Graphene Oxide Quantum Dots Immobilized on Mesoporous Silica: preparation, characterization and electroanalytical application

Albina Mikhraliieva, Vladimir Zaitsev*, Oleg Tkachenko, Michael Nazarkovsky, Yutao Xing, and Edilson V. Benvenutti

Supplementary information

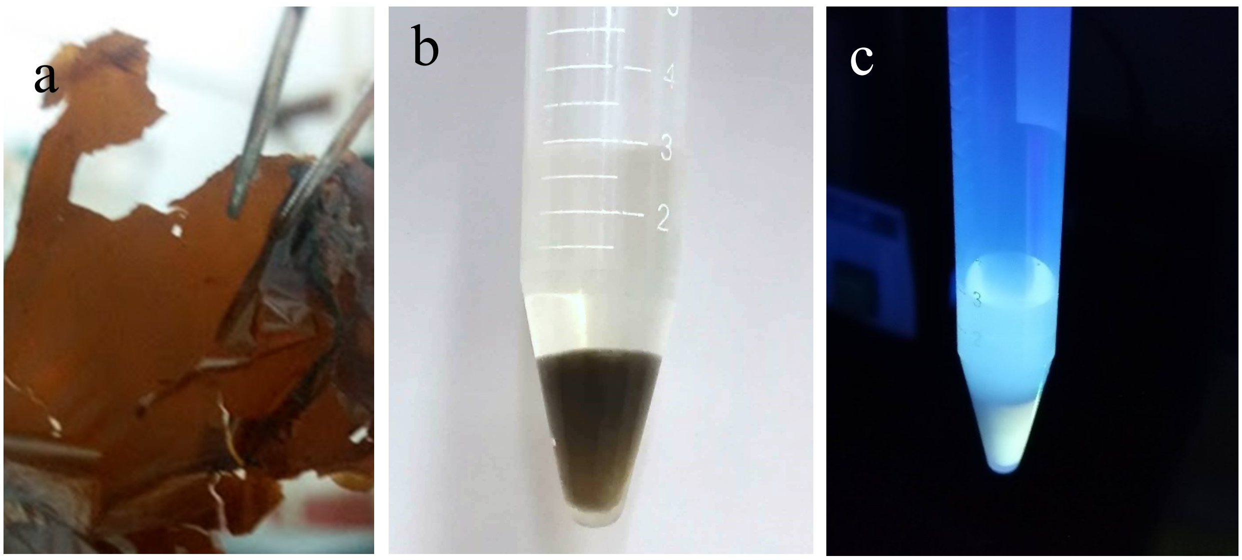

Fig. S1. Digital photos of vacuum-dried GO (a) and SiO_2-GOQDs under illumination with white (b) and ultraviolet (c) light with λ = 365 nm.

Table S1 – Elemental composition of SiO_2-NH_2 and SiO_2-GOQDs determined from CHN analysis, and concentration of immobilised aminopropyl fragment calculated from Eq. 1

Material	N,%	C,%	H,%	C_{NH_2}, mmol/g
SiO_2-NH_2	1.05	2.89	0.84	0.75
SiO_2-GOQDs	1.00	3.22	0.86	

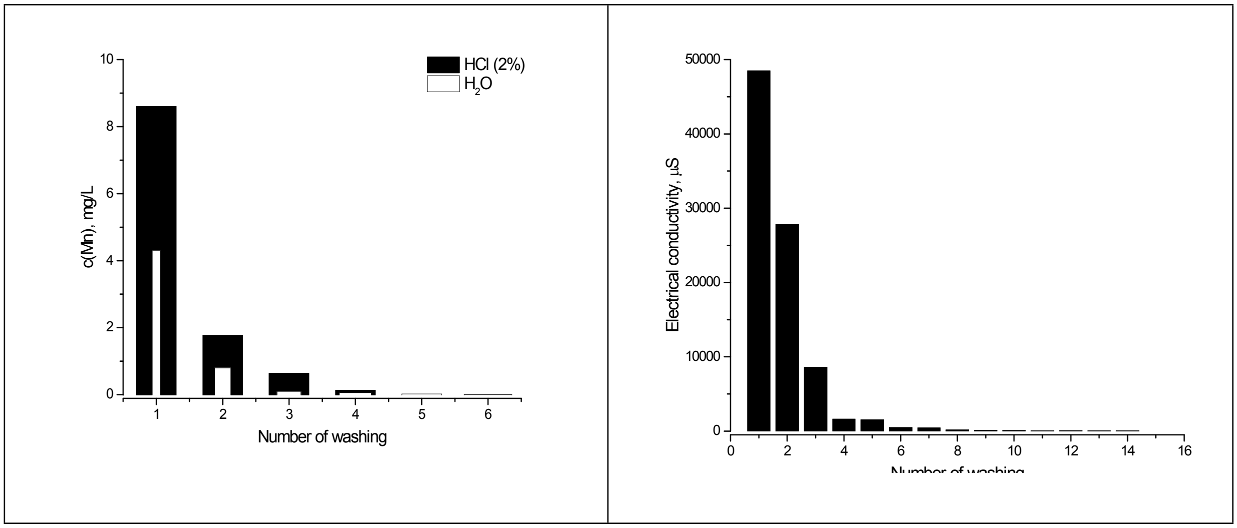

Fig. S2 Effect of washing on c(Mn) in supernatants (a) and monitoring of electrical conductivity with water washing (b)

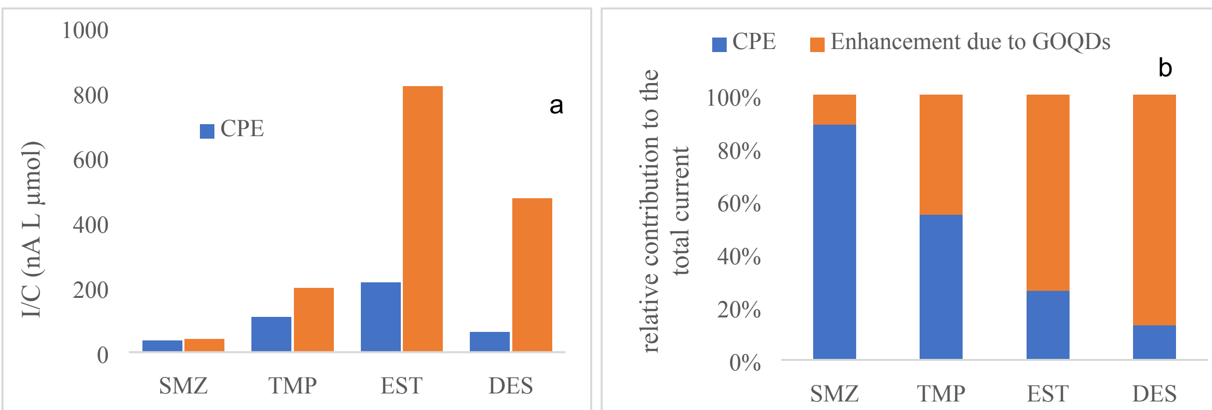

Fig. S3 Electrochemical sensibility (a) and relative enhancement of the current (b) on CPE and CPE/SiO2-GOQDs to the selected analytes.

Table S2 Analytical characteristics of the different electrodes modified with carbogenic nanomaterials in determination of EST, DES, SMZ and TMP

Material	Analyte	Linear range, $\mu mol\ L^{-1}$	LOD, $\mu mol\ L^{-1}$	LOQ. $\mu mol\ L^{-1}$	Equation (y(nA)vsC($\mu mol\ L^{-1}$))	Sensitivity, $nA\ L\ \mu mol^{-1}$	Ref.
CPE/SiO_2-GOQDs	EST	0.01-0.6	0.009	0.029	y=500*C+4.1	500	This work
GCE/CNB/AgNPs		0.2-3	0.16	0.5	n.d.	131	[1]
GCE/rGO/AgNPs		0.1-3	0.021		y=590*C+590	590	[2]
GCE/rGO/SbNPs		0.2-1.4	0.0005		y=2.13*C+0.57	2.13	[3]
GCE/Pt/CNTs		0.5-15	0.62		y=790*C+22040	790	[4]
CPE/SiO_2-GOQDs	DES	0.15-0.5	0.18	0.6	y=270*C+32	270	This work
CPE		0.1-15	0.01	0.03	n.d.	n.d.	[5]
GCE		2-100	0.08		y=337*C+264	337	[7]
GCE/GO/CS		0.015-30	0.003	0.01	y=−69.1*C−1.83	69	[8]
GCE/rGO/CD		0.01-13	0.004		n.d.	n.d.	[9]
CPE/SiO_2-GOQDs	SMZ	4-20	0.46	1.53	y=19*C+95.90	19	This work
CPE/MCM-41		98-327	3.1		y=2.43*C+11352	2.43	[10]
CPE/CNTs		1.4-119	0.4	1.33	n.d.	24.1	[11]
SPE/rGO		0.5–50	0.04	0.13	n.d.	n.d.	[12]
MIP/BDD		0.1-100	0.024	0.080	y=314.22*C+7.17	314	[13]
CPE/SiO_2-GOQDs	TMP	0.7-3.5	0.191	0.63	y=100*C+106	100	This work
SPE/CNTs/PBnc		0.1-10	0.06	0.2	y=108.31*C+70.7	108	[14]
CPE/CNTs/SbNPs		0.1–0.7	0.031	0.1	y=0.37*C+30	0.37	[15]

Electrodes: CPE – carbon paste electrode; GCE - glassy carbon electrode; MIP - molecularly imprinted polymer; SPE - screen-printed electrode.

Modifiers: CNB – carbon black nanoballs; AgNPs - silver nanoparticles; SbNPs - antimony nanoparticles; AuNPs - gold nanoparticles; rGO - reduced graphene oxide; CoPc - cobalt phtolocyanine; CS - chitosan; CD - β-cyclodextrin; CNTs – carbon nanotubes; BDD - boron-doped diamond; PBnc - Prussian blue nanocubes.

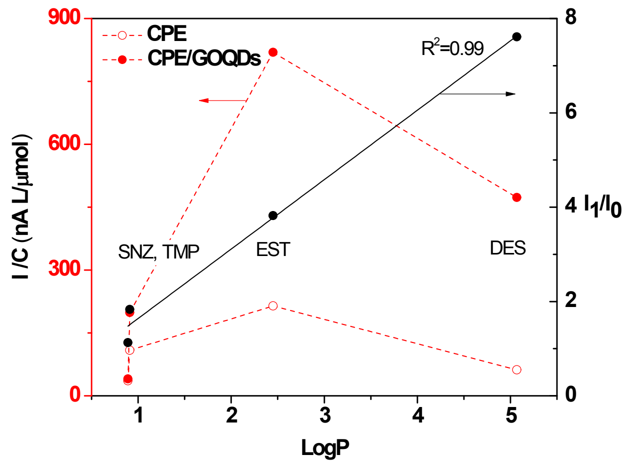

Fig. S4 Relationship between normalised peak currents (I(nA)/C(µmol L^{-1}) on CPE and CPE/SiO_2-GOQDs (left axis), and relative enhancement of the peak current on modified (I_1) and bulk (I_0) CPE (right axis), versus LogP of the analytes.

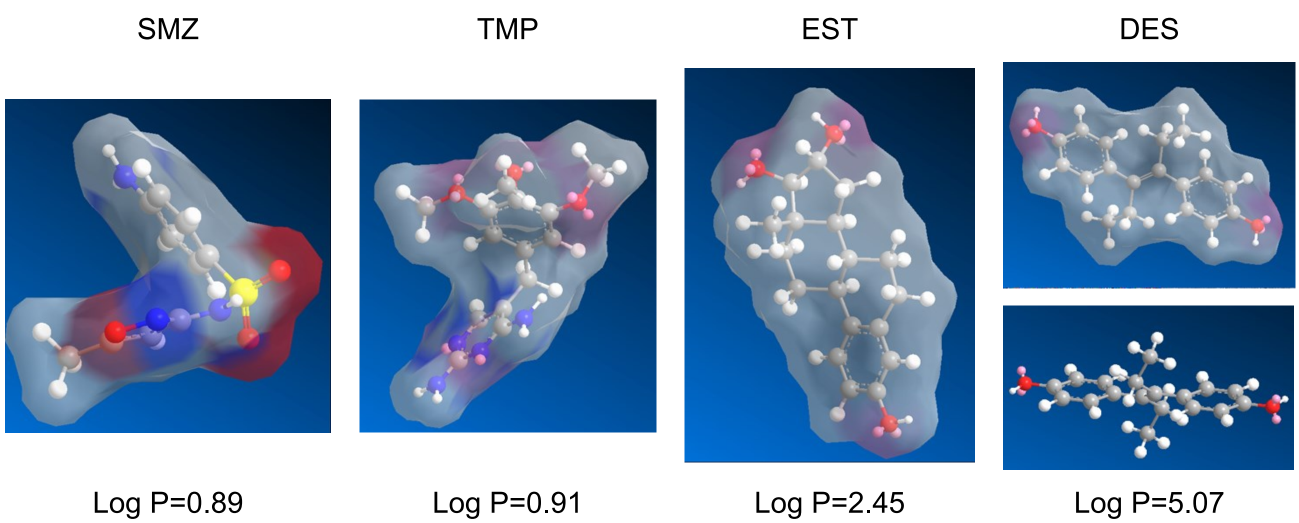

Fig. S5 Topological polar surface area of the selected analytes visualised by ChemDraw Ultra 12.0

References.

1 P. A. Raymundo-Pereira, A. M. Campos, F. C. Vicentini, B. C. Janegitz, C. D. Mendonça, L. N. Furini, N. V. Boas, M. L. Calegaro, C. J. L. Constantino, S. A. S. Machado and O. N. Oliveira, *Talanta*, 2017, **174**, 652–659.

2 C. A. Donini, M. K. L. da Silva, R. P. Simões and I. Cesarino, *J. Electroanal. Chem.*, 2018, **809**, 67–73.

3 I. Cesarino, F. H. Cincotto and S. A. S. Machado, *Sensors Actuators, B Chem.*, 2015, **210**, 453–459.

4 X. Lin and Y. Li, *Biosens. Bioelectron.*, 2006, **22**, 253–259.

5 S. Zhang, K. Wu and S. Hu, *Talanta*, 2002, **58**, 747–754.

6 X. Xie, D. Sun, G. Liu and Q. Zeng, *Anal. Methods*, 2014, **6**, 1640–1644.

7 Q. Bin, W. Wei, Y. Chi and G. Chen, *Anal. Biochem.*, 2005, **336**, 196–201.

8 C. Yu, W. Ji, Y. Wang, N. Bao and H. Gu, *Nanotechnology*, , DOI:10.1088/0957-4484/24/11/115502.

9 D. Lu, S. Lin, L. Wang, X. Shi, C. Wang and Y. Zhang, *Electrochim. Acta*, 2012, **85**, 131–138.

10 L. V. de Souza, D. S. da Rosa, O. S. Tkachenko, A. de A. Gomes, T. M. H. Costa, L. T. Arenas and E. V. Benvenutti, *Ionics (Kiel).*, 2019, **25**, 3259–3268.

11 A. Rana, N. Baig and T. A. Saleh, *J. Electroanal. Chem.*, 2019, **833**, 313–332.

12 C. Chen, Y. C. Chen, Y. T. Hong, T. W. Lee and J. F. Huang, *Chem. Eng. J.*, 2018, **352**, 188–197.

13 Y. Zhao, F. Yuan, X. Quan, H. Yu, S. Chen, H. Zhao, Z. Liu and N. Hilal, *Anal. Methods*, 2015, **7**, 2693–2698.

14 L. F. Sgobbi, C. A. Razzino and S. A. S. Machado, *Electrochim. Acta*, , DOI:10.1016/j.electacta.2015.11.151.

15 I. Cesarino, V. Cesarino and M. R. V. Lanza, *Sensors Actuators, B Chem.*, , DOI:10.1016/j.snb.2013.08.047.