

An Efficient Sensor for Determination of Concentrated Hydrogen Peroxide Based on Nickel Oxide Modified Carbon Paste Electrode

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A new sensor for the analytical determination of hydrogen peroxide is proposed. This sensor was constructed by immobilizing nickel oxide film on the surface of carbon paste electrode, which was performed by derivatization of nickel hexacyanoferrate (NiHCF) in alkaline solution. Cyclic voltammetry experiments yielded evidence that nickel oxide facilitates hydrogen peroxide oxidation, showing excellent catalytic activity. Electrocatalytic oxidation of hydrogen peroxide occurs at a potential less positive than unmodified carbon paste electrode. This modified electrode has many advantages such as simple preparation procedure, good reproducibility and catalytic activity toward the hydrogen peroxide oxidation. Such characteristics were explored for the specific determination of hydrogen peroxide in cosmetics product sample, giving results in excellent agreement with those obtained by standard method.

Keywords: Nickel hexacyanoferrate, modified electrode, hydrogen peroxide, nickel oxide, electrocatalytic oxidation

1. INTRODUCTION

Hydrogen peroxide has wide applications in many fields. Its concentrations typically range from micromolar to tens of millimolar [1]. Most reports have been focused on determination of low concentrations of hydrogen peroxide, and upper limits of detection achieved with these methods are of a few tens of millimolars (10-20 mM) [2-7]. The rapid determination of concentrated hydrogen peroxide, which is demanding for control of some industrial processes, is much less successful [1].

Also, all the electrochemical methods reported for determination of concentrated hydrogen peroxide are based on platinum-based electrodes [1, 8].

Nickel and nickel-based chemically modified electrodes such as nickel-hexacyanoferrates, hydroxides and complex modified nickel-electrodes have been utilized for a variety of electrooxidation [9-13] and reduction [14] purposes. Electrochemical studies using nickel-based electrodes have established that various electroreactant species can be determined with a high rate of heterogeneous electron transfer, good sensitivity, and reproducibility. In these studies, the presence of various Ni-based surface species has been detected, and extensive analysis of the composition of the nickel oxide films on the electrodes has been performed [15-17]. The anodic behavior of nickel in alkaline media has also been studied [18, 19] and formations of nickel oxide as well as nickel oxy-hydroxide and various phases of the species have been reported. The formation of nickel oxide has been achieved in principle in four different ways: potentiostatic and galvanostatic anodic sweeps, cathodic deposition of a pH-controlled salt of nickel in alkaline solution, and the electrode processing of a pre-crystallized nickel salt in alkaline solutions [10, 12] and derivatization of NiHCF [20] in alkaline solutions. In all of these studies, the layer consisting of NiOOH / Ni(OH)₂ was detected.

In our previous works, we used the advantageous features of polymer modification, dispersion of metallic particles into organic polymers and carbon paste technology. Nickel ions were incorporated into the polymeric matrix by immersion of the polymeric modified electrodes in a nickel chloride solution. These electrodes were used for electrocatalytic oxidation of various carbohydrates [21, 22], methanol [23-26] and ethanol [27]. Also, we used of other modified electrode for electrooxidation and determination of hydrogen peroxide [28].

In this communication, we report the results of the catalysis of nickel oxide, obtained through surface derivatization of NiHCF on a carbon paste electrode (CPE), on electrooxidation of hydrogen peroxide known to be not easily oxidizable. Comparison of the collected on the above with reported information is made wherever possible.

2. EXPERIMENTAL PART

2.1. Reagents and materials

The solvent used in this work was twice distilled water. The Nickel chloride, Potassium hexacyanoferrate (III) and total chemical reagents from Fluka were used as received. Sodium hydroxide and hydrogen peroxide used in this work were analytical grade of Fluka origin and used without further purification. High viscosity paraffin (density = 0.88 g cm⁻³) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter = 0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

2.2. Preparation of working electrode

A mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass

tube (internal radius = 1.7 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

The precursor modification of the carbon paste electrode with NiHCF was achieved by cycling the electrode between 0 and 1 V at 50 mV s^{-1} for 6 min in a clear solution of 0.01 M NiCl_2 in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.1 M KCl. Then the electrode with NiHCF film is cycled between 0 and 0.65 V in 0.1 M NaOH 9 times. On cycling the NiHCF electrode in alkaline solution $\text{Ni}(\text{OH})_2 \rightleftharpoons \text{NiOOH}$ film is formed which was identified by its characteristic cyclic voltammetric peak potential data [29]. CPE derivatized thus was found to be extremely stable for two weeks and it lasted for several hundreds of cycles.

2.3. Instrumentation

The electrochemical experiments were carried out using a Metrohm potentiostat/galvanostat model 764 VA trace analyzer instrument. Voltammetry was conducted using a three-electrode cell. A CPE, a platinum electrode and $\text{Ag}|\text{AgCl}|\text{KCl}$ (3M) were used as working electrode, counter electrode and reference electrode respectively.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical behavior of the NiHCF – modified carbon paste electrode

Fig. 1 shows the typical cyclic voltammograms describing the deposition process of NiHCF.

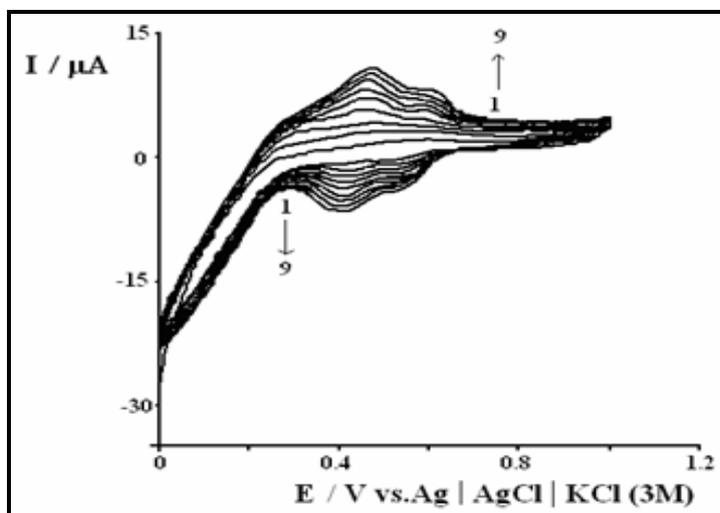


Figure 1. Repetitive cyclic voltammograms of a carbon paste electrode modified with a NiHCF film synthesized from 0.01 M Ni^{2+} and 0.01 M $\text{Fe}(\text{CN})_6^{3-}$ in 0.1 M KCl solution, $v = 50 \text{ mV s}^{-1}$.

The formation and growth of NiHCF film on a carbon paste electrode is verified by two pair of redox peaks at about 0.44 and 0.58 V, which grows with potential-scan cycling repetitively. The two redox peaks/waves can be ascribed to the $\text{Fe}(\text{CN})_6^{3-/4-}$ transition in the NiHCF [30] which can be described as: $\text{Ni}_{1.5}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6] / \text{KNi}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{KNi}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6] / \text{K}_2\text{Ni}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$.

Fig. 2 presents comparative cyclic voltammograms for the NiHCF-modified CPE in three kinds of solutions with different supporting electrolytes. It is well known that metal hexacyanoferrate films are permeable membranes for cations [31-34]. These alkali metal cations can react with the inorganic film by incorporation into their net structures. For the NiHCF-modified CPE, NiHCF supported on carbon paste acts as a zeolite in which hydrated cations may enter into the cage. Potassium cation can be expected to fit within the zeolite cage more easily than other cations. The cyclic voltammograms of the NiHCF film on carbon paste electrodes and then transferred to aqueous solutions with the same cations and different anions are compared. The cyclic voltammograms almost overlap and the peak heights are close (not shown). The anion dependence is not obvious for the electrode modified with the NiHCF redox couple.

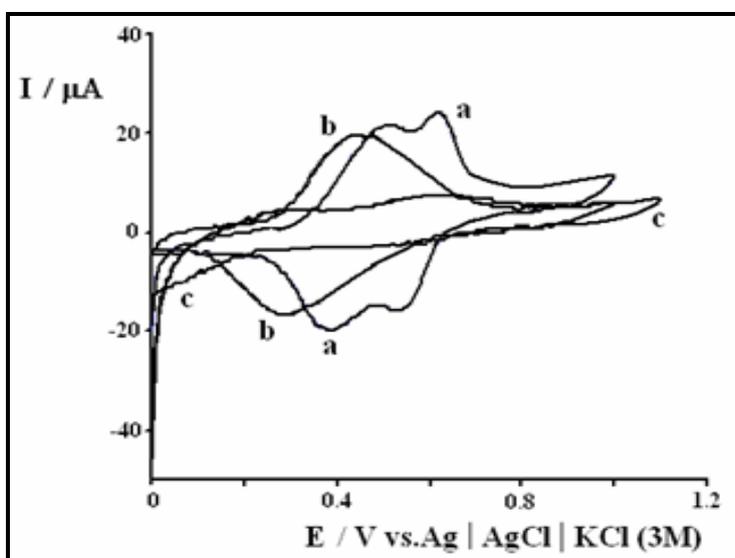


Figure 2. Cyclic voltammograms of a NiHCF film synthesized from 0.1 M aqueous KCl solution on the carbon paste electrode, which was then transferred to 0.1 M aqueous solution of (a) KCl, (b) NaCl and (c) HCl, $v = 50 \text{ mV s}^{-1}$.

The cyclic voltammograms of the NiHCF-based modified carbon paste electrode are shown in Fig. 3 in a solution containing 0.1 M KCl as supporting electrolyte in the absence of any electroactive material in solution. A pair of well-defined redox peaks provides evidence for prolonged surface attachment. As shown in Fig. 3 (B and C), at lower scan rates ($50\text{-}300 \text{ mV s}^{-1}$), currents of anodic and cathodic peaks are linearly proportional to the scan rate (v), which is expected for surface confined redox processes; however, at higher scan rates ($v > 300 \text{ mV s}^{-1}$), the plot of peak current versus $v^{1/2}$

indicates diffusion-controlled processes, which may be related to the relatively slow diffusion of potassium ions into the electrode wetting.

Also, we have observed two pair peaks at lower scan rate ($< 100 \text{ mV s}^{-1}$) but one pair redox peak at higher scan rate. The peak-to-peak separation increase with scan rate and potential separation between anodic and cathodic peaks is non-zero ($\Delta E_p = 0$ expected for a reversible surface redox process) which might arise due to non-ideal behavior.

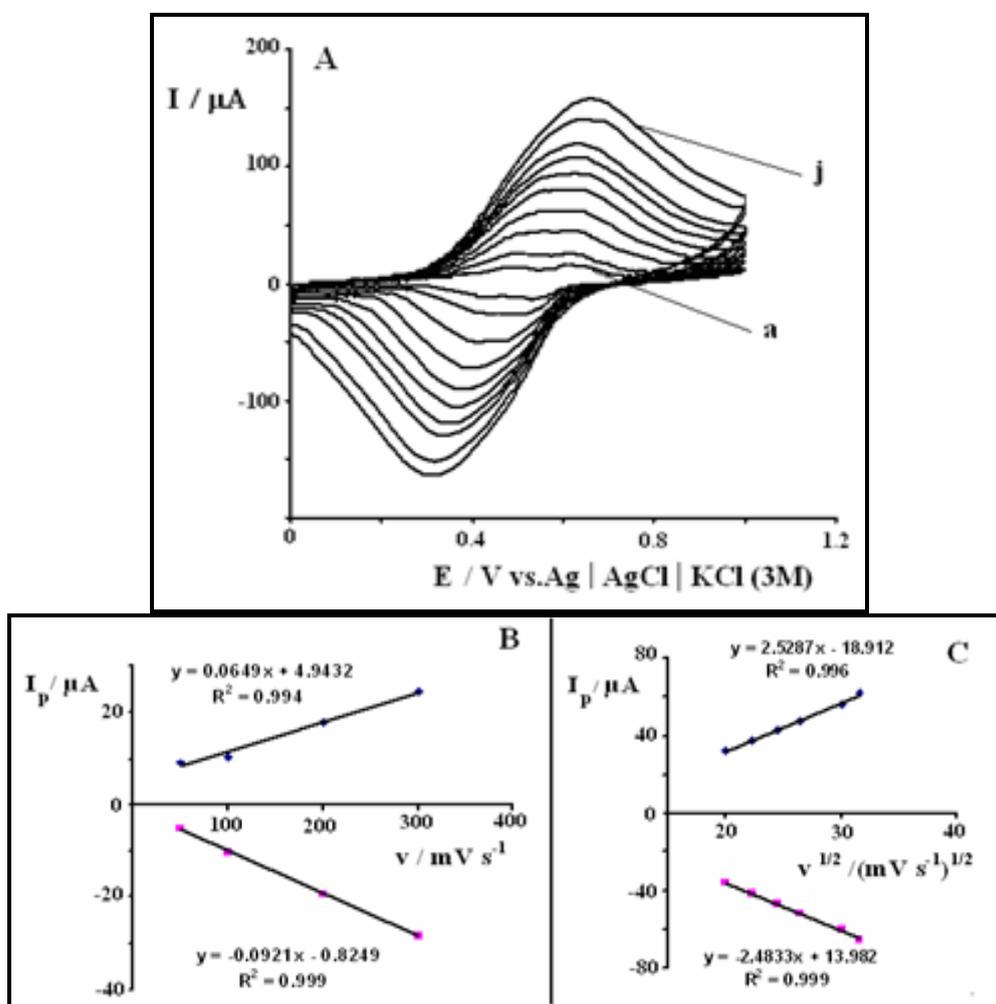
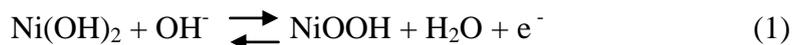


Figure 3. Scan rate dependence of the peak current for carbon paste electrode modified with NiHCF, scan rates: (a) 50, (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, (g) 600, (h) 700, (i) 900 and (j) 1000 mV s^{-1} in 0.1 M KCl solution (A), Plot of I_p vs. v (B) and Plot of I_p vs. $v^{1/2}$ (C).

3.2. Electrochemical behavior of the nickel oxide film

Fig. 4 shows the response of the NiHCF modified electrode in 0.1 M NaOH at 50 mV s^{-1} . The electrode becomes derivatised to the oxide species quantitatively. After about 9 potential cycling the redox behavior of CPE modified with nickel oxide becomes very stable and no change in peak current

is observed. The anodic and cathodic peaks occur at 0.43 and 0.50 V respectively. The redox reaction of this derivatised oxide electrode is presented as follows:



The current grows with the number of potential scans, indicating the progressive enrichment of the electroactive species Ni(OH)_2 and NiOOH in the surface. The change of anodic peak potential with increasing the number cycles was because of altering in phase composition of nickel oxides. At potentials positive of 0.60 V, there is a sharp rise in anodic current due to oxygen evolution.

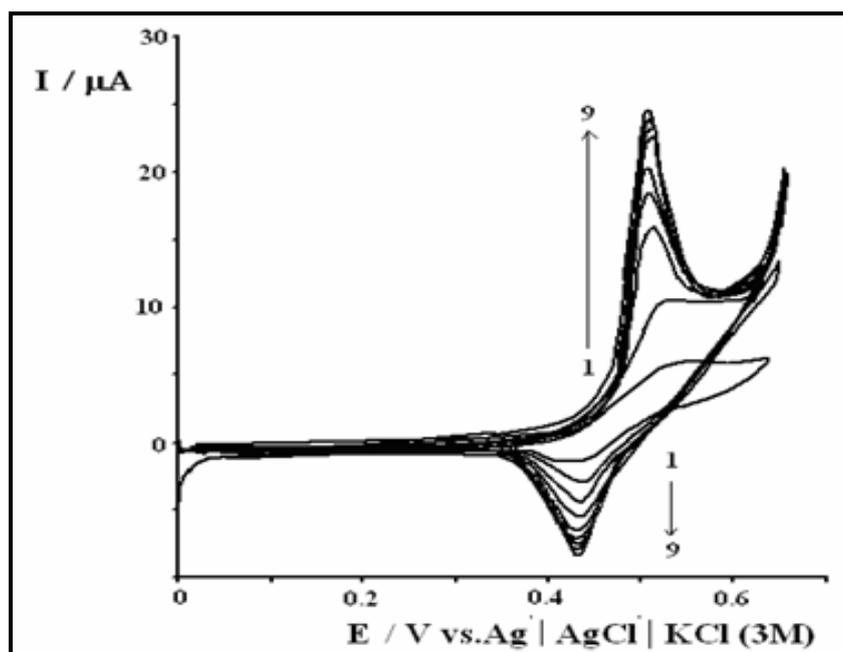


Figure 4. Electrochemical response of a NiHCF-modified electrode in 0.1 M NaOH and during nine consecutive potential scan, $\nu = 50 \text{ mV s}^{-1}$.

Fig. 5 represents the cyclic voltammograms of the electrode modified with nickel oxide in 0.1 M NaOH at different scan rates. The anodic and cathodic peaks occur at 0.52 and 0.44 V at a scan rate of 50 mV s^{-1} . The anodic peak potential shifted towards the positive direction with increasing scan rates, while the cathodic peak shifted to a more negative potential. For example, a peak potential separation of 0.08 and 0.136 V were observed at 50 and 300 mV s^{-1} respectively. Also, the anodic and cathodic peak currents increase linearly with scan rate as predicted for a diffusionless system (Fig. 5B). The surface coverage Γ^* of the redox species of nickel oxide was determined from the slope of these lines and using the following equation [35]:

$$I_p = (n^2F^2/4RT)\nu A\Gamma^* \quad (2)$$

Where I_p is the peak current, A is the electrode surface area and Γ^* is the surface coverage of the redox species and taking the average of both cathodic and anodic currents, the surface coverage of the immobilized film was obtained $2.93 \times 10^{-9} \text{ mol cm}^{-2}$. This surface concentration would correspond to a thickness of a few hundreds of monolayers.

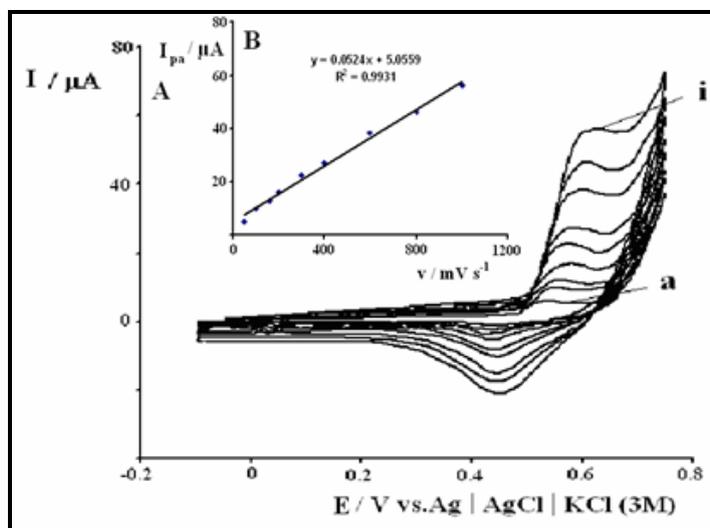


Figure 5. Cyclic voltammograms of CPE modified with nickel oxide at different scan rates: (a) 50, (b) 100, (c) 160, (d) 200, (e) 300, (f) 400, (g) 600, (h) 800 and (i) 1000 mV s^{-1} in 0.1 M NaOH solution (A), Plot of I_{pa} vs. v (B).

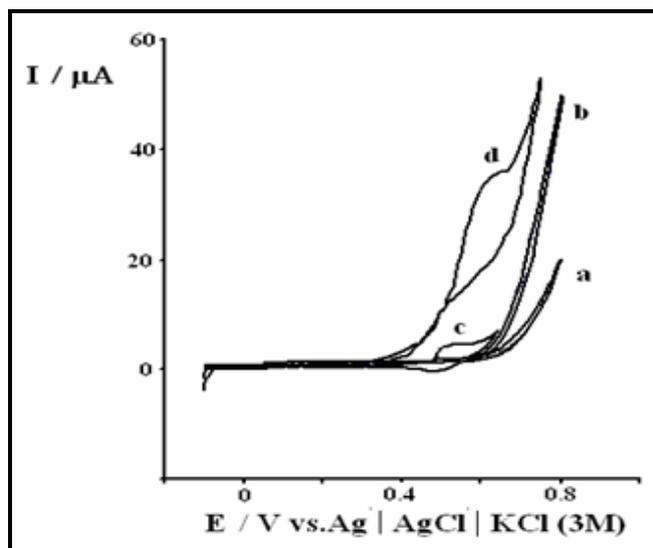
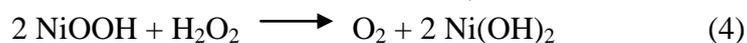


Figure 6. Cyclic voltammetric behavior of CPE at a scan rate of 20 mV s^{-1} : (a) 0.1 M NaOH solution, (b) 0.1 M NaOH solution containing 4 mM hydrogen peroxide, (c) CPE modified with nickel oxide in the same conditions of (a) and (d) CPE modified with nickel oxide in the same conditions of (b).

3.3. Electrooxidation of hydrogen peroxide on the modified electrode

In this work, in order to investigate whether the CPE modified with nickel oxide has excellent electrocatalytic property, control experiments were carried out by using bare CPE and CPE modified with nickel oxide. Voltammetric responses of these electrodes with addition of 4 mM hydrogen peroxide are presented in Fig. 6. As shown in Fig. 6, no obvious response can be observed at bare CPE (Fig. 6 curve b), which shows that it is difficult for hydrogen peroxide to be oxidized at bare CPE.

If the CPE coated with nickel oxide and placed into the same hydrogen peroxide containing cell, a well defined and reproducible peak is observed (Fig. 6 curve d). The oxidation peak potential of hydrogen peroxide on CPE modified with nickel oxide is about 0.6 V. The significant decrease of overpotential (> 200 mV) during electrooxidation of hydrogen peroxide demonstrates that CPE modified with nickel oxide has a good catalytic activity toward the hydrogen peroxide oxidation as follows (EC' mechanism):



Also, redox process is affected by the presence of hydrogen peroxide in bulk solution. The response of CPE modified with nickel oxide to hydrogen peroxide was examined and the corresponding calibration curves are shown (Fig. 7 and Fig. 8). Two linear ranges from 0.6 to 6 mM and 17 to 54 mM ($\text{LOD} (2\delta) = 0.34$ mM) have been observed for modified electrode. We ascribe this to a change in the catalytic reaction conditions arising from the formation of oxygen gas bubbles at the surface of modified electrode, as has already been reported [36-38].

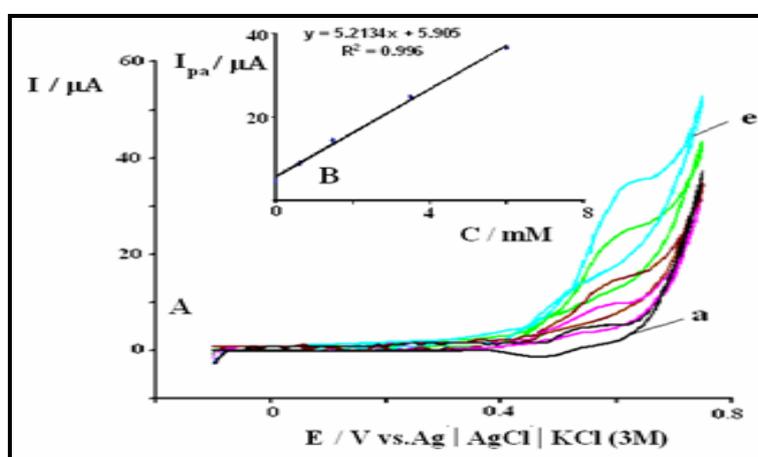


Figure 7. Voltammetric responses of CPE modified with nickel oxide in the presence of various hydrogen peroxide concentrations: (a) 0, (b) 0.6, (c) 1.1, (d) 3 and (e) 6 mM, $v = 20 \text{ mV s}^{-1}$ (A) and Calibration curve for the determination of hydrogen peroxide derived from voltammetric data (B).

Table 1. Comparison of the efficiency of some mediators used in electrocatalysis of hydrogen peroxide oxidation

Working electrode	Linear range (mM)	pH	LOD (mM)	Reference
Graphite paste electrode	15-30	7.0	_____	[39]
CPE/Nanostructured cryptomelane-type manganese oxides	0.10-0.69	7.4	0.002	[40]
MWCNT paste electrode	0.5-35	7.0	_____	[39]
Activated SWCNH ^a paste electrode	0.5-100	7.0	0.05	[39]
SWCNT ^b ensemble networks	1.9-24	6.9	1.0	[41]
CPE/PNMA(SDS)/Co	0.03-12	13	0.018	[28]
CPE/nickel oxide	0.6-6 17-54	13	0.34	Present work

^a Single-walled carbon nanohorn

^b Single-walled carbon nanotube

Indeed at low concentrations of hydrogen peroxide, the formed gas being negligible has no effect on the diffusion of hydrogen peroxide toward electrode surface. However, at high concentrations of hydrogen peroxide, gas evolution at the electrode surface reduces to some extent the normal diffusion of the substrate.

Also, the electrocatalytic oxidation of hydrogen peroxide in this work has been compared with other research work (Table 1). The results show that CPE modified with nickel oxide is suitable electrode in comparison with other previous mediators.

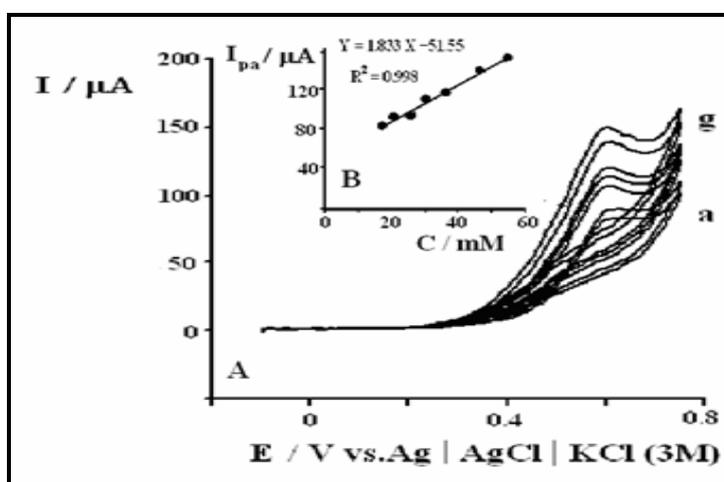


Figure 8. As same as Fig. 7 but for concentrated hydrogen peroxide: (a) 17, (b) 20, (c) 25, (d) 30, (e) 36, (f) 46 and (g) 54 mM, $v = 20 \text{ mV s}^{-1}$.

3.4. Analysis of hydrogen peroxide in real sample

The new method based on the CPE modified with nickel oxide was employed for the quantification of hydrogen peroxide in some commercial samples of cosmetics products. The determination of hydrogen peroxide in a sample was carried out by the standard addition method for prevention of any matrix effect. Fig. 9A shows the related voltammograms for this purpose. As can be seen in this Figure, adding hydrogen peroxide to the solution of 3×10^3 order diluted cosmetics products in the presence of 0.1 M NaOH (curve a) caused an increase in the oxidation peak height (curves b-f). Thus, the peak was attributed to hydrogen peroxide.

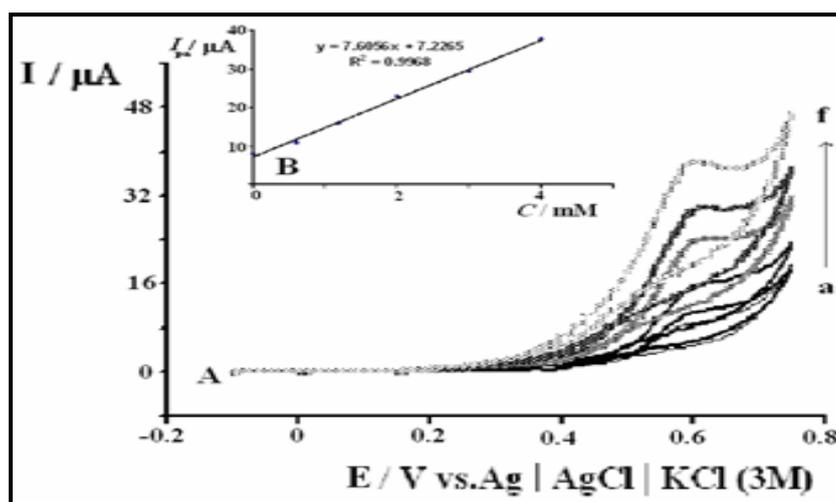


Figure 9. Cyclic voltammograms: (a) CPE modified with nickel oxide + 3×10^3 order diluted solution of cosmetics products in 0.1 M NaOH solution, (b-f) after adding hydrogen peroxide 0.6, 1.2, 2.0, 3.0 and 4.0 mM, respectively; $v = 20 \text{ mV s}^{-1}$ (A); Plot of I_{pa} as a function of added hydrogen peroxide concentration to sample (B).

Also Fig. 9B is a diagram of I_{pa} versus hydrogen peroxide concentration that shows the linear region usable for determination of hydrogen peroxide. By this method hydrogen peroxide concentration in real sample was about 2.9 M. Accuracy was examined by comparison of data obtained from this method with a recognized common method for determination of hydrogen peroxide (oxidation-reduction titration in acid solution of KMnO_4). The results from the statistical calculation indicate good agreement between the mean values (t-test) and precision (F-test) for two methods (for $p = 0.05$).

4. CONCLUSIONS

A simple method was introduced to modified CPE with nickel oxide. Cyclic voltammetric studies show this modified electrode has an electrocatalytic effect the hydrogen peroxide. The good

linearity between the electrooxidation current and the concentration of hydrogen peroxide makes it practically usable in determining concentrated hydrogen peroxide. Our study shows that CPE modified with nickel oxide is promising alternative to platinum electrode that conventionally used for determination of concentrated hydrogen peroxide. This modified electrode was used for the quantification of hydrogen peroxide in commercial samples of cosmetics product giving excellent analytical results.

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