

Full Paper

Non-Enzymatic Glucose Sensor based on Electrodeposition of Platinum Particles on Polyaniline Modified Pt Electrode

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Abstract- A non-enzymatic glucose sensor was successfully developed based on platinum (Pt) particles immobilized on Pt electrode modified with polyaniline film (PANI) modified Pt electrode. The optimal conditions for maximum dispersion of Pt particles on PANI were evaluated. The electrochemical behavior of the Pt/PANI/Pt sensor towards oxidation of glucose was studied in both alkaline (NaOH) and neutral (PBS) electrolytes using cyclic voltammetry and chronoamperometry techniques. The sensor showed a wide linear response to the glucose concentration from 0.1 mM to 12 mM with linear regression coefficient of 0.997. Furthermore, high sensitivity of 215.8 $\mu\text{A mM}^{-1}\text{cm}^{-2}$ is obtained with fast response time of less than 2 s. The as prepared sensor showed good stability, excellent reproducibility, and high selectivity to only glucose in presence of interferences. Finally, the applicability of the sensor was successfully verified with detection of glucose in juice samples. The results obtained were in good agreement with commercial glucose meter. These observations indicate that our sensor is promising in the field of non-enzyme based glucose sensors.

Keywords- Glucose Sensors, Electrochemical, Cyclic Voltammetry, Non-Enzymatic

1. INTRODUCTION

The need for development of simple, sensitive, stable, and selective glucose sensors is vital in various fields such as food industry, pharmaceutical research, clinical science and

biotechnology [1]. The literature study reveals that various techniques have been employed to detect the levels of glucose intermittently or continuously. These include amperometry [2], voltammetry [3], capillary electrophoresis [4], chemiluminescence [5], chromatography [6], spectrophotometry [7], fluorometry [8], and colorimetry [9]. The electrochemical methods are preferred to detect glucose due to easy measurements, high selectivity and sensitivity, portability, low cost, and rapid response [10].

With the development of enzyme-based glucose sensor in 1962 [11], research based on glucose oxidase (GOx) enzyme have taken great attention [12-15]. However, these sensors are not stable as enzyme losses its activity due to change in the environmental conditions such as pH, humidity, and temperature [16]. Many studies have been reported to overcome the drawbacks of enzyme-based glucose sensors for detection of glucose by using non-enzymatic sensors [17]. The mechanism in non-enzymatic glucose sensor is based on electron transfer on electrode surface without the presence of enzymes [18]. The catalytic action in these sensors has been attained with the incorporation of metals and alloys [19].

An ideal sensor should be one that is highly stable, sensitive, reproducible, and fast responsive. All these analytical parameters can be achieved in a single electrode by its modification using conducting polymer/ metal particles composites [20]. Conducting polymers have great contribution towards fabrication of non-enzymatic glucose sensor due to their mechanical stability and long orders of conductance [21]. Of the numerous conducting polymers that are being used in non-enzymatic glucose sensors, PANI has contributed most due to long range of conductivity (over 11 orders) and of its stability to environmental and thermal conditions [22].

In an acid solution, PANI exists in three redox forms. Of these, emeraldine salt (ES) is conductive form that can either be reduced or oxidized to the other two forms, termed as pernigraniline salt (PS) and leucomeraldine salt (LS), respectively. However, only ES form of PANI is conducting and therefore used in fabrication of sensors [23].

Recently, metal nanoparticles have been a source of interest in the development of non-enzymatic glucose sensors as they act as the catalyst in the polymer matrix and has contributed to the increased surface area as well as electrocatalytic properties of the electrode [19,24]. The electrocatalytic behavior of metal nanoparticles is greatly affected by various factors such as substrate concentration, method of preparation, deposition time, particle size, and temperature. In general, the catalytic behavior increases with increasing concentration of substrate and reducing particle size [25]. Numerous studies have been published related to the incorporation of Pt nanoparticles in the development of highly stable non-enzymatic glucose sensors [26-30]. The large surface area of Pt nanoparticles is responsible for the kinetically controlled reaction that results in high sensitivity towards oxidation of glucose in non-enzymatic sensors [31].

Herein, we fabricated a non-enzymatic glucose sensor based on Pt particles immobilized on PANI film modified Pt electrode. The electrocatalytic activity of the proposed sensor towards oxidation of glucose is investigated in both alkaline and neutral electrolytes. The optimum concentration of K_2PtCl_6 solution and number of cycles in CV scan were selected for maximum dispersion of Pt particles on the PANI film. The as-prepared sensor was evaluated for various analytical parameters such as selectivity, sensitivity, stability, detection limits, response time, and reproducibility using cyclic voltammetry and chronoamperometry techniques. Finally, the applicability of the sensor was successfully confirmed by detection of glucose in various commercial juice samples.

2. EXPERIMENTAL SECTION

2.1. Materials & Chemicals

Potassium hexachloroplatinate (IV) (K_2PtCl_6 , 98%, Aldrich, USA), aniline ($C_6H_5NH_2$, $\geq 99.5\%$, Aldrich, USA), hydrochloric acid (HCl, 36.0–38.0%, Fisher Scientific, USA), sulfuric acid (H_2SO_4 , 2N, LabChem, USA), phosphate buffer solution (PBS, 20X, ThermoFisher Scientific, USA), sodium hydroxide (NaOH, 99.4%, Fisher Scientific, USA), uric acid (UA, Nutritional Biochemicals Corporation, USA), ascorbic acid (AA, Acros Organics, USA), sucrose (Aldrich, USA), and D-Glucose (Macron Fine Chemicals, USA). All the chemicals used were of analytical grade. Glucose solutions were prepared in 0.1 M NaOH and 0.1 M PBS.

2.2. Apparatus

The electrochemical studies were conducted at room temperature and carried out using electrochemical analyzer (CHI750C Electrochemical Workstation). In all the experiments, the reference electrode used was saturated calomel electrode (SCE). Pt wire electrode was used as the counter electrode and the modified Pt electrode was the working electrode. The electrochemical analyzer and electrodes were purchased from CH Instruments, Inc., USA. The working electrode was stored in air when it is not use.

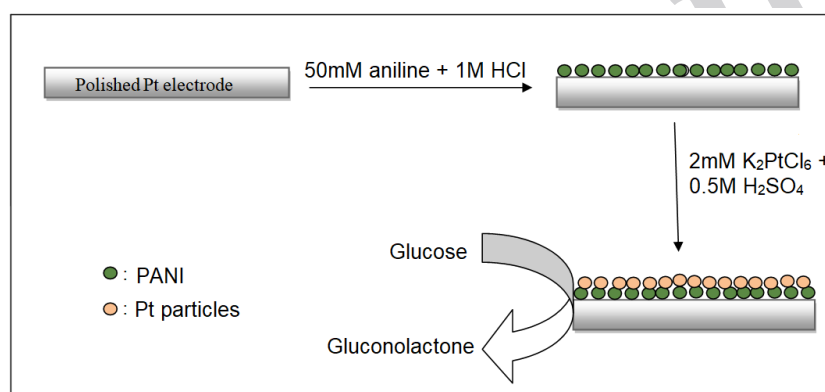
2.3. Preparation of Pt immobilized on PANI modified Pt electrode

Firstly, bare Pt electrode was polished using alumina slurries (0.1, 0.3 and 0.05 μm), rinsed thoroughly till shiny surface and then ultrasonicated in deionized water for 15 min. The polished electrode was further subjected to CV scans in 1 M H_2SO_4 solution to obtain clean Pt electrode (sweep potential: -0.2 V to +0.7 V; scan rate: 50 mVs^{-1}). Further, the electrode was dried in air before electrodeposition of PANI film.

The PANI film was electrodeposited on the Pt electrode from 50 mM aniline in 1 M HCl solution using CV scans for 20 cycles at 50 mVs^{-1} [32]. The green color coating of PANI film

on Pt electrode was observed. This electrode was rinsed with deionized water and dried in air for a day before electrodeposition of Pt particles.

The immobilization of Pt particles on PANI film was done from a solution of 2 mM K_2PtCl_6 in 0.5 M H_2SO_4 using CV. The potential was swept between -0.2 V to and +0.7 V at 10 mVs^{-1} for 30 cycles. The electrode was dried at room temperature and then rinsed with deionized water. The as-prepared electrode was labeled as Pt/PANI/Pt electrode. Another electrode with PANI film modified Pt was prepared by the same method except that Pt nanoparticles were not electrodeposited on it. This was labeled as PANI/Pt electrode. The current response of the Pt/PANI/Pt electrode towards oxidation of glucose was studied in both neutral (0.1M PBS) and alkaline (0.1 M NaOH) electrolytes. The analysis of glucose oxidation was carried out between potentials of -0.8 V and +0.9V at 50 mVs^{-1} . The entire procedure for fabrication of Pt/PANI/Pt electrode is shown in Scheme 1.



Scheme 1. Preparation of Pt particles immobilized on PANI film on modified Pt electrode

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of aniline

The electropolymerization of aniline on the Pt electrode was done through CV technique. For this, bare Pt electrode was dipped in the solution of 50 mM aniline in 1 M HCl, potential swept between -0.2 V and + 1.0 V at scan rate of 50 mVs^{-1} for 20 cycles. Fig. 1 shows the voltammograms obtained during the polymerization of aniline. Two well defined redox couples at potential +0.24 V and +0.81 V represent the formation of PANI polymer film. The peak at +0.20 V is attributed to the transition from the leucoemeraldine (LS) to emeraldine (ES) oxidation states while the peak at +0.81 V is due to the oxidation from the emeraldine (ES) to pernigraniline (PS) oxidation state [32]. The increase in current with cycles indicates that the thickness of the polymer film increases with each cycle. After the complete polymerization, the surface of the modified electrode is coated with green color indicating the formation of conductive ES-PANI.

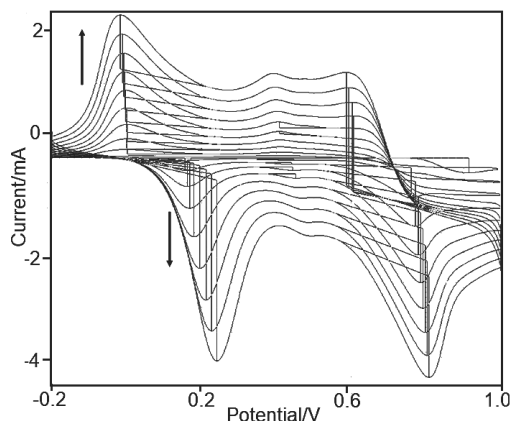


Fig.1. Cyclic voltammogram of electropolymerization of PANI film on Pt electrode. Scan rate: 50 mVs^{-1}

3.2. Effect of K_2PtCl_6 concentration for electrodeposition of Pt particles

The optimum concentration of K_2PtCl_6 solution required for electrodeposition of Pt particles on polymer film was determined by varying concentration of K_2PtCl_6 solution and recording response current with each concentration. The working electrode was modified with different concentrations of K_2PtCl_6 (0.5 mM-6 mM) in 0.5 M H_2SO_4 solution and the corresponding response current was recorded. It is clear from Fig. 2 that the maximum response current is observed at 2 mM K_2PtCl_6 concentration after which the current decreases. Hence, the concentration of K_2PtCl_6 solution was chosen to be 2mM for carrying the electrodeposition of Pt particles on PANI film.

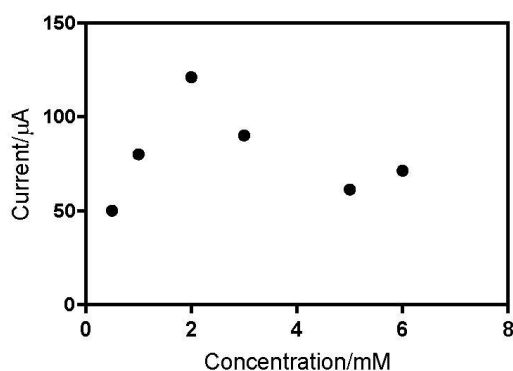


Fig. 2. Behaviour of Pt/PVF/Pt electrode with different concentrations of K_2PtCl_6 solution

3.2.1. Effect of number of cycles during electrodeposition of Pt particles

The electrodeposition of Pt particles on PANI film was carried out through CV technique. The optimum number of cycles during CV scan was determined by subjecting the PANI/Pt electrode in 2 mM K_2PtCl_6 solution for varying number of cycles (5, 10, 15, 20, 25, 30, 35,

and 40). As observed from Fig. 3, the current response increases from 5 cycles to 30 cycles for 5 mM glucose in 0.1 M NaOH after which it gradually falls. This indicates that the maximum number of Pt particles can be immobilized on PANI film for 30 cycles. The decrease in current response at higher scans might be due to the accumulation of Pt particles which resulted in a decrease in surface area available for oxidation of glucose.

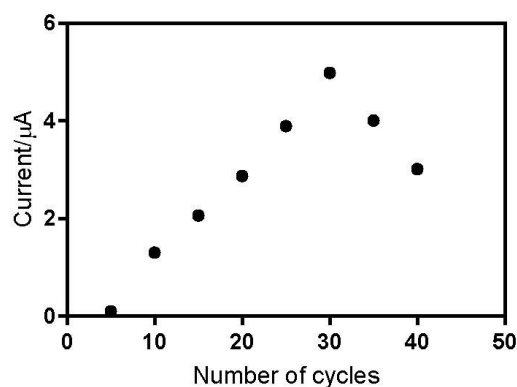


Fig. 3. Behaviour of Pt/PANI/Pt electrode in 5 mM glucose after different number of cycles during CV scans in 2 mM K_2PtCl_6 solution

3.3. Electrocatalytic behavior of Pt/PANI/Pt modified electrode to glucose in different electrolytes

The response of Pt/PANI/Pt electrode towards oxidation of glucose was studied in both alkaline (0.1 M NaOH) and neutral (0.1 M PBS) solutions.

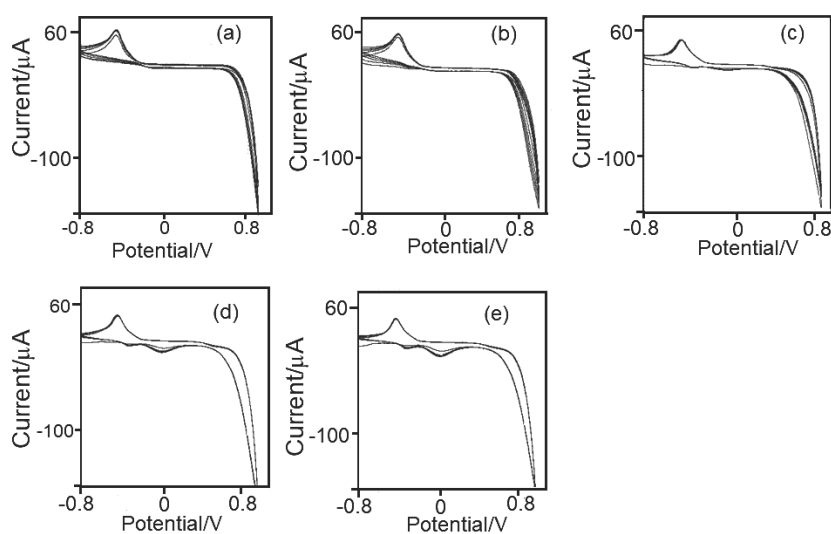


Fig. 4. Cyclic voltammograms of Pt/PANI/Pt modified electrode in 0.1 M NaOH with (a) 0 mM; (b) 4 mM; (c) 8 mM; (d) 12 mM and (e) 16 mM of glucose. Scan rate: 50 mVs^{-1}

The potential was applied between -0.8 V and +0.9 V at scan rate of 50 mVs^{-1} . The current response was recorded for Pt/PANI/Pt electrode without glucose and with different concentrations of glucose (4-16 mM). Fig. 4 shows the response of the Pt/PANI/Pt electrode towards oxidation of glucose in 0.1 M NaOH. As observed, no obvious peak of glucose appears in the blank solution while prominent peak of glucose can be observed at onset of potential -0.33 V for increasing concentrations of glucose with simultaneous increase in the response current (Fig.4 (b)-(e)).

Not only in alkaline solution, Pt/PANI/Pt modified electrode also showed electrocatalytic behavior towards oxidation of glucose in neutral PBS solution. Fig. 5(b-e) displays the oxidation peak of glucose at +0.07 V for different concentrations of glucose in PBS while no obvious peak was observed in the blank solution (Fig. 5(a)). Similar to the behavior observed in NaOH solution, the response current of Pt/PANI/Pt electrode does increase with the increase in concentration of glucose in PBS. However, the current response towards oxidation of glucose in NaOH is larger than in PBS. For instance, comparing the results for 8mM glucose in NaOH and PBS, a current of $4.25 \times 10^{-6} \text{ A}$ at -0.33 V observed in NaOH, which is larger than the current of $3.92 \times 10^{-6} \text{ A}$ at +0.07 V observed in PBS. This can be attributed to the fact that in NaOH solution the protons generated during the dehydrogenation step of the reaction are quickly neutralized by the presence of hydroxyl ions [33,34]. While, in case of PBS the same reaction steps occur slowly due to the absence of hydroxyl ions.

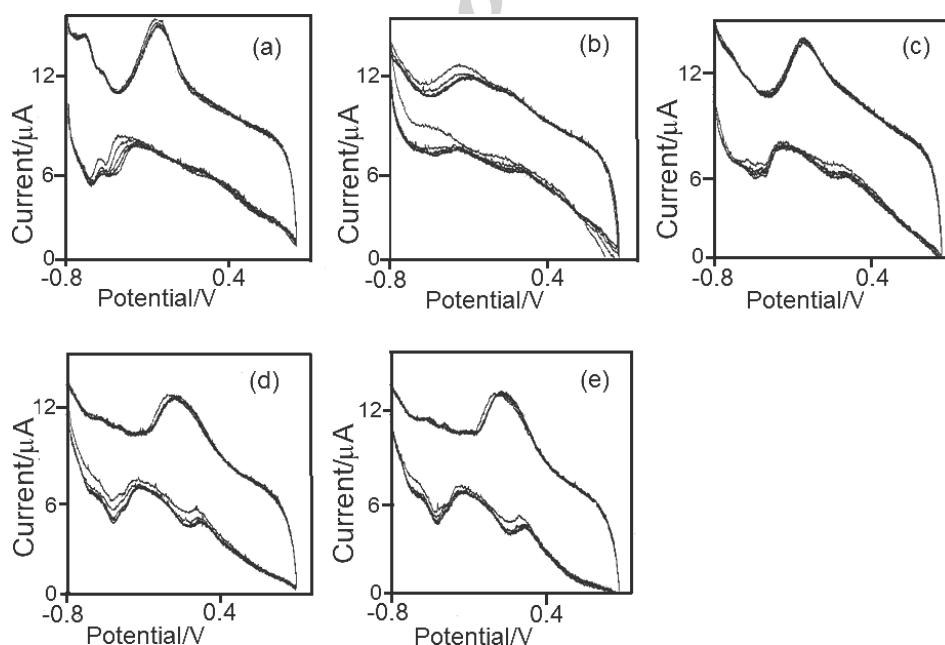


Fig. 5. Cyclic voltammograms of Pt/PANI modified Pt electrode in 0.1 M PBS with (a) 0mM; (b) 4 mM; (c) 8 mM; (d) 12 mM and (e) 16 mM of glucose. Scan rate: 50 mVs^{-1}

3.4. Scan rate

The variation of scan rate towards oxidation of glucose is also an important parameter that has to be considered in development of modified electrode. CV technique was used to study the variation of current response with scan rate in both NaOH and PBS electrolytes. CV was performed at various scan rates (between 10 to 100 mVs^{-1}) in 20 mM glucose solution with Pt/PANI/Pt electrode. Figs. 6 and 7 show the variation of glucose peak current (I_p) with scan rate in NaOH and PBS media, respectively.

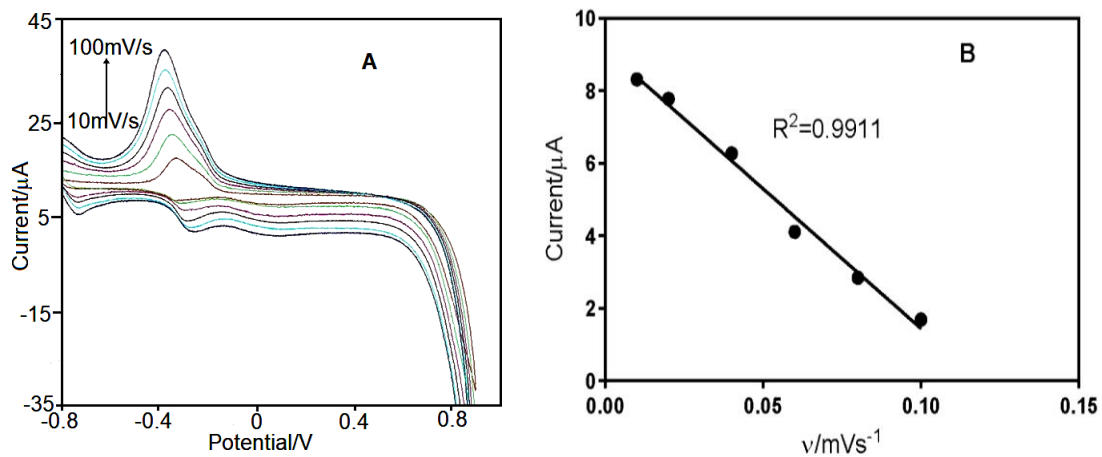


Fig. 6. (A) Cyclic voltammograms of Pt/PANI/Pt electrode examined at various scan rates: 10, 20, 40, 60, 80, and 100 mVs^{-1} in 20 mM glucose in NaOH media; (B) Calibration curve of I_p vs scan rate

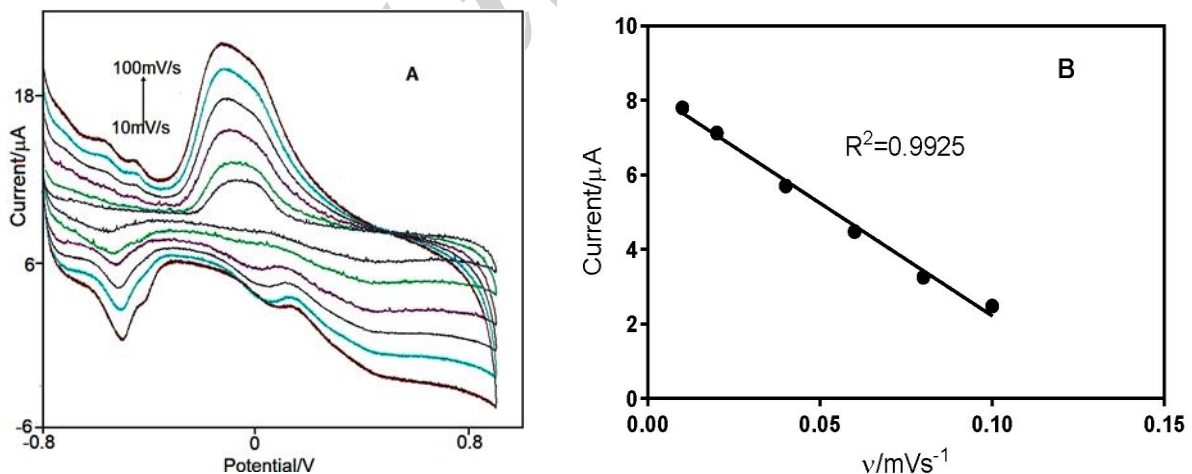


Fig. 7. (A) Cyclic voltammograms of Pt/PANI/Pt electrode examined at different scan rates: 10, 20, 40, 60, 80, and 100 mVs^{-1} in 20 mM glucose in PBS media; (B) Calibration curve of I_p vs. scan rate

As observed from both figures, I_p of glucose increases with the increase in subsequent scan rates. The graph plot between I_p vs. scan rate (Figs. 6B and 7 B, for NaOH and PBS respectively) was linear which indicates that electrochemical kinetics in both NaOH and PBS is surface controlled phenomenon that is an essential requirement for oxidation of glucose [33].

3.5. Chronoamperometric response of Pt/PANI/Pt sensor

After optimizing the conditions for the fabrication of sensor, its analytical parameters were evaluated using CA technique. First, the applied potential was selected where the substantial current is observed due to oxidation of glucose. We studied the effect of applied potential using Hydrodynamic Modulation Voltammetry (HMV) technique. The current response of Pt/PANI/Pt electrode towards oxidation of 5mM glucose (in both NaOH and PBS) was studied at varying potentials (-0.6 V to +0.8 V), keeping the other experimental conditions constant. As shown in Figs. 8(A) and (B), the response current initially increased with an initial increase of potential after which it gradually decreases. In case of NaOH, the current gradually increases and reaches a maximum at -0.03 V after which it decreases. While, in case of PBS the current increases to maximum at potential +0.29 V after which it gradually falls. Therefore, potential of -0.03 V was chosen as operational potential for the chronoamperometric experiments performed in 0.1 M NaOH and +0.29 V for PBS.

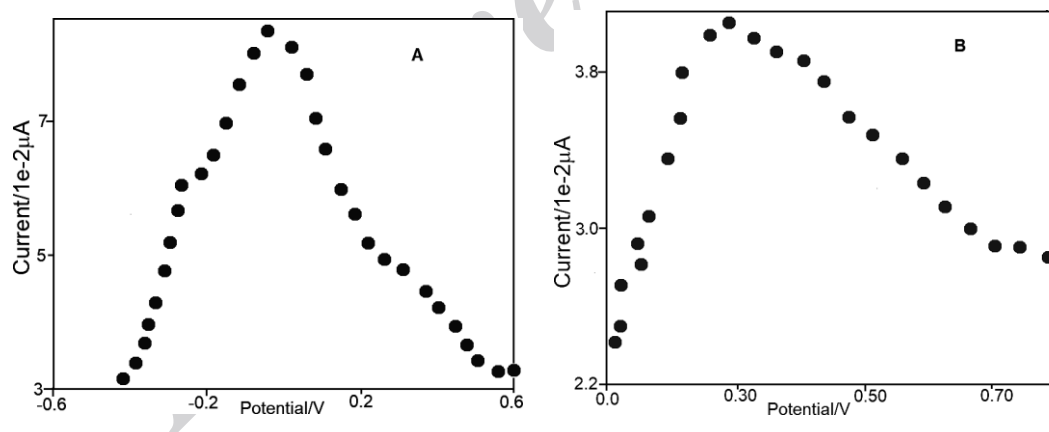


Fig. 8. Effect of varying applied potential on Pt/PANI/Pt electrode to the oxidation of glucose in (A) 0.1 M NaOH; (B) 0.1 M PBS

As observed in section 3.3, the current response of Pt/PANI/Pt electrode towards oxidation of glucose is much higher in NaOH than in PBS, hence we chose to study the chronoamperometric behavior in NaOH media. Figs. 9(A) and (B) display the current response of Pt/PANI and Pt/PANI/Pt electrodes, respectively, with successive additions of glucose concentration at an interval of 50 s at applied potential of -0.03 V. As observed, Pt/PANI/Pt exhibit higher current response towards oxidation of glucose compared to

PANI/Pt that showed unclear steps. It is clear that the Pt particles present in Pt/PANI/Pt electrode are responsible for initiating the electron transfer in the oxidation process of glucose.

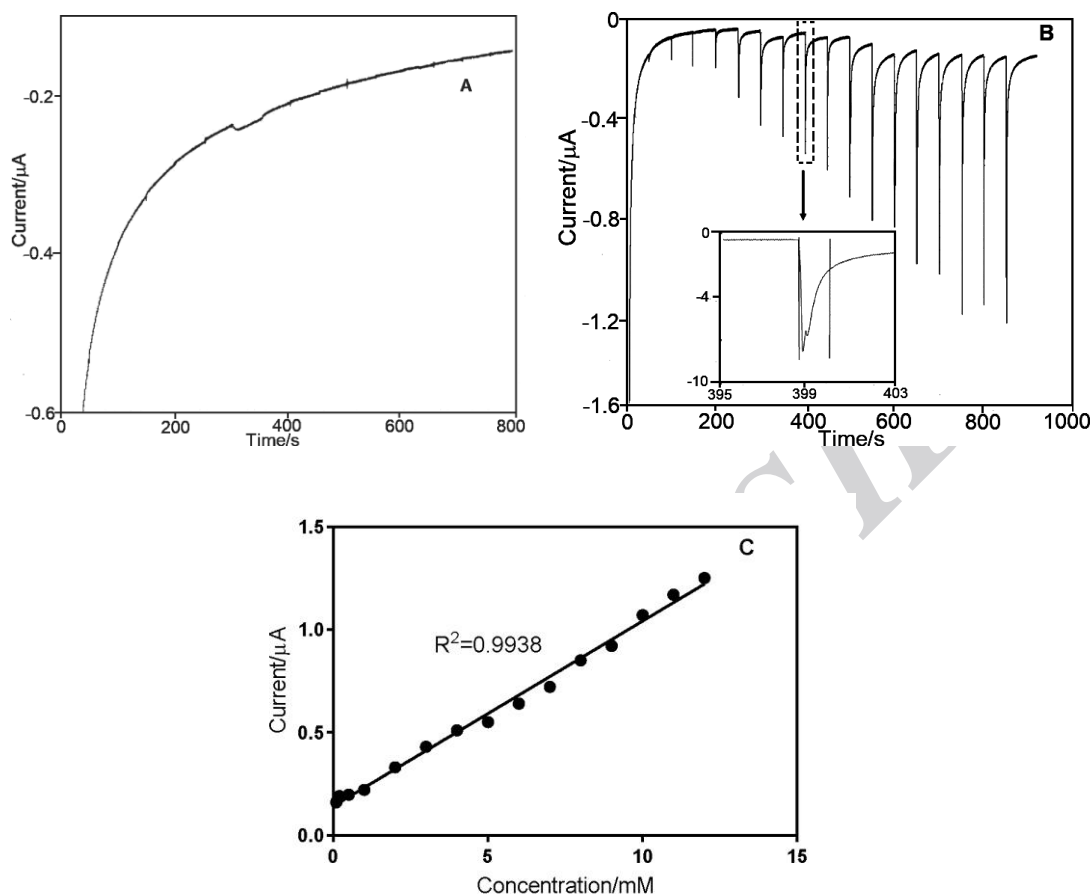


Fig. 9. Chronoamperometric responses of glucose at -0.03 V subject to various concentrations of glucose at (A) Pt/PANI electrode; (B) Pt/PANI/Pt electrode. Insert displays the enlargement of response time towards glucose; (C) Calibration curve obtained for amperometric response of Pt/PANI/Pt electrode

The response current for Pt/PANI/Pt electrode is linear with respect to the increasing glucose concentrations ($R^2=0.9938$) and displays linear range from 0.1 mM– 12 mM (Fig. 9C). The proposed sensor displays fast response time of less than 2 s (insert in Fig. 9B) with detection limit 0.01 mM ($S/N=3$), calculated from the Eq. (1) [35]

$$\text{LOD} = \frac{3\sigma}{s} \quad (1)$$

where, σ = standard deviation of blank solution (10 readings), s = slope of the calibration curve

The sensitivity of the Pt/PANI/Pt electrode was calculated according to the Eq. (2)

$$\text{Sensitivity} = \frac{\text{Slope of the Chronoamperometric Calibration Curve}}{\text{Active Surface Area}} \quad (2)$$

The active surface area can be calculated from the Randles–Sevcik equation at temperature 25°C (Eq. (3)), as the method described by Fotouhi et al [36].

$$I_p = 268600 n^{3/2} A D^{1/2} C v^{1/2} \quad (3)$$

Where, I_p =peak current, n =number of electrons transferred, A =active surface area, D =diffusion coefficient, C =concentration of solution, v =scan rate. Briefly, the voltammograms of the modified electrode was recorded in 0.01 mM of potassium ferrocyanide [$K_4Fe(CN)_6$] redox couple at various scan rates (10, 20, 40, 60, 80 and 100). The slope obtained from linear calibration curve of I_p vs. $v^{1/2}$ is substituted in Eq. (3). From this, the active area of the modified electrode is calculated as 0.000417 cm^2 . The sensitivity of Pt/PANI/Pt electrode from Eq. (2) is calculated as 215.8 $\mu A mM^{-1} cm^{-2}$. The active area obtained seems to be very less as compared to the actual geometrical area. It can be contributed here that the concentrations of PANI and Pt particles used for modification of electrode surface are very less. However, even with this small active surface area our sensor showed high sensitivity. Table 1 shows the performance parameters of our sensor compared with other Pt particles based non-enzymatic sensors reported recently.

Table1. Performance parameters of the proposed sensor compared with other Pt particles based non-enzymatic glucose sensor

Electrode	Potential (V)	Sensitivity ($\mu A mM^{-1} cm^{-2}$)	Response time	LOD	Linear range of detection	Ref.
Pt/GOH	+0.1	137.4	5s	NA	5–20 mM	[26]
PtNCs/graphene	+0.05	1.21	3s	30 μM	1–25 mM	[27]
Pt@TiO ₂ NTAs	-0.4	0.056*	-	0.02×10^{-3} M	-	[28]
Pt ₃ Ru ₁ /GCE	+0.1	31.3	2 s	0.3 μM	5×10^{-7} – 10^{-2} M	[29]
BH-Ag/Pt NPs	-	7.0 [#]	NA	0.013 mM	1–12 mM	[30]
Fe@Pt/C	-0.35	11.75	-	300 μM	1–16 mM	[37]
Pt _x Co _{1-x} /C	+0.10	73.6	3s	0.03 mM	0.10–14.20 mM	[38]
Pt/PANI/Pt	-0.03	215.8	<2s	0.01 mM	0.1–12 mM	This work

NCs: Nanoclusters; NFs: Nanoflowers; NTAs: Nanotube arrays; BH: Bimetallic hollow; * unit of sensitivity is $mAmM^{-1} cm^{-2}$; # unit of sensitivity is $\mu A mM^{-1}$

3.6. Selectivity, Stability & Reproducibility

The interfering species such as ascorbic acid (AA), uric acid (UA) and sucrose have similar activities to glucose and interfere in the oxidation of glucose. The normal physiological level of glucose is much higher than these interfering substances, about 30 times in human blood and more than that in food samples [39]. The selectivity of the Pt/PANI/Pt sensor was examined in presence of interfering species, 0.1 mM AA, 0.1 mM UA and 0.1 mM sucrose. These three interferents along with 1 mM and 5 mM glucose were successively added at interval of 100s in 0.1 M NaOH. As observed from Fig. 10, the current response towards oxidation of glucose is much higher than the other interfering species. Hence, we can conclude that our sensor is able to show specificity and selectivity to glucose only in presence of interfering species.

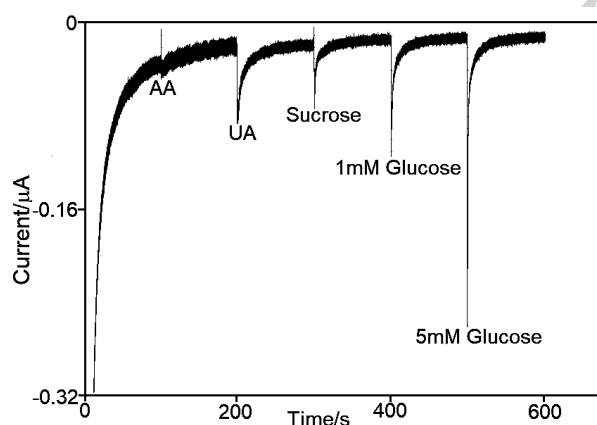


Fig. 10. Chronoamperometric current responses of the Pt/PANI/Pt electrode upon addition of 0.1 mM AA, 0.1 mM UA, 0.1 mM sucrose, 1 mM glucose and 5 mM glucose at -0.03 V

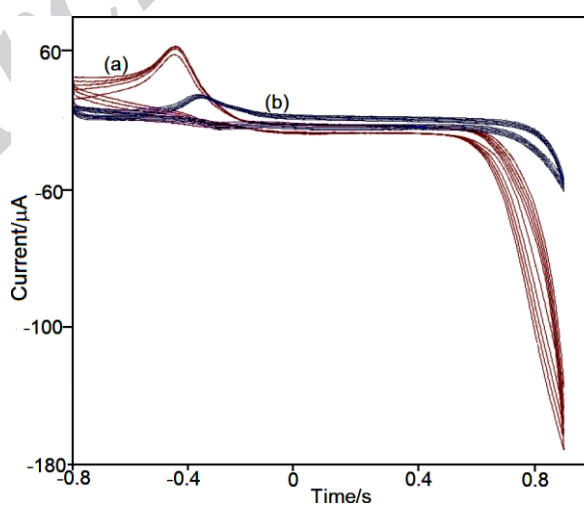


Fig. 11. Current response of 5 mM glucose in 0.1 M NaOH on (a) Day 1 (b) Day 25. Scan rate: 50 mVs⁻¹

To investigate the stability of prepared Pt/PANI/Pt modified electrode its current response was measured for 5 mM glucose over a period of 25 days. During this period, the sensor was continuously used for experiments such as chronoamperometric detection, specificity examination and detection of different concentrations of glucose. After 25 days, only 11.4% loss in current was observed (Fig.11), indicating that our sensor exhibits good stability.

The reproducibility of the proposed sensor was investigated by fabricating three sensors with same procedure under same conditions. The current response of these identical sensors towards 15 mM glucose in 0.1 M NaOH was recorded (Fig. 12). The sensor exhibited excellent reproducibility with RSD of only 2.81%.

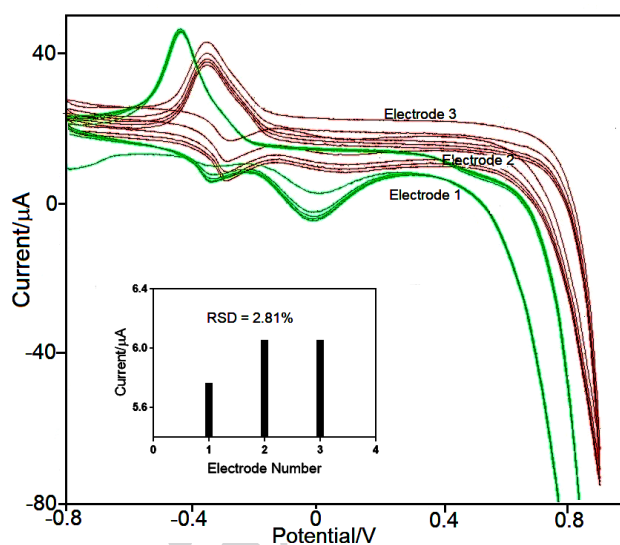


Fig. 12. Current response of three identical Pt/PANI/Pt sensors towards 15 mM glucose fabricated with same method. Insert shows the bar graph comparing peak current of three sensors

3.7. Analysis of Juice Samples

The practical applicability of our sensor was verified with detection of glucose in different commercial juice samples. The concentration of glucose obtained from our method in these juices was compared to the values obtained from glucose meter available in market (TRUEtrack®). Three different varieties of juice samples (mango, pineapple, and orange) were obtained from local store and were made to 1:100 dilution in 0.1 M NaOH. The concentration of the glucose was examined by standard addition method for which the diluted juice sample was spiked with 1 mM, 2 mM, 3 mM and 4 mM glucose [40]. Equal volume of sample and the standard solutions were added at interval of 50 s in 0.1M NaOH (Figs. 13A, B, and C). The graph obtained for I_p against glucose concentration was extrapolated to determine the concentration of glucose in sample (insert of Figs. 13A, B and C). Table 2 displays the results obtained from our method compared to the commercial glucose meter.

These results confirm that our sensor has the potential to be used for routine analysis of glucose.

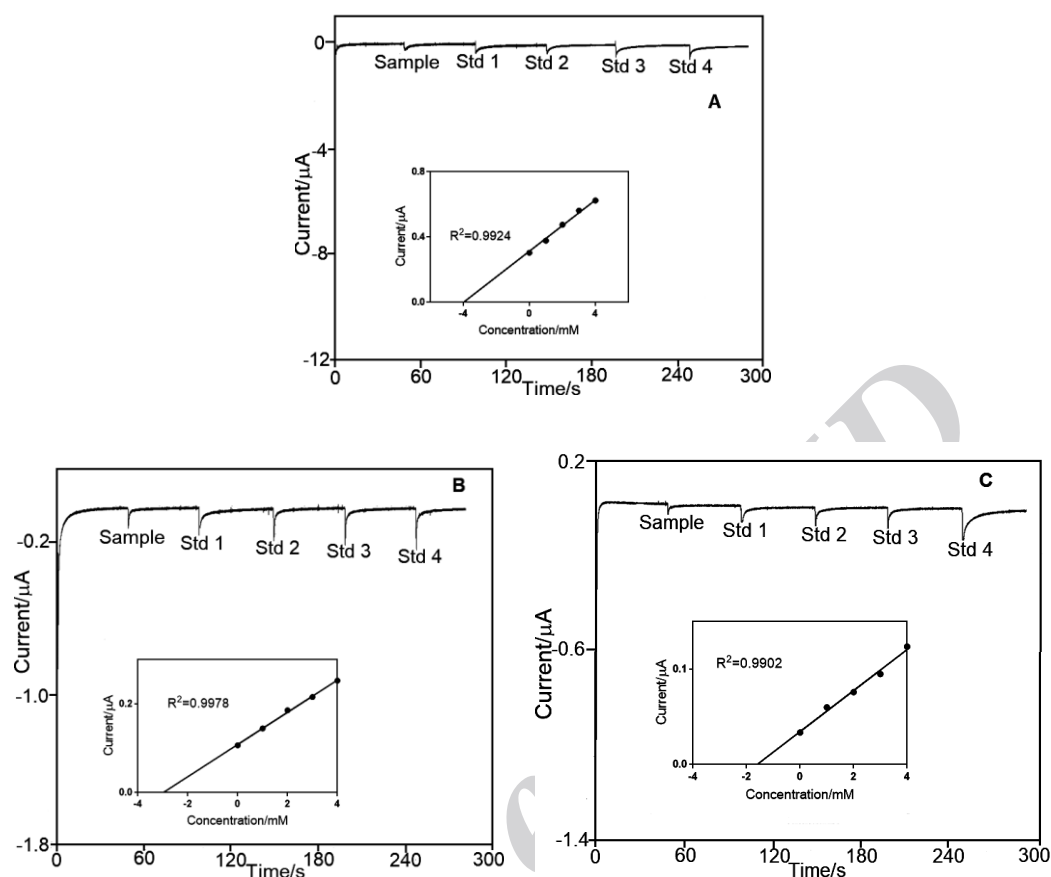


Fig. 13. Chronoamperometric response of Pt/PANI/Pt electrode in determination of glucose in (A) mango juice; (B) pineapple juice ;(C) orange juice. Std1:1 mM, Std2: 2 mM, Std3: 3 mM, Std4: 4mM glucose. Insert shows the respective standard addition curves

Table 2. Glucose detection in different boxed juice samples

Juice Sample	Glucose determined by Pt/PANI/Pt sensor (mmol/L)	Glucose found by Glucose meter (mmol/L)	Bias
Mango	17.7	19.5	-1.8
Pineapple	14.9	15	-0.1
Orange	8	8.88	-0.88

4. CONCLUSION

A non-enzymatic glucose sensor based on electrodeposition of platinum particles on polyaniline film modified on platinum electrode (Pt/PANI/Pt) has been developed. The

Pt/PANI/Pt sensor exhibits high electrochemical activity towards the oxidation of glucose in alkaline electrolyte compare to neutral electrolyte. The proposed sensor showed wide linear response to glucose concentrations in the range of 0.1 mM to 12 mM with high sensitivity of $215.8 \mu\text{AmM}^{-1}\text{cm}^{-2}$ and fast response time of less than 2 s. The sensor displayed good selectivity, stability and reproducibility. Finally, the practical applicability of the proposed sensor was confirmed from successful detection of glucose in various boxed juices.

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