



Short communication

Fabrication of enzymatic glucose biosensor based on palladium nanoparticles dispersed onto poly(3,4-ethylenedioxythiophene) nanofibers

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ABSTRACT

A new methodology involving the combination of a soft template (surfactant) and an ionic liquid (co-surfactant) is used to electrodeposit poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers. Electrochemical deposition of palladium nanoparticles and glucose oxidase (GOx) immobilization are done sequentially into nanofibrous PEDOT to fabricate the modified electrode (ME) (denoted as PEDOT-Pd/GOx-ME). The PEDOT-Pd/GOx-ME displays excellent performances for glucose at +0.4 V (vs. Ag/AgCl) with a high sensitivity ($1.6 \text{ mA M}^{-1} \text{ cm}^{-2}$) in a wider linear concentration range, 0.5 to 30 mM (correlation coefficient of 0.9985). Further, the electrode is insusceptible to the electroactive interfering species.

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1. Introduction

Several enzyme-based amperometric glucose biosensors have been developed by exploiting the advantages of the enzyme, glucose oxidase (GOx) and the synergistic properties of components in the modifying layer of the electrodes. Nanostructured materials have become the focus of scientific researchers due to their inherent characteristics. ZnO nanorods [1], carbon nanotubes [2], nanostructured polymers [3,4] etc. have been successfully employed to immobilize enzymes due to their high surface area. A glucose sensor has been fabricated utilizing the functional properties of poly(3-aminophenyl boronic acid) and the high surface area of a nanofibrous polymer matrix [5]. Further, matrices for enzyme immobilization were developed by dispersing metal nanoparticles into conducting polymers. They possess large surface area and high catalytic activity and utilized for biosensor applications [6,7].

Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the conducting polymers, exhibits long term electrochemical stability and electroactivity in phosphate buffer (pH 7) and hence finds applications in biosensors [8]. PEDOT-poly (styrene sulfonate) (PSS) composite based organic thin film transistors have been exploited as glucose sensor [9,10]. Setti et al. [11] developed an electrochemical biosensor utilizing inkjet printing technology. A thin layer of PEDOT-PSS was inkjet printed on top of an indium tin oxide coated glass slide and used as a probe for glucose detection. PEDOT-gold nanoparticles composites were synthesized and their sensing capability toward dopamine and

uric acid in the presence of excess ascorbic acid was demonstrated [12]. In addition, gold nanoparticles were dispersed onto PEDOT-PSS thin film and used as an electrochemical transducer for sensing β -nicotinamide adenine dinucleotide and alcohol [7].

However, nanostructured PEDOT has not been utilized so far for the fabrication of a glucose sensor. And, to the best of our knowledge, there is no report on the synthesis of nanostructured PEDOT with dispersion of metal nanoparticles and used for biosensing application. Among the transition metals, palladium (Pd) is a preferred one to modify the electrode because of its various advantageous properties [13]. Different methodologies have been attempted to incorporate Pd particles into polymer matrices and modify the surface of electrodes [14].

In this report, we have utilized a “micellar assisted soft template” approach for the electrodeposition of nanofibrous PEDOT onto the surface of electrode. A surfactant and an ionic liquid were collectively used toward this purpose. Further, Pd nanoparticles and GOx were incorporated into PEDOT nanofibers. Thus, PEDOT-Pd/GOx-ME was fabricated and tested for its electrochemical activity towards glucose. PEDOT-Pd/GOx-ME exhibits excellent performances to the synergistic augmentation from nanofibrous PEDOT and Pd nanoparticles.

2. Experimental

Glucose oxidase (GOx; 256 U mg^{-1}) and other chemicals/reagents were purchased from Aldrich. Aqueous solutions of glucose were prepared afresh in 0.1 M phosphate buffer saline (PBS, pH 7). Cyclic voltammetry and amperometry measurements were performed using EG&G PAR 283 Electrochemical Analyzer. Field emission transmission electron microscope (FETEM) measurement was performed with JOEL

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JEM-2000EX transmission electron microscope. Electrochemical Quartz Crystal Microbalance, EQCM (Autolab-Maxtek PM-710) was used to estimate the enzyme activity.

Electrodeposition of PEDOT was performed on the surface of glassy carbon electrode (3 mm in diameter) by cyclic voltammetry. In a typical experiment, solution of EDOT (0.1 M), prepared in the mixture of ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-[BF₄]) and the surfactant, sodium dodecyl sulfate (SDS) with a molar ratio of 0.2:0.8, was subjected to potential cycles between -1.0 V and 1.3 V (vs. Ag/AgCl) at a sweep rate of 20 mV s^{-1} for 30 cycles. Deposition of Pd nanoparticles and GOx incorporation were done sequentially through electrochemical method. Further, a thin layer of Nafion (3.0 μl) was coated on the surface of the PEDOT-Pd/GOx-ME.

3. Results and discussion

3.1. Fabrication and morphology of PEDOT-Pd/GOx-ME

Fig. 1 presents the consecutive cyclic voltammograms (CVs) recorded during the electrochemical polymerization of EDOT in a solution containing a mixture of [bmim]-[BF₄] and SDS (molar ratio, 0.2:0.8). In the CV of the first potential scan, a peak was observed around $+1.20$ V for the oxidation of EDOT. In the subsequent potential scans, redox peaks corresponding to PEDOT were noticed around 0.0 and $+0.40$ V and 0.0 V and -0.80 V during anodic and cathodic potential scans, respectively. The current values at the redox peaks increased steadily with the number of potential scans. Thus, formation of an electroactive PEDOT film was evident. A current loop could be seen (Fig. 1) at the end of positive potential scan. This signifies the nucleation/growth mechanism for the formation of PEDOT [15]. Further, peak positions of PEDOT redox processes were found to be shifted for the electro-polymerization of EDOT performed in the absence of SDS. Redox peaks were observed around -0.38 V and $+0.32$ V (during anodic scan) and -0.64 V and $+0.13$ V (during cathodic scan), respectively [16]. The inset shows the CV recorded for the PEDOT film in a monomer free electrolyte solution. Typically, three oxidation peaks were observed around -0.4 , $+0.1$ and $+0.5$ V. On the reverse scan, three broad peaks were observed around $+1.0$, $+0.3$ and -0.2 V. These redox peaks indicate that PEDOT was p-doped.

Electro-deposition/stripping of Pd particles was performed in a solution containing PdCl₂ (0.5 mM) in 0.5 mM [bmim]-[BF₄] at a scan rate of 100 mV s^{-1} (Fig. 2a). During the cathodic sweep, a reduction wave

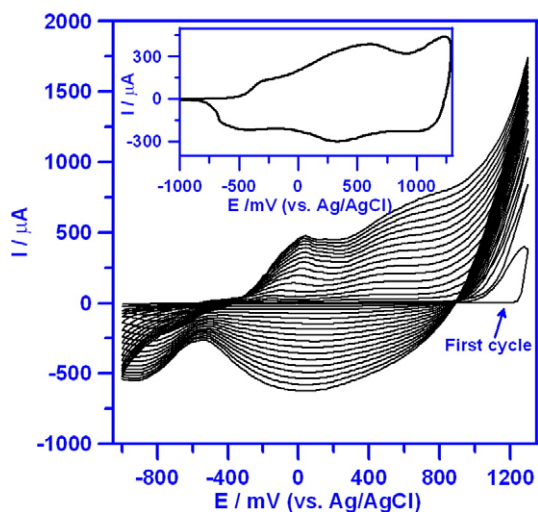


Fig. 1. Cyclic voltammograms recorded during the electrochemical polymerization of 0.1 M EDOT in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-[BF₄]) and sodium dodecyl sulfate (SDS) (0.2:0.8); scan rate: 20 mV s^{-1} . Inset shows the CV recorded at PEDOT electrode in monomer free electrolyte solution.

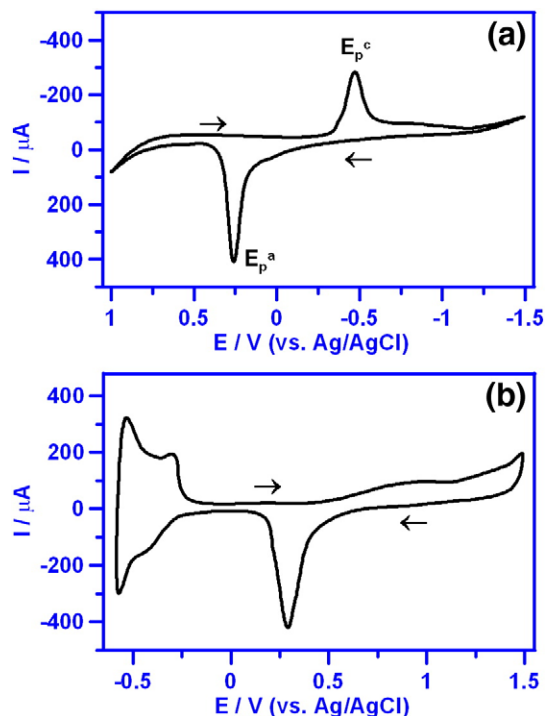


Fig. 2. (a) Cyclic voltammogram recorded at PEDOT electrode in the solution containing 0.5 mM PdCl₂ and 0.5 mM [bmim]-[BF₄]. (b) Cyclic voltammogram of Pd nanoparticles deposited PEDOT electrode in 0.1 M H₂SO₄ at a scan rate of 100 mV s^{-1} .

corresponding to the conversion of Pd²⁺ to Pd⁰ was observed at -0.5 V. In the reverse scan, a peak for the stripping of Pd⁰ was observed at $+0.25$ V. However, when electro deposition of Pd⁰ was performed in [bmim]-[Cl], the reduction wave was observed at -0.61 V [17]. The shift in the peak potential for Pd⁰ deposition is attributed to the donor property of [bmim]-[Cl].

CV of the Pd⁰ particles loaded PEDOT modified electrode was recorded in 0.1 M H₂SO₄ solution (pH 1.2) at a scan rate of 100 mV s^{-1} (Fig. 2(b)). CV exhibits the typical features of a polycrystalline Pd electrode [18]. One could observe two pairs of well defined anodic and cathodic peaks in the "hydrogen region". The redox pair observed around -0.6 V is due to the oxidation/reduction of dissolved hydrogen. The other redox pair at -0.3 V corresponds to the oxidation/reduction of

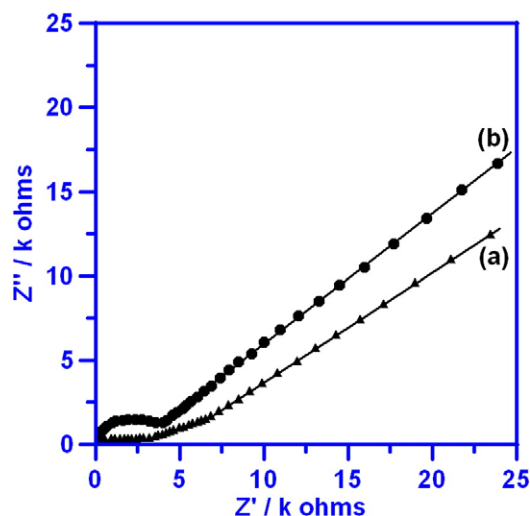


Fig. 3. Electrochemical impedance spectra recorded before (a) and after (b) immobilization of GOx at Pd nanoparticles deposited PEDOT electrode in the solution containing 1 mM K₃[Fe(CN)₆] in KCl and PBS mixture (0.1 mM each).

chemisorbed hydrogen. Pd particles are oxidized to the higher oxidation state, Pd^{4+} , leading to the formation of PdO_2 when the potentials were beyond +0.70 V [19]. The peak observed in the reverse scan of potential at +0.3 V is due to the reduction of PdO_2 to Pd^0 .

Subsequently, GOx was immobilized into PEDOT–Pd–ME to fabricate PEDOT–Pd/GOx–ME. Typically, a constant potential of –1.0 V was applied for 10 min to PEDOT–Pd–ME in an aqueous solution containing 1.0 mg ml^{-1} GOx. After the application of potential, the electrode was washed with distilled water to remove the enzyme molecules which were not strongly bound to the PEDOT–Pd matrix.

In order to authenticate the immobilization of GOx onto PEDOT–Pd–ME, electrochemical impedance spectra (EIS) were recorded. Fig. 3 shows the EIS responses of PEDOT–Pd and PEDOT–Pd/GOx electrodes for 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in KCl and PBS (0.1 mM each). The Nyquist plots show a semicircle at higher frequencies corresponding to the electron-transfer-

limited process. The linear portion that appeared at lower frequency corresponds to the diffusion-limited process. The charge transfer resistance (R_{ct}) values for PEDOT–Pd–ME and PEDOT–Pd/GOx–ME were determined to be 2.51 k Ω and 4.89 k Ω , respectively. The value of R_{ct} depends on the dielectric and insulating properties at the electrode/electrolyte interface. The increase in R_{ct} for PEDOT–Pd/GOx–ME is attributed to the hindrance of electron-transfer kinetics by the presence of GOx. This signifies the successful immobilization of GOx to the electrode. The enzyme activity of GOx was determined by measuring the amount of H_2O_2 formed using the o-dianisidine method [20]. The value was found to be 8.32×10^{-2} U. Further, we have estimated the enzyme activity of GOx immobilized onto PEDOT–Pd–ME through EQCM as 8.58×10^{-2} U.

FETEM image of PEDOT–Pd–ME (Fig. 4a) reveals the existence of bundles of nanofibers (PEDOT) with diameters of the individual fiber in

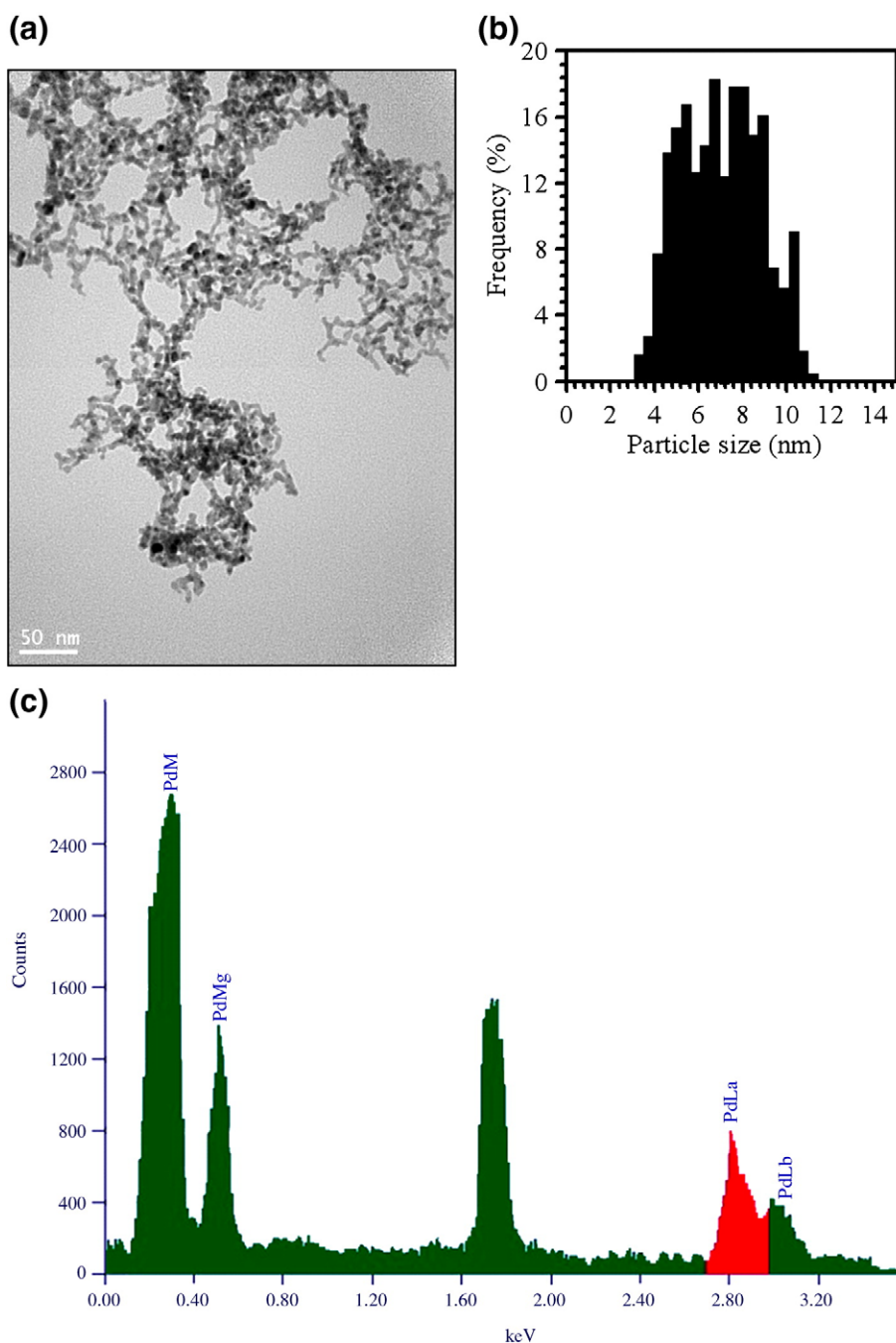


Fig. 4. FETEM image (a), size distribution curve of Pd nanoparticles (b) and EDAX spectrum (c) of PEDOT–Pd–ME.

the range of 5 to 10 nm. Pd nanoparticles with sizes of about 5–10 nm (Fig. 4b) were found to be dispersed on the surface of PEDOT nanofibers. The presence of Pd nanoparticles was further confirmed by EDAX analysis (Fig. 4c).

The roles of [bmim]-[BF₄] and SDS in the formation of PEDOT nanofibers is detailed. PEDOT nanofibers were formed through a self-assembled micellar soft-template approach [21] in the presence of mixture of [bmim]-[BF₄] and SDS. This is based on earlier reports [21–23]. Efforts have been earlier invested to bring out the behaviour of surfactant and the self assembly of surfactant molecules within ionic liquids [22]. The formation of micelles was demonstrated for different combinations of ionic liquids and surfactants [22]. Surfactants generally tend to form aggregates or micelles in a number of different types of solvents [23]. In water, normal micelles that spontaneously form from surfactant molecules are expected. However, the dissolution of a surfactant in an ionic liquid alters the surface tension at the air–water interface. This has been ascribed due to solvatophobic interactions of the ionic liquid with hydrocarbon portion of the surfactant [23]. The micelles formed with a mixture of ionic liquid and a surfactant could influence the salvation interactions between the added solute and ionic liquid. Thus, the ratio of surfactant to ionic liquid decides the size and structure of the micelles [24]. In the present work, a mixture of [bmim]-[BF₄] and SDS (molar ratio of 0.2:0.8) was used to form micelles. Upon addition of EDOT into the mixture of [bmim]-[BF₄] and SDS, molecules of EDOT prefer to be present within the cylindrical micelles probably due to its hydrophobicity. Upon application of potential, the self-assembled EDOT molecules inside the cylindrical micelles were oxidized and transformed into nanofibrous PEDOT [21]. Importantly, the absence of SDS or [bmim]-[BF₄] in the electrolyte did not result PEDOT with fibrous morphology. This clearly demonstrates the role of combined presence of [bmim]-[BF₄] and SDS to generate nanofibrillar morphology. It is to be noted that when polystyrene sulfonate was used as an electrolyte during the electrodeposition of PEDOT, film of PEDOT with microrings/arrows morphology has been deposited through ‘micro bubbles assisted’ growth mechanism [25]. In the present work, [bmim]-[BF₄] also functions as the dopant for PEDOT besides its role as a co-surfactant along with SDS to form micelles and to result PEDOT nanofibers.

3.2. Hydrodynamic response of glucose at PEDOT–Pd/GOx–ME

PEDOT–Pd/GOx–ME was tested for the electrochemical detection of glucose. Hydrodynamic voltammograms were recorded in the potentials between –0.5 V and 0.6 V (interval of 50 mV) for a solution of glucose (20 mM in PBS) at PEDOT–Pd/GOx–ME (line a in Fig. 5) and PEDOT/GOx–ME (line b in Fig. 5). PEDOT–Pd/GOx–ME exhibited excellent electrocatalytic activity towards the reduction and oxidation of enzymatically formed H₂O₂ (line a). However, no obvious reduction

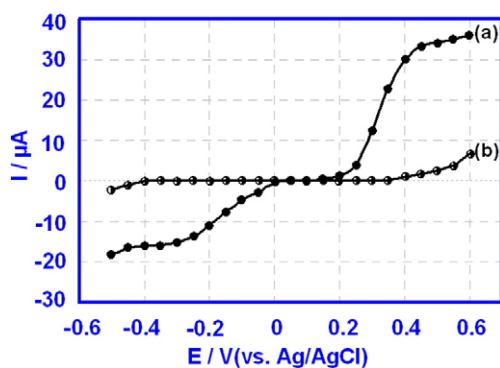


Fig. 5. Hydrodynamic voltammograms recorded at PEDOT–Pd/GOx–ME (a) and PEDOT/GOx–ME (b) to 20 mM glucose in PBS.

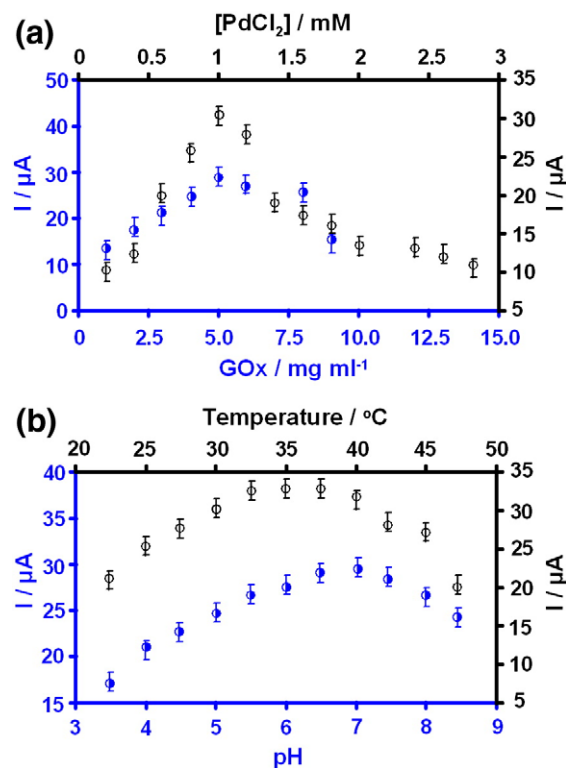


Fig. 6. Amperometric current responses observed at PEDOT–Pd/GOx–ME as a function of (a) PdCl₂ and GOx loading, (b) pH and temperature; *E* = +0.4 V, [glucose]: 20 mM.

or oxidation current was observed between –0.5 and 0.5 V (line b) for PEDOT/GOx–ME (without loading of Pd nanoparticles). These observations clearly reveal that Pd nanoparticles that are dispersed in the PEDOT nanofibers facilitate the electrochemical reduction/oxidation of enzymatically formed H₂O₂ [26]. Pd nanoparticles provide larger surface area with specific interaction towards the substrate. It can be seen that oxidation current is predominant over the reduction process (line a) and hence, an operating potential of +0.4 V was chosen for the further experiments.

3.3. Optimization of experimental parameters

Amperometric measurements were further performed to study the influence of various experimental parameters on the sensitivity of PEDOT–Pd/GOx–ME. Fig. 6 shows the influence of current responses towards glucose using varieties of electrodes prepared with different amounts of enzyme and Pd nanoparticles. Experiments were also done for various pHs and temperature. The calibration curve was deduced from the average of amperometric current responses of six different electrodes. It can be seen from Fig. 6(a) that the amount of PdCl₂ and GOx used in the fabrication of PEDOT–Pd/GOx–ME has a profound influence on the electrochemical behavior of electrode towards glucose. The response current increases with increase in the loading of GOx. However, a substantial decrease in current response was observed at higher enzyme loading (>5.0 mg ml^{–1}). This could be due to the decrease in electron relaying capacity by higher enzyme loading and its insulation effect. A maximum current response was noticed with PEDOT–Pd/GOx–ME prepared with PdCl₂ of about 1 mM. PEDOT–Pd/GOx–ME fabricated with a higher concentration of Pd (>1 mM) showed a lower current response. The amount of Pd nanoparticles deposited from 1 mM of PdCl₂ was found to be 63 μg cm^{–2} [27].

PEDOT–Pd/GOx–ME displayed a larger plateau in current response between the selected range of pHs, with a maximum response at

pH 7 (29.45 μA) (Fig. 6(b)). With an increase in temperature, the current response showed an increasing trend. However, a temperature of 25 °C was selected to avoid the denaturation of GOx. In all, an optimum response was obtained at PEDOT-Pd/GOx-ME toward glucose for a GOx loading of 5.0 mg ml⁻¹ and Pd nanoparticles of 63 $\mu\text{g cm}^{-2}$ in pH 7 at 25 °C. Hence, further amperometric measurements were performed with these optimized conditions.

3.4. Analytical performance of PEDOT-Pd/GOx-ME

The current–time response of the PEDOT-Pd/GOx-ME recorded at +0.4 V is shown in Fig. 7. The current shows a linear function with glucose concentration in the range between 0.5 and 30 mM. (Fig. 7-inset). However, beyond the concentration of 30 mM, the response current reached a saturation with increase in concentration which informs that the enzyme–substrate interaction follows a typical Michaelis–Menton kinetics [2,3]. The sensitivity of the PEDOT-Pd/GOx-ME is estimated to be 1.6 mA M⁻¹ cm⁻², a value comparable to polypyrrole nanotubes [28] and carbon nanofiber [29] based sensors. The detection limit was calculated to be 75 μM (glucose concentration giving a signal equal to the blank signal y_B (intercept) plus five standard deviation of y -residuals $s_{y/x}$).

3.5. Influence of interference at PEDOT-Pd/GOx-ME

The selectivity of the PEDOT-Pd/GOx-ME towards glucose was also evaluated. The electroactive substances such as ascorbic acid (AA), uric acid (UA) and acetaminophen (AP) had no interference on the detection of 5 mM glucose (Fig. 8). It is to be noted that a thin layer of Nafion was coated over the modified surface as an effective perm-selective membrane for the anionic redox active species (AA and UA) [2,3]. However, in the absence of the Nafion layer over the surface of PEDOT-Pd/GOx-ME, current signal due to the oxidation of interfering species was witnessed (Fig. 8-inset).

3.6. Repeatability, reproducibility and life time

The repeatability of the amperometric measurements at PEDOT-Pd/GOx-ME was tested with seven calibration plots by using the same PEDOT-Pd/GOx-ME in the range of glucose concentration between 0.5 and 30 mM (R.S.D. = 1.85%). In order to evaluate the reproducibility of the

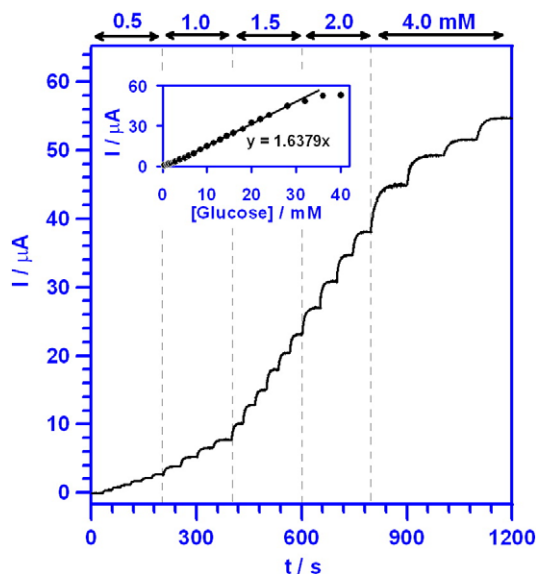


Fig. 7. Amperometric responses of PEDOT-Pd/GOx-ME to the successive addition of glucose at the potential of +0.4 V in PBS. Inset shows the calibration curve.

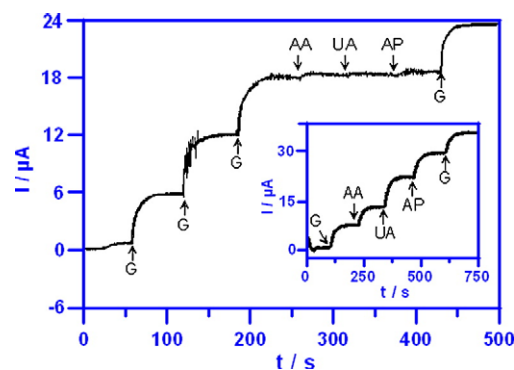


Fig. 8. Amperometric responses of PEDOT-Pd/GOx-ME with and without Nafion layer (inset figure) to 5 mM glucose (G) and ascorbic acid (AA), uric acid (UA) and acetaminophen (AP) of 1 mM each in PBS.

responses at the PEDOT-Pd/GOx-ME, six different electrodes were fabricated concurrently and the amperometric measurements were made. The PEDOT-Pd/GOx-ME was reliable and reproducible with a R.S.D. value of 8.5%.

The life time of the PEDOT-Pd/GOx-ME was evaluated by performing repetitive calibration graphs for glucose concentration between 0.5 and 30 mM. After each measurement, the electrode was stored in PBS (pH 7) at 4 °C. Five consecutive calibration graphs were plotted and the mean value of the slopes was obtained for every day. Interestingly, no significant change in mean value of the slope was observed for first 12 days. However, after this, the electrode yielded only 75% of the original response. The decrease in response may be due to denaturation of the enzyme which was immobilized onto the modified surface. As well, there could be deterioration of the electronic conductivity of PEDOT caused by the oxidation products of enzymatically formed H₂O₂.

3.7. Real sample analysis

Reliability and practical use of PEDOT-Pd/GOx-ME were tested by estimating the glucose concentration in human serum sample and comparing the value with a commercial glucose meter (EZ Smart blood glucose monitoring system; ME-3301). The sample was diluted to half of its concentration using PBS (pH 7). The glucose level was determined to be 7.58 mM and 7.33 mM at PEDOT-Pd/GOx-ME and glucose meter, respectively. The results obtained at PEDOT-Pd/GOx-ME agreed well with an error value of 3.24%. With a R.S.D. value of 2% ($n=6$), PEDOT-Pd/GOx-ME is proved to be useful in real sample analysis for the detection of glucose.

4. Conclusions

A new methodology involving the combined use of a soft template and an ionic liquid was successfully utilized to electrodeposit nanofibrous PEDOT. Pd nanoparticles and GOx were subsequently incorporated into nanofibrous PEDOT to fabricate the glucose biosensor, PEDOT-Pd/GOx. The glucose biosensor exhibited high sensitivity, good linear in current response for a wider concentration and high selectivity towards glucose. The methodology adapted in the present study to fabricate the glucose biosensor could form the basis for development of varieties of other biosensors.

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