

EVALUACIÓN PRELIMINAR DE UN SENSOR ELECTROQUÍMICO PARA PERÓXIDO DE HIDRÓGENO BASADO EN UN ELECTRODO DE GRAFITO MODIFICADO CON AZUL DE PRUSIA DEPOSITADO ELECTROQUÍMICAMENTE SOBRE NANOTUBOS DE CARBONO DOPADOS CON HIDROXIAPÁTITA

PRELIMINARY EVALUATION OF AN ELECTROCHEMICAL SENSOR FOR HYDROGEN PEROXIDE-BASE ON A PRUSSIAN BLUE MODIFIED GRAPHITE ELECTRODE ELECTROCHEMICALLY DEPOSITED ON CARBON NANOTUBES DOPED WITH HYDROXYAPATITE

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Resumen

Se evaluó un sensor electroquímico para la detección de peróxido de hidrógeno (H₂O₂). El montaje del sensor se realizó utilizando un electrodo de grafito fabricado y modificado con una película de nanotubos de carbono de pared múltiple (MWCNT) dopados con nanopartículas de hidroxiapatita (HAp) y azul de Prusia (PB) como transductor electrocatalítico. La caracterización de los MWCNT funcionalizados (fMWCNT) y los HAp-fMWCNT modificados se realizó mediante espectroscopia infrarroja transformada de Fourier, difracción de rayos X y microscopía electrónica de transmisión. El desempeño electroquímico del sensor se evaluó por voltametría cíclica (CV) y cronoamperometría, utilizando [Fe(CN)₆]^{3-/4-} como sistema redox de referencia. Los voltamogramas cíclicos mostraron la actividad electrocatalítica del PB hacia la reducción del peróxido de hidrógeno. Se encontró una dependencia lineal sobre el sensor de la corriente catalítica versus la concentración de H₂O₂ de 1 a 10 mM (R²=0,9763), con una sensibilidad de detección de 119 μA mM⁻¹cm⁻². Este reporte muestra la viabilidad del ensamblaje sobre electrodos de grafito para construir un sensor de H₂O₂ además, de evidenciar el potencial de los nanomateriales de carbono, como los fMWCNT dopados con HAp, para la construcción de dispositivos bioelectrónicos.

Palabras clave: sensor electroquímico; peróxido de hidrógeno; azul de Prusia; nanotubos de carbono dopados con hidroxiapatita; voltametría cíclica.

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ABSTRACT

An electrochemical sensor for detection of hydrogen peroxide (H_2O_2) based on multiwalled carbon nanotubes (MWCNT) doped with hydroxyapatite nanoparticles (HAp) was evaluated. The assembly of the sensor was performed using a graphite electrode (GE) manufactured and modified by layers with a film of HAp-MWCNT and Prussian Blue (PB) as electrocatalytic transducer. The characterization of functionalized MWCNT (fMWCNT) and modified HAp-fMWCNT was performed by Fourier Transform Infrared Spectroscopy, X-Ray Diffraction, and Transmission Electron Microscopy. The electrochemical performance of the developed sensor were carried out by cyclic voltammetry (CV) and chronoamperometry, using $[Fe(CN)_6]^{3-/4-}$ as reference redox system. Cyclic voltammograms revealed the electrocatalytic activity of the PB toward reduction of hydrogen peroxide. A linear dependence on H_2O_2 concentration from 1 mM to 10 mM ($R^2 = 0,9763$), with a detection sensitivity of $119 \mu A mM^{-1}cm^{-2}$. This work demonstrates the feasibility of assembled of graphite electrode to build up a H_2O_2 sensor, and also evidence the great potential of carbon nanomaterials, such as MWCNT doped with Hap, for the construction of bioelectronics devices and biosensors.

Keywords: electrochemical sensor; hydrogen peroxide; prussian blue; hydroxyapatite-doped carbon nanotubes; cyclic voltammetry

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Introduction

Hydrogen peroxide (H_2O_2) is a simple inorganic compound, and its determination plays an important role in various areas such as medicine, biology, environmental, mining, textile and industrial processes. In the area of Medicine, H_2O_2 reacts easily and can decompose into hydroxyl radicals ($\bullet\text{OH}$), which are highly reactive and harmful to the human body¹. Many of the cell damage and tissue malfunction are related to the overproduction of reactive species such as $\bullet\text{OH}$ and superoxide ($\text{O}_2^{\bullet-}$)². Hydrogen peroxide is also involved in several biological events and intracellular pathways and is the by-product of enzymatic processes such as those involving, for example, glucose oxidase, cholesterol oxidase, and alcohol oxidase³. Hydrogen peroxide is also a substrate for the enzyme horseradish peroxidase⁴.

On the other hand, carbon nanotubes (CNTs) have received a great deal of attention of research in recent years due their high surface areas, their excellent electrical, mechanical and electrochemical properties, therefore, the modification of these biosensors with CNTs create a new generation of ultrafast and ultrasensitive biosensors⁵.

Modification of CNT walls with different nanoparticles in biosensors also provide a faster electron transfer rate and catalytic activity towards many biomolecules⁶.

Some modified biosensors markedly improve their behavior to immobilize enzymes⁷. Hydroxyapatite (HAP) has a high capacity of adsorption of biomolecules, and also possess exceptional biocompatibility and bioactivity properties⁸. Therefore, the combination of CNTs doped with HAP nanoparticles can offer a synergistic effect as biosensors.

Considering the foregoing, this work deals with the development of an electrochemical sensor with a nanostructured system based on multi-walled carbon nanotubes (MWCNTs) doped with HAP nanoparticles for the detection of H_2O_2 . The electrochemical sensor measured an electrochemical

response when an inorganic electrocatalytic transducer (Prussian Blue) was electrodeposited directly onto the surface of the modified graphite electrode using a Hap-fMWCNT film. Prussian Blue (PB) will be used as an electrocatalyst towards hydrogen peroxide reduction^{9,10}.

MATERIALS AND METHODS

Materials and Reagents

All chemicals used in this work were from commercial sources with an analytical purity and used as received. Aqueous solutions were prepared using distilled/deionized water (18.4 M Ω resistivity) water. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), potassium ferricyanide [$\text{K}_3(\text{Fe}(\text{CN})_6)$], potassium chloride (KCl) and sodium chloride (NaCl) were from BDH Chemicals (Philadelphia, PA, USA), hydrochloric acid (HCl, 37%) was from Fisher Scientific (Waltham, MA, USA). Concentrated solution of hydrogen peroxide (H_2O_2 , 30%) was purchased from Sigma-Aldrich (Steinheim, Germany).

Potassium phosphate monobasic (KH_2PO_4 , 99%) and sodium hydroxide (NaOH, 99.9%) were purchased from Fisher Scientific (Waltham, MA, USA). The electrolyte solution used for every experiment was a phosphate-buffered saline (PBS, 100 mmol.L⁻¹ KH_2PO_4 + 200 mmol.L⁻¹ NaOH, pH 7.4). All the carbon nanotubes were donated, with a previous characterization and functionalization¹¹.

A conventional three-electrode system was used, consisting of a platinum (Pt) wire as a counter electrode (CE) was from (Metrohm, Utrecht, Netherlands), an Ag/AgCl (sat. KCl) as a reference electrode (RE), polishing pads and 1 μm , 0.3 μm , 0.05 μm alumina polish (Al_2O_3) were from CH-Instruments (Austin, TX, USA). The working electrode (WE) was a graphite electrode (GE) fabricated using a commercial 2H-pencil leads (Staedtler, Germany) as a source of graphite. N-Dimethylformamide (DMF) was purchased from Fisher Scientific (Waltham, MA, USA) and poly(diallyldimethylammonium chloride) (PDDA, $M_w < 100.000 \text{ g mol}^{-1}$ in 35wt% aqueous solution) was purchased

from Sigma-Aldrich (Darmstadt, Germany).

Apparatus

The following equipment was used: Branson 3800 ultrasound bath, Biologic SP-150 Potentiostat, EC-Lab V11.26 software, one-compartment electrochemical cell, GC electrode as working electrode, Ag/AgCl electrode as reference electrode, graphite as counter-electrode; Mettler Toledo pH meter, SIEMENS D5005 diffractometer (with a 1.54178 \AA wavelength in a 2θ range from 10° to 80° at a $0.02^\circ/0.52\text{s}$ speed), FTIR Nicolet iS10 spectrometer that uses 64 swept with a 2 cm^{-1} resolution, JEOL 1220 microscope at 100 kV and 200 kV voltages.

Synthesis of Hap-fMWCNT

The MWCNT functionalization was carried out to provide the CNTs walls with functional groups that allow the chemical bonding between the CNTs and the HAp, and to eliminate possible impurities on its surface. The procedure described by González et al.¹⁵ was used, briefly: 1.0 g of CNTs was added to a $3 \text{ mol L}^{-1} \text{ HNO}_3 + 1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution using a 3:1 proportion, under reflux and magnetic agitation at 80°C for 6 hours.

The resulting material was filtered, and then washed with deionized H_2O , vacuum dried for 12 h at 60°C , and it was finally grounded in a mortar for its later functionalization. The formation of carboxyl and hydroxyl groups on the material's walls was done by mixing pre-functionalized CNTs with 80 mL of HNO_3 under ultrasonic agitation during 30 s. This mixture was refluxed at 80°C for 2 h, then diluted with H_2O , filtered, and dried at 60°C for 16 h. Then the functionalized carbon nanotubes (fMWCNT) were ground, and the final material was passed through a $125 \mu\text{m}$ particle-size sieve.

The coating of fMWCNT walls with HAp was carried out by means of biomimetic process using 1.5SBF (simulated body fluid). 1.5SBF was prepared by the method reported by Kokubo et al.¹⁶: 80 mg of fMWCNT was added to a simulated corporal fluid solution inside a sealed container that was then submerged into a water bath at 35 to 42°C . The aging

time of this solution was set at two levels, 36 (fMWCNT /HAp(36)) and 100 (fMWCNT /HAp(100)) days. Subsequently, the samples were later separated by decantation from the solution, and then dried under vacuum at 60°C during 14 h¹⁶.

Graphite electrode fabrication

A 2H pencil lead cut to a length of 8.0 cm was used as the source of graphite for the electrode assembly. The pencil lead was cleaned in an ultrasonic bath of acetone/water for 10 minutes and dried at room temperature. The graphite lead was placed into the center of a tubing glass of 7.0 mm of inner diameter and 6.5 cm of length and then sealed on one side with epoxy resin. To remove the excess of resin and smooth the surface of the electrode surface mechanical polishing with emery paper #500, #1200, #2500, and washing with distilled water was necessary. Finally, an electrode with a homogeneous surface is obtained. The 2H-GE surface requires a pretreatment to remove the impurities and residues, the most common treatment is alumina polishing. At first step, the 2H-GE surface requires an activation, through creation of defects¹², by mechanical polishing with an emery paper #A99-240. Afterwards, the 2H-GE was polished with water-alumina slurry of $1.0 \mu\text{m}$, $0.3 \mu\text{m}$ and $0.05 \mu\text{m}$ alumina powder with figure-eight motions on a cloth polishing pad during 5 minutes and rinsed with deionized water. Subsequently, to remove any residual alumina particles from the electrode surface, an ultrasonic vibration for 5 minutes in acetone/water solution (1:1) was required. Finally, the electrode was dried at 50°C for 5 minutes and cooled at room temperature. As a result, a 2H-GE with a diameter (\varnothing) of 2.0 mm is obtained, ready to be subjected to be modified and electrochemical tests.

Preparation of the modified electrode

A concentration of 5.0 mg mL^{-1} of fMWCNT and Hap-fMWCNT were suspended in DMF into a 1.5 mL vial and were sonicated for 10 min each one^{13,14}. The dispersed solutions were stored in a dark place at room temperature. Then, onto the surface of each graphite

electrodes (GE) previously treated, 10 μL of the fMWCNT and fMWCNT/HAp dispersions were pipetted covered uniformly the electrodes surface. The modified electrodes HAp-fMWCNT/GE were dried in an oven at 50 $^{\circ}\text{C}$ for 10 min and were then cooled. A solution of poly(diallyldimethylammonium chloride) (PDDA) was prepared in 0.5 mol.L⁻¹ NaCl at a concentration of 1 mg.mL⁻¹.

Then, 10 μL of PDDA solution was dropped uniformly over the surface of the modified electrodes, and once again proceed to dry at 50 $^{\circ}\text{C}$ for 10 min. Finally, the fMWCNT/PDDA/GE and Hap-fMWCNTs/PDDA/GE modified electrodes were obtained. PDDA was used as an electrostatic stabilizer between the layers of carbon nanotubes and the surface of graphite electrode. The modification of the electrode was based on a layer-by-layer electrostatic assembly, such as the case of the positively charged PPDA layer attached electrostatically to negatively charged carbon nanotube layer.

Electrochemical deposition and activation of Prussian Blue at the modified electrodes

The electrochemical deposition of Prussian Blue (PB) film at the fMWCNTs/PDDA/GE and Hap-fMWCNT/PDDA/GE modified electrodes surface were carried out by chronoamperometry, respectively⁹. Therefore, for each electrodeposition of PB film, two aqueous solutions were employed. Solution 1: 2.5 mmol L⁻¹ K₃[Fe(CN)₆] + 2.5 mmol L⁻¹ FeCl₃.6H₂O + 0.1 mol.L⁻¹ HCl + 0.1 mol.L⁻¹ KCl. Solution 2: 0.1 mol L⁻¹ HCl + 0.1 mol L⁻¹ KCl with pH 2.0. Consequently, the PB film was deposited onto the modified electrode surface when dipped into solution 1, applying a constant potential of +0.4 V (vs. Ag/AgCl) for 60 s. Then, the electrode was carefully washed with distilled water and transferred into solution 2, where the activation, growth and stabilization the PB film was checked by electrochemical cycled for various times in the potential range of -0.15 V to +0.5 V (vs. Ag/AgCl), with a scan rate of 50 mV.s⁻¹, until obtained a stable voltammetric response (25 cycles). Then, the PB-modified electrode was washed several times with deionized water, dried at 50 $^{\circ}\text{C}$

for 10 min, and cooled at room temperature. As a final step of the layer-by-layer process, 10 μL of the polyelectrolyte (PDDA) solution was place onto the PB-modified electrode surface, acting as a supporting matrix of PB layer due to the maintenance of electrostatic force between layers. Then, the electrode was dried at 50 $^{\circ}\text{C}$ for 10 min. Finally, PB-fMWCNT/PDDA/GE and PB-Hap/MWCNTs/PDDA/GE modified electrodes were obtained. Then, they were stored at a temperature of 4 $^{\circ}\text{C}$, ready to be characterized and used electrochemically.

Voltammetric detection of hydrogen peroxide

The behavior of modified electrodes toward electrocatalytic reduction of H₂O₂ was investigated using cyclic voltammetry. The voltammetric response was analyze, adding aliquots of different H₂O₂ concentrations, into of PBS (pH 7.4), at a constant potential range from -1.0 V to +0.5 V (vs. Ag/AgCl) with a scan rate of 50 mV.s⁻¹. Hydrogen peroxide solution (0.1 M) (stock solution) was prepared by dissolving 250 μL of H₂O₂, 30 % in 25 mL of distilled water and stored at 4 $^{\circ}\text{C}$ when not in use. The working standard solutions from 1mM to 10 mM H₂O₂, were prepared by dilution of the stock solution with 0.1 M PBS (pH 7.4). All working solutions were freshly prepared before used and purged with pure N₂ gas, during 60 s, to eliminate de oxygen during the tests.

Results and Discussion

Characterization of the nanostructured material

Fourier transformed infrared spectroscopy Figure 1 shows that the nanostructured compounds fMWCNT/HAp(36) and fMWCNT/HAp(100) exhibit the same bands as Hap synthesized in the laboratory, with the exception of the band at 3570 cm⁻¹, which represents the OH⁻ groups of this substance. This result indicates the existence of some interaction between the fMWCNT and the HAp. Also, it is observed that the bands corresponding to HAp are more intense in the fMWCNT/HAp(36) material than in the fMWCNT/HAp(100) material, which shows

that there is a greater amount of HAp in fMWCNT/HAp(36). Significant differences of these compounds with respect to HAp can be observed in the right part of Figure 1, where the fMWCNT/Hap materials have

characteristic bands of the fMWCNT, in the region ranging from 400 to 515 cm^{-1} .

Figure 2 show the XRD patterns of the fMWCNT, HAp, fMWCNT/HAp(36) and fMWCNT/HAp(100). In the fMWCNT/Hap

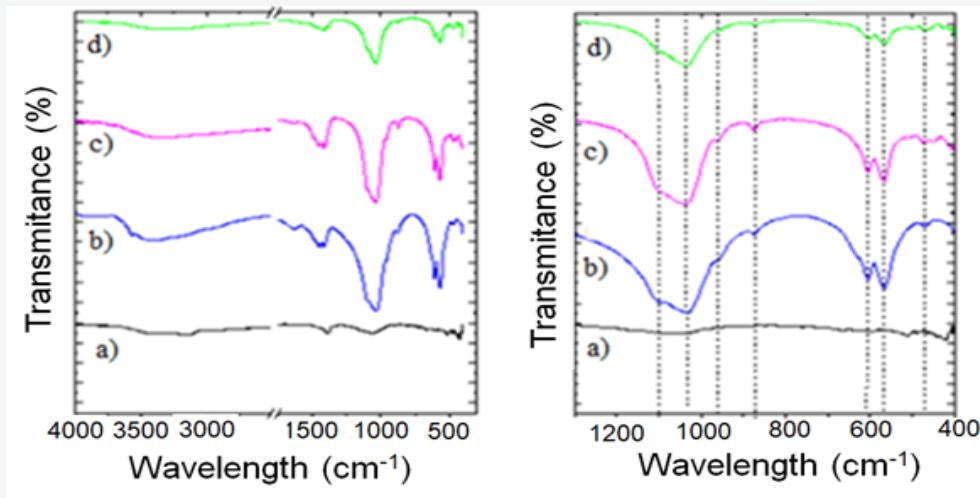


Figure 1. FTIR spectra of CNTf / HAp nanostructured systems: a) fMWCNT, b) HAp, c) fMWCNT/HAp(36) and d) fMWCNT/HAp(100).

(100) material the intensity of the peak of the plane (002) at $2\theta = 25.9^\circ$ increases with respect to that of HAp, since it overlaps with the peak of the fMWCNT. In addition, it is observed that the width of the peaks in both compound increases with respect to the HAp, being greater in the fMWCNT/HAp(100); It is expected that the crystal size will be smaller than that of the fMWCNT/HAp(36). The crystal size decreased in the following order HAp > fMWCNT/HAp(36) > fMWCNT/HAp(100).

Transmission electron microscopy

In Figures 3 and 4 it is observed that the HAp particles are located in areas where the fMWCNT are agglomerated, which seems to indicate that the HAp is supported on the nanotubes and not chemically bound to them. Also, it is observed that there is more quantity of HAp in the fMWCNT/HAp(36) than in the fMWCNT/HAp(100) material, as obtained in the FTIR and XRD analyzes. HAp particles in these systems are spherical in shape, whereas of HAp particles synthesized without the fMWCNT are rod-shaped. The average size of HAp particles in the fMWCNT/HAp(36) material, shown in Figure 3-B, is 7.6 nm.

Electrochemical characterization

The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used as reference redox system, to determine the electrochemical behavior of the electrode through cyclic voltammetry studies. Before start with the electrochemical characterization, in order to clean and active the surface of bare and modified 2H graphite electrodes, a cyclic voltammetry potential sweep between -1.2 V and +1.5 V in 0.1 mol L^{-1} PBS was carried out, a sweep rate of 100 mV s^{-1} , during 25

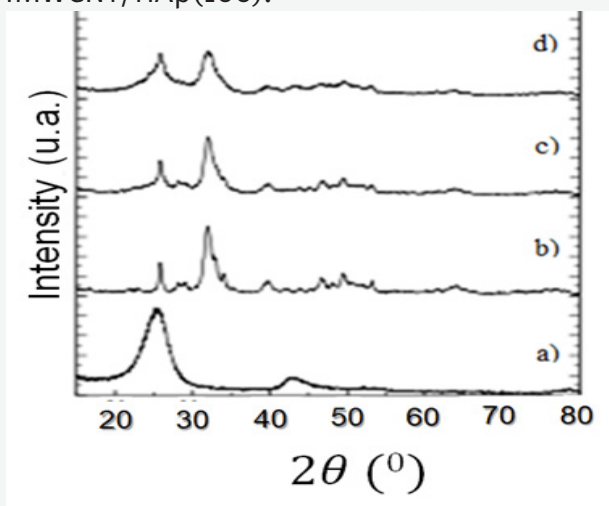


Figure 2. XRD patterns of the: a) fMWCNT, b) HAp, c) fMWCNT/HAp(36) and d) fMWCNT/HAp(100)

cycles. As illustrated in Figure 5, not peaks are shown on the cyclic voltammograms of bare and Hap (36)-MWCNTs/ PDDA/GE modified electrodes, in the range of potential range used, so there have not been reduction and oxidation reactions . However, on

the MWCNTs/PDDA/GE electrode, a high capacitive current and current signal (at 0.0 V) were obtained that can be associated with quinone groups present on the surface of the nanotubes.

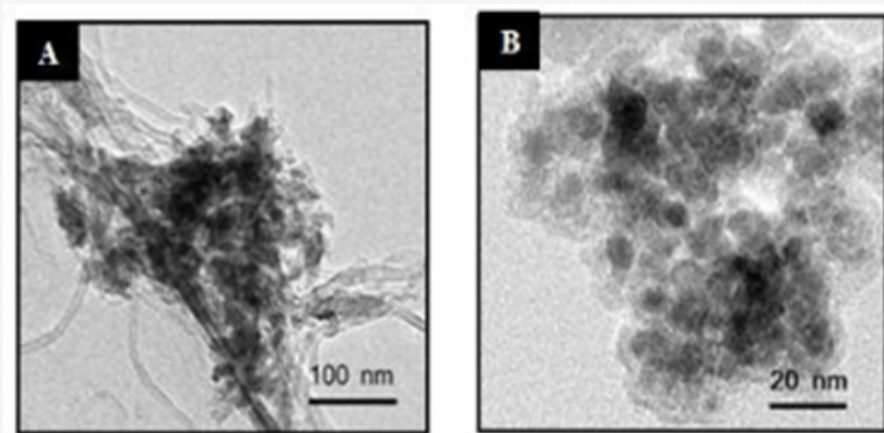


Figure 3. Transmission electron micrographs of the fMWCNT/HAp(36)

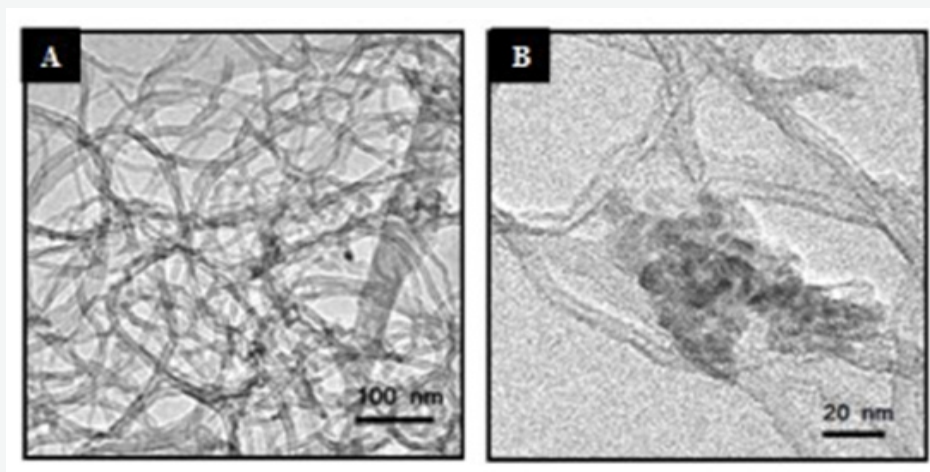


Figure 4. Transmission electron micrographs of the fMWCNT/HAp(100)

In this research the modification of Hap(36)-MWCNTs/PDDA/GE electrode implies coating its surface with Prussian Blue (PB), in order to enhance the properties of those electrodes to H₂O₂ electrocatalytic detection.

Once the PB film was electrodeposited at the surface of modified Hap(36)/MWCNTs/PDDA/GE, during 60 s, the films require electrochemically activation by cyclic scan in the same supporting electrolyte (0.1 M HCl +0.1 M KCl), in the potential range of -150 mV and +500 mV, at a scan rate of 50 mVs⁻¹, for the purpose of growing and stabilizing the Prussian Blue film. Figure 6 shows typical cyclic voltammograms obtained after

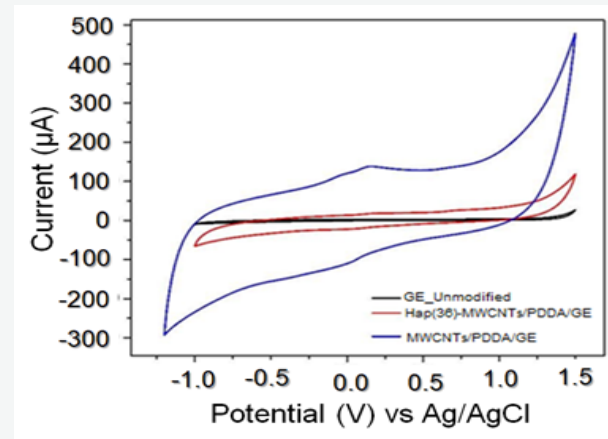


Figure 5. Cyclic voltammogram of bare and modified electrodes in 0.1 mol L⁻¹ PBS, at scan rate of 100 mV s⁻¹.

electrodeposition of PB, for PB-MWCNTs/PDDA/GE and Hap(36)/MWCNTs/PDDA/GE modified electrodes. A pair of redox peaks appeared located at 0.152 V (vs. Ag/AgCl), values consistent with the reported in the literature^{21,22}. The redox peaks cor-

responding to redox conversion between Prussian Blue (PB, $K_2Fe^{III}[Fe^{II}(CN)_6]$) and Prussian White (PW, $K_2Fe^{II}[Fe^{II}(CN)_6]$) in their reduced form, according to the reversible equation (1).

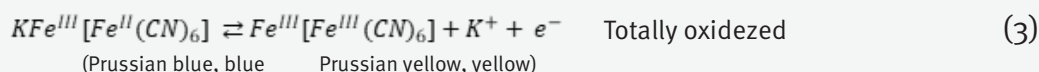
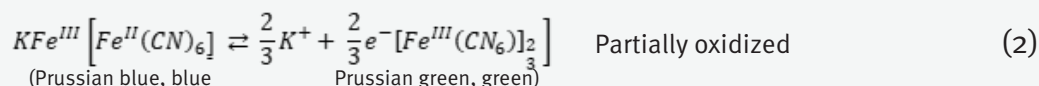
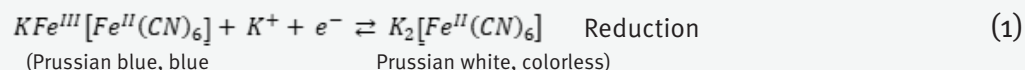


Figure 6(B) shows that the PB-Hap(36)/MWCNTs/PDDA/GE modified electrode presents a lower potential peak separation, (ΔE_p) of 70.8 mV (vs. Ag/AgCl), in comparison with the PB-MWCNTs/PDDA/GE modified electrode which reaches 124 mV (vs. Ag/AgCl). The lower value of ΔE_p indicates better reversibility and fast charge transfer in the modified film occurs. This can be attributed to the synergy related to the high capacity of adsorption of hydroxy-apatite nanoparticles⁶ and the good electrochemical conductivity of multiwalled carbon nanotubes¹⁷. After 25 cycles, there was no decrease in peaks current and no expressive changes on the cyclic voltammogram obtained for PB-Hap(36)/MWCNTs/PDDA/GE electrode, while for the PB-MWCNT/PDDA/GE electrode there was an appreciable decrease in current (approximately 50%), this indicates a good adsorption of PB at the surface of electrode¹⁸, and as results a stable transition between PW and PB.

According to the literature that follows the same procedure to electrodeposition and activation the PB-films, estimated the amount of deposited Prussian Blue about to $\sim 6 \text{ nmol cm}^2$, assuming a transfer of 4 electrons per unit cell¹⁹.

Evaluation of modified electrodes in the electrocatalytic reduction of hydrogen peroxide

The behavior of different modified electrodes toward H_2O_2 reduction was carried out by cyclic voltammetry. The voltametric response was analyzed in of 1mM in 0.1 M PBS in 1 mM H_2O_2 (pH = 7.4), at potential range from -1 to +0.5 V (vs. Ag/AgCl) with a scan rate of 50 mVs⁻¹. As can see of Figure 7 H_2O_2 presence: a) the Hap(36)/MWCNTs/PDDA/GE electrode presents a reduction current peak located at -0,42 V (vs. Ag/AgCl) with a slightly reduction current response, which indicates the electrocatalytic activity of H_2O_2 , meanwhile,

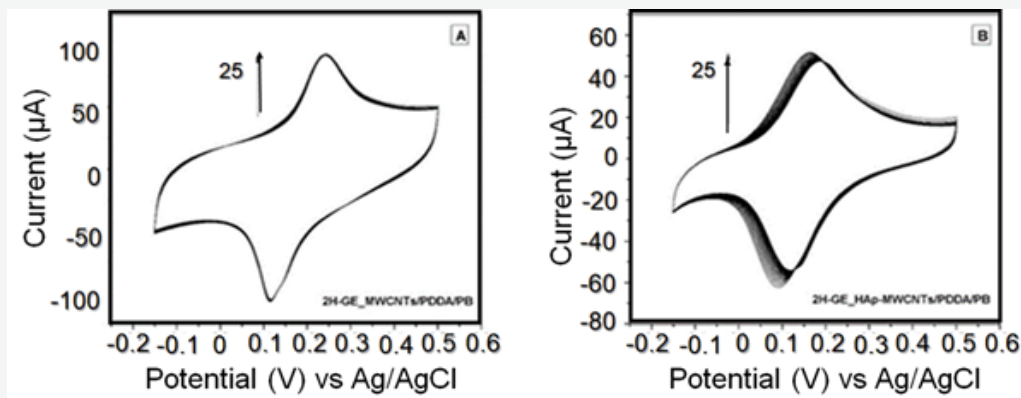
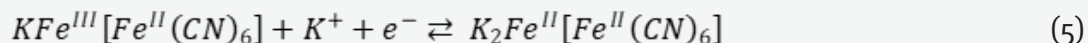


Figure 6. Cyclic voltammograms of PB films activated in 0.1 M HCl + 0.1 M KCl solution on: a) PB-MWCNTs/PDDA/GE and b) PB-Hap(36)/MWCNTs/PDDA/GE modified electrode

b) in MWCNTs/PDDA/GE electrode, the peak current had almost disappeared, because MWCNTs are not good electrocatalysts for reducing H_2O_2 ¹⁷, c) in PB-MWCNTs/PDDA/GE not remarkable peak and current response is observed; however, d) the voltammogram at PB-Hap(36)/MWCNTs/PDDA/GE electrode shows a reduction current peak located at -0.35V(vs.Ag/AgCl) with a reverse remarkable current response. In the presence of H_2O_2 at the electrode PB-Hap(36)/MWCNTs/PDDA/GE, the reversed current decreased and the forward current increased with the increase in the H_2O_2 concentration (Data not showed),



demonstrating that the electrocatalytic reduction of hydrogen H_2O_2 on this electrode. According to the results, it might be can say that hydroxyapatite nanoparticles could accelerate the catalytic rate at low potentials, due their zeolite structure which can allow diffusion of small molecules, such O_2 and H_2O_2 , into the lattices²⁰. Therefore, this indicate that modifications of 2H-GE electrode with PB-Hap(36)/MWCNTs/PDDA film show a synergistic effect and might be sensitive by cyclic voltammetry in presence of H_2O_2 . The electrocatalytic mechanism of Prussian blue for H_2O_2 reduction could be

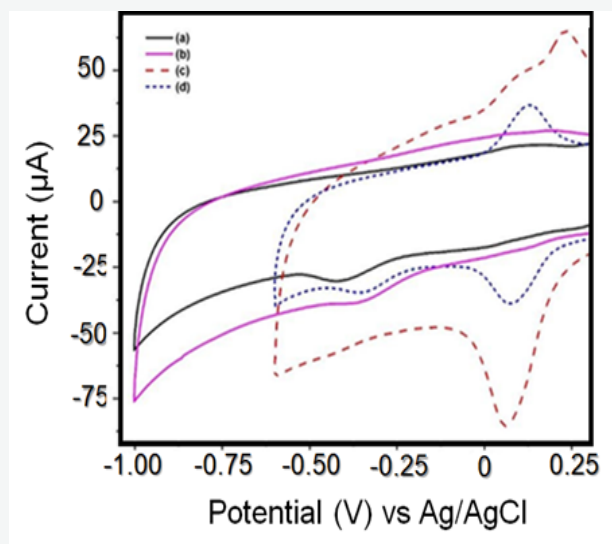


Figure 7. Cyclic Voltammograms of 2H-GE modified by a) Hap(36)/fMWCNTs/PDDA, b) fMWCNTs, c) PB-fMWCNTs and d) PB-Hap(36)/fMWCNT in 0.1 M PBS in 1mM H_2O_2 , at pH 7.4. Scan rate of 50 mVs^{-1} .

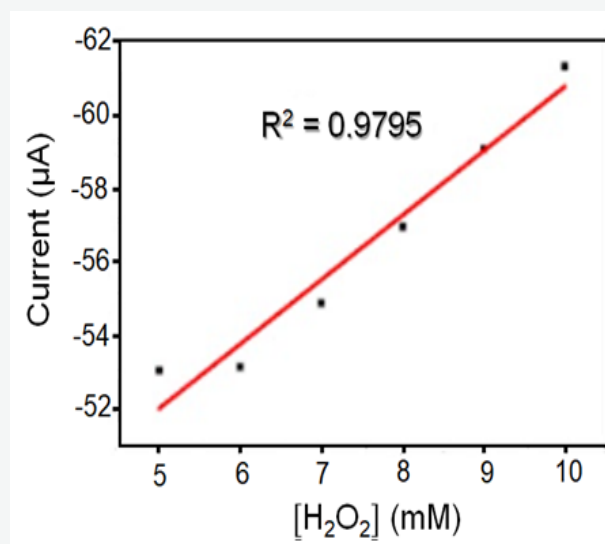


Figure 8. H_2O_2 calibration plot at PB-Hap(36)/MWCNTs/PDDA/GE. Detection potential +0.75 mV vs Ag/AgCl

expressed as follows:

A linear dependence on H_2O_2 concentration from 1 to 10 mM ($R_2 = 0.9795$), with a detection sensitivity of $119 \mu\text{A mM}^{-1}\text{cm}^{-2}$

shows Figure 8. Based on a signal-to-noise ratio of 3, a detection limit of 1.01 mM H_2O_2 was obtained, and based on a signal-to-noise ratio of 10, a quantification limit of 6.44 was obtained.

Conclusions

The modification of the Graphite electrode fabricated based on commercial 2H pencil graphite lead by carbon nanomaterials allows to obtain the sensor labeled as PB-Hap/MWCNTs/PDDA/GE, which showed a good electrocatalytic response to the reduction of hydrogen peroxide with a sensitivity of $119.77 \mu\text{A mM}^{-1}\text{cm}^{-2}$ in a range of concentration of 1 to 10 mM with a detection limit of 230 μM . According to preliminary results, it is a simple, robust and

reliable sensor for sensing H₂O₂ and has many potential applications in environmental, biomedical and industrial monitoring.

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