

New materials based on nanostructured Prussian blue for development of hydrogen peroxide sensors

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Abstract

We have been reported before on the possibility for nanostructuring of Prussian blue (PB) by its electrodeposition through liquid crystal template for improving of analytical performances. In this paper, we propose further development of PB based microelectrodes by simplification of nanostructuring procedure. It is possible by electrodeposition of nanostructured PB films without using template.

Analytical performances of the resulting PB based nanoelectrode arrays have been studied in course of hydrogen peroxide detection in FIA mode. The value of sensitivity for obtained sensors was $0.2 \text{ A M}^{-1} \text{ cm}^{-2}$, which is two times more than for electrodes modified by PB electrodeposited through liquid crystal template. Detection limit was 10^{-8} M and a linear calibration range was extending over six orders of magnitude of H_2O_2 concentrations, which are the most advantageous analytical performances in hydrogen peroxide electroanalysis nowadays. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Sensitive, selective and not expensive analysis of hydrogen peroxide is a very important analytical task. Hydrogen peroxide is necessary to detect as in underground and rainwater, which resulted of industrial and atomic power stations emissions as in food industry [1,2]. At the other hand, H_2O_2 is the most valuable marker for oxidative stress, recognized as one of the major risk factors in progression of disease-related pathophysiological complications in diabetes, atherosclerosis, renal disease, cancer, aging and other conditions [3–7]. Hydrogen peroxide sensor also is needed for the development of biosensors based on enzymes oxidases [8].

The most progressive method of H_2O_2 monitoring is its amperometric detection on electrode, modified by Prussian blue (PB). The latter allows low-potential H_2O_2 detection with advantageous analytical characteristics: (i) the sensitivity of $0.7 \text{ A M}^{-1} \text{ cm}^{-2}$, which is at the upper limiting

sensitivity level [9]; (ii) the detection limit of 10^{-7} M in FIA mode; (iii) linear calibration range starting from the detection limit and extending over more than three orders of magnitude of hydrogen peroxide concentration [8,10,11].

The use of the sensors in clinic diagnostic and for ecological monitoring requires further reduction of the detection limit.

The using of microelectrodes instead of conventional ones allows to decrease the detection limit of electrochemical sensor [12–14]. However, single microelectrodes generate low current, which is hardly detectable using the conventional electrochemical technique. With the purpose of current increase microelectrodes arrays have been proposed [15,16].

The common procedure to produce microelectrode arrays involves photolithography or electronic beam techniques. However, except for their cost and complexity, they are not suitable for structuring of needle-type electrode with the working lateral surface and for microelectrodes.

We have reported to develop the microelectrode arrays by nanostructuring of the electrocatalyst on the electrode surface [17]. Among known methods for nanostructuring of the electrodeposited material, we have chosen electrochemical

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deposition through liquid crystal templates. Generally, the nanostructuring with LCT is used for different metals to obtain higher surface area [18–21]. We propose to use nanostructuring of electrocatalyst to improve analytical characteristics of the hydrogen peroxide sensors, and, in particular, to decrease its detection limit [17].

In this paper, we proposed further development of PB based microelectrodes by electrodeposition of the thin film without using of template.

2. Experimental

2.1. Materials

Experiments were carried out with MilliQ water from a Millipore MilliQ system. All inorganic salts and hydrogen peroxide (30% solution) were obtained at the highest purity from Reachim (Moscow, Russia) and used as received.

2.2. Instrumentation

Electrochemical experiments were made in a three-compartment electrochemical cell containing a platinum net auxiliary electrode and a Ag|AgCl reference electrode in 1 M KCl. The cell construction allowed deaeration of the working electrode space. Glassy carbon disk electrodes (2 mm in diameter) were used as working electrodes. Prior to use, the glassy carbon electrodes were mechanically polished with alumina powder (Al_2O_3 , 0.03 μm) until a mirror finish was observed.

The flow injection system consisted of a Cole Parmer (Vernon Hills, IL) peristaltic pump (7519-10), homemade flow-through wall-jet cell with 0.5-mm nozzle positioned at 1/2-mm distance from the surface of disk electrode, (Ag|AgCl|1 M KCl) reference, homemade injector and Metrohm potentiostat (641-VA) or Solartron electrochemical interface model 1286 interfaced to an IBM PC. Flow rates used were in the range 0.5/1 mL min^{-1} . In FIA experiments, the peak current values were taken for data treatment, sample volume was 50 μL and working electrode potentials were 0.00/0.05 V, allowing hydrogen peroxide reduction on PB-modified electrodes.

Concentration of hydrogen peroxide in stock solutions was controlled by optical density at 230 nm with an LKB-Ultraspec U11 spectrophotometer (Broma, Sweden).

Atomic force microscope (AFM) image was obtained in contact regime on scanning sonde microscope Solver P47 (NT-MDT, Moscow, Zelenograd). Silicic cantilever with constant of resilience 0.03 N/m (Ultrasharp CSG, NT-MDT, Moscow, Zelenograd) was used as a sonde.

Electrodeposition of PB was made in cyclic voltammetric conditions with switching potentials of 0.3/0.4 V (cathodic) and of 0.7/0.8 V (anodic) at a sweep rate of 20 mV s^{-1} as described elsewhere. Growing solution contained 4 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 4 mM FeCl_3 . A solution of 0.1 M HCl and

0.1 M KCl was used as supporting electrolyte. After deposition, PB films were electrochemically activated in the same supporting electrolyte by cycling in the range $-0.05/0.35$ V at a rate of 40 mV s^{-1} until a stable voltammogram was obtained. Then, the electrodes were heated at 100 $^\circ\text{C}$ for 1 h.

3. Results and discussion

We have show before that the nanostructuring of PB on the electrode surface allows one to decrease detection limit in hydrogen peroxide detection [17]. However, electrodes modified by PB electrodeposited through liquid crystal template did not show the good repeatability. Moreover, the sensitivity of the analysis with developed electrodes was seven times lower in comparison with ones modified by conventional PB. The value of sensitivity was 0.1 $\text{A M}^{-1} \text{cm}^{-2}$.

Recently, it was shown that nanoPB film could be grown without using template [22]. In this work, we proposed nanostructuring of the electrocatalyst by stop of growing in the initial stage of the electrodeposition. This procedure is most advantageous in comparison with the previous one [17] because of its simplicity. Electrodeposition of PB was carried out in solutions with concentrations decreased up to 10 times and the sweep rate was varied in the range from 20 to 100 mV s^{-1} . The best results were obtained for sweep rates 20 and 40 mV s^{-1} and growing solution containing 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 mM FeCl_3 . These correspond to solutions with eight times lower concentrations in comparison with electrodeposition of the conventional PB film.

Detection limit of the electrodes modified by nanostructured PB layers in course of hydrogen peroxide detection in FIA mode was 10^{-8} M and a linear calibration range was extending over six orders of magnitude of H_2O_2 concentrations ($1 \times 10^{-8}/1 \times 10^{-2}$ M). The value of sensitivity related

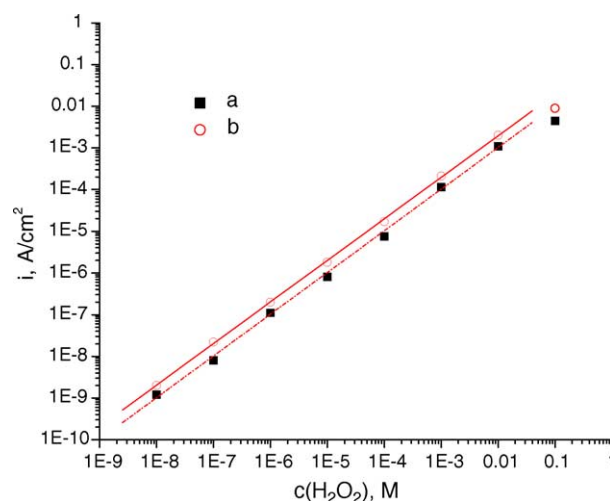


Fig. 1. Calibration plot for hydrogen peroxide detection in flow-injection mode with electrode modified by nanostructured PB: (a) electrodeposited through liquid crystal template and (b) from dilute growing solution under sweep rate 20 mV s^{-1} .

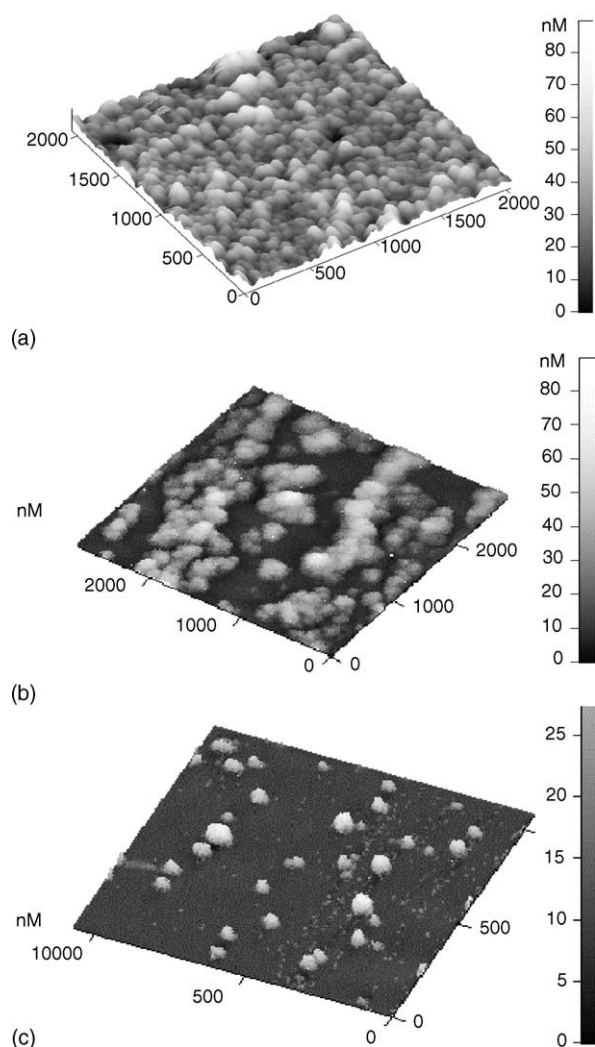


Fig. 2. AFM-images of PB modified monocrystalline graphite: (a) conventional PB deposited without surfactants, (b) PB electrodeposited from dilute growing solution under sweep rate 20 mV s^{-1} and (c) 40 mV s^{-1} .

to visible electrode surface square were $0.2 \text{ A M}^{-1} \text{ cm}^{-2}$ for sweep rate 20 mV s^{-1} which is two times more than for electrodes modified by PB electrodeposited through liquid crystal template (Fig. 1).

The morphology of obtained PB films was investigated by atomic force microscopy (Fig. 2). In the AFM image of conventional PB film, it is seen that it completely covers electrode surface. When PB has been electrodeposited from the growing solutions with decreased concentration it is seen the separate polycrystals of electrocatalyst. Hence, the resulting nanostructured PB can be considered as nanoelectrode arrays in relation to H_2O_2 detection.

4. Conclusion

In this work, we report on simplification of PB nanostructuring procedure in comparison with electrodeposition

through liquid crystal template. It is possible to carry out by stop of the growing on the initial stage of the electrodeposition. Investigation of the obtained PB films by atomic force microscopy confirms that they can be considerate as nanoelectrode arrays in hydrogen peroxide analysis. The value of sensitivity related to visible electrode surface square for obtained sensors was $0.2 \text{ A M}^{-1} \text{ cm}^{-2}$, which is two times more than for electrodes modified by PB electrodeposited through liquid crystal template. Detection limit was 10^{-8} M and a linear calibration range was extending over six orders of magnitude of H_2O_2 concentrations. The obtained characteristics are the most advantageous in the hydrogen peroxide electroanalysis reported.

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