



Electrocatalytic reduction of hydrogen peroxide and its determination in antiseptic and soft-glass cleaning solutions at phosphotungstate-doped-glutaraldehyde-cross-linked poly-L-lysine film electrodes

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ABSTRACT

The present work describes the electrocatalytic behavior of phosphotungstate-doped glutaraldehyde-cross-linked poly-L-lysine (PLL-GA-PW) film electrode towards reduction of hydrogen peroxide (H_2O_2) in acidic medium. The modified electrode was prepared by means of electrostatically trapping the phosphotungstate anion into the cationic PLL-GA coating on glassy carbon electrode. The PLL-GA-PW film electrode showed excellent electrocatalytic activity towards H_2O_2 reduction in 0.1 M H_2SO_4 . Under the optimized conditions, the electrochemical sensor exhibited a linear response for H_2O_2 concentration over the range 2.5×10^{-6} to 6.85×10^{-3} M with a sensitivity of $1.69 \mu\text{A mM}^{-1}$. The curvature in the calibration curve at high concentration is explained in terms of Michaelis–Menten (MM) saturation kinetics, and the kinetics parameters calculated by three different methods were compared. The PLL-GA-PW film electrode did not respond to potential interferents such as dopamine, ascorbic acid and uric acid. This unique feature of PLL-GA-PW film electrode allowed selective determination of H_2O_2 . Finally, the proposed electrochemical sensor was successfully applied to determine H_2O_2 in commercially available antiseptic solution and soft-contact lenses cleaning solution and the method has been validated using independent estimation by classical potassium permanganate titration method. Major advantages of the method are simple electrode fabrication, stability and high selectivity towards hydrogen peroxide.

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1. Introduction

An accurate and reliable method for the determination of hydrogen peroxide (H_2O_2) is important because of the fact that H_2O_2 plays significant role in many fields including food, pharmaceutical, chemical and biochemical industries and in clinical control and environmental protection [1–4]. In addition, H_2O_2 is one of the products of reactions mediated by almost all oxidases [5]. Numerous methods have been reported for the determination of H_2O_2 based on spectrophotometry [6], fluorometry [7], chemiluminescence [8] and electrochemical [9,10] techniques. Among these, electrochemical methods have been considered to be an effective way for H_2O_2 determination because of their high sensitivity, quick response, low cost, simple instrumentation and possibility of miniaturization. However, the direct reduction of H_2O_2 at bare electrode is not suited for analytical application due to slow electrode

kinetics on many electrode materials. To overcome this problem, chemically modified electrodes have been suggested for promoting the electrochemical reduction and detection of H_2O_2 . Most of the modified electrodes proposed for H_2O_2 determination are enzyme-based amperometric biosensors [11–13]. However, there are some disadvantages with enzyme electrodes; for example, optimal operational conditions of the biosensors are generally limited by the properties of native enzymes. Further, native enzyme gradually loses its catalytic activity after repeated measurements [14,15]. Therefore, development of non-enzymatic hydrogen peroxide sensing electrodes that can overcome the disadvantages of native enzymes is desired.

A number of non-enzymatic hydrogen peroxide sensors based on the use of different electron transfer mediators such as Prussian Blue [16,17], polyoxometalates [18,19], Fe_3O_4 [20], vanadium-doped zirconias [21] and lead pentacyanonitrosylferrate [22] have been reported. Among potential electrocatalysts used for electrode modification, polyoxometalates (POMs) have been demonstrated as efficient systems to facilitate electrocatalytic reduction of H_2O_2 [23–25]. POMs can accept and release a certain number of electrons, thus serving as multi-electron relays [26]. A detailed discussion on the electrochemical properties and electrocatalytic applications of

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POMs has been presented by Sadakane and Steckhan [27]. POMs can be immobilized on electrode surfaces by: (i) irreversible adsorption to form monolayers [28]; (ii) electrodeposition [29]; (iii) entrapping into polymer matrices [30]; (iv) layer-by-layer approaches [31]; and (v) sol-gel methods [32]. Among these, immobilization of POMs in a polymer matrix is attractive strategy for sensor applications due to flexibility in selecting suitable mediator and simple fabrication procedure. In the recent studies, we have shown the potentiality of polymer-entrapped POMs film modified electrodes for sensor applications [19,33].

In the present investigation, an amperometric electrode for hydrogen peroxide was developed based on phosphotungstate-doped-glutaraldehyde-cross-linked poly-L-lysine film by electrostatically binding the negatively charged $PW_{12}O_{40}^{3-}$ (PW) mediator into positively charged PLL-GA coatings. The modified electrode is stable and exhibits electrocatalytic activity towards hydrogen peroxide only among the electroactive substrates studied such as dopamine, ascorbic acid, and uric acid. Thus, PLL-GA-PW film coated electrode provides a new means for the selective detection of hydrogen peroxide. The non-linear amperometric response is explained in terms of Michaelis–Menten (MM) kinetics, and the associated kinetics parameters are calculated. The practical applicability of the proposed electrochemical sensor was successfully demonstrated from the determination of H_2O_2 in commercially available antiseptic solution and soft-contact lenses cleaning solution.

2. Experimental

2.1. Reagents and chemicals

Sodium phosphotungstate nHydrate ($Na_3[PO_4 \cdot 12WO_3] \cdot nH_2O$; Wako), hydrogen peroxide (Wako) were used as received. Poly-L-lysine hydrobromide (mol. wt = 70,000–150,000) and glutaraldehyde 25% solution in water were obtained from Sigma. All other chemicals used were of analytical grade and used without further purification. As phosphotungstate anion is unstable in neutral and basic aqueous solution and undergoes a series of hydrolysis process, 0.1 M H_2SO_4 was used as a supporting electrolyte. For real sample analysis, the required concentration of real sample was prepared in 0.1 M H_2SO_4 (without giving any special treatment to the real sample) and the measurements were made. Aqueous solutions were prepared using doubly distilled deionized water.

2.2. Electrochemical measurements

All electrochemical experiments were carried out with a single compartment cell, in which a BAS (Bioanalytical Systems, West Lafayette, IN) glassy carbon electrode (area = 0.07 cm^2) was used as working electrode and a platinum wire served as counter electrode. An Ag|AgCl (sat KCl) reference electrode was used to monitor the cell potentials. Cyclic voltammetry (CV) and amperometric experiments were performed with CH Instruments. Constant-potential amperometric measurements were carried out under stirred condition. All the solutions were purged with high purity nitrogen gas for about 20 min before performing electrochemical experiments. Also, a continuous flow of nitrogen over the aqueous solution was maintained during measurements. All the experiments were carried out at room temperature ($\approx 25^\circ \text{C}$).

2.3. Preparation of PW-doped-PLL-GA film modified electrode

Glassy carbon (GC) electrode was polished with $0.05 \mu\text{m}$ alumina on Buehler felt pads and then ultrasonically cleaned for about a minute in water. Finally, the electrode was thoroughly washed

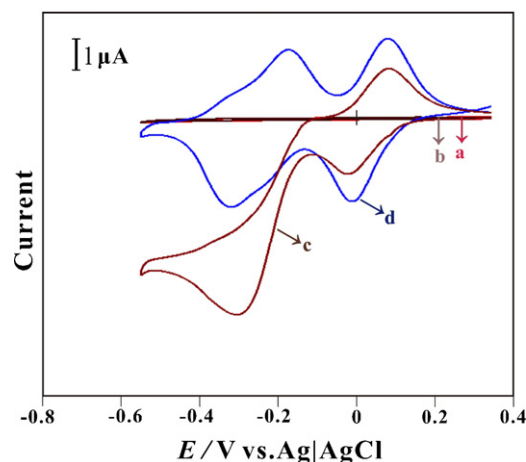


Fig. 1. Cyclic voltammograms in 0.1 M H_2SO_4 containing 1 mM H_2O_2 for different electrodes: (a) bare GCE; (b) PLL-GA coated GCE and (c) PW-incorporated-PLL-GA modified GCE. (d) Response of PW-incorporated-PLL-GA modified GCE in pure 0.1 M H_2SO_4 . Scan rate = 2 mV s^{-1} .

with double distilled water and dried at room temperature. Solutions of product of poly-L-lysine and glutaraldehyde were prepared by mixing 97.5% PLL and 2.5% GA. For this purpose, 1% (w/v) PLL and 0.05% (w/v) GA solutions were used. $10 \mu\text{L}$ of the product solution was placed on the polished electrode surface and allowed in room temperature to evaporate the solvent. The inverted electrode was then placed in a drying oven at 80°C for 5 min. After this drying procedure, the PLL-GA-coated electrode was rinsed with distilled water and immersed in 0.1 M H_2SO_4 solution containing 1 mM phosphotungstic acid, and the electrode potential was cycled continuously 50 times at a scan rate of 100 mV s^{-1} between +0.6 and -0.6 V . After modification, the electrode was rinsed with supporting electrolyte and used for further studies. The amount of PW incorporated into PLL-GA-coating, Γ_{PW} , was calculated using the following equation [34]:

$$\Gamma_{PW} = \frac{Q}{nFA} \quad (1)$$

where Q is the charge consumed, which is obtained from integrating the peak area of cyclic voltammograms of PLLGA-PW electrode at low scan rate in pure supporting electrolyte, n is the number of electrons consumed and A is the geometric area of the electrode.

3. Results and discussions

3.1. Electrocatalytic reduction of hydrogen peroxide at PW-doped-PLL-GA film electrode

Curve 'd' of Fig. 1 shows cyclic voltammetric response of PW-doped-PLL-GA film modified electrode in pure 0.1 M H_2SO_4 . As can be seen, two sets of redox peaks were observed in the potential range +0.35 to -0.55 V corresponding to two one-electron reversible redox processes [35,36]. Upon addition of 1 mM H_2O_2 , there was a dramatic enhancement in the cathodic current of second peak with disappearance of anodic peak, while the peak currents of first redox couple remained unchanged as illustrated by curve 'c'. The voltammetric responses suggested that H_2O_2 was electrocatalytically reduced by the two-electron reduced species of $PW_{12}O_{40}^{3-}$ anion. At the same time, H_2O_2 reduction did not take place at bare GCE as well as on PLL-GA-coated electrode as shown by curves 'a' and 'b', respectively. The electrocatalytic activity of PW-doped-PLL-GA film electrode was further evaluated by investigating the effect of concentration on the peak current response. As shown in Fig. 2, the cathodic peak current of more negative redox

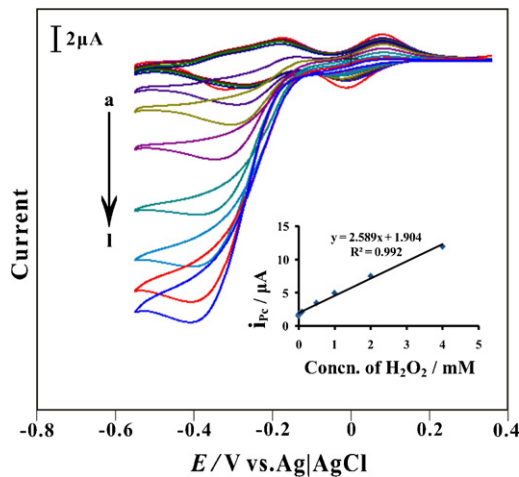


Fig. 2. Cyclic voltammograms of different concentrations of H_2O_2 at PW-incorporated-PLL-GA film modified electrode. Concentrations of H_2O_2 from (a) to (l) are 0, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 2, 4, 7, 10 and 15 mM, respectively. Scan rate = 2 mV s^{-1} . Inset shows calibration curve.

couple increases with increasing concentration while its anodic counterpart disappeared. This behavior is typical of that expected for a mediated electrochemical reaction. Further, the reduction peak current increases with increasing H_2O_2 concentration and the calibration curve was linear from 5×10^{-7} to $4 \times 10^{-3} \text{ M}$ with a sensitivity of $2.59 \mu\text{A mM}^{-1}$ ($R^2 = 0.992$; $n = 8$) as shown in the inset. Based on the voltammetric results, the electrocatalytic behavior of PW-doped-PLL-GA film electrode towards H_2O_2 reduction can be explained by the following mechanism:

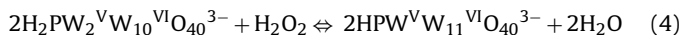
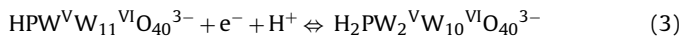


Fig. 3A shows cyclic voltammograms of PW-doped-PLL-GA film electrode at different scan rates in $1 \text{ mM H}_2\text{O}_2$. It can be seen in Fig. 3B that the peak current of H_2O_2 reduction is proportional to square root of scan rate, suggesting that electrocatalytic reduction process is controlled by the diffusion of H_2O_2 from bulk to the electrode/solution interface. Also, a plot of scan rate normalized current vs scan rate, Fig. 3C, exhibits the characteristic shape of an EC_{cat} process [37]. The cyclic voltammetric results of concentration and scan rate dependence study clearly showed that PW-doped-PLL-GA film electrode can effectively catalyze H_2O_2 reduction, and can be advantageously used for quantitative applications.

3.2. Optimization of applied potential for H_2O_2 sensing

Because of higher current sensitivity, amperometry under stirring condition was adopted to evaluate the analytical application of PW-doped-PLL-GA film electrode for H_2O_2 determination. In order to determine the best working potential for hydrogen peroxide sensing, a plot of amperometric current vs working potential was made as illustrated in Fig. 4. The study was performed in $0.1 \text{ M H}_2\text{SO}_4$ applying different potentials in the range from 0 to -600 mV and analysing the response for the same H_2O_2 concentration of 5 mM . It can be noticed that the response was negligible until -100 mV then the steady-state current increases with increasing applied potential with a maximum current at -300 mV . Therefore, -300 mV was selected as the working potential for amperometric detection of H_2O_2 .

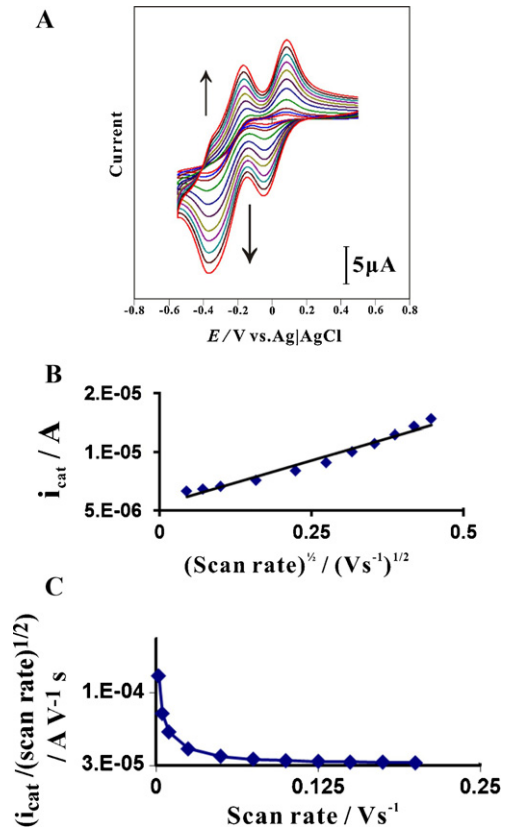


Fig. 3. (A) Cyclic voltammograms of $1 \text{ mM H}_2\text{O}_2$ at PW-incorporated-PLL-GA film modified electrode at different scan rates (inner to outer voltammograms correspond to 2, 5, 10, 25, 50, 100, 125, 150, 175 and 200 mV s^{-1}). (B) Dependence of reduction current vs square root of scan rate. (C) Variation of scan rate-normalized current with scan rate.

3.3. Amperometric response and calibration curve

Curve 'a' of Fig. 5 shows a typical current-time plot for PLL-GA-PW film electrode at -300 mV on successive injection of different concentrations of H_2O_2 into $0.1 \text{ M H}_2\text{SO}_4$. When an aliquot of H_2O_2 is added into $0.1 \text{ M H}_2\text{SO}_4$ solution, the reduction current rises steeply. As demonstrated in the inset of Fig. 6, the steady-state reduction current varies linearly with H_2O_2 concentrations between 2.5×10^{-6} and $6.85 \times 10^{-3} \text{ M}$. The sensitivity of PLL-GA-PW film electrode was $1.69 \mu\text{A mM}^{-1}$. The linear calibration range and sensitivity of PLL-GA-PW film coated electrode are comparable with the values summarized in Table 1 for other POMs-modified electrodes [18,19,23–25,38–40]. Further, it is worthy to mention that the linear range of PW-doped-PLL-GA film electrode is about two orders of magnitude wider, and the sensitivity also nearly 3 times higher compared to SiMo-doped-PLL-GA film electrode [19]. For comparison, similar experiments were performed with bare GCE but the response was poor as shown by curve 'b' of Fig. 5.

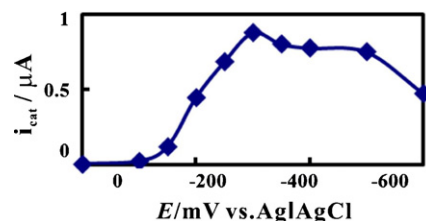


Fig. 4. Dependence of hydrodynamic amperometric response of PW-incorporated-PLL-GA modified electrode on applied potential towards $5 \text{ mM H}_2\text{O}_2$ in $0.1 \text{ M H}_2\text{SO}_4$.

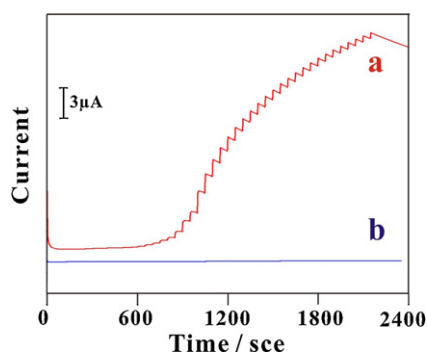


Fig. 5. Amperometric responses of PW-incorporated-PLL-GA modified electrode (a) and bare GCE (b) upon successive injections of different concentrations of H_2O_2 to 10 mL 0.1 M H_2SO_4 under stirred condition. Applied potential = -300 mV.

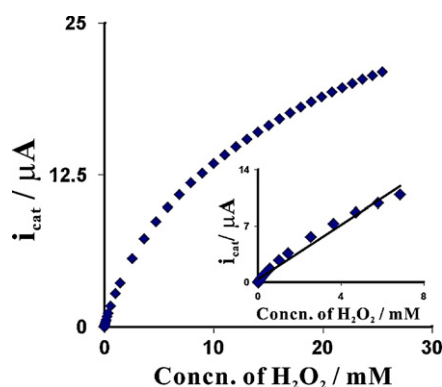


Fig. 6. Calibration curves of PW-incorporated-PLL-GA modified electrode in Fig. 5. Inset shows the linear region of calibration curve.

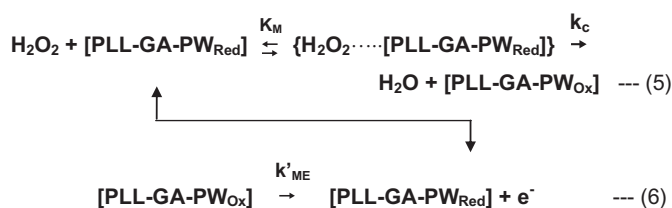
At higher concentrations (above 7 mM) of hydrogen peroxide, the reduction current deviates from linearity and became curvature as shown in Fig. 6. The curvature from the initial straight line shows the characteristics of saturation kinetics, similar to Michaelis–Menten (MM) type kinetics observed in biological system, involving formation of an intermediate complex between the mediator and substrate followed by its slow decomposition to form pre-catalyst and product [41–49] according to Scheme 1.

Here, PW_{Red} and PW_{Ox} represent reduced ($\text{H}_2\text{PW}_2\text{V}_{10}\text{O}_{40}^{3-}$) and oxidized ($\text{HPW}^{\text{V}}\text{W}_{11}\text{O}_{40}^{3-}$) form of second (more negative) redox couple of PW (incorporated into PLL-GA film), respectively. The intermediate complex formed between PW and H_2O_2 is represented by $\{\text{H}_2\text{O}_2 \cdots [\text{PLL-GA-PW}_{\text{Red}}]\}$. K_M is the Michaelis–Menten constant related to the equilibrium step and k_c is the complex decomposition rate constant (s^{-1}).

Table 1

Experimental conditions and analytical parameters for H_2O_2 determination using different POMs-modified electrodes.

Electrode	Method	E_p (mV)	Electrolyte	Linear range (M)	Sensitivity ($\mu\text{A mM}^{-1}$)	LOD (M)	Reference
1. PPy/PMo ₁₂ /Au	FIA	+100 (SCE)	0.5 M H_2SO_4	1×10^{-5} to 1×10^{-2}	–	1×10^{-6}	[24]
2. α_2 - $\text{K}_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ /graphite/organoceramic composite	CA	+435 (Ag/AgCl)	0.1 M Na_2SO_4 + 0.5 M H_2SO_4	1×10^{-4} to 2×10^{-2}	0.8	4×10^{-5}	[18]
3. PMo ₁₂ -doped gel film/Pt	CA	0 (SCE)	0.5 M H_2SO_4	2×10^{-5} to 3×10^{-2}	3.6	7×10^{-6}	[38]
4. Vanadium-17-molybdophos- phate/graphite/methylsilicate composite	CA	+205 (Ag/AgCl)	0.5 M H_2SO_4	1×10^{-3} to 7.5×10^{-2}	324 nA mM^{-1}	4×10^{-4}	[39]
5. PMo ₁₂ -PPy bulk-modified CPE	CA	+180 (SCE)	0.1 M Na_2SO_4 + 0.5 M H_2SO_4	2×10^{-4} to 3×10^{-2}	1.1	5×10^{-5}	[40]
6. P ₂ Mo ₁₈ /OMC/GCE	CA	0 (Ag/AgCl)	1 M H_2SO_4	1.6×10^{-4} to 4.4×10^{-2}	–	5.3×10^{-5}	[25]
7. (APS-PFeW ₁₁)-modified CPE	FIA	0 (Ag/AgCl)	0.5 M H_2SO_4	1×10^{-5} to 2×10^{-4}	0.183 nA μM^{-1}	7.4×10^{-6}	[23]
8. PLL-GA-SiMo-modified GCE	CA	-50 (Ag/AgCl)	0.1 M H_2SO_4	5×10^{-5} to 5×10^{-4}	0.6	–	[19]
9. PLL-GA-PW-modified GCE	CA	-300 (Ag/AgCl)	0.1 M H_2SO_4	2.5×10^{-6} to 6.85×10^{-3}	1.69	–	Present study



Scheme 1.

Lyons et al. [43,44] have proposed a theoretical model for the Michaelis–Menten analysis of amperometric responses of microheterogeneous systems uniformly dispersed in thin polymer film. For the present case, the electrochemical version of Michaelis–Menten equation, in terms of i_{cat} , can be written as:

$$i_{\text{cat}} = \frac{nFAk_c c_{\text{H}_2\text{O}_2}^b \Gamma_{\text{PW}}}{K_M + c_{\text{H}_2\text{O}_2}^b} = \frac{i_M c_{\text{H}_2\text{O}_2}^b}{K_M + c_{\text{H}_2\text{O}_2}^b} \quad (7)$$

where i_M is the maximum catalytic current measured under substrate saturation condition, and all other symbols have their usual significance. The i_M is given by:

$$i_M = nFAk_c \Gamma_{\text{PW}} \quad (8)$$

The electrochemical version of Lineweaver–Burk (L–B; Eq. (9)), Eadie–Hofstee (E–H; Eq. (10)), and Hanes (Eq. (11)) equations, which are useful to evaluate the kinetic parameters K_M , k_c , and i_M , can be obtained by rearranging the Michaelis–Menten equation.

$$\frac{1}{i_{\text{cat}}} = \frac{K_M}{i_M c_{\text{H}_2\text{O}_2}^b} + \frac{1}{i_M} \quad (9)$$

$$i_{\text{cat}} = -\frac{K_M i_{\text{cat}}}{c_{\text{H}_2\text{O}_2}^b} + i_M \quad (10)$$

$$\frac{c_{\text{H}_2\text{O}_2}^b}{i_{\text{cat}}} = \frac{c_{\text{H}_2\text{O}_2}^b}{i_M} + \frac{K_M}{i_M} \quad (11)$$

The kinetic parameters K_M , k_c , and i_M can be readily obtained from the analysis of slopes and intercepts of L–B [$(i_{\text{cat}})^{-1}$ vs $(c_{\text{H}_2\text{O}_2}^b)^{-1}$], E–H [(i_{cat}) vs $(i_{\text{cat}}/c_{\text{H}_2\text{O}_2}^b)$], and Hanes [$(c_{\text{H}_2\text{O}_2}^b/i_{\text{cat}})$ vs $(c_{\text{H}_2\text{O}_2}^b)$] plots [47]. The kinetic parameters calculated using such plots are summarized in Table 2. The average values of K_M , i_M and k_c are found to be 13.6 ± 0.42 mM, 31.73 ± 0.56 μA , and 0.75 ± 0.02 s^{-1} , respectively. The plots (Fig. 7) for L–B, E–H and Hanes analysis showed good straight lines with regression coefficients of 0.9979, 0.9923 and 0.9985, respectively. This is strong evidence to prove that $[\text{PLL-GA-PW}_{\text{Red}}]$ acts as an enzyme-mimic catalyst. Further, the K_M value, 13.6 ± 0.42 mM, is reasonably comparable or even smaller than most of the hydrogen peroxide electrochemical biosensor

Table 2

Comparison of kinetics parameters obtained from different methods for H₂O₂ reduction at PLL-GA/PWA film electrode.

Method	K _M (mM)	i _M (μA)	k _c ^a (s ⁻¹)	R ²	k' _{ME} ^b (×10 ⁻⁴ cm s ⁻¹)
L-B	13.19	31.15	0.73	0.9979	1.73
E-H	13.58	31.79	0.75	0.9923	1.72
Hanes	14.03	32.26	0.76	0.9985	1.69
Average	13.6±0.42	31.73±0.56	0.75±0.02	–	1.71±0.02

^a From $i_M = nFAk_c\Gamma_{PW}$ with $\Gamma_{PW} = 3.12 \times 10^{-9}$ mol cm⁻², $n = 2$.

^b From $k'_{ME} = (k_c\Gamma_{PW}/K_M)$ with $\Gamma_{PW} = 3.12 \times 10^{-9}$ mol cm⁻².

[50–53], which implies that the PLL-GA-PW film exhibits higher affinity for H₂O₂ than that of biomacromolecules immobilized on electrode surface [50,52,53]. Finally, the average value of heterogeneous modified electrode rate constant, k'_{ME} , calculated by substituting k_c and Γ_{PW} values in $k'_{ME} = (k_c\Gamma_{PW}/K_M)$ is found to be 1.71×10^{-4} cm s⁻¹.

3.4. Influence of interference at GCE/PLL-GA/PW electrode

Interference due to other electroactive compounds such as ascorbic acid (AA), dopamine (DA), and uric acid (UA) presents a serious problem in electrochemical sensing of H₂O₂. Therefore, the selectivity of proposed sensor towards amperometric determination of H₂O₂ was evaluated. Fig. 8 illustrates amperometric response of PLL-GA-PW film electrode for the successive injection of H₂O₂ as well as AA, DA, and UA. None of them cause any observable interference to H₂O₂. The experimental results strongly suggest that PLL-GA-PW film coated electrode has high selectivity to H₂O₂.

3.5. Detection and fabrication reproducibility

The applicability of any sensor depends on its reproducibility for successive uses. To characterize the reproducibility, repetitive measurements were performed 5 times in 1 mM H₂O₂ by cyclic voltammetry using the same PLL-GA-PW film electrode. The rela-

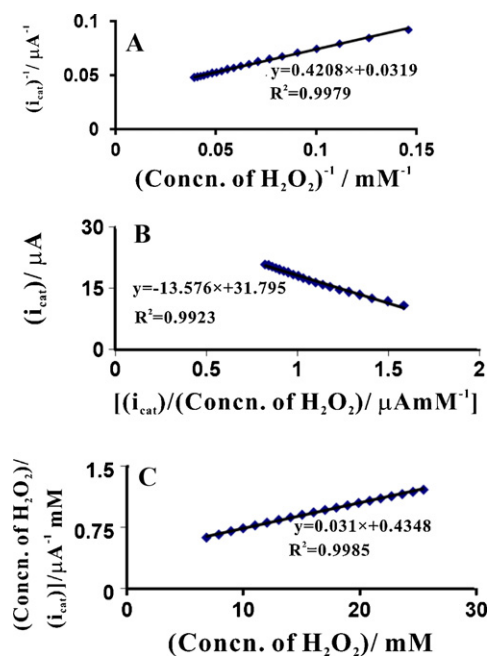


Fig. 7. (A) Lineweaver–Burk plot, (B) Eadie–Hofstee plot, and (C) Hanes plot for PW-incorporated-PLL-GA modified electrode for the data in Fig. 6.

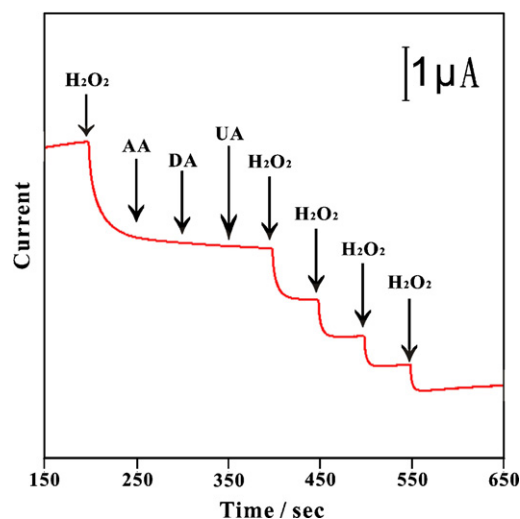


Fig. 8. Amperometric response of PW-incorporated-PLL-GA modified electrode to the additions of 100 μL of various electroactive molecules under stirred condition: 5 mM H₂O₂ (at 200, 400, 450, 500 and 550 s); 5 mM AA (250 s); 5 mM DA (300 s), and 1 mM UA (350 s). Applied potential = –300 V.

tive standard deviation (RSD) of the current values was found to be 6.4% for five measurements, which indicated that PLL-GA-PW film electrode displayed acceptable reproducibility. Also, fabrication reproducibility of three electrodes made independently showed an acceptable reproducibility.

3.6. Stability of PLL-GA-PW film electrode

An important requirement of any modified electrode for the sensor application is its stability in contacting solution or sample. Therefore, the stability of PW-doped-PLL-GA film electrode was checked in pure supporting electrolyte by performing 50 successive cyclic voltammograms. After 50 cycles, the modified electrode shows stable response and the peak currents and peak potentials remain nearly unchanged (not shown), indicating that PW-doped-PLL-GA film modified electrode was relatively stable and can be conveniently used for sensor applications.

In order to assess the long-term operational stability, cyclic voltammetric response of modified electrode in 1 mM H₂O₂ was monitored for seven days. During the test period (between measurements), the PLL-GA-PW film electrode was stored in 0.1 M H₂SO₄. The stability of the modified electrode was evaluated in terms of surface coverage, Γ_{PW} . It was found that negligible amount of mediator was leached out from the film. However, the original electrocatalytic activity of the modified electrode could be restored easily by reloading the same film, after which further measurement were possible. It is worthy to mention that the PLL-GA film, once formed on the electrode surface, could be used continuously for several measurements (we tested up to two weeks). The easy regeneration of the modified electrode to the original electrocatalytic activity makes PLL-GA-PW film electrode attractive for sensor application.

3.7. Real sample analysis

The analytical applicability of the electrochemical sensor developed in the present investigation towards real sample detection was assessed with commercially available antiseptic solution and soft-contact lenses cleaning solution by chronoamperometrically (Fig. 9). The analyses were performed without any sample treatment and the results were compared with those obtained from the classical potassium permanganate titration method [54]. As

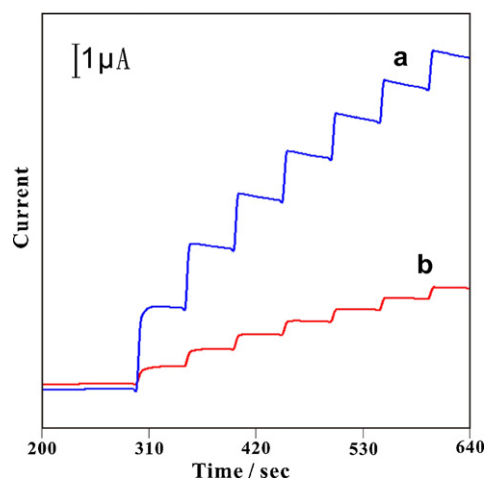


Fig. 9. Amperometric response of PW-incorporated-PLL-GA modified electrode for sequential additions of 100 μL of (a) antiseptic solution and (b) soft-contact lenses cleaning solution. Applied potential = -300 mV .

Table 3

Determination of concentration of H_2O_2 in commercial antiseptic solution and soft-contact lenses cleaning solution by using proposed electrochemical (EC) sensor based on PLL-GA/PWA film electrode and reference method.

Sample	Concentration of H_2O_2 (M)		Relative error (%)
	EC sensor ^a	Reference method ^b	
Antiseptic solution	1.2379 ± 0.062 ($n = 7$) ^c	1.2575^c	-1.6
Soft-contact lenses cleaning solution	0.7416 ± 0.093 ($n = 7$) ^d	0.7421^d	-0.07

^a By amperometry using GCE/PLL-GA/PWA electrode. EC sensor results are obtained by comparison to calibration curve (inset of Fig. 6).

^b From classical titration method with potassium permanganate.

^c Amount of H_2O_2 (in mol l^{-1}).

^d Amount of H_2O_2 (in mol l^{-1}).

summarized in Table 3, the results obtained by using our electrochemical sensor were in close agreement with those determined by titration method and satisfactory. These results indicate the suitability of PLL-GA-PW film based electrochemical sensor for practical application towards quick analysis of hydrogen peroxide solutions.

4. Conclusions

We have demonstrated successful application of PW-doped-PLL-GA film based electrode as simple electrochemical sensor for the selective determination of H_2O_2 . The sensor displays rapid response to H_2O_2 and possesses good stability and reproducibility. The mechanism of electrocatalytic reduction of H_2O_2 at PLL-GA-PW film electrode involves an EC_{cat} process. The linear range covers over three orders of magnitude with a sensitivity of $1.69\ \mu\text{A mM}^{-1}$. The plateau region of calibration curve was explained in terms of Michaelis–Menten saturation kinetics, and the average values of kinetics parameters K_M , i_M , and k_c calculated by using Lineweaver–Burk, Eadie–Hofstee, and Hanes plots were $13.6 \pm 0.42\ \text{mM}$, $31.73 \pm 0.56\ \mu\text{A}$, and $0.75 \pm 0.02\ \text{s}^{-1}$, respectively. Although the modified electrode showed electrocatalytic activity towards hydrogen peroxide, it did not respond to other electroactive interferents such as dopamine, ascorbic acid and uric acid. Thus, PW-doped-PLL-GA film electrode developed in the present investigation shows great potentiality as electrochemical sensor for selective determination of hydrogen peroxide. The application of proposed method for the determination of hydrogen peroxide in

commercially available antiseptic solution and soft-contact lenses cleaning solution was successful.

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