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Sensing and biosensing with screen printed electrodes modified with nanostructured nickel oxide thin films prepared by magnetron sputtering at oblique angles



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ABSTRACT

This work reports about the sensing and biosensing applications of a novel screen printed electrode (SPE) modified by nanostructured nickel oxide thin films obtained by reactive magnetron sputtering under an oblique angle configuration. Using these films as electrodes we demonstrate their ability to detect hydrogen peroxide under neutral pH conditions. Furthermore, as a proof-of-concept, NiO-modified SPEs have been developed and their cholesterol biosensing properties determined by cyclic voltammetry and chronoamperometry.

1. Introduction

Hydrogen peroxide (H_2O_2) determination is of outmost importance in biochemistry and biomaterials because its pervasive presence as major oxygen reagent in living organisms and as essential mediator molecule in biology and medicine, where it acts as messenger molecule in various redox-dependent cellular signaling transductions [1-3]. Applications of this molecule have been also reported in cosmetic, pharmaceutical, agro-food, textile and paper industries [4-6]. Due to its importance, several analytical methods relying on spectrophotometry, fluorometry, chemiluminescence or titration detections have been proposed for determining H₂O₂ [4]. Among the existing approaches, electrochemical methods are very attractive because of their high sensitivity and selectivity, real-time response, low device dimensions and the possibility to develop user-friendly devices [7, 8]. These advantages have given rise to the development of a large variety of electrochemical biosensors for the detection of H_2O_2 [9, 10]. Due to its outstanding electrocatalytic properties and high sensitivity for H2O2 detection, Pt has been the most common material used for the fabrication of the first generation of this type of sensing and biosensing devices. However, the relative low cost and abundance of other metals (Fe, Ni, Cu) and their oxides (NiO, CuO, Co2O3) have favored the use of these materials as useful biosensing alternatives [11]. To increase sensitivity of detection, a key issue is the fabrication of metal and/or metal oxide nanostructures with high surface area-to-volume ratio and therefore good electrocatalytic properties [12]. With this purpose, Magnetron Sputtering (MS) under an oblique angle configuration (OAD) has been used for the fabrication of nanocolumnar and porous thin films possessing a large surface area and an open microstructure that are particularly well suited to improve the electron and mass transfer processes at the interface between electrode and electrolyte [11]. Unlike the high compactness of films obtained by MS in a normal configuration [13], this geometrical configuration renders films with a high porosity and a nanocolumnar microstructure.

Ni-based electrodes (*under extremely high basic conditions*) have revealed a remarkably high catalytic activity towards H_2O_2 detection through the involvement of the redox couple Ni(OH)₂/NiOOH [14]. Herein we demonstrate that screen printed electrodes (SPEs) modified by the deposition of nanocolumnar NiO electrodes prepared by MS-OAD can be used for the electrocatalytic detection of H_2O_2 *under physiological pH*. The sensitivity and selectivity of these hydrogen peroxide electrodes have resulted comparable to those of classical electrochemical methods [9, 10]. Then, as *proof-of-concept*, these electrodes have been assembled together with cholesterol oxidase to develop a first-generation cholesterol biosensor where the enzymatically generated H_2O_2 has been used to sense the cholesterol concentration with excellent results.

2. Materials and methods

2.1. Reagents, materials and solutions

Cholesterol oxidase (ChOx) (C8868, from microorganism) and all

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Fig. 1. (a) General XPS spectra obtained for NiO-modified SPEs. (a-d) Fitted high resolution Ni2p_{3/2}, O1s and C1s spectra.

other chemicals were obtained from Sigma. The nickel target for MS was supplied by Alfa Aesar and consisted of a 50 mm diameter disk of high purity nickel (99.99%). Gold-modified screen-printed electrodes (AT220) were supplied by Dropsens (Spain). Phosphate buffer solutions (0.1 M, pH7.4) were prepared in doubly distilled (DI) water (18.2 M Ω cm, Millipore-Q). ChOx was dissolved (2 mg mL⁻¹) in 50 mM PBS with 0.1 M NaCl. Cholesterol solutions. Cholesterol solutions and electrochemical tests were carried out at room temperature according to the common methodology as described in previous works [15].

2.2. Thin film deposition

NiO thin films were prepared by reactive pulsed Direct Current (DC) sputtering MS using a 50 mm diameter nickel target. A mask was placed over the electrodes to exclusively deposit the film on a 4-mm diameter area of the working electrode. Experimental setup may be consulted in reference [12] and in *Supporting information SO*.

2.3. NiO thin film characterization

Field emission scanning electron micrographs SEM) and Energydispersive X-ray spectroscopy (EDX) of NiO films were obtained using a HITACHI S 4800 microscope after dicing for cross-section observation. X-ray photo-electron spectroscopy (XPS) was carried out in a Phoibos-100 spectrometer, working in the pass energy constant mode, with Mg K α as excitation source and using the C1s line at 284.6 eV for referencing the binding energy (BE) scale. Electrochemical analysis was carried out with a DRP-STAT400 BiPotentiostat/Galvanostat provided with a Dropview 8400 software (DropSens). Tests were carried out in an electrochemical cell incorporating the SPE consisting of a 4-mm diameter NiO-covered gold working electrode layer, a gold counter electrode and an Ag pseudo-reference electrode (hereafter, these electrodes will be named as SPE-Au/NiO).

2.4. Cholesterol biosensor

Enzymatic immobilization on the NiO layer was achieved by casting the working electrode with $5 \,\mu$ L of a ChOx solution ($2 \,\text{mg mL}^{-1}$). The electrode layer was dried at room temperature for 3 h, newly casted with $2 \,\mu$ L of a Nafion solution (dilution 1/10 in PBS) and dried during 2 h. Last polymeric film is used for entrapping ChOx enzyme and as anti-interference film against the most common anionic interference substance found in biological samples Then, these modified biosensors were stored overnight at 4 °C, washed several times with DI water to remove the non-immobilized enzyme, dried with a N₂ flow and stored at 4 °C until their use.

3. Results and discussions

NiO thin films presented a nanocolumnar microstructure with open pores with variable diameters ranging from 10 to 20 nm and high surface area as characterized by SEM and EDX (consult additional results in *Supporting information*, *Fig. S1*).

The XPS spectra of the NiO-modified SPE displayed in Fig. 1 confirmed that its outmost layers (2-3 nm) presented a NiO composition. General spectra (see Ni2p peak inset in Fig. 1a) depicted the typical features of NiO-based materials. The Ni2p expanded signal (Fig. 1b) was characterized by two main peaks corresponding to the 2p_{3/2} and 2p_{1/2} spin-orbital levels, respectively at 855.4 and 874.3 eV, and two strong satellite peaks at about 862.2 and 880.5 eV which can be attributed to multi-electron excitation processes [11]. Meanwhile, the O1s and C1s spectra revealed the presence of a high concentration hydroxyl and carbonate species as evidenced by the spectra in Fig. 1c and d [16] (for details see Supporting information S2). The main Ni2p_{3/2} and Ni2p_{1/2} peaks presented a doublet structure which was compatible with the presence of both Ni²⁺ (in NiO/Ni(OH)₂) at ca. 854.8 eV and Ni³⁺ species (in NiO(OH)) at ca. 856.9 eV. The existence of highly oxidized nickel species justifies the outstanding H2O2 sensing properties of the NiO sensor layer under neutral pH conditions (see below).

The cyclic voltammetry (CV) characterization of the SPE-Au/NiO

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