Quantification of Hydrogen Peroxide using Poly Fe (III)-5-amino 1, 10 Phenanthroline

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Quantification of hydrogen peroxide using poly Fe (III)-5-Amino 1, 10 phenanthroline

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This work reports the results obtained with a composite prepared by dispersing multiple-wall carbon nanotubes in mineral oil (CNTPE) modified with a polymeric matrix of poly Fe(III)-5-Amino 1,10 phenanthroline (MCNTPE). The MCNTPE was used as electrochemical sensor for hydrogen peroxide quantification based on the polymer electrocatalytic effects. The amperometric response to H_2O_2 on MCNTPE was evaluated at -0,100 and 0,700 V vs Ag/AgCl. At -0,100 V, the sensitivity of the MCNTPE was increased by a factor of 2 orders of magnitude in comparison with the one obtained at CNTPE. At 700 mV, the sensitivity of the modified electrode was increased by a factor of 268 with respect to the non-modified electrode. The sensor also demonstrated to be very stable after continuous use. These results show that a new composite with remarkable electrocatalytic properties can be proposed for the future development of electrochemical (bio)sensors for the quantification of hydrogen peroxide.

Introduction

In the last years, the quantification of hydrogen peroxide has been the focus of attention in different scientific fields due to its multiple applications in the food industry, pharmaceutics, clinical and environmental studies (phytoremediation) (1). Hydrogen peroxide has been used in many industrial processes as oxidant, bleaching agent and sterilization agent. At NASA, hydrogen peroxide is used as rocket fuel in monopropellant engines, oxygen generator in bipropellant engines and turbopump propellant (2). Because of the importance of this compound, many researchers have tried to find the way to generate it and store it efficiently. The fact that hydrogen peroxide is a product generated by several enzymatic reactions, playing a major role in the enzymatic quantification of cholesterol, glucose, triglycerides and in the cancer study from the antioxidant effects on cells and tissues (3-5). Therefore, the importance of H_2O_2 in biochemical reactions and at biological level, have motivated the development of new alternatives for its analytical quantification. Chemical and biological sensors are examples of these new alternatives, where electrochemical transduction sensors are the most studied (6, 7).

The electrochemical determination of hydrogen peroxide by means of carbon electrodes has been widely used, although it presents the disadvantage of requiring high overpotentials for the oxidation of hydrogen peroxide. In order to avoid this inconvenience, some strategies have been applied to diminish the reduction - and/or the oxidation overpotential of H_2O_2 by using carbon, vitreous carbon and graphite electrodes (8). A very common strategy is the modification of these electrodes by catalytic species that accelerate the H_2O_2 reaction.

In the last decades, sensors and biosensors with chemical/electrochemical transduction have been synthesized by employing nanostructured materials like metallic-nanoparticle type and carbon nanotubes (CNT) (9). NTCs represent a new group of nanomaterials with unique properties such as high surface area and good electronic conductivity. There are two types of nanotubes: i) single wall nanotubes, which consist of rolled-up bidimensional graphite layers that form cylinders with lengths of tenths of micron and nanometric radii with fullerene semistructures in the edges and ii) multiple-wall nanotubes, which consist of cylindrical concentric layers that are approximately separated by a distance that is similar to the graphite interplanar distance (10). Carbon nanotubes are a very interesting option for the production of sensors that have to be small, portable, fast and energy-saving (11).

Due to their electric properties, which strongly depend on their atomic and electronic structures, it is possible to determine any physical or chemical modification produced by a change in their properties. CNTs have been used as semiconductors, sensor components, chips, optical devices, chemical and genetic probes, mechanic memory elements, nanoforceps and supersensible sensors. Nanotubes have also been used in the storage of hydrogen and ions (12-14) and in the study of different electrochemical processes (electrodes) (15).

This work presents the results obtained by using a composite for the quantification of hydrogen peroxide. This composite was obtained by dispersing multiple-wall carbon nanotubes in mineral oil (CNTPE) and modified with a polymeric matrix of Fe (III)-5-Amino 1,10 phenanthroline (MCNTPE).

Experimental conditions

Solutions and reagents

The formation of the Fe (III) metallic complex was carried out by using a solution consisting of $Fe_2(SO_4)_3 \bullet nH_2O$ ($2.5x10^{-4}$M) (100% J.T.Baker) and 5-Amino 1,10 phenantroline (5-Aphen) ($7.5x10^{-4}$ M) (Polysciences Inc). Since 5-Aphen is not very soluble in water, the initial mixture was stirred until a totally homogeneous mixture was obtained. H_2SO_4 (0.5 M) was added and a pH close to (6.00 ± 0.01) was obtained by adding a saturated aqueous solution of NaOH (99%, Merck). The solution was deoxygenated with nitrogen for 30 min in order to have a totally inert atmosphere. Afterwards, the solution was stored in a plastic flask at room temperature and protected from light until the system reaches its chemical equilibrium (16).

For the amperometric experiments, a phosphate buffer solution was prepared by using Na_2HPO_4 (J.T. Baker) and $NaH_2PO_4 \cdot H_2O$ (J. T. Baker). The hydrogen peroxide solution, H_2O_2 (20 mM), was prepared from a 30 % w/w H_2O_2 (Baker) solution that was dissolved in phosphate buffer (0.050 M) at pH=7.40.

Preparation of the carbon nanotube electrode paste

The CNTPE was prepared by mixing 70 % w/w of multiple-wall nanotube powder (diameter = 30 ± 15 nm, length= 50- 20 μm) (Nanolab, 95%) and 30 % w/w of nujol oil (Fluka). The carbon nanotube paste (CNTP) was placed within the cavity of a Teflon rod with a stainless steel screw as electric contact.

Electrochemical measurements

The electrochemical measurements were carried out by using a TEQ-02 potentiostat with a typical cell consisting of a three-electrode system. A platinum wire and a Ag/AgCl (3M NaCl) were used as auxiliary and reference electrode, respectively. CNTPE and MCNTPE were used as working electrodes.

The electrode was then activated (pretreated) by scanning the potential between 2000 and -1000 mV for 10 min in supporting electrolyte. The electropolymerization was performed by cyclic voltammetry experiments, scanning the potential between -1147 and 453 mV (70 successive cycles) in electrolytic solution of Fe(III)-5-Aphen ($2.5x10^{-4}$ M), with a stoichiometric ratio of 1:3 and pH=6.2. The supporting electrolyte for amperometric studies was phosphate buffer solution (0.050M) at pH=7.40.

The hydrodynamic voltammograms were carried out in a phosphate buffer solution at pH=7.40 by additions of 20 mM H_2O_2 from -400 to 800 mV. The solution was stirred in a 5.0 mL cell at a constant rate of 250 rpm.

Results and Discussion

Electroplymerization of poly Fe (III)-5-Aphen on carbon nanotube paste electrode

The formation of the poly Fe (III)-5-Aphen film on the CNTPE was performed by cyclic voltammetry applying 70 successive potential cycles from -1147 to 453 mV with a scanning speed of 100 mV/s.

Figure 1 shows the behavior obtained during the electrochemical polymerization of the Fe (III)-5-Aphen over a CNTPE reported. In this voltammogram, the redox processes concerning to the electropolymerization of poly Fe (III)-5-Aphen can be seen. Two oxidation peaks are obtained at -569 mV (I) and at -373 mV (I$_a$), while two reduction peaks are found at 537 mV (II$_a$) and at -829 mV (II). In the first electropolymerization cycle can be seen a peak at 55mV (a), which disappears in the second cycle. This behavior could be due to the high overpotential required for the oxidation of the monomer species at the electrode interface, or that the film formed on the surface of CNTPE modifies the electron transfer process.

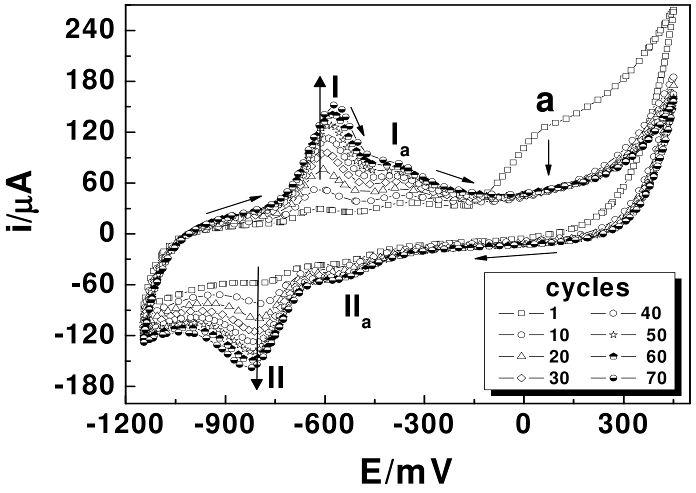


Figure 1. Cyclic voltammogram of the electropolymerization of Fe(III)-5-Aphen solution (2.5x10^{-4}M, pH 6.2) on CNTPE. Potential interval: -1147 to 453 mV. Scanning speed: 100 mV/s

The oxidation-reduction peaks (I/II) that appear at more cathodic potential values are related to the 5-Aphen redox properties in the film (17). The redox process corresponding to the (I$_a$/II$_a$) peaks is associated with the transformation of the Fe (III)/Fe (II) process in the polymer matrix. The system shows the typical behavior of the species adsorbed over the electrode surface. Figure 2 shows I$_p$ vs number of potential cycles for the I$_a$ and II$_a$ redox processes shown in Figure 1. In both cases, linear relationships are found, indicating that ~~a~~ the poly Fe (III)-5-Aphen film has been formed on the electrode surface.

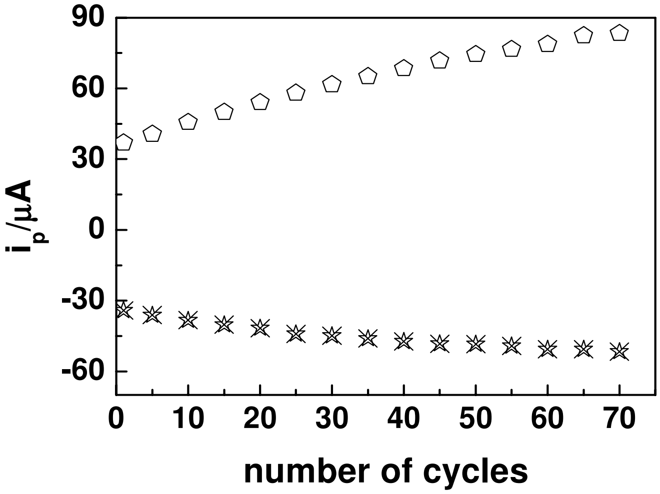


Figure 2. Evaluation of the peak current associated with the Fe (II)/Fe(III) redox pair processes on CNTPE. Fe(III)-5-Aphen solution (2.5x10^{-4}M, pH 6.2). Potential interval: -1147 to 453 mV. Scanning speed: 100 mV/s

Once the polymeric film was formed, a hydrodynamic voltammetry study was performed in order to determine the electrochemical behavior of hydrogen peroxide at CNTPE electrode modified with poly Fe (III)-5-Aphen (MCNTPE).

Hydrodynamic voltammetry of hydrogen peroxide on MCNTPE

By means of the hydrodynamic voltamperometry technique, the potential intervals at which H_2O_2 was oxidized and reduced at MCNTPE were determined in comparison to the electrochemical behavior at CNTPE. This study was performed using a 0.050 M phosphate buffer solution pH 7.40 as supporting by additions of 20 mM H_2O_2. At MCNTPE hydrogen peroxide oxidation starts at higher potentials than 400mV. The reduction takes place at lower potentials than 0.00 mV (Figure 3). The electrochemical behavior shown in Figure 3 clearly evidences the catalytic effects of poly Fe (III)-5-Aphen, where a decrease in the oxidation and reduction H_2O_2 overpotentials can be seen. In addition, an increase in the currents associated with both processes was found.In comparison, at CNTPE higher oxidation and reduction overpotentials for hydrogen peroxide are required and smaller associated currents are obtained, demonstrating the advantages of using MCNTPE for evaluating the electrochemical behavior of hydrogen peroxide.

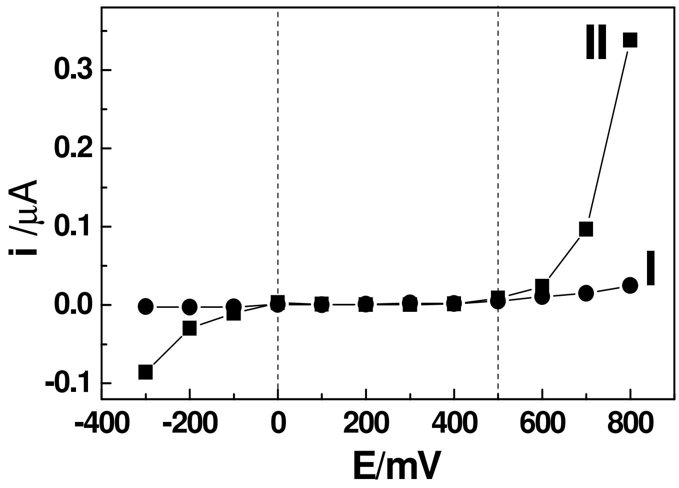
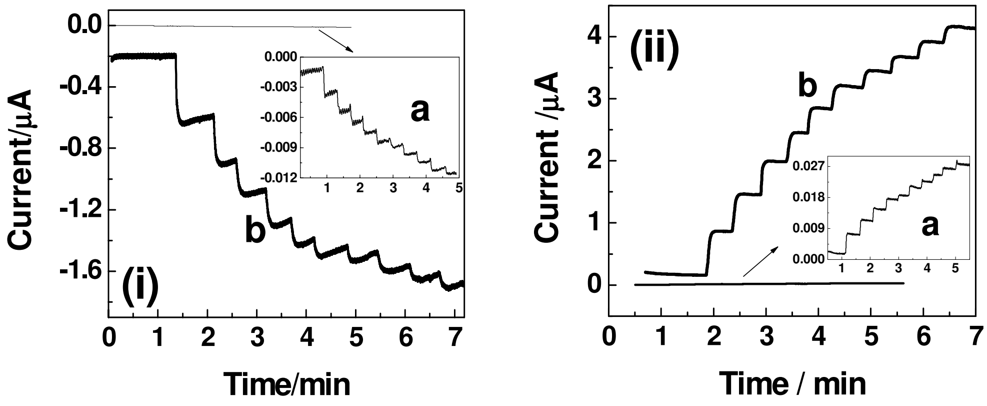
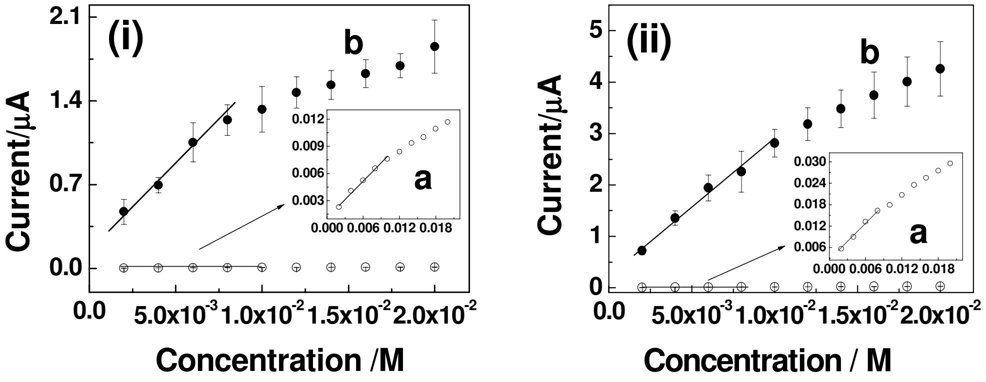


Figure 3. Hydrodynamic voltammogram for 20 mM H_2O_2. Potential interval: -400 to 800 mV vs Ag/AgCl at: I) CNTPE and at II) CNTPE modified with Fe (III)-5-Aphen (MCNTPE).

Once the oxidation and reduction potentials of hydrogen peroxide at the MCNTPE, the experimental conditions to perform an amperometric study for the determination of H_2O_2 were established from successive addition of 2.0 mM hydrogen peroxide. The applied working potentials were -100 mV (i) for the reduction and 700 mV (ii) for the oxidation of the analyte. Figure 4 shows the amperometric recordings (A) and the calibration curves (B) for the oxidation and reduction of H_2O_2 at CNTPE (a) and MCNTPE (b).



A



B

Figure 4. Comparison of the amperometric recordings (A) and the corresponding calibration curves (B) obtained for successive additions of 20 mM hydrogen peroxide and working potentials of (i) E =-100mV and (ii) E =700mV for a) CNTPE and b) MCNTPE**.**

At MCNTPE the sensitivity towards H_2O_2 is 2 orders of magnitude higher than the one obtained at CNTPE, as can be seen in Figure 4. These evidences are consistent with the fact that poly Fe (III)-5-Aphen deposited at CNTPE presents higher catalytic activity towards the oxidation and reduction of hydrogen peroxide in comparison to the behavior observed at CNTPE.

Table 1 shows the analytic parameters for the different calibrations plots obtained for 2.0 mM H_2O_2 at MCNTPE and CNTPE at -100 mV and 700 mV . In all cases, It can be seen that the sensitivities towards H_2O_2 obtained from the amperometric calibration plots at -100 and 700 mV were remarkably improved in the MCNTPE (b) with respect to the CNTPE (a).

TABLE I. Statistical parameters obtained from amperometric calibrations curves for 2.0 mM H_2O_2 at CNTPE and CNTPE modified with Fe (III)-5-Aphen (MCNTPE).

Working Potential (mV)	Sensibility (μAM)	r	Linearity up to (mM)	Detection limit (μM)
-100 (CNTPE)	0.7 ±0.1	0.998	2.0 - 10.00	1.37
-100 (MCNTPE)	**$(1.3 \pm 0.3) \times 10^2$**	**0.994**	**2.0 - 8.0**	**0.27**
700 (CNTPE)	1.8±0.3	0.9991	2.0 - 8.0	3.76
-700 (MCNTPE)	**$(2.7 \pm 0.3) \times 10^2$**	**0.996**	**2.0 - 10.0**	**0.48**

The quantification of H_2O_2 at MCNTPE is highly sensitive and the detection limits are largely enhanced compared to other already existing methodologies for the analysis of H_2O_2 (18). This improved behavior is related to the ability of poly Fe (III)-5-Aphen to catalyze the oxidation and reduction of hydrogen peroxide.

The stability of the response to hydrogen peroxide at MCNTPE was also evaluated. The MCNTPE was challenged and after six successive amperometric recordings obtained for 2.0 mM additions of H_2O_2 (four hours of continuous use) the sensitivity of the sensor was around 94% of the original value. This fact clearly indicates that the sensor could be use during six succesive calibrated without significant loosing of activity towards H_2O_2.

Conclusions

This work reports the results concerning the quantification of H_2O_2 with laboratory solutions using an MCNTPE as working electrode. This electrode showed excellent electrocatalytic properties for the oxidation and reduction of H_2O_2. An increment in the sensitivity by two orders of magnitude and a diminution in the detection limit (DL) by one order of magnitude were found at MCNTPE. According to these characteristics, the MCNTPE can be a good candidate to develop an electrochemical sensor for the determination of hydrogen peroxide in different processes such as the oxidation of phenols in industrial wastewaters (19) and the enzymatic quantification of glucose using glucose oxidase that generates hydrogen peroxide as a product of the enzymatic oxidation of glucose.

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