

# Tin Hexacyanoferrate Nanoparticles Based Electrochemical Sensor for Selective and High Sensitive Determination of H<sub>2</sub>O<sub>2</sub> in Acidic Media

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In this paper, a thin film of tin hexacyanoferrate (SnHCF) nanoparticles as a new Prussian blue analogue was deposited on the surface of carbon ceramic electrode (CCE) and used as a high sensitive hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) electrochemical sensor. The SnHCF film was prepared by electrochemical derivatization of metallic Sn doped in the CCE matrix prepared by sol-gel method. The morphology of the SnHCF-modified CCE was characterized by scanning electron microscopy (SEM). The proposed modified electrode exhibited sufficient mechanical and electrochemical stability and high sensitivity in compare with other electrochemical H<sub>2</sub>O<sub>2</sub> sensors. The sensor showed a good linear response for H<sub>2</sub>O<sub>2</sub> over a concentration range 4 – 50 μM with a detection limit of ca. 1.47 μM (S/N=3), and sensitivity of 0.588 μA M<sup>-1</sup> cm<sup>-2</sup>. The quality of experimental results demonstrates the feasibility of the sensor for practical sensing applications.

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**Keywords:** tin hexacyanoferrate, nanoparticles, carbon ceramic, hydrogen peroxide, amperometric sensor.

## 1. INTRODUCTION

Metal hexacyanoferrates (MHCFs) are important inorganic compounds that have been used for modification of electrode surfaces [1-2]. These compounds are able to form stable crystalline structure films showing reversible redox processes without dissolution in solution [3-4]. These valuable properties of MHCFs attracted much attention due to their important role in the various research areas such as electrochemical sensors, solid state batteries, ion selective electrodes, and electrophoresis detectors [5]. Preparation of modified electrodes based on the use of MHCFs was started after the pioneering work of Neff et al. [6], who reported the deposition of Prussian blue (PB) films on an

electrode surface for the first time. Afterwards the preparation and use of PB analogues for various applications have become a great research field in electrochemistry. Various kinds of transition metals such as Pd [7-8], V [9], Ru [10], Co [11], Ni [12], Zn [13-14] have been used to prepare MHCFs based modified electrodes by chemical or electrochemical methods. However, studies on rare earth MHCFs such as Tb [15], Nd [16], Dy [17], Sm [18] have attracted much attention in recent years.

Among the various kinds of the metals, p-block metals can be good candidates for substitution with these elements due to their special properties and uncounted applications. The first attempt in this field was carried out by the use of Ga [19], Bi [20] and Pb [21]. To our knowledge there is no report about the preparation and investigation of tin hexacyanoferrate (SnHCF) film modified electrode. Tin is silvery malleable poor metal that is not easily oxidized in air and resists against corrosion. Tin is mainly obtained from the mineral cassiterite where it appears as an oxide. The use of pure tin or tin alloyed with other metals is rapidly supplanting the use of previously common lead-containing alloys in order to eliminate the problems of toxicity caused by lead [22].

One of the main aims of this work is to evaluate the suitability of tin element for constructing of a new PB analogue on carbon ceramic composites (CCCs) as an electrode substrate which was rarely used for fabricating modified electrodes. The carbon ceramic electrodes (CCEs) are prepared by sol-gel method via mixing of graphite powders with sol-gel precursors, which result in a porous brittle composite matrix after gelation and drying [23]. CCEs were found to have a wide range of applications in electroanalysis, biosensing, electrocatalysis, gas diffusion electrodes and energy storage devices [24]. However, their applications are focused in the field of chemical sensors and biosensors [25]. We are interested in immobilizing of tin hexacyanoferrate (SnHCF) film on a sol-gel derived CCE surface. In order to obtain information about the electrocatalytic properties of SnHCF modified CCE (SnHCF|CCE), the electroreduction of hydrogen peroxide ( $H_2O_2$ ) was studied in details. The determination of hydrogen peroxide through electrochemical process is important in both biomedical and environmental studies. Electrochemical detection of hydrogen peroxide in the presence of oxygen is usually accomplished by the oxidation of hydrogen peroxide at high potential (0.6 V vs. Ag|AgCl). However, most biological samples contain a series of reductants, such as bilirubin, ascorbic acid, and uric acid, which are easily co-oxidized at the similar potential and produce an additional response current [26-27].

The use of MHCFs modified electrode for the electrocatalytic determination of  $H_2O_2$  was extensively reported in the literatures. A general overview on the electrochemistry and sensing aspects of Prussian blue based hydrogen peroxide sensors have been presented in the comprehensive review of Ricci and Palleschi [28]. Chemically modified electrodes (CMEs) provide a convenient method with simplicity, good selectivity and high sensitivity for the determination of  $H_2O_2$  at low electrode potential compared to the bare substrate due to an electrocatalytic process [29-30].

In the present work, preparation, surface morphology and electrochemistry of SnHCF-modified CCE as well as its catalytic effect toward the reduction of  $H_2O_2$  were studied in details. The sensitivity and selectivity of the proposed sensor were good, making it attractive for routine analysis of  $H_2O_2$  in real samples which is under investigation in our laboratory.

## 2. EXPERIMENTAL

### 2.1. Reagents and Materials

Methyltrimethoxysilane (MTMOS) was purchased from Merck and used without any further purification. Fine powdered graphite and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were obtained from Merck. The concentration of the  $\text{H}_2\text{O}_2$  solution was determined by volumetric titration using a standard solution of potassium permanganate. Tin powder (diameter 2-3  $\mu\text{m}$ ), potassium hexacyanoferrate ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ), and all other reagents were of analytical grade from Merck and Flucka. The acetate buffer solution (0.1 M) was prepared from  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ . All solutions were prepared with doubly distilled water.

### 2.2. Apparatus

The electrochemical experiments were carried out using an AUTOLAB PGSTAT-100 (potentiostat/galvanostat) equipped with an USB electrochemical interface and driven GPES 4.9 software package (Eco Chemie, The Netherlands) in conjunction with a three-electrode system and a personal computer for data storage and processing. A three-electrode cell system composed of a saturated calomel electrode (KCl 3 M: SCE) as the reference electrode, a platinum wire as an auxiliary electrode and SnHCF-modified CCE (geometric surface area of  $0.119 \text{ cm}^2$ ) as a working electrode (prepared as follows) were employed for the electrochemical studies.

### 2.3. Preparation of bare and SnHCF-modified CCE

The Sn modified carbon ceramic modified electrode was prepared according to the procedure described by Lev and co-workers [31]. The fabrication procedure were as follows: 0.6 mL MTMOS, 0.9 mL methanol and 0.6 mL HCl 0.1 M were mixed and stirred for 20 min until a homogeneous gel solution appeared, then 0.3 g graphite powder and 0.06 tin powder were added and the resultant mixture was shaken for additional 5 min. Then the mixture was packed into a Teflon tube (7 mm length and 3.9 mm inner diameter) and dried for 24 h at room temperature. Then the electrode was polished with polishing paper and rinsed with distilled water. The electric contact was made with a copper wire through the back of the electrode. The Sn modified carbon ceramic electrode was immersed in 30 mM aqueous solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  + 0.5 M  $\text{KNO}_3$  and was swept for 70 cycles over the potential range -0.3 - 1.25 V. After washing the electrode with distilled water, it was dried at room temperature over a night and used for electrochemical studies.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical Behavior of the SnHCF-modified CCE

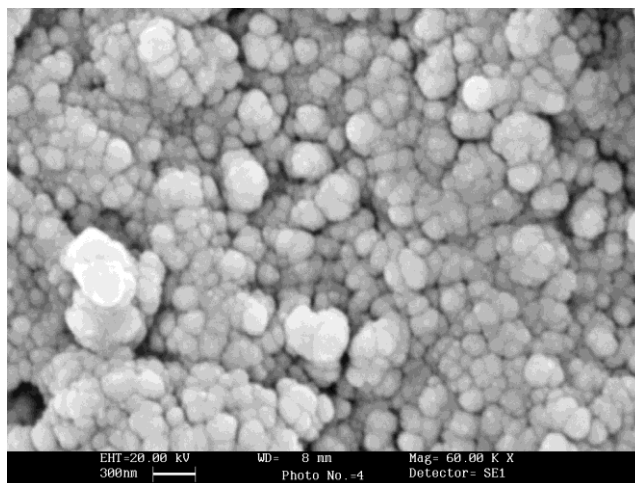
#### 3.1.1. General aspects

Electrochemical formation of SnHCF film was carried out by the repetitive cycling of the Sn-doped CCE in solution of 30 mM hexacyanoferrate (HCF) and 0.5 M  $\text{KNO}_3$ , between -0.3 and 1.25 V

/ SCE. Two redox couples are observed and the peak currents increased by the repetitive potential scanning, indicating that the electro-formation of SnHCF film is taking place. During the anodic scan metallic Sn at the surface of CCE is probably oxidized to Sn(II) and /or Sn(IV), that can react instantaneously with ferrocyanide or ferricyanide ions and form SnHCF solid film.

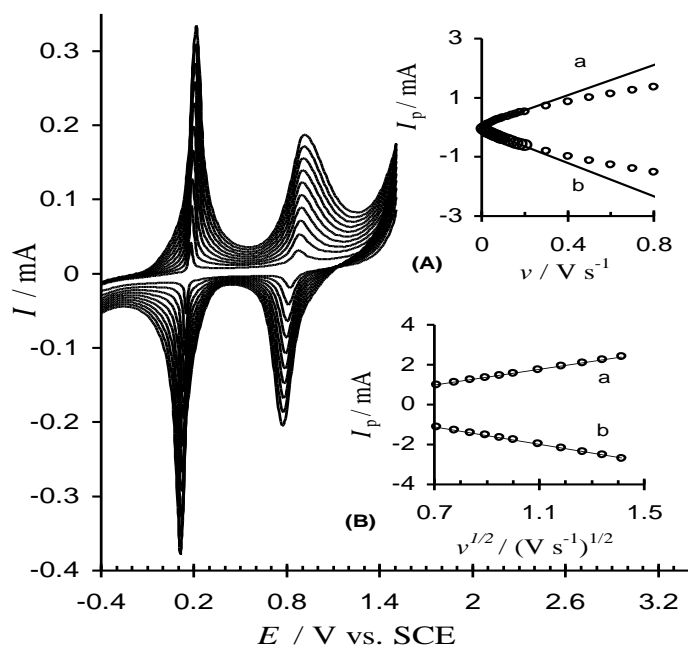
In order to have an intuitive understand about the conformation of SnHCF particles, the SEM image of the modified carbon ceramic electrode was provided (Fig. 1). As can be seen the electrode surface, covered with clusters which formed by joining of spherical SnHCF particles with average size of ca. 100 nm. Also, the SEM image of the modified electrode displays a three-dimensional and porous structure. This shows that solid SnHCF materials are entrapped in the jagged network of the carbon ceramic electrode. These structures showed sufficient suitability and catalytic activity.

The electrochemical behavior of SnHCF has been thoroughly investigated in 0.5 M  $\text{KNO}_3$  solution. It showed two well defined redox couples with the formal potentials of 0.14 V and 0.84 vs. SCE at a scan rate of  $20 \text{ mV s}^{-1}$  for the first and second redox couples (figure not shown). Peak-to-peak separations were 80 and 60 mV for the first and second couples confirming reversibility of the redox systems at low scan rates. These peaks were not affected by stirring of the solution, which is another proof to conclude that the materials were well adsorbed on the surface of the CCE. The ratios of  $I_{pa}/I_{pc}$  were close to unit at different scan rates as expected for adsorbed species.



**Figure 1.** A typical SEM image of a carbon ceramic electrode modified with SnHCF nanoparticles.

The effect of different scan rates on the voltammetric behavior of SnHCF modified CCE was investigated (Fig. 2). The peak currents increase with potential scan rate. The linear dependence of anodic and cathodic peak currents are proportional to scan rates up to  $200 \text{ mV s}^{-1}$  for the both redox couples (inset A to Fig. 2), which is typical for adsorbed species. This behavior illustrates that the materials are well cramped on the CCE surface. At higher scan rates the peak currents deviate from the linearity and are proportional to the square root of scan rate (inset B to Fig. 2), where, overall electrode process of the SnHCF is dominated by the diffusion of single-charged alkali metal cations through the solid film.



**Figure 2.** Cyclic voltammograms of the SnHCF|CCE at different scan rates (from inner to outer curve): 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, and 200  $\text{mV s}^{-1}$ . Supporting electrolyte: acetate buffer solution (0.1 M) pH = 4 containing 0.5 M  $\text{KNO}_3$ . Insets: Plots of peak currents vs. scan rate (A) and the square root of scan rate (B) for the first redox couple.

### 3.1.2. Effect of solution pH

The effect of pH on the voltammetric behavior of SnHCF|CCE over the pH range 2-8 was investigated by cyclic voltammetry in 0.1 M phosphate buffer solution (figure not shown). The peak current of the SnHCF modified electrode decreases by increase in the pH value, and completely disappears at pH 10, while the anodic and cathodic peak potentials remain constant. Although stable and reproducible peaks were obtained at a pH range 1-6, but well-behaved voltammograms were recorded at pH range 3 - 4. Therefore, the pH=4 was chosen as the optimum value.

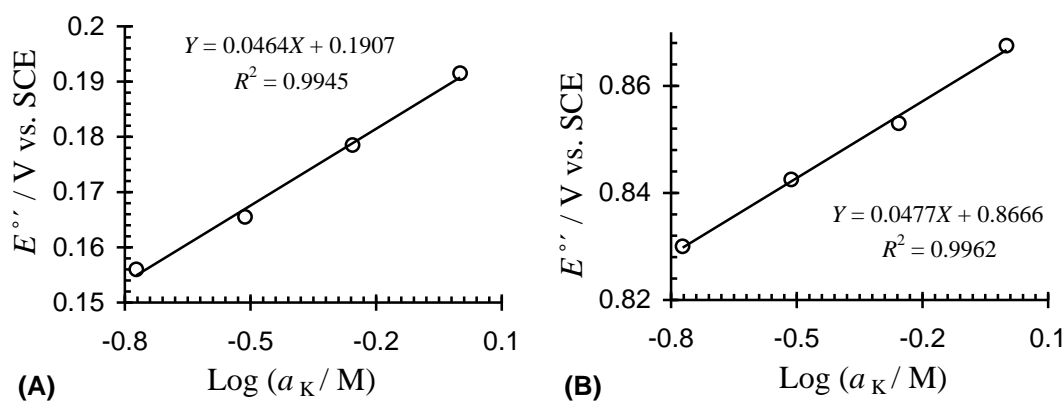
It seems that both  $\text{H}^+$  and  $\text{K}^+$  ions can be exchanged between the solution and SnHCF film. In acidic solutions,  $\text{H}^+$  overcomes  $\text{K}^+$  and makes less reversibility on the voltammetric behavior of the modified electrode. In optimum pH range (3-4),  $\text{K}^+$  overcomes  $\text{H}^+$  in this competition and well-behaved voltammograms are obtained. In alkaline solutions (pH>10) film degradation occurs due to complex interactions between  $\text{OH}^-$  and metallic cations in the film ( $\text{Sn}^{\text{II/IV}}$ ,  $\text{Fe}^{\text{II/III}}$ ).

### 3.1.3. Effect of various supporting electrolytes

The electrochemical behavior of MHCFs modified electrodes are changed in the presence of various supporting electrolytes. When the potential of a MHCF modified electrode is scanned, an

electron exchange reaction occurs, and in a parallel phenomenon, cations of the supporting electrolyte enter into or get out of the film to keep electroneutrality of the film [32-33].

In this study various alkali supporting electrolytes solutions including  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{CsNO}_3$  were separately used as supporting electrolytes and cyclic voltammogram of the SnHCF|CCE was recorded in each solution (0.5 M) at scan rate of  $100 \text{ mV s}^{-1}$ . The results showed that two redox couples appeared in all examined supporting electrolytes. Although all alkali cations could enter into the cavities of SnHCF, but the potential of redox couples shifted to positive or negative potentials depending on the kind and nature of the corresponding cation. Among various alkali cations  $\text{K}^+$  could easily penetrate into the crystalline lattice of SnHCF and exhibits higher peak current than the others. So  $\text{KNO}_3$  is selected as a supporting electrolyte for this present study.



**Figure 3.** Dependence of formal potentials of SnHCF film on the logarithms of  $\text{K}^+$  activities obtained for the first (A) and second redox couple (B) derived from voltammetric data.

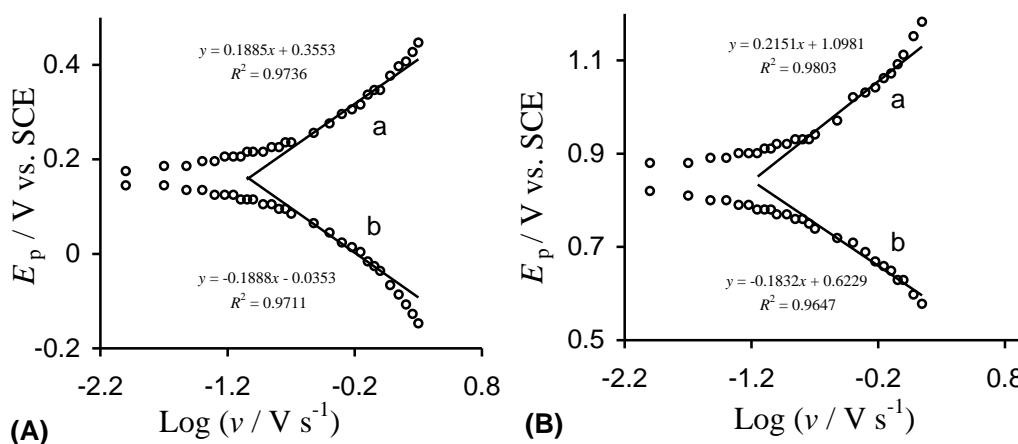
The affect of various concentrations of  $\text{KNO}_3$  as supporting electrolyte on the formal potential of the modified electrode was investigated. Fig. 3A indicates that the formal potential of the first redox couple shifts to positive potentials by increasing in  $\text{KNO}_3$  concentration and a liner relationship was found between the formal potential and  $\text{Log}(a_{\text{K}^+})$  with a slope of 46.40 mV/decade, which is close to the theoretical value of 59.16 mV/decade for one electron transfer (Nernst equation), indicating this fact that the electrochemical reaction of the first couple occurs with the transfer of one electron and a counter cation. Similar behavior was observed for the second redox couple with the slope 47.70 mV/decade (Fig. 3B), showing a Nernsian behavior of the second couple. So it is observed that the electrochemical reaction occurred through transportation of one electron and a counter ion for the second couple as well as for the first one.

#### 3.1.4. Charge transfer rate through the film

Despite the fact that for an ideal limited surface redox process the peak separation ( $\Delta E$ ) of the redox couples must be zero [34], the peak separation of SnHCF modified electrode is about 127 mV,

indicating a divergence from the ideal redox surface process, due to certain kinetic limitations that take place during reduction process. This deviation may be attributed to interactions between doping cations and crystal lattice of the film [35]. At higher scan rates divergence from ideal peak separation ( $\Delta E$ ) increased (up to 470 mV), indicating that there is a limitation in charge transfer kinetics.

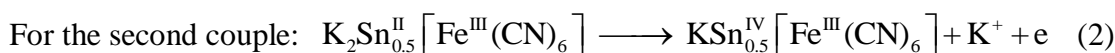
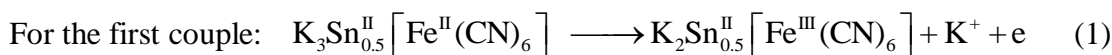
According to Laviron theory [36], variations in the peak potential values as a function of logarithms of scan rates (Fig. 4 A & B), the electron transfer rate constant ( $k_s$ ) for the first and the second couples are 0.627 and 0.86. The transfer coefficient ( $\alpha$ ) for the first and the second couples were found to be 0.68 and 0.73, respectively.



**Figure 4.** Plots of  $E_p$  vs.  $\text{Log} v$  derived from cyclic voltammograms of SnHCF|CCE for the first (A) and second (B) redox couples in presence of 0.5 M  $\text{KNO}_3$  as supporting electrolyte (pH 4). Lines (a) and (b) were drawn for the anodic and cathodic peaks, respectively.

### 3.1.5. Electrochemical process of the peaks

The electrochemical process of PB modified electrodes can be explained by these series:  $\text{MF}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] / \text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  and  $\text{M}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6] / \text{MFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ . Kulesza and co-workers claimed that there are two redox peaks in CoHCF modified electrode [37-38] which can be explained by below series:  $\text{MCo}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6 / \text{M}_2\text{Co}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$  and  $\text{Co}^{\text{II}}_{1.5}\text{Fe}^{\text{III}}(\text{CN})_6 / \text{MCo}_{1.5}\text{Fe}^{\text{II}}(\text{CN})_6$  whereas M is an alkali cation that is necessary for electroneutrality of the film. According to experimental observations such as peak potential, electrocatalytic properties and shape of the peak, on the other hand according to Nernstian behavior of the electrode in different concentration of  $\text{K}^+$ , it can be concluded that transportation of one electron and one counter ion are carried out. The electrochemical behavior of the SnHCF is similar to PB, so the redox processes can be written as follows:



### 3.2. Electrocatalytic reduction of $H_2O_2$ on SnHCF modified electrode

It is well known that most of the MHCF have excellent electrocatalytic activity; therefore they are important in analytical chemistry. In order to show electrocatalytic activity of SnHCF modified electrode, hydrogen peroxide has been selected as a model compound. Cyclic voltammetry of bare and SnHCF modified electrode carbon ceramic electrode has been studied in the absence and presence of 5 mM  $H_2O_2$  in 0.1 M acetate buffer containing 0.5 M  $KNO_3$  (pH 4) (figure not shown). As a result, that with the addition of 5 mM  $H_2O_2$ , the cathodic peak current increased and the anodic peak current decreased, indicating an electrocatalytic reduction of  $H_2O_2$  in potential rang examined from 0.5 to -0.3 V. On the other hand no specific increase in current was observed on the bare CCE in the presence of 5 mM  $H_2O_2$ .

For better performance of the SnHCF modified electrode as a sensor, the effect of pH on the electrode response to 3 mM  $H_2O_2$  was investigated by CV in acetate buffer solution with different pH values changing from 2 to 7 (not shown). By increasing of the pH values from 2 to 4 the catalytic current increased and reached to a maximum in pH 4, and the hydrogen peroxide reduction peak potential slightly shifted to positive value. The catalytic current was constant in pH range 4-5 and finally, by increasing the pH from 5 to 7 the peak current started to decrease gradually. As the most repetitive and the highest catalytic activity of SnHCF were observed in pH 4, it is chosen as an optimum pH for hydrogen peroxide determination.

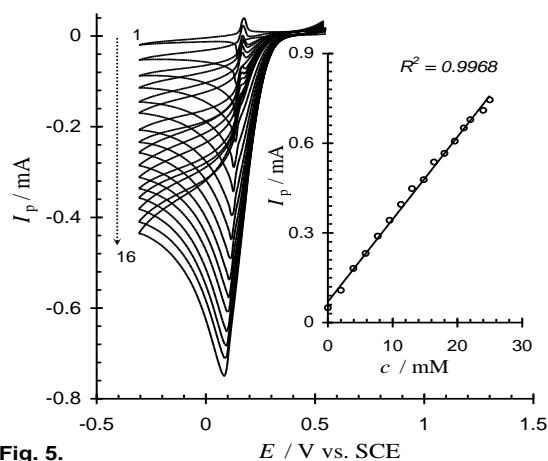


Fig. 5.

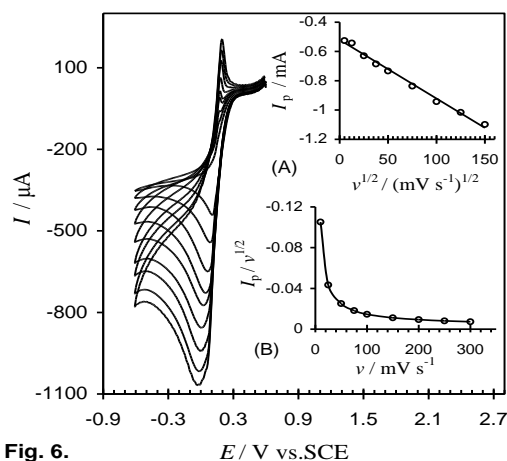


Fig. 6.

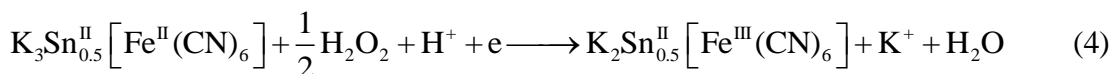
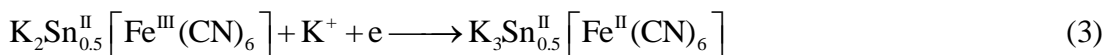
**Figure 5.** Cyclic voltammograms of SnHCF|CCE in presence of increasing concentration  $H_2O_2$  at a scan rate of  $20 \text{ mV s}^{-1}$ . Supporting electrolyte was as in Fig. 3. Inset: Calibration graph obtained from the data of main panel.

**Figure 6.** Cyclic voltammograms of SnHCF|CCE in presence of 36 mM  $H_2O_2$  at various potential scan rates of 10, 25, 50, 75, 100, 150, 200, 250, and 300  $\text{mV s}^{-1}$ . Insets: (A) and (B) represent  $I_p$  vs.  $v^{1/2}$  and  $I_p/v^{1/2}$  vs.  $v$ , respectively.

The dependence of cathodic peak current on the hydrogen peroxide concentration was investigated by CV. According to Fig. 5 by adding increasing concentration of hydrogen peroxide, the relationship between  $I_{pc}$  and  $c$  was found to be linear over the concentration range 2 - 30 mM.



In order to get information about the catalytic reaction mechanism, cyclic voltammograms of the modified electrode were recorded in the presence of 36 mM H<sub>2</sub>O<sub>2</sub> at various scan rates (Fig. 6). Inset A to this figure specifies a linear relationship between cathodic current and square root of scan rate, indicating a mass transfer controlled reaction; furthermore the current function,  $I_p/v^{1/2}$  vs.  $v$  plot, (inset B to Fig. 6) indicates that exchange process between hydrogen peroxide and the redox site of SnHCF modified electrode is controlled by an EC' mechanism as follows:



Tofel plots which are resulted from polarization curves recorded at low scan rates specify the dependence of current on applied potential. The rising parts of these curves obtained for various concentrations of hydrogen peroxide are used to derive Tofel plots (figure not shown), which revealed an average slope of 126 mV/decade indicating one electron takes part in the rate determining step assuming  $\alpha = 0.49$ .

More information about the electrocatalytic reaction was obtained from chronoamperometric data. Fig. 7A shows the current-time plots recorded by adjusting the working electrode potential at -0.2 V in the absence and presence of hydrogen peroxide in the range 6 – 30 mM. The variation of diffusion controlled current is described by Cottrell equation [34]:

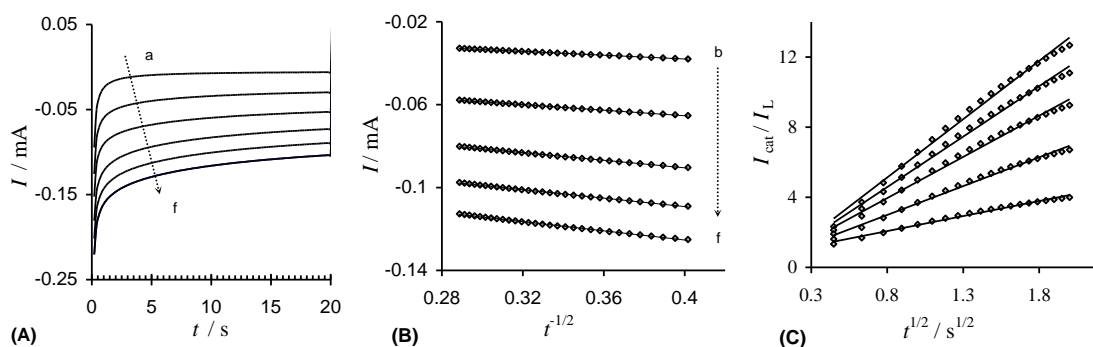
$$I = nFAD^{1/2} c_o (\pi t)^{-1/2}, \quad (5)$$

where  $D$  and  $c_o$  are diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) and bulk concentration ( $\text{mol cm}^{-3}$ ) of hydrogen peroxide, respectively.  $A$  is the electrode surface area ( $0.119 \text{ cm}^2$ ),  $I$  is a current controlled by diffusion of hydrogen peroxide from the bulk of the solution to the electrode /solution interface. The plot of  $I$  vs.  $t^{-1/2}$  at various concentration of hydrogen peroxide was linear (Fig. 7B), and the slopes of resulting straight lines are then used to estimate the diffusion coefficient. The average value of  $D$  was calculated equal to  $1.15 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

Chronoamperometry can also be used for the evaluation of the catalytic rate constant ( $k_{\text{cat}}$ ). At intermediate time, when the current is dominated by the rate of the electrocatalyzed reduction of hydrogen peroxide, the catalytic current ( $I_{\text{cat}}$ ) can be written as follows [40]:

$$I_{\text{cat}} / I_L = \pi^{1/2} (k_{\text{cat}} c_o t)^{1/2}, \quad (6)$$

where  $I_L$  is the current of the SnHCF-modified CCE in the absence of hydrogen peroxide, and  $I_{\text{cat}}$  is the catalytic current due to addition of hydrogen peroxide.  $k_{\text{cat}}$ ,  $c_o$  and  $t$  are the catalytic reaction rate constant ( $\text{M}^{-1} \text{s}^{-1}$ ), the bulk concentration (M) of hydrogen peroxide and time elapsed (s), respectively. In a small elapsed time, the values of  $I_{\text{cat}}/I_L$  are linearly changed with  $t^{1/2}$  (Fig. 7C) and from the slope, the value of  $k_{\text{cat}}$  for a given concentration of hydrogen peroxide can be calculated. The value of  $k_{\text{cat}}$  for the reaction between SnHCF and H<sub>2</sub>O<sub>2</sub> was found to be  $6.16 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ .



**Figure 7.** (A) Chronoamperograms obtained from SnHCF/CCE in the absence (a) and in the presence of (b – f): 0.0, 0.0059, 0.011, 0.016, 0.0216, 0.028 M  $\text{H}_2\text{O}_2$ , potential was adjusted at  $-0.2$  V / SCE. The plots of  $I_p$  vs.  $t^{-1/2}$  (B), and  $I_{\text{cat}}/I_L$  vs.  $t^{1/2}$  (C) for various  $\text{H}_2\text{O}_2$  concentrations obtained from the chronoamperograms.

### 3.3. Amperometric determination of hydrogen peroxide at SnHCF modified CCE

The current-time response of SnHCF-modified CCE in the hydrodynamic conditions was recorded to evaluate the limit of detection and the calibration curve for hydrogen peroxide detection. The sensor response at an applied potential of  $-0.1$  V vs. SCE toward increasing concentration of hydrogen peroxide was recorded in  $0.1$  M acetate buffer solution containing  $0.5$  M  $\text{KNO}_3$ . Fig. 8 specifies the sensor response for successive addition of hydrogen peroxide from stock solution of  $4$   $\mu\text{M}$  by  $0.1$  mL increments to electrochemical cell containing  $10$  mL acetate buffer solution. The resulted calibration curve is linear in the range  $4 - 50$   $\mu\text{M}$  with the slope of  $0.5884$   $\mu\text{A mM}^{-1}$  and correlation coefficient is  $0.9952$ , the limit of detection was calculated equal to  $1.47$   $\mu\text{M}$ .

### 3.4. The selectivity and stability study of SnHCF/CCE

The voltammetric stability of SnHCF/CCE was evaluated by repetitive potential sweep at the scan rate of  $50$   $\text{mV s}^{-1}$  in the acetate buffer solution of pH 4 containing  $0.5$  M  $\text{KNO}_3$ . The result showed that the peak current remained ca. 90 % of the initial one after 150 repetitive scans, confirming a satisfied stability of SnHCF. Electrodes stored in the air at room temperature for several months showing only a few percent losses in surface material.

### 3.5. Effect of electroactive interference

Fig. 9 shows the effect of  $15$   $\mu\text{M}$  ascorbic acid (AA), acetaminophen (ACT) and Dopamine (DA) on the sensor response to  $15$   $\mu\text{M}$   $\text{H}_2\text{O}_2$ . At an applied potential of  $-0.1$  V, these interferents have no influence on the response of the sensor and the sensor response for  $15$   $\mu\text{M}$   $\text{H}_2\text{O}_2$  is not changed by these interferents. These results indicate that the response of proposed sensor is really free from these biological compounds due to the low applied potential.

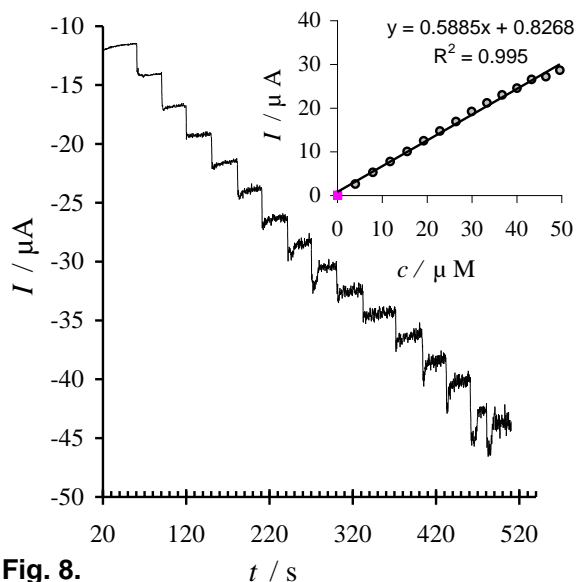


Fig. 8.

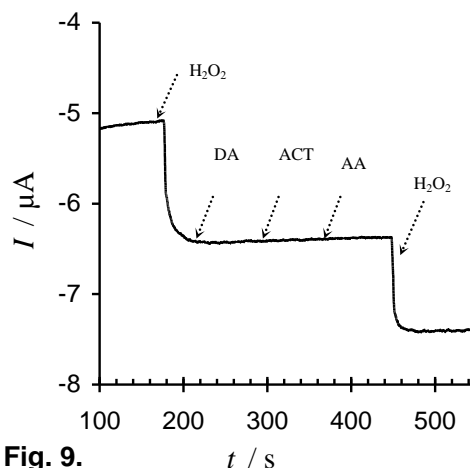


Fig. 9.

**Figure 8.** Amperometric response of SnHCF|CCE for the successive addition of  $\text{H}_2\text{O}_2$ , applied potential was  $-0.1$  V vs. SCE. Other conditions are as in Fig. 6. Inset: The calibration graph obtained from data of main panel.

**Figure 9.** Amperometric response of SnHCF|CCE for successive addition of  $15 \mu\text{M}$   $\text{H}_2\text{O}_2$ , DA, ACT, AA,  $\text{H}_2\text{O}_2$ . Applied potential was  $-0.1$  V vs. SCE, other conditions is as in Fig. 6.

#### 4. CONCLUSION

In the present study a new SnHCF-modified electrode was successfully fabricated by electrochemical method. The morphological and electrochemical characteristics of SnHCF modified CCE was studied thoroughly by various methods. SnHCF modified CCE shows two well defined redox couples with the formal potential of  $0.14$  V for the first redox couple and  $0.84$  V for the second one. More ever the modified electrode shows an excellent electrocatalytic behavior toward hydrogen peroxide. The calibration plot for amperometric determination of hydrogen peroxide was linear in the range  $4$ - $50 \mu\text{M}$  with correlation coefficient  $0.992$  and the detection limit  $1.47 \mu\text{M}$ . The linear response range as well as detection limit of the proposed sensor are better than that reported on glassy carbon electrode (GCE) modified with multiwalled carbon nanotubes, a gold-chitosan colloid, Prussian blue composite [40].

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