



Nickel–copper bilayer nanoporous electrode prepared by physical vapor deposition at oblique angles for the non-enzymatic determination of glucose

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ABSTRACT

This work presents a novel bilayer Ni/Cu porous nanostructured film electrode prepared by physical vapor deposition (PVD) in an oblique angle configuration. Scanning electron microscopy (SEM) data revealed that the film, with an approximate thickness of 200 nm, is formed by tilted nanocolumns of around 50 nm of diameter and an inclination of 30° with respect to the surface normal. X ray photoelectron spectroscopy (XPS) data confirmed a bilayer configuration with Cu and Ni located at the top and bottom parts of the film, respectively. A porosity of ca. 45–35% as determined by Rutherford back scattering (RBS) offered a large exposed area and excellent diffusion properties that, combined with a very good catalytic activity, rendered these films excellent electrodes for the quantitative determination of glucose. Under optimized working conditions of detection these electrodes presented a high sensitivity of $2.53 \text{ A M}^{-1} \text{ cm}^{-2}$ (R^2 : 0.999), a limit of detection of $0.23 \mu\text{M}$ and a time response of ca. 2 s. The sensors did not show any loss of response during a period of 4 months. The selectivity of the sensor was checked against various interferences, including physiological compounds, different sugars and ethanol, in all cases with excellent results. The feasibility of using of this sensor for practical applications was confirmed by successfully determining the glucose content in different commercial beverages.

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1. Introduction

Glucose is an important fuel source to generate the universal energy molecule ATP [1–5]. Blood glucose level is a key diagnostic parameter for many metabolic disorders such as diabetes mellitus [5–7]. Consequently, during the last decades many researches have tried to develop and improve different methods for a reliable and strict glycemic control [6,8]. Biotechnology or food and beverages processes are other important areas where control of glucose is a clear need [9–11].

At present, electrochemical glucose biosensors have reached remarkable features in sensitivity and reproducibility [5,6,12,13]. However, although this enzymatic approach of glucose analysis is rather generalized, it still suffers from important drawbacks such as low temporal, thermal and pH stability, high oxygen dependency and the influence of interference artifacts due to the presence of other electroactive species [14,15]. An attractive alternative to biosensors is that of non-enzymatic electrodes,

transition metals (Pd, Pt, Ni) [16–18], metal alloys (PtIr, PtPb, NiCr) [19–21], oxides (NiO, Co_3O_4 , MnO_2) [22–24] or composite electrodes [25–29] capable of inducing the direct oxidation of glucose. These electrocatalytic sensors generally present high sensitivity, stability and simplicity, although their actual capacity for the direct non-enzymatic electrooxidation of glucose uses to be quite dependent on the material and microstructure of the electrode. Electrocatalytic reaction generally occurs via the adsorption of the analyte onto the electrode surface, a process that presumably involves the d-electrons and d-orbitals of the metal substrate [14,15]. Among different material options presenting a good electrocatalytic response, copper, nickel and their oxides are materials of choice due to their natural abundance, relatively low-cost and good catalytic properties [14,24,30–37]. Metal alloys have been also intended with the purpose of setting a favorable electronic structure to enhance the electrocatalytic activity [38–40]. Unfortunately, some authors reported that although alloying two metals may improve the electrode long-stability and surface resistance to biofouling, the obtained sensitivity is generally lower than that of single metal electrodes [41–43].

Recently, metallic bilayers (MBs) and multilayers (MMs), have been proposed as a new kind of electrode configuration with

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improved electronic and structural properties [44] and better responses than pure metals or alloys [45,46]. The electrocatalytic activity of MBs and MMs has been tested for the oxidation of small organic molecules such as methanol, ethanol, formaldehyde and formic acid [44–49] but, to the best of our knowledge, they have not been used for the non-enzymatic detection of glucose.

The aim of the present work is to develop a nanostructured Ni/Cu bilayer electrode film on an ITO substrate (ITO/Ni/Cu) and to investigate its electrocatalytic activity against glucose oxidation. The sensor films have been prepared by physical vapor deposition (PVD) in an oblique angle configuration (oblique angle deposition OAD) [50–52]. This one step procedure avoids the drawbacks associated to chemical synthesis procedures of bilayers (handling of residues, deposition of a second layer without affecting the first one, etc.) and yields porous and nanocolumnar films with a high surface to bulk ratio. The work encompasses the study of the chemical and microstructural characteristics of the Ni/Cu bilayers and a thorough analysis of the main experimental variables and working conditions by their use as electrochemical glucose sensors. Finally, the performance of these electrodes for real practical applications has been proved with different essays of glucose determination in different commercial beverages.

2. Materials and methods

2.1. Reagents and solutions

Ni and Cu metallic pellets (99.9999% purity) were purchased in Goodfellow. Indium tin oxide (ITO) plates were supplied by Visiontek Systems Ltd. After assembling the electrode the working area was ca. 1.5 cm². Glucose, NaOH and interference species were obtained from Sigma–Aldrich and prepared in doubly distilled water (18.2 MΩ cm, Millipore-Q). Stock solutions of 0.1 or 1 M glucose were prepared in water, left for 24 h at room temperature to allow equilibration of the anomers and then stored at 4 °C.

2.2. Preparation and characterization of nanoporous Cu/Ni thin films and ITO-supported electrodes

Nanocolumnar porous Ni/Cu thin films were prepared on a silicon wafer and on ITO-supported nanoelectrodes by physical vapor oblique angle deposition (PV-OAD). Briefly, Ni metallic pellets were electron beam evaporated under vacuum conditions (pressure ca. 10^{−6} mbar) at a zenithal angle of 80° between the evaporation flux and the perpendicular to the substrate. The distance between the vapour source and the samples was 80 cm and the deposition rate was adjusted to ca. 1 Å s^{−1}. After depositing a first layer (Ni) of approximately 100 nm, an upper layer (Cu) of a similar thickness was deposited in an analogous way to obtain the bilayer film supported on ITO (i.e., ITO/Ni/Cu).

Field emission scanning electron micrographs (FE-SEMs) were obtained using a HITACHI S 4800 microscope for doped silicon supported films conveniently diced for cross section observation. Raman spectra were recorded with a HORIBA HR-800-UV microscope. For these measurements a green laser (532.14 nm) working at 600 lines per mm and a 100× objective were used. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Phoibos-100 spectrometer working in the pass energy constant mode with Mg Kα as excitation source. The binding energy scale was referenced at 284.5 eV for the C 1s peak of some minor contamination of carbon present on the electrode surface. X-ray diffraction spectra in a grazing angle configuration were acquired using a Panalytical X'PERT PRO diffractometer.

Rutherford back scattering (RBS) spectra were obtained in a tandem accelerator (CNA, Sevilla, Spain) with a beam of alpha particles

with energy of 2.1 MeV, 1.7 nA of intensity and ca. 1 mm diameter. The recorded spectra were analysed with the SIMRA6.0 program.

2.3. Electrochemical tests

Electrochemical measurements (cyclic voltammetry (CV) and constant potential amperometry (CPA) and chronoamperometry) were performed with a DRP-μSTAT400 BiPotentiostat/Galvanostat and data were acquired with Dropview 8400 software (DropSens) in a 10 mL glass cell at room temperature. For all electrochemical measurements, the ITO/Ni/Cu bilayer electrode was used as the working electrode and a commercial Ag/AgCl (3 M KCl) and a Pt wire used as reference and counter electrodes, respectively. Firstly, each ITO/Ni/Cu electrode was stabilized using CV by cycling from −0.8 to +0.8 V at 50 mV s^{−1} ($n = 0, 25, 50, 100$ cycles) until constant repetition of the voltammogram shape. Glucose calibrations (using CPA) were performed under stirred conditions using 0.1 M NaOH as supporting electrolyte, unless stated otherwise. When the current achieved steady-state conditions (i.e., after ca. 100 s), several glucose aliquots (0.1 or 1 M) were added each ca. 20 s, time enough to reach the steady-state current again. Applied potential, NaOH concentration and stirring rate were optimized for the analysis. Commercial beverages were conveniently diluted in water (1:100) and measured using the Ni/Cu bilayer sensor under optimized conditions.

3. Results and discussion

3.1. Electrochemical conditioning

Since glucose sensing involves oxi/hydroxide (i.e., CuOOH, NiOOH) species [14], the nanoporous metallic ITO/Ni/Cu electrodes were electrochemically conditioned prior to their use for glucose detection. Therefore, a stable oxide and/or hydroxide (MO, M(OH)₂ where M = Cu, Ni) surface layer was previously generated by cycling the electrode in the range −0.8 to 0.8 V (scan rate: 0.05 V s^{−1}) in a 0.1 M NaOH solution. This conditioning step allows the enrichment of MO and M(OH)₂ species at the surface of the electrode, resulting in a thickening of the electrocatalytically active outer layers [53] involved in the detection of glucose. Fig. 1 shows the cyclic voltammogram (CV) of the ITO/Ni/Cu electrode during this activation treatment. The obtained voltammogram clearly depicts

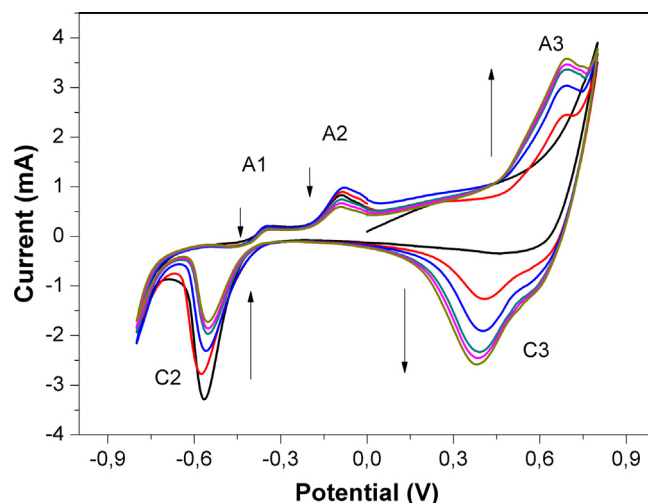


Fig. 1. Cyclic voltammogram (1st, 10th, 20th, 30th, 40th, 50th cycles) during the conditioning procedure of a nanoporous ITO/Ni/Cu electrode in a 0.1 M NaOH medium at scan rate of 0.05 V s^{−1}. Arrows indicate the evolution of peak intensities along the successive voltammograms.

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