



# Non-enzymatic hydrogen peroxide detection at NiO nanoporous thin film- electrodes prepared by physical vapor deposition at oblique angles



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## ARTICLE INFO

### Article history:

Received 9 December 2016

Received in revised form 31 January 2017

Accepted 11 March 2017

Available online 15 March 2017

### Keywords:

nickel  
hydrogen peroxide  
non-enzymatic sensor  
physical vapor deposition  
oblique angle deposition

## ABSTRACT

In this work we report a non-enzymatic sensor for hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) detection based on nanostructured nickel thin films prepared by physical vapor deposition at oblique angles. Porous thin films deposited on ITO substrates were characterized by X-ray diffraction analysis, scanning electron microscopy (SEMs), X-ray photoelectron spectroscopy (XPS) and electrochemical techniques such as Cyclic Voltammetry (CV) and Constant Potential Amperometry (CPA). The microstructure of the thin films consisted of inclined and separated Ni nanocolumns forming a porous thin layer of about 500 nm thickness. Prior to their use, the films surface was electrochemically modified and the chemical state studied by CV and XPS analysis. These techniques also showed that  $\text{Ni}^{2+}/\text{Ni}^{3+}$  species were involved in the electrochemical oxidation and detection of  $\text{H}_2\text{O}_2$  in alkaline medium. Main analytical parameters such as sensitivity ( $807 \text{ mA M}^{-1} \text{ cm}^{-2}$ ), limit of detection ( $3.22 \mu\text{M}$ ) and linear range ( $0.011\text{--}2.4 \text{ mM}$ ) were obtained under optimal operation conditions. Sensors depicted an outstanding selectivity and a high stability and they were successfully used to determine  $\text{H}_2\text{O}_2$  concentration in commercial antiseptic solutions.

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## 1. Introduction

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a prevailing oxidizing agent widely utilized in pharmaceutical, cosmetic, paper, agro-alimentary and textile industries [1–3]. It is used as cleaning solvent in the electronic industry and as an additive for the treatment of liquid, solid and gaseous wastes. Many countries have also accepted its use as food additive to control the growth of microorganisms, disinfectant and bleaching. However, due to its detrimental cell and genotoxicity properties, residual concentrations of  $\text{H}_2\text{O}_2$  in food may be harmful to humans, and many countries have specific regulations to limit the residual concentration of  $\text{H}_2\text{O}_2$  [1].

Conventional analytical approaches to determine  $\text{H}_2\text{O}_2$  concentration in solutions are based on titration methods with potassium permanganate ( $\text{KMnO}_4$ ) [3]. However, this method requires long analysis times, presents low sensitivity and presents the inconvenient that  $\text{H}_2\text{O}_2$  vapor inhalation during titration may result harmful [3]. To circumvent these problems, other methods such as spectrophotometry, fluorometry, electrochemistry and chemiluminescence have been recently proposed [1]. Among these methods, amperometric enzyme-based biosensors making use of the peroxidase (HRP) enzyme have become rather popular because of their high selectivity and sensitivity, easy implementation and low instrumentation costs [4–9]. These properties have prompted many researches to enhance the sensitivity and stability of these biosensors through the improvement of enzymatic immobilization techniques on solid electrode surfaces and/or nanostructured devices. Nonetheless practical applications of these biosensors are often hampered by the low temporal, thermal and pH stability of the HRP enzyme [10]. Therefore, efforts have been dedicated to develop alternative non-enzymatic methods that might compete in sensitivity, stability and

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reproducibility. In this context, various noble metals (Pt, Ag, Au, Pd) and their metallic alloys have been reported as useful electrodes for non-enzymatic  $\text{H}_2\text{O}_2$  electrochemical detection [11–16]. However, due to the high cost of noble metals, other non-precious metals (Cu, Ni, Mn, Fe) and their oxides ( $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ) have been also essayed for  $\text{H}_2\text{O}_2$  sensor applications [17–23]. In particular, it has been shown that Ni based electrodes are good candidates for ethanol, glucose or  $\text{H}_2\text{O}_2$  detection [24–28]. Their high performance has been attributed to the outstanding electrocatalytic properties of oxydioxide species ( $\text{NiOOH}$ ) that, in alkaline conditions and relative high applied potentials (ca. +0.5 V), form at this metal surface [25–27].

Unlike wet chemical synthesis fabrication methods which are time-consuming, tedious and involve multiple steps, [25–27] physical methods such as Physical Vapor Deposition (PVD) under an oblique angle configuration (OAD) enable the fabrication in one step and on any kind of substrate of nanocolumnar and porous thin films with a high surface to volume ratio [25–27,29,30]. Herein, we report the fabrication by PV-OAD of a nanostructured  $\text{H}_2\text{O}_2$  sensor based on nanostructured nickel thin film electrodes deposited on indium tin oxide (ITO) substrates, and demonstrate that they act as efficient transducers for the electrocatalytic detection of  $\text{H}_2\text{O}_2$ . In addition, we show a thorough electrochemical and surface analysis characterization of these films and determine main analytical parameters for  $\text{H}_2\text{O}_2$  detection, such as sensitivity, limit of detection, linear range, selectivity and stability. Furthermore, to prove the use of these sensors for real analytical applications, the  $\text{H}_2\text{O}_2$  concentration in commercial antiseptic solutions has been carried out and successfully compared with their actual value determined by alternative methods.

## 2. Materials and methods

### 2.1. Reagent and materials

Ni pellets (99.999% purity) and Indium tin oxide (ITO) substrates were purchased from Visiontek Systems and Goodfellow respectively. After their assembling these ITO-based plates presented an electrochemical working area of  $1.5\text{ cm}^2$ .  $\text{NaOH}$ ,  $\text{H}_2\text{O}_2$  and interferences were obtained from Sigma-Aldrich. All solutions were prepared in doubly-distilled (DI) water ( $18.2\text{ M}\Omega\text{ cm}$ , Millipore-Q).  $\text{H}_2\text{O}_2$  stock solutions were daily prepared in DI water.

### 2.2. Preparation of nano NiO-modified electrodes

Nanocolumnar porous Ni thin films were prepared by PVD/OAD on ITO-supported plates and silicon wafers, film thickness was controlled using a quartz crystal microbalance during deposition. Ni was electron-beam evaporated in a residual vacuum of  $\sim 10^{-6}$  mbar at a zenithal angle of  $80^\circ$  between the perpendicular to the substrate and the evaporation flux. The distance between samples and vapor source was 50 cm. Fig. 1a displays the experimental setup employed for thin film deposition under PVD approach. More details of the experimental setup can be seen in previous publications [26,27].

### 2.3. Measurements and apparatus

Scanning electron micrographs (SEMs) were obtained using a HITACHI S 4800 microscope for silicon wafer supported films conveniently diced for cross section analysis. X-ray diffraction

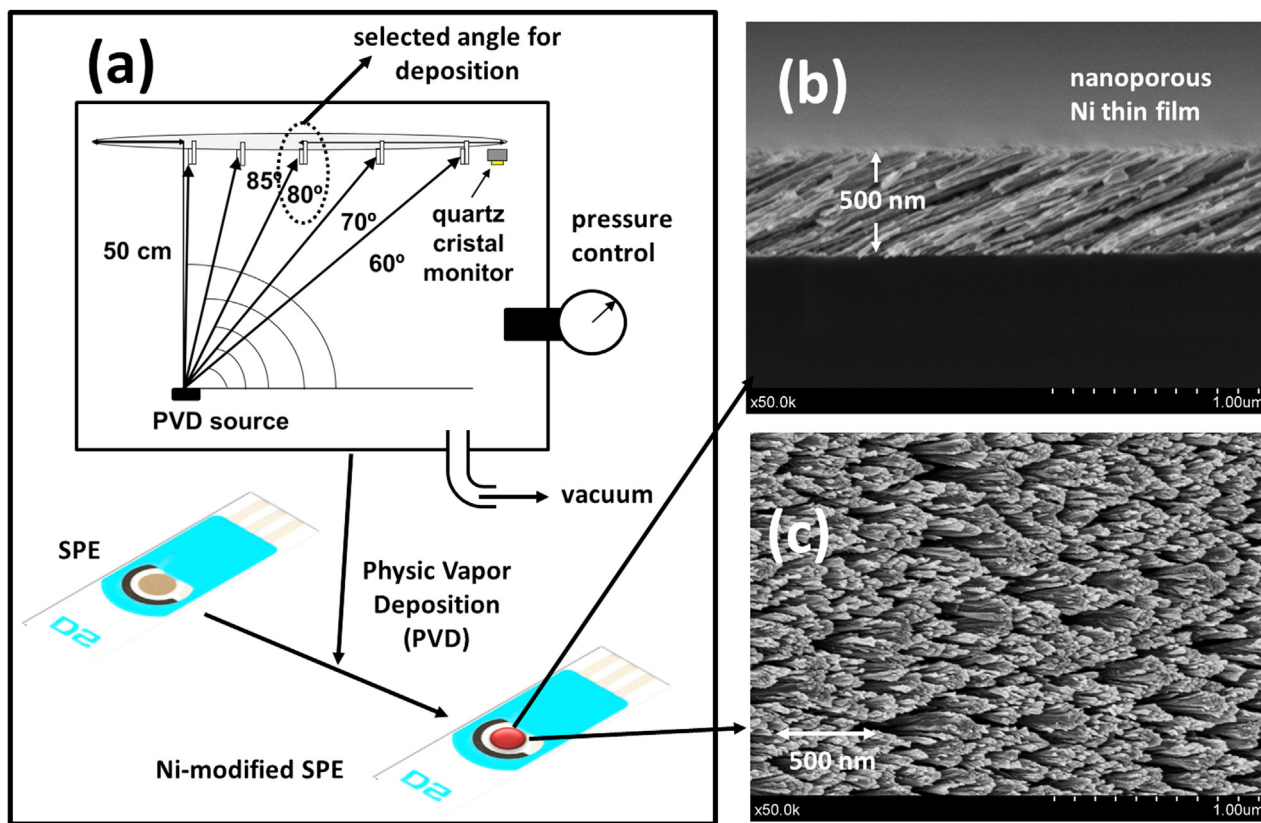


Fig. 1. (a) Schematic image of a PVD (Physical Vapor Deposition) chamber employed in this work. Cross-section (b) and plan-view (c) images of the nickel thin films.

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