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Co_2SnO_4/CARBON PASTE ELECTRODE AS ELECTROCHEMICAL SENSOR FOR HYDROGEN PEROXIDE

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ABSTRACT

Hydrogen peroxide (H_2O_2) plays an important role as an intermediary in different biological, chemical and environmental systems. It has been widely used as an oxidizing and antimicrobial agent, in germicides production and textile and paper bleaching. However, it is well known, that H_2O_2 is a possible responsible in many diseases and is a chemical agent that threatens the environment, so it becomes important to detect peroxide with high accuracy. In this study, carbon paste electrode (CPE), modified with Co_2SnO_4 was synthesized and tested. It was successfully obtained a non-enzymatic H_2O_2 detection type sensor, based on Co_2SnO_4/CPE composite, showing good linear response in concentration of H_2O_2 in the range of 88 – 605.9 µM.

Keywords: Hydrogen peroxide, Carbon paste electrode, Co_2SnO_4

INTRODUCTION

Hydrogen peroxide (H_2O_2) plays an important role as an intermediary in different biological, chemical and environmental systems. It has been widely used as an oxidizing and antimicrobial agent, in germicides production and textile and paper bleaching [1,2]. However, it is well known, that H_2O_2 is a possible responsible in many diseases and is a chemical agent that threatens the environment, so it becomes important to detect peroxide with high accuracy [3]. For the chemical determination of H_2O_2 it is usually used methods such as volumetric analysis [4], spectrophotometry [5], fluorescence [6], electrochemistry [7] and chromatography [8]. In particular, several electrochemical methods have been reported as sensors for detecting H_2O_2 because they are a high sensitivity alternative at low cost and easy operation [7]. Recently, many biosensors have been studied as H_2O_2 detectors, such as enzymes/proteins immobilized in different materials, such as hemoglobin, carbon nanotubes, cytochrome C, etc. [9, 10, 11]. However the applications of these biosensors are restricted, because immobilization processes are complicated and activity is drastically affected by external factors such as temperature, humidity and pH [7, 12]. In this regard, it is important to develop non-enzymatic H_2O_2 sensors, presenting high sensitivity, stability, hardiness, economical and easy preparation. In this context, metal oxides (Fe_3O_4, V_2O_5, NiO, SnO_2, MnO_2, etc.), metal compounds such as ternary MCo_2O_4 (M = Zn, Ni, etc.), MFe_2O_4 (M = Ni, Mn, etc.), nanocomposites of PDAG/reduced graphene oxides (GRO) [13] and recently, electroceramic oxide composite such as Co_2SnO_4/ graphene have been considered as promising candidates for H_2O_2 detection[14]. Co_2SnO_4, is frequently used as conductive electrode in lithium ion batteries and as supercapacitor because of its electrical properties [15-16].

In this study, Co_2SnO_4/CPE electrode was prepared and tested. It was successfully obtained a non-enzymatic H_2O_2 detection type sensor. Co_2SnO_4/CPE composite showed good linear response in concentration of H_2O_2 in the range of 88 – 605.9 µM.

EXPERIMENTAL

Reagents:

All chemicals were of analytical grade from Merck. Mineral oil was purchased from Sigma and sodium chloride and hydrochloric acid were from J.T Baker. Hydrogen peroxide was from Merck, 30%. The H_2O_2 standard solution was standardized by $KMnO_4$ 0.2N which was previously standardized by $Na_2C_2O_4$. A stock solution of 29.4 mM H_2O_2 was prepared by 30% H_2O_2 solution and diluted with deionized and bidistilled water. 0.5M NaCl as the electrolyte and drops of concentrated HCl and NaOH were used to change the pH of the solution.

Equipment:

X-ray diffraction (XRD) measurements were performed using a MTI diffractometer, model MD-10 with a Cu radiation source ($k\alpha 1/\alpha 2$) = 1.54178 Å λ in a range of 2Θ = 15 - 70. The analysis of crystalline phases was performed using the Crystal Impact Match program with PDF-2 database. Parameter lattices were calculated using the STOE XPOW software. Morphological characterization was carried out in a scanning electron microscope (SEM), TESCAN, Vega 3 model. Compositional study was conducted by analysis of energy dispersive spectroscopy (EDS) using a Bruker probe, model QUANTAX 400a series. To perform electrochemical measurements 900B CH Instruments potentiostat was used at room temperature (25 ± 2 °C).

Electrochemical experiments: a conventional three electrode cell was employed where the working electrode is the composite electrode (Teflon tubes with a metal connection were used for making working electrodes, Teflon hollow electrodes of geometrical area 0.031 cm^2), Ag/AgCl (3M KCl) reference electrode, and a platinum wire was the counter electrode. Before each experiment, the working electrodes were polished and washed with deionized and double distilled water and cycled in the electrolyte solution 0.5M NaCl until a stable voltammetric response was obtained.

Electrode modification: The modification was performed by direct mixing 10% electroceramic oxide with 60% graphite and 30% of mineral oil by weight in an agate mortar. Then, it was added 10 mL of diethyl ether for homogenizing until solvent evaporation [17-18].

Cyclic voltammetry (CV): For electrochemical characterization carbon paste electrode (CPE) and Co_2SnO_4/CPE were measured in a potential range of -0.8V to 0.6 V at a scan rate of 0.05 V/s in a 0.5M NaCl solution which was previously purged with N_2 for 20 minutes.

Amperometry: In the electrochemical cell with electrolyte solution 0.5M NaCl (and drops of NaOH) pH = 10.2, aliquots of a standard solution of 29.4 mM H_2O_2 were added every 150 s for a total time 1300 s. Measurements were performed at a potential of -0.27 V.

RESULTS AND DISCUSSION

Synthesis of Co_2SnO_4

For the synthesis it was mixed CoO and SnO_2 in molar ratio 2: 1 in agate mortar. Acetone was added until a smooth paste is formed. Finally the resulting mixture was calcined in a furnace at 1000 °C for 24 h for obtaining ceramic oxide particles [14].

The reactions is described as follows (eq. 1)

$$SnO_2 + 2CoO \rightarrow Co_2SnO_4 \qquad \text{equation 1}$$

Structural characterization

X-ray diffraction (XRD)

Ceramic oxide Co_2SnO_4 corresponds to a spinel structure with Fd3m space group. The structural formula that defines the distribution of the cations in a normal and reverse spinel is (eq. 4):

$$^{IV}(A_{1-x}B_x)^{VI}(B_{2-x}A_x)O_4 \qquad \text{equation 2}$$

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Where IV corresponds to tetrahedral sites and VI to octahedral sites. At low temperatures, when T → 0K and X → 0, the structure correspond to a normal spinel, namely all atoms A occupy tetrahedral sites and B are located in octahedral sites. When X → 1 the spinel becomes an inverse spinel. This is the specific case of the Co_2SnO_4 ceramic oxide. In this case a new spatial distribution of cations A and B takes place. A percentage of cation A is occupying tetrahedral sites and the other percentage of A and B are in octahedral sites [19-20]. Figure 1 shows the diffraction pattern of Co_2SnO_4.

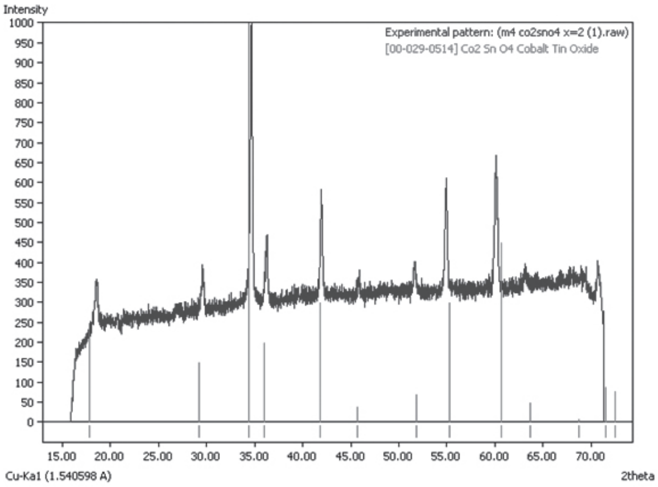

Figure 1: XRD Pattern of Co_2SnO_4

Figure 1a shows that XRD pattern of the synthesized material compared with the data base correspond to Co_2SnO_4, crystallizing in the Fd3m space group and a calculated cell parameter of 8.847 Aº. There are no secondary phases or evidence of unreacted raw materials assuring a pure crystalline phase.

Scanning electron microscopy (SEM)

Figure 2 shows morphology of Co_2SnO4 In this case, it can be observed a granular grain morphology and an average grain size of 0.57 µm.

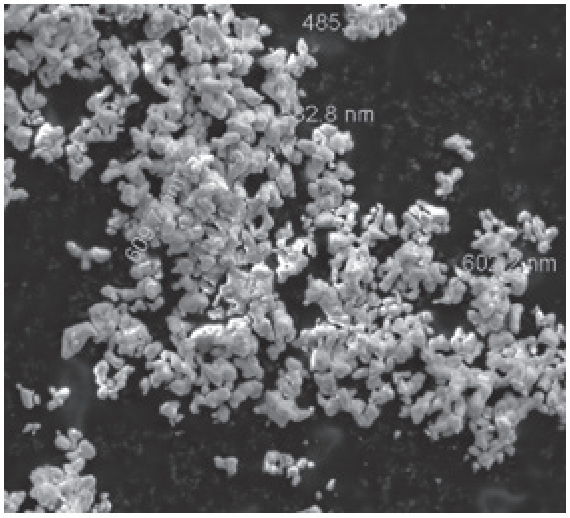

Figure 2: Scanning electron microscopy (SEM) of Co_2SnO_4

Modified electrodes

The modified electrodes were tested using the ferri-ferrocyanide redox couple. A solution of potassium hexacyanoferrate was dissolved in 0.5 M NaCl and the response was recorded at a scan rate of 50 mV/s. The electroactive area was determined using the Randles -Sevcik equation [21] (eq.3).

$$i_p = [\![(2.69 \cdot 10]\!]^5)n^{\frac{3}{2}}D^{\frac{1}{2}}v^{\frac{1}{2}}AC \qquad \text{Equation 3}$$

Where D is the parameter of diffusional coefficient of the species Fe (II) ($7,6 \cdot 10^{-6}$ cm^2/s) [21], n is the number of electrons transferred (n=1), C is the concentration of Fe (II)/Fe (III) (2 mM), ν is the scan rate (50 mV/s). The geometric area measured for the CPE electrode was 0.031 cm^2. Table 1 summarizes the electroactive area values calculated according to equation 5. The relative roughness factor (R = electroactive area area/geometrical area) and ΔE of the couple Fe (II)/Fe (III) for composites electrodes and CPE are also summarized.

Table 1: Electroactive area, relative roughness factor and ΔE for composites electrodes and CPE.

Electrode	electroactive area [cm^2]	relative roughness factor: R	**ΔE [V]**
CPE	0.035	1.15	0.24
Co_2SnO_4/CPE	0.039	1.26	0.19

Electrochemical characterization of the electrodes in the presence of H_2O_2

Cyclic voltammetry

The redox behavior of the composite and CPE were studied by cyclic voltammetry. Fig. 3 shows the cyclic voltammograms of the composite and CPE in 0.5M NaCl solution (pH=10.2) in the presence of H_2O_2. It is interesting that the modified electrode showed high activity compared to the CPE shifting the potential and increasing the current density. When comparing CPE vs. Co_2SnO_4/CPE system shows that H_2O_2 does not present redox peak but instead a current discharge at the bare CPE electrode. In contrast, the composite Co_2SnO_4/CPE shows a redox peak at −0.22 V.

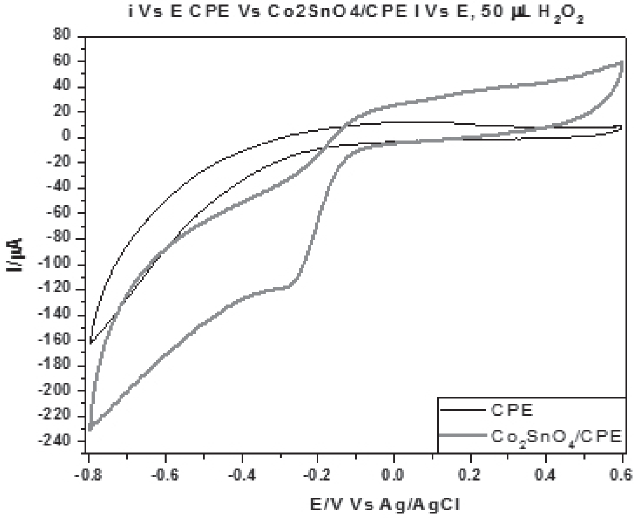

Figure 3: Cyclic voltammetry profiles of composite electrodes and CPE in the presence of 48.9 mM H_2O_2 0.5 M NaCl at pH=10.2. Scan rate: 0.05 V/s. a) (thin line) CPE, (bold line) Co_2SnO_4/CPE

Figure 4 shows cyclic voltammetry responses of CPE/Co_2SnO_4 when changing the concentration of H_2O_2. It can be seen that increasing the H_2O_2 concentration, the reduction current increases, suggesting that this electrode has an amperometric sensor behavior.

Amperometry

The amperometric study of the reduction of hydrogen peroxide with Co_2SnO_4/CPE composite electrode was performed adding aliquots of 30 µL 29.4 mM H_2O_2 to 10 mL of solution each 150 s during 1300 s applying a constant potential -0.27 V.

Figure 5a shows the amperometric response of the Co_2SnO_4/CPE composite electrode in the presence of increasing concentrations of H_2O_2 concentration from 88.0 to 605.0 µM. It can be seen that the current signal increases when concentration increases, showing a linear correlation (R = 0.9888), indicating that this composite electrode can be used as amperometric sensor for H_2O_2 (see figure 5b). The calibration curve of J Vs C shows the following analytical parameters: detection limit (µM)= 65.38, sensitivity ($µAcm^2/µM$) = $3,81x10^{-8}$, linear range [88 – 605,9 µM].

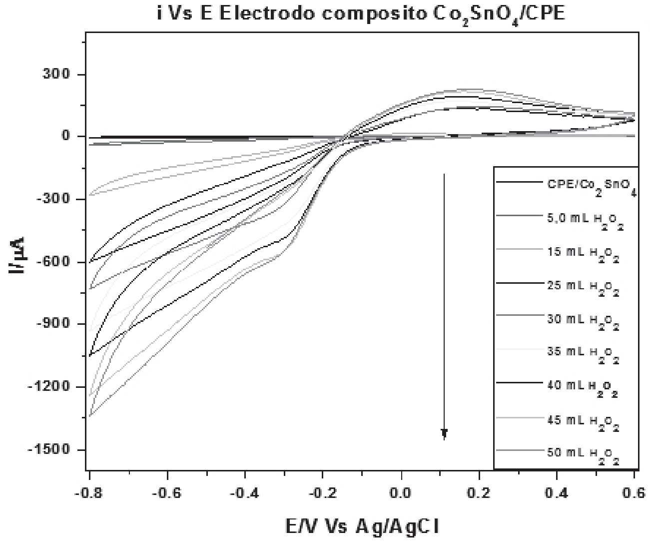

Figure 4: Cyclic voltammetry responses of composite electrode Co_2SnO_4/CPE at growing concentrations of H_2O_2 in solution of 0.5 M NaCl at pH=10.2 (see the arrow). Scan rate: 0.05 V/s.

Table 2 compares different sensors for peroxide showing that the composite electrode is cheap, stable, has good sensitivity and can be used easily for the detection of H_2O_2 in the range of linearity 88 µM - 605 µM.

Table 2: Comparison of different sensors for detecting H_2O_2

Sensor	Sensitivity: µAcm²/µM	linear range: mM	Ref
HRP/GO-Co_3O_4 - nafion	0.018	1-30	13
Ag NPs/CNT/rGO	--	0.01 – 10	22
PdAg/rGO	0.248	0.05 – 28	12
Fe_3O_4–rGO	0.028	0.1 – 6	23
Cu_2O–rGOis/GCE	0.019	0.1 – 7.8	24
Co_2SnO_4-rGO/GCE	0.43	0.01 – 0.80	14
CPE/Co_2SnO_4	0.038	0.08 – 0.61	This work

* rGO: Reduced graphene oxide, GO: Graphene oxide NPs: Nanoparticles, HRP: Horseradish peroxidase; GCE: Glassy carbon electrode

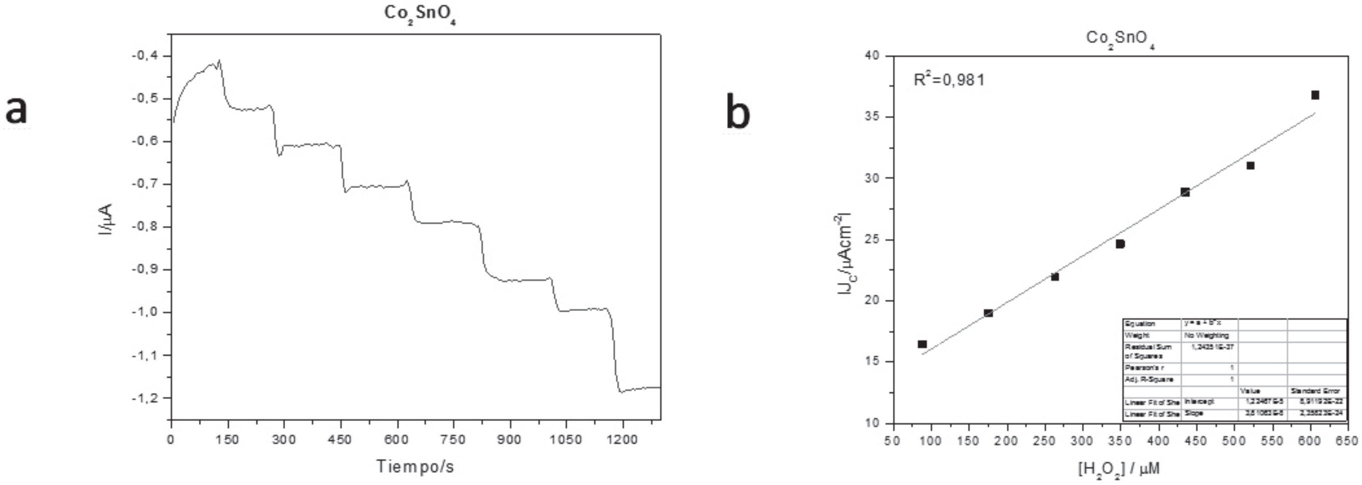

Figure 5: a) J Vs t response of the CPE/Co_2SnO_4 composite when adding aliquots of 30 µL 29.4 mM of H_2O_2 each 150 s. b) Calibration curve for the Co_2SnO_4/CPE composite electrode between 88 µm – 605.9 µm of H_2O_2 in 0.5M NaCl at pH=10.2.

CONCLUSIONS

It was obtained a stable, low cost, amperometric electrode sensor for hydrogen peroxide using a carbon paste electrode modified with Co_2SnO_4 ceramic compound.

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