Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Sensitive Electrochemical Detection of Metabisulphite in Gastrointestinal Fluids

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Table S1. Formulations of the stimulated salivary fluid (SSF) and the simulated gastric fluid (SGF) at the specified pH values.

			SSF		SGF	
			pH 7		pH 3	
Constituent	Stock conc.		Vol. of stock	Conc. in SSF	Vol. of stock	Conc. in SGF
	g L^{-1}	**mol L^{-1}**	**mL**	**mmol L^{-1}**	**mL**	**mmol L^{-1}**
KCl	37.3	0.5	15.1	15.1	6.9	6.9
KH_2PO_4	68	0.5	3.7	3.7	0.9	0.9
$NaHCO_3$	84	1	6.8	13.6	12.5	25
NaCl	117	2	—	—	11.8	47.2
$MgCl_2(H_2O)_6$	30.5	0.15	0.5	0.15	0.4	0.1
$(NH_4)_2CO_3$	48	0.5	0.06	0.06	0.5	0.5
For pH adjustment						
	mol L^{-1}		**mL**	**mmol L^{-1}**	**mL**	**mmol L^{-1}**
NaOH	1		—	—	—	—
HCl	6		0.09	1.1	1.3	15.6
$CaCl_2(H_2O)_2$ is not added to the simulated digestion fluids, see details in legend						
	g L^{-1}	**mol L^{-1}**		**mmol L^{-1}**		**mmol L^{-1}**
$CaCl_2(H_2O)_2$	44.1	0.3		1.5 (0.75*)		0.15 (0.075*)

[a] * in brackets is the corresponding Ca^{2+} concentration in the final digestion mixture.

Table S2. Comparison of the performance of different electrochemical sensors for the detection of sulphite and bisulphite.

No	Method	Sensor Element/Analyte	Linear range (µM to mM)	Sensitivity (µA/µM cm^{-2})	LOD (µM)	Reference
1	Electrochemical	Sulfite oxidase/sulphite	200 - 1.8	-	200	S1
2	Electrochemical	MWCNT/COOH /Sulphite	400 - 4.4	2.2	80	S2
3	Electrochemical	NiPCNF/AI /Sulphite	40 - 4.2	-	3	S3
4	Electrochemical	NiO nanoplate /Sulphite	16.2 -0.6	2.8	8.8	S4
5	Electrochemical	Zn nanoparticles /Bisulphite	5 - 0.41	-	-	S5
6	HPIC	Bisulphite	3-165 µg/ml			S6
7	UV spectroscopy	Bisulphite	50- 375 µg.ml		1 µg/ml	S7
8	Bisulphite	Au/F-rGO	10 – 1.0	4.9	0.67	This work

High performance ion chromatography

S1. D.J. Shawk, S.S. Dritz, R.D. Goodband, M.D. Tokach, J.C. Woodworth, J.M. Derouchey, F.A. Sem, H.L. Frobose, M.D. Tokach, E.L. Hansen, L.J. McKinney, J.M. Derouchey, R.D. Goodband, J.L. Nelssen, S.S. Dritz, T. City, D. Moll, D., F. Ahmadi, W.H. Lee, Y.K, Oh, K. Park, W.S. Kwak, *Arch. Anim. Nutr*., 2019, **389**, 143–152.

S2. M.H. Pournaghi-Azar, M. Hydarpour, H. Dastangoo, *Anal. Chim. Acta* 2003, **497**, 133–141.

S3. R. Rawal, S. Chawla, T. Dahiya, C.S. Pundir, *Anal. Bioanal. Chem*.,2011**, 401,** 2599–2608.

S4. V. Sudha, S.M. Senthil Kumar, R. Thangamuthu, ., *J. Alloys Compd*. 2018, **749**, 990–999.

S5. V. Sudha, S.M. Senthil Kumar, R. Thangamuthu, . *J. Alloys Compd*., 2018, **744**, 621–628.

S6. K. Wang, E.P.C. Lai, K. Wang, K. Lai, P.C Edward, *Chemosensors*, 2022, **10**, 145-163.

S7. L. Geiser, E. Varesio, J.L. Veuthey, *J. Pharm. Biomed. Anal.* 31 2003, **31**, 1059– 1064

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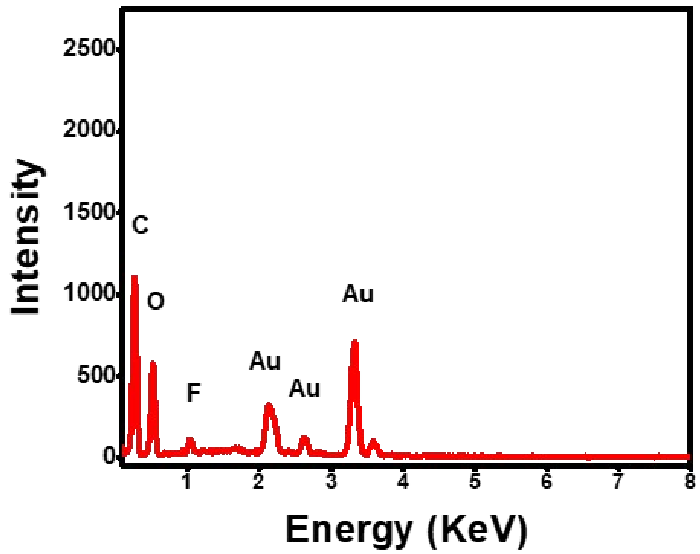

Figure S1. Energy-dispersive X-ray spectrum of the Au/F-rGO nanocomposite.

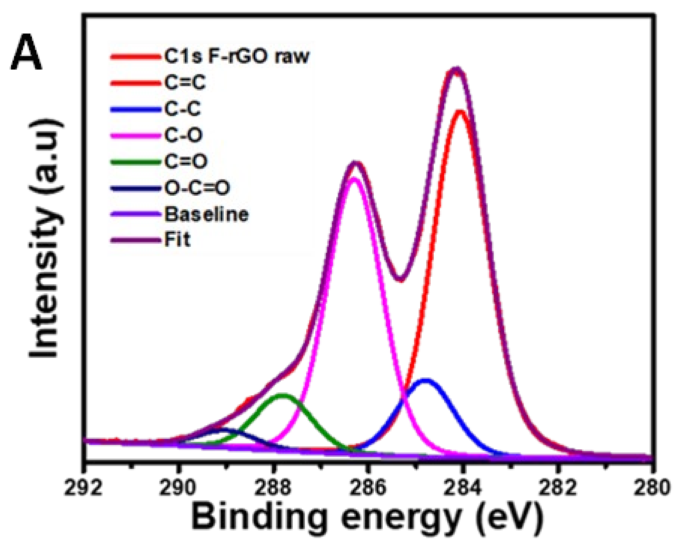

Figure S2. High resolution C1s X-ray photoelectron spectrum of the F-rGO.

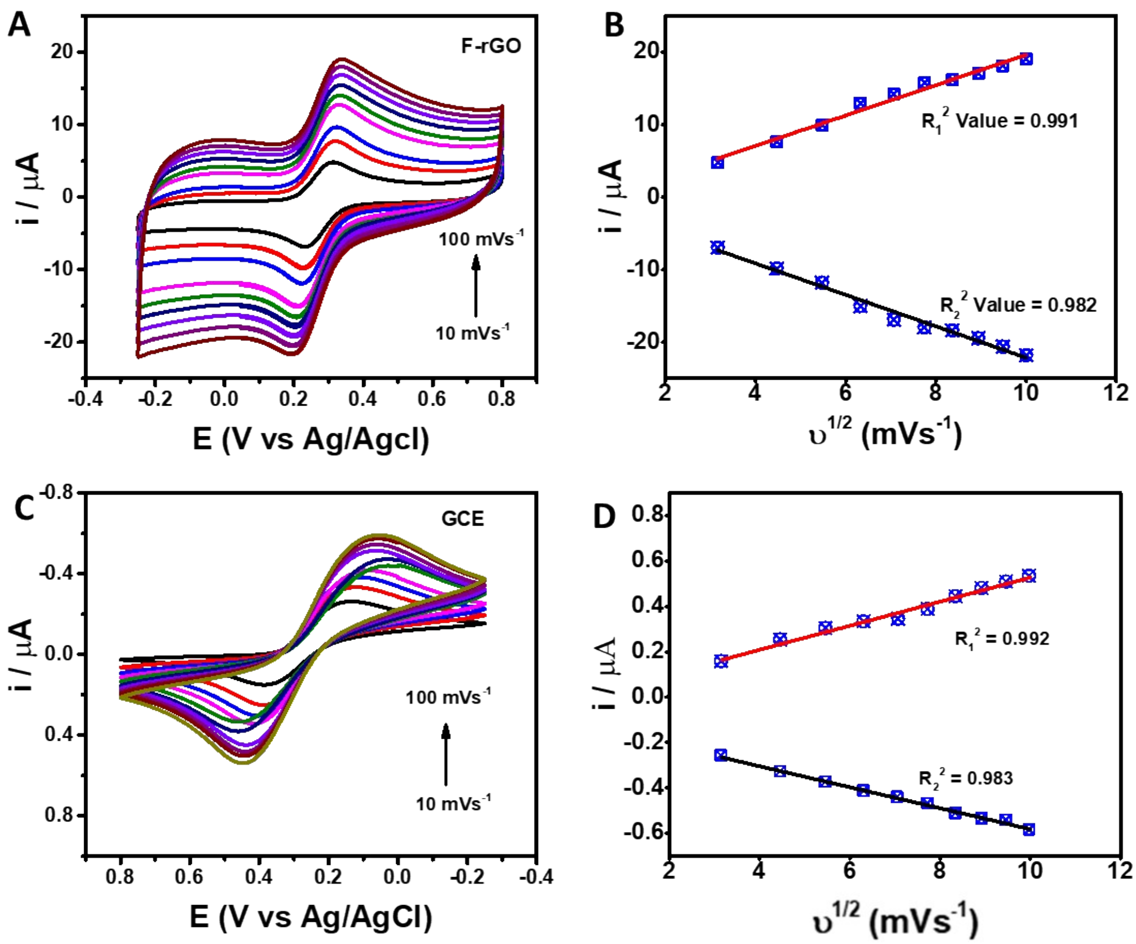

Figure S3. Cyclic voltammograms of the F-rGO/GCE (A) and the GCE (C) recorded in 0.1 M KCl containing 5.0 mM $[Fe(CN)6]^{3-/4-}$ at the scan rates varying from 10 to 100 mV s^{-1}. Plots of the redox peak currents vs. the squared root of the scan rate (mVs^{-1}) for the F-rGO/GCE (B) and the GCE (D).

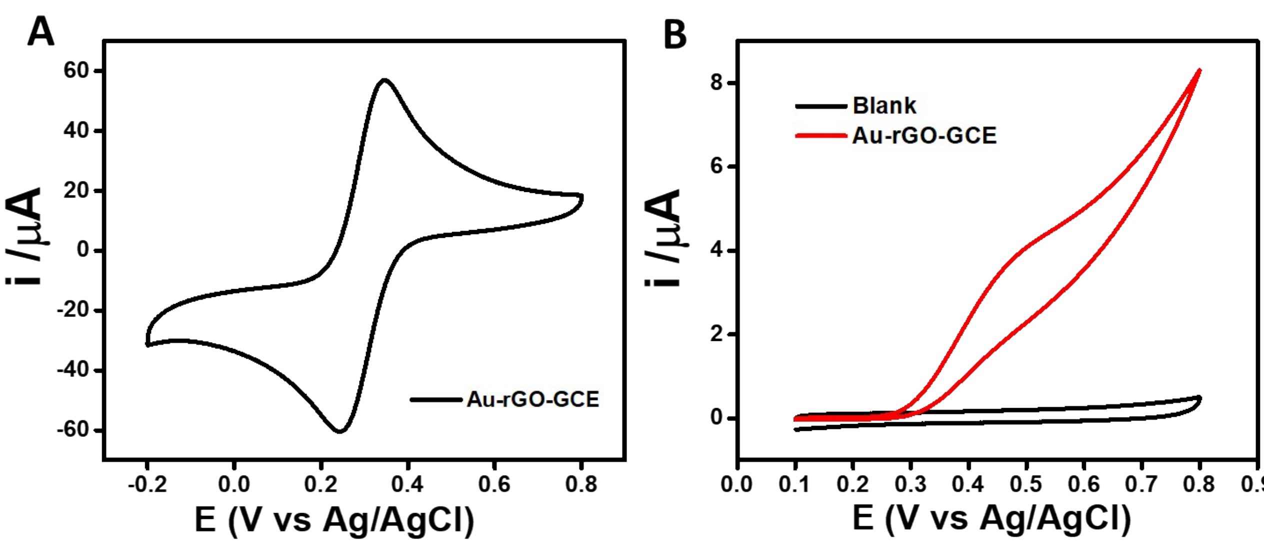

Figure S4. (A) Cyclic voltammogram (CV) of the Au/rGO/GCE recorded in 0.1 M KCl containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ at the scan rate of 50 mVs^{-1}. (B) CVs of the Au/rGO electrode recorded in 0.1M PBS at pH 7.4 in the absence (black) and in the presence of 100 μM SMBS at a scan rate of 50 mV s^{-1}.

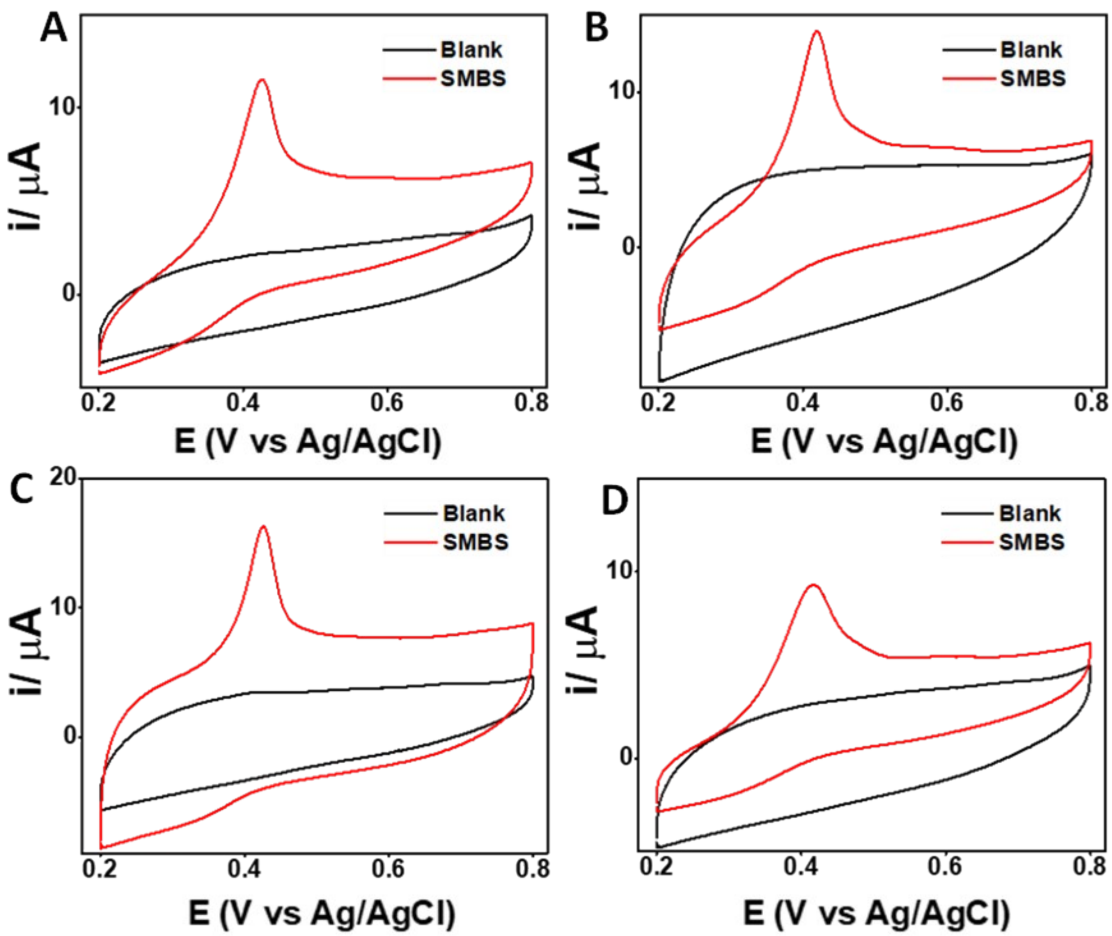

Figure S5. Effect of the electrochemical Au deposition time on the CVs of the Au/F-rGO/GCE recorded in 0.1 M PBS (pH 7.4) in the absence of (black) and in the presence of 100 μM SMBS at the scan rate of 50 mVs^{-1}. The electrochemical deposition of Au was carried out in a 2 mM $AuCl_3$ + 0.1M KNO_3 electrolyte at -0.4 V (vs Ag/AgCl) for (A) 60 s, (B) 150 s, (C) 300 s and (D) 400 s.

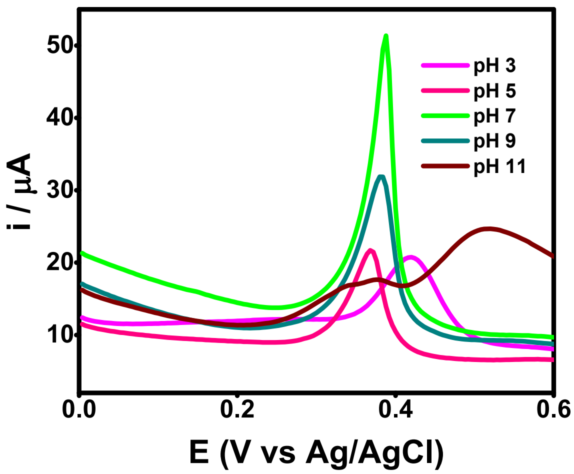

Figure S6. Effect of the pH of the electrolyte on the oxidation peak current at the Au/F-rGO/GCE obtained from the LSV recorded in 0.1 M PBS containing 100 µM SMBS at the scan rate of 50 mVs^{-1}.