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A novel nonenzymatic hydrogen peroxide amperometric sensor based on AgNp@GNR nanocomposites modified screen-printed carbon electrode

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Abstract

A nonenzymatic hydrogen-peroxide sensor was developed by utilization of silver nanoparticles and graphene nanoribbons. The mentioned composite was inflicted on a screen-printed carbon electrode which provides disposable, ready-to-use sensor. The structure and morphology of the nanocomposite were analyzed by scanning electron microscopy and X-ray diffraction. The sensor has excellent performance toward H₂O₂ amperometric detection. Figures of merit include dynamic response range from 0.05 to 5 mM and detection limit of 20 μM (at S/N = 3). The fabricated sensor was used for the determination of H₂O₂ in milk samples. The obtained results showed that the proposed AgNp@GNR/SPCE sensor can be used for the determination of hydrogen peroxide in real samples.

Keywords: graphene nanoribbons, screen printed carbon electrode, hydrogen peroxide, enzyme-less hydrogen peroxide sensor

Introduction

Hydrogen-peroxide is a very important mediator in clinical, environmental and food analysis. Accurate and precise determination of this molecule is of great importance. Several methods, such as chromatography [1,2], spectrophotometry [3–5] or titrimetric methods can be used to determinate hydrogen peroxide in real samples. However, these methods are often very complex

and expensive. On the other hand, electrochemical methods enable fast, usually simple and often the inexpensive determination of this analyte [6,7].

Recently, various forms of nanomaterials based on carbon- and/or graphene have been developed for sensory purposes, such as single or multi-walled carbon nanotubes, graphene nanosheets, graphene nanoribbons etc [8–14]. Graphene nanoribbons (GNR) are narrow strips of graphene or single-layer graphite [15]. This configuration gives the material outstanding properties such as large surface area, high mechanical strength, high electrical conductivity, high elasticity and thermal conductivity [16,17].

Although these mentioned carbon and graphene materials possess excellent electrocatalytic properties, they are usually enriched with metal nanoparticles [18–20] or metal oxides [21,22] in order to increase their selectivity. Noble metal nanoparticles, gold, silver, platinum, palladium and rhodium play important role in the development of new biosensors as means of increasing sensitivity and improving selectivity [23]. Among these noble metal nanoparticles, silver nanoparticles (AgNp) have become the subject of increasing research as they have characteristics suitable for the use in clinical research and biological sensing [23]. These characteristics include good biocompatibility, low toxicity, good catalytic activity, high conductivity and also antibacterial activity [24–27].

Different combination of graphene and/or carbon nanomaterials with metal/metal oxide nanoparticles are frequently used for the sensor/biosensor construction. These composites are then used to modify screen-printed electrodes or glassy carbon electrode, as materials that improve the characteristics of the bare carbon electrode [28]. Screen-printed electrodes are more preferably than other electrodes used in biosensing, because they have appropriate characteristics for the analysis of biological samples [11].

The main goal of this paper was to develop a new enzyme-less, disposable electrochemical sensor for the determination of hydrogen peroxide. We used graphene nanoribbons reinforced with silver nanoparticles, as a composite made of materials with excellent properties toward electrochemical detection, for modifications of screen-printed carbon electrodes (SPCE).

Experimental part

Reagents and instruments

All electrochemical measurements (cyclic voltammetry and amperometric measurements) were performed using a potentiostat/galvanostat CHI 760b (CH Instruments, Inc., Austin, USA). Glass cell (total volume of 10 ml) with three electrodes was used for all electrochemical experiments. As reference electrode, an Ag/AgCl electrode (3 M KCl) was used while as counter electrode we used Pt wire. As a working electrode, the modified screen-printed electrode was used. Each potential reported in this paper is given against Ag/AgCl/3 M KCl electrode at a laboratory temperature of 25 ± 1 °C. For pH measurements pH meter model Orion 1230 equipped with combined glass electrode model Orion 9165BNWP (USA) was used.

The crystal structure of AgNp@GNR was analysed by X-ray powder diffraction (XRPD) technique performed on dried powders in a high-resolution SmartLab[®] X-ray diffractometer (Rigaku, Japan) using Cu K α radiation ($\lambda = 1.542$ Å). The diffraction patterns were collected within of $20\text{--}70^\circ$ 2θ in a scan rate of $0.05^\circ/\text{min}$ with divergent slit of 0.5 mm and operated at 30 mA and 40 kV.

The morphology of synthesized AgNp and prepared composite were investigated employing a field emission-scanning electron microscopy (FE-SEM) with a MIRA3 microscope (Tescan, Czech Republic) which operated at 30 kV. The carbon-coated copper grids were prepared by placing a drop of particles suspended in water on it and allowing them to dry at room temperature (RT) for FE-SEM observations.

All chemical used in this paper were of analytical grade and used as supplied. Graphene nanoribbons (GNR, length 2-15 μm , width 40-250 nm), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) and potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) were all supplied by Sigma Aldrich (Darmstadt, Germany). Phosphate buffer solutions were prepared by dissolving corresponding amounts of phosphate salts (K_2HPO_4 and KH_2PO_4 , Merck) in ultra-pure water. All other chemical used in this work was supplied from Merck, Germany.

Preparation of working electrodes

Screen-printed carbon electrodes (SPCE) were prepared by applying thick layers of carbon ink (No. C2030519P4, Gwent, Pontypool, UK) to laser pre-etched ceramic supports (No. CLS 641000396R, Coors Ceramics GmbH, Chattanooga, TN, USA). With the aid of a screen-printing

device (SP-200, MPM, Franklin, MA, USA), the ink was brushed through an etched stencil (thickness 100 μm , electrode printing area 105 mm^2) onto the substrates. The resulting plates were dried overnight at room temperature.

In order to get AgNp@GNR/SPCE working electrode, the synthesis of silver nanoparticles (AgNp) was firstly performed, following the procedure described in the literature [29,30]. Briefly, 21.7 mg of AgNO_3 was dissolved in 250 ml of ultra-pure water, and heated until boiling, with continuous stirring. Then, in this solution, 4 ml of 1% solution of sodium-citrate was added and heating was continued until the color of the solution became yellow. After this, solution was only stirred, without heating for 15 more minutes. Composite made of AgNp and GNR was obtained in the following way. First, graphene nanoribbons (10 mg) were suspended in 10 ml of ultra-pure water and this mixture was sonicated for 1 hour. Then, in this suspension, 2 ml of obtained AgNp colloid solution was added and the mixture was sonicated for 15 min. After this period, the solution was leave at room temperature for 12 h. After 12h, solution was centrifuged and washed three times with ultra-pure water and one time with ethanol. Prior use, AgNp@GNR particles was dried, dissolved in dimethylformamide (DMF, concentration of the solution was 5 mg/ml) and sonicated for 3 hours. After this period, 5 μL of the obtained composite was deposited on the SPCE electrode and allowed to dry at room temperature. In the described way, AgNp@GNR/SPCE modified electrode was obtained. This procedure has also been performed without GNR, in order to compare the electrochemical properties of obtained materials. One electrode was prepared by applying only nanoparticles of silver on the SPCE surface.

Results and discussion

Characterization of synthesized AgNp@GNR composite

The morphologies of synthesized Ag nanoparticles and AgNp@GNR composite were investigated by scanning electron microscopy. The FE-SEM micrographs of synthesized Ag nanoparticles were shown in Fig 1A. As illustrated, AuNPs are small spheres densely packed in the form of grape-like clusters, stacked on top of each other. The particle's size of individual particles was less than 20 nm. As can be seen in Fig. 1B, graphene nanoribbons are long curved nanorods with granular-shaped aggregates at the end of each ribbon. The average length of individual ribbon was in the range of few micrometers, while the width was between 100-200

nm, making great support for the attachment of small Ag nanoparticles. The morphology of AgNp@GNR composite is shown in Fig. 1C. The microstructure of the prepared AgNp@GNR analyzed by XRPD is presented in Fig. S1. While it is difficult to identify all of the reflections, it is clear that the composite was prepared successfully, because the pattern of (002) GNR plane reflection at 26.2° is present in both samples [31].

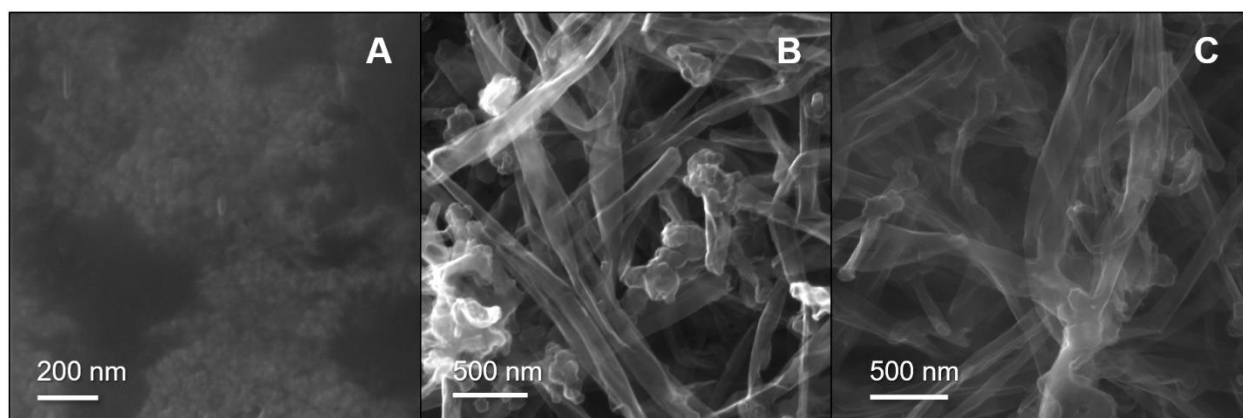


Figure 1. FE-SEM images of: (A) Ag nanoparticles, (B) GNR and (C) AgNp@GNR composite.

Characterization of working electrodes

In order to investigate electrochemical properties of the obtained electrode, cyclic voltammograms of a solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ in 0.1 M PBS solution (pH 7.4) was recorded. Obtained voltammograms are present in Fig. 2. As can be seen, the CVs of bare SPCE and SPCE decorated with GNR shows a pair of poorly defined redox peaks in contrary to SPCE decorated with silver nanoparticles and SPCE modified with composite material (AgNp@GNR), where presence of two oval-shaped and well-defined redox peaks are notable. Oxidation peaks appeared in the potential ranges from 0.53 up to 0.92 V and reduction peaks in the potential range from -0.27 to -0.60 V. Peak-to-peak separation is smallest in the case of SPCE decorated with AgNp, followed AgNp@GNR modified electrode. The highest current intensity was achieved using the AgNp@GNR/SPCE modified electrode which can be attributed to the presence of GNR and Ag nanoparticles, which provided a synergistic effect increase of electrochemical signal. Anodic to cathodic peak current density ratios (I_{pa}/I_{pc}) are 1.12; 1.10; 1.09 and 1.05 for SPCE, GNR/SPCE, AgNp/SPCE and AgNp@GNR/SPCE, respectively. Based on these results, we can exclude SPCE and GNR/SPCE electrodes further consideration due to their poorer performance. Both of AgNp/SPCE and AgNp@GNR/SPCE modified electrodes

showed good electrochemical characteristics whereby latter one showed significantly higher signal current intensities as well as better reversibility.

In order to confirm that the AgNp@GNR/SPCE modified electrode is applicable for our analyte, cyclic voltammograms of PBS solution containing 25 mM H_2O_2 was recorded. Results are given in Fig. S2. Only with a modified electrode an oxidative peak of hydrogen peroxide was observed. So, based on these results, AgNp@GNR/SPCE modified electrode was used for all further experiments as an electrode of choice.

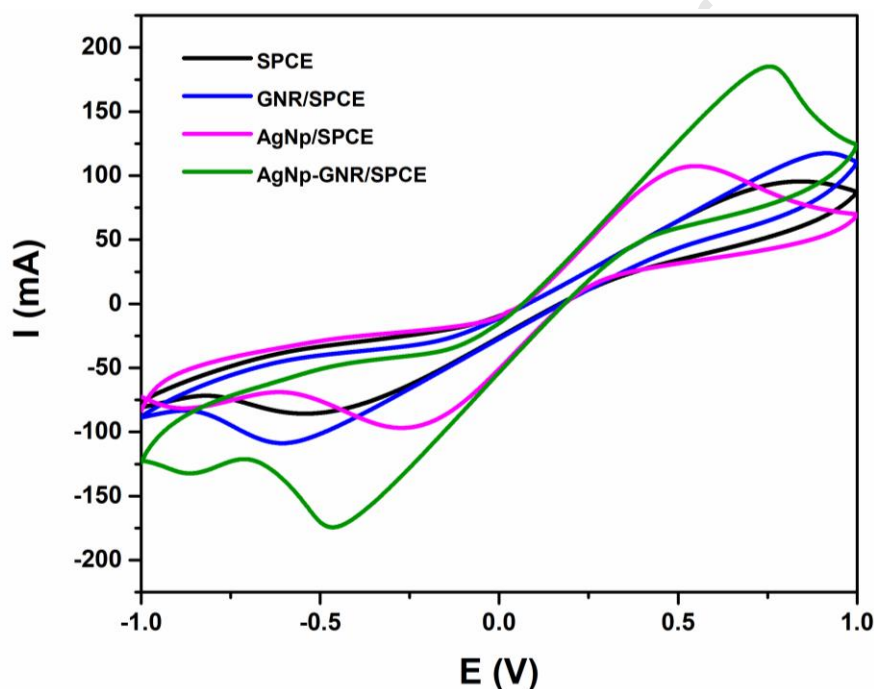


Figure 2. Cyclic voltammograms for each electrode in 0.1 M PBS solution (pH 7.4) containing 5 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$. Scan rate 50 mV/s

Optimization of analytical parameters

Once we confirmed that our electrode possesses the best electrochemical characteristic, we proceeded to develop an analytical procedure for the detection of H_2O_2 . Firstly, we optimized analytical parameters: pH value of supporting electrolyte and operating potential. For optimization study, we used chronoamperometry instead of cyclic voltammetry since this method offers better sensitivity and higher signal-to-noise ratio.

The effect of pH values of working solutions was investigated in the range from 6.2 to 8.0, using PBS solution (Fig. 3A). For each tested pH value, current was monitored after addition of hydrogen peroxide standard solution: aliquot containing 0.2 mM, 4 times. Results were presented in the Fig. 3A, as calibration curve in the range 0.2 mM – 0.8 mM, while obtained currents for each aliquot at selected pH were calculated as current difference after and before aliquot addition, and summarized, as mean value (ΔI , $n=4$), in the Figure 3B. It was observed that the current response of the AgNp@GNR/SPCE toward H_2O_2 , increases with increasing pH value up to pH value of 7.8. There was no significant increase in current response after this value, while at the same time a greater instability of the signal became noticeable (Fig. 3B). We chose pH value of 7.8 for all further experiments considering current response intensity as well as signal stability when this buffer solution was used.

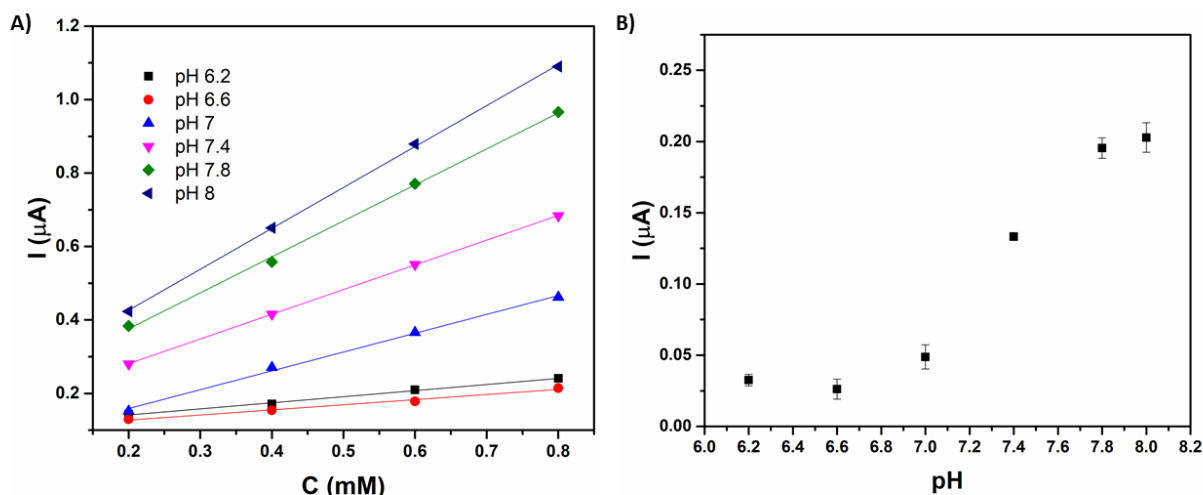


Figure 3. Optimization of pH value of supporting electrolyte A) Amperometric response of AgNp@GNR/SPCE toward successive addition of 0.2 mM of hydrogen peroxide standard solution to PBS of different pH values B) dependence of amperometric current response after hydrogen peroxide addition in PBS of different pH values

The effect of operating potential was investigated at chosen pH value, in the range from 0.40 to 0.56 V. Amperometric measurements in stirred solution at optimized pH and at different operating potentials (Fig. 4A and Fig. 4B) were performed. To compare influence of the used working potentials, a similar approach was used as for pH studies: 0.2 mM aliquot H_2O_2 , $\Delta I = I_{\text{after addition}} - I_{\text{before addition}}$, $n=5$, results summarized as calibration curve in the range 0.2 mM – 1

mM. With increasing operating potential, the current response of the AgNp@GNR /SPCE was also increasing (Fig. 4B). However, in the same way, the signal instability increased as did the baseline current values. Based on these results, we have chosen for all further works potential of 0.52 V as optimal potential value.

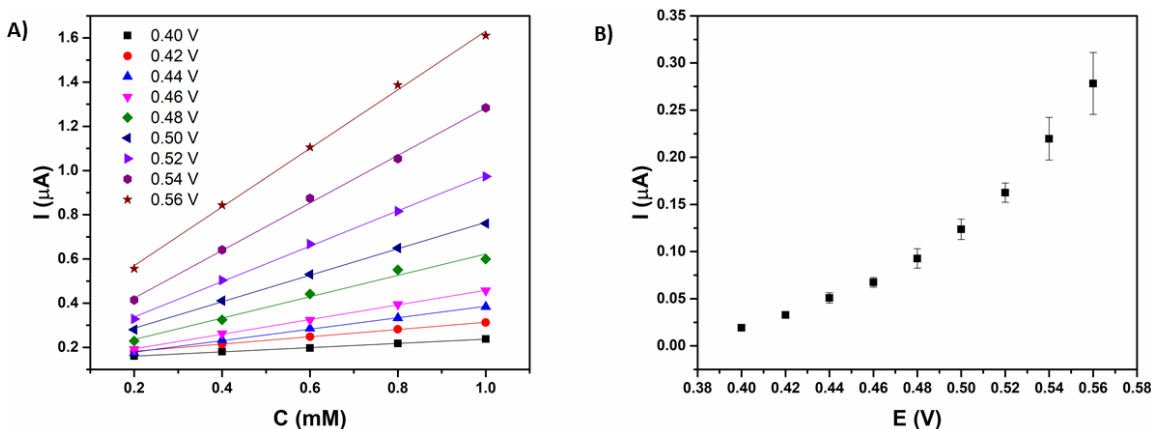


Figure 4. Optimization of operating potential A) Amperometric response of AgNp@GNR/SPCE toward successive addition of hydrogen peroxide standard solution at different operating potential B) dependence of amperometric current response after hydrogen peroxide addition at different operating potential

Analytical performance of proposed sensor

Using optimal experimental parameters, we proceeded to investigate a method for H_2O_2 determination. Firstly, we examined the sensitivity and the linear range of proposed sensor. In this purpose, we used amperometry as a method of choice. Amperometric response in stirred PBS solution was recorded for successive addition of a known amount of H_2O_2 standard solution (Fig. 5A). On this way, a calibration curve showing two linear ranges was obtained (Fig. 5B). The first linear range corresponds to concentration values from 0.05 to 1.8 mM and was determined by the equation $y=0.2490+1.2540x$ ($R^2=0.9984$). The second linear range corresponds to concentration values from 1.8 to 5 mM and was determined by the equation $y=1.0623+0.8185x$ ($R^2=0.9963$). The limit of detection was calculated according to the 3 Sa/b [32] as 0.02 mM, based on first linear range.

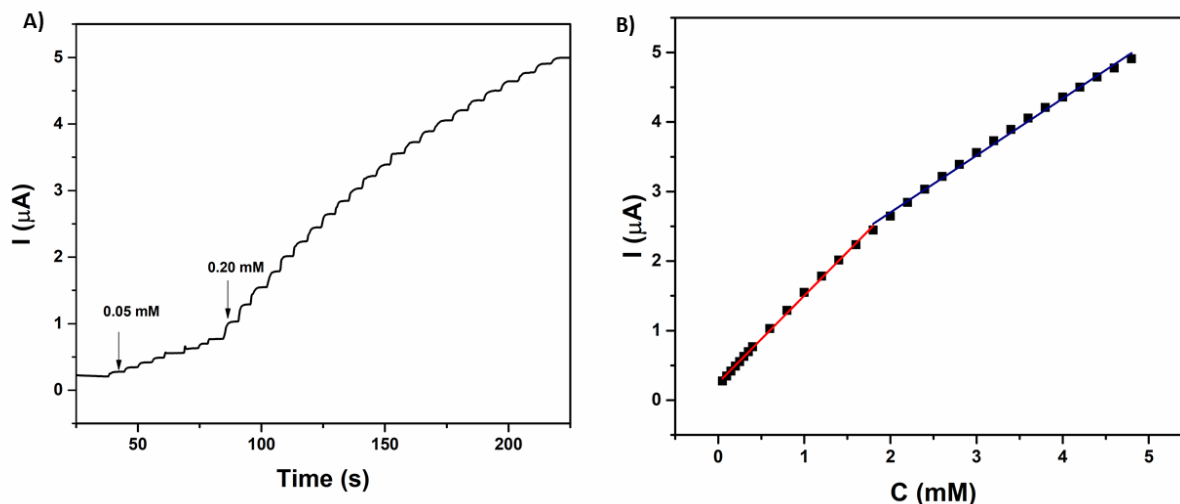


Figure 5. (A) Amperometric response toward successive addition of hydrogen peroxide standard solution (B) Calibration curve

Looking at the literature data for electrochemical hydrogen peroxide sensors obtained by various electrode modifications and simultaneously using silver nanoparticles, we can conclude that the here proposed sensor is comparable to the previously reported ones (Table 1). Also, in several reports linear range of sensors is wider and LOD often lower than in our case, preparation of mentioned electrodes is more complicated and time-consuming. Also, GNRs are poorly investigated toward sensor development and this paper is one of few that deal with this research.

Table 1. Comparison of non-enzymatic electrochemical hydrogen peroxide sensors with Ag nanoparticles reported previously with the AgNp@GNR/SPCE sensor.

Electrode	Dynamic range (mM)	Detection limit (μ M)	Reference
AgNp@GNR/SPCE	0.05 – 5	20	<i>This work</i>
MWCNT/Ag nanohybrids/Au	0.05–17	0.5	[33]
Ag NPs/Cu-TCPP/GCE	0.0037 - 5.8	1.2	[34]
RGO/Ag-Au/Cu ₂ O	0.05 - 50.75	0.1	[35]
LSG-Ag	0.1 – 10	7.9	[36]
Ag NPs/GC	0.025-5.5	10	[37]
Ag microspheres GCE	0.2 - 4	1.2	[38]
Ag NW array	0.1-3	29.2	[39]
GCE/PVP-AgNWs	0.02-3.26	2.3	[40]
GCE/GO-Ag nanocomposite	0.1-11	28.3	[41]

Selectivity, repeatability and reproducibility

The selectivity of the proposed sensor was evaluated using several different compounds commonly present in biological samples: glucose, ethanol, ascorbic and uric acid. Influence of the each interfering compound was tested during construction of the calibration plot under optimized experimental conditions. After two consecutive additions of H_2O_2 (0.2 mM), the same amount of interference was added. The response of the electrode was monitored by a potential increase in current. For all tested interferences this procedure was repeated two times. Results are given in the Electronic Supplementary Material, Fig S3. As can be seen, after the addition of ethanol and glucose there were not electrode response. On the other hand, ascorbic acid, and uric acid to a lesser extent, interfere with H_2O_2 determination.

The performance of the obtained sensor toward the detection of H_2O_2 was evaluated during 5 weeks in order to examine its durability. The measurements were performed on every seven days and in meanwhile electrode was kept at 4 °C. After this period, the sensor retained 92.3 % of its initial current response which approve its great durability (Fig. 6A). For the reproducibility studies, amperometric measurements at five individual electrodes were recorded in PBS (pH 7.8) towards 3 mM of H_2O_2 and obtained and calculated RSD value 4.5 % (Fig. 6B). For the repeatability studies, five repeated measurements were performed at one modified electrode (PBS solution, pH 7.8, 3 mM H_2O_2) and obtained and calculated RSD value was 2.9% (Fig. 6C). According to these results can be concluded that the proposed sensor has good repeatability as well as reproducibility.

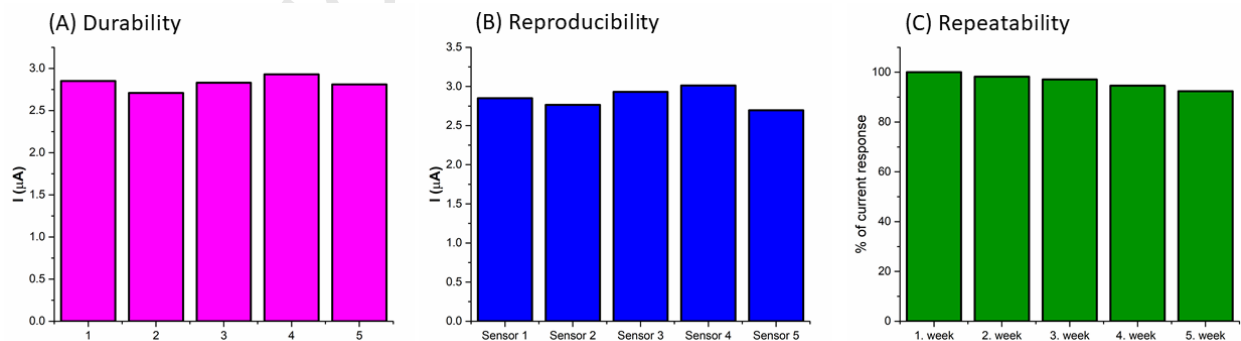


Figure 6. Durability, reproducibility and repeatability studies for proposed sensor

Real sample analysis

The developed sensor is not suitable for clinical samples, having in mind interfering studies. However, it can be applied to testing of H_2O_2 concentration in different disinfectants or food analysis. Namely, H_2O_2 can be used as a preservative in milk or juices [42,43]. The applicability of the AgNp@GNR/SPCE sensor for H_2O_2 determination was carried out by testing H_2O_2 concentration in milk samples using the standard addition method. For every sample, three individual measurements were performed. The amperograms are recorded in PBS solution (pH 7.8). Obtained results are given in Table 2. Recovery values were in the range from 96.0 to 104.0 % (Table 2). These results imply the potential of the use of the proposed electrode for future practical application.

Table 2. Determination of H_2O_2 in real samples

Sample	Added (mM)	Found (mM)	Recovery (%)
1	0.50	0.48 ± 0.02	96.0
	4.00	4.02 ± 0.12	100.5
2	0.50	0.52 ± 0.03	104.0
	4.00	3.98 ± 0.11	99.5
3	0.50	0.51 ± 0.02	102.0
	4.00	4.05 ± 0.10	101.3

Conclusion

Composite made of silver nanoparticles, obtained by easy synthesis and graphene nanoribbons was inflicted on the surface of the SPCE to provide a portable, disposable sensor, easy to use. The proposed sensor was further used for quantification of hydrogen peroxide. Material was characterized using spectroscopic and electrochemical methods. Amperometric method was optimized and used for estimation of analytical performance of the sensor. Obtained linear range (from 0.05 to 5 mM), as well as low detection limit (20 μM), allow utilization of AgNp@GNR/SPCE sensor for hydrogen peroxide detection. Additionally, effect of several interfering compounds was tested. Practical application of the sensors was investigated toward peroxide quantification in food samples. These results showed excellent accuracy and precision of the proposed procedure.

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