

# Carbon paste electrode modified by cobalt ions dispersed into poly (*N*-methylaniline) preparing in the presence of SDS: application in electrocatalytic oxidation of hydrogen peroxide

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Received: 26 August 2008 / Revised: 15 February 2009 / Accepted: 4 March 2009 / Published online: 20 March 2009  
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**Abstract** Conducting and stable poly (*N*-methylaniline) film was prepared by using the repeated potential cycling technique in aqueous solution containing *N*-methylaniline, sulfuric acid, and sodium dodecyl sulfate (SDS) at the surface of carbon paste electrode (CPE). The transition metal ions of Co(II) were incorporated to the polymer by immersion of the modified electrode in 0.1 M cobalt chloride solution for 10 min. The electrochemical characterization of this modified electrode exhibits stable redox behavior of Co(II)→Co(III) and formation of insoluble oxide/hydroxide cobalt species on the CPE surface. The modified electrode showed well-defined and stable redox couples in alkaline aqueous solution. The modified electrode showed excellent electrocatalytic activity for oxidation of hydrogen peroxide. The response of modified electrode toward the H<sub>2</sub>O<sub>2</sub> oxidation was examined using cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, and chronoamperometry. This modified electrode has many advantages such as simple preparation procedure, good reproducibility, and high 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** Modified electrode · Carbon paste electrode · Conducting polymer · Hydrogen peroxide · Cobalt oxide

## Introduction

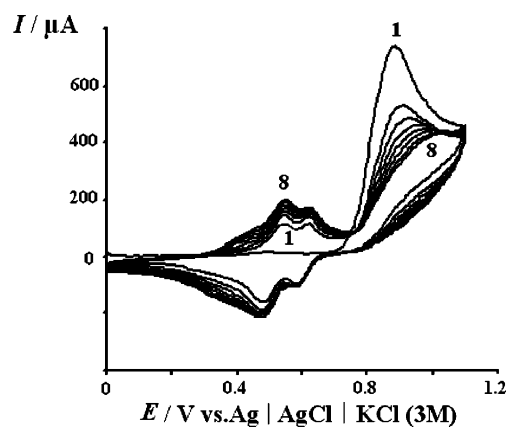
Conducting polymers are novel organic semiconducting materials with great promise because of their wide range of potential technological applications. Among the conducting polymers, polyaniline has been studied extensively due to the commercial availability of the monomer, its easy synthesis, well-behaved electrochemistry, good environmental stability, high conductivity, and multiple redox and protonation states [1]. *N*-substituted polyanilines are interesting materials for several reasons. First, an intermediate with high stability is formed during electropolymerization of various *N*-alkyl substituted anilines in acidic aqueous solutions [2, 3]. Second, the electrochemistry of poly (*N*-alkylaniline) is less complicated in comparison to polyaniline [4]. It has been shown recently the interest of using aqueous anionic micellar media, based mainly on sodium dodecyl sulfate (SDS), for electrosynthesizing conducting polymers, such as polypyrroles [5] and polythiophenes [6]. The presence of anionic micelles leads to an increase of the monomer solubility in aqueous solution and a lowering of its oxidation potential, thus making possible the electrodeposition of adherent films in aqueous media. The polymeric components can provide, for instance, mechanical strength and thermal stability, while the surfactants retain their tendency to assemble in layered structures. This may be particularly useful for fabrication of multifunctional materials for technological application, e.g., electronic devices, microsensors, separation membrane, and biomembranes, etc. [7–10].

On the other hand, hydrogen peroxide is the product of the reactions catalyzed by a large number of oxidases. Detection of hydrogen peroxide, which is a byproduct in an enzymatic reaction, is important in the field of biosensor

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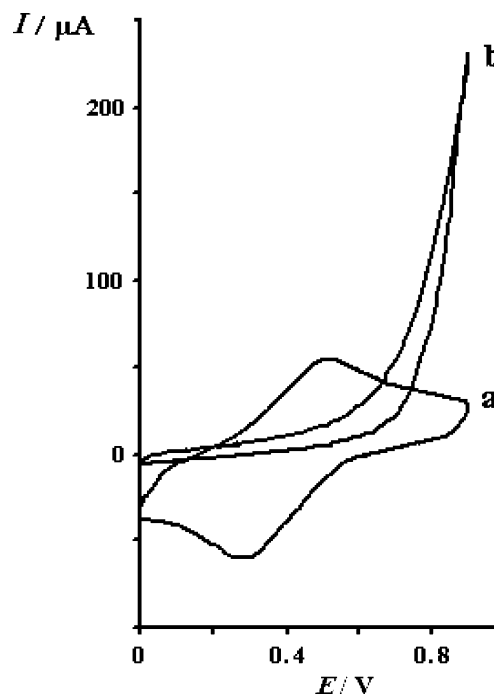
fabrication [11]. Many methods such as titrimetry, spectrophotometry, and chemiluminescence have been developed for this purpose [12–15]. Electrochemical methods have been proven to be an inexpensive and effective way for hydrogen peroxide determination. The direct reduction or oxidation of hydrogen peroxide at bare electrode is not suited for analytical application due to slow electrode kinetics and high overpotentials required for redox reactions of  $\text{H}_2\text{O}_2$  on many electrodes materials. For this reason, redox mediators have been widely used in order to decrease the overpotential and increase the electron transfer kinetics. Different electron transfer mediators such as cobalt phthalocyanine [16], water soluble dyes [17], platinum and iridium [18], vanadium-doped zirconias [19], iodine [20], Prussian blue [21], nickel Schiff base complex [22], and copper complex [23] have been used for determination of hydrogen peroxide. Furthermore, immobilization of different peroxidase enzymes has been used for fabrication hydrogen peroxide biosensors [24–27]. Although modified electrodes have been shown interesting ability toward hydrogen peroxide detection, they also display many problems related to the immobilization of the mediator and its toxicity, low sensitivity and stability, and mediator leakage. In addition, high cost, low reproducibility, and poor repeatability are also the disadvantages of these sensors. Hence, developing simple and reliable methods for fabrication of novel sensor for hydrogen peroxide detection have been always a goal for research groups.

The preparation of coatings of transition metals such as Co, Fe, Ni, Cu, etc. has attracted considerable attention in view of their potential applications in scientific and technological fields. Cobalt oxide-based materials, in particular, are used for the production of magnetoresistive devices [28], electrochromic thin films [29, 30], energy storage systems [31, 32], and heterogeneous catalysts [33–36]. Generally, cobalt oxide films are prepared at high temperatures, namely by sol–gel [37–40], spray pyrolysis [41, 42], or sputtering [43, 44] methods, whose main drawback is the formation of defects by thermally induced stress, impairing the catalytic activity of the films. Choosing an electrodeposition technique for the preparation of thin oxide films or their alloys offers a number of unique advantages in comparison to other procedures. For instance, very thin and homogeneous films with specific morphological and chemical properties can be prepared. Electrochemical methods are interesting tools for the deposition of such materials at room temperature, but the low solubility of the cobalt hydroxide should be overcome. The physical properties of the relevant deposits can be easily modulated by means of the various experimental parameters affecting the electrodeposition process such as electrolyte composition, pH, applied potentials, time of polarizations, and electrode substrate.



**Fig. 1** Cyclic voltammograms (eight cycles) recorded during potentiodynamic growth of PNMA film in a solution containing 0.01 M NMA, 0.01 M SDS, and 1 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$

In our previous works, we combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer, and carbon paste technology by construction of poly (1-naphthylamine)/nickel [45] and poly (1,5-diaminonaphthalene)/nickel [46] modified carbon paste electrode (CPE) for successful electrocatalytic oxidation of some carbohydrates and small organic molecule such as methanol, respectively. According



**Fig. 2** Electrochemical responses of CPE/PNMA (SDS) in: **a** 1.0 M  $\text{H}_2\text{SO}_4$ , **b** 0.1 M NaOH solution,  $\nu=50 \text{ mV s}^{-1}$

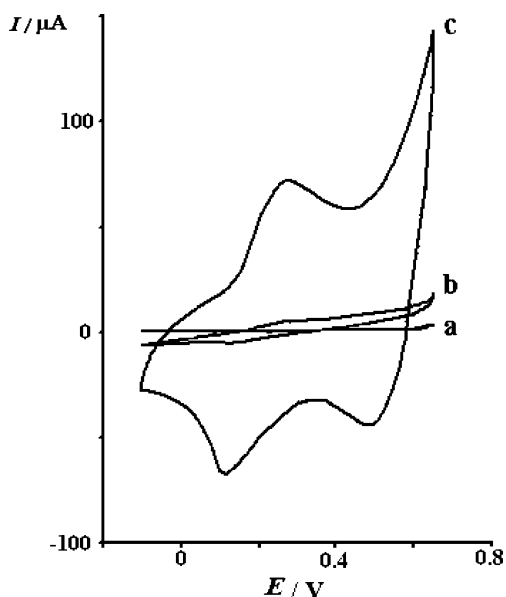
to our recent study, the polymer films of poly (*N*-methylaniline) (PNMA) can easily be formed on CPE in 1 M H<sub>2</sub>SO<sub>4</sub> solution and in the presence of SDS. It was observed that the PNMA film growth was greatly facilitated in the presence of SDS.

In this work, we decided to combine the advantageous features of PNMA film in the presence of SDS, dispersion of cobalt particles into the polymeric film, and carbon paste technology. In this paper, at the first step, *N*-methylaniline monomer is electropolymerized at the surface of CPE. Then, cobalt ions were incorporated into the polymeric matrix by immersion of the polymeric-modified electrode in a cobalt chloride solution. Efficiency of this cobalt-modified polymeric CPE toward the catalytic oxidation of hydrogen peroxide in alkaline medium was investigated. The high stability and electrocatalytic activity of this new substrate for the hydrogen peroxide oxidation, as well as its application for the preparation of a new sensor for determination of hydrogen peroxide in cosmetics products are described.

## Experimental

### Reagents and materials

The solvent used in this work was twice distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. The *N*-methylaniline and SDS from Fluka were used as received. Sodium hydroxide and hydrogen peroxide used in this work were analytical grade of Fluka origin and



**Fig. 3** Electrochemical responses of electrodes: **a** CPE/Co, **b** CPE/PNMA/Co, and **c** CPE/PNMA (SDS)/Co in 0.1 M NaOH solution, scan rate=50 mV s<sup>-1</sup>

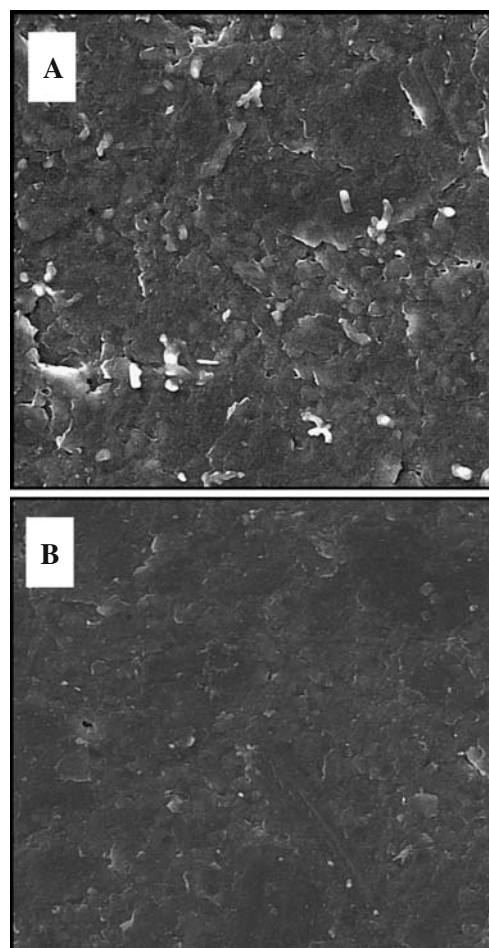
used without further purification. High viscosity paraffin (density=0.88 g cm<sup>-3</sup>) from Fluka was used as the pasting liquid for the CPE. Graphite powder (particle diameter=0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

### 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 Ag|AgCl|KCl (3 M) were used as WE, counter electrode, and reference electrode, respectively.

### Preparation of the WE

A mixture of graphite powder and paraffin were blended by hand mixing with a mortar and pestle for the preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius=1.7 mm). The



**Fig. 4** SEM photograph of: **a** PNMA (SDS), **b** PNMA (SDS)/Co deposited on CPE

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. In addition, PNMA film in the presence of SDS [PNMA (SDS)] was synthesized using a (*N*-methylaniline) monomer solution [0.01 M (*N*-methylaniline) and 0.01 M SDS in 1 M H<sub>2</sub>SO<sub>4</sub>]. The electropolymerization was carried out on the surface of CPE by potential cycling (eight cycles at a scan rate of 50 mV s<sup>-1</sup>) between 0.0 and 1.1 V versus Ag|AgCl|KCl (3 M).

Incorporation of Co (II) ions into different matrix

Deposition of cobalt oxide on three different types of electrode surfaces—(a) CPE, (b) CPE modified with PNMA, and (c)

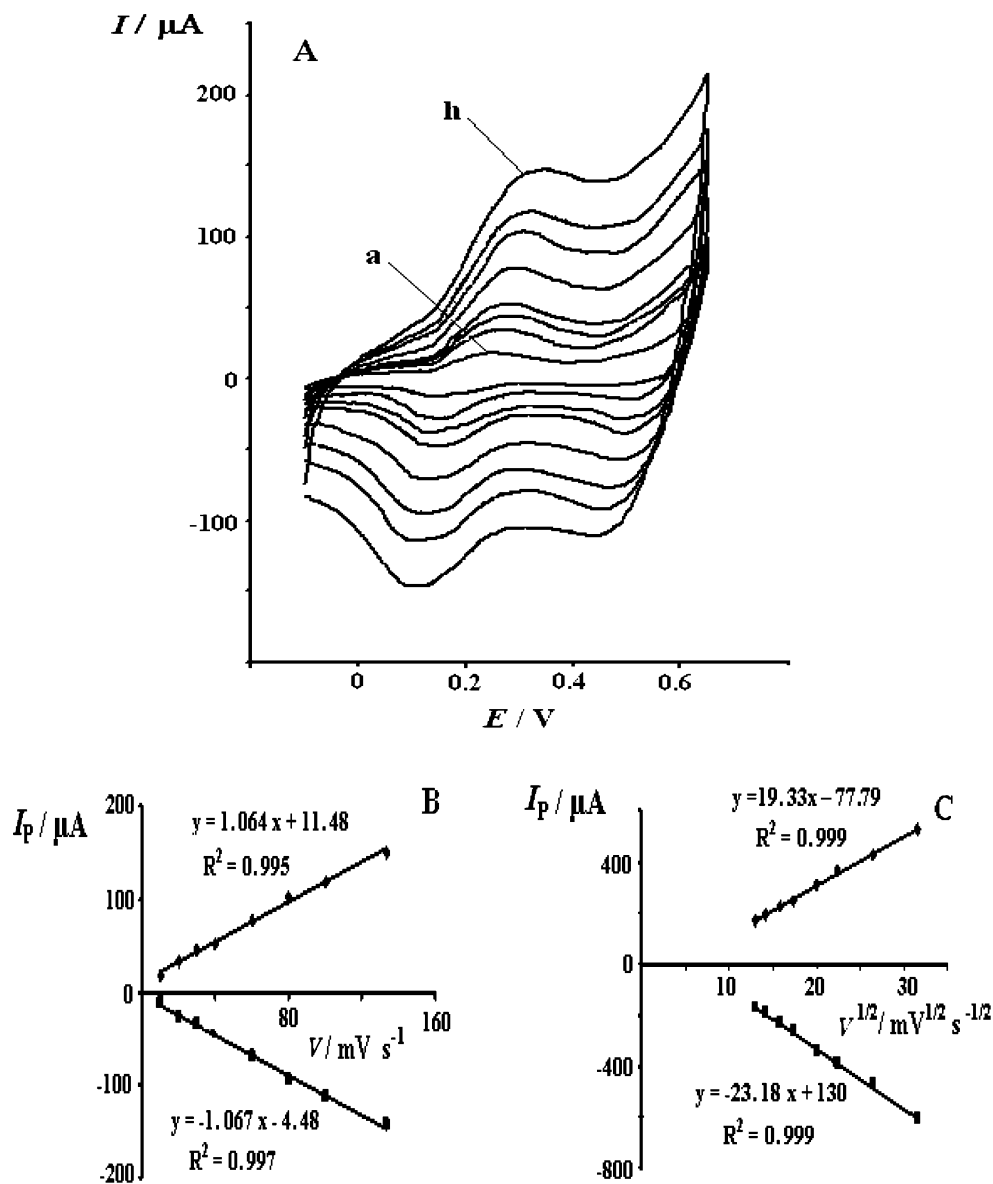
CPE modified with PNMA (SDS)—was achieved in same conditions. The electrodes were placed at open circuit in a well-stirred aqueous solution of 0.1 M CoCl<sub>2</sub>, for a given period of time (*t*<sub>a</sub>, accumulation time=10 min).

## Results and discussion

Electrosynthesis of PNMA in the presence of SDS

Figure 1 shows the typical multisweep cyclic voltammograms during electropolymerization in the presence of SDS. As can be seen, at the first cycle and in the forward scan, oxidation of monomer occurs about 900 mV, and in the reverse scan, two reduction peaks appear at the potentials about 0.6 and 0.5 V related to the polymer formed,

**Fig. 5** **a** Scan rate dependence of the peak current for CPE/PNMA(SDS)/Co, scan rates: *a* 10, *b* 20, *c* 30, *d* 40, *e* 60, *f* 80, *g* 100, *h* 133.3 mV s<sup>-1</sup> in 0.1 M NaOH solution. **b** Plot of *I*<sub>p</sub> vs. *v*. **c** Plot of *I*<sub>p</sub> vs. *v*<sup>1/2</sup>



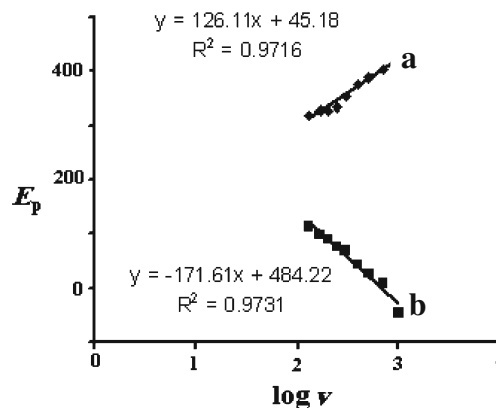
respectively. At the second cycle, also two new oxidation peaks related to the polymer can be observed. In the higher cycles, the peak height of polymer growth increases, but the peak height related to the monomer oxidation decreases. This indicates the build-up of an electroactive polymeric material on the CPE surface. Moreover, a pair of shoulders was observed around 0.4 V, which can be attributed to the presence of SDS in the film. According to our study, it was observed that the PNMA film growth was greatly facilitated in the presence of SDS compared with the absence of it. The current–potential behavior of a PNMA (SDS) coated CPE in monomer-free, SDS-free, and 1.0 M sulfuric acid is depicted in Fig. 2a. As can be seen in this figure, the redox behavior of the film was strongly dependent on the pH of the electrolyte solution. Therefore, the obtained polymer shows a well-defined redox behavior in an acidic solution. The response obtained in an alkaline solution (0.1 M NaOH) shows a complete loss of electrode activity in the potential range from 0.0 to 0.9 V (Fig. 2b). Furthermore, the anodic peak current at 0.8 V correspond to oxidation of hydroxide ion (OH<sup>-</sup>). However, the film was not degraded under these experimental conditions, and its response was recovered when the electrode was immersed in an acidic solution.

#### Electrochemical behavior of CPE modified with PNMA (SDS)/Co film

The results about the influence of the surface modification on the formation of cobalt oxide particles were checked by recording the cyclic voltammograms of the modified electrodes in alkaline solution (pH=13) without cobalt ions (Fig. 3).

Figure 3 shows the variation of peak current for the three different electrode surfaces exposed to the solution of Co (II) ions. Curve c corresponds to the signal of the modified electrode with PNMA and SDS. The peak current is completely different from the preceding two cases (its value is the most). However, deposition of cobalt on the surface of CPE/PNMA (in the absence of SDS; Fig. 3b) was very negligible, and it was not deposited at the surface of CPE at all (Fig. 3a). Such behavior indicates that the deposition process is favored by the presence of the negatively charged SDS within the polymeric film on the electrode surface. Regardless of the actual structure of the polymeric film, in the fact, the excess of negative charge due to the presence of SDS at the interface is capable of attracting positively charged cobalt ions, and accumulation of cobalt ions was carried out by complex formation between Co (II) and amine sites in the polymer backbone.

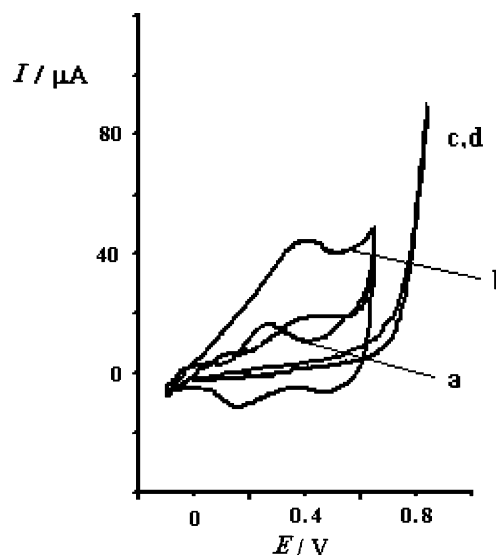
It can be seen in Fig. 3c that oxidation peak was observed at 0.25 V during the positive potential scan. These results can be attributed to the conversion between cobalt



**Fig. 6** Plot of  $E_p$  vs.  $\log v$  for cyclic voltammograms recorded at the surface of CPE/PNMA (SDS)/Co in 0.1 M NaOH solution; **a** for anodic peaks and **b** for cathodic peaks

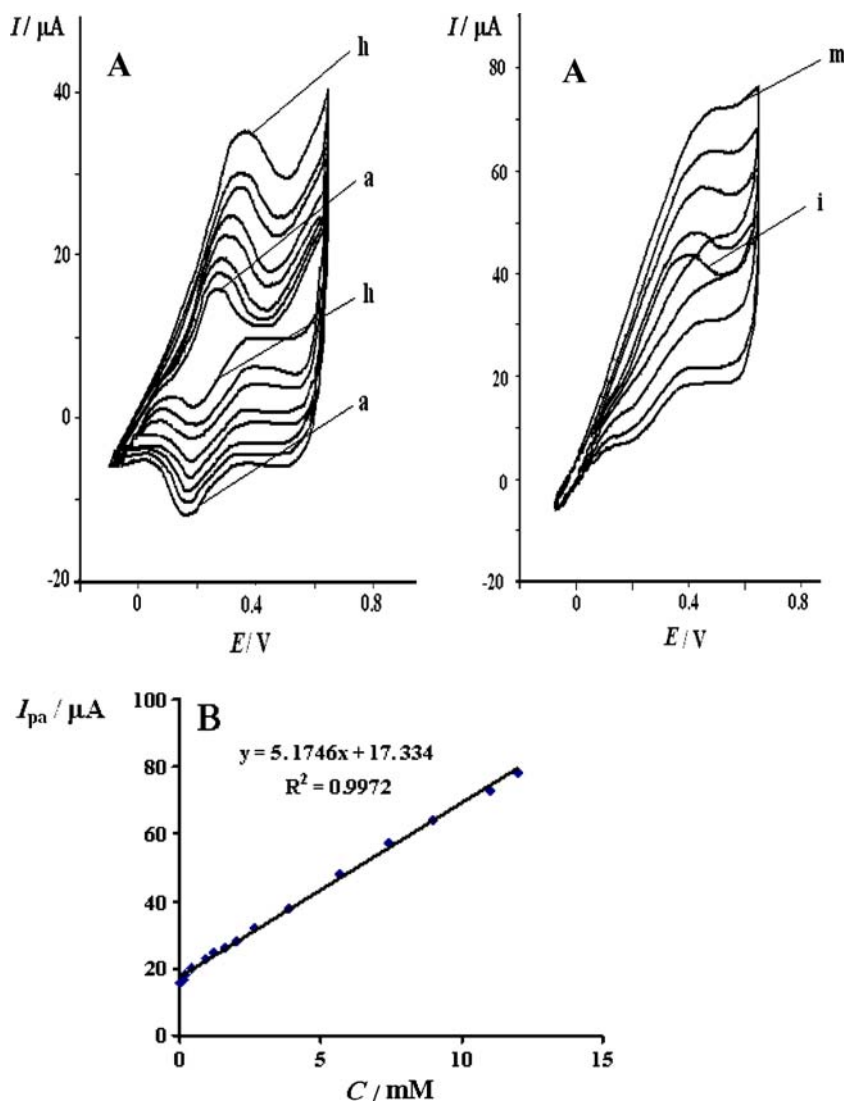
oxidation phases of Co(OH)<sub>2</sub>, CoOOH, and CoO<sub>2</sub>, which are stable at alkaline pH [47]. At potentials positive of 0.65 V, there is a sharp rise of anodic current due to the evolution of oxygen. During the cathodic scan, two reduction peaks at 0.52 and 0.14 V were observed, corresponding to the reduction of the various cobalt oxide species formed during the positive sweep.

To understand the surface morphology of the electrodeposited cobalt film on the polymeric film, the electrode surfaces were examined by SEM. After preparation, the electrodeposited cobalt oxide films were thoroughly rinsed with pure water before being inspected by SEM. Figure 4 shows the morphology of the cobalt deposition on the surface of CPE/PNMA (SDS). As can be seen in this figure (subpanel B), the film shows a very uniform and compact structure. In comparison with the polymeric film in the



**Fig. 7** Cyclic voltammograms of CPE/PNMA (SDS)/Co in 0.1 M NaOH solution at scan rate of 10 mV s<sup>-1</sup> in **a** 0 and **b** 4 mM of H<sub>2</sub>O<sub>2</sub>. Subpanels **c** and **d** are same results as **a** and **b** for CPE/PNMA (SDS)

**Fig. 8** **a** Cyclic voltammograms for electro-oxidation of hydrogen peroxide at the surface of CPE/PNMA (SDS)/Co in 0.1 M NaOH solution with different concentrations of hydrogen peroxide: *a* 0, *b* 0.05, *c* 0.1, *d* 0.2, *e* 0.4, *f* 0.9, *g* 1.6, *h* 2.7, *i* 5.7, *j* 7.4, *k* 9, *l* 11, *m* 12 mM. **b** Plot of anodic peak current vs.  $\text{H}_2\text{O}_2$  concentrations



absence of cobalt ions (subpanel A), it is interesting that the formation of cracks and/or voids was not observed.

Figure 5a shows the cyclic voltammograms of CPE/PNMA (SDS)/Co in 0.1 M NaOH solution at different potential sweep rates, as can be seen anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values from 10 to  $133 \text{ mV s}^{-1}$  (Fig. 5b). This can be attributed to an electrochemical activity of an immobilized redox couple at the electrode surface. From the slope of this line and using [48]:

$$I_p = (n^2 F^2 / 4RT) \nu A \Gamma^* \quad (1)$$

where  $I_p$  is the peak current,  $A$  the electrode surface area, and  $\Gamma^*$  is the surface coverage of the redox species, and taking the average of both cathodic and anodic currents, the surface coverage of the immobilized active substance [Co (II)] in the films of about  $1.3 \times 10^{-8} \text{ mol cm}^{-2}$  was

derived. In the higher range of potential sweep rates ( $166$ – $1,000 \text{ mV s}^{-1}$  (Fig. 5c), the peak currents depend on square root of the potential sweep rate, signifying the dominance of a diffusion process as the rate limiting step in the total redox transition of the modifier film. The effect of  $\nu$  on peak potential was also investigated by voltammetry. With the increase of  $\nu$ , the oxidation peak potential is positively shifted, and the reduction peak potential is negatively shifted, indicating that the redox reversibility of cobalt oxide film was impaired. Under the surface controlled redox process, the electron transfer kinetics of this film on the surface of CPE modified with PNMA can be obtained by using the approach developed by Laviron [49]; when peak to peak separation is higher than  $0.20 \text{ V/n}$ , the relationship between the peak potential,  $E_p$ , and the scan rate can be expressed in Eq. 2:

$$E_p = f(\log \nu) \quad (2)$$

Figure 6 provided the variations of peak potentials with the logarithm of the scan rate. From the slope of the oblique asymptotes, where for cathode peak, the slope value is  $-2.3RT/\alpha nF$ , and for anode peak,  $2.3RT/(1-\alpha)nF$ , the electron transfer coefficient ( $\alpha$ ) of cobalt oxide film was calculated. Furthermore, the standard rate constant of reaction,  $k_s$ , is expressed in Eq. 3 [49]:

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log(RT/nFv) - [\alpha(1 - \alpha)nF\Delta E_p]/[2.3RT] \quad (3)$$

where  $n$  is the number of electrons involved in the reaction, and  $\Delta E_p$  is the peak to peak potential separation. We known that the number of electrons involved in the reaction of cobalt oxide film is 1. Therefore, the resulting values of  $\alpha$  and  $k_s$  were obtained 0.59 and  $3.4 \times 10^{-1} \text{ cm s}^{-1}$ , respectively.

Electrocatalytic oxidation of hydrogen peroxide

Voltammetric studies

Biosensors developed for medical biodiagnostic applications typically use enzymes in order to catalytically generate a redox active product, such as hydrogen peroxide. It can be electrochemically detected. In order to verify the electrocatalytic activity of this modified electrode for hydrogen peroxide oxidation, the electrochemical experiments in the presence of hydrogen peroxide were carried out. Figure 7 shows the cyclic voltammograms of CPE/PNMA (SDS) and CPE/PNMA (SDS)/Co in the absence and presence of  $\text{H}_2\text{O}_2$  (4 mM). As shown for CPE/PNMA (SDS), no redox response of  $\text{H}_2\text{O}_2$  can be seen in the potential range from  $-0.1$  to  $0.65$  V. As can be seen, at the surface of CPE/PNMA (SDS)/Co, upon hydrogen peroxide addition, there is an increase in the anodic peak current and a decrease in the cathodic peak current (Fig. 7b). The decrease of overvoltage (400 mV) and increased peak current of hydrogen peroxide oxidation confirm that cobalt oxide has catalytic ability for  $\text{H}_2\text{O}_2$  oxidation. This behavior is typical of that expected for mediated oxidation (EC' mechanism) as follows:

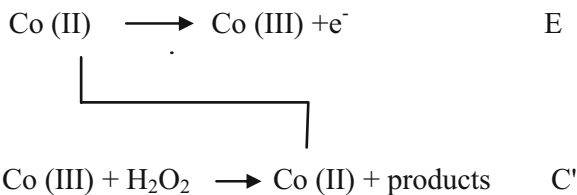


Figure 8 shows the cyclic voltammograms of the PNMA (SDS)/Co film on the surface of CPE with various

concentrations of hydrogen peroxide in 0.1 M NaOH solution. When the excessive concentrations of hydrogen peroxide were added, the oxidation peak current increased noticeably (Fig. 8a). The catalytic oxidation peak current showed a linear dependence on the hydrogen peroxide concentration from 0.03 to 12 mM. The linear regression equation is obtained as  $I (\mu\text{A}) = 5.175 C (\text{mM}) + 17.334$ ,  $R^2 = 0.997$  (Fig. 8b). The detection limit is estimated to be  $1.8 \times 10^{-5} \text{ M}$  when the signal-to-noise ratio is 3.

In addition, the above modified electrode was applied to the electrocatalytic oxidation of hydrogen peroxide using the differential pulse voltammetry and square wave voltammetry methods. Figure 9 shows the differential pulse voltammograms that were obtained for a series of hydrogen peroxide solutions with various concentrations (5–48  $\mu\text{M}$ ). The calibration plot was linear in this range, and the value of LOD ( $2\delta$ ) was calculated 3  $\mu\text{M}$  by this method. Figure 10 shows square wave voltammograms in the range of 1–12  $\mu\text{M}$ . It was linear dependent on the hydrogen peroxide concentration. The value of LOD ( $2\delta$ ) was calculated 0.9  $\mu\text{M}$ . The results show that an increase in concentration of

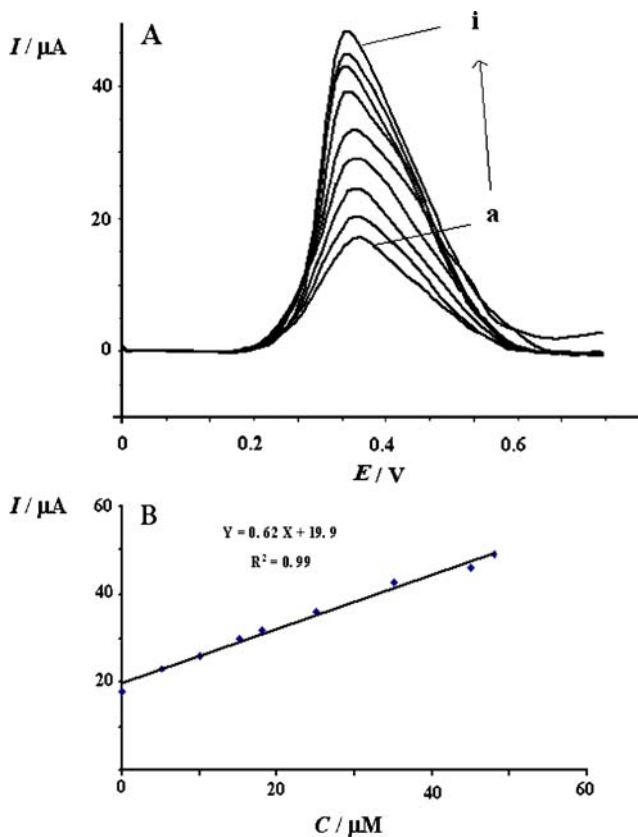
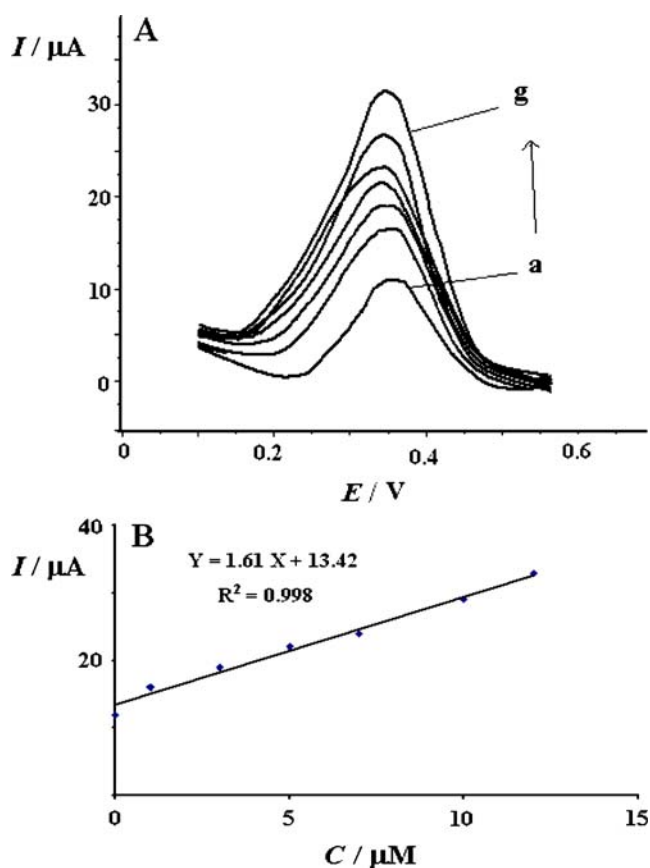


Fig. 9 a Differential pulse voltammograms of carbon paste electrode modified with PNMA (SDS)/Co in the presence of different concentrations of hydrogen peroxide: a 0, b 5, c 10, d 15, e 18, f 25, g 35, h 45, and i 48  $\mu\text{M}$ . b Plot of electrocatalytic current vs. concentration of hydrogen peroxide



**Fig. 10** **a** Square wave voltammograms of carbon paste electrode modified with PNMA (SDS)/Co in the presence of different concentrations of hydrogen peroxide: *a* 0, *b* 1, *c* 3, *d* 5, *e* 8, *f* 10, and *g* 12  $\mu\text{M}$ . **b** Plot of electrocatalytic current vs. concentration of hydrogen peroxide

hydrogen peroxide was accompanied by an increase in anodic current. However, the electrocatalysis of hydrogen peroxide in this work has been compared with other research works (Table 1). The results show that PNMA (SDS)/Co film is comparable with other previous mediators.

#### Chronoamperometric studies

Chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrode processes at chemically modified electrodes. Figure 11 shows chronoamperometric measurements for hydrogen peroxide on the surface of CPE/PNMA (SDS)/Co.

Figure 11 a presents the current–time behavior of CPE/PNMA (SDS)/Co by setting the WE potential at 0.3 V (first potential step) and 0.1 V (second potential step) in the absence (subpanel a) and in the presence (subpanels b–d) of hydrogen peroxide in 0.1 M NaOH solution. The transition current is obviously due to the mediated oxidation of hydrogen peroxide by cobalt oxide and is substantiated upon increasing the concentration of hydrogen peroxide. Furthermore, chronoamperometry was employed to investigate the kinetic aspect of chemical reaction at the modified electrode for hydrogen peroxide. The rate constant for the catalytic chemical reaction between hydrogen peroxide and redox sites of CPE/PNMA (SDS)/Co, can be evaluated by chronoamperometry according to the method described in the literature [56].

$$I_C/I_L = \lambda^{1/2} [\pi^{1/2} \text{erf}(\lambda^{1/2}) + \exp(-\lambda)/\lambda^{1/2}] \quad (4)$$

Where  $I_C$  is the catalytic current of the CPE/PNMA (SDS)/Co in the presence of hydrogen peroxide,  $I_L$  is the limiting current in the absence of hydrogen peroxide and  $\lambda = kc_0 t$  ( $c_0$  is

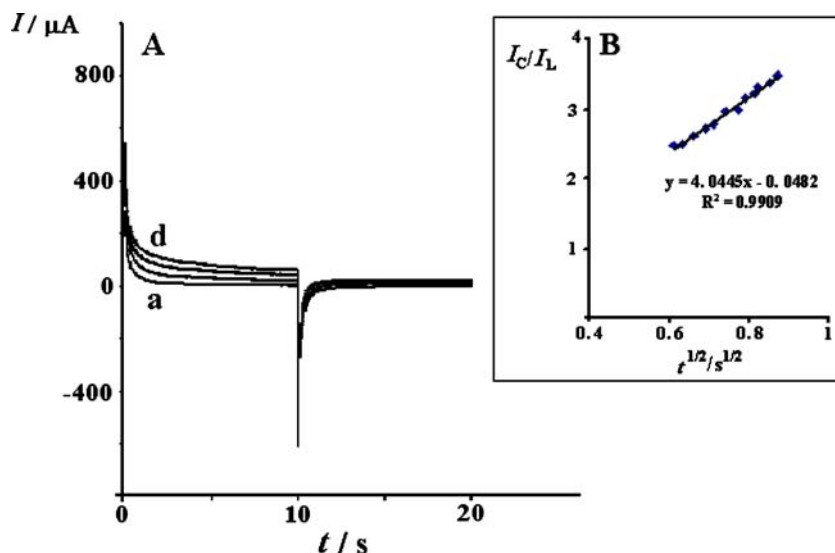
**Table 1** Comparison of the efficiency of some mediators used in electrocatalysis of hydrogen peroxide

Electrode	Mediator	pH	Electrocatalytic effect (mV)	LOD( $\mu\text{M}$ )	LDR( $\mu\text{M}$ )	Reference
GC	CoHCF	7	–	0.27	4.3–1.5 $\times 10^3$	[50]
GC	Cobalt (II)–tartrate complexes	11.6	–	–	700–4 $\times 10^3$	[51]
GC	Cobalt oxide nanoparticles	7.4	250	4 $\times 10^{-4}$	4 $\times 10^{-3}$ –8 $\times 10^{-2}$	[52]
CPE	Manganese oxide	7.4	200	2	100–690	[53]
Pt	Pt / silver nanoparticles	7	120	1	1.25–1 $\times 10^3$	[54]
SWCNH paste electrode <sup>a</sup>	activated SWCNH	7	–	50	500–1 $\times 10^5$	[55]
CPE	PNMA (SDS) / Co	13	400	18 (CV) 3 (DPV) 0.9 (SWV)	30–12 $\times 10^3$ 5–48 1–12	Present work

<sup>a</sup> Single-walled carbon nanohorn



**Fig. 11 a** Chronoamperograms obtained at the CPE/PNMA (SDS)/Co in the *a* absence and presence of *b* 0.05, *c* 0.07, and *d* 0.1 mM of hydrogen peroxide; first and second potential steps were 0.3 and 0.1 V respectively, in 0.1 M NaOH solution. **b** Dependence of  $I_C/I_L$  on  $t^{1/2}$  derived from the data of chronoamperograms of *a* and *d* in *a*



the bulk concentration of hydrogen peroxide) is the argument of the error function. In the cases where  $\lambda > 1.5$ ,  $\text{erf}(\lambda^{1/2})$  almost equals unity and Eq. 4 reduces to:

$$I_C/I_L = \pi^{1/2} \lambda^{1/2} \quad (5)$$

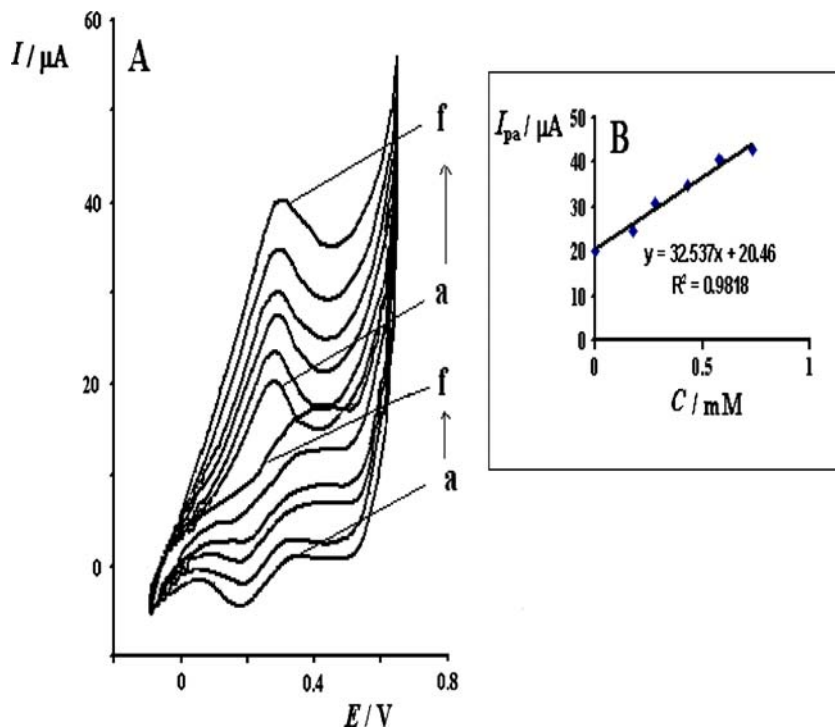
where  $k$ ,  $c_\infty$ , and  $t$  are the catalytic rate constant ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ), hydrogen peroxide concentration ( $\text{mol cm}^{-3}$ ), and time elapsed (s), respectively. From the slope of the  $I_C/I_L$  vs.  $t^{1/2}$  plot, we can simply calculate the value of  $k$  for a given concentration of substrate. Figure 11b shows one such plot, constructed from the chronoamperograms of the CPE/PNMA

(SDS)/Co in the absence and presence of 0.1 mM hydrogen peroxide. The mean value for  $k$  was found to be  $2.98 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

#### Analysis of hydrogen peroxide in real sample

The new method based on the CPE/PNMA (SDS)/Co 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 the prevention of

**Fig. 12 a** Cyclic voltammograms: *a* CPE/PNMA (SDS)/Co +  $5 \times 10^3$  order diluted solution of cosmetics products in 0.1 M NaOH solution, *b–f* after adding hydrogen peroxide 0.18, 0.28, 0.38, 0.53, and 0.68 mM, respectively;  $v = 10 \text{ mV s}^{-1}$ . **b** Plot of  $I_{pa}$  as a function of added hydrogen peroxide concentration to sample



any matrix effect. Figure 12a shows the related voltammograms for this purpose. As can be seen in this figure, adding hydrogen peroxide to the solution of  $5 \times 10^3$  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 current was attributed to hydrogen peroxide. In addition, Fig. 12b 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 3.14 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  $\text{KMnO}_4$ ). The results from the statistical calculation indicate good agreement between the mean values ( $t$  test) and precision ( $F$  test) for two methods (for  $p=0.05$ ).

## Conclusion

A new substrate was described herein, consisting of cobalt ions loaded into a PNMA-modified CPE, by immersion of the polymeric modified electrode in a cobalt chloride solution. The experimental conditions for the preparation of CPE/PNMA (SDS)/Co were carefully evaluated in order to obtain optimized conditions for hydrogen peroxide quantification in alkaline medium. The electro-oxidation of hydrogen peroxide solutions at reduced overpotential was performed using this modified electrode. The kinetic process of the catalytic reaction can be explained using cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, and chronoamperometry. The values for the rate constant,  $k$ , obtained from the chronoamperometric method indicated that the modified electrode can overcome the kinetic limitations for hydrogen peroxide oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction of hydrogen peroxide. Modified electrode was used for the quantification of hydrogen peroxide in commercial samples of cosmetics product giving excellent analytical results.

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