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AMPEROMETRIC DETECTION OF GLUCOSE BY ELECTROCATALYTIC REDUCTION AT A COPPER-MODIFIED ELECTRODE

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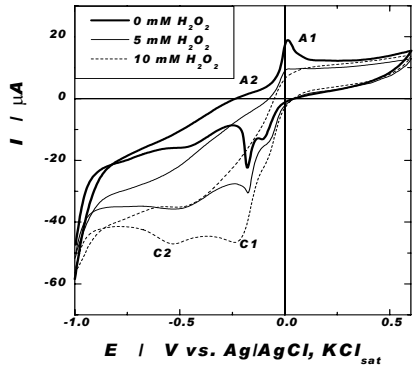
The performance of an amperometric bioelectrode (Cu/CuO/Gox) based on a glucose oxidase membrane immobilized on a Cu surface modified by an electrodeposited CuO film for the detection of glucose is reported. The electrochemical investigation of the modified electrode by cyclic voltammetry shows that the copper oxide promotes an excellent electrocatalytic activity for the reduction of hydrogen peroxide, allowing a large decrease in the reduction overpotential, as well as an important enhancement of the corresponding current. By chronoamperometry, it is possible to detect the glucose at low potentials where are no interferences. The obtained Cu/CuO/Gox bioelectrode shows a fast response (10 s), a linear domain for glucose concentration up to 20 mM glucose (*i.e* 3.60 g L^{-1} glucose) and a detection limit of 1.6 mM glucose (0.29 g L^{-1} glucose).



INTRODUCTION

The investigation of carbohydrates like glucose is essential in numerous circumstances and plays an important role, particularly in the clinical and industrial applications.[1-2] Thus, between many bioelectrochemical systems reported in the literature, systems based on glucose oxidase (GOx) attract a great interest, perhaps due to the use of this enzyme in the commercialized biosensor, which was intensively investigated in the last 50 years, after Updicke and Hicks[3] in 1967 have developed the first, and the most popular amperometric glucose oxidase based biosensors. Although the fact that there are many devices commercially available, the interest in developing new electrode materials more sensitive and highly selective is still increasing. In the last years, different techniques for the transduction step and different protocols (indirect and direct measurements) have been proposed. The direct glucose detection could be achieved either by oxidation, as well as by reduction of enzymatically generated hydrogen peroxide (H_2O_2). Because the oxidation of H_2O_2 could not always be coupled to the active site of an oxidase, the detection based on the H_2O_2 reduction has been frequently used in the electrochemical sensor's field. However, in some practical cases when the operating at low applied potential avoids the interferences, the H_2O_2 reduction might be more helpful.[4]

One issue in high sensitivity[5] and more selective detection[6] of H_2O_2 involves the improving of the electron transfer rate at a supporting electrode matrix used for the immobilization of the enzyme. Between the numerous types of matrices used today, especially carbonaceous electrodes, which need elevated

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overpotentials,[7-8] are expensive and sometimes involved complicated electrode preparation process,[5] recently the enzyme based metalized electrodes and inorganic nanostructured materials have been shown to be very promising due to their regular structure, high active surface area for protein binding, good chemical and thermal stability and excellent electrocatalytic properties towards the oxidation or reduction of the enzymatically generated hydrogen peroxide.[9]

The reduction of H_2O_2 on copper was first studied by Delahay in 1950. Since, in the literature it was reported the possibility to use the Cu-modified electrode as a transducer for glucose detection due to its advantages, *e.g.*, low resistivity 1.7 μΩ cm at 20 °C, high conductive property, low cost, commercial availability and mainly its electrocatalytic properties towards the reduction of H_2O_2.[4-5] The CuO as a modifier is an important *p*-type transition-metal oxide with a narrow-band gap (E_g = 1.2 eV), a potential field emission material, a main catalyst and a gas-sensing medium.[10] As consequence, for H_2O_2 detection Cu micro-band electrode,[4] platinum,[11] gold[12] or carbon ionic liquid electrodes[13] modified with CuO nanoparticles[11, 13] or Cu nanostructure[12] was used.

To enhance the performance of glucose biosensor, a substantial progress in glucose detection has been achieved during recent years by using of glassy carbon,[10,14-16] carbon paste,[8,17] screen-printed,[18-19] gold,[2,6,20,21] platinum,[11] Si/Ti/Pt,[22] Cu[1,5,23-25] electrodes as a supporting matrix for different type of Cu nanobelt,[19] Cu nanocluster,[16] CuO nanowires,[10] Cu nanoparticles,[11,17,22-23,26] Cu microparticles,[8] CuO film.[2,14,15,20,22,24-25] Generally, the above mentioned composite electrode matrix is obtained by simple deposition from a suspension[2] or by potentiostatic[24]/ galvanostatic anodisation.[25] In the same time, other metallic nanostructures (inorganic/organic nanoparticles, nanowires, nanotubes, porous and composites[27]) were used for glucose detection: *e.g.*, ITO glass/ZnO nanorods film,[28] GC/$Ni(OH)_2$/ NiOOH[29] or Ti/TiO_2 nanotubes/Au/Prussian Blue/ GOx.[9] Between these numerous reports, the opportunity to develop a facile and low-cost strategy using a simple cyclic voltammetry method in view to achieve a reproducible CuO film having electrocatalytic properties seems to be a great advantage.

The aim of this work was to demonstrate the possibility to obtain a reproducible CuO film by cycling the potential at a low scan rate in an appropriate potential window, a limited number of cycles in view to obtain a Cu/CuO modified electrode applied as an electrochemical interface for the electroreduction of H_2O_2. Then, a glucose biosensor Cu/CuO/Gox was built-up by the immobilization of a glucose oxidase pre-prepared membrane on the tip of Cu/CuO modified electrode. Using the cyclic voltammetry and chronoamperometry investigations' methods, the kinetic and analytical parameters of the prepared electrodes were estimated.

RESULTS AND DISCUSSION

Electrochemistry of Cu/CuO modified electrode

As discussed above, the opportunity to develop a simple electrochemical strategy in view to obtain a reproducible CuO/Cu modified electrode having electrocatalytic properties looks to be very interesting. Thus, Fig. 1A shows the cyclic voltammograms obtained with the Cu immersed in a neutral phosphate buffer in view to obtain the modified Cu/CuO electrode. When a clean Cu surface is immersed in the phosphate buffer, after few cycles, are visible two cathodic peaks' pairs C1 and C2, each attributed to a monoelectronic redox electron transfer. The peak located at E_{C1} = - 0.180 V *vs*. Ag/AgCl, KCl_{sat} was attributed to the reduction of Cu(II) to Cu(I), whereas the peak placed at E_{C2} = - 0.490 V *vs*. Ag/AgCl, KCl_{sat} to the reduction of Cu(I) to Cu(0), according to the similar behaviour of the Cu nanoparticles immobilised on Pt surface by Nafion.[11] As previously indicated,[4] the peak A1 appearing during the anodic scan, before formation of the copper oxide, is attributed to its electrosorption (Fig. 1A) and is described by reaction 1. The supplementary anodic peak (A2) is probably due to the CuO formation following the reactions 2 and 3:[4]

Peak A1 $Cu + H_2O \rightleftharpoons Cu(OH)_{ads} + H^+ + e^-$ (1)

Peak A2 $2Cu + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2e^-$ $E^0 = 0{,}471 - 0{,}0591\ pH$ (2)

and $Cu_2O + H_2O \rightleftharpoons 2CuO + 2H^+ + 2e^-$ $E^0 = 0{,}669 - 0{,}0591\ pH$ (3)

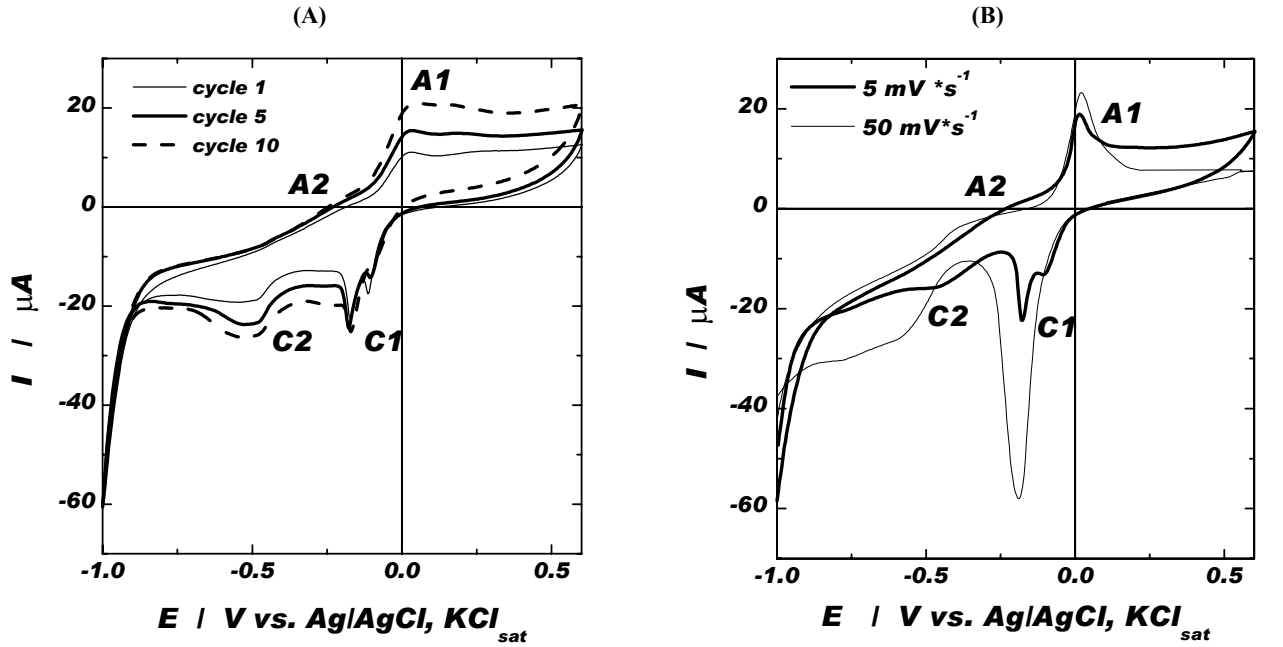

Fig. 1 – (A) Preparation of Cu/CuO modified electrode and (B) the influence of the scan rate on the preparation of the Cu/CuO modified electrode. Experimental conditions: electrolyte, phosphate buffer 0.1 M (pH 7); starting potential, -1 V *vs.* Ag/AgCl, KCl_{sat}; scan rate, 5 mV s^{-1} (A, B), 50 mV s^{-1} (B, thin line); number of cycles, 1, 5, 10 (A), 20 (B).

As previously described,[4] the electrosorption anodic reaction would involve co-adsorbed anions (abbreviated L, *e.g.,* phosphate or hydroxyl groups). Thus, the cathodic peaks probably represent a combination between the reduction of copper oxides and CuL. Furthermore, it should be noted that the area of the cathodic peaks is greater than the area of the anodic peak, indicating an essential catalytic effect of the reduction of ambient oxygen. Moreover, the *I–E* characteristics of the obtained voltammograms are in good agreement with the earlier reported.[21]

Additionally, from Fig. 1A is evident that the increase of the number of cycles leads to increase the C2 peak current intensity and consequently, the weight of the deposited CuO on the Cu surface electrode. Thus, a number of 20 cycles is considered enough to obtain a satisfactory thickness of the CuO film.

The influence of the scan rate on the modification of the Cu electrode with a CuO film was studied. As it can be seen in Fig. 1B, the increase 10 times of the scan rate lead to obtain a greatest C1 peak area and the disappearance of the shoulder preceding the C1 peak is observed. Despite that all peaks' intensities of currents are not significantly different, and because at low scan rate values, it is possible to observe slow processes, for obtaining Cu/CuO electrode surface, the optimal value of scan rate used during all work was 5 mV s^{-1}.

Cu/CuO electrode as Amperometric Sensor for H_2O2

Hydrogen peroxide is the product of the reactions catalyzed by many oxidases and, consequently, its determination is of considerable importance in medical, food and environmental analysis.[30-31]

Taking into account the well-known ability of CuO to catalyze the H_2O_2 reduction, cyclic voltammetry measurements at the Cu/CuO modified electrode, in the absence and in the presence of different concentrations of H_2O_2, were performed. As it can be seen from Fig. 2, a substantial electrocatalytic effect was identified. This effect is noticeable for A1/C1 peak pair, but especially marked at C2 peak. Thus, the anodic peak A1 for the formation of CuO disappears, suggesting that in the buffer system Cu(0) and/or Cu(I) are oxidised chemically by H_2O_2.[4] Furthermore, in the reduction window is noticeable an increase in the peaks' intensities for both systems Cu(II)/Cu(I) and Cu(I)/Cu(0). This behaviour suggests that the main catalytic mechanism for the H_2O_2 reduction involves the generation of Cu(I) at the electrode, following the reactions 4-6:[4, 8]

$$2\,Cu + H_2O_2 \xrightarrow{k_1} Cu_2O + H_2O \qquad (4)$$

$$Cu_2O + H_2O + 2e^- \xrightarrow{k_2} 2Cu + 2OH^- \quad (5)$$

combined with:

$$Cu_2HPO_4 + 2e^- \xrightarrow{k_3} 2Cu + HPO_4^{2-} \quad (6)$$

Because of the low stability of Cu(I) in the presence of buffer, during the potential scan the Cu(I) formed is immediately reduced to Cu(0), before it can be oxidized by H_2O_2. This is the explanation why H_2O_2 reacts mainly with Cu(0) and not with Cu(I).[4]

The corresponding electrocatalytic efficiency (estimated as the ratio between the increase of the catalytic peak current in the presence of H_2O_2 and the value of peak current in the absence of H_2O_2) was found to be 66.8% for 5 mM H_2O_2 (at -0.5 V *vs.* Ag/AgCl, KCl_{sat}, pH 7).

Consequently, the important catalytic effect of copper oxide towards the reduction of H_2O_2 makes possible the determination of glucose (from the H_2O_2 enzymatically generated, see reaction 7) at lower potentials, where the interferences of different compounds are negligible.[17]

$$\text{Glucose} + O_2 + H_2O \xrightarrow{\text{GOx}} \xrightarrow{\text{GOx}} \text{gluconic acid} + H_2O_2 \quad (7)$$

$$H_2O_2 \xrightarrow{E_{app}} 2H^+ + O_2 + 2e^- \quad (8)$$

Cu/CuO/Gox bioelectrode as Amperometric Sensor for Glucose

Following the reactions step 7-8, the chronoamperometric response for addition of different concentrations of glucose was carried out by using the Cu/CuO/Gox biosensor at different applied potential of -0.1, 0 and +0.1 V *vs.* Ag/AgCl, KCl_{sat}, respectively.

At all applied potential, the corresponding calibration curves have a typically hyperbolic Michaelis–Menten shape (Fig. 3). The kinetic parameters of the Cu/CuO/GOx electrode can be calculated from different linearization equations as synthesised in Table 1. As expected, no significant differences are obtained for the kinetic parameter values using different linearization methods. The values of the kinetic parameters at an applied potential of -0.1 V *vs.* Ag/AgCl, KCl_{sat} are not included in the table, because their values are very low. Furthermore, the apparent Michaelis-Menten constant (K_M), which is a reflection of the enzymatic affinity, has a value between 8-16 mM despite the used linearization method, which is in concordance with those obtained in literature (8.7 ± 0.2 mM).[2] All kinetic parameters, including sensitivity (S, estimated as I_{max}/K_M ratio) are highest for Cu/CuO/GOx electrode operated at 0 V *vs.* Ag/AgCl, KCl_{sat} (table 1), then for an applied potential of +0.1 V *vs.* Ag/AgCl, KCl_{sat}. Further, because the differences between sensitivities are not significant in the both mentioned case, the recommended applied potential may be between 0 and +0.1 V *vs.* Ag/AgCl, KCl_{sat}.

Concerning the analytical parameters, regardless of the applied potential, a linear relationship between current and glucose concentration was obtained from 1 mM up to 20 mM glucose (*i.e.* 3.60 g L^{-1}), thereafter, as expected for biocatalytic reactions, a non-linearly current increase with the substrate concentration is observed. In addition, the dynamic range covers not only physiological values, but also pathological ones (normal range: 0.70–1.10 g L^{-1} glucose). The detection limit (calculated as signal-to-noise ratio = 3) was ~1.6 mM glucose (0.29 g L^{-1} glucose).[17] Furthermore, the time required to reach the 95% steady-state response is within 10 s, for both applied potentials at Cu/CuO/GOx bioelectrode.

Real sample analysis

The Cu/CuO/GOx bioelectrode was used for glucose determination in some commercial food products or medicine, like orange juices and lemon ice tea and glucose ampoules. Using the standard addition method, recovery studies were carried out in the batch chronoamperometric system using the Cu/CuO/GOx bioelectrode polarised at an applied potential of 0 V *vs.* Ag/AgCl, KCl_{sat}.

The samples were diluted for 100 times in 0.1 M phosphate buffer (pH 7) and were analysed without any additional treatment. The results reported in Table 2 indicated an excellent recovery of glucose in the food samples, even if several additives like ascorbic acid are present. Furthermore, a very good result is obtained when the bioelectrode was used in the medicine sample, where the possible redox interferences are absent.

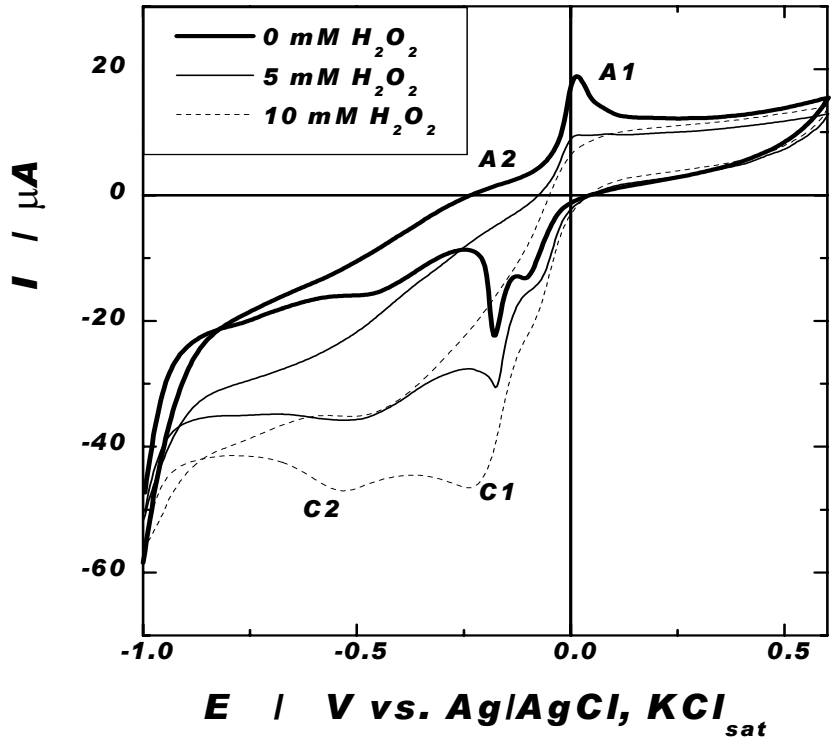

Fig. 2 – The electrocatalytic effect of Cu/CuO modified electrode towards H_2O_2 electroreduction. Experimental conditions: electrolyte, phosphate buffer 0.1 M (pH 7); starting potential, -1 V *vs.* Ag/AgCl, KCl_{sat}; scan rate, 5 mV s^{-1}.

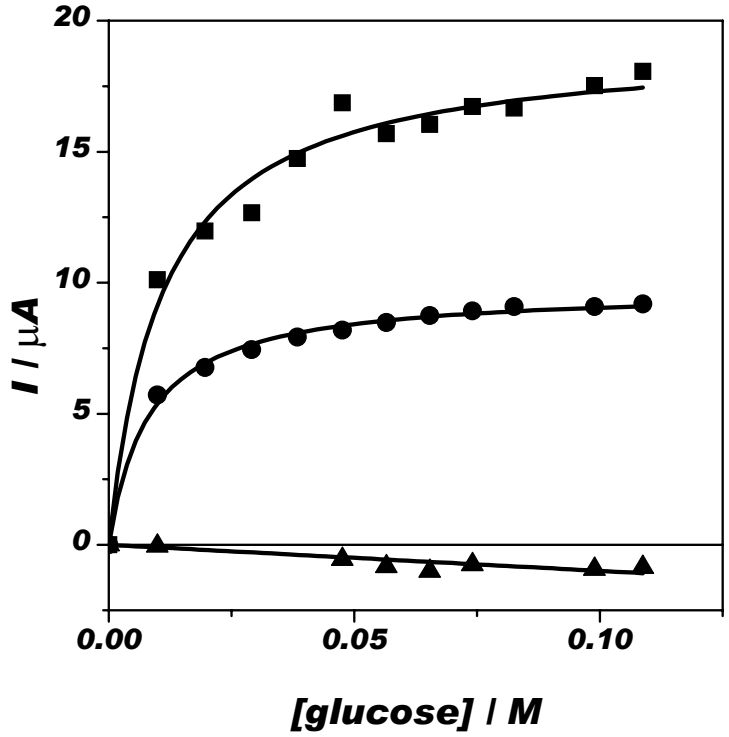

Fig. 3 – Amperometric calibration plot for glucose at Cu/CuO/Gox electrode. Experimental conditions: supporting electrolyte, phosphate buffer 0.1 M (pH 7); applied potential, -0.1 (▲), 0 V (●) and +0.1 V (■) *vs*. Ag/AgCl, KCl_{sat}; continuous stirred aerated solution.

Table 1

Kinetic parameters of Cu/CuO/Gox bioelectrode. Experimental conditions: see Fig. 3

Type of linearisation	K_M (mM)	I_{max} (μA)	S (mA M^{-1})	R/n
	Cu/CuO/Gox at 0 V *vs.* Ag/AgCl, KCl_{sat}			
Lineweaver –Burk	16.56 ± 7.40	20.62 ± 2.24	1.25 ± 0.42	0.9296/9
Eadie-Hoffstee	13.16 ± 6.89	19.75 ± 2.75	1.50 ± 0.83	0.9149/10
Hanes-Woolf	12.48 ± 1.15	19.66 ± 1.19	1.58 ± 0.17	0.9968/11
Origin fitting	10.90 ± 1.63	20.00 ± 0.57	1.83 ± 0.35	0.9900/12
	Cu/CuO/Gox at +0.1 V *vs.* Ag/AgCl, KCl_{sat}			
Lineweaver –Burk	9.62 ± 0.92	9.99 ± 0.18	1.04 ± 0,08	0.9952/10
Eadie-Hoffstee	9.74 ± 0.75	10.01 ± 0.18	1.03 ± 0.10	0.9926/10
Hanes-Woolf	9.10 ± 1.56	9.96 ± 0.21	1.10 ± 0.02	0.9996/11
Origin fitting	8.08 ± 0.59	9.78 ± 0.12	1.21 ± 0.20	0.9980/12

where: K_M is the Micheaelis Menten constant, I_{max} is the maximum current measured under saturated substrate conditions, S is the sensitivity calculated as the ratio of I_{max}/K_M. K_M and I_{max} confidence intervals were estimated as $s_{A/B}*t_{N\text{-}2;\ 0.95}$ and $s_{1/B}*t_{N\text{-}2;\ 0.95}$, respectively; $s_{A/B}$ is the standard deviation of the ratio A/B; $s_{1/B}$ is the standard deviation of 1/B; A and B are the Lineweaver-Burk linear regression parameters; N is the number of experimental data; t is the Student's variable corresponding to (N-2) degrees of freedom and 95% probability.

Table 2

Glucose determination in real sample using a Cu/CuO/GOx bioelectrode

Samples	Found (mM)	Added (mM)	Expected after addition (mM)	Found after addition (mM)	Recovery (%)
Orange juice (Santal Tetra Pak)	150	50	200	183	91.5
Lemon Ice Tea (Santal)	125	50	175	171	97.7
Glucose ampoules	148	50	198	196	99.0

EXPERIMENTAL

Reagents

Glucose oxidase membrane (YSI 2365) was purchase from YSI Co. (USA). Hydrogen peroxide (30% v/v aqueous solution) and glucose were obtained from Merck (Germany). Stock solutions of 1 M H_2O_2 and 1 M glucose were freshly prepared in 0.1 M phosphate buffer (pH 7); the glucose solution is let to mutarotate at room temperature overnight before use. A 0.1 M phosphate buffer (pH 7) prepared by mixing appropriate amounts of $Na_2HPO_4 \cdot 12H_2O$) and NaH_2PO_4 (Merck, Germany) was employed as a supporting electrolyte. All chemicals were of analytical grade and were used without further purification.

Real samples of food and medicine were commercially available, *i.e.* the orange juices (Santal, Tetra Pak) and the lemon ice tea (Santal) were purchased from a supermarket and the glucose ampoule from the pharmacy.

Apparatus

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about redox reactions and consist in recording the current of the working electrode during the scanning of the potential under a constant value of the scan rate. Contrarily, in the chronoamperometric methods, the recorded current *versus* time is obtained at a constant potential value. The cyclic voltammetry and the batch chronoamperometric measurements were performed using a PC controlled Autolab voltammetric analyzer (PGSTAT 10, EcoChemie, Netherlands). All experiments were carried out using a typical undivided three-electrode cell equipped with an Ag|AgCl, KCl_{sat} as reference electrode and a platinum plate as a counter electrode. As working electrodes a copper surface (3 mm diameter) was employed. All experiments were carried out at room temperature.

Modification of copper electrode (Cu/CuO)

The electrodeposition of the CuO film was realised by cyclic voltammetry at a low scan rate, between -1 V and +0.6 V *vs*. Ag/AgCl, KCl_{sat} on a freshly polished surface of a copper electrode immersed in 0.1 M phosphate buffer (pH 7). After electrodeposition, the electrode was thoroughly rinsed with distilled water.

Preparation of Cu/CuO/Gox bioelectrode

On the tip of the obtained modified Cu/CuO electrode the pre-prepared membrane containing GOx was fixed using a nylon mesh (lattice).

CONCLUSIONS

The advantages of the used Cu-CuO system which can greatly increase the electrocatalytic activity and faster promote the electron transfer at

the interface, lead to provide a simple method to develop a new amperometric bioelectrode for H_2O_2 and glucose detection. The excellent electrocatalytic activity showed by CuO film to the electroreduction of the enzimatically generated H_2O_2 has allowed detecting glucose at potentials negative enough to avoid the interferences of many compounds. The resulting Cu/CuO/GOx bioelectrode demonstrated very good analytical and kinetic parameters comparable and even better than those observed for other metalized glucose biosensors.

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