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Nanostructured screen-printed electrodes based on titanate nanowires for biosensing applications

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ABSTRACT

This work demonstrates the successful modification of screen-printed electrodes using functionalized titanate nanowires for producing a peroxide biosensor. Titanate nanowires were synthesized by the hydrothermal method and characterized using physico-chemical techniques. The surface of the nanowires was modified with (3-aminopropyl)trimethoxysilane and glutaraldehyde to immobilize horseradish peroxidase through covalent bound, obtaining a surface coverage of 1.62 mg of enzyme/m^2. The surface of screen-printed carbon electrodes was modified with peroxidase-containing nanowires. Cyclic voltammetry and chronoamperometry were employed to study the electrochemical properties of the nanostructured electrode. A low hydrogen peroxide reduction potential around −0.98 V (*vs* Ag, pH 7.0) was observed, with linear response in the range of 40 to 560 μmol L^{-1}, detection limit of 10.7 μmol L^{-1} and good stability. Reproducibility relative standard deviation was as low as 4.7%. For repeatability, deviation was 3.3%.

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1. Introduction

The global market for biosensing devices was over US$ 13 billion in 2013, with projection of a growth mainly driven by their application in medical diagnostics, in addition to the environmental monitoring field [1]. The quantification of hydrogen peroxide (H_2O_2) has drawn particular interest due to the great importance of peroxide in clinical and environmental applications and in mining, textile and food industries [2–5].

Devices based on enzymes immobilized on nanomaterials have proven high sensitivity to H_2O_2. Metal, carbon or polymer nanomaterials can be used to develop biosensors with high sensitivity and stability. Their excellent conductivity increases the electron transfer between the protein redox center and the electrode surface. Because of their high surface-volume ratio and enhanced electrons transport, their electrical properties are very sensible to minimal changes in the system [6–9]. These properties provide fastness and sensitivity to biosensors for direct electron detection [10–11]. Due to the biocompatibility, lower detection limits can be achieved and the detection potential is close to the enzyme redox potential, minimizing interfering reactions [11–12].

Various types of enzyme biosensors based on nanomaterials have been reported [13–17]. Studies have shown that modification of electrodes with titanate nanostructures can increase the direct transport of electrons *via* surface reactions [18–22].

Table 1 shows a comparison of nanostructured biosensors reported in the literature for H_2O_2 detection. In our previous work [23] we developed a biosensor for H_2O_2 using HRP immobilized on titanate nanowires surface. The fabricated biosensor exhibited a low reduction potential (around −0.38 V *vs* Ag/AgCl at pH 7.0), electrons transfer rate of 3.5 s^{-1}, linear range of 250 to 6.760 μmol L^{-1} and a detection limit of 1.2 μmol L^{-1}. In that work, an electrochemical stirred cell was used as biosensor platform.

For biosensing applications, other important characteristics are simplicity, robustness and portability. Regarding this matter, the development of screen-printed electrodes has met this demand, offering a complete system of electrodes designed with great simplicity and economy [28–29]. Some studies on the modification of screen-printed electrodes through HRP deposition reported low detection limit of hydrogen peroxide [30–31]. Immobilization of HRP on gold (nano)particles [32–33] or graphene structures [34–35] are strategies adopted to improve the biosensor performance in terms of detection limit and linear range. This work aimed at the modification of screen-printed electrodes through the deposition of HRP immobilized onto titanate nanowires.

2. Experimental

2.1. Materials

Horseradish peroxidase type IV (HRP, MM 44 kDa, RZ 3.0), bovine serum albumin (BSA), (3-aminopropyl)trimethoxysilane (APTMS, 97%) and hydrogen peroxide (H_2O_2, 30% *w*/*w*) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Glutaraldehyde ($C_5H_8O_2$, 25%), sodium hydroxide [NaOH (PA)], nitric acid [HNO_3, 65% (PA)] and

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Table 1
H_2O_2 biosensors based on titanate nanostructures.

Biosensor	E (V *vs* Ag/AgCl)	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	Reference
TNW/CHIT/GOx	0.60	10–6980	10.0	[24]
TNT/HRP	−0.50	11–2000	1.2	[20]
TNT/Au/HRP	−0.40	5–1000	2.1	[25]
TNW/HRP	−0.38	250–6760	1.2	[23]
TNT/Hb	−0.24	0.5–100	0.1	[26]
TNT/GOx	−0.10	15–4000	5.0	[27]

TNW – titanate nanowires; TNT – titanate nanotubes; CHIT – Chitosan; GOx – glucose oxidase; Hb – Hemoglobin.

dichloromethane (CH_2Cl_2, 99.5%) were purchased from Vetec-Sigma (Rio de Janeiro, Brazil).

2.2. Synthesis and characterization of titanate nanowires

Titanate nanowires (TNW) were synthesized by hydrothermally processing the titania (TiO_2, anatase) powder with 10 mol L^{-1} NaOH solution. The temperature was raised at a heating rate of 10 °C/min from room temperature to 130 °C [36]. The final temperature (130 °C) was held constant for 24 h. After cooling overnight under stirring, the product was filtered and rinsed with 1 M HNO_3 to obtain sodium-free TNW. After a final wash with distilled water to lower pH to 7.0, nanowires were dried overnight at 100 °C.

TNW morphology, composition and textural properties were characterized using field-emission scanning electron microscopy (FEG/SEM) (FEI Company Quanta 200), powder X-ray diffraction (XRD) analysis (Rigaku Miniflex equipment with CuKα radiation, λ = 15,418 Å), semi-quantitative powder X-ray fluorescence (XRF) analysis (Rigaku RIX 3100, with Rd tube, 4 kW), Raman spectroscopy (LabRam Horiba HR-800 UV-resolution 1 μm^3, with He—Ne laser – wavelength 632 nm) and N_2 physisorption (77 K, ASAP 2020 Micromeritics instrument, with pretreatment under vacuum at 573 K for 12 h). Specific surface was calculated by using the classic BET equation in the P/Po range of 0.06–0.21.

2.3. Immobilization of HRP on TNW

HRP immobilization through covalent bond was carried out according to previously described procedure [23]. Briefly, after treatment with APTMS and glutaraldehyde, 1 mL of 1 mg·mL^{-1} HRP solution in 0.1 mol L^{-1} phosphate buffer (PB) was added to 10 mg of functionalized TNW under stirring, for 2 h, at room temperature. Non-bound HRP was separated using 100 kDa Amicon filters under centrifugation.

The amount of immobilized HRP was quantified using Bradford assay from the difference between the protein concentration in solution before and after adsorption. Specific enzymatic activity (U/mg) was determined by spectrophotometry using an oxidative reaction catalyzed by HRP. In this case, hydrogen peroxide reacts with 4-aminoantipyrine forming the complex quinoneimine, which is detected at 510 nm. Immobilization efficiency was evaluated by infrared analysis (FTIR) (Perkin Elmer, Spectrum 100).

2.4. Modification of screen-printed electrodes

Screen-printed electrodes (IS-1 Florence sensors) with graphite as working electrode (3 mm in diameter, 0.071 cm^2 of area) were modified by deposition of HRP-containing TNW. The reference and counter-electrodes were made of silver paste (E_0 = 0.799 mV) and carbon past, respectively. For modification, 30 μL of TNW suspension in PB 0.1 mol L^{-1} pH 7.0, was dropped onto the working electrode surface. After drying, 30 μL of a 10% alcoholic solution of Nafion® was used to cover the electrode surface. When not in use, the modified electrode was stored in 0.1 mol L^{-1} PB pH 7.0 at 4 °C.

Electrochemical measurements were conducted using a PalmSens® workstation. Cyclic voltammetric (CV) analysis of the biosensor were performed at room temperature (23 °C) in the presence of 0.1 mol L^{-1} KCl in 0.1 mol L^{-1} PB pH 7.0, with and without the presence of H_2O_2, at a scanning rate of 0.1 V·s^{-1}.

2.5. Biosensor reproducibility, repeatability and stability

To evaluate the biosensor reproducibility, cyclic voltammograms were obtained for the same biosensor in three different days. Repeatability was evaluated from 10 consecutive measurements using the same biosensor. To evaluate the biosensor stability, the response of the biosensor was followed every day for 30 days. All analysis were performed with 2×10^{-4} mol L^{-1} peroxide solution in 0.1 mol L^{-1} PB (pH 7.0) at a scan rate of 0.1 V·s^{-1}. After each measurement, the biosensor was stored in 0.1 M PB at 4 °C.

2.6. Analytical curve

Chronoamperometry was used to obtain the biosensor analytical curve, through consecutive additions of 20 μL of 0.02 mol L^{-1} H_2O_2

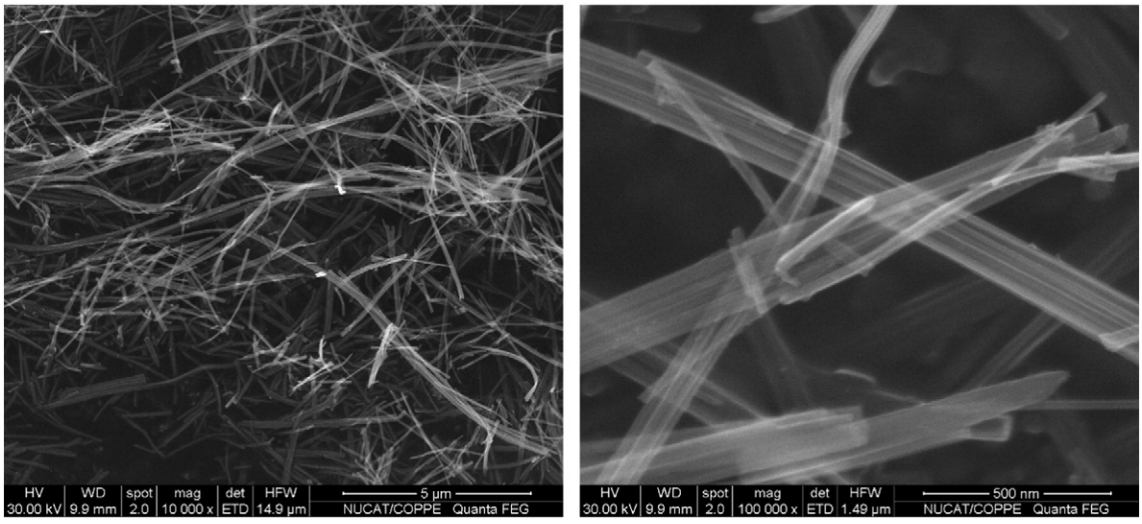

Fig. 1. FEG/SEM micrographs of synthesized of titanate nanowires (TNW).

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