Electrochemical detection of 8-Hydroxy-2'-Deoxyguanosine biomarker with new graphene modified carbon electrodes

C Varodi, F Pogacean, M Coros, V Mirel, L Magerusan, L-B Tudoran and S Pruneanu

National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat Street, 400293 Cluj-Napoca, Romania

E-mail: codruta.varodi@itim-cj.ro

Introduction – 8-Hydroxy-2'-Deoxyguanosine Biomarker (8-OH-dG) is a cancer biomarker for tumors and it is used for the evaluation of oxidative damage processes in DNA. Graphite exfoliation with pulses of current has a lot of advantages for the graphene synthesis. In this work we prepared two graphene-based materials doped with nitrogen, sulfur and boron in different proportions, following denoted EXF-1, and EXF-2. Both materials were morphologically and structurally characterized by SEM, FTIR, and XRD and they were used for the modification of two glassy carbon electrodes, denoted GC/EXF-1 and GC/EXF-2. The electroanalytical parameters of the new electrodes were determinate and tested in artificial plasma experiment with standard addition of 8-OHdG.

Experimental – The graphene samples were obtained and characterized by different techniques: SEM, X-Ray powder diffraction, FTIR, XPS, and elemental analysis. The electrodes were modified by drop-casting on their surfaces the graphene suspension in DMF and the electrochemical measurements were recorded with an AUTOLAB 302N electrochemical work-station (Metrohm-Autolab B.V., Netherlands). The Linear Sweep Voltammetry (LSV) measurements were generally run between 0.1 and 0.7 V vs Ag/AgCl, with a scan rate of 10 $mV \cdot s^{-1}$ and chronoamperometric determinations were registered at +0.46 V..

Results and Discussions

Synthesis of graphene co-doped with heteroatoms: boron and nitrogen or sulfur

Table 1. Reaction conditions for graphene co-doped with heteroatoms: boron and nitrogen or sulfur (electrochemical) in pulsed current

Probe	Electrolit Conc.	Reaction time (min)	Applied Voltage (V)	Obs
EXF-1	0,05M $(NH_4)_2SO_4$+0,05M $B(OH)_3$+ 0.05M NaCl	240	12	Pulsed current 0,4-0,8A
EXF-2	0,05M $(NH_4)_2SO_4$+0,1M $B(OH)_3$+ 0.05M NaCl	270	12	Pulsed current 0.50-0.55A, with tap water cooling

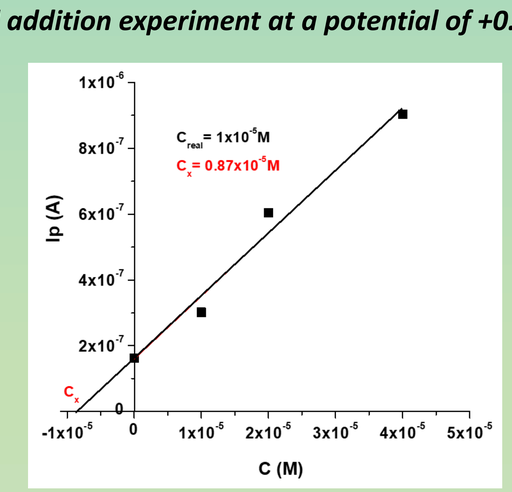
Structural characterization of graphene co-doped with heteroatoms: boron and nitrogen or sulfur

Table 2. Structural parameters obtained from X-ray diffractograms: crystallite size (D), interplanare distance (d), average number of layers (n) and quantity (%) of each type of graphene obtained

Probe	2θ (grade)	*D* (nm)	*d* (nm)	*n*	Obs
EXF-1	9.401	2.342	0.951	2	19% GO
	23.390	1.048	0.381	3	53% FLG
	26.387	18.72	0.338	55	28% MLG
EXF-2	9.664	2.483	0.917	3	17% GO
	21.685	1.181	0.410	3	69% FLG
	26.224	10.103	0.341	30	14% MLG

Standards addition of of 8-OHdG in artificial plasma

Figure 3. Standard addition experiment at a potential of +0.46 V - calibration plot



Electrochemical detection of of 8-OHdG

Figure 1. Linear voltammograms recorded with electrode GC/EXF-1 (A, C), GC/EXF-2 (B, D) modified with graphene electrochemically co-doped with heteroatom - boron and nitrogen or sulfur, in standard laboratory solutions (pH 6 PBS) containing increasing concentrations of 8-OHdG (10^{-7}– 10^{-3} M). Calibration curves obtained for three distinct measurements.

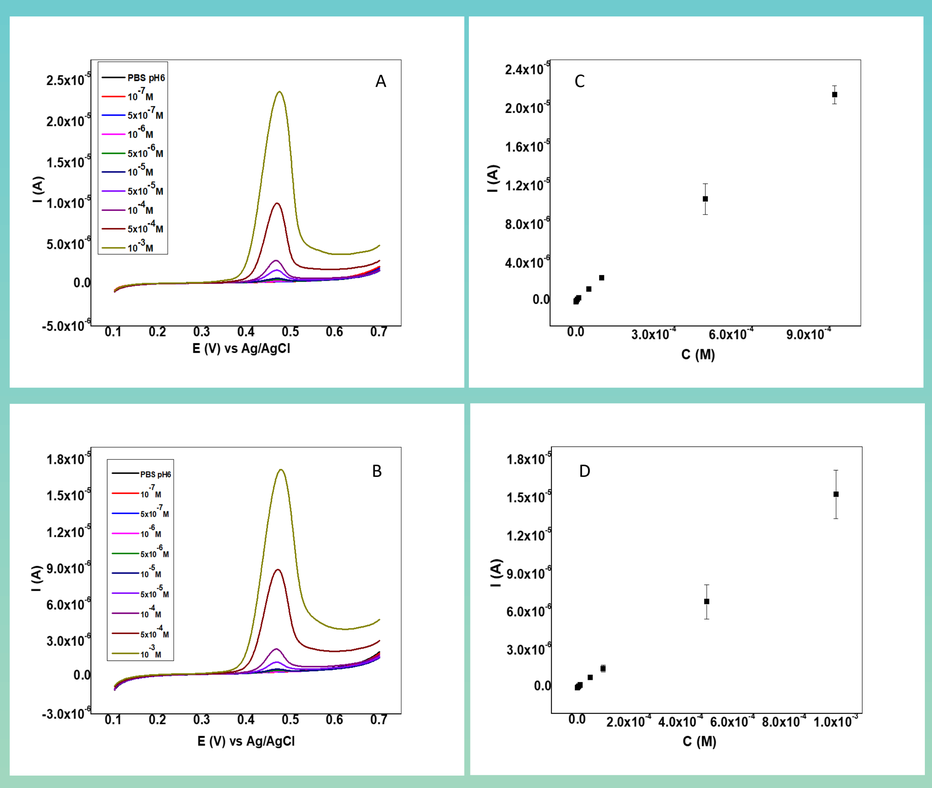
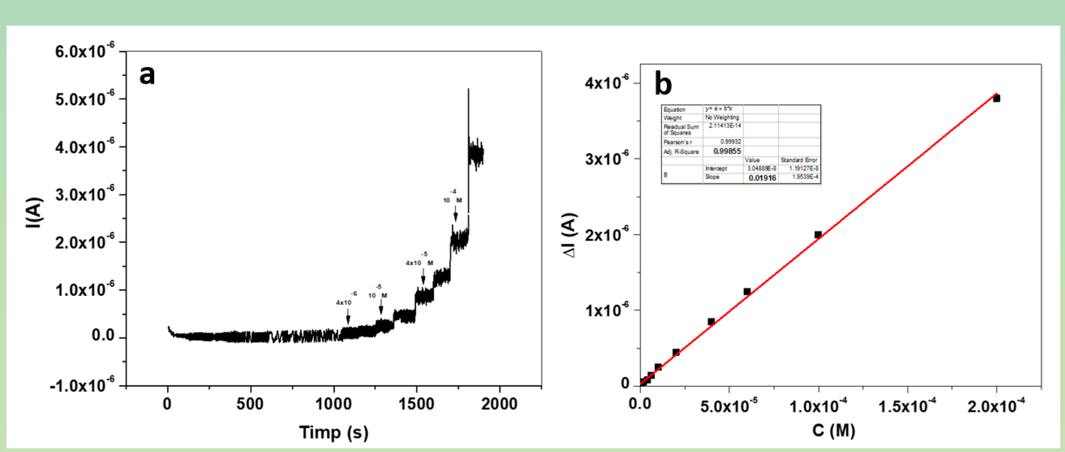


Figure 2. Amperometric curves recorded with GC/EXF-1 electrode in pH6 PBS supporting electrolyte, after the addition of known concentrations of 8-OHdG (a); The corresponding calibration plots (b).



Conclusions –There were prepared two graphene-based materials doped with nitrogen, sulfur and boron in different proportions, following denoted EXF-1, and EXF-2. Both materials were morphologically and structurally characterized and they were used for the modification of two glassy carbon electrodes, denoted GC/EXF-1 and GC/EXF-2. The electrochemical performances obtained for the 8-OH-dG biomarker detection with these new graphene-modified electrodes are very good (Detection limit of 0.9x 10^{-7} M, Linear range between 5x10^{-6}– 10^{-3} M, sensitivity of 19 mA/M*)* and promising for real sample analysis.

Acknowledgement

This work was supported by a grant of Romanian Ministry of Research, Innovation and Digitization, CNCS/CCCDI-UEFISCDI within PNCDI III, project number PN-III-P4-ID-PCCF-2016-0006