Carbonaceous materials modified with iridium oxide as an electrochemical sensing platform

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The electrochemical sensor devices provide the opportunity for sensitive, selective, interference-free, fast, cost-effective and susceptible to automation analysis, and are a promising alternative of the traditional analytical techniques. In this work the modification of carbonaceous carriers (glassy carbon, spectroscopic graphite and pyrolytic graphite) with iridium oxide applying two-step electrodeposition procedure is described. Developed electrodes showed attractive performance for electroanalytical applications, proving to be suitable for the sensitive and selective electrochemical detection of ascorbic acid, sulfite and hydrogen peroxide – analytes of interest in food quality and safety. The electrochemical behavior of the modified electrodes was explored by means of cyclic voltamperometry (CV), differential pulse voltamperometry (DPV) and constant potential amperometry. The effect of carrier type on the electrocatalytic activity of the modified electrodes in reduction of hydrogen peroxide was also evaluated. The results obtained from the quantitative detection measurements offer potential application of the modified with iridium oxide electrodes in electrochemical sensor devices for quick and accurate monitoring of these analytes.

Keywords: *electrochemical sensor, iridium oxide, ascorbic acid, sulfite, hydrogen peroxide*

INTRODUCTION

The strong antioxidant activity of ascorbic acid (AA), also known as vitamin C, and its ability to protect oxidizable constituents, including phenolic and flavor compounds, is the main factor AA to be frequently used in food industry to prevent unwanted changes in color or flavor. Additives, based on AA, are widely used in production of foods and drinks such as beer, jam, sweets, fruit juices, fish products and meats. AA is used as well as in cosmetics as a skin conditioning agent and in pharmaceutical industry as a diet supplement in various forms. Normal AA intake is about 70 – 90 mg for adults [1]. Sulfite (SO_3^{2-}) has an antioxidant and inhibitory characteristics in enzymatic activity and it is utilized as a preservative for various food, meat products and wine to prevent oxidation and bacterial growth [2]. Hydrogen peroxide (H_2O_2) is an industrially relevant analyte – it is widely used as an oxidizing, disinfecting and bleaching agent in the pharmaceutical, textile, cosmetic and paper industries; as a sterilizing agent in food processing and packing. In medicine, H_2O_2 is one of the most important markers for oxidative stress.

Due to the crucial role of the above-mentioned substances in food quality and in industrial applications, recently there is a considerable research interest to develop electrochemical sensors for quantitative detection in various samples including foods and biological fluids [3-18]. In this connection, novel modified carbonaceous electrodes have been fabricated applying cyclic voltammetry (CV) to form iridium oxide layers at the electrode surface as the fastest and simplest electrodeposition technique, that not requires expensive equipment or special experimental conditions. The developed electrodes showed good performances and potential application in electroanalysis for quantitative detection of ascorbic acid, sulfite and H_2O_2 with sensitivity and selectivity comparable to or better than existing nonenzymatic sensors.

EXPERIMENTAL

Materials

Na_2IrCl_6, HCl, H_2SO_4, 30 % H_2O_2, NaOH, $NaOOCCH_3$, NaCl, Na_2CO_3, Na_2SO_3, KBr, KI, $MgCl_2$ were purchased from Fluka; $Na_2HPO_4.12H_2O$, $NaH_2PO_4.2H_2O$, sodium citrate ($Na_3C_6H_5O_7$), ascorbic acid ($C_6H_8O_6$) and D-glucose ($C_6H_{12}O_6$) were purchased from Sigma-Aldrich. All chemicals used were of analytical grade and double distilled water was used to prepare aqueous solutions. Buffer solution, 0.1 M, was made of monobasic and dibasic sodium phosphates dissolved in double distilled water with pH 7.0 adjusted with NaOH. Three different types of carbonaceous materials were used as working electrodes: glassy carbon (GC) with visible surface area 7.07 mm^2 (Metrohm), spectroscopic graphite (Gr) with area *ca.* 25 mm^2 and pyrolytic graphite (PGr) with area *ca.* 26.4 mm^2 (RWO, Ringsdorff, Germany).

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Apparatus and measurements

All the electrochemical measurements were performed using potentiostat EmStat2 (PalmSens BV, The Netherlands) interfaced with a computer and controlled by 'PSTrace 2.5.2' software. A conventional thermostated three-electrode cell including a working electrode, an Ag/AgCl (3 M KCl) as a reference electrode, and a platinum wire as a counter electrode was used. Before the measurement the background electrolyte was purged with pure argon for 15-20 min to remove dissolved oxygen. The modified electrode was investigated using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and amperometry at a constant potential. The DPV parameters were chosen as follows: scan rate 9 mV s^{-1}, pulse amplitude 50 mV, pulse interval 70 ms. Amperometric (*i-t*) curves were monitored at a constant applied potential under hydrodynamic condition. The experimental data analysis was performed using software package 'OriginPro 8.0'. The value of the electrode sensitivity was calculated from the slope of the corresponding regression line and normalized to the electrode geometric surface area.

Electrodeposition of iridium oxide

The electrodeposition of IrO$_x$ onto the electrode surface (polished and sonicated in double distilled water) was carry out in two-step procedure as follows: deposition of iridium from 2.0 % Na$_2$IrCl$_6$ in 0.1 M HCl solution using CV from –0.3 to 0.3 V applying 100 cycles at scan rate of 100 mV s^{-1} and subsequent oxidation of iridium applying 100 cycles from –0.3 to 1.4 V in electrolyte 0.5 M H$_2$SO$_4$. The modified electrodes will be denoted in the text as: IrO$_x$/GC, IrO$_x$/Gr and IrO$_x$/PGr, respectively.

RESULTS AND DISCUSSION

Electrocatalytic oxidation of ascorbic acid

To study the application of the modified electrode IrO$_x$/GC in electrochemical sensing of AA and sulfite, electrooxidation and quantitative detection of each of the substances in neutral medium was evaluated using two electrochemical techniques – DPV and constant potential amperometry, according to the sensitivity, linear range and detection limit.

DPV technique was first employed to study the electrochemical oxidation of AA on IrO$_x$/GC and bare GC electrode in PBS, pH 7.0 (Fig. 1A). The electrooxidation of AA was shown in the form of peak shaped differential pulse voltammogram with maximum current intensity at 0.25 V on bare GC and at 0.025 V on IrO$_x$/GC, respectively. The oxidation peak potential of AA at the modified electrode is significantly shifted (by ~0.225 V) in the negative direction compared with the bare GC, and 2.5-fold increase in the peak current at the modified IrO$_x$/GC was observed. This result clearly shows that the modified electrode possesses a better sensitivity and selectivity in comparison to the bare GC. The oxidation potential value (0.025 V) is significantly lower than the AA oxidation potential reported in previous research articles [3-7], indicating that the presented modified electrode IrO$_x$/GC is distinguished by a higher efficiency in the selective detection of AA compared to other electrocalysts. Measurements (n = 7) done with the presented modified electrode in presence of 1.0 mM AA showed current signal of 9.315 ± 0.125 µA featuring extremely high reproducibility (relative standard deviation R.S.D. equal to 1.34 %). A clear increase in DPV peak current was observed upon increasing the concentration of AA and the peak current was found to increase linearly (correlation coefficient of 0.999) as a function of the concentration up to 1.9 mM (Fig. 1B); the electrode sensitivity was calculated 135 µA mM^{-1} cm^{-2}. Fig. 1B (Inset) presents the authentic current-time response of IrO$_x$/GC recorded after successive additions of AA into stirred PBS (pH 7.0) at a constant potential of 0.025 V. The proposed electrode shows sensitivity of 96.2 µA mM^{-1} cm^{-2} in the range from 0.01 to 3.0 mM AA (I$_p$ (µA) = 6.8042 C (mM) + 0.9428, R^2 = 0.994). From the comparative review presented in Table 1, it can be seen that the analytical parameters of the proposed IrO$_x$/GC electrode are superior in working potential, sensitivity and linear concentration range, as compared to the previously reported modified electrodes for AA detection.
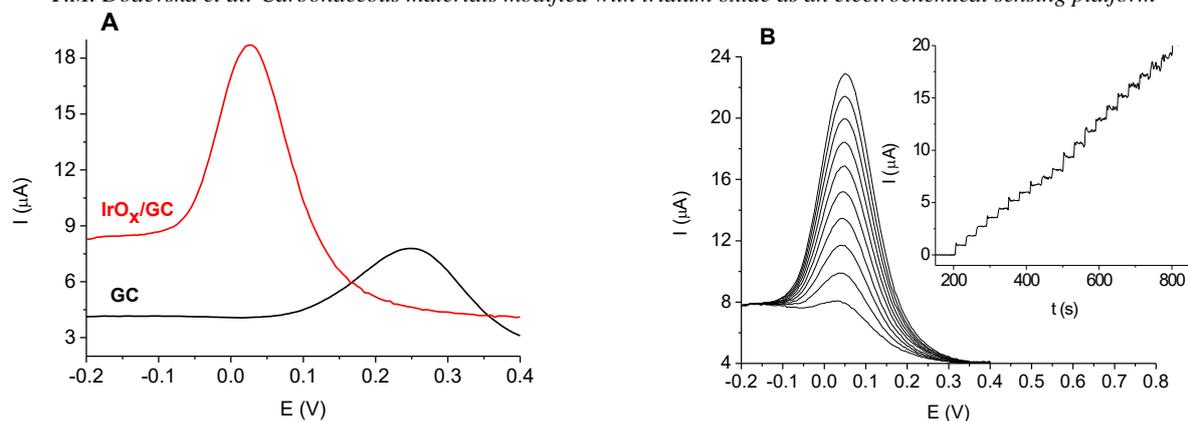
Fig. 1. A) DPV response of bare GC and modified IrOx/GC for 1.0 mM ascorbic acid in PBS (pH 7.0); B) DPVs of modified electrode IrOx/GC in the presence of various concentrations of AA (in mM) as follows: 0.2, 0.4, 0.6, 0.78, 0.97, 1.15, 1.34, 1.52, 1.7, 1.88. Inset: Amperometric response of IrOx/GC for successive additions of AA (10 injections of 0.1 mM and 11 injections of 0.2 mM) at an applied potential of 0.025 V.

Table 1. Comparison of the operational characteristics of electrochemical sensors for quantitative detection of AA, sulfite and H_2O_2, with the achieved in the present work.

Sensing platform/Support electrode*	E, V	Sensitivity, $\mu A\ mM^{-1}\ cm^{-2}$	Linearity, M	Ref.
Sensors for ascorbic acid				
AuNPs/GO/GC	0.15[a]	101.86	1.1×10^{-7}–6×10^{-4}	3
Q–chitosan/C	0.1[a]	76	1×10^{-5}–5×10^{-3}	4
Au/EPA/CPE	0.3[a]	21.7[c]	5×10^{-5}–7.5×10^{-4}	5
GDSP/CPE	0.4[b]	21.879[c]	1.5×10^{-4}–8×10^{-3}	6
EMGON/CPE	0.38[b]	78.63[c]	up to 1×10^{-3}	7
IrOx/GC	0.025[a]	96.2	1×10^{-5}–3×10^{-3}	This work
Sensors for sulfite				
BFCNTs/CPE	0.4[a]	0.05[d]	1×10^{-7}–4×10^{-4}	8
FeHCF/GC	0.85[b]	2.18[c]	up to 4×10^{-3}	9
GC	0.75[a]	5.37[e]	1×10^{-5}–1×10^{-3}	10
CS–Fc/MWCNTs/GC	0.35[b]	13.08[c]	5×10^{-6}–1.5×10^{-3}	11
PrHCF/GC	0.65[a]	36	up to 8×10^{-3}	12
IrOx/GC	0.5[a]	81	5×10^{-5}–9.1×10^{-3}	This work
Sensors for H_2O_2				
AgNPs–PANI–HNTs/GC	-0.2[b]	74.8	5×10^{-7}–4.7×10^{-3}	13
Ag–HNTs–MnO$_2$/GC	-0.3[b]	11.9	2×10^{-6}–4.71×10^{-3}	14
RuNPs/CRGR/GC	-0.6[a]	1.1[d]	1×10^{-5}–1.7×10^{-4}	15
PtIr/MWCNTs/GC	0.25[b]	58.8	2.5×10^{-6}–7.25×10^{-5}	16
Au@Ag@C/GC	-0.55[a]	76.02	5×10^{-6}–7.5×10^{-5}	17
PdNPs/PEDOT/GC	-0.2[b]	215.3	2.5×10^{-6}–1×10^{-3}	18
IrOx/Gr	-0.2[a]	240	5×10^{-6}–1.09×10^{-2}	This work

[a] referred to an Ag/AgCl (3 M KCl) electrode; [b] referred to a saturated calomel electrode (SCE); [c] the unit is: $\mu A\ mM^{-1}$; [d] the unit is: $\mu A\ \mu M^{-1}$; [e] the unit is: $mA\ mM^{-1}$; * NPs – nanoparticles, GC – glassy carbon, Gr – graphite, CPE – carbon paste electrode, GO – graphene oxide, Q-chitosan – hydroquinone modified chitosan, Au/EPA – gold/aniline-pentamer-based electroactive polyamide, GDSP – gold decorated SiO$_2$@polyaniline (PANI) core-shell microspheres, EMGON – electroactive mesoporous gold-organosilica nanocomposite, BF – benzoylferrocene, CNTs – carbon nanotubes, CS – chitosan, Fc – ferrocene, HCF – hexacyanoferrate, MWCNTs – multiwall carbon nanotubes, PANI – polyaniline, HNTs – halloysite nanotubes, CRGR – chemically reduced graphene, PEDOT – poly(3,4-ethylenedioxythiophene).

The selectivity of the modified electrode IrOx/GC for AA detection was also studied by amperometric measurements at potential of 0.025 V in the presence of eight different electroactive species. Fig. 2 shows the authentic response of electrode IrOx/GC for the interval additions of 0.3 mM AA and a 10-fold concentration (3.0 mM) of the above mentioned interfering substances. A well defined amperometric response was observed for AA. Obvious additional signals were not observed for the modified electrode

after injection of interfering substances and the electrode response for AA after adding interfering substances was not changed. The results reveal the application potential of IrO$_x$/GC for precise sensing of AA in real samples.
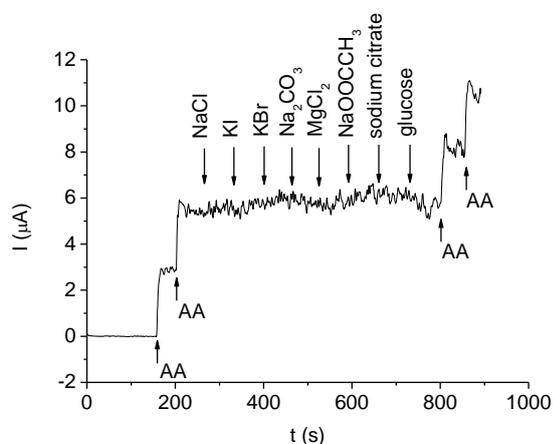

Fig. 2. Amperometric curve of IrO$_x$/GC for the determination of 0.3 mM ascorbic acid (AA) in the

presence of 3.0 mM of different interfering species, added one by one with an interval of 60 s to 0.1 M PBS (pH 7.0) at an applied potential of 0.025 V.

Electrocatalytic oxidation of sulfite

Fig. 3A shows DPVs recorded for the modified electrode IrO$_x$/GC and the bare GC electrode in presence of 1.0 mM sulfite in PBS, pH 7.0. The peak potential was determined to be 0.5 V and 0.78 V at the IrO$_x$/GC and GC electrodes, respectively. This result indicated that the IrO$_x$-deposit also had an electrocatalytic activity for the sulfite oxidation. The DPV response of IrO$_x$/GC upon subsequent addition of sulfite ranging from 0.1 to 1.5 mM is presented in Fig. 3B. The electrocatalytic current for the oxidation of sulfite increased with increasing sulfite concentration. The oxidation peak currents were proportional to the sulfite concentration, following linear regression equation $I_p (\mu A) = 4.7774\,C\,(mM) + 0.0027$. The plot showed good linearity with a 0.995 correlation coefficient (Fig. 3B, Inset).
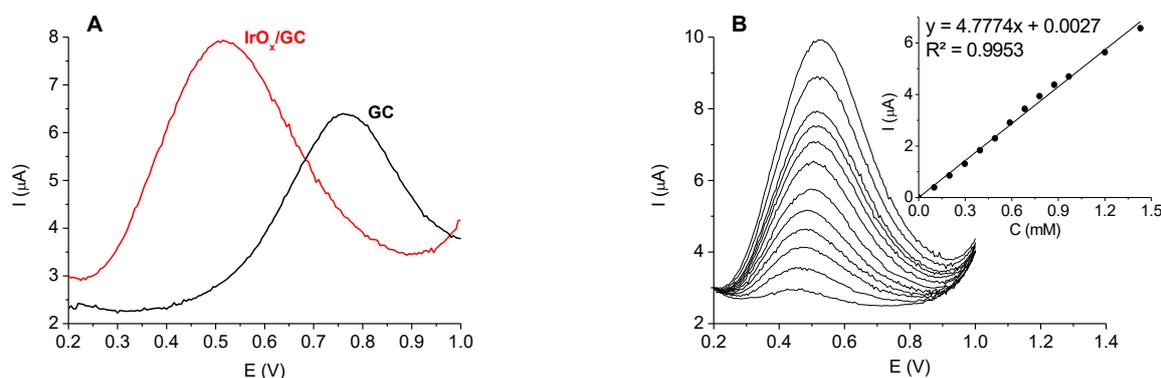

Fig. 3. A) DPV response of bare GC electrode and modified electrode IrO$_x$/GC for 1.0 mM sulfite in PBS (pH 7.0); B) DPVs of IrO$_x$/GC in the presence of various concentrations of sulfite; *Inset*: the corresponding calibration plot.
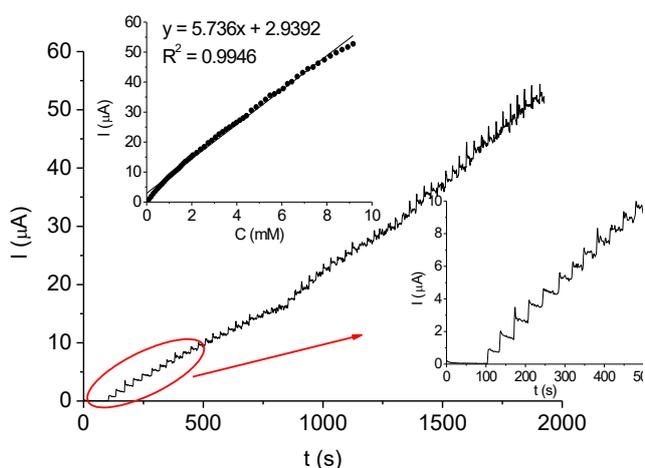

Fig. 4. Amperometric response of modified electrode IrO$_x$/GC to successive additions of Na$_2$SO$_3$ stock solution into stirring 0.1 M PBS (pH 7.0) at an applied potential of 0.5 V; *Inset*: calibration plot and enlarged initial section of the same graph.

Constant potential amperometry also was applied to determine the capability of IrO$_x$/GC for quantitative determination of sulfite. Fig. 4 displays the authentic record of the amperometric response of IrO$_x$/GC to successive additions (in 30 s intervals) of Na$_2$SO$_3$ stock solution into magnetically stirred PBS (pH 7.0) at a working potential of 0.5 V. Upon injection of sulfite the modified electrode shows increasing staircase current response, corresponding to the electrochemical oxidation of the analyte, which evidences that IrO$_x$/GC efficiently promoted the electrooxidation of sulfite. The response time of the sensor system was 10 s. The background subtracted steady-state response of the electrode was proportional to the sulfite concentration up to 9.1 mM (correlation coefficient of 0.995) with a sensitivity of 81 $\mu A\ mM^{-1}\ cm^{-2}$, calculated on the basis of 58 points. The IrO$_x$/GC sensor showed a

comparatively lower working potential and better sensitivity toward sulfite detection [8-12] (Table 1).

It is well known that the long-term stability is one of the main factors that determine the possibility of using the modified electrode as a sensing element. The developed electrode IrO_x/GC was stored at room temperature and measured every 4 days. After 20 days storage the current response to 1 mM sulfite (measured by constant potential amperometry at 0.5 V) retained 94 % of the initial value, demonstrating the good stability of the electrodeposited catalytically active phase.

Electrocatalytic reduction of hydrogen peroxide

The catalytic activity of the proposed IrO_x in the electroreduction of H_2O_2 was also evaluated. In order to assess the impact of type of carbonaceous carrier on the activity of the electrocatalysts, spectroscopic graphite and pyrolytic graphite electrodes have been modified applying the same procedure for electrodeposition of IrO_x. It is well known that the applied potential strongly affects the amperometric response of the electrochemical sensors. Therefore, we have investigated the impact of the applied potential on the amperometric response on the three types of carbonaceous electrodes modified with IrO_x (IrO_x/GC, IrO_x/Gr, IrO_x/PGr) towards reduction of H_2O_2. Chronoamperometric measurements of different concentrations of H_2O_2 at the modified electrodes were done by setting the working potential at –0.1, –0.2 and –0.3 V, respectively. The results indicate that for all types of modified electrodes the reductive current increased stepwise upon introducing in the buffer aliquots of the H_2O_2 stock solution. Table 2 summarizes the operational parameters in terms of sensitivity and linearity of the modified electrodes. The data clearly show that the modified graphite IrO_x/Gr possesses optimal operational characteristics. At an applied potential of –0.2 V the analytical detection of H_2O_2 with IrO_x/Gr is distinguished by the highest sensitivity (240 µA mM^{-1} cm^{-2}) in extended linear range (up to 10.9 mM). The merits of the presented modified electrode IrO_x/Gr can be evaluated by the comparative review presented in Table 1. As can be seen, the IrO_x/Gr exhibits better analytical performance than other published electrochemical sensors for H_2O_2 detection [13-18]. The low working potential of H_2O_2 detection suggests successful application of IrO_x-modified carbonaceous electrodes for quantitative analysis in real samples.

From the data presented it is evident that the electrode type IrO_x/PGr exhibits much lower current response than the other two modified electrodes. It is well known that the activity of heterogeneous catalysts strongly depends on the content and the dispersity of the catalytically active phase. The observed low activity of IrO_x/PGr is probably due to the lower amount of catalytically active phase deposited onto the pyrolytic graphite surface. We are convinced that the sensitivity of the proposed electrodes could be improved by optimizing the scan rate and the number of cycles applied for modification of the carbonaceous carrier. In this regard, the aim of our future research is to determine how the parameters of electrodeposition process affect shape and size of the structures formed onto electrode surface and to establish correlation with catalytic activity of the modified electrodes in the target reaction.

Table 2. Operational parameters of carbonaceous electrodes modified with IrO_x for amperometric sensing of H_2O_2; background electrolyte 0.1 M PBS (pH 7.0).

Modified electrode	E, V	Sensitivity, µA mM^{-1} cm^{-2}	R^2	Linearity, mM
	-0.3	135	0.999	7.2
IrO_x/GC	-0.2	117	0.988	6.3
	-0.1	61	0.996	7.2
	-0.3	215	0.983	9.1
IrO_x/Gr	-0.2	240	0.985	10.9
	-0.1	180	0.994	8.0
	-0.3	35	0.997	9.5
IrO_x/PGr	-0.2	41	0.999	10.9
	-0.1	37	0.983	10.9

CONCLUSIONS

In the present study, we have fabricated iridium oxide-based electrochemical sensor platform for sensitive detection of AA, sulfite and H_2O_2 through a fast and simple electrochemical strategy for surface modification. The developed sensor platform exhibited a remarkable direct electrocatalytic activity towards the oxidation of AA and sulfite as well as reduction of H_2O_2 in the absence of any other electron transfer mediators or enzyme immobilization at the electrode surface. The results obtained from the quantitative detection measurements offer potential application of the carbonaceous electrodes modified with iridium oxide in electrochemical sensor devices for quick and sensitive monitoring of these analytes for environment security and food safety. In addition, the modified electrodes may have potential applications in biosensing.

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