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Scientific paper
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New H_2O_2 sensors based on silver nanowire arrays

Owing to its strong oxidizing properties, hydrogen peroxide (H_2O_2) has a wide range of applications. It is a key component for many industrial applications, such as pharmaceutical and cosmetic production or sterilization. Moreover, H_2O_2 is produced in the human body by immune system cells and is a product of glucose oxidation. Therefore, creating an effective and selective method of H_2O_2 detection has been of great importance. A novel glucose sensor, based on silver nanowires deposited into nanoporous anodic aluminum oxide (AAO) templates has been proposed. AAO templates has been prepared via anodization of Al in three electrolytes: oxalic, sulphuric and phosphoric acids. Silver nanowires has been created by deposition of silver in AAO templates. Electrodes based on silver nanowires were then investigated for electrocatalytical properties. H_2O_2 reduction on silver nanowires was tested using cyclic voltammetry (CV) and chronoamperometry (ChA). An influence of interfering substances like ascorbic acid was also examined.

Key words: *sensors, hydrogen peroxide, silver nanowires, electrocatalytical properties*

INTRODUCTION

In recent years the development of nanotechnology has influenced the modification and reformation of various systems and devices in almost every field of science and industry. Thanks to special properties, nanomaterials are used in microelectronics, optoelectronics or construction of magnetic devices. Recently, also sensors and biosensors used in medicine are based on various types of nanomaterials.

Applying new materials to medicine means that they will have contact with living organisms. Therefore, such materials should have special properties such as biocompatibility, bioavailability and non-toxicity. Biosensors should not only be very efficient and sensible towards detected substances, but also give a rapid response in human body environment.

A perfect example of such substances are silver nanomaterials. Silver is a transition metal, that has the highest specific and thermal conductivity from all known metals. Moreover, it has positive standard potential and is not very reactive. Taking all of this properties into account, silver is applied in different fields of life. Due to its glittery and possibility for polishing, silver is used in jewelry and as a material for coinage. It is also used in a production of contacts. In chemistry it is used as a catalyst. Silver compounds and nanometric silver has bacteriocidal properties and are used in disinfectant products. In medicine, silver compounds are used as additives to anitbiotics. An amalgam with silver additions is commonly used in stomatology as a filler. There are certain silver compounds that are harmless for human beings, but at the same time are highly toxic toward some kinds of bacteria, fungus and viruses. It allows for silver nanoparticles to be used in deodorants and as a coat in laptops' keyboards. Silver nanoparticles have much better optical, electrical, thermal and magnetic properties than bulk silver. Therefore, their use in optics [1], electronics [2], catalysis [3] or surface enhance Raman spectroscopy (SERS) [4] became more popular.

Hydrogen peroxide (H_2O_2) is a very strong oxidizer. Its diluted form is well known as a paper bleach agent and component of various pharmaceutical or cosmetic products. It is also used in food production, sterilization and clinical applications [5-8]. High concentrated H_2O_2 is used as either monopropellantor as the oxidizer component of bipropellant rocket. Moreover, H_2O_2 is produced in the human body by immune system cells [9, 10]. For instance, an enzymatic oxidation of glucose, interceded with glucose oxidase (GOx), leads to hydrogen peroxide's release [11]. Therefore, detection of H_2O_2 is of great importance in the field of many sciences such as chemistry, biology, environmental sciences, bioanalytics or medicine [12 – 15].

Both electrochemical and non – electrochemical methods are used to determine H_2O_2. Among the latter, spectrophotometry [16], fluorimetry [17], chemiluminescence [18] and titration [19] are the most popular. However, electrochemical methods [15] seem to be the most preferable, due to their high

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sensitivity, efficiency and operation simplicity at relatively low cost, as well as possibility of miniaturization. The main problem that occurs during detection of H_2O_2 is interference of biological compounds such as uric acid, ascorbic acid and acetaminophen that are present in blood and oxidize at similar potential as H_2O_2 (+0.6 V vs. Ag/AgCl) [2]. There were few effective methods used to overcome that problem. One of them was modification of electrode with enzymes (e.g. horseradish peroxidase) but it is too expensive and enzymes are relatively unstable [20]. Another method was to modify the surface of electrodes with Prussian blue (PB) [21,22]. This popular dye and mediator, known as “artificial peroxidase”, indicates electrocatalytic reduction at the relatively low potential. Such electrodes have nevertheless limitation, which is a quick desorption of PB from electrode surface. As a result it loses its catalytic properties. There is a need for finding electrodes that will operate at low potential and characterize with high sensitivity, efficiency and stability during long – term usage.

Nanomaterials play an important role in modifying electrodes because of their properties, such as high surface to volume ratio, unique optical and catalytic properties [15, 23]. Among various noble metal nanomaterials, silver nanowires and nanotubes have aroused interest in recent years. Their low toxicity and biocompatibility would allow to use them in electrochemical sensor applications in the near future. Another important factor that should be taken into consideration while constructing H_2O_2 sensor are other organic substances that occurs in human blood and may interfere. Among them, ascorbic acid, uric acid or acetaminophen have similar oxidizing potential as hydrogen peroxide and cannot be present, while detecting H_2O_2. It is crucial to create a biosensor that will allow to determine H_2O_2 in presence of interfering substances [24].

In this work a novel sensor based on silver nanowires is proposed. Silver nanowire-based electrodes created from anodic aluminum oxide (AAO) templates are very sufficient and effective [25-28]. Synthesis of both AAO templates and silver nanowires is very simple and cost-effective. Having high surface to volume ratio, Ag nanowires allow for rapid response of small amounts of hydrogen peroxide that can be easily calculated for an amount of glucose. The problem of interfering substances may to be avoided by applying negative potential for the measurements.

MATERIAL AND METHODS

Fabrication of silver nanowires

Porous anodic aluminum oxide (AAO) templates were fabricated by two-step anodization of aluminum in different electrolytes, For each electrolyte a set of conditions, such as temperature, potential and time of anodization, were established. In presented studies three electrolytes were used: 0.3 M oxalic acid, 0.3 M sulfuric acid and 2 % phosphoric acid in mixture of water and methanol. For oxalic acid, anodization was carried out under potential of 45 V in 20 °C. Time for the first anodizing step was 1 h, whereas for the second it was 5 h. Anodization in sulphuric acid was performed in temperature of 1 °C, under 25 V for 6 h for the first and 12 h for the second anodizing step. Anodization in phosphoric acid was performed under constant voltage of 175 V in 0 °C. Anodization lasted for 12 and 36 h for the first and second anodizing steps, respectively. As a result a highly ordered porous Al_2O_3 membranes were received. Membranes with different pore diameters and interpore distances were obtained for different sets of anodizing conditions (Fig. 1A). Those parameters directly reflect diameters of silver nanowires. Afterwards, Al was removed from the AAO template and then the barrier-layer was removed. As a result, open membranes were received. A layer of gold was sputtered on AAO templates in order to get better conductivity. As-prepared templates can be used for metal deposition. Synthesis of AAO templates and silver deposition are shown in Figure 1.

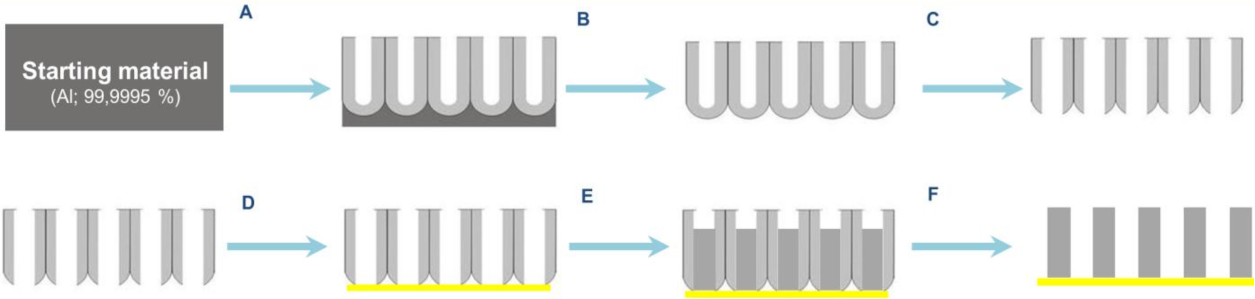

Figure 1 - Diagram of synthesis of silver nanowires using AAO templates. (A) Two-step anodization. (B) Al removal; (C) Pore opening and widening; (D) Sputtering conducting layer; (E) Metal electrodeposition; (F) Template dissolution

The electrochemical deposition of silver was carried out from a commercially available electrolyte containing 28g/dm^3 Ag^+. Process was carried out in three-electrode cell, where AAO template was used as a working electrode and platinum wires were used as both counter and reference electrodes. Deposition of silver nanowires was carried out for 5, 10 and 15 min at the current density of 1 mA/cm^2. The last step was dissolution of templates in NaOH. As a result, a free-standing silver nanowires were received.

Study on electrocatalytical properties of silver nanowires

Cyclic voltammetry (CV) and chronoamperometry (ChA) were used for testing electrocatalytical properties of silver nanowires.

Cyclic voltammetry was used to determine the reduction potential of H_2O_2 on silver nanowires. The process was carried out in air-tight three-electrode cell. Silver nanowires were used as a working electrode, platinum wire as a counter electrode and saturated calomel electrode (SCE) was used as a reference. The system was deoxidized using argon stream. CV measurements were performed in a 0.01 M phosphate buffer solution of pH 7.4 (the same as a blood pH). CV was performed between 0.0 and -0.6 V over a wide range of scan rates (5, 10, 20, 30, 40, 50, 100 and 300 mV/s). Before first measurements, the solution was deoxidized for 30 minutes. First registered curve was always for solution without hydrogen peroxide. Afterwards, a portion of 310 µL of 30 % hydrogen peroxide was added to the solution. Such experiments were performed for all kind of prepared silver nanowires.

Chronoamperometric measurements were performed for determination of a sensitive region of silver nanowires for H_2O_2. Measurements were conduced at the constant voltage of -0.2 V in the exact same cell and solution as CV tests. H_2O_2 portions (3.5 µL each) were added in 50 s intervals for 1500 seconds. ChA method was also used to determine the influence of interference substances. Ascorbic acid (AA) was used as an interfering substance. Tests were carried out under a constant voltage of -0.2 V for 200 s in the same system as previously. Firstly a portion of hydrogen peroxide was added to the system, later a portion of ascorbic acid. The changes in current were registered.

A summary of techniques used for electrocatalytic tests is gathered in table in figure 2.

Cyclic voltammetry	Chronoamperometry
• Purpose: estimating reduction potential of H_2O_2 • Conditions: three-electrode cell: working electrode – Ag; reference electrode – SCE; counter electrode – Pt 0.01 M phosphate buffer of pH 7.4 310 mM, 30 % H_2O_2 potential range: from 0.0 to – 0.6 V scan rates: 5, 10, 20, 30, 50, 100, 300 mV/s	• Purpose: response of H_2O_2 sensor towards successive addition of H_2O_2 • Conditions: three-electrode cell: working electrode – Ag; reference electrode – SCE; counter electrode – Pt 0.01 M phosphate buffer of pH 7.4 successive addition of 3.5 mM of 30 % H_2O_2 every 50 s for 1500 s applied potential: – 0.2 V

Figure 2 - Detailed information on electrochemical techniques (cyclic voltammetry and chronoamperometry) used for electrocatalytic tests of silver nanowires.

RESULTS AND DISCUSSION

Figure 3 shows FE-SEM images of silver nanowires deposited in Al_2O_3 templates made by anodization in three electrolytes: oxalic, sulphuric and phosphoric acids. The time of silver deposition was 15 minutes. Silver nanowires have different diameters: 40, 80 and 300 nm, respectively.

All silver nanowires were tested towards electrocatalytical properties. Cyclic voltammetry curves were registered in phosphate buffer solution. Seven different scan rates were used to determine the value of H_2O_2 reduction potential. Reference curve for solution without presence of H_2O_2 was registered for every sample. Results are shown in Figure 4 (A – C). Peak current versus scan rate ($v^{1/2}$) plots were also compiled for better understanding of the process. For each set of results linear regression was applied (Figure 4D).

CV curves clearly shows that reduction of H_2O_2 occurs for all three types of silver nanowires. In solution without an addition of hydrogen peroxide, current value oscillate around 0 A. Single addition of H_2O_2 implicates a significant reduction peak in each examined system. Reduction peaks occurs around -0.4 V. It is also visible that with increasing scan rate, the reduction potential shifts towards more negative potential values. The dependence between peak current and scan rate is linear. It proves that Randles – Sevćik equation (characteristic for cyclic voltammetry) is fulfilled:

$$i_p = 0.4463 \cdot n \cdot F \cdot A \cdot c \cdot \sqrt{\frac{n \cdot F \cdot D \cdot \vartheta}{R \cdot T}},$$

i_p – current maximum [A];
n – number of electrons transferred in the redox event;
A – electrode area [cm^2];
F – the Faraday Constant [C/mol];
D – diffusion coefficient [cm^2/s];
c – concentration in [mol/cm^3];
ν – scan rate [V/s]

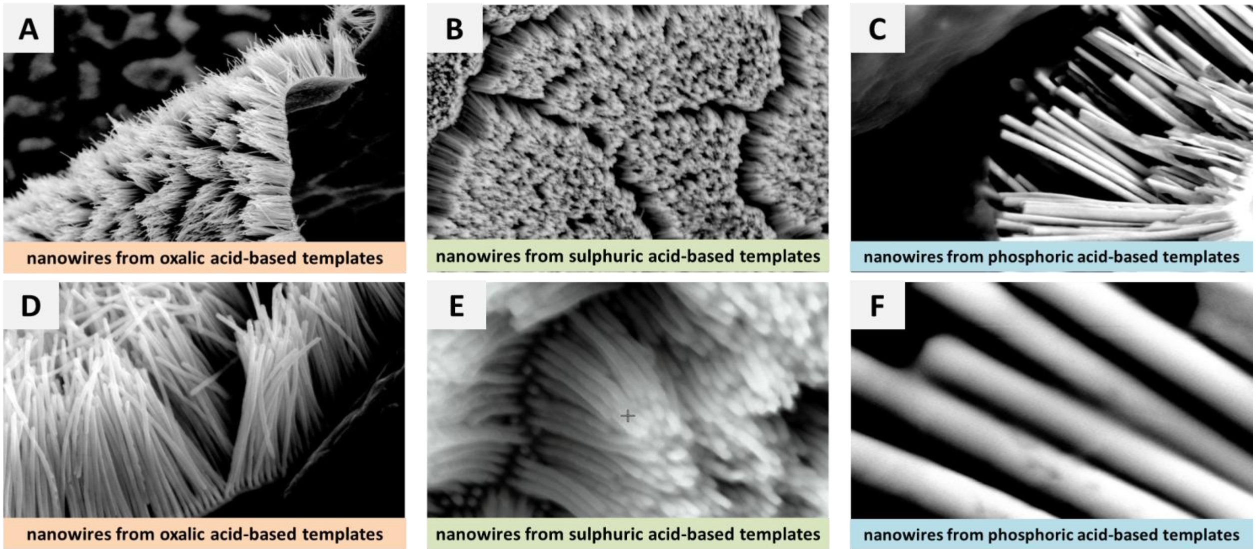

Figure 3 - FE - SEM images of Ag nanowires after AAO templates removal. Ag nanowires were deposited in AAO templates from $H_2C_2O_4$ (A, D), H_2SO_4 (B, E) and H_3PO_4 (C, F)

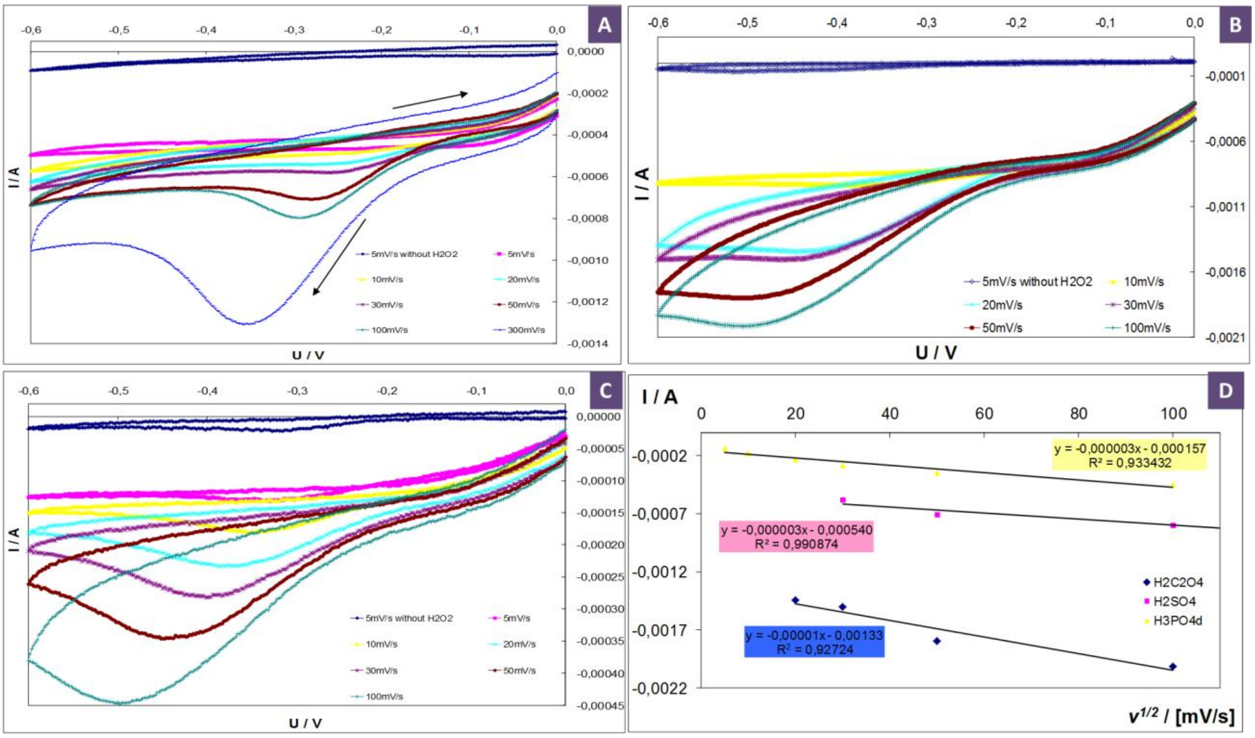

Figure 4 - Cyclic voltammograms of Ag nanowires electrodes deposited in different AAO templates, recorded in 0.01 M pH 7.4 phosphate buffer in the absences and presence of 10 mM H_2O_2 (A, B, C) at different scan rates: 5, 10, 20, 30, 50, 100, 300 mV/s. (D) Plots of peak current vs. scan rate $v^{1/2}$

In order to determine if silver nanowires can be used as H_2O_2 sensor, response to successive addition of small portions of H_2O_2 was examined. Chronoamperometric method was applied. Current vs. time plots were registered (Figure 5A – C) for all examined nanowires. Taking into account the system response to increasing concentration of hydrogen peroxide, the calibration plots between the steady-state current and H_2O_2 concentration were established (Figure 5D).

Chronoamperograms show that successive addition of H_2O_2 generate the system response, which is increased current value. We can observe very characteristic "steps" that allows us to trace changes of current value connected with an addition of hydrogen peroxide. The most significant changes are observed for silver nanowires made from AAO templates anodized in oxalic acid. Also calibration plots shows that the smallest amounts of hydrogen peroxide can be determined using silver nanowires with diameter of 80 nm. From calibration plots, knowing the calibration equation, we can squarely determine the concentration of H_2O_2 that is present e.g. in human blood and then the concentration of glucose. The system response to an addition of H_2O_2 is very quick – 2 s.

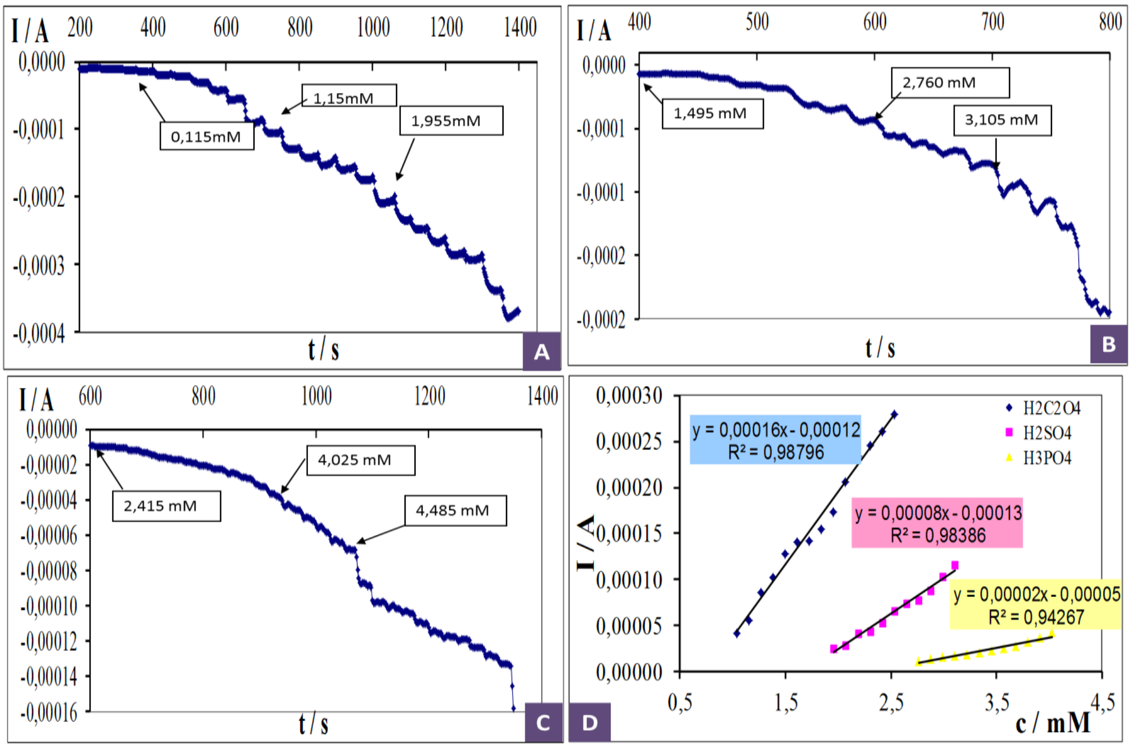

Figure 5 - Typical amperometric response of the sensor at -0.2 V to successive addition of 3.5 mM H_2O_2. (A) $H_2C_2O_4$ templates, (B) H_2SO_4 templates and (C) H_3PO_4 templates. Calibration plots between the steady-state current and H_2O_2 concentration (D)

As it was mentioned before, one of the biggest problem with constructing biosensors for H_2O_2 is presence of interfering substances. Compounds like ascorbic acid or uric acid have similar oxidative potential as hydrogen peroxide. Therefore, working under positive voltage makes it impossible to detect H_2O_2 alone. In this work, the applied potential had negative values, thus an influence of interfering substances had to be examined. Figure 6 shows that addition of ascorbic acid does not increase current value. That proves that sensors based on silver nanowires, working under negative potential, may work in presence of interfering substances, such as ascorbic acid.

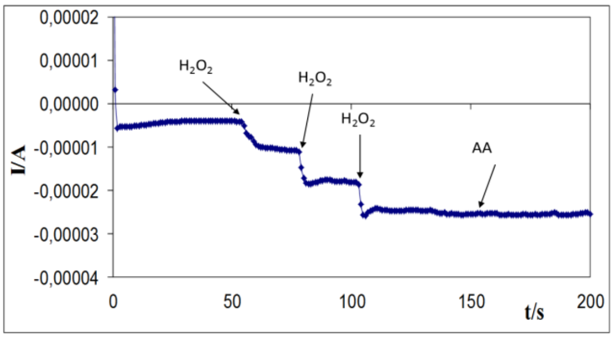

Figure 6 - An amperometric response of the sensor at -0.2 V to addition of 3.5 mM H_2O_2 and ascorbic acid. After additions of H_2O_2 a visible drop of current occurs, whereas after addition of ascorbic acid such a drop does not occur

CONCLUSION

Silver nanowires received from anodic aluminum oxide templates show catalytic properties towards H_2O_2 reduction. Reduction potential occurs around -0.4V. Chronoamperometric tests proves that Ag nanowires may be used as a potential glucose sensor. This kind of sensor, as opposed to currently used sensors, work under negative potential. This feature allows to determine glucose in blood next to other substances that might interfere. Therefore, one of the biggest problems considering glucose sensors was overcame.

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IZVOD

NOVI H_2O_2 SENZORI NA BAZI NIZOVA SREBRO NANOŽICA

Zahvaljujući svojim jakim oksidacionim svojstvima , vodonik peroksid (H_2O_2) ima širok spektar primene. To je ključna komponenta za mnoge industrijske aplikacije, kao što su farmaceutski i kozmetički proizvodi ili sterilizacija. Šta više, H_2O_2 se proizvodi u ljudskom telu u ćelijama imunog sistema i predstavlja proizvod oksidacije glukoze. Dakle, stvaranje efikasnog i selektivnog načina H_2O_2 detekcije je bilo od velikog značaja. Novi senzor glukoze, na osnovu srebro nanožica deponovanih u nanoporozni anodni aluminijum-oksida (AAO) je predložen. AAO šabloni su pripremljeni preko anodne oksidacije aluminijuma u tri elektrolita: oksalne, sumporne i fosforne kiseline. Srebro nanožice stvorene su taloženjem srebra u AAO šablone. Elektrode na osnovu srebro nanožica su zatim ispitivane na elektrokatalitička svojstva . Redukcija H_2O_2 na srebrnim nanožicama je testirana primenom ciklične voltametrije (CV) i hronoamperometrije (CHA). Uticaj smeša supstanci, kao što su askorbinska kiselina, je takođe ispitivan.

Ključne reči: *senzori, vodonikperodsid, srebro nanožice, elektrokatalitička svojstva*

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