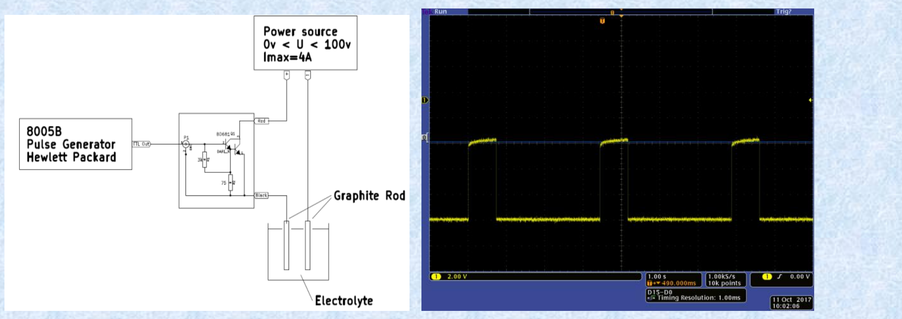
Electrochemical detection of His-Tagged CA19-9 Antigen with triple-doped graphene modified electrode

F Pogacean, C Varodi, 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, 400293 Cluj-Napoca, Romania
E-mail: florina.pogacean@itim-cj.ro

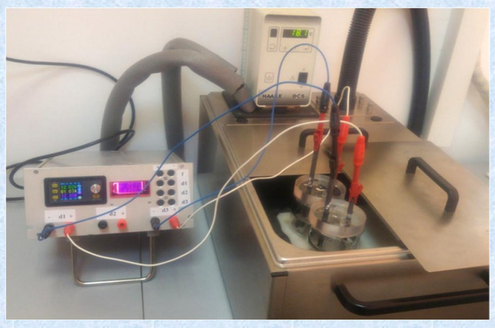
INCDTIM

Abstract

His tag CA19–9 (Carbohydrate antigen N-terminal His Tag) is a typical biomarker for gastrointestinal cancer tumors and represents a highly sialylated glycoprotein showing 85% carbohydrate by weight, that attaches to O-glycans on the surface of cells and plays a vital role in the cell-to-cell recognition processes. Two graphene-based materials were prepared by exfoliation of graphite rod with pulses of current. The first material (denoted EGr-1) was exfoliated in a mixture of ammonium sulfate, boric acid and sodium chloride (1:1:1 ratios). The second material (denoted EGr-2) was prepared by exfoliation of the graphite rod in a mixture of ammonium sulfate, boric acid and sodium chloride (0.5:1:0.5 ratios). Both materials were morphologically and structurally characterized by XRD, XPS, and SEM. After preparation, the materials were used for the modification of two screen printed electrodes, denoted DS/EGr-1 and DS/EGr-2, respectively and used for electrochemical detection .



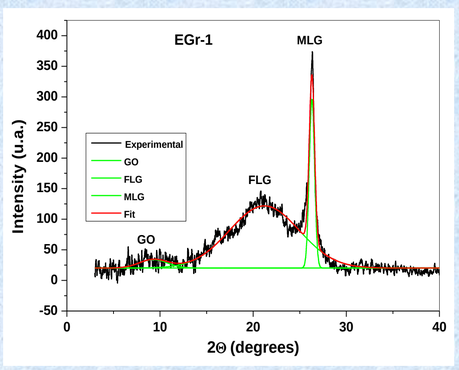
The experimental set-up employed for pulse exfoliation of graphite rods



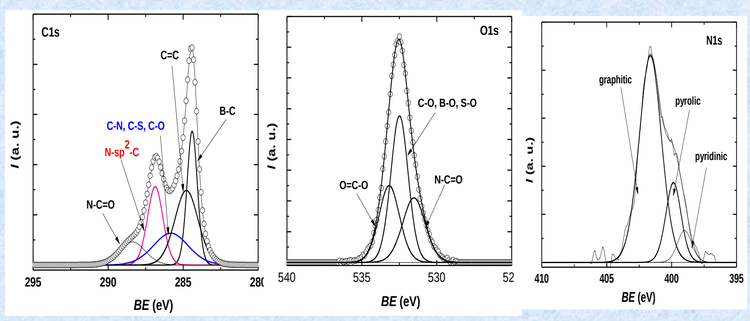
Experimental set-up for electrochemical exfoliation of graphite .

Experimental set-up for electrochemical measurements; Modifield electrodes with triple-doped graphene

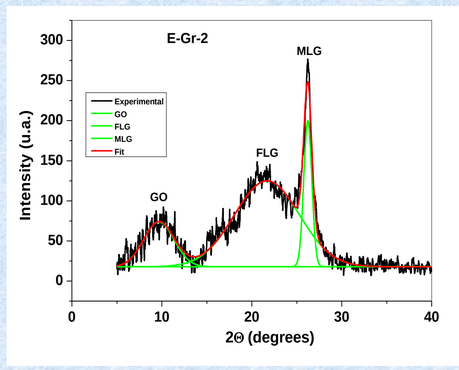
Morphological and structural characterization of EGr-1 and EGr-2



The XRD pattern of graphene sample and the corresponding deconvoluted peaks



Core level high-resolution *C 1s*, *O 1s and N1s* XPS spectra of EGr-1



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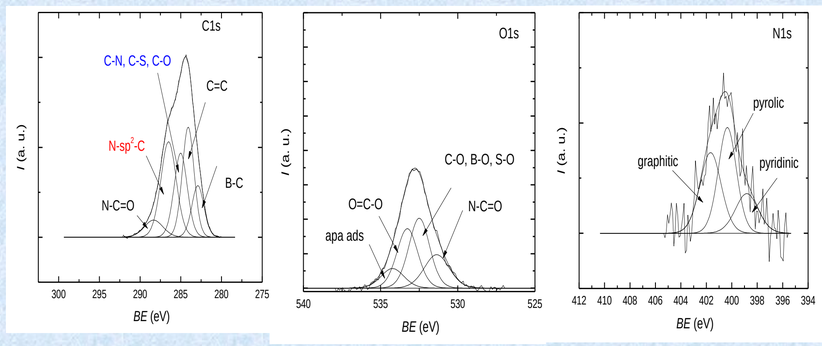
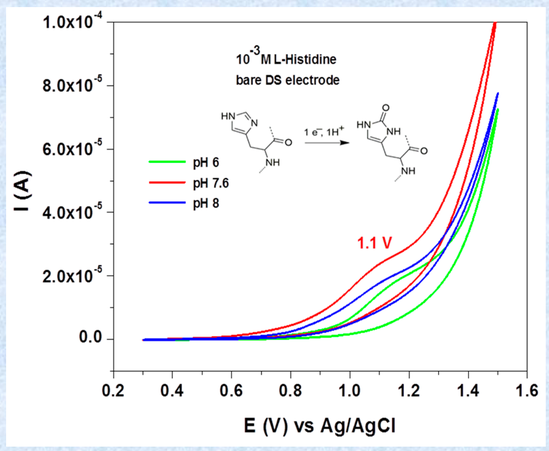


Core level high-resolution *C 1s*, *O 1s and N1s* XPS spectra of EGr-2

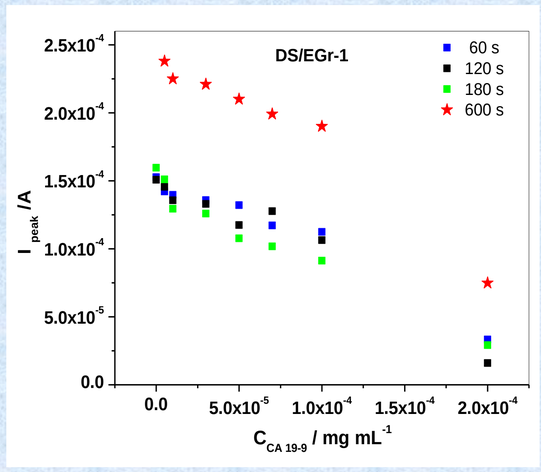
Sample	*2θ* (deg)	*D* (nm)	*d* (nm)	*n*	*Amount%*
EGr-1	9.28 (GO)	2.79	0.96	~3	4
	21.20(FLG)	1.13	0.42	~3	80
	26.30 (MLG)	16.23	0.33	~48	16

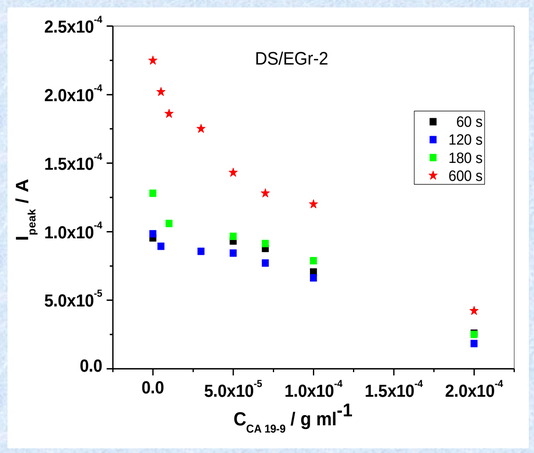
Sample	*2θ* (deg)	*D* (nm)	*d* (nm)	*n*	*Amount%*
EGr-2	9.66 (GO)	2.48	0.91	~2	17
	21.68(FLG)	1.18	0.41	~3	68
	26.22 (MLG)	10.10	0.34	~30	15

Electrochemical studies

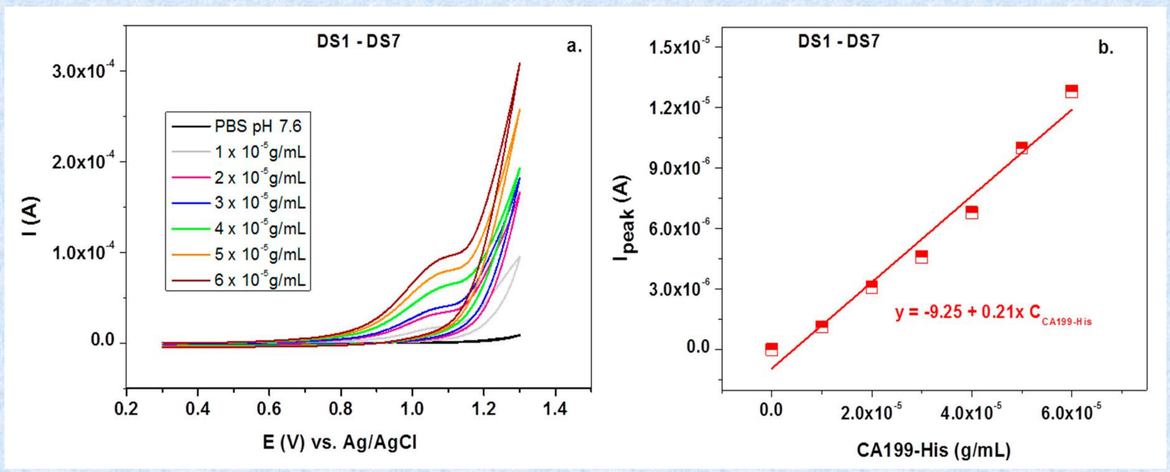


CVs recorded with bare DS electrode in solution containing 10^{-3}M L-Histidine; PBS supporting electrolyte: pH 6 (green); pH 7.6 (red); pH 8 (blue); scan rate 10 mV/s; inset: the electrochemical oxidation of L-Histidine

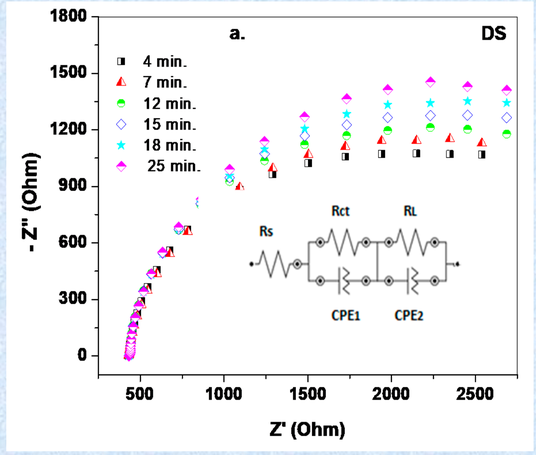




Calibration curves obtained with modified electrodes with triple doped graphene DS/EGr-1 and DS/EGr-2 for His-Tagged CA19-9 Antigen .



CVs recorded with bare DS electrodes in the presence of CA19-9-His having various concentrations, from $1x10^{-5}$ to $6x10^{-5}$ g/mL; scan rate 10 mV/s (a). Calibration curve obtained with bare DS electrodes for CA19-9-His (b).



Nyquist plots recorded over time with the bare DS electrode in pH 7.6 PBS solution containing 0.07 mg/mL CA19-9-His; applied potential: +1.1 V; 0.1–106 Hz frequency range (a); inset: electrical equivalent circuit employed for fitting the recorded EIS data;

Conclusions

Triple doped (N; S; B) graphene sample was prepared by electrochemical exfoliation of graphite rods with pulses of current in the appropriate electrolyte. After structural and morphological characterization the materials were deposited on top screen printed electrode. Next, their electrochemical performances toward the detection of His-Tagged CA19-9 Antigen were tested in laboratory solutions. The best results were obtained with triple-doped graphene-modified electrode.

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