



Prussian blue-modified nanoporous gold film electrode for amperometric determination of hydrogen peroxide

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ABSTRACT

In this manuscript, the electrocatalytic reduction of hydrogen peroxides on Prussian blue (PB) modified nanoporous gold film (NPGF) electrode is described. The PB/NPGF is prepared by simple anodizing of a smooth gold film followed by PB film electrodeposition method. The morphology of the PB/NPGF electrode is characterized using scanning electron microscopy (SEM). The effect of solution pH and the scan rates on the voltammetric responses of hydrogen peroxide have also been examined. The amperometric determination of H₂O₂ shows two linear dynamic responses over the concentration range of 1 μM–10 μM and 10 μM–100 μM with a detection limit of 3.6 × 10⁻⁷ M. Furthermore, this electrode demonstrated good stability, repeatability and selectivity remarkably.

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1. Introduction

Hydrogen peroxide is the main product of enzyme-catalyzed reactions and an essential mediator for the analysis of biological reactions. Furthermore, hydrogen peroxide is used in industrial processes such as pharmaceutical, food and plastic processing industries, intensively. High concentration of H₂O₂ can cause serious damages in the skin and human health. Therefore, highly sensitive, accurate, rapid and economical determination of H₂O₂ is very important in both biomedical and environmental studies [1,2].

Although many techniques have been reported for the determination of H₂O₂ including volumetric titration [3], fluorescence [4–6], chemiluminescence [7,8] and spectrophotometry [9,10]; but most of them have some limitations such as low sensitivity, time-consuming, susceptibility to interferences, and in some cases, these techniques require complex and expensive instrumentations [11]. Electrochemical techniques are the powerful methods for the detection of analytes due to their particular characteristics [12,13]. These methods are preferred compared to other techniques for monitoring of H₂O₂.

Most of the employed electrodes in the fabrication of electrochemical H₂O₂ sensors are based on enzymes [14,15]. By the way, these electrodes have some practical restrictions related to the use of enzyme; enzymes are relatively expensive and unstable [16,17]. Moreover, enzyme-based electrodes are the electrochemical sensors that generate anodic current during electrooxidation of hydrogen peroxide. The redox reaction of hydrogen peroxide has a relatively high potential at these

electrodes. However, electrochemically active interfering species, which are usually present in real samples, are easily oxidized at that potential and influence the biosensor sensitivity dramatically by producing an interfering current [18–20]. Consequently, the main problem of these analytical devices is their sensitivity to the interferences, present in analyte solution [21]. By considering these aspects, it is necessary to develop a simple and effective non-enzymatic sensor for measurement of hydrogen peroxide. An efficient approach to lower over-potential and selective reduction of H₂O₂ is its amperometric detection on the modified electrode by Prussian blue [22].

Prussian blue (PB) or potassium iron (III) hexacyanoferrate (II) is an inorganic polycrystalline complex with well-known electrochromic [23], electrochemical [24], photophysical [25], magnetic [26] and especially electrocatalytic properties [27]. Prussian blue shows the electrocatalytic activity for the reduction of hydrogen peroxide at relatively low potentials with considerable high activity and selectivity [28–30]; therefore, it is usually considered as an “artificial peroxidase” and has been extensively used in the fabrication of electrochemical biosensors [31]. The development of amperometric sensors on the basis of Prussian blue modified electrodes was reported by Karyakin group for the first time in 1994 [32]. Selective determination of H₂O₂ by electroreduction in the presence of O₂ allows a remarkable decrease in the electrode potential, avoiding the influence of interfering species [33].

Recently, increasing attention has been paid on the nanoscale materials (nanoparticles and nanoporous metals) due to their unique characteristics, such as the catalytic activities, optical, electronic and magnetic properties that cannot be observed by their bulk complement [2,34]. Compared with the modified electrodes by metal nanoparticle, the metal electrodes with nanoporous structure have much higher surface

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area and better electron transport [35]. Furthermore, the complexity of adsorbing methods can affect the reproducibility of electrode preparation, the electrochemical behavior and mechanical stability of these electrodes [36]. Metal nanoporous films (NPFs) could be directly formed on the surface of an electrode and overcome these drawbacks [37]. The hydrogen peroxide reduction has been studied with nanoscale gold materials such as gold nanowires [38], gold nanorods [39] and gold nanoparticles systemically [30,40]. Although nanoparticles could be attached onto the electrodes for subsequent application by simple spin coating or drop casting method the adhesion is normally restricted to weak physical or chemical interaction. The complicated nature of these processes can influence the reproducibility of electrode preparation and consequently, the electrochemical behavior and mechanical stability of electrodes prepared in this manner. Growing nanostructured materials directly onto the electrode surface can overcome this problem, while simplifying the fabrication process.

In this manuscript, the electrocatalytic activity of the Prussian blue modified nanoporous gold film electrode (PB/NPGF) toward the electrochemical reduction of H_2O_2 with emphasis on the high sensitivity and selectivity and simplicity and reproducibility of the electrode is presented. Cyclic voltammetry (CV) and amperometry techniques were used in the investigation of H_2O_2 reduction on PB/NPGF. Moreover, the detection limit, linear range, selectivity and stability are further investigated.

2. Experimental

2.1. Apparatus

All electrochemical studies were performed using the potentiostat/galvanostat μ -Autolab PGSTAT101. Experiments were carried out using a conventional three electrode system containing a PB modified nanoporous gold CDtrode as the working electrode; a platinum wire and a Ag/AgCl/3.0 M KCl as the counter electrode and the reference electrode, respectively. All potentials throughout the manuscript are referred to the Ag/AgCl/3.0 M KCl electrode. The morphology of the electrodes was characterized using scanning electron microscope (SEM) (Seron, Model AIS-2100). A Metrohm pH/mV meter model 827 was used for pH measurements. All the experiments were done at room temperature.

2.2. Reagents and solutions

All inorganic salts and reagents were received from commercial resources in analytical grade or better and were used without further purification. The concentration of diluted H_2O_2 was determined by the classic potassium permanganate titration method.

Phosphate buffer solutions (0.1 M) were prepared from NaH_2PO_4 in the pH range of 2–8 and pH of these solutions was adjusted using HCl and NaOH. Deionized-double distilled water was used throughout the manuscript.

2.3. Preparation of the electrodes

The working electrodes were prepared using small pieces of recordable disks (CD-R) made of gold (CDtrode) as previously reported in the literature [36,41,42]. Briefly, a piece of CD was cut and the protective layer was removed by putting it in the concentrated HNO_3 . Then it was washed with water thoroughly. Now the gold surface is exposed and it could be used as a working electrode. Usually, the chemical attack to the protective films requires just a few minutes and after that, the remaining material can be easily removed with water.

The NPGF electrode was prepared in two steps. In the first step, the gold CDtrode is anodized in a phosphate buffer solution (pH 7.4) for three minutes, by applying a potential step from the open-circuit potential (OCP) to 4 V. The progression of oxide film was accompanied by gas production at all time until anodizing process was finished. In the second step, the reduction of gold oxide to metallic gold was performed using ascorbic acid as a non-toxic and inexpensive reducing agent. The anodized gold substrate incubated in a solution of ascorbic acid (1.0 M) for 3 min. The color of the gold surface became dark due to its high surface area and nanometer crystal size [36,37].

The modification of the NPGF electrode surface using Prussian blue film was accomplished by repetitive potential cycling over -0.1 to $+0.5$ V (10 cycles) at a scan rate 20 mV/s in an oxygen-free solution containing 0.1 mM FeCl_3 and 0.1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. A solution of 0.1 M HCl and 0.1 M KCl was used as supporting electrolyte. After film deposition, electrochemical activation of PB film was performed by cycling at a scan rate 50 mV/s in the same supporting electrolyte until a stable voltammogram was obtained [22].

3. Results and discussion

3.1. Characterization of PB/NPGF electrode

The morphology of the smooth gold film, nanoporous gold film and PB modified NPGF was characterized using SEM. The images of SEM are shown in Fig. 1. The surface micrograph of NPGF reveals a nanoporous film, while that of the gold film substrate showed a smooth film.

Furthermore, it is very clear that PB/NPGF electrode surface is coated by a uniform PB film with tiny and regularly PB grains. Moreover, the cyclic voltammetric experiments in 0.5 M sulfuric acid solution demonstrates that NPGF electrode roughly has a six-fold surface area rather than smooth gold electrode following electrode processing (Fig. S-1).

Cyclic voltammetry (CV) is a powerful method in the investigation of electrochemical modification of electrodes and has been used in the present study to characterize the modified electrodes. Fig. S-2 implies the typical cyclic voltammograms of the electrodeposition of PB film on the surface of NPGF in PB solution containing 0.1 mM FeCl_3 and 0.1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. As it can be seen, pair of redox peaks grows gradually as the cycles increase. The current increases incessantly that indicates PB film is accumulating on the modified electrode. After 10 cycles, the currents of voltammograms don't increase more, which demonstrates

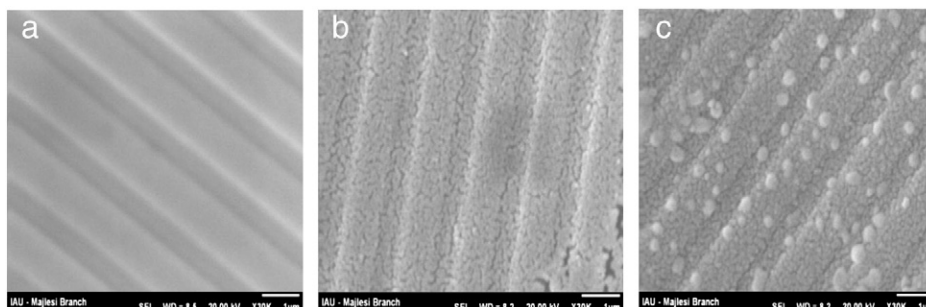


Fig. 1. SEM images of (a) the smooth gold film (b) the nanoporous gold film and (c) the PB modified NPGF.

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