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New Copper wide range nanosensor electrode prepared by physical vapor deposition at oblique angles for the non-enzimatic determination of glucose

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ABSTRACT

In this work a novel Cu nanostructured electrode is presented. Cu tilted nanocolumnar and porous thin films have been prepared by physical vapor deposition (PVD) in an oblique angle configuration and characterized by different techniques. Cyclic voltammetry and amperometry were used to study the sensing ability of the copper films deposited on ITO to quantitatively determine glucose and to optimize the experimental conditions of detection. Scanning electron microscopy data revealed that the film microstructure consists of tilted nanocolumns of around 70 nm of diameter and an inclination of 65° with respect to the surface normal that extend through the total thickness of the layer of ca. 300 nm. X ray photoelectron spectroscopy and Raman, used to determine the oxidation state of Cu, revealed that an oxy/hydroxide external layer formed around the nanocolumns is the active phase responsible for the electrocatalytic detection of glucose. Under optimized conditions, the CuO/Cu nanoporous/ITO electrode presented a sensitivity of 1.41 A mol dm^{-3} cm^{-2} (R^2:0.999) with a limit of detection of 0.36 μmol dm^{-3} and a reproducibility of 3.42%.The selectivity of the proposed sensor was checked against various interferences, including physiological compounds, different sugars and ethanol, thereby showing excellent anti-interference properties. The CuO/Cu nanoporous/ITO electrode was also used successfully to determine glucose in blood samples showing a performance comparable to that of a commercial glucometer. An extended working range covering from 1 to 5×10^{-3} mol dm^{-3} was determined for these sensor films which, in this way, could be applied for different analytical purposes including agro industrial liquids.

1. Introduction

In recent years the *European Society of Cardiology* and *European Association for the Study of Diabetes* presented the guidelines on the management of diabetes mellitus (DM), pre-diabetes, and cardiovascular disease [1]. This study revealed the increasing prevalence of DM worldwide, where approximately 360 million people had DM in 2011, of whom more than 95% would have had type 2 DM (T2DM). In addition, this number is estimated to increase to 552 million by 2030 and it is thought that about half of them will be unaware of their diagnosis. Furthermore, it is estimated that another 300 million individuals had symptoms indicating future risk of developing T2DM. This study showed that the majority of new cases of T2DM occur in the context of westernized lifestyles with high-fat diets and decreased exercise. The diagnosis and management of DM requires a tight monitoring of blood glucose levels. Thus, during the last decades the main objective of many researches has been to develop a method that provides a reliable and strict glycemic control [2]. Thanks to this huge effort, a great number of commercial devices, industrial developments and patents have been developed with this purpose [2–4].

Nowadays, the need to control industrial processes and ensure the high quality of products in the agro-alimentary industry has generated high interest in the development of new, robust and user-friendly monitoring technologies, where biosensors and sensors are the most promising approach [5–7]. These sensors and biosensors should offer high sensitivity and selectivity, a wide operational range, low cost, user-friendly instrumentation, real-time output and ready-to-use bio/sensor appliances [8].

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Amperometric glucose biosensors incorporating glucose oxidase (Gox) are one of the most commonly used methods for glucose detection [2–4,9–12]. Although the enzymatic approach is rather generalized, this procedure suffers some important drawbacks such as a high oxygen dependency [2,4,13] and the occurrence of artifacts due to the presence of other electroactive species in real samples [2,14]. Finally, other important problem is that enzymes present a low temporal stability [15,16] and are affected by the temperature, pH and the ambient humidity levels [17–19].

To overcome these problems, in recent years electrocatalytic metals, oxides and novel carbon materials have been proposed as non-enzymatic glucose sensors and an alternative to the biosensors approach [15,16]. With this aim, metals (Pd, Pt, Ni) [20–22], metal alloys (PtIr, PtPb, NiCr) [23–25] and oxides (NiO, Co_3O_4, MnO_2) [26–28] electrodes have been reported in the literature. However, novel metals and metallic alloys usually presents low sensitivities and selectivities, are expensive and suffer from the poising of intermediate compounds and chloride ions [15–17,29–31]. To overcome these constrains, during the last years much effort has been dedicated to develop other cost-effective, sensitive, selective and stable non-enzymatic electrodes [16]. In this context, Cu and its oxides have deserved an increasing attention because of their high electrocatalytic activity, good stability, low cost and high anti-poisoning resistance against chloride ions [16]. To improve the performance with respect to the bulk material, the introduction of new nanostructures (nanoparticles, nanowires, nanocolumns) with higher surface/volume ratio and better electrocatalytic properties has constituted a real breakthrough in the design of advanced electrodes for this application [18,28–30,32–36]. These nanostructured electrodes have been prepared using different approaches including wet chemical methods, thermal oxidation or dehydration and others [16]. In addition, hybrid configurations where copper is combined with electrocatalytic materials such as carbon nanotubes and graphene have been also reported [30,33,34,37,38]. In general, chemical methods are usually tedious, time-consuming and involve multiple steps where $Cu(OH)_2$, firstly synthetized onto a sacrificial surface and then subjected to thermal treatments for activation, cannot be applied on sensitive substrates [18,29,31,32]. Consequently, for advanced sensing applications, there is still a strong need for simple synthesis processes of novel nanostructured sensors with good catalytic properties.

Physical vapor deposition (PVD) in an oblique angle configuration (oblique angle deposition OAD) avoids the drawbacks associated to a chemical synthesis while enabling the fabrication of porous and nanocolumnar films with a high surface to bulk ratio on any type of substrates [39,40]. In this paper, we report the use of this methodology for the fabrication of CuO/Cu nanoporous thin films on ITO substrates and their use for electrochemical non-enzymatic detection of glucose. The work encompasses the study of the chemical and microstructural characteristics of the copper films and the analysis of the main experimental electrochemical variables controlling the detection process. Based on these data a comparative assessment of glucose blood concentrations obtained with our sensor and a commercial device is also carried out. The wide concentration range of glucose where these copper sensors can be applied sustains their suitability for a large variety of applications from physiological samples to agro industrial liquids.

2. 2 Experimental

2.1. Reagents and solutions

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 cm^2. 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 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 CuO/Cu thin films and ITO-supported electrodes

Nanocolumnar porous Cu thin films with an approximate thickness of 300 nm were prepared on a silicon wafer and ITO-supported nanoelectrodes by physical vapor oblique angle deposition (PV-OAD). Briefly, Cu metallic pellets were electron beam evaporated under vacuum conditions (pressure ca. 10^{-4} Pa) at a zenithal angle of 80° between the evaporation flux and the perpendicular to the substrate. The distance between the vapor source and the samples was 80 cm. More details of the experimental setup can be seen in [40].

Field emission scanning electron micrographs (FE-SEMs) were obtained using a HITACHI S 4800 microscope for 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 x objective were used. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a VG-ESCALAB 210 spectrometer working in the pass energy constant mode and using the Mg Kα as excitation source. The binding energy scale was referenced was at 284.5 eV for the C 1s peak of some minor contamination of carbon on the electrode films. X-ray diffraction spectra in a grazing angle

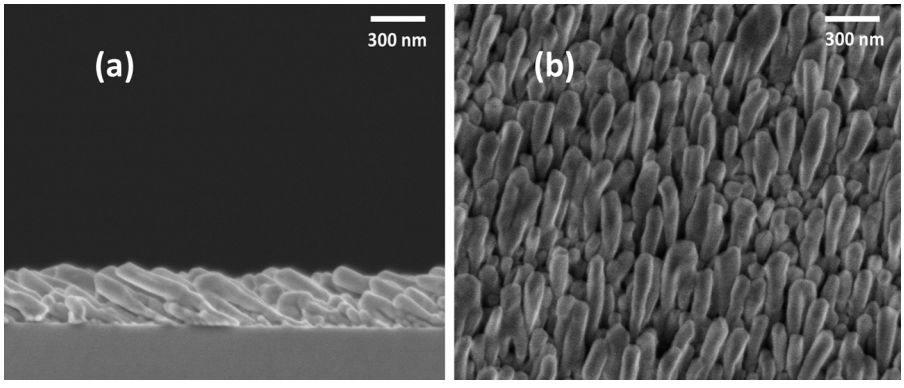

Fig. 1. SEM images of a Cu nanoporous thin film grown on silicon wafer showing the cross-section (a) and plan-view micrographs (b).