



Ag or Au Nanoparticles Decorated Multiwalled Carbon Nanotubes Coated Carbon Paste Electrodes for Amperometric Determination of H₂O₂

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Abstract

Composite materials made of multiwalled carbon nanotubes and silver (Ag-MWCNT) or gold particles (Au-MWCNT) were synthesized and characterized by XRD and SEM/EDS techniques. The composites and the MWCNTs were applied as surface modifiers of carbon paste electrodes (CPEs). The mediator based electrocatalytic activity of the modified electrodes was investigated for H₂O₂ oxidation/reduction by electrochemical measurements. All voltammetric working electrodes (Ag-MWCNT/CPE, Au-MWCNT/CPE, MWCNT/CPE and the bare CPE) were characterized by cyclic voltammetry (CV) in acetate and phosphate supporting electrolytes (0.1 mol L⁻¹, pH 4.50 and 7.50, respectively) in the absence and presence of the H₂O₂ analyte. Amperometric experiments were performed in stirred solutions at selected constant working potentials, in accordance with the CV responses, for developing new analytical methods for the determination of H₂O₂. In the case of the Ag-MWCNT/CPE the most promising working potentials in the acetate buffer solution were -0.40 V and +0.80 versus SCE; in phosphate buffer solution these values were between -0.20 and -0.30 V and from +0.60 to +1.0 V. The Au-MWCNT/CPE is applicable in acetate buffer supporting electrolyte in the working potential close to -0.30 V versus SCE and from +0.70 to +1.0 V; in the phosphate buffer solution only from +0.60 V versus SCE and higher values. Due to the presence of the signal enhancement effect of Au and Ag nanoparticles, the sensitivity of the obtained methods is significantly higher in comparison to the results obtained by the MWCNT/CPE and bare CPE. The relative standard deviation of the measurements was lower than 10%. The practical application using the Ag-MWCNT/CPE was shown for the determination of H₂O₂ in real nursing product sample. It was proven that the developed mediator based (electro)catalytic platform exhibits low detection limit, high selectivity, reproducibility and stability.

Keywords Au-MWCNT · Ag-MWCNT · H₂O₂ determination · Voltammetry · CPE · Nursing product · Mediator based electrocatalytic signal enhancement

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1 Introduction

Hydrogen-peroxide (H₂O₂) is an analyte of great importance because of its large involvement in different fields of application such as environmental protection/analysis, pharmaceutical research, textile industry, medical diagnostics, etc. [1–3]. It is a powerful oxidant and found applications in many organic compound synthesis and for removal of pollutants from wastewater by advanced oxidation processes [4–7]. Moreover, H₂O₂ is an active ingredient of different disinfection and nursing products, with 3% of H₂O₂. Therefore, there is a need for development of sensitive and reliable analytical methods for determination of this target analyte in different complex matrices.

Electroanalytical measurements compared to other ones enable low-cost, selective, sensitive, simply and fast detection/determination of H_2O_2 [8]. In analytical voltammetry carbon paste presents a convenient electrode material (CPE) for the amperometric determination of H_2O_2 due its direct oxidation or reduction which occurs at highly positive or negative working potentials. In order to reduce the overpotential of H_2O_2 redox processes on such simpler carbonaceous electrodes different modifiers/mediators/catalysts are incorporated into the electrode bulk or at electrode surface [9, 10] with aim to improve the selectivity and in some cases the sensitivity of the working electrode and on this way the sensitivity of the related analytical method as well. The modification of carbon paste electrodes with mono- or bimetallic micro- and nanoparticles (Pt, Pd, Cu, Ag) or other nanostructures (carbon nanotubes) for the determination of H_2O_2 has received considerable attention [11–13]. The benefited properties of CNTs such as chemical stability, high surface area, excellent electrical conductivity and electrocatalytic activity makes them suitable for preparation/modification of electrochemical working electrodes/sensors. They can be functionalized with organic molecules, polymers, enzymes, proteins, DNA and with different metal (nano)particles which expand their application [12]. Combination of CNTs and metal (nano)particles produce the hybrid materials which are often important for catalysis (including electrocatalysis) and nanotechnology [14]. Such materials can be incorporated in/on working electrodes upgrading their catalytic activity towards H_2O_2 sensing and improving the selectivity and/or sensitivity of its determination. Beside Pt and Pd nanoparticles deposited onto the CNTs surface for determination of H_2O_2 [10, 15–20], the Ag and Au (nano)particles are also found application for similar purposes. Different substrate electrodes (such as glassy carbon or gold) were surface modified with multiwalled carbon nanotubes (MWCNTs) or ionic liquid functionalized MWCNTs decorated with Ag nanoparticles for determination of H_2O_2 [21–24]. The gold electrode surface modified with composite of polyaniline, MWCNTs and Au nanoparticles and functionalized CNTs with Au nanoparticles have proven to be suitable as electrochemical sensors for determination of H_2O_2 [13, 25]. Furthermore, fluorine-doped tin oxide electrode modified with ZnO nanorods and Ag nanoparticles [26] and Pt electrode modified with Ag nanoparticles [27] were used as well for amperometric sensing of H_2O_2 . Another one, the ceramic electrode modified with a nanohybrid composite made from singlewalled carbon nanotubes and Ag nanoparticles was successfully applied for determination of H_2O_2 in a complex sample as honey [28]. Also, the composite material Ag-CNTs was used as a building element during the preparation of nanocomposites with polypropylene and polystyrene improving

the electrical conductivity and mechanical properties of polymers compared to non-functionalized CNTs [29].

The aim of this work was to prepare silver or gold nanoparticle modified MWCNTs based nanocomposite materials (Ag-MWCNT and Au-MWCNT), their incorporation into the simply paraffin oil and graphite powder containing carbon paste working electrode sensor surface, and the investigation/comparison of the voltammetric behavior and applicability of these electrodes in the determination of H_2O_2 with special attention to a real sample/nursing product.

2 Experimental

2.1 Chemicals and Solutions

All chemicals used were of analytical reagent grade. As supporting electrolytes two 0.1 mol L^{-1} buffers, acetate pH 4.50 and phosphate pH 7.50 were applied. The acetate buffer solution was made from required volumes of 0.1 mol L^{-1} sodium acetate (tri-hydrate) (13.6 g L^{-1}) (p.a., Sigma-Aldrich) and 0.1 mol L^{-1} acetic acid (p.a., Sigma-Aldrich) solutions. The phosphate buffer solution (0.1 mol L^{-1} , pH 7.50) was prepared by appropriate mixing of aqueous solutions of 0.1 mol L^{-1} sodium dihydrogenphosphate (p.a., Sigma-Aldrich), and 0.1 mol L^{-1} disodium hydrogenphosphate (p.a., Sigma-Aldrich). The pH values of the prepared buffer solutions were measured by pH-meter. Standard solutions of H_2O_2 were daily prepared from the 30% H_2O_2 (INK, Inzenjering, Beograd) by appropriate dilutions, while the concentration of the stock was controlled by permanganometric titration. All solutions were prepared with doubly distilled water.

2.2 Apparatus

Cyclic voltammetric (CV) and amperometric measurements at constant potential were performed at an electrochemical analyzer AUTOLAB PGSTAT12 operated via GPES 4.9 software. The voltammetric vessel with reduced bottom included a three-electrode system with reference saturated calomel (SCE) and auxiliary platinum (Amel) electrodes and the following working electrodes: native CPE, MWCNT/CPE, Au-MWCNT/CPE, and Ag-MWCNT/CPE. All potentials are quoted to the SCE.

pH measurements were performed on a digital pH-meter (Radiometer) using a glass electrode in combination with SCE.

Surface morphology characterization and semi-quantitative chemical analysis of the Au-MWCNT and Ag-MWCNT composites was performed with a HITACHI S-4700 Type II cold field emission scanning electron microscope (SEM) by using an integrated Röntec QX2

EDS detector. Spectra were analyzed by the factory standard software after automatic background subtraction and peak fitting.

Powder X-ray diffraction (XRD) patterns for the synthesized materials were obtained by a Rigaku Miniflex II instrument using Cu $K\alpha$ radiation.

2.3 Procedures

2.3.1 Preparation of MWCNT, Ag-MWCNT and Au-MWCNT

MWCNTs in their native and functionalized forms were used as surface modifier of the CPE. MWCNTs were prepared in our laboratory by catalytic chemical vapor deposition described elsewhere [30]. The as-grown MWCNTs were subjected to acid treatment for purification and functionalization (since acid treatment results in attachment of mainly—COOH groups at defect sites). The Ag-MWCNT and Au-MWCNT (nano)hybrid materials were prepared by a sonication assisted reduction method [31, 32]. Briefly, the required amount of AgNO_3 (or in case of Au-MWCNT sodium tetrachloroaurate(III) salt) was dissolved in water and 100 mg MWCNT was added to the solution. After 15 min sonication the reduction was carried out using NaBH_4 resulting in formation of Ag-MWCNT (or in case of gold Au-MWCNT) (nano)hybrid material. After this treatment the resulting substances were washed 3 times with ethanol and dried for overnight at 90 °C.

2.3.2 Preparation of Working Electrodes

The carbon paste was prepared by hand-mixing of 0.5 g graphite powder (< 20 μm , synthetic, Sigma Aldrich) with 0.2 mL paraffin oil (Kemika, Croatia) in agate mortar. The paste was packed into piston-driven Teflon holders with a diameter of 2 mm [33] and left for 24 h at room temperature. The CPE surface was formed/cleaned mechanically by squeezing out a small amount of paste from the holder by the micrometer screw of the electrode and wiping the surface with a piece of clean Teflon to obtain the appropriate shape of the renewed native/substrate CPE. The suspensions for the CPE modifications were prepared by dispersing 1.5 mg MWCNT, Au-MWCNT or Ag-MWCNTs in 1.0 mL of ethanol and sonicated in sonication bath (Bandelin) for cc. 20 min at room temperature. 3.0 μL of the resulting suspensions was dropped on a freshly generated CPE surfaces and the modified working electrodes (MWCNT/CPE, Au-MWCNT/CPE and Ag-MWCNT/CPE) were dried at room temperature cc. 15 min in accordance with our similar earlier procedure [10].

2.3.3 SEM–EDS Study of MWCNT, Au-MWCNT and Ag-MWCNT

The surface modifiers were analyzed by the accelerating voltage of 10.00 or 20.00 kV at different magnifications. The EDS measurements were performed at different representative locations of the investigated materials.

2.3.4 X-Ray Diffraction Measurements

Four different samples: native MWCNT, oxidized MWCNT, Ag-MWCNT and Au-MWCNT were characterized in the range from 0° to 90° 2θ .

2.3.5 Cyclic Voltammetric Measurements in Model Solutions

CVs were recorded in phosphate and acetate buffer solutions (0.1 mol L^{-1} , 10.0 mL, pH 7.50, and 4.50, respectively) with all investigated electrodes in the absence and presence of H_2O_2 in a potential range from 1.00 to -1.00 V with a scan rate of 50 mV s^{-1} starting in cathodic direction.

2.3.6 Amperometry in Model Solutions

Into the both buffer supporting electrolytes (0.1 mol L^{-1} , pH 7.50 and 4.50) equal aliquots of H_2O_2 standard solution were added by micropipette in the concentration range from 0.86 to 5.81 mmol L^{-1} in appropriate time intervals and constant potential of the working electrode versus SCE under permanent stirring of the solution (300 rpm). The widest investigated potential range for the selection of appropriate working potential(s) was from 1.00 to -1.00 V. Such measurements were recorded by Au-MWCNT/CPE, Ag-MWCNT/CPE, MWCNT/CPE and bare CPE. Detailed analysis was performed at pH 7.50 at the operation potentials from -0.20 to -0.30 V in the lower concentration range of H_2O_2 with the Ag-MWCNT/CPE. As the optimal working potential -0.25 V was chosen under mentioned circumstances, which later served for real sample analysis as well. In all cases the limit of detection (LOD) and quantitation (LOQ) values were evaluated as signal/noise 3 and 10, respectively.

2.3.7 Analysis of H_2O_2 Active Ingredient Content in the Selected Nursing Product

The 2.50 mL aliquot of the sample Oto aqua clean (spray solution) was directly added into volumetric flask of 25.0 mL which was flipped to the mark with doubly distilled water. Aliquot of 15.0 μL of such diluted sample was added by micropipette into the voltammetric vessel

with 10.0 mL of phosphate buffer supporting electrolyte pH 7.50 (0.1 mol L^{-1}) during the amperometric measurement under constant potential and stirring. In the same run in the next steps three times the equal volumes of H_2O_2 standard solution were added into the system. On such way the sample was analyzed by standard addition method. The applied working potential was -0.25 V . The experiments were repeated in triplicates by three times renewed Ag-MWCNT/CPE surface.

3 Results and Discussion

3.1 Physical Characterization of the MWCNT, Ag-MWCNT and Au-MWCNT

The SEM micrographs (Fig. 1) obtained for the MWCNT (a) and composites Ag-MWCNT (b, c) and Au-MWCNT

(d) confirmed a very similar carbon nanomaterial based frameworks where the MWCNTs are densely and randomly oriented. It can be stated that the structure was not affected during the nanoparticle decoration process. For both nanocomposites the Ag and Au nanoparticles, recognized as bright and mainly spherical unites, are surrounded by the carbon nanotubes. The average diameter of the metal particles was between 50 and 200 nm, the metal content was around 5 wt% for both composites.

The X-ray diffractograms at Fig. 2a, b showed the characteristic diffraction patterns of the synthesized materials: MWCNT (curve 1), Ag-MWCNT (curve 2) and Au-MWCNT (curve 3) in their full diffractograms (a) and in a section plot with characteristic signals (b), respectively. The aim of the XRD measurements was to characterize the Au and Ag-rich phase and to determine the possible impact of this phase on the composites by means of identifying the types of the metal-based particles. As it is well known, the

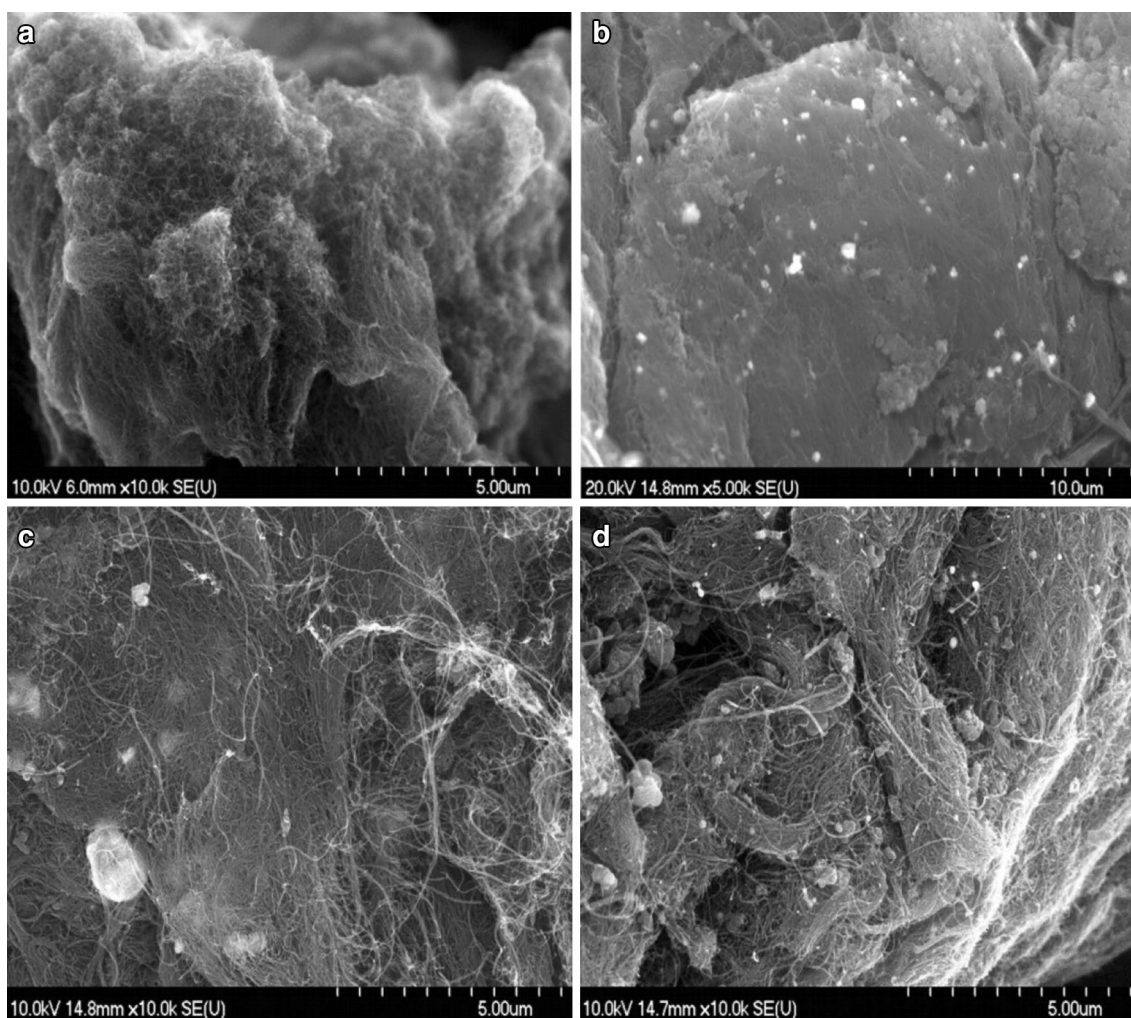


Fig. 1 Micrographs of the prepared nanomaterials: **a** MWCNT, **b, c** Ag-MWCNT and **d** Au-MWCNTs. In the case of the micrographs at **b** and **c** the Ag-MWCNT composite was observed under two different magnifications

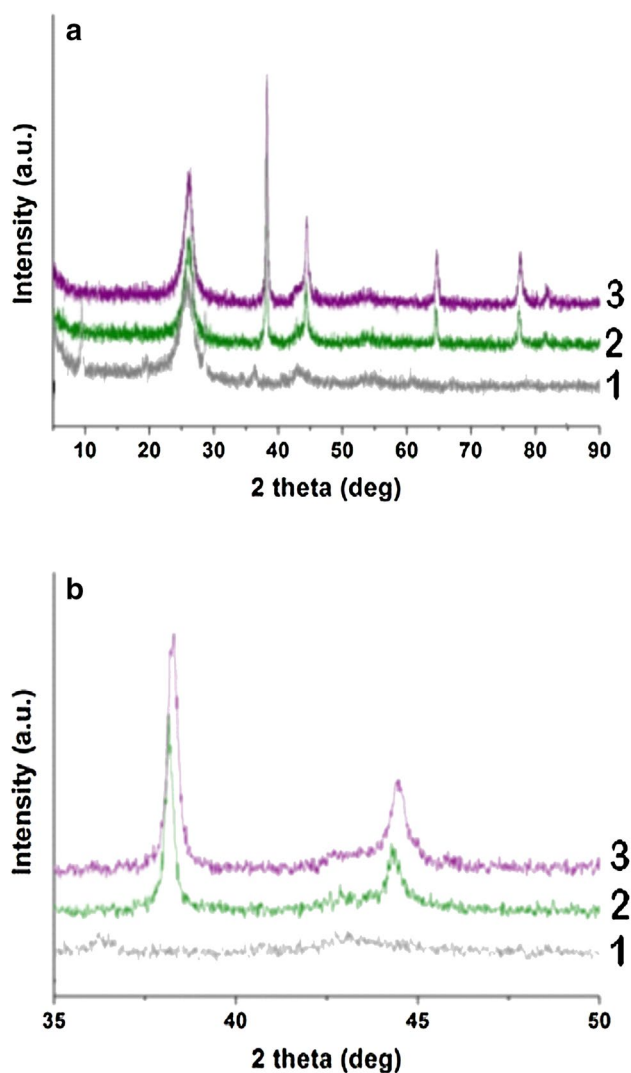


Fig. 2 XRD pattern of the nanomaterials: **a** full diffractograms of (1) MWCNT, (2) Ag-MWCNT and (3) Au-MWCNT and **b** section plots of the diffractograms of (1) MWCNT, (2) Ag-MWCNT and (3) Au-MWCNT

XRD patterns for all MWCNT based materials revealed the presence of a broad peak at 25.8° corresponding to the interlayer spacing (0.34 nm) of the nanotubes (d_{002}) which is in good agreement with the literature [34] for the native MWCNT (not shown) and oxidized form of MWCNTs (grey line marked as CNT). The XRD patterns of the (nano)hybrid material confirmed the presence of face-centered cubic (fcc) structured Au (JCPDS 4-784) and Ag (JCPDS 4-783) nanoparticles beyond the graphitic carbon structure. The section plot (b) showed the received information with more details concerning the peak positions of Ag and Au particles in the angle range between 35° and 50° .

3.2 Electrochemical Characterization of Au-MWCNT and Ag-MWCNT Modified Carbon Paste Electrodes

As first, cyclic voltammetric (Fig. 3) and amperometric (Figs. 4, 5) responses of the H_2O_2 analyte were investigated on native CPE (not shown), and by nanomaterials modified ones (MWCNT/CPE (not shown), Au-MWCNT/CPE (Figs. 3a, 4) and Ag-MWCNT/CPE (Figs. 3b, 5) in slightly alkaline (0.1 mol L^{-1} phosphate buffer, pH 7.50) and acidic (0.1 mol L^{-1} acetate buffer, pH 4.50) supporting electrolytes. Figure 3 illustrates the CV signals of the composite nanomaterials modified working electrodes in the absence (dashed lines) and presence (full lines) of H_2O_2 in the polarization range from 1.00 to -1.00 V in both buffer solutions (red lines pH 7.50, black lines pH 4.50). The native CPE has poor electrocatalytic properties toward the target analyte which is in accordance with our recent work where it was found that the H_2O_2 responses at the CPE belong to its direct electrochemical oxidation and reduction [10]. For the MWCNT/CPE in the slightly alkaline media the improvement of the H_2O_2 reduction signal intensity was obtained at potentials lower than -0.40 V . The effect is much significant in the case of the composite modified electrodes due to the presence of noble metal mediator (nano)particles into the MWCNT framework at the sensor surfaces. Namely, based on the recorded CVs, the Ag-MWCNT/CPE (Fig. 3b) showed pronounced reduction signal from -0.10 V and at lower potentials. Moreover, the electrode showed significant H_2O_2 response at 0.10 V and higher values. Concerning the Au-MWCNT/CPE (Fig. 3a), in the negative polarization mode from -0.30 V significant H_2O_2 reduction signal was observed, but the electrode is promising for H_2O_2 detection at positive polarizations at 0.40 V and higher potential values as well. Differences were observed for the composite nanomaterial-modified electrodes in acetate buffer supporting electrolyte (black lines) in the presence (full lines) and absence (dashed lines) of the H_2O_2 . In the acidic media the Ag-MWCNT/CPE and Au-MWCNT/CPE showed sharp reduction signals which started close to -0.25 and -0.65 V , respectively.

It should be noted that the MWCNTs on the CPE enhanced the H_2O_2 signal intensity mainly because of the increased sensor surface, and due to the changed/reduced overpotential of H_2O_2 redox processes which indicates the mediator based behavior of the working electrode. The two noble metal (nano)particles in combination with MWCNTs additionally changed/enhanced the H_2O_2 signal intensities and reduced the overpotentials because of their pronounced mediator/catalytic effects on the electrode surface concerning the reduction or oxidation of the target analyte. The tested supporting electrolytes influence the H_2O_2 signal

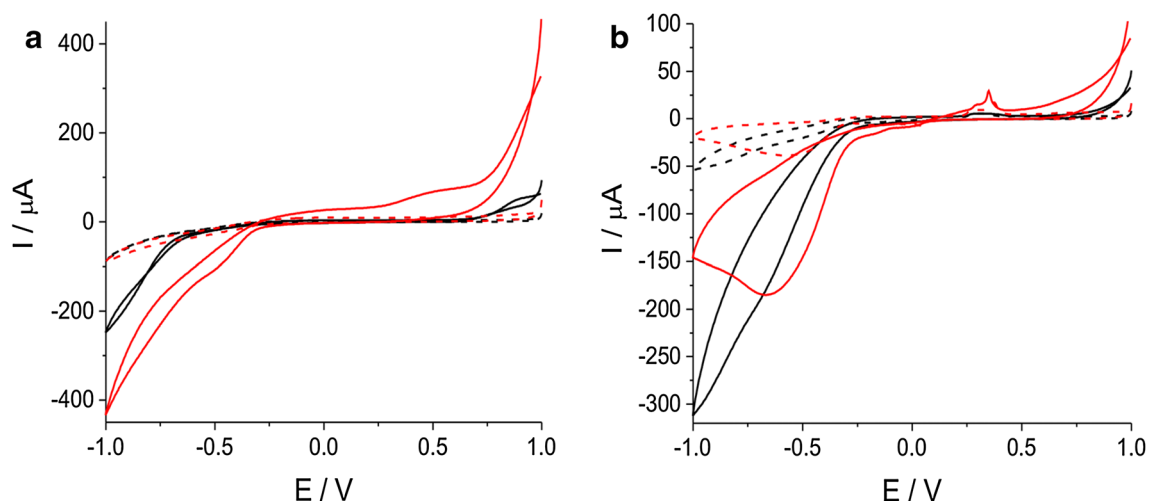


Fig. 3 Cyclic voltammograms recorded in acetate (black curves) and phosphate (red curves) buffer supporting electrolytes by: Au-MWCNT/CPE (a) and Ag-MWCNT/CPE (b). CVs recorded in the

supporting electrolytes (dashed line) and in the presence of $0.02 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ (full line). Scan rate 50 mV s^{-1}

generation in the case of all four electrodes, but particularly in the case of the composite modified ones.

It is important to emphasize that the simple graphite powder and paraffin oil containing carbon past electrode showed appropriate affinity to the MWCNTs, Ag-MWCNTs and Au-MWCNTs modifiers. These electrodes are stable during few days, except in the case of mechanical damaging of their surfaces. The electrochemical activation/conditioning of the working electrodes was required before each set of measurements by recording 10 CVs in the appropriate supporting electrolytes in the potential span from 1.00 to -1.00 V versus SCE. Additionally, the total renewing of the surface is possible by simply mechanical cleaning of the

electrode by squeezing out a small amount of paste from the holder and wiping the surface with a piece of clean Teflon to obtain the appropriate shape of the renewed substrate CPE as it is elaborated with details in “Procedures”.

The first screening by amperometric measurements performed in wider working potential range and at higher concentrations of the target analyte (e.g. from 0.86 to 5.81 mmol L^{-1}) in both supporting electrolytes can offer more detailed information to compare the behavior of the Au-MWCNT/CPE and Ag-MWCNT/CPE with the MWCNT/CPE and bare CPE. Some illustrative staircase shaped current–time response curves of H_2O_2 recorded on Au-MWCNT/CPE and Ag-MWCNT/CPE are presented on Figs. 4 and 5,

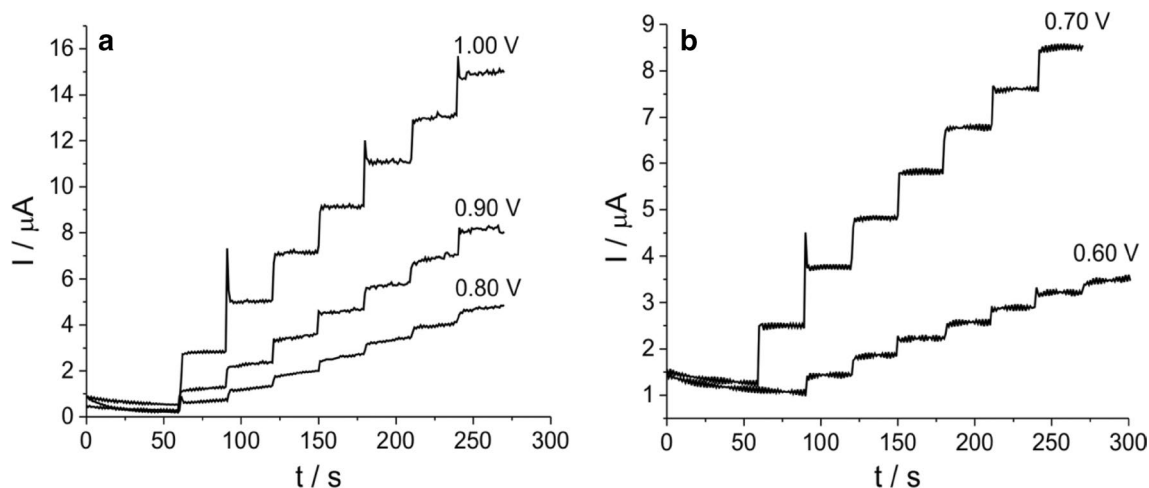


Fig. 4 Amperograms recorded by Au-MWCNT/CPE in acetate pH 4.50 (a) and phosphate 7.50 (b) buffer supporting electrolytes (0.1 mol L^{-1}) for the H_2O_2 analyte in concentration range from 0.86 to 5.81 mmol L^{-1} . Working potentials marked on the curves

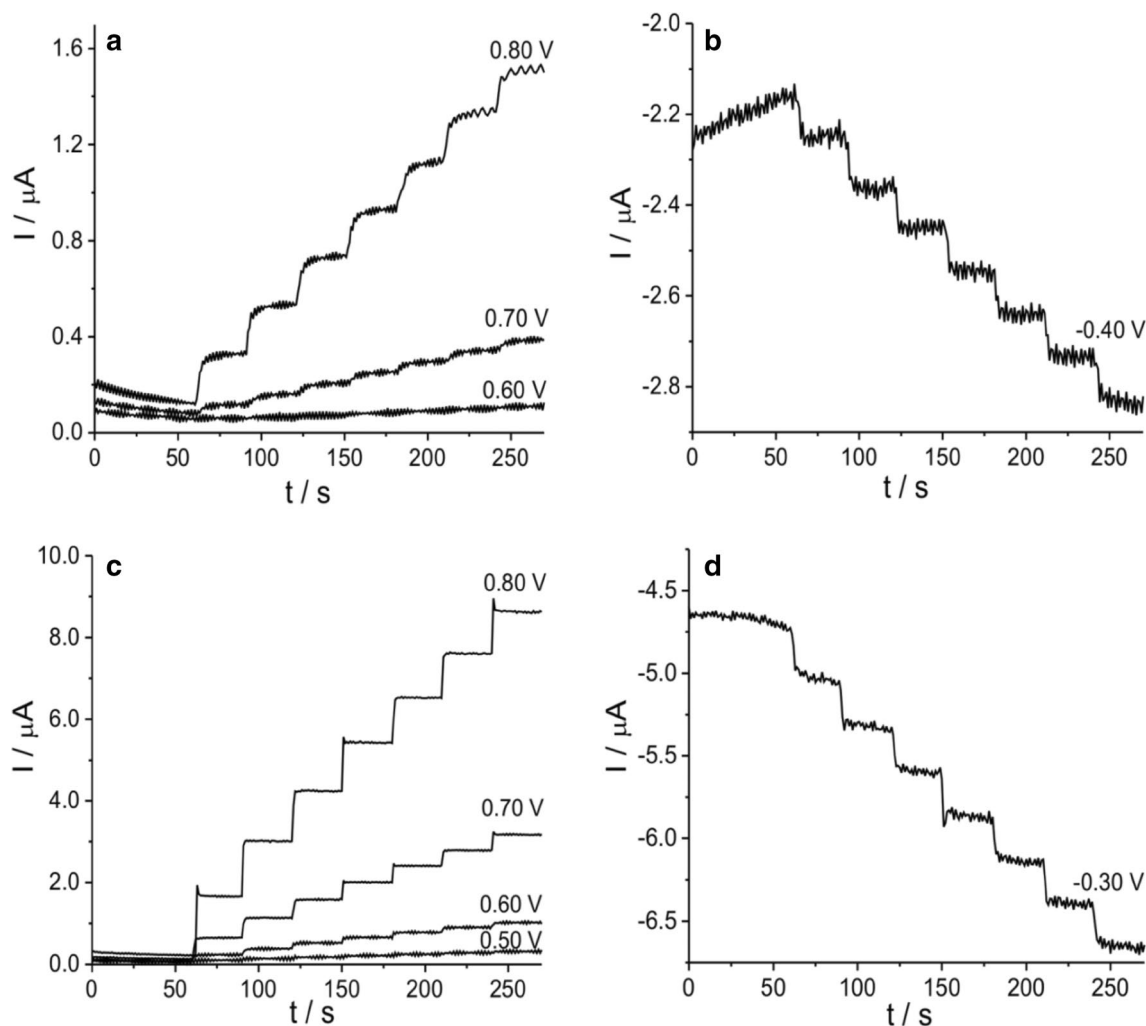


Fig. 5 Amperograms recorded by Ag-MWCNT/CPE in acetate pH 4.50 (**a**, **b**) and phosphate 7.50 (**c**, **d**) buffer supporting electrolytes (0.1 mol L^{-1}) for the H_2O_2 analyte in concentration range from 0.86 to 5.81 mmol L^{-1} . Working potentials marked on the curves

respectively. As for the Au-MWCNT/CPE, it is applicable for the development of the analytical methods for H_2O_2 determination in both investigated media but mainly at positive working potentials starting from 0.70 V in the case of acetate (Fig. 4a) and 0.60 V in phosphate (Fig. 4b) buffer solutions. Some outlines of the parameters for the methods based on the Au-MWCNT/CPE are elaborated in the Table 1. Concerning the Ag-MWCNT/CPE based H_2O_2 amperometric responses in the acetate buffer supporting electrolyte (pH 4.50) in the positive potential range they are poor (Fig. 5a), so the development of the analytical method under all described experimental conditions is possible still at 0.80 V and higher potential values. Concerning the negative working potentials (Fig. 5b) an applicable working condition was found at -0.40 V . It can be noted that the signal to noise ratio is not favored for the both polarization mode at such conditions. As for the slightly alkaline media the Ag-MWCNT/CPE showed acceptable analytical behavior from

the working potential 0.60 V and higher values (Fig. 5c), and between -0.20 and -0.30 V in the negative working potential range (Fig. 5d). However the CV signals prognoses excellent H_2O_2 reduction responses in negative potential range, the amperometric measurements showed that the signal to noise ratio is unfavorable in many cases of investigated negative working potentials. Therefore such potential values are not suitable for analytical purposes. The analytical parameters of the amperometric methods at selected usable working potentials are presented in the Table 2 for the Ag-MWCNT/CPE.

The RSD of the methods did not exceed 10% in all investigated cases based on the three times repeated measurements considering all investigated staircase steps on amperometric curves.

As for the MWCNT/CPE, and especially the native CPE, in the investigated electrolytes the H_2O_2 signals are with significantly lower intensities, so the Ag-MWCNT/CPE and

Table 1 Analytical parameters of the amperometric method with Au-MWCNT/CPE obtained in two different supporting electrolytes for the H₂O₂ responses in the concentration range 0.86–5.81 mmol L⁻¹

Parameters	Au-MWCNT/CPE							
	Acetate buffer, pH 4.50				Phosphate buffer, pH 7.50			
Working potential (V)	0.70	0.80	0.90	1.00	-0.30	0.60	0.70	
Intercept (μA)	-0.070	-0.194	-0.192	0.170	0.021	0.060	0.255	
Slope (μA L mmol ⁻¹)	0.274	0.790	1.37	2.47	-0.141	0.427	1.24	
Correlation coefficient	0.997	0.998	0.999	0.999	0.999	0.999	0.998	
LOD (mmol L ⁻¹)	0.26	0.17	0.13	0.09	0.26	0.26	0.13	
LOQ (mmol L ⁻¹)	0.86	0.57	0.43	0.29	0.86	0.86	0.43	

the Au-MWCNT/CPE are the favored ones. Based on the obtained responses, both composite modified electrodes are with excellent mediator supported electrocatalytic behavior under defined experimental conditions. Because of the lower price of the Ag-MWCNT/CPE, this electrode was selected for the further measurements and optimization.

3.3 Optimization of the Analytical Method Based on the Ag-MWCNT/CPE

To get deeper insight into the possibilities and limits of the analytical method based on the Ag-MWCNT/CPE and amperometry in phosphate buffer pH 7.50 (0.1 mol L⁻¹) different working potentials as -0.20, -0.25 and -0.30 V were investigated while the H₂O₂ concentration range was nearly three times lower (0.29–1.99 mmol L⁻¹, Fig. 6) in comparison to those applied for the first screening measurements. The working potential of -0.20 V (Fig. 6a) is suitable analytical condition, but in the case of the -0.25 V (Fig. 6b) the H₂O₂ signal intensity is enhanced. Further working potential changes till -0.30 V (Fig. 6c) lead to the significant noise enhancement receiving the lower, unfavorable, signal to noise ratio. This reflects on the analytical parameters of the developed methods which are elaborated in the Table 3.

Additionally, it can be mentioned that as it is illustrated on the Fig. 6d, the MWCNT/CPE is not applicable under the same conditions for the H₂O₂ measurements.

The -0.25 V was selected for next experiments when an additional investigation was performed to define with more details the analytical parameters of the Ag-MWCNT/

CPE based method concerning the working electrode sensitivity. The lowest investigated concentration range was 0.07–0.49 mmol L⁻¹ and a representative amperometric response is presented at the Fig. 7a together with the belonging liner calibration curve in the inset with the following equation: $y = 0.002 - 0.564x$, $r = 0.999$. The LOD of the method is 0.02 mmol L⁻¹ and the LOQ is 0.07 mmol L⁻¹.

The measurements were repeated six times with same Ag-MWCNT/CPE surface, and the H₂O₂ signals at the amperometric staircase steps has lower RSD than 6%, considering each staircase steps, which proved that the electrode is usable for higher number of measurements without significant changes of the Ag-MWCNT/CPE sensor surface. Additionally, the surface renewing by mechanical cleaning and drop coating was repeated three times and with such prepared Ag-MWCNT/CPEs all measurement procedures were repeated in triplicates. The results showed that the RSDs are lower than 8%.

Furthermore, beside the H₂O₂ determination, test experiments were performed for direct glucose sensing on the Ag-MWCNT/CPE. The tested 0.04 and 0.07 mmol L⁻¹ of glucose did not give recognizable response at -0.25 V in phosphate buffer solution pH 7.50. Furthermore, the both concentrations of glucose, 0.04 mmol L⁻¹ (not shown) and 0.07 mmol L⁻¹ (Fig. 7b) were introduced into the system after the first added aliquot of H₂O₂ (0.07 mmol L⁻¹). Next addition of equal amount of H₂O₂ in the same run produces the expected current intensity increase in both investigated cases, which proved that the presence of the glucose at such concentration levels did not affect on the H₂O₂ sensing.

Table 2 Analytical parameters of the amperometric method with Ag-MWCNT/CPE obtained in two different supporting electrolytes for the H₂O₂ in the concentration range 0.86–5.81 mmol L⁻¹

Parameters	Ag-MWCNT/CPE					
	Acetate buffer, pH 4.50			Phosphate buffer, pH 7.50		
Working potential (V)	0.80	-0.40	0.60	0.70	0.80	-0.30
Intercept (μA)	-0.003	0.002	0.018	0.073	0.220	-0.010
Slope (μA L mmol ⁻¹)	0.239	-0.115	0.161	0.519	1.44	-0.330
Correlation coefficient	0.999	0.999	0.999	0.999	0.999	0.999
LOD (mmol L ⁻¹)	0.26	0.26	0.26	0.13	0.09	0.09
LOQ (mmol L ⁻¹)	0.86	0.86	0.86	0.43	0.29	0.29

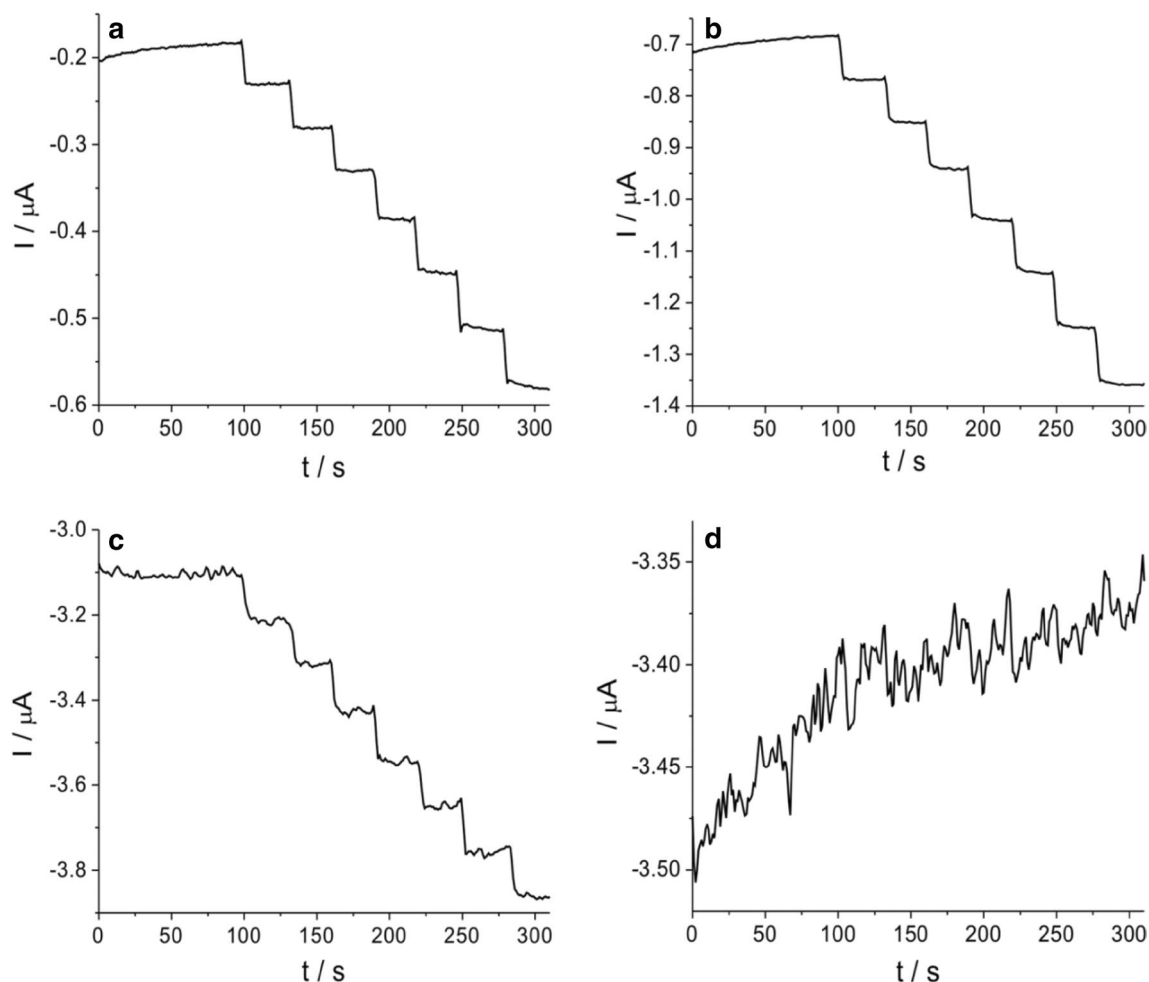


Fig. 6 Optimization of the amperometric working potentials by Ag-MWCNT/CPE in phosphate buffer supporting electrolyte pH 7.50 (0.1 mol L^{-1}) for H_2O_2 measurements in the concentration range from

0.29 to 1.99 mmol L^{-1} : **a** -0.20 V , **b** -0.25 V and **c** -0.30 V . **d** The amperogram recorded by MWCNT/CPE at analogues measurement conditions at working potential of -0.25 V

Table 3 Analytical parameters of the amperometric method with Ag-MWCNT/CPE obtained in phosphate buffer supporting electrolyte pH 7.50 (0.1 mol L^{-1}) at different working potentials for the H_2O_2 in concentration range 0.29 – 1.99 mmol L^{-1}

Parameters	Working potential (V)		
	-0.20	-0.25	-0.30
Intercept (μA)	0.012	0.018	0.001
Slope ($\mu\text{A L mmol}^{-1}$)	-0.199	-0.339	-0.384
Correlation coefficient	0.997	0.998	0.999
LOD (mmol L^{-1})	0.09	0.02	0.09
LOQ (mmol L^{-1})	0.29	0.07	0.29

3.4 Amperometric Method in Combination with Ag-MWCNT/CPE for Determination of H_2O_2 Content in a Nursing Product

To investigate the applicability of the Ag-MWCNT/CPE for the determination of H_2O_2 in a nursing product concerning its active ingredient the commercially available products was selected with an expected content as 3% of H_2O_2 . Figure 8 shows amperograms recorded with two Ag-MWCNT/CPE surfaces at -0.25 V in phosphate buffer solution during the determination of the target analyte. The amperograms were recorded on the way that after 100 s of baseline recording firstly the defined volume of diluted sample was introduced into the supporting electrolyte by micropipette, and after that three times the equal volume of standard H_2O_2 solution was added. The steps of the staircase signals presented the full measurement run. On this way the standard addition method was used for analysis. The outlines of the experiments

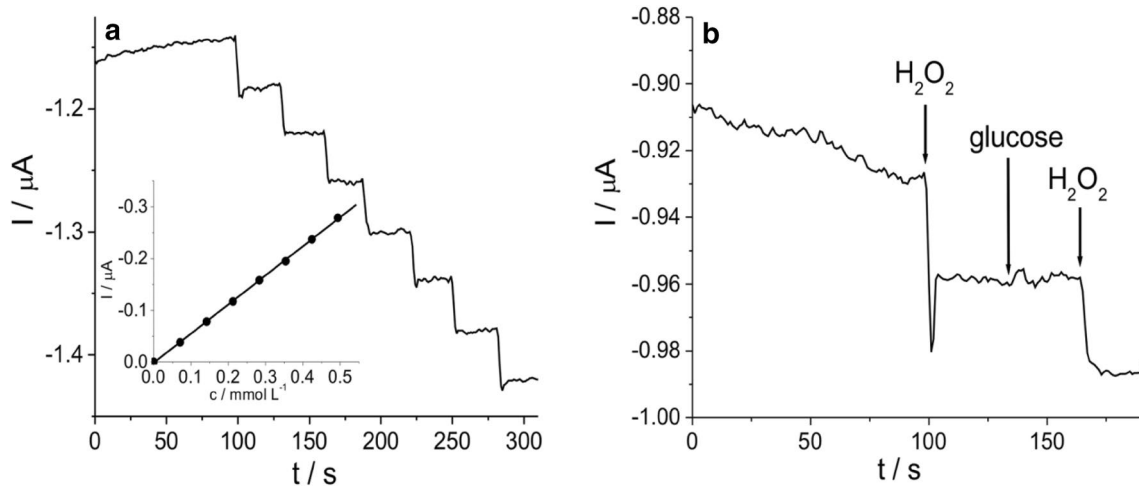


Fig. 7 Amperograms of the H_2O_2 recorded by Ag-MWCNT/CPE in phosphate buffer pH 7.50 at working potential of -0.25 V versus SCE: **a** target analyte concentration range of 0.07 – 0.49 $mmol L^{-1}$

(inset with the appropriate calibration curve) and **b** interference study of glucose at 0.07 $mmol L^{-1}$ of target analyte and 0.07 $mmol L^{-1}$ of added glucose (arrow showed the introduced chemicals)

performed with three different Ag-MWCNT/CPE surfaces are summarized in the Table 4.

The found average amount of the H_2O_2 is 2.8%, and the highest RSD was 5.3%. It can be concluded that here is an easy to perform, and reliable analytical method, based on the mediator/catalyst signal enhancement of H_2O_2 on Ag-MWCNT modified CPE for determination of the H_2O_2 target analyte in a selected nursing product.

Concerning the design of ecologically and economically acceptable, reliable working electrodes, further detailed investigations are planned with composite nano-materials. For this purpose, nanoparticles as contemporary building unites of chemical sensors or enzymatic layers as

constituents of simple biosensors will be applied. In this way the determination of different target analytes of biological, physiological or environmental importance becomes possible by a sensitive bioelectrochemical detection.

4 Conclusions

In this study, the link between the preparation of Ag-MWCNT or Au-MWCNT modified carbon based electrodes, the consequent structure and the amperometric measurements of H_2O_2 determination are discussed. Carbon paste electrode (CPE) surfaces were modified with Ag-MWCNT

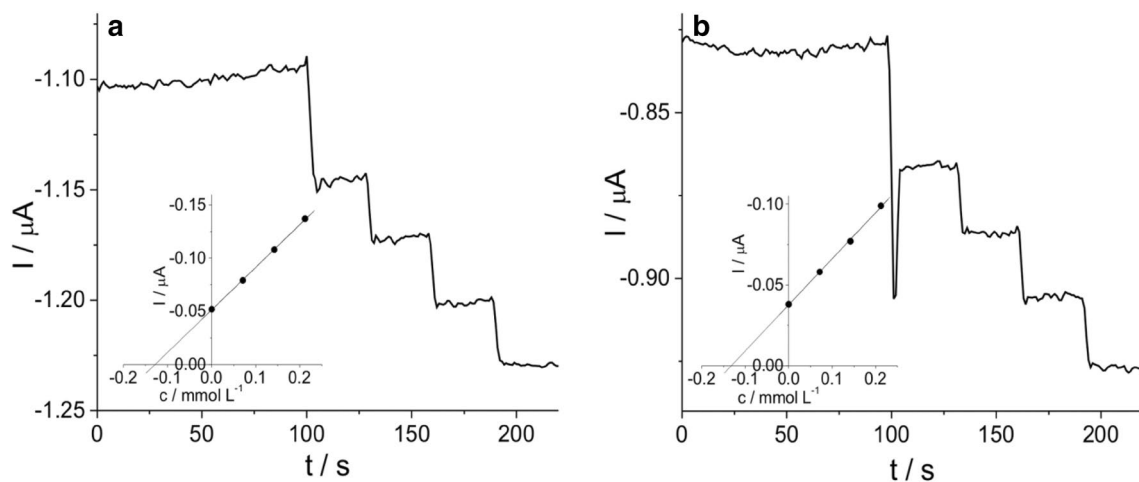


Fig. 8 Standard addition based amperometric determination of the H_2O_2 content in a nursing product by Ag-MWCNT/CPE in phosphate buffer supporting electrolyte pH 7.50 (0.1 $mol L^{-1}$) at working poten-

tial of -0.25 V versus SCE. Response of the: **a** first working electrode and **b** second working electrode

Table 4 Determination of the H₂O₂ content in a nursing product by the Ag-MWCNT/CPE based amperometric method in the phosphate buffer solution pH 7.50 (0.1 mol L⁻¹) at working potential of -0.25 V

Number of measurement	Found amount of H ₂ O ₂ (%)		
	First electrode	Second electrode	Third electrode
1	2.8	2.9	2.9
2	2.7	2.7	3.0
3	2.8	2.9	2.7
Mean value (%)	2.8	2.8	2.9
RSD (%)	2.1	4.1	5.3

and Au-MWCNT by simple drop coating method. The modifier components were characterized by XRD, SEM and the prepared working electrodes by electrochemical techniques. Cyclic voltammetric and amperometric experiments were performed at two different pHs (7.50 and 4.50) for the basic characterization of the H₂O₂ responses in order to compare the performance of the MWCNT/CPE, bare CPE and composite modified electrodes. The results showed that the composite based sensor surfaces exhibit remarkable improved electrochemical response towards H₂O₂ compared to unmodified CPE, and MWCNT/CPE under defined experimental conditions in the appropriate supporting electrolytes, and at the applied working potentials. This indicates a mediator based electrocatalytic effect of the Ag and Au particles in the composite materials. For practical application, the choice of adequate working potential and pH of the supporting electrolyte are very important experimental parameters for Ag-MWCNT/CPE which depends on the complexity and type of the sample. Optimized Ag-MWCNT/CPE based analytical method was applied for determination of H₂O₂ in a nursing product with the following experimental parameters: working potential -0.25 V, phosphate buffer supporting electrolyte 0.1 mol L⁻¹, pH 7.50.

The developed amperometric method is simple and reliable for receiving information in short response time about the H₂O₂ content in selected nursing product.

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