68E-07	8.9E-07	9.19E-07	1.73E-07	3.4E-07	5.65E-07	4.03E-07	8.62E-07	7.41E-07	1.05E-06	8.8E-07	8.83E-07	2.14E-07	6.75E-07	5.35E-07	1.12E-06	8.67E-07	1.22E-07
GSH 100	7.34E-07	8.3E-07	8.85E-07	1.85E-07	3.51E-07	5.66E-07	4.59E-07	9.57E-07	7.69E-07	1.02E-06	9.5E-07	9.89E-07	1.15E-07	5.76E-07	5.04E-07	1.9E-06	1.2E-06	3.57E-07
GSH 100	7.45E-07	8.47E-07	9.09E-07	1.69E-07	3.36E-07	5.89E-07	5.22E-07	1.07E-06	9.01E-07	1.08E-06	1.06E-06	1.17E-06	3.98E-07	8.8E-07	7.08E-07	1.04E-06	7.08E-07	-3.4E-08
Hcys 100	9.8E-07	8.59E-07	9.85E-07	9.82E-07	9.51E-07	1.08E-06	3.88E-07	7.19E-07	7.87E-07	1.91E-06	1.32E-06	1.24E-06	4.68E-07	9.58E-07	7.91E-07	1.43E-06	3.51E-07	-1.8E-07
Hcys 100	1.04E-06	8.87E-07	1.03E-06	1.24E-06	1.24E-06	1.31E-06	5.53E-07	1E-06	1.08E-06	1.8E-06	1.25E-06	1.22E-06	5.16E-07	1.09E-06	9.61E-07	1.89E-06	6.01E-07	7.93E-08
Hcys 100	1.07E-06	9.15E-07	1.07E-06	1.24E-06	1.21E-06	1.26E-06	5.43E-07	9.92E-07	1.09E-06	1.53E-06	9.78E-07	9.33E-07	6.02E-07	1.23E-06	1.06E-06	1.77E-06	3.66E-07	-1.3E-07
Hcys 100	1.15E-06	9.74E-07	1.13E-06	1.16E-06	1.22E-06	1.27E-06	6.78E-07	1.23E-06	1.26E-06	1.6E-06	1.05E-06	1.02E-06	4.98E-07	1.22E-06	1.05E-06	2.18E-06	7.51E-07	1.68E-07
Hcys 100	1.15E-06	9.83E-07	1.14E-06	1.07E-06	1.14E-06	1.19E-06	6.14E-07	1.11E-06	1.17E-06	1.4E-06	8.89E-07	8.81E-07	4.18E-07	1.11E-06	9.41E-07	1.88E-06	5.13E-07	-6.4E-08
Hcys 100	1.18E-06	1.01E-06	1.18E-06	1.09E-06	1.19E-06	1.24E-06	6.2E-07	1.19E-06	1.24E-06	1.61E-06	1.04E-06	1.02E-06	4.93E-07	1.13E-06	1.02E-06	1.78E-06	2.62E-07	-2.6E-07
Hcys 100	1E-06	8.44E-07	1E-06	1.08E-06	1.2E-06	1.2E-06	6.34E-07	1.18E-06	1.23E-06	1.54E-06	9.47E-07	8.84E-07	3.6E-07	1.1E-06	9.67E-07	1.88E-06	5.16E-07	-7E-08

Table S3. Shows the oxidation peak potentials of different biothiols in presence of RIs. Each voltammogram shows peak currents at two potentials. Comparison of the data shows, three values (0.38, 0.48, and 0.48 V) are qualified for the LDA and PLS-R process.

Electrode	Analyte	Potential 1 (mV)	Potential 2 (mV)
CuPc (**1'**)	Cys	0.41	0.57
	GSH	0.41	0.57
	Hcys	0.38	0.58
MnPc (**2'**)	Cys	0.38	0.48
	GSH	0.38	0.48
	Hcys	0.38	0.44
GO-CuPc-PDA (**3'**)	Cys	0.46	0.57
	GSH	0.48	0.60
	Hcys	0.39	-
GO-MnPc-PDA (**4'**)	Cys	0.38	0.57
	GSH	0.42	0.6
	Hcys	0.41	0.64
rGO-CuPc-PDA (**5'**)	Cys	0.37	0.46
	GSH	0.37	0.48
	Hcys	0.37	0.48
rGO-MnPc-PDA (**6'**)	Cys	0.33	0.47
	GSH	0.36	0.48
	Hcys	0.36	0.48

Table S4. Shows the cross-validation results:

from \ to	Cys	Cys 100	Cys 5	GSH	GSH 100	GSH 5	Hcys	Hcys 100	Hcys 5	P-1	Total	% correct
Cys	6	0	0	1	0	0	0	0	0	0	7	85.71%
Cys 100	0	7	0	0	0	0	0	0	0	0	7	100.00%
Cys 5	0	0	7	0	0	0	0	0	0	0	7	100.00%
GSH	1	0	0	6	0	0	0	0	0	0	7	85.71%
GSH 100	0	0	0	0	7	0	0	0	0	0	7	100.00%
GSH 5	0	0	0	0	0	7	0	0	0	0	7	100.00%
Hcys	1	0	0	0	0	0	6	0	0	0	7	85.71%
Hcys 100	0	0	0	0	0	0	0	7	0	0	7	100.00%
Hcys 5	0	0	0	0	0	0	0	0	7	0	7	100.00%
P-1	0	0	0	0	0	0	0	0	1	5	6	83.33%
Total	8	7	7	7	7	7	6	7	8	5	69	94.20%

Table S5. Results of the fitted regression curves for predicted vs. experimental values and RMSE, for the calibration and validation measurements of the individual samples (Cys, GSH, and Hcys). (Intervals calculated at the 95% confidence level)

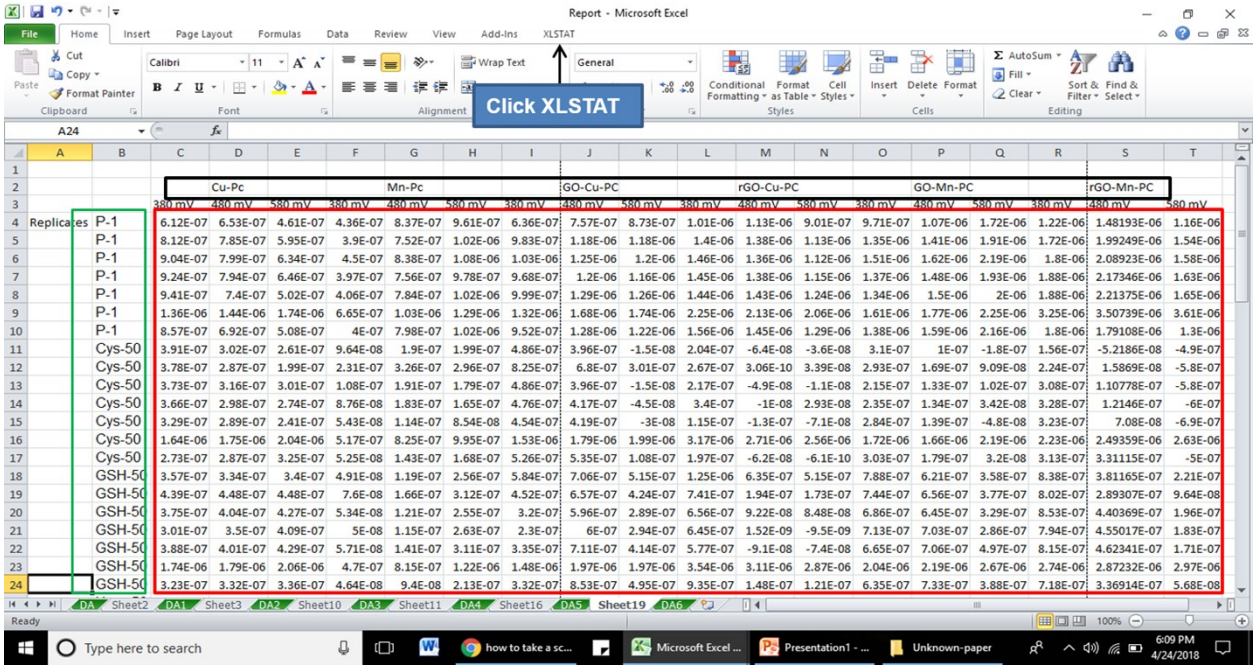
Analytes	R^2_{Cal} value	R^2_{Val} value	$RMSE_{Cal}$	$RMSE_{Val}$
Cys	0.833	0.966	15.88	7.28
GSH	0.902	0.977	12.18	5.57

Hcys	0.974	0.942	6.29	9.48

R Square values - Redox Indicators			
Electrode	**AA** **i vs $(\upsilon)^{1/2}/(mVs^{-1})^{1/2}$**	**DA** **i vs $(\upsilon)^{1/2}/(mVs^{-1})^{1/2}$**	**UA** **i vs $(\upsilon)^{1/2}/(mVs^{-1})^{1/2}$**
1' (CuPc)	0.95907	0.96251	0.98701
2' (MnPc)	×	0.96132	0.97094
3' (GO-CuPc-PDA)	0.97512	0.989	0.9903
4' (GO-MnPc-PDA)	×	0.97748	0.98284
5' (rGO-CuPc-PDA)	0.94267	0.98016	0.96895
6' (rGO-MnPc-PDA)	×	0.94961	0.98693

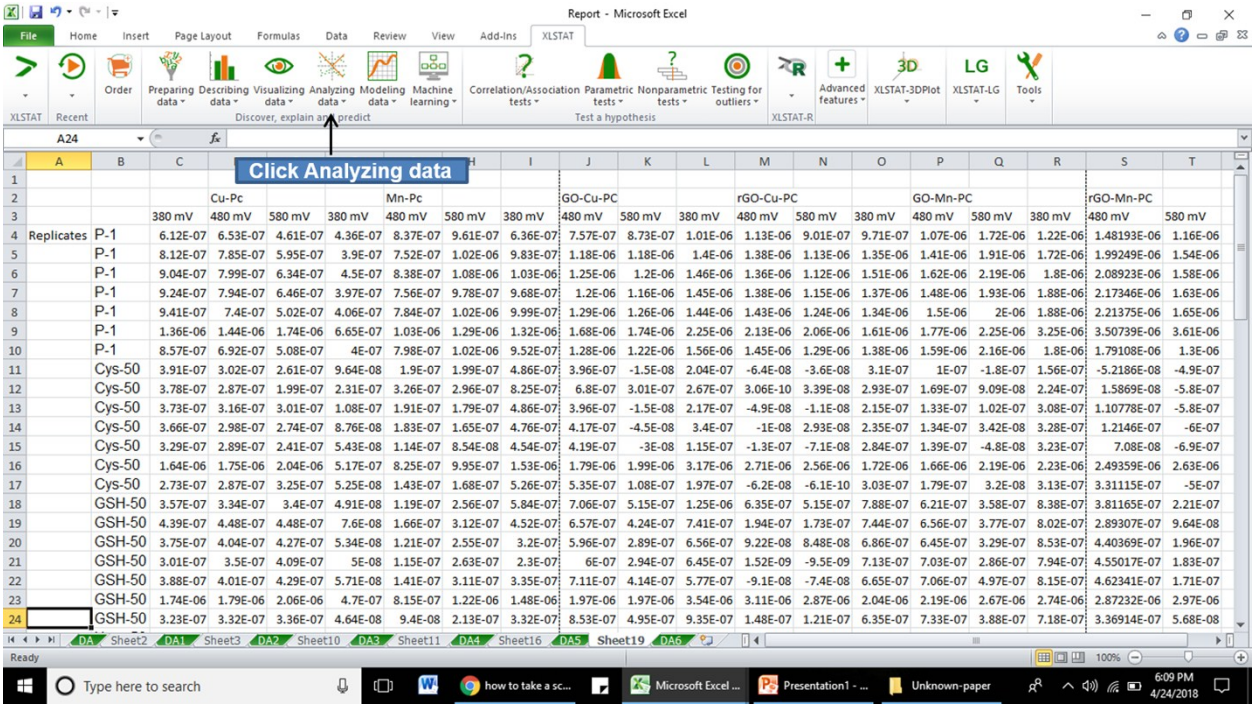
Table S6. Shows the R^2 value obtained from the plot of current as a function of square root of scan rate.

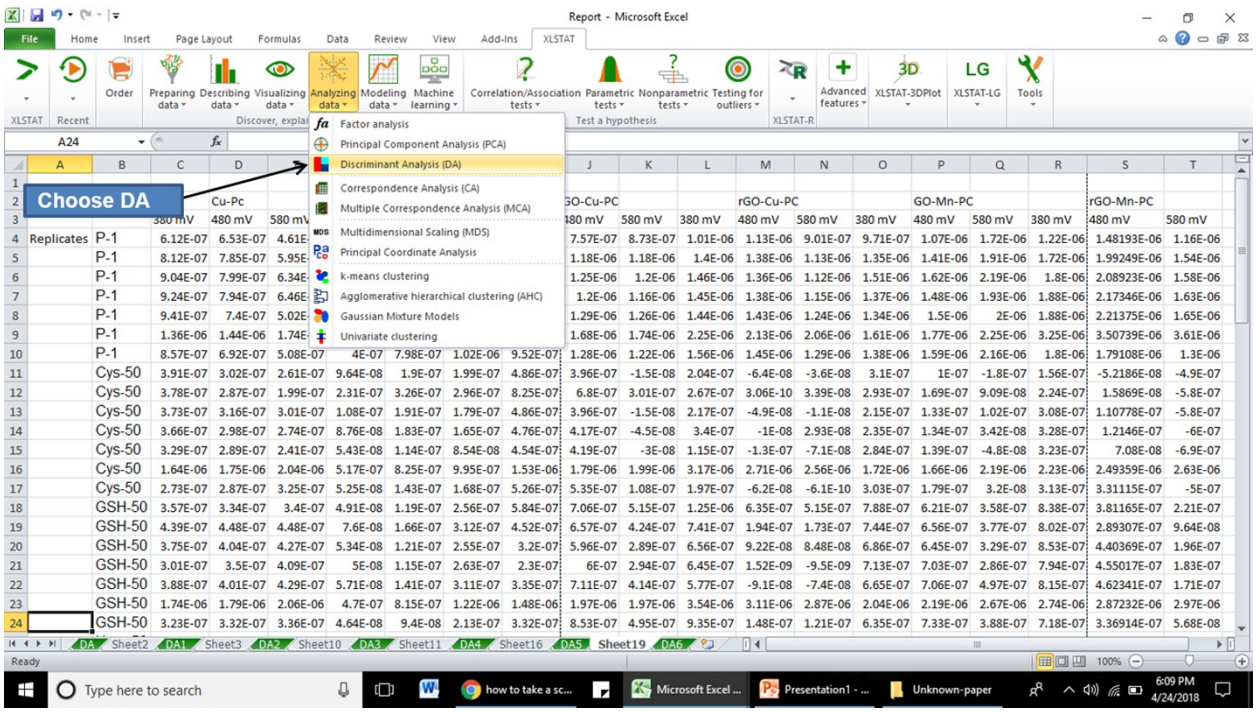
×- Refers the absence of oxidation current signal.



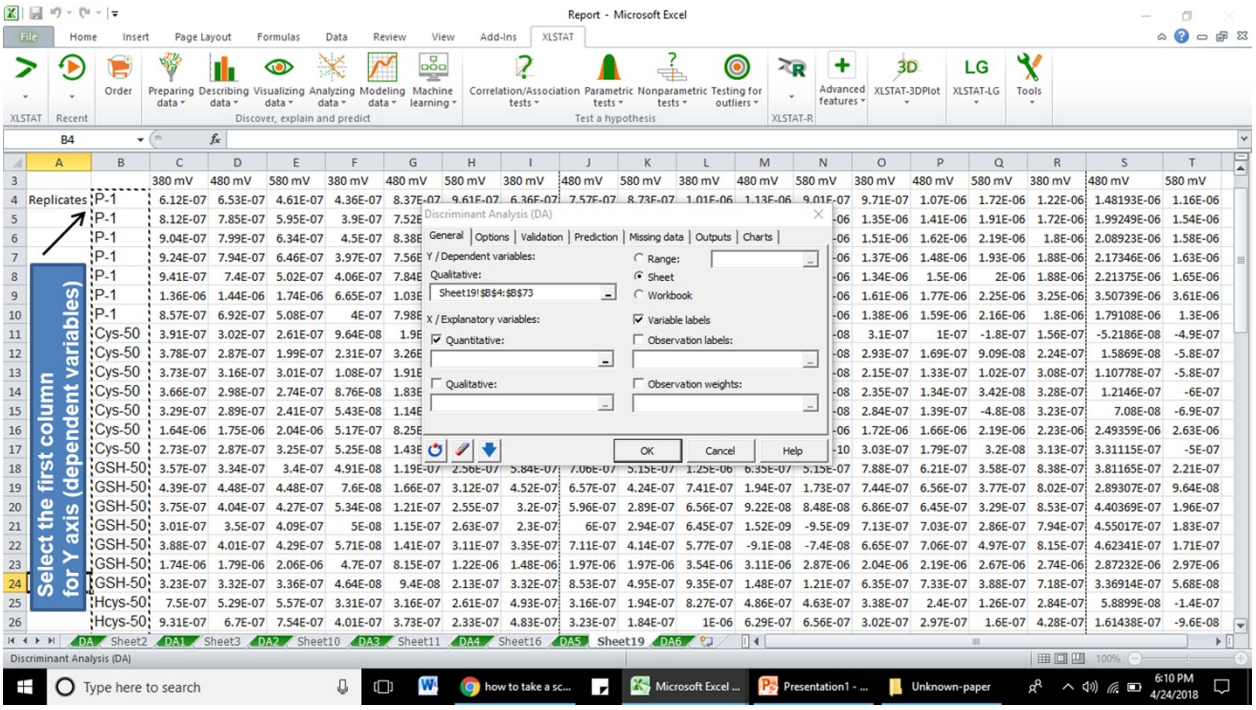
5. Step wise procedure for generating LDA score plot shown in Figure 10

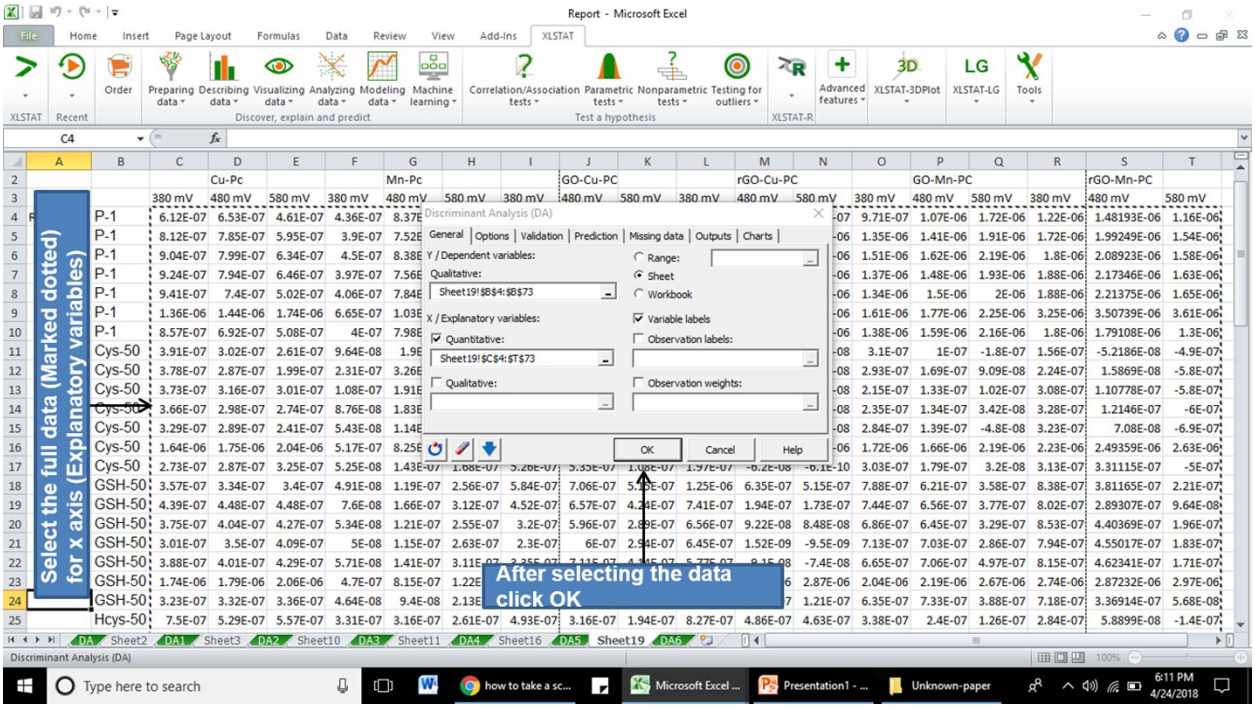
Red Box: Contains difference in current value at particular potential (380 mV, 480mV and 580 mV) obtained from the LSV. **Green Box**: Shows the label of the replicates. **Black Box**: Shows the name the electrodes used as working electrode.

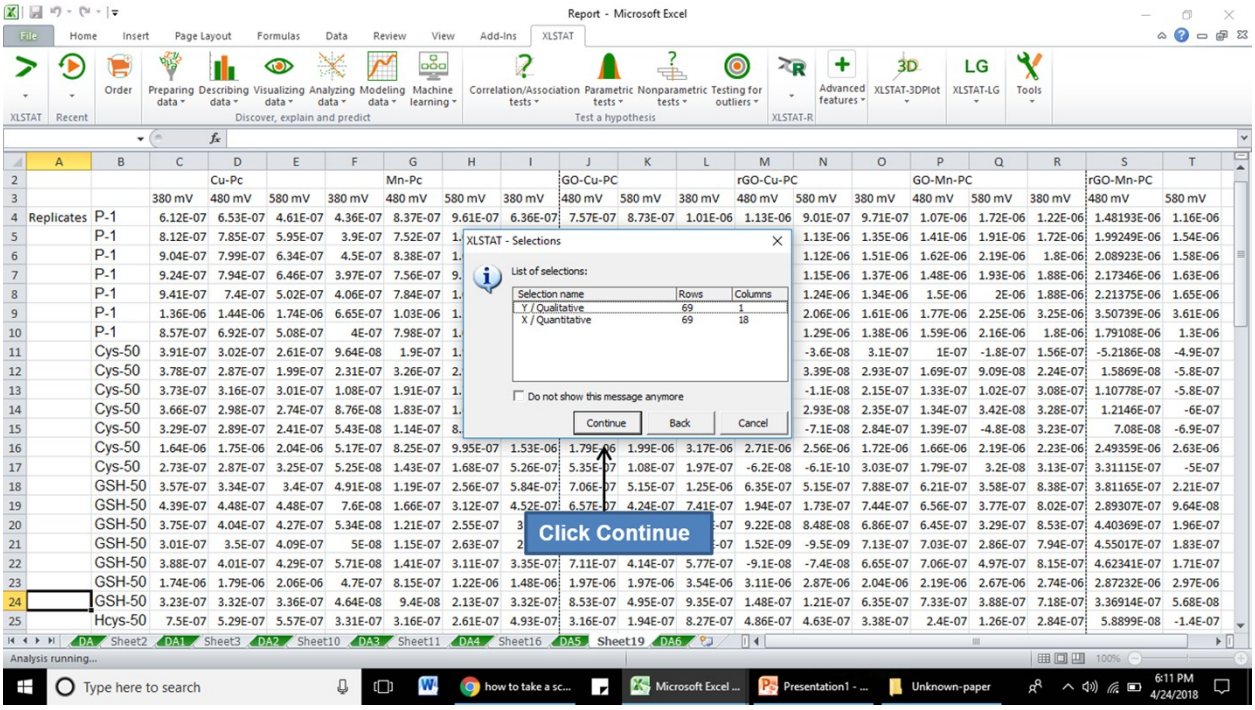




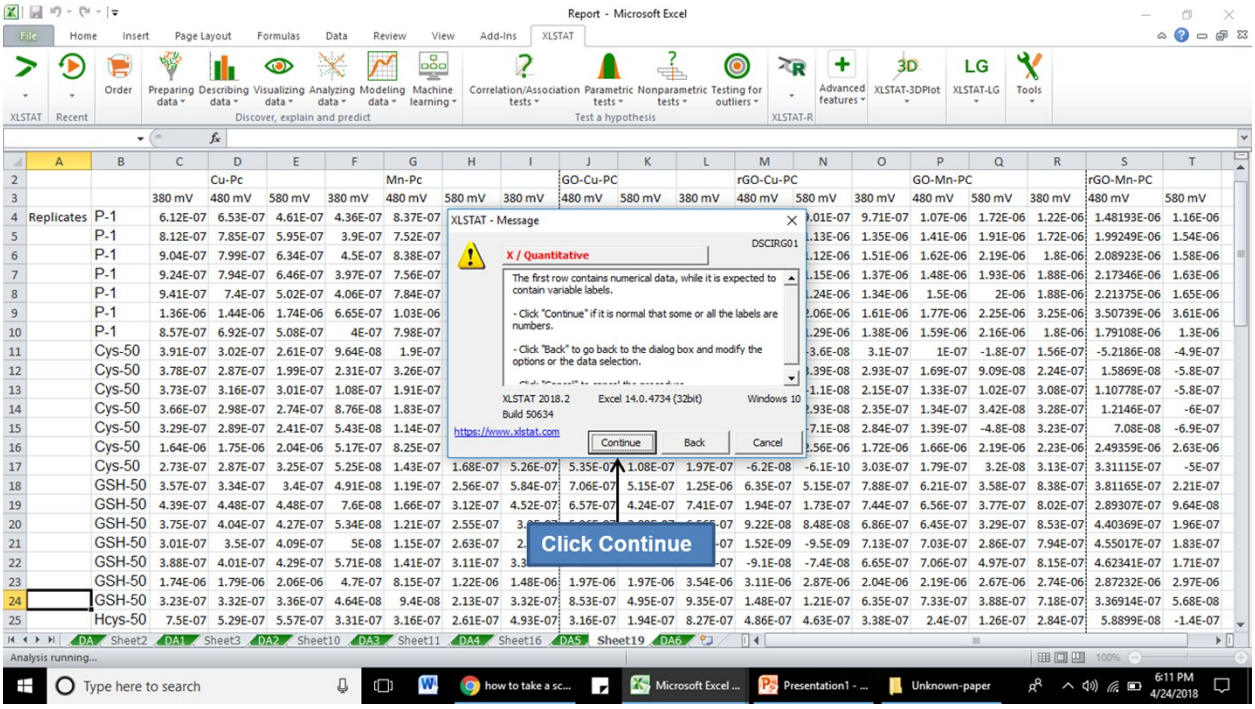
		Cu-Pc			Mn-Pc			GO-Cu-PC			rGO-Cu-PC			GO-Mn-PC			rGO-Mn-PC	
		380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV	380 mV	480 mV	580 mV
Replicates	P-1	6.12E-07	6.53E-07	4.61E-07	4.36E-07	8.37E-07	9.61E-07	6.36E-07	7.57E-07	8.73E-07	1.01E-06	1.13E-06	9.01E-07	9.71E-07	1.07E-06	1.72E-06	1.22E-06	1.48193E-06	1.16E-06
	P-1	8.12E-07	7.85E-07	5.95E-07	3.9E-07	7.52E-07	1.02E-06	9.83E-07	1.18E-06	1.18E-06	1.4E-06	1.38E-06	1.13E-06	1.35E-06	1.41E-06	1.91E-06	1.72E-06	1.99249E-06	1.54E-06
	P-1	9.04E-07	7.99E-07	6.34E-07	4.5E-07	8.38E-07	1.08E-06	1.03E-06	1.25E-06	1.2E-06	1.46E-06	1.36E-06	1.12E-06	1.51E-06	1.62E-06	2.19E-06	1.8E-06	2.08923E-06	1.58E-06
	P-1	9.24E-07	7.94E-07	6.46E-07	3.97E-07	7.56E-07	9.78E-07	9.68E-07	1.2E-06	1.16E-06	1.45E-06	1.38E-06	1.15E-06	1.37E-06	1.48E-06	1.93E-06	1.88E-06	2.17346E-06	1.63E-06
	P-1	9.41E-07	7.4E-07	5.02E-07	4.06E-07	7.84E-07	1.02E-06	9.99E-07	1.29E-06	1.26E-06	1.44E-06	1.43E-06	1.24E-06	1.34E-06	1.5E-06	2E-06	1.88E-06	2.21375E-06	1.65E-06
	P-1	1.36E-06	1.44E-06	1.74E-06	6.65E-07	1.03E-06	1.29E-06	1.32E-06	1.68E-06	1.74E-06	2.25E-06	2.13E-06	2.06E-06	1.61E-06	1.77E-06	2.25E-06	3.25E-06	3.50739E-06	3.61E-06
	P-1	8.57E-07	6.92E-07	5.08E-07	4E-07	7.98E-07	1.02E-06	9.52E-07	1.28E-06	1.22E-06	1.56E-06	1.45E-06	1.29E-06	1.38E-06	1.59E-06	2.16E-06	1.8E-06	1.79108E-06	1.3E-06
	Cys-50	3.91E-07	3.02E-07	2.61E-07	9.64E-08	1.9E-07	1.99E-07	4.86E-07	3.96E-07	-1.5E-08	2.04E-07	-6.4E-08	-3.6E-08	3.1E-07	1E-07	-1.8E-07	1.56E-07	-5.2186E-08	-4.9E-07
	Cys-50	3.78E-07	2.87E-07	1.99E-07	2.31E-07	3.26E-07	2.96E-07	8.25E-07	6.8E-07	3.01E-07	2.67E-07	3.06E-10	3.39E-08	2.93E-07	1.69E-07	9.09E-08	2.24E-07	1.5869E-08	-5.8E-07
	Cys-50	3.73E-07	3.16E-07	3.01E-07	1.08E-07	1.91E-07	1.79E-07	4.86E-07	3.96E-07	-1.5E-08	2.17E-07	-4.9E-08	-1.1E-08	2.15E-07	1.33E-07	1.02E-07	3.08E-07	1.10778E-07	-5.8E-07
	Cys-50	3.66E-07	2.98E-07	2.74E-07	8.76E-08	1.83E-07	1.65E-07	4.76E-07	4.17E-07	-4.5E-08	3.4E-07	-1E-08	2.93E-08	2.35E-07	1.34E-07	3.42E-08	3.28E-07	1.2146E-07	-6E-07
	Cys-50	3.29E-07	2.89E-07	2.41E-07	5.43E-08	1.14E-07	8.54E-08	4.54E-07	4.19E-07	-3E-08	1.15E-07	-1.3E-07	-7.1E-08	2.84E-07	1.39E-07	-4.8E-08	3.23E-07	7.08E-08	-6.9E-07
	Cys-50	1.64E-06	1.75E-06	2.04E-06	5.17E-07	8.25E-07	9.95E-07	1.53E-06	1.79E-06	1.99E-06	3.17E-06	2.71E-06	2.56E-06	1.72E-06	1.66E-06	2.19E-06	2.23E-06	2.49359E-06	2.63E-06
	Cys-50	2.73E-07	2.87E-07	3.25E-07	5.25E-08	1.43E-07	1.68E-07	5.26E-07	5.35E-07	1.08E-07	1.97E-07	-6.2E-08	-6.1E-10	3.03E-07	1.79E-07	3.2E-08	3.13E-07	3.31115E-07	-5E-07
	GSH-50	3.57E-07	3.34E-07	3.4E-07	4.91E-08	1.19E-07	2.56E-07	5.84E-07	7.06E-07	5.15E-07	1.25E-06	6.35E-07	5.15E-07	7.88E-07	6.21E-07	3.58E-07	8.38E-07	3.81165E-07	2.21E-07
	GSH-50	4.39E-07	4.48E-07	4.48E-07	7.6E-08	1.66E-07	3.12E-07	4.52E-07	6.57E-07	4.24E-07	7.41E-07	1.94E-07	1.73E-07	7.44E-07	6.56E-07	3.77E-07	8.02E-07	2.89307E-07	9.64E-08
	GSH-50	3.75E-07	4.04E-07	4.27E-07	5.34E-08	1.21E-07	2.55E-07	3.2E-07	5.96E-07	2.89E-07	6.56E-07	9.22E-08	8.48E-08	6.86E-07	6.45E-07	3.29E-07	8.53E-07	4.40369E-07	1.96E-07
	GSH-50	3.01E-07	3.5E-07	4.09E-07	5E-08	1.15E-07	2.63E-07	2.3E-07	6E-07	2.94E-07	6.45E-07	1.52E-09	-9.5E-09	7.13E-07	7.03E-07	2.86E-07	7.94E-07	4.55017E-07	1.83E-07
	GSH-50	3.88E-07	4.01E-07	4.29E-07	5.71E-08	1.41E-07	3.11E-07	3.35E-07	7.11E-07	4.14E-07	5.77E-07	-9.1E-08	-7.4E-08	6.65E-07	7.06E-07	4.97E-07	8.15E-07	4.62341E-07	1.71E-07
	GSH-50	1.74E-06	1.79E-06	2.06E-06	4.7E-07	8.15E-07	1.22E-06	1.48E-06	1.97E-06	1.97E-06	3.54E-06	3.11E-06	2.87E-06	2.04E-06	2.19E-06	2.67E-06	2.74E-06	2.87232E-06	2.97E-06
	GSH-50	3.23E-07	3.32E-07	3.36E-07	4.64E-08	9.4E-08	2.13E-07	3.32E-07	8.53E-07	4.95E-07	9.35E-07	1.48E-07	1.21E-07	6.35E-07	7.33E-07	3.88E-07	7.18E-07	3.36914E-07	5.68E-08


Report - Microsoft Excel
Select the first column for Y axis (dependent variables)
Discriminant Analysis (DA)
Step 4


Report - Microsoft Excel
Select the full data (Marked dotted) for x axis (Explanatory variables)
After selecting the data click OK
Discriminant Analysis (DA)
Step 5

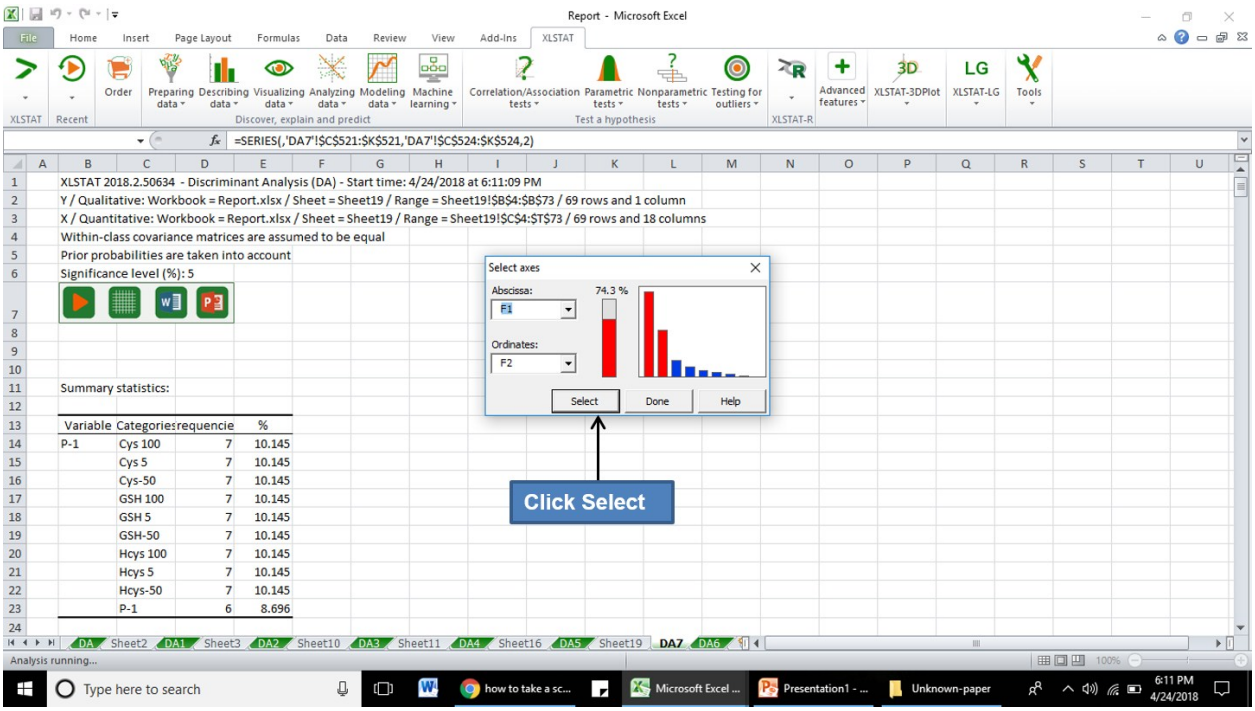

Report - Microsoft Excel
XLSTAT - Selections
List of selections:
Selection name
Rows
Columns
Y / Qualitative
69
1
X / Quantitative
69
18
Do not show this message anymore
Continue
Back
Cancel
Click Continue

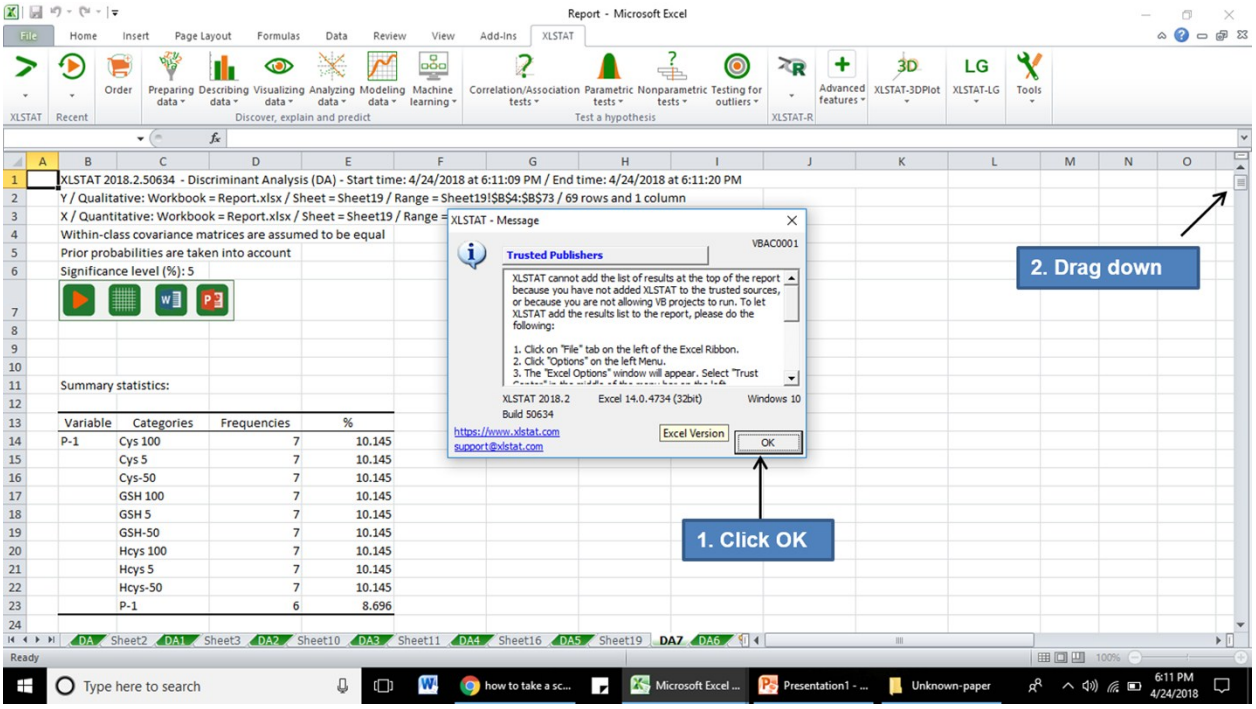
Step 6


Report - Microsoft Excel
XLSTAT - Message
X / Quantitative
DSCIRG01
The first row contains numerical data, while it is expected to contain variable labels.
- Click "Continue" if it is normal that some or all the labels are numbers.
- Click "Back" to go back to the dialog box and modify the options or the data selection.
XLSTAT 2018.2
Excel 14.0.4734 (32bit)
Windows 10
Build 50634
https://www.xlstat.com
Continue
Back
Cancel
Click Continue

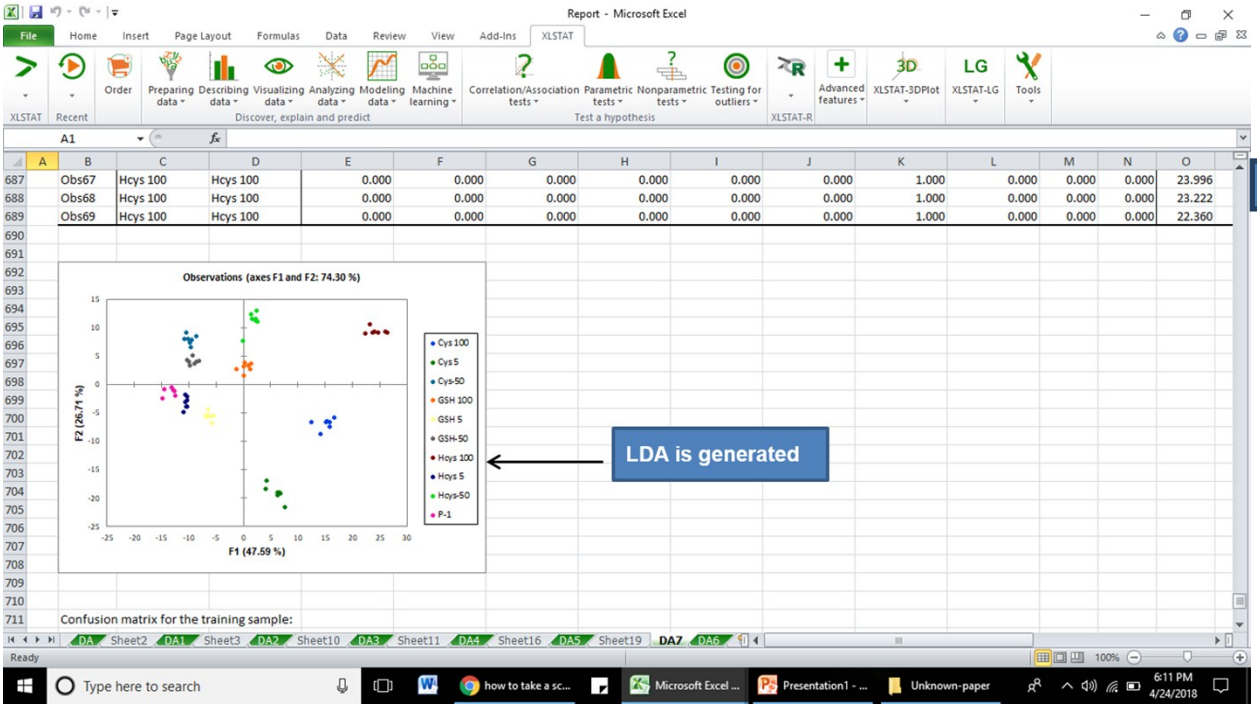
Step 7

Step 8


Report - Microsoft Excel
=SERIES(,'DA7'!$C$521:$K$521,'DA7'!$C$524:$K$524,2)
XLSTAT 2018.2.50634 - Discriminant Analysis (DA) - Start time: 4/24/2018 at 6:11:09 PM
Y / Qualitative: Workbook = Report.xlsx / Sheet = Sheet19 / Range = Sheet19!$B$4:$B$73 / 69 rows and 1 column
X / Quantitative: Workbook = Report.xlsx / Sheet = Sheet19 / Range = Sheet19!$C$4:$T$73 / 69 rows and 18 columns
Within-class covariance matrices are assumed to be equal
Prior probabilities are taken into account
Significance level (%): 5
Summary statistics:
Variable Categories Frequencie %
P-1 Cys 100 7 10.145
Cys 5 7 10.145
Cys-50 7 10.145
GSH 100 7 10.145
GSH 5 7 10.145
GSH-50 7 10.145
Hcys 100 7 10.145
Hcys 5 7 10.145
Hcys-50 7 10.145
P-1 6 8.696
Select axes
Abscissa:
F1
74.3 %
Ordinates:
F2
Select
Done
Help
Click Select

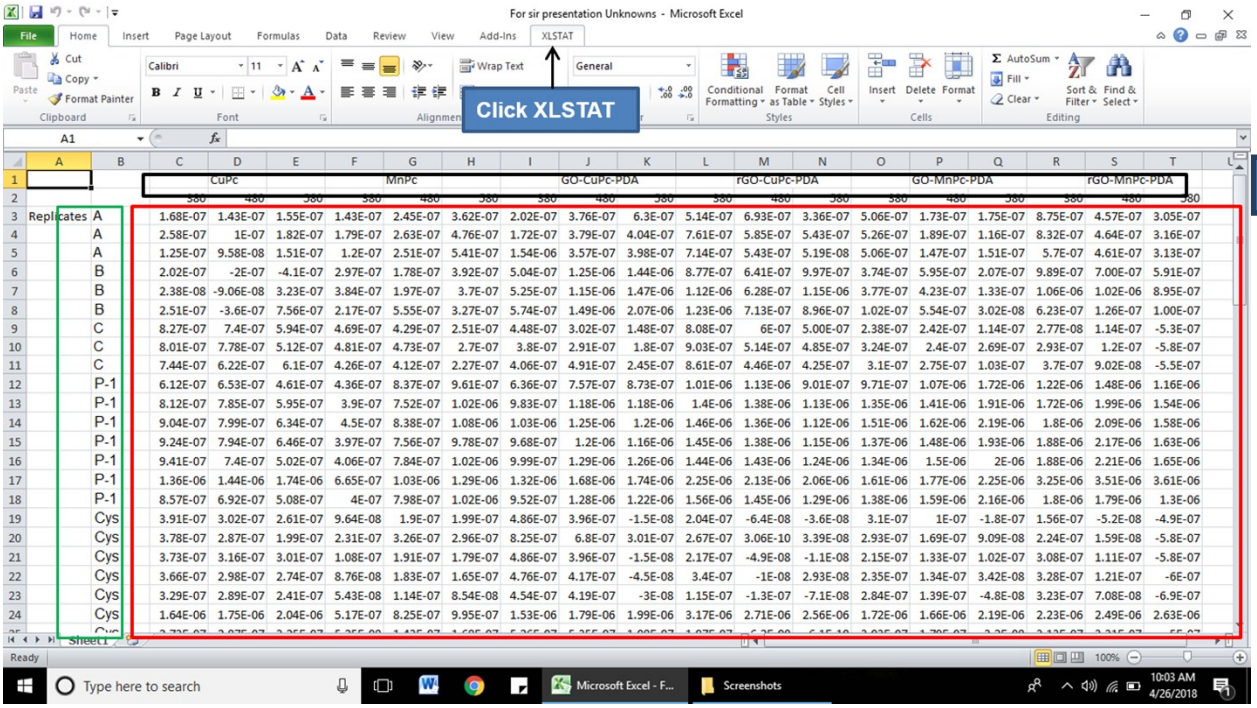

Report - Microsoft Excel
XLSTAT 2018.2.50634 - Discriminant Analysis (DA) - Start time: 4/24/2018 at 6:11:09 PM / End time: 4/24/2018 at 6:11:20 PM
Y / Qualitative: Workbook = Report.xlsx / Sheet = Sheet19 / Range = Sheet19!$B$4:$B$73 / 69 rows and 1 column
X / Quantitative: Workbook = Report.xlsx / Sheet = Sheet19 / Range =
Within-class covariance matrices are assumed to be equal
Prior probabilities are taken into account
Significance level (%): 5
Summary statistics:
Variable Categories Frequencies %
P-1 Cys 100 7 10.145
Cys 5 7 10.145
Cys-50 7 10.145
GSH 100 7 10.145
GSH 5 7 10.145
GSH-50 7 10.145
Hcys 100 7 10.145
Hcys 5 7 10.145
Hcys-50 7 10.145
P-1 6 8.696
XLSTAT - Message
VBAC0001
Trusted Publishers
XLSTAT cannot add the list of results at the top of the report because you have not added XLSTAT to the trusted sources, or because you are not allowing VB projects to run. To let XLSTAT add the results list to the report, please do the following:
1. Click on "File" tab on the left of the Excel Ribbon.
2. Click "Options" on the left Menu.
3. The "Excel Options" window will appear. Select "Trust
XLSTAT 2018.2 Excel 14.0.4734 (32bit) Windows 10
Build 50634
https://www.xlstat.com
support@xlstat.com
Excel Version
OK
2. Drag down
1. Click OK

Step 9

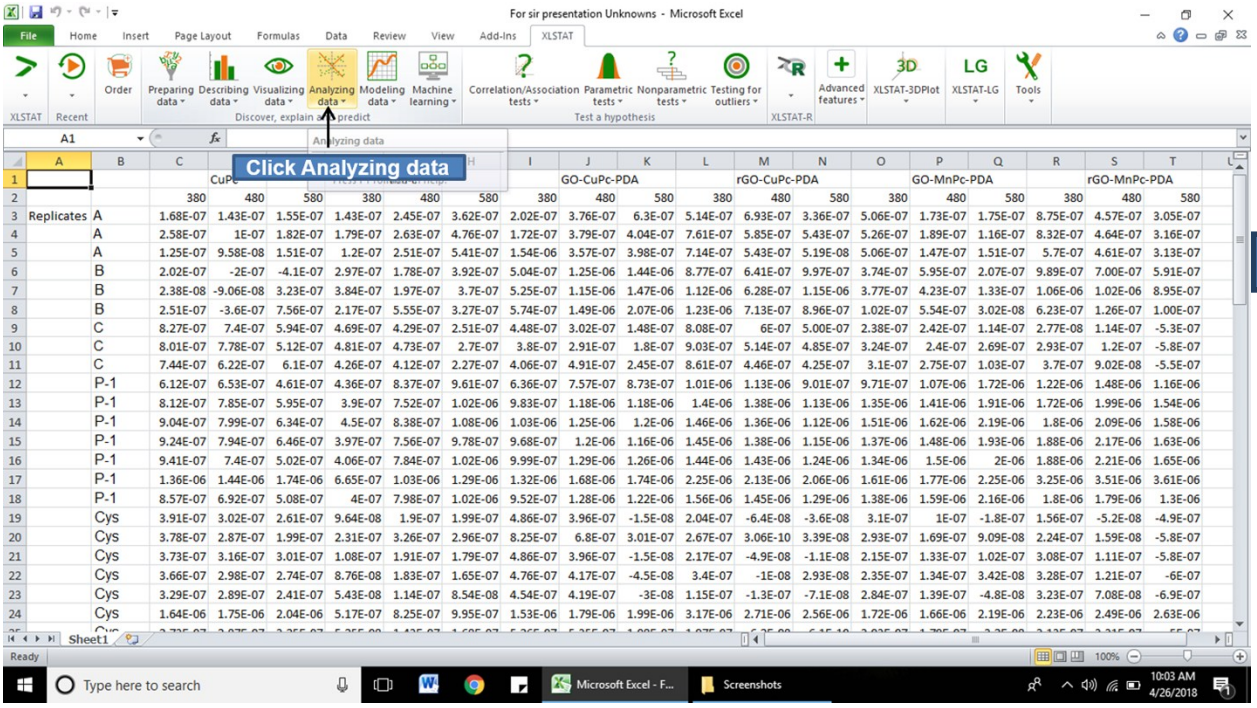

Report - Microsoft Excel
Observations (axes F1 and F2: 74.30 %)
F2 (26.71 %)
F1 (47.59 %)
Cys 100
Cys 5
Cys-50
GSH 100
GSH 5
GSH-50
Hcys 100
Hcys 5
Hcys-50
P-1
LDA is generated
Confusion matrix for the training sample:

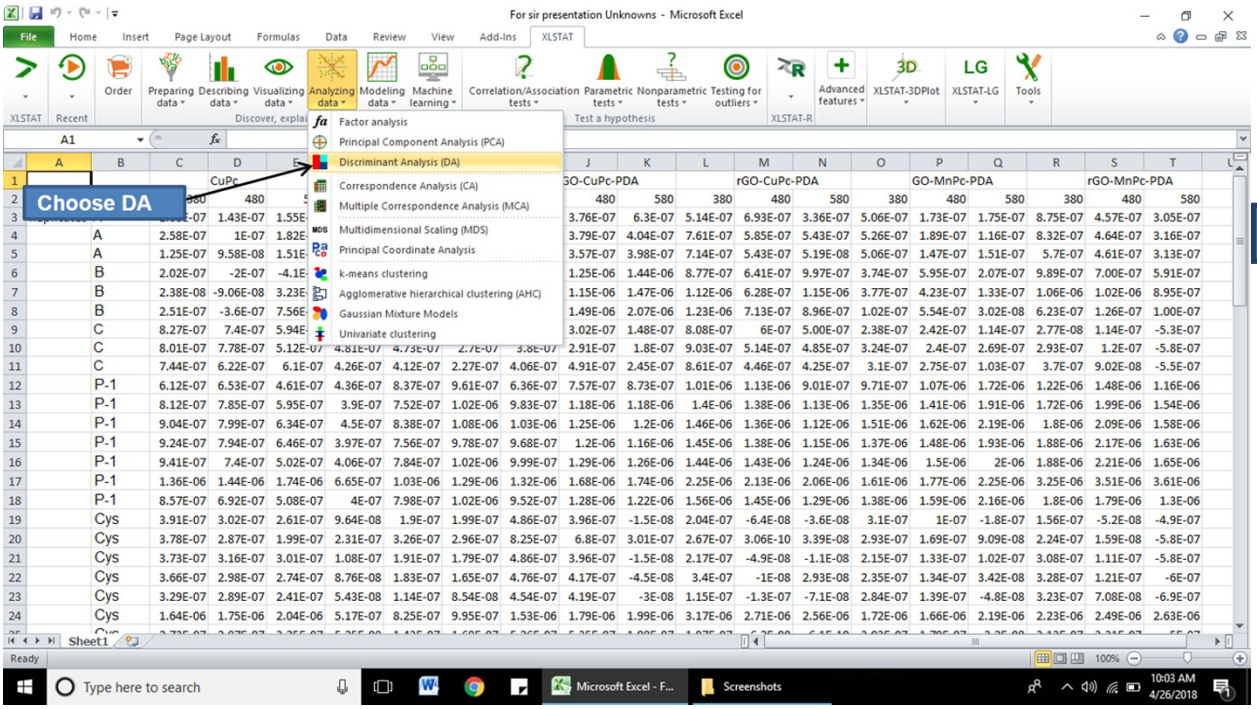
Step 10

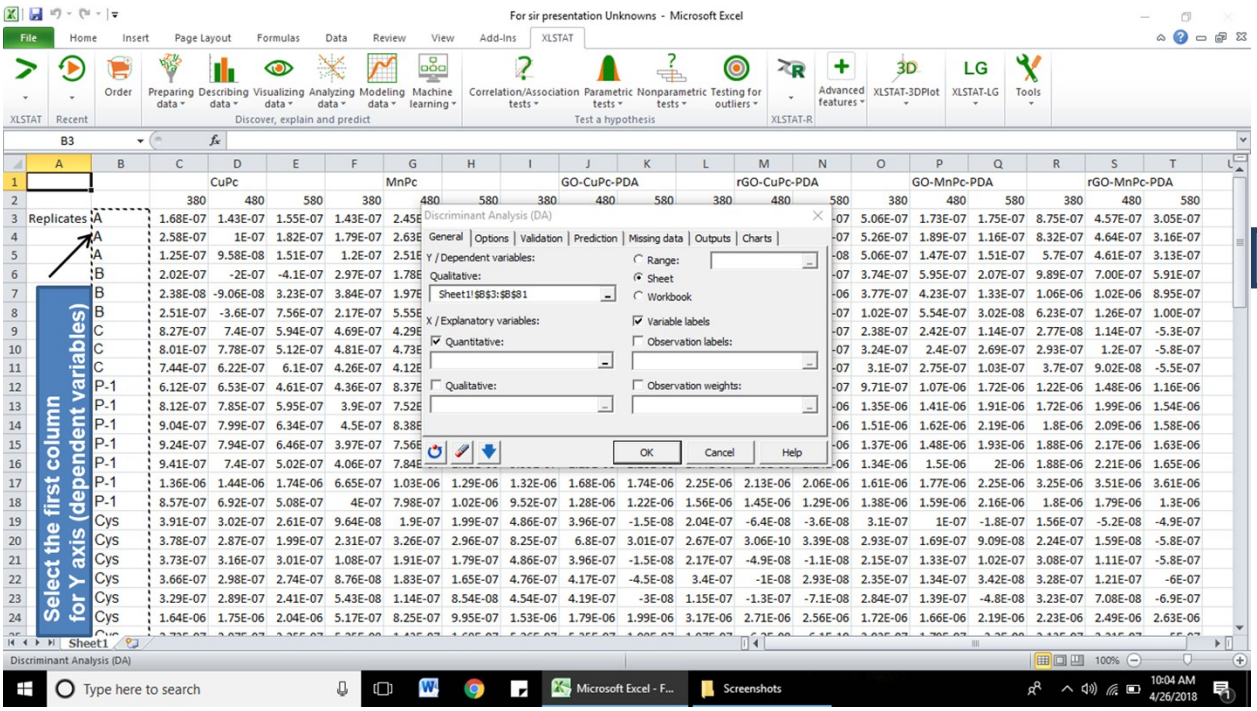
Step wise procedure for generating LDA score plot shown in Figure 11b.

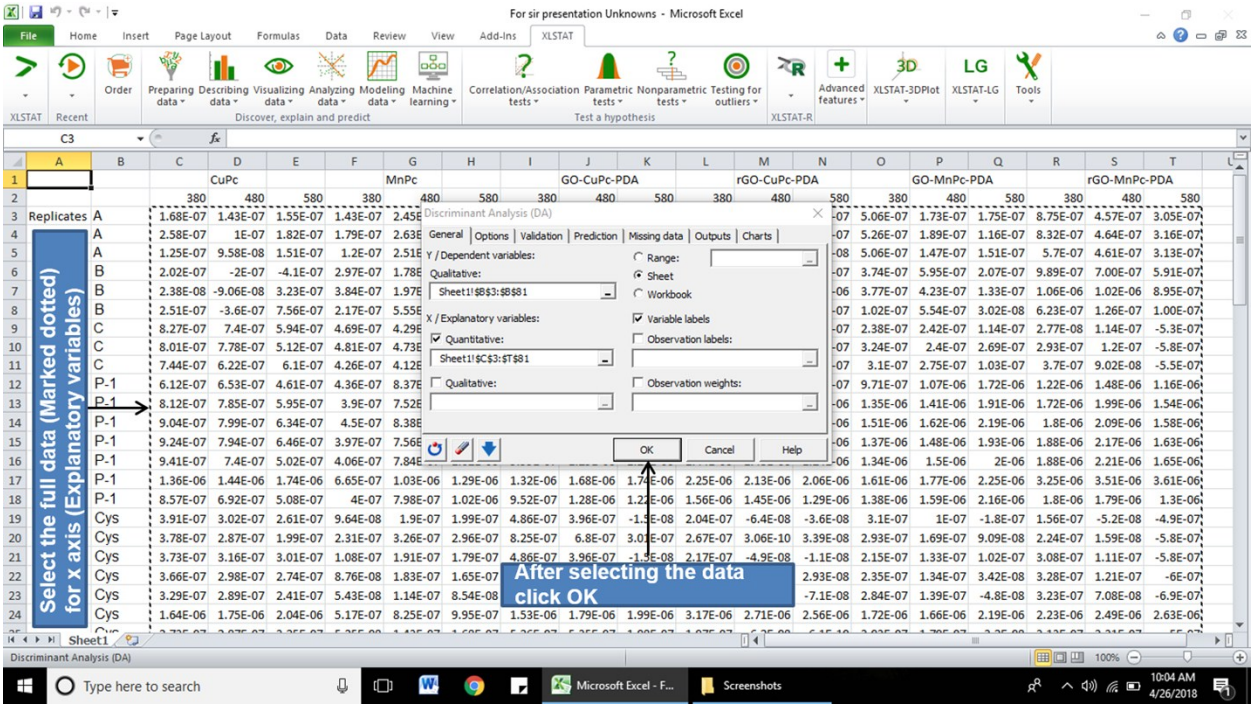


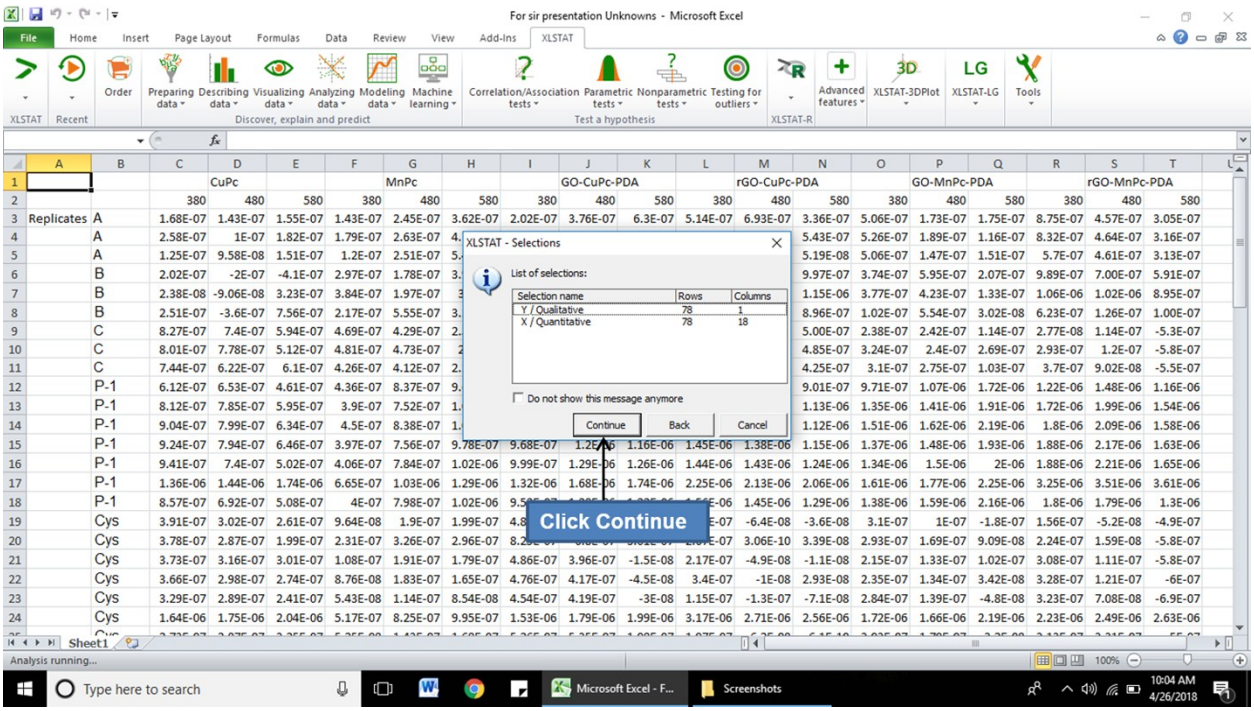
Red Box: Contains difference in current value at particular potential (380 mV, 480mV and 580 mV) obtained from the LSV. **Green Box**: Shows the label of the replicates. **Black Box**: Shows the name the electrode used as working electrode.


For sir presentation Unknowns - Microsoft Excel
Click Analyzing data
Analyzing data
Step 2

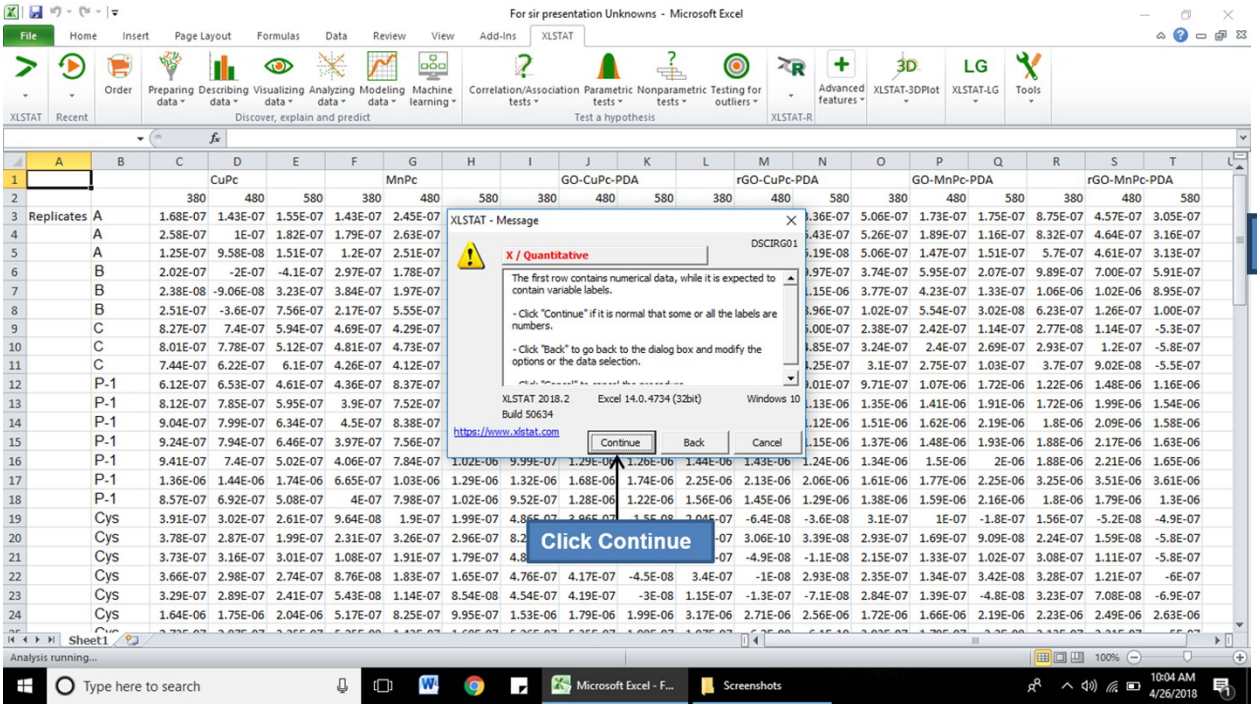

For sir presentation Unknowns - Microsoft Excel
Choose DA
Factor analysis
Principal Component Analysis (PCA)
Discriminant Analysis (DA)
Correspondence Analysis (CA)
Multiple Correspondence Analysis (MCA)
Multidimensional Scaling (MDS)
Principal Coordinate Analysis
k-means clustering
Agglomerative hierarchical clustering (AHC)
Gaussian Mixture Models
Univariate clustering
Step 3


Select the first column for Y axis (dependent variables)
Step 4


Select the full data (Marked dotted) for x axis (Explanatory variables)
After selecting the data click OK
Step 5


For sir presentation Unknowns - Microsoft Excel
XLSTAT - Selections
List of selections:
Selection name | Rows | Columns
Y / Qualitative | 78 | 1
X / Quantitative | 78 | 18
Do not show this message anymore
Continue
Back
Cancel
Click Continue

Step 6


For sir presentation Unknowns - Microsoft Excel
XLSTAT - Message
X / Quantitative
DSCIRG01
The first row contains numerical data, while it is expected to contain variable labels.
- Click "Continue" if it is normal that some or all the labels are numbers.
- Click "Back" to go back to the dialog box and modify the options or the data selection.
XLSTAT 2018.2
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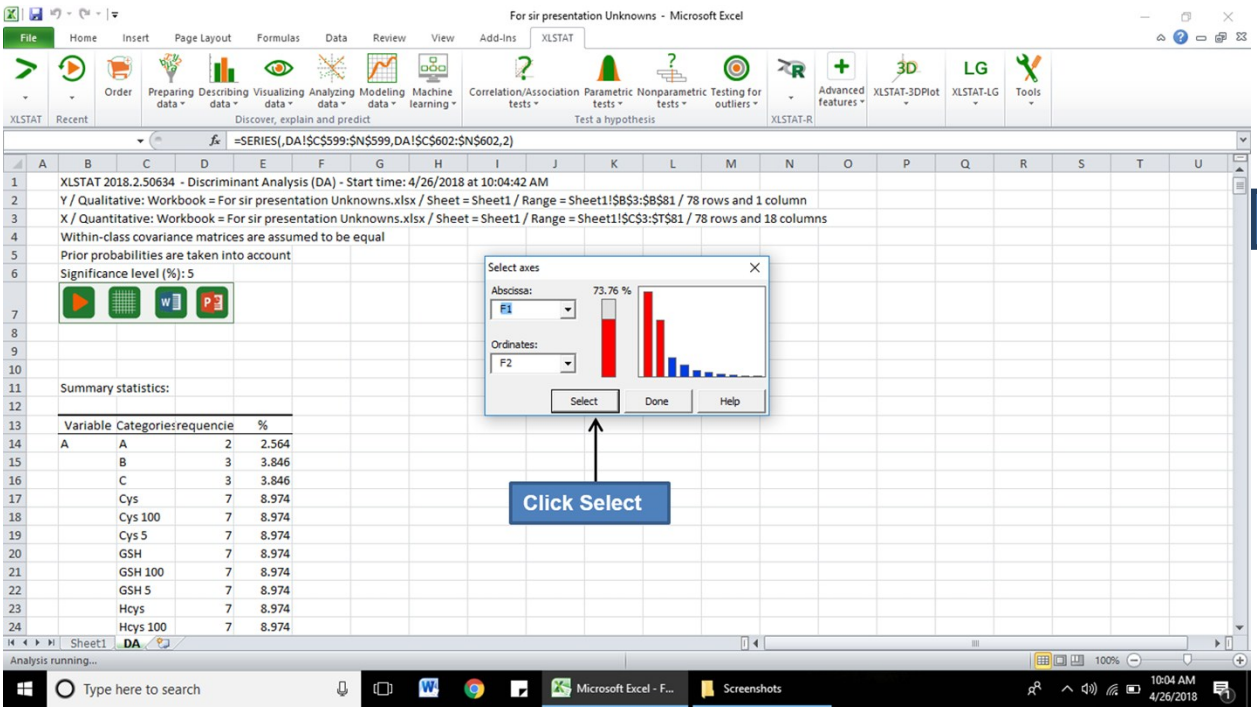
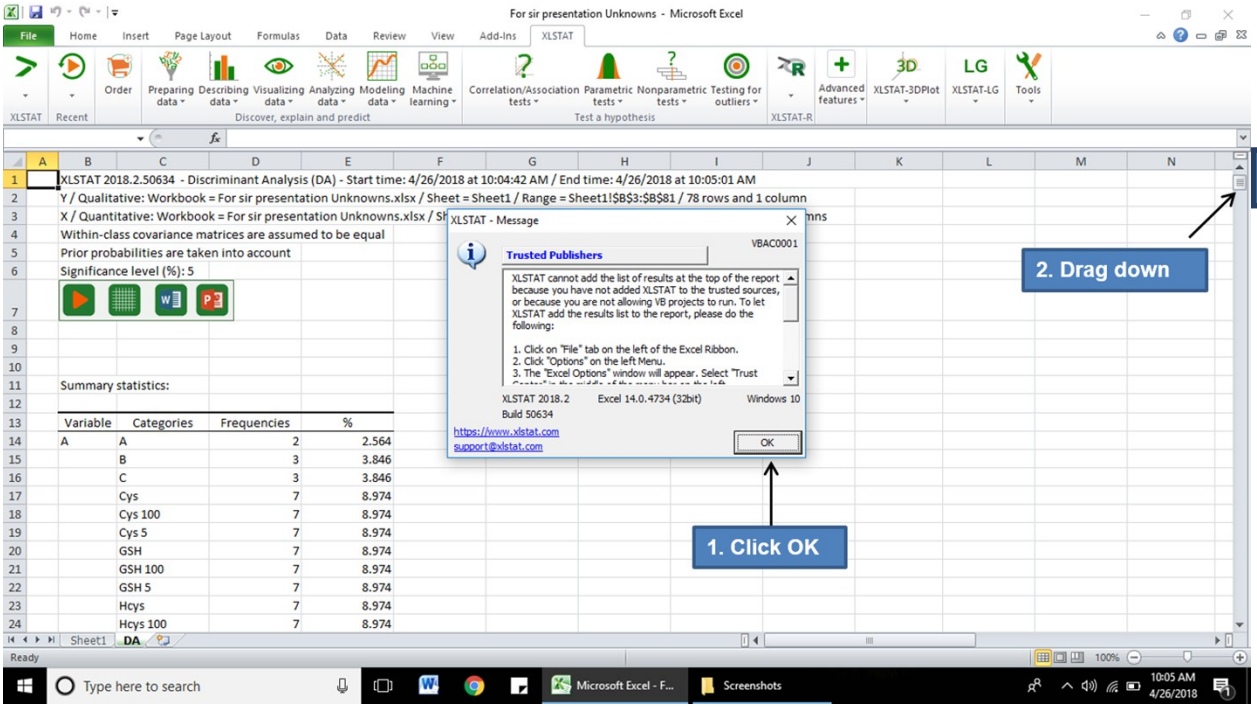
Continue
Back
Cancel
Click Continue

Step 7


For sir presentation Unknowns - Microsoft Excel
=SERIES(,DA!$C$599:$N$599,DA!$C$602:$N$602,2)
XLSTAT 2018.2.50634 - Discriminant Analysis (DA) - Start time: 4/26/2018 at 10:04:42 AM
Y / Qualitative: Workbook = For sir presentation Unknowns.xlsx / Sheet = Sheet1 / Range = Sheet1!$B$3:$B$81 / 78 rows and 1 column
X / Quantitative: Workbook = For sir presentation Unknowns.xlsx / Sheet = Sheet1 / Range = Sheet1!$C$3:$T$81 / 78 rows and 18 columns
Within-class covariance matrices are assumed to be equal
Prior probabilities are taken into account
Significance level (%): 5
Summary statistics:
Variable Categories Frequencies %
A A 2 2.564
B 3 3.846
C 3 3.846
Cys 7 8.974
Cys 100 7 8.974
Cys 5 7 8.974
GSH 7 8.974
GSH 100 7 8.974
GSH 5 7 8.974
Hcys 7 8.974
Hcys 100 7 8.974
Select axes
Abscissa:
F1
73.76 %
Ordinates:
F2
Select
Done
Help
Click Select
Step 8


For sir presentation Unknowns - Microsoft Excel
XLSTAT 2018.2.50634 - Discriminant Analysis (DA) - Start time: 4/26/2018 at 10:04:42 AM / End time: 4/26/2018 at 10:05:01 AM
Y / Qualitative: Workbook = For sir presentation Unknowns.xlsx / Sheet = Sheet1 / Range = Sheet1!$B$3:$B$81 / 78 rows and 1 column
X / Quantitative: Workbook = For sir presentation Unknowns.xlsx / Sheet = Sheet1 / Range = Sheet1!$C$3:$T$81 / 78 rows and 18 columns
Within-class covariance matrices are assumed to be equal
Prior probabilities are taken into account
Significance level (%): 5
Summary statistics:
Variable Categories Frequencies %
A A 2 2.564
B 3 3.846
C 3 3.846
Cys 7 8.974
Cys 100 7 8.974
Cys 5 7 8.974
GSH 7 8.974
GSH 100 7 8.974
GSH 5 7 8.974
Hcys 7 8.974
Hcys 100 7 8.974
XLSTAT - Message
VBAC0001
Trusted Publishers
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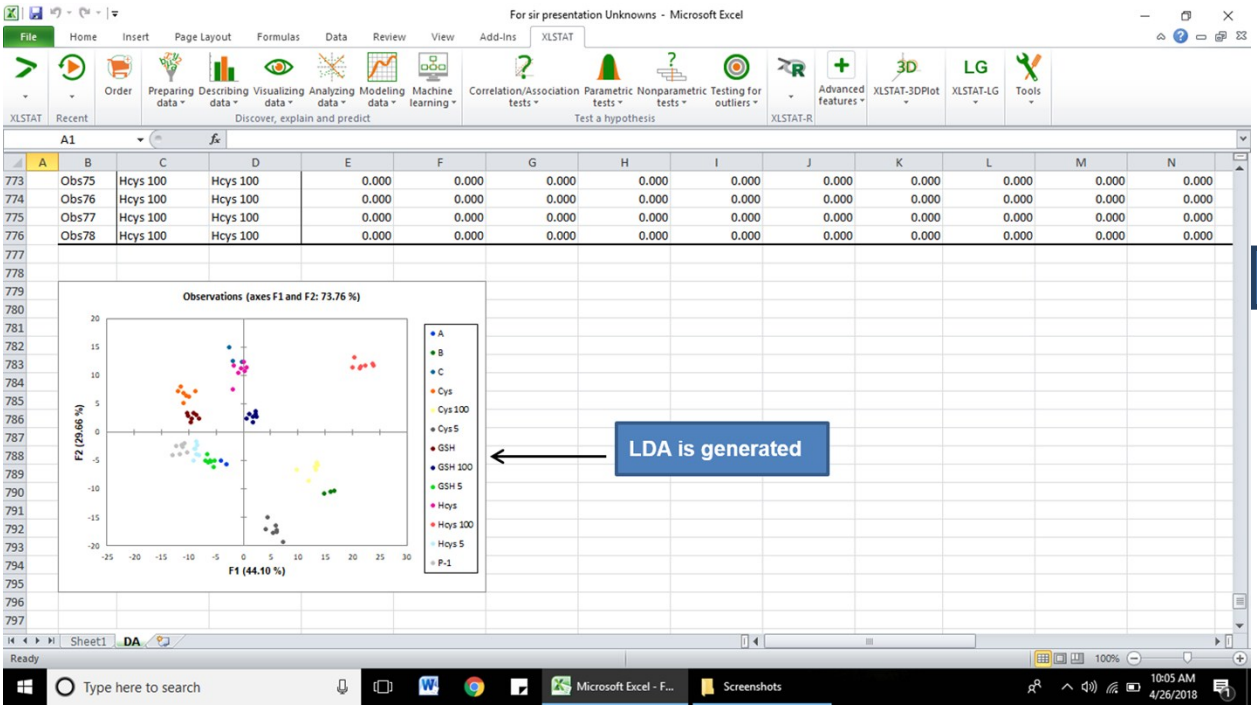
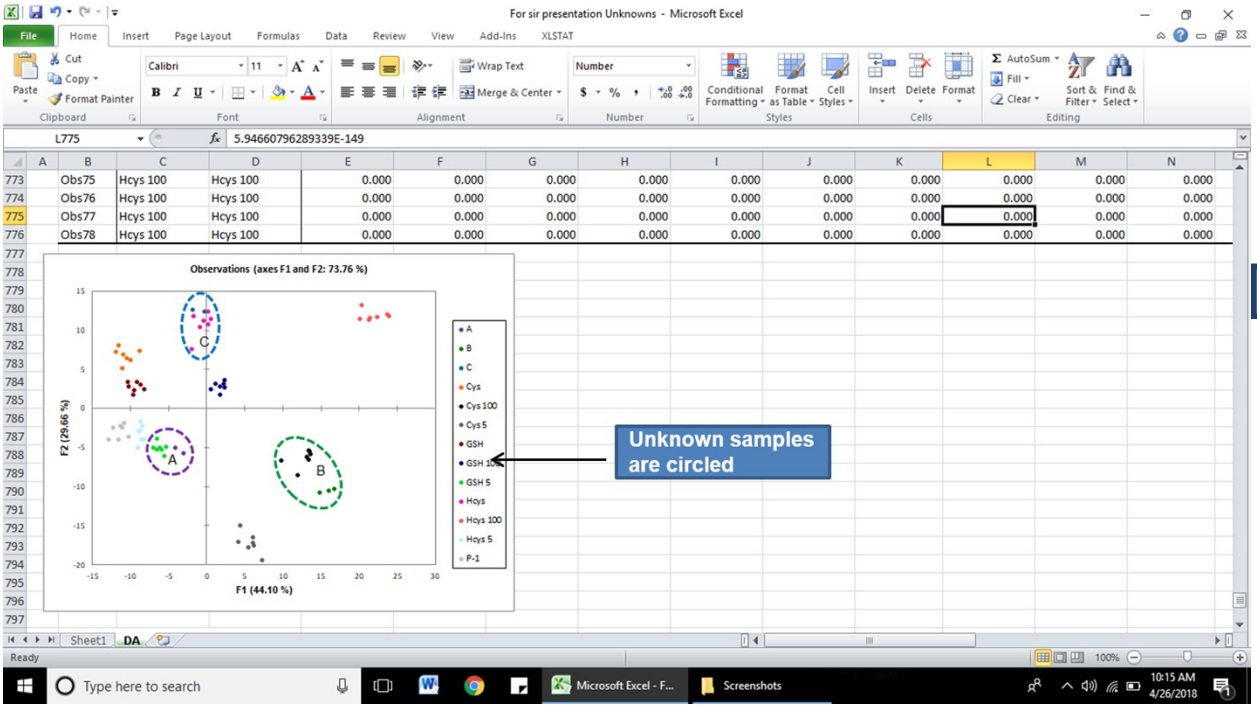
1. Click on "File" tab on the left of the Excel Ribbon.
2. Click "Options" on the left Menu.
3. The "Excel Options" window will appear. Select "Trust
XLSTAT 2018.2 Excel 14.0.4734 (32bit) Windows 10
Build 50634
https://www.xlstat.com
support@xlstat.com
OK
1. Click OK
2. Drag down
Step 9



Step 10



Step 11

6. Reference

1. S. Moeno, R.W. M. Krause, E. A. Ermilov, W. Kuzyniak and M. Höpfner, *Photochem. Photobiol. Sci.*, 2014, **13**, 963970
2. H. Xu, Q. Yang, F. Li, L. Tang, S. G. B. Jiang, X. Zhao, L. Wangand and C. Fan. *Analyst*, 2013, **138**, 2678–2682.
3. Z. Yang, Q. Zheng, H. Qiu, J. LI and J. Yang, *New Carbon Mater*., 2015, **30**, 41–47.
4. C. M. Parnell, B. Chhetri, A. Brandt, F. Watanabe, Z. A. Nima, T. K. Mudalige, A. S. Biris and A. Ghosh, *Sci. Rep.,* 2016, **6**, 31415.
5. S. Palanisamy, B. Thirumalraj, S.-M. Chen, Y.-. Wang, V. Velusamy and K. Ramaraj, *Sci. Rep*., 2016, **6**, 33599.
6. rice.edu, http://www.ruf.rice.edu/~bioslabs/methods/protein/abs280.html, (accessed April 2018).