Supplementary data

For

Manganese sulfanyl porphyrazine–MWCNT nanohybrid electrode material as a catalyst for H_2O_2 and glucose biosensors

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Figure S1. CVs of GC (A), and GC/MWCNT (B) electrodes. An experiment was recorded in PB (pH 7.4) before (a, marked by black line) and after (b, marked by blue line) 2 mM H_2O_2 addition. Scan rate 10 mV s^{-1}.

Figure S2. The results of cyclic voltammetry studies of (A) GC, (C) GC/MWCNT, (E) GC/MWCNT/Pz3, and (G) GC/MWCNT/Pz3/GOx in phosphate buffer (pH 7.4) containing 1 mM $K_3[Fe(CN)_6]$ at the scan rate range 0.01–0.05 V s^{-1}. (B, D, F, H) Change in peak cathode currents as a function of the applied square root of the scan rate for appropriate electrodes.

Figure S3. Chronoamperometric response to the addition of 1 mM Glu for the GC/MWCNT/GOx (a, marked by black line), and GC/MWCNT/Pz3/GOx (b, marked by blue line) electrode at an applied potential of +0.6 V.

Figure S4. Cyclic voltammograms of the 7 newly prepared GC/MWCNT/Pz3/GOx electrodes recorded in PB buffer at 50 mV s^{-1}. RSD is equal 4.6% (n = 7).

Figure S5. Stability of the GC/MWCNT/Pz3/GOx biosensor to a 1 mM Glu response recorded over time. with an applied potential of +0.6 V.

Figure S6. Chronoamperometric responses recorded at the GC/MWCNT/Pz3/GOx biosensor upon the addition of glucose and selected interferents with an applied potential of +0.6 V. The supporting electrolyte: phosphate buffer (PB, pH 7.4).

Figure S7. (A) Chronoamperometric curve recorded at +0.6 V in PB after additions of real sample and 1 mM glucose standard solutions. (B) Standard addition curve corresponding to curve presented in (A). RSD = 0.7% (n = 3).

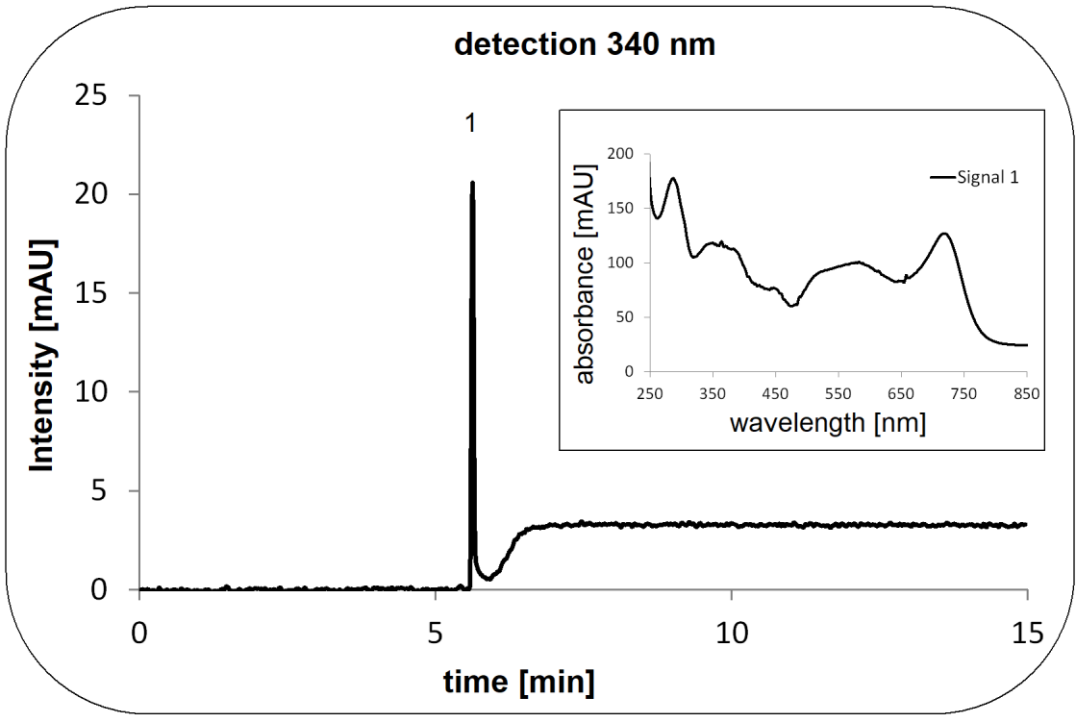
1. HPLC purity

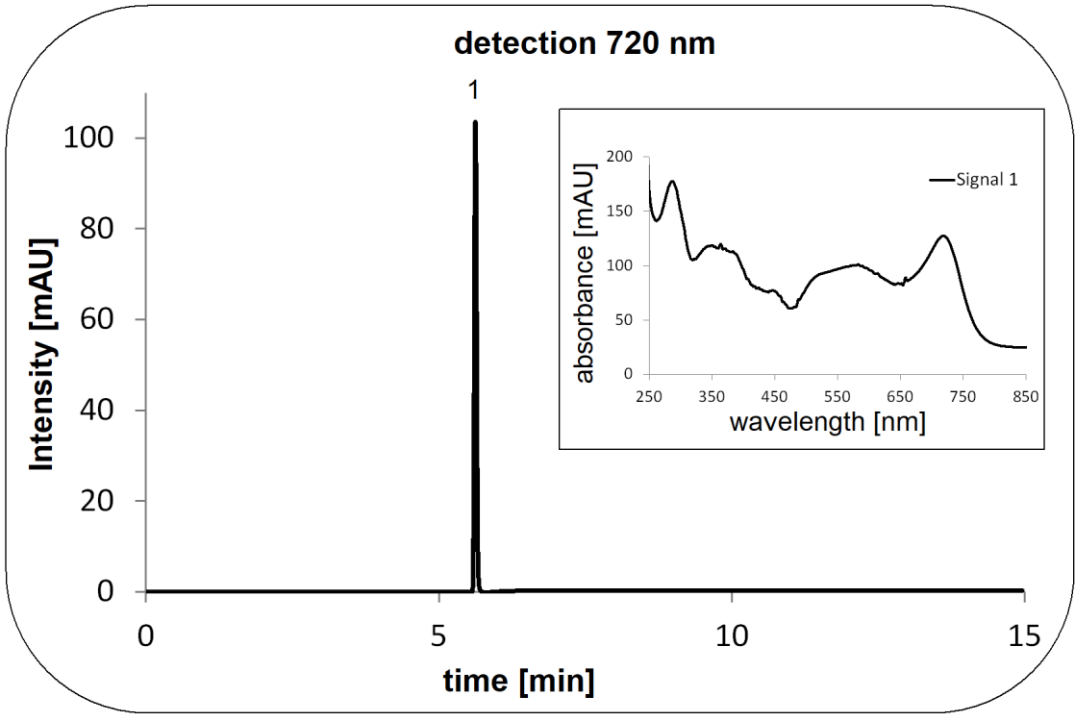
The HPLC analysis using an Agilent 1200 instrument equipped with a UV-DAD detector was utilized to assess the purity of macrocycle **3**. An octadecylsilane-coated column (Eclipse XDB-C18, 150 mm × 4.6 mm, 5 μm, Agilent) was used for chromatographic separations with gradient elution conditions at a 1 mL/min flow rate. Band dispersion and additional peaks from aggregates significantly hampered HPLC analysis. The best conditions for the compounds are shown below.

Manganese(III) porphyrazine (3)

Configuration 1

Phase		
time [min]	**dichloromethane**	**methanol**
0	100	0
3	100	0
4	75	25
15	75	25

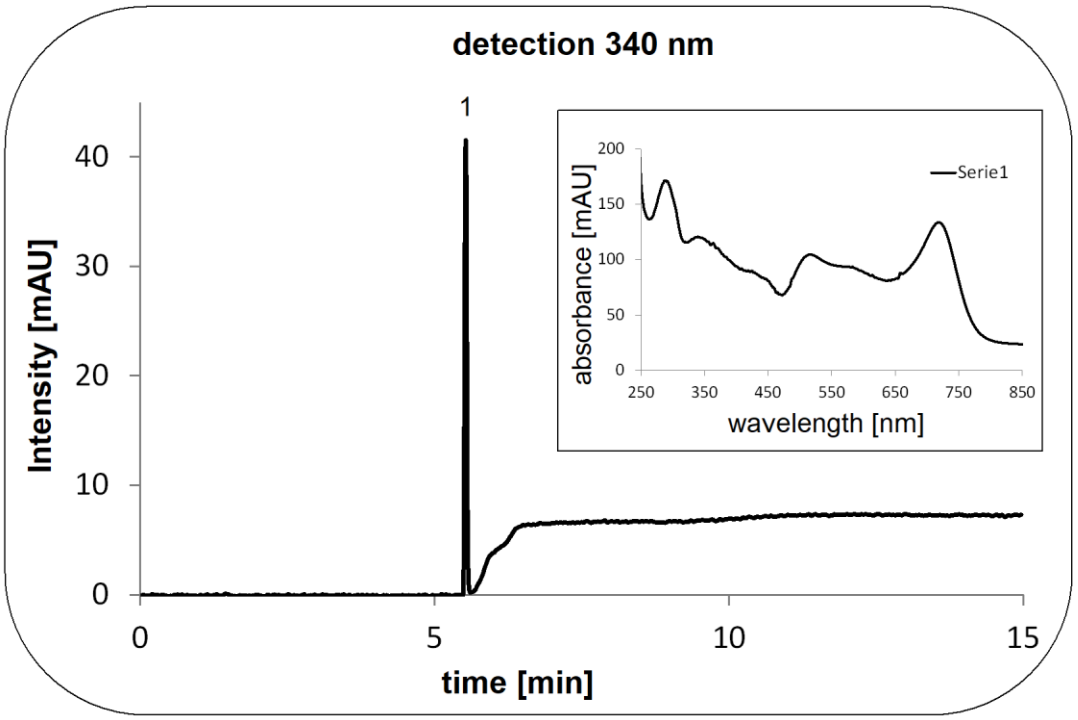


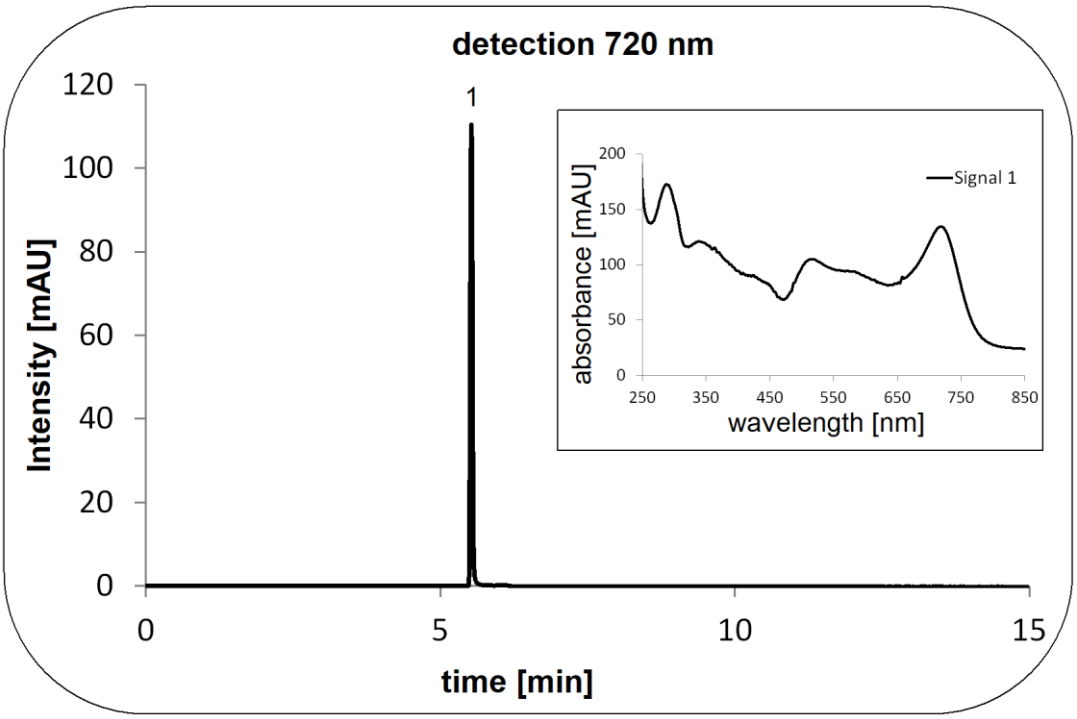


Results			
signal	**retention time [min]**	**area**	**purity [%]**
detection 340 nm			
1	5.6	59.7	100.0
detection 720 nm			
1	5.6	104.5	100.0

Configuration 2

Phase		
time [min]	**dichloromethane**	**2-propanol**
0	100	0
3	100	0
4	40	60
15	40	60

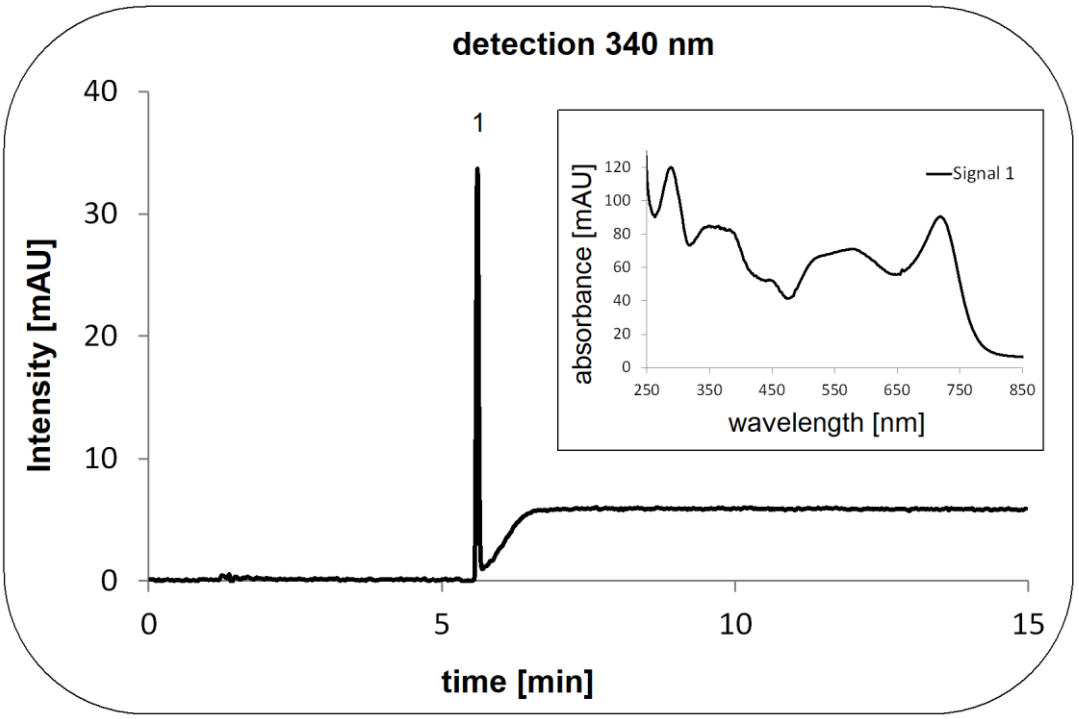


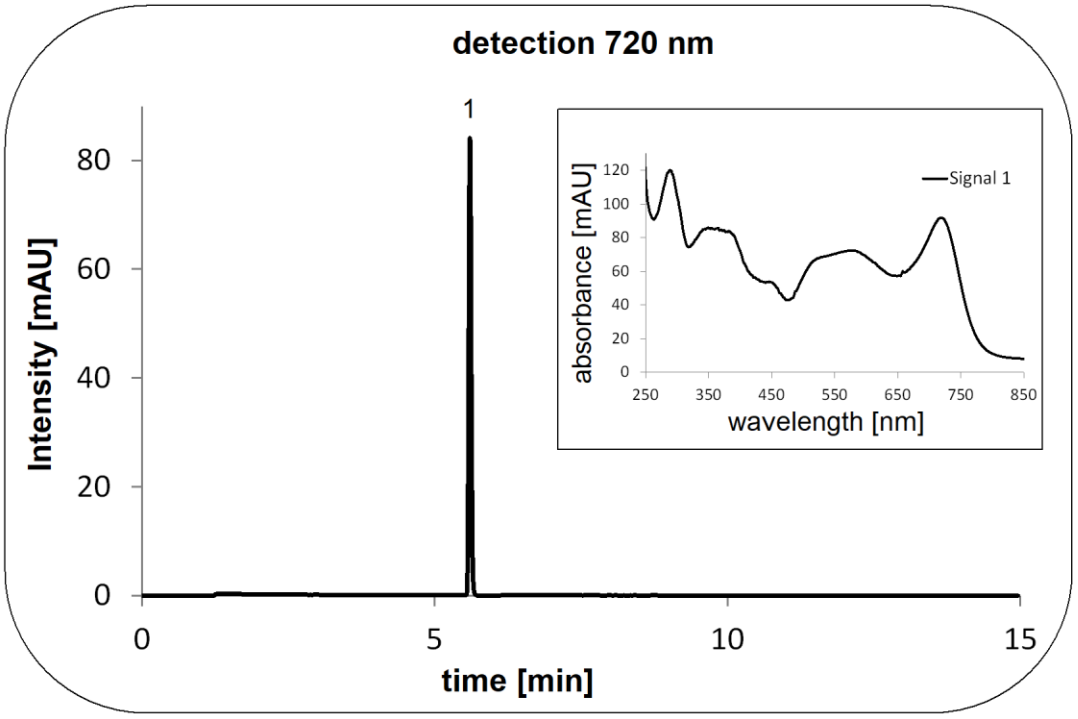


Results			
signal	**retention time [min]**	**area**	**purity [%]**
detection 340 nm			
1	5.5	106.6	100.0
detection 720 nm			
1	5.5	287.9	100.0

Configuration 3

Phase				
time [min]	**dichloromethane**	**acetonitrile**	**methanol**	**2-propanol**
0	80	20	0	0
3	80	20	0	0
4	60	10	20	10
15	60	10	20	10





Results			
signal	**retention time [min]**	**area**	**purity [%]**
detection 340 nm			
1	5.6	99.2	100.0
detection 720 nm			
1	5.6	246.6	100.0

2. Electrochemical studies

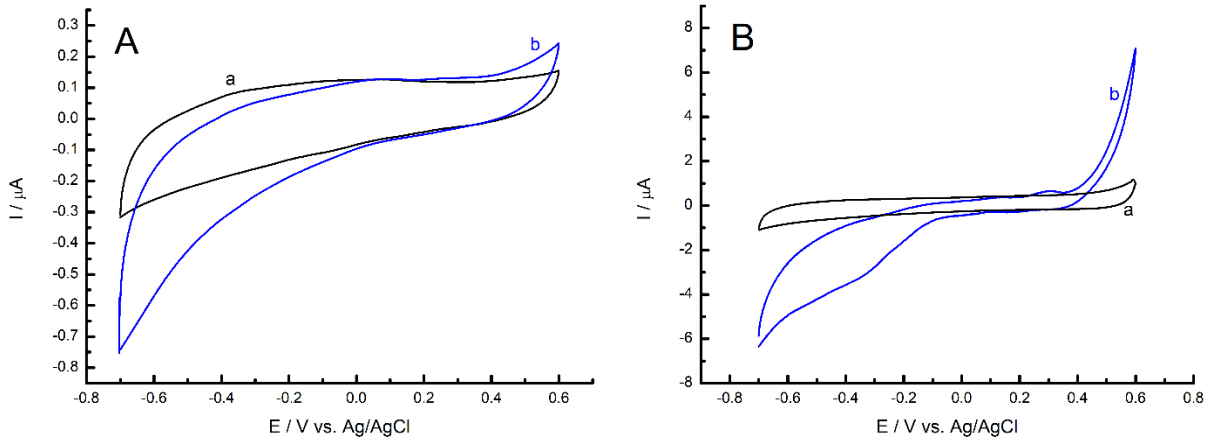


Figure S1. CVs of GC (A), and GC/MWCNT (B) electrodes. An experiment was recorded in PB (pH 7.4) before (a, marked by black line) and after (b, marked by blue line) 2 mM H_2O_2 addition. Scan rate 10 mV s^{-1}.

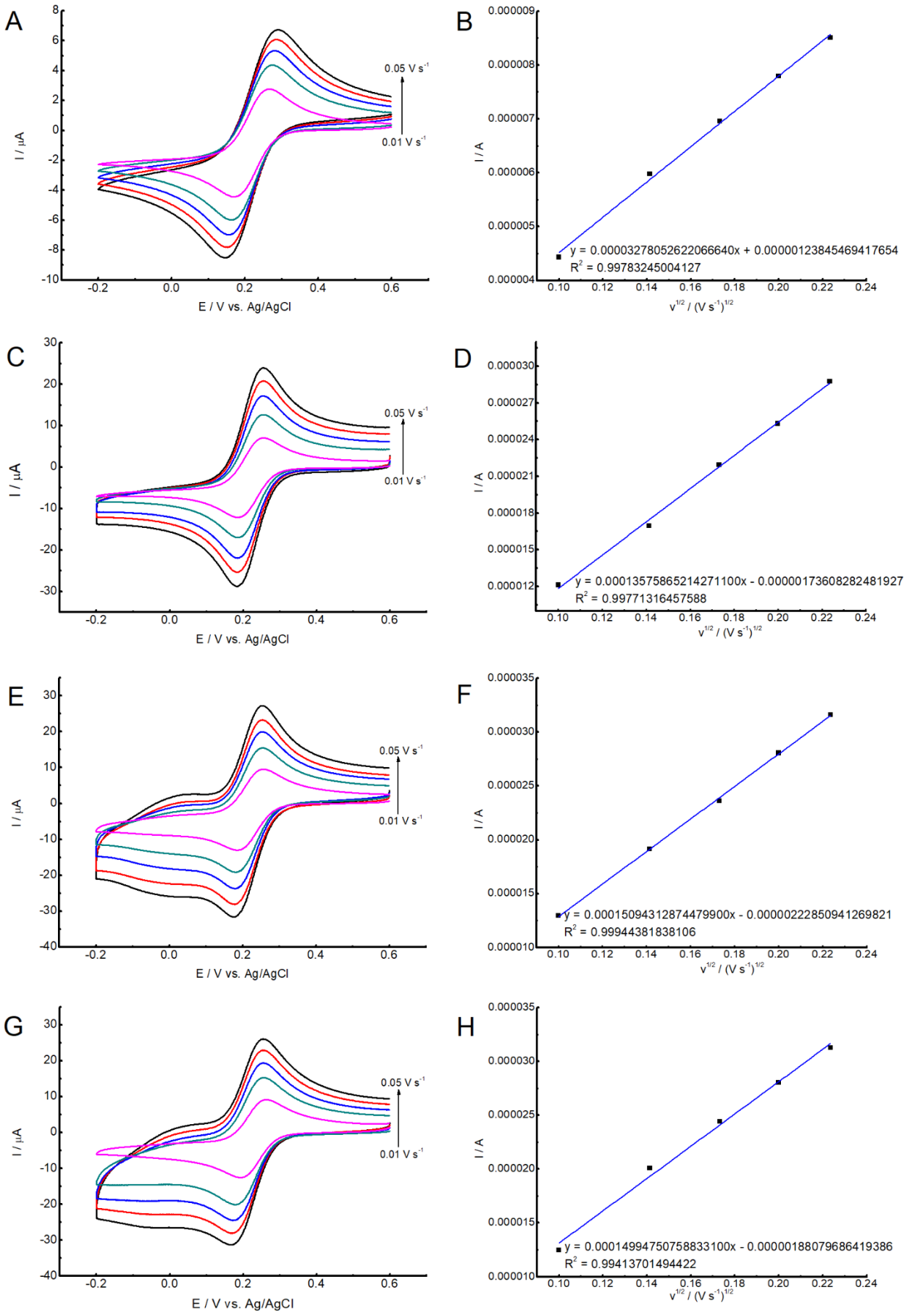

A
I / μA
E / V vs. Ag/AgCl
0.05 V s-1
0.01 V s-1
B
I / A
v1/2 / (V s-1)1/2
y = 0.00003278052622066640x + 0.00000123845469417654
R2 = 0.99783245004127
C
I / μA
E / V vs. Ag/AgCl
0.05 V s-1
0.01 V s-1
D
I / A
v1/2 / (V s-1)1/2
y = 0.00013575865214271100x - 0.00000173608282481927
R2 = 0.99771316457588
E
I / μA
E / V vs. Ag/AgCl
0.05 V s-1
0.01 V s-1
F
I / A
v1/2 / (V s-1)1/2
y = 0.00015094312874479900x - 0.00000222850941269821
R2 = 0.99944381838106
G
I / μA
E / V vs. Ag/AgCl
0.05 V s-1
0.01 V s-1
H
I / A
v1/2 / (V s-1)1/2
y = 0.00014994750758833100x - 0.00000188079686419386
R2 = 0.99413701494422

Figure S2. The results of cyclic voltammetry studies of (A) GC, (C) GC/MWCNT, (E) GC/MWCNT/**Pz3**, and (G) GC/MWCNT/**Pz3**/GOx in phosphate buffer (pH 7.4) containing 1 mM $K_3[Fe(CN)_6]$ at the scan rate range 10–50 mV s^{-1}. (B, D, F, H) Change in peak cathode currents as a function of the applied square root of the scan rate for appropriate electrodes.

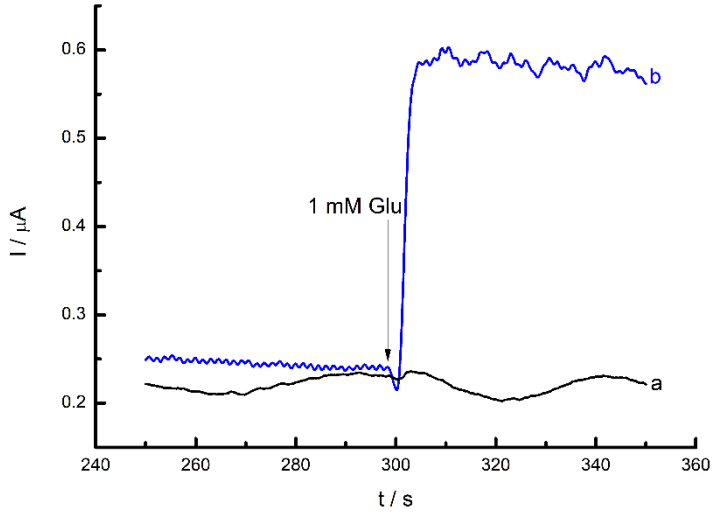


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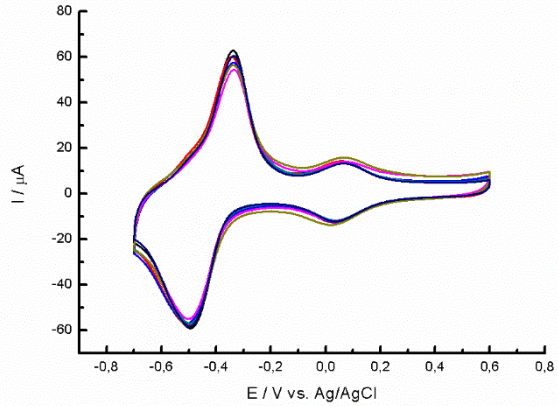


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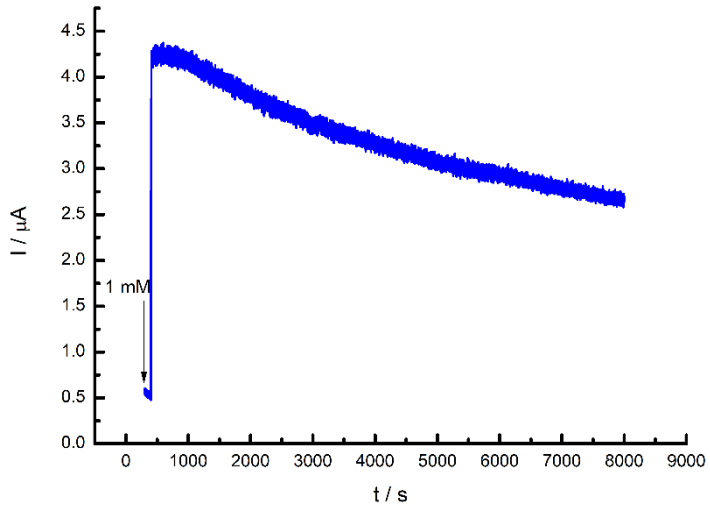


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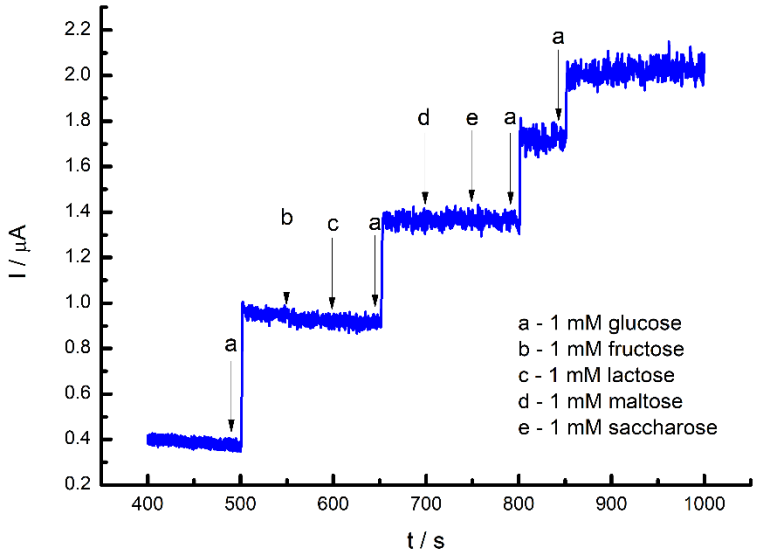


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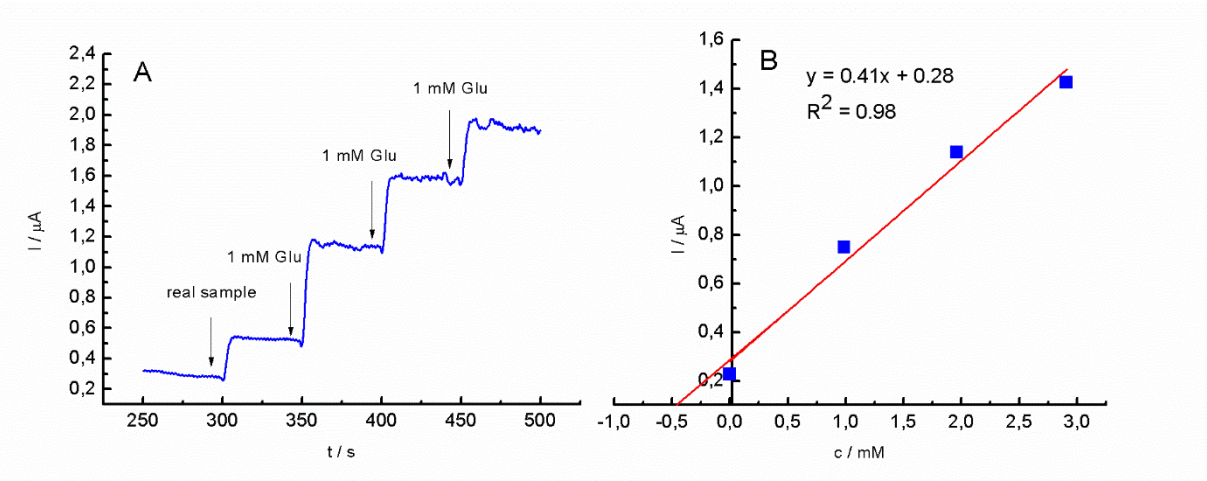


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