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Simultaneous determination of dopamine and ascorbic acid on poly (3,4-ethylenedioxythiophene) modified glassy carbon electrode

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Abstract Detection of dopamine (DA) in the presence of excess of ascorbic acid (AA) has been demonstrated using a conducting polymer matrix, poly (3,4-ethylenedioxythiophene) (PEDOT) film in neutral buffer (PBS 7.4) solution. The PEDOT film was deposited on a glassy carbon electrode by electropolymerization of EDOT from acetonitrile solution. Atomic force microscopy studies revealed that the electrodeposited film was found to be approximately 100 nm thick with a roughness factor of 2.6 nm. Voltammetric studies have shown catalytic oxidation of DA and AA on PEDOT modified electrode and can afford a peak potential separation of ~ 0.2 V. It is speculated that the cationic PEDOT film interacts with the negatively charged ascorbate anion through favorable electrostatic interaction, which results in pre-concentration at a less anodic value. The positively charged DA tends to interact with the hydrophobic regions of PEDOT film through hydrophobic–hydrophobic interaction thus resulting in favorable adsorption on the polymer matrix. Further enhancement in sensitivity to micro molar level oxidation current for DA/AA oxidation was achieved by square wave voltammetry (SWV) which can detect DA at its low concentration of $1 \mu\text{M}$ in the presence of 1000 times higher concentration of AA (1 mM). Thus the PEDOT modified electrode exhibited a stable and sensitive response to DA in the presence of AA interference.

Keywords Conducting polymer · Poly (3,4-Ethylenedioxythiophene) · PEDOT · Dopamine · Ascorbic acid · Hydrophobic

Introduction

Conducting polymers (CP) offer myriad opportunities to couple analyte–receptor interactions into observable (transducible) responses. The advantages of CP-based sensors over devices using small molecule (chemosensor) elements are the potential of the CP to exhibit collective properties that are sensitive to very minor perturbation [1]. Thus, CPs obtained elegantly by electropolymerization, offer a simple approach to construct a sensor electrode. The advantages of electropolymerization are: (a) thin, uniform and adherent polymer films can be obtained; (b) polymer film can be deposited on a small surface area with a high degree of geometrical conformity and controllable thickness using a specific number of growth cycles in potentiodynamic mode and (c) deposition can be effected on selected areas, especially in the case of microsensors. Among the numerous polymeric materials developed and studied over the past few decades, polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) constitute an important class [2]. Among those, PEDOT has received a significant amount of attention as an electrode material for a variety of applications in organic light-emitting devices, polymer batteries, electrochromic windows, etc. [3–4]. It shows a very high conductivity of the order of 500 S cm^{-1} in the *p*-doping range [5] and good stability and transparency in the oxidized state and can serve as the most promising CP for practical applications. Further it can be synthesised electrochemically from both aqueous and non-aqueous media [6–8] and the conductivity of the PEDOT film does not change significantly with the counter ion [9].

Dopamine (DA), belonging to the class of catecholamines, plays a vital role in the function of central nervous, renal, hormonal and cardiovascular systems. The development of methods for quantification of DA in blood and biological fluids is currently a subject of intense investigations [10–14]. Since DA is easily

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oxidisable, electrochemical method offers itself as an ideal choice for its quantitative determination. However, electrochemical oxidation of DA at conventional electrodes is found to be difficult because of (a) fouling of the electrode surface due to the adsorption of oxidation products, (b) interference due to the co-existence of ascorbic acid (AA) in biological fluids, which also undergoes oxidation more or less at the same potential and (c) concentration of AA being relatively higher ($\sim 10^3$ times) than that of DA in these samples, which results in poor selectivity and sensitivity for DA detection. Hence, development of a DA sensor using voltammetric protocols for the detection of DA in the presence of excess of AA is a challenging task. Attempts to detect DA using electrochemical approaches based on surface coatings [15], carbon paste electrodes [16], self-assembled monolayers [17–19], interfaces between two immiscible electrolyte solutions (*ITIES*) [20] etc., each one associated with its own advantages and limitations, have been reported.

Studies on the behavior of PEDOT in phosphate buffer solutions show a high degree of stability when compared to other CPs, thereby showing that PEDOT can be a potential candidate for sensor applications and hence chosen for the detection of DA in our investigations. In an earlier preliminary communication [21], we have reported the possibility of detecting DA in the presence of excess of AA using PEDOT/Au coated GC electrode by achieving significant separation between the oxidation peak potentials of DA and AA. The peak potential separation was tentatively explained using the argument that DA tends to reside on the hydrophobic regions of the PEDOT electrode and AA on the hydrophilic regions (energetically different), leading to their preferential oxidation at these sites. Interestingly, other factors such as electrostatic interactions based on the forms that DA and AA exist in solution can also afford this kind of peak separation. The investigations described in this study offer insights into this aspect. Detailed investigations have been carried out on the simultaneous detection of DA in the presence of excess of AA on a PEDOT modified GC electrode. The PEDOT film on GC was prepared by electropolymerization from a non-aqueous medium and its characteristics were also examined.

Experimental

Materials

3,4-ethylenedioxythiophene (EDOT, Baytron M) was a gift sample provided by Bayer-AG (Germany). Dopamine (Acros), ascorbic acid (E-Merck, India), tetrabutylammonium perchlorate (TBAPC) (Aldrich), potassium dihydrogen phosphate (E-Merck, India), sodium hydroxide (E-Merck, India) were used as received. The aqueous solutions were prepared using Milli-Q water (18.3 Ω) (Millipore).

For voltammetric studies, a glassy carbon (ϕ 3 mm, BAS, Inc.) working electrode, a platinum wire coil auxiliary electrode and an Ag⁺/AgCl (3 M NaCl) reference electrode were used and the potential values mentioned in this text are against this reference electrode unless otherwise mentioned. Phosphate (0.1 M) buffer solution of pH 7.4 was employed as the electrolytic medium.

Instrumentation

Voltammetric experiments were carried out using a Potentiostat/Galvanostat BAS 100 B (Bioanalytical Systems Inc.) at ambient temperature ($25 \pm 1^\circ\text{C}$). To record the square wave voltammograms (SWV), the following input parameters were used: step potential, 4 mV; square wave amplitude, 25 mV; frequency, 15 Hz; quiet time, 2 s; and sensitivity, 10 μA . Peak currents were determined either after subtraction of a manually added baseline or as absolute peak heights above zero.

Poly (3, 4-ethylenedioxythiophene) films (coated on ITO glass substrates supplied by Donnelly Corp., USA) were characterized by PicoSPM Atomic Force Microscopy (Molecular Imaging, USA) operated in 'contact' mode. Gold coated SiN₃ cantilever (Force Constant 0.12 N/m) was used as the force sensor and the radius of curvature of the probe tip was about 5–10 nm. The measurement was made with the "small" 6 μm piezoelectric z-scanner, which was standardized using calibration gratings supplied by molecular imaging.

Methods

Preparation of PEDOT modified GCE

The GC electrode surface was polished first with fine emery paper and then with 1.0 and 0.06 μm alumina powder, and finally sonicated with Milli-Q water for 5 min. Before electropolymerization, the polished electrode was pretreated by cycling it between -0.9 and $+1.5$ V at 10 V/s in acetonitrile containing TBAPC for 10 min. Then PEDOT was electrodeposited on the electrode from a solution of 10 mM EDOT + 0.1 M tetrabutyl ammonium perchlorate in acetonitrile by potential cycling between -0.9 V and 1.5 V vs. Ag wire pseudo-reference electrode. PEDOT film was allowed to grow on GC surface for five successive scans, as seen from the increasing anodic and cathodic peak current densities. The electropolymerization of EDOT was highly reproducible and the cyclic voltammograms obtained for the electropolymerization agreed closely with that reported earlier [22]. The modified electrode is hereafter referred to as GC | PEDOT.

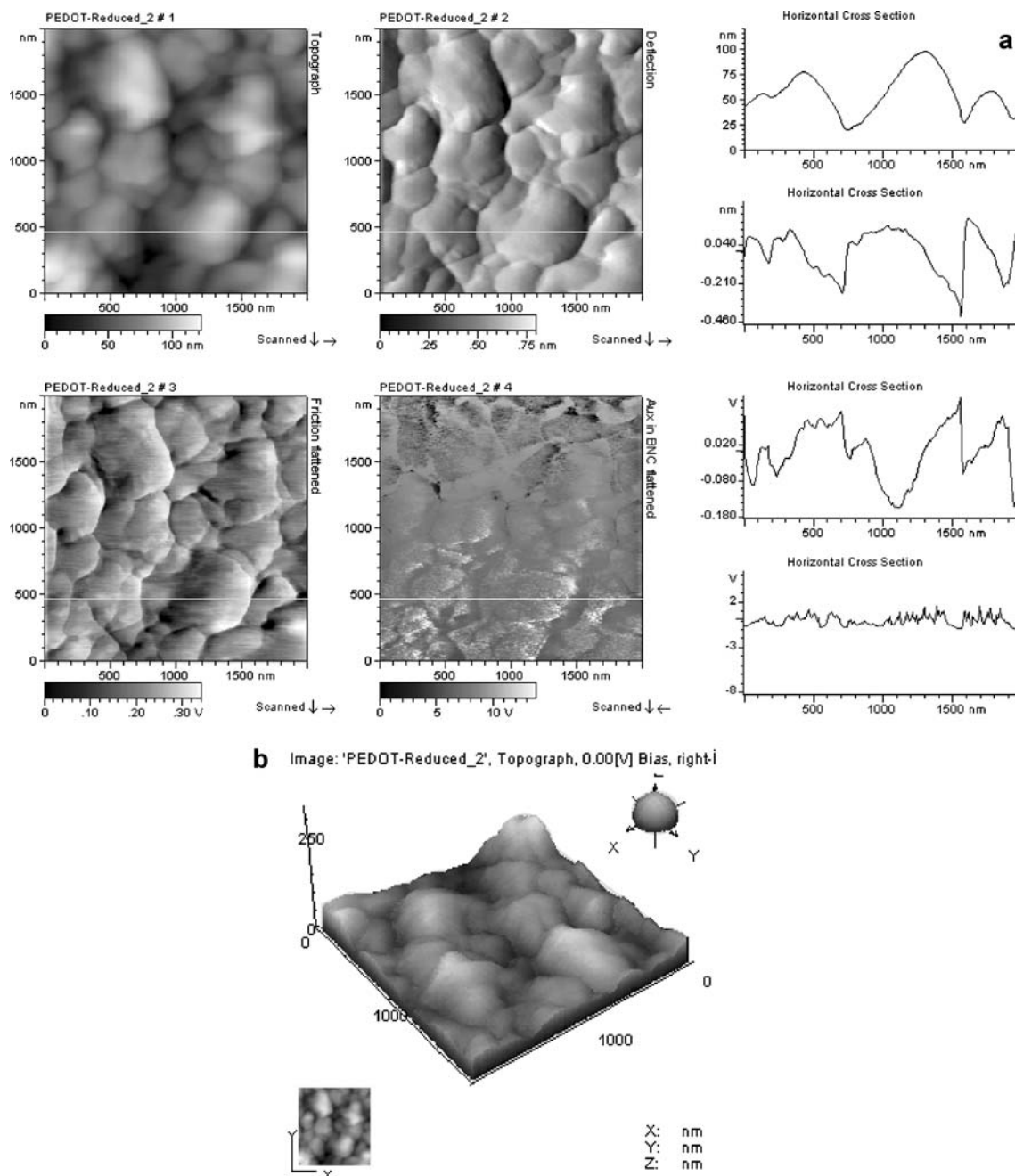
Results and discussion

Characterisation of GC|PEDOT

The surface characteristics of the PEDOT film coated on an ITO glass substrate were examined by AFM. The film was grown by cycling the electrode potential between -0.9 V and 1.5 V vs. Ag wire pseudo-reference (five cy-

cles) in acetonitrile solution containing TBAPC. Figure 1a shows the typical topography, deflection, friction and current images obtained simultaneously for the same area of the film. Since the topographic image could not be sharpened further, it is also shown in its three-dimensional version (Fig. 1b), which gives a clear image of the surface. The deflection and friction images reveal a non-uniform globular structure, which is densely packed. From the horizontal cross section analysis, the minimum and maximum globule size was estimated to be in the range of 50 – 500 nm. The thickness of the film was measured to be 100 ± 20 nm. The surface smoothness of the film was found to have ~ 10 nm variations in the z direction, which shows the deposition of a smooth film.

Fig. 1 a Typical topography, deflection, friction and current images obtained for an as-grown PEDOT film in a 0.1 M TBAPC acetonitrile solution and their cross section analysis. The scan was 2×2 μm . **b** Three-dimensional view of the topographic image



The current image shows that the current flow is uniform over the entire surface area of the PEDOT film except for some small areas (darker ones). It is relevant to note that 100 nA is the maximum limit of the Pico-Scan current amplifier employed in these experiments. It is likely that currents higher than 100 nA could have resulted at fully oxidized (fully doped) areas of the film even at a bias potential of 1.0 V. Similar observations in the case of 3-methylthiophene have been reported by Su-Moon Park et al. [23].

Roughness analysis of polymer films was carried out and the value of the mean roughness R_a was calculated as the deviations in height from the profile mean value

$$R_a = \frac{1}{N} \sum_{i=1}^N |Z_i - Z| \quad (1)$$

where Z is defined as the sum of all height values divided by the number of data points (N) in the profile. The roughness value, estimated from these images using Eq. 1 was 2.6 nm, which is very close to the values reported for polyaniline film deposited from a solution containing sodium dodecylsulfate [24].

Cyclic voltammetry

Figure 2 shows the cyclic voltammograms (CVs) of DA (1 mM) on GC and GC | PEDOT electrodes. On bare GC, DA is oxidized at around 0.190 V yielding an oxidation peak current of $31 \pm 3 \mu\text{A}$, while on the reverse scan a reduction peak at around 0.115 V is observed.

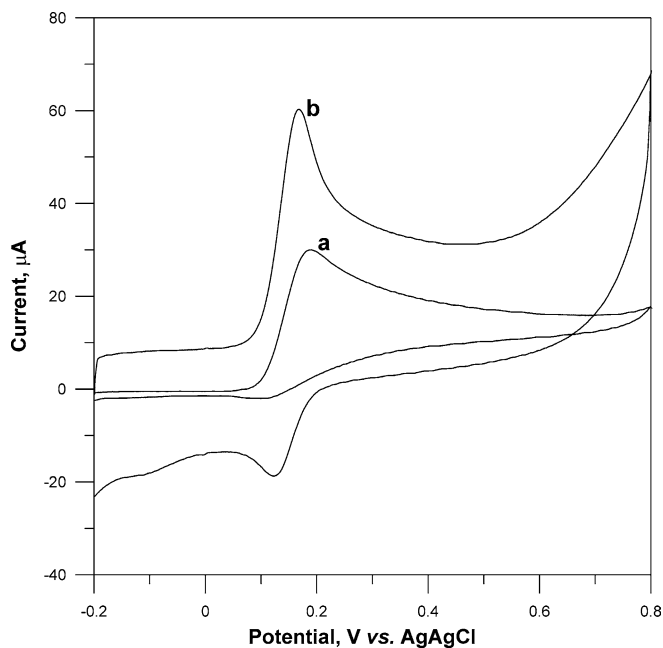
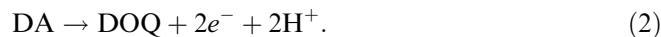


Fig. 2 Cyclic voltammetric behaviour of DA (1.0 mM) at **a** bare GC and **b** GC | PEDOT electrodes in PBS of pH 7.4. Scan rate 0.05 V s^{-1}

The peak separation ($\Delta E_p = 0.075 \pm 0.002 \text{ V}$) reveals that the oxidation process is quasi-reversible, which agrees very well with previous reports [25]. DA undergoes oxidation to its *o*-quinone form, DOQ that involves a two-electron transfer



On GC | PEDOT, DA gets oxidized at around 0.17 V, yielding an oxidation peak current of $52 \pm 3 \mu\text{A}$. When compared to bare GC, there is no appreciable potential shift for the DA oxidation on GC | PEDOT. However, the oxidation peak current has increased by 1.7 times, which indicates the catalytic oxidation of DA on the modified electrode. During reverse scan, a cathodic peak is observed at around 0.125 V and ΔE_p is found to be $0.045 \pm 0.002 \text{ V}$, which corresponds to a near-reversible process.

The CVs for the oxidation of AA (1 mM) on GC and GC | PEDOT electrodes are depicted in Fig. 3. On bare GC, AA is oxidized at around 0.22 V and a peak current of $15 \pm 2 \mu\text{A}$ is noticed. The oxidation peak is found to be broad and no peak in the reverse scan is observed, which reveals that the oxidation of AA at bare electrode is totally irreversible. During successive cycles, the reproducibility of the electrode response suffers possibly due to the fouling effect caused by the adsorption of the oxidation product of AA on the electrode surface.

On GC | PEDOT electrode, AA oxidation peak occurs at around -0.035 V , indicating a cathodic shift of 0.25 V when compared to the bare electrode. Further, the oxidation peak is sharp on the modified electrode

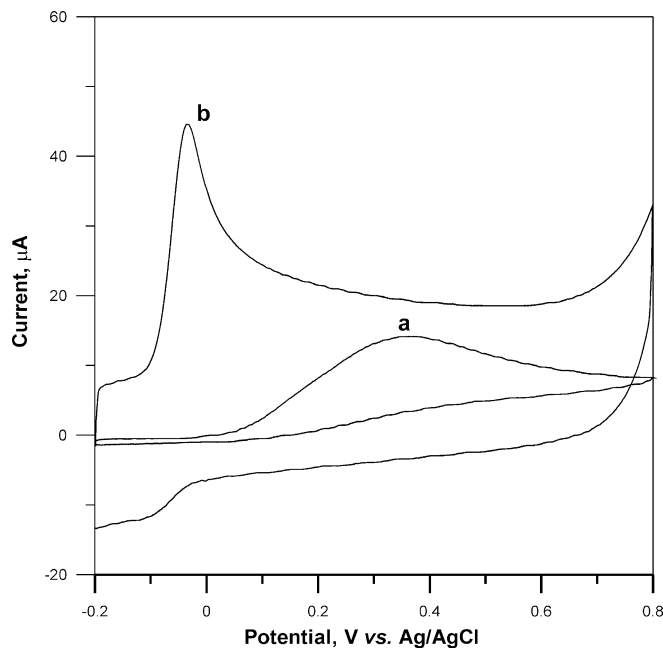


Fig. 3 Cyclic voltammetric behaviour of AA (1.0 mM) at **a** bare GC and **b** GC | PEDOT electrodes in PBS of pH 7.4. Scan rate 0.05 V s^{-1}

and no peak in the reverse direction is observed. A comparison of peak currents reveals that oxidation current at GC | PEDOT is 2.4 times higher, which shows the catalytic oxidation of AA at the modified electrode. The observed large negative shift (~ 0.25 V) in the oxidation peak potential and the enhanced oxidation current are attributed to electrostatic interactions between the surface groups and the reactant species in the solution. The cationic charges on the PEDOT film leads to accumulation of ascorbate anions at the interface. This is corroborated by an earlier finding that metal like electrodes with fixed cationic sites can enhance the oxidation rates of anion when compared to bare electrode, by means of electrostatic attraction [26].

The peak potentials for the oxidation of DA and AA at GC/PEDOT are observed to shift anodically with the increase in scan rate. The plot of oxidation peak current versus the square root of scan rate in the range from 0.01 V s $^{-1}$ to 0.1 V s $^{-1}$, yields a straight line passing through origin, which suggests that the oxidation of AA and DA at GC | PEDOT is to be diffusion controlled (Fig. 4).

Having examined individually the oxidation behavior of AA and DA on GC | PEDOT, the details of the interdependence of AA and DA oxidation at the modified electrode is in order. Figure 5 depicts CVs for the oxidation of DA (1 mM) and AA (1 mM) on GC and GC | PEDOT electrodes from a solution containing them both. On bare GC, the two species get oxidized and their oxidation peaks are found to coalesce and appear as a strong oxidation signal at around 0.22 V, yielding a peak current of 46 ± 3 μ A, which corresponds approximately to the sum of the oxidation peak currents noticed individually for the oxidation of AA and DA.

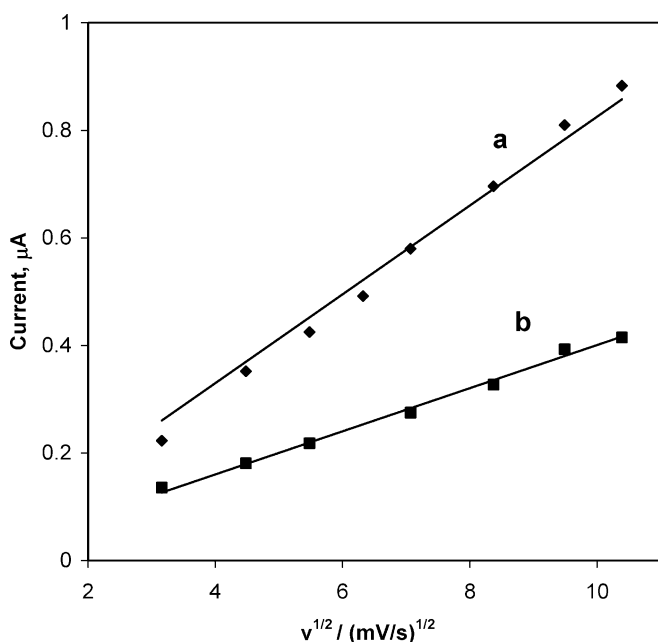


Fig. 4 Plot of oxidation peak current vs. square root of scan rate **a** 1 mM DA and **b** 1 mM AA

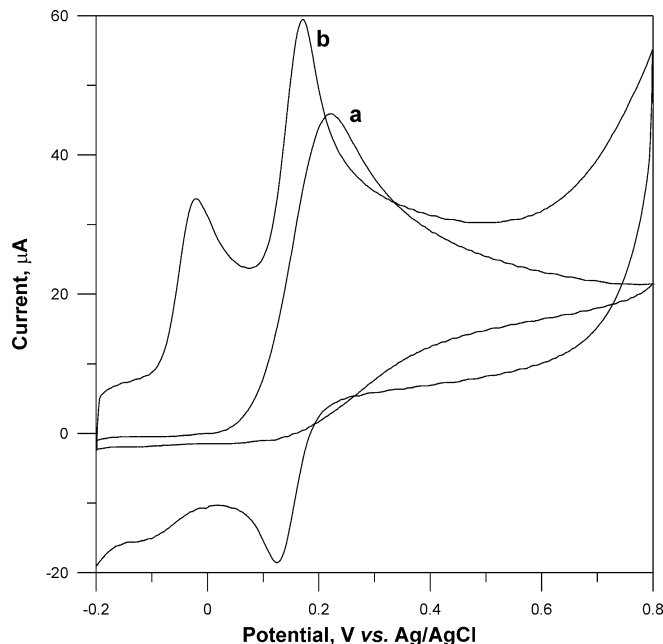


Fig. 5 Cyclic voltammetric behaviour of DA (1 mM) + AA (1 mM) at **a** bare GC **b** GC | PEDOT electrodes in PBS of pH 7.4. Scan rate 0.05 V s $^{-1}$

On the other hand, on GC | PEDOT electrode two distinct oxidation peaks are observed at around -0.025 and 0.17 V corresponding to the oxidation of AA and DA, respectively. In other words, GC | PEDOT electrode affords a significant peak separation of about 0.195 V for the oxidation of DA and AA. This allows one to measure simultaneously and quantitatively AA and DA present in the sample.

The distinct peak separation achieved above is mainly attributed to the cationic (electrostatic) and hydrophobic characteristics of PEDOT film. At physiological pH, DA exists as a cation with a positively charged amino group and DA is more hydrophobic than AA [21]. So, DA does not have any electrostatic interaction with the PEDOT matrix (being a cationic in nature), as its peak potential shift is negligibly small on modification with PEDOT. It is reasoned that the conducting polymer films (ca. polypyrrole) coated on the electrode surfaces contain a distribution of “reduced” and “oxidized” regions [27, 28] and the reduced regions are more hydrophobic [29] in nature and the same is expected in the case of PEDOT. In our earlier work [21], the increase in oxidation current was attributed to only a weak hydrophobic interaction. It is well known that hydrophobic anions are generally bound strongly to hydrophobic binding sites and the hydrophobicity can influence the selectivity process [30]. It is likely that DA interacts with the ‘reduced’ regions of PEDOT through hydrophobic–hydrophobic interactions, whereas AA does not. This is understandable since the ‘reduced’ form of the film, acts as a mere redox polymer [31] and can mediate the electron transfer for oxidation of DA. It is also reported that hydrophobicity of the polymer is one

of the important factors that is responsible for the selective DA receptor ligand bonding [32]. This can further be interpreted by the non-specific adsorption property of dopamine with the polymer matrix [33].

In the case of AA oxidation on PEDOT film, a large potential shift (~ 0.25 V) was observed. This shift can be interpreted to be due to the pre-concentration of the negatively charged ascorbate anion in the CP matrix because of the electrostatic attraction of the PEDOT polymer in its oxidized state (-0.05 to 0.0 V). This can be explained based on the cyclic voltammograms of PEDOT modified electrode in solutions containing redox couples such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$. In these experiments, current enhancement was observed for both redox couples, whereas the formal peak potential shifts to negative values in the case of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (Figures not given). This is due to the fact that the cationic form of PEDOT strongly attracts the negative redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ into the film, whereas it repels the positive redox couple $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$. However, the enhancement in the peak current on both the redox couples is due to the large surface area of the porous polymeric film/increase in the surface roughness in nanometer region (see Fig. 1 AFM images). An additional factor that can contribute to the shift of peak potential to less anodic values is catalysis through electron transfer mediation. The CP's are known to work as electron mediators, which promote electron shuttling between the electrode surface and the electrolyte through their redox mediation. PEDOT polymer is electronically conducting in nature when it is in oxidized state and is selective to cations in the neutral form as reported by Higgins et al. [34]. It is well known that the electrocatalytic activity of the polymer films arises from the formation of polarons, that is of positive charges on the polymer backbone. The oxidation of AA can be facilitated by the negative charge of the molecule and, at the same time, oxidation of possible interferences which are positively charged like, for example, DA, could be made more relatively difficult due to the positively charged electric field surrounding the active centers on the polymer which are more localized than electric charges on a metal electrode surface.

We have now established, through voltammetric studies, that the PEDOT polymeric film favors the separation of the voltammetric peaks of DA and AA through a combination of effects as discussed above. This large peak separation can be explained based on the observations that electrostatic interactions and redox mediation by PEDOT are responsible for the negative shift of peak potential of oxidation of AA and weak hydrophobic interactions of DA with the polymer matrix.

Rotating disc electrode

In order to understand the electrocatalytic activity of GC | PEDOT and to elucidate the kinetics of the DA

oxidation at GC | PEDOT electrodes, measurements at the rotating disk electrode were performed at different rotation rates. Figure 6 shows the steady-state I-E curves recorded for the oxidation of 1.0 mM DA in the presence and absence of 1.0 mM AA at GC | PEDOT electrode for different rotation speeds, at a sweep rate of 0.002 V s^{-1} . As can be seen from the Fig. 6, the limiting current increases with increasing rotation speeds only at lower rotation rates. At higher rotation rates, that is above $2,400$ rpm, the current attains a limiting value in view of faster electrode kinetics. When the rotation speed is increased the mass transfer in solution becomes fast enough to reveal kinetic limitations, that is electron transfer between DA and PEDOT becomes rate limiting and not diffusion in the polymer film. It is pertinent to note that a similar observation has been made earlier for a polymer modified RDE that low rotation rates allow a flux from the solution to establish a limiting current dependent on the square root of rotation rate, while high rotation rates confine the diffusion layer to the polymer, causing the limiting current to be independent of the rate of rotation [35]. When the rotation rate is low, the diffusion of DA through the diffusion layer controls the current and at higher rotation rate, the thickness of the diffusion layer decreases and the magnitude of the current is controlled by the kinetics. Under these conditions, the Koutecký-Levich plot can be used to determine the reaction rate constant, k_p , between surface-deposited PEDOT and diffusing DA.

The Koutecký-Levich plots obtained at an oxidation potential of 0.4 V from the i-E plots are shown in Fig. 7 a and b. The plot shows a linear dependence between $1/i_l$ as a function of $\omega^{-1/2}$ and the catalytic rate constant (k) which can be calculated from the intercepts of the Koutecký-Levich plots. The positive intercept value clearly indicates a kinetic limitation associated with the polymeric film. The value of k was found to be 2.4×10^5 and 8.3×10^5 $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for a DA and DA in presence of AA. The diffusion coefficient of DA, 'D', in the solution phase has been estimated from the slope of the Koutecký-Levich plot and is found to be in close agreement with the values reported in the literature [36]. The 'D' values which were in this medium was found to be 0.89×10^{-5} and 1.09×10^{-5} $\text{cm}^2 \text{s}^{-1}$ for a DA concentration of 1 mM in the presence and absence of 1 mM of ascorbic acid, respectively. A large difference in the catalytic rate constant data in the presence and absence of AA proves that there exists a definite influence of AA on DA oxidation kinetics.

Thus, in this present study, GC | PEDOT is found to favour separation of DA and AA oxidation peaks. Yet, the sensitivity of these polymeric modified electrodes towards DA sensing is found to be low due to the presence of a large capacitive current arising during voltammetric analysis. It is reasonable to expect that increasing the thickness of the polymer film can enhance the current signal. But, thicker films are usually associated with a greater extent of porosity. Increased film thickness also results in unwanted charging current

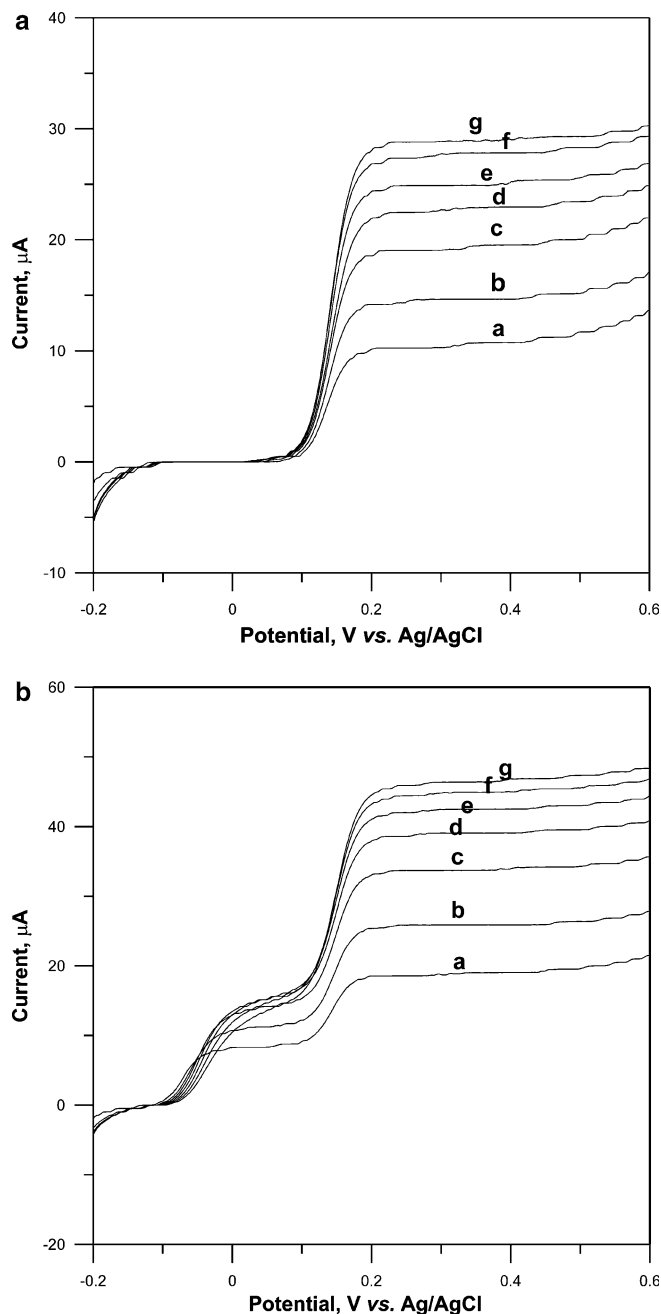


Fig. 6 Voltammograms for the oxidation of **a** 1 mM DA and **b** 1 mM DA in the presence of 1 mM AA at the rotating disk PEDOT modified GC electrode in PBS of pH 7.4. Electrode rotation rate: **a** 200, **b** 400, **c** 800, **d** 1,200, **e** 1,600, **f** 2,000 and **g** 2,400 rpm

enhancement, thus limiting their detection at sub-micromolar levels usually with low signal-to-noise ratio (S/N). It is likely that the analyte molecules (DA/AA) can be trapped inside the porous polymeric matrix through specific/non-specific interactions in thicker porous films, limiting the scope of renewal of the surface for repeated analysis (ca. fouling effect). In order to minimize the charging current, the PEDOT film is kept as thin as possible, at the same time ensuring complete coverage of the electrode surface. In order to minimize

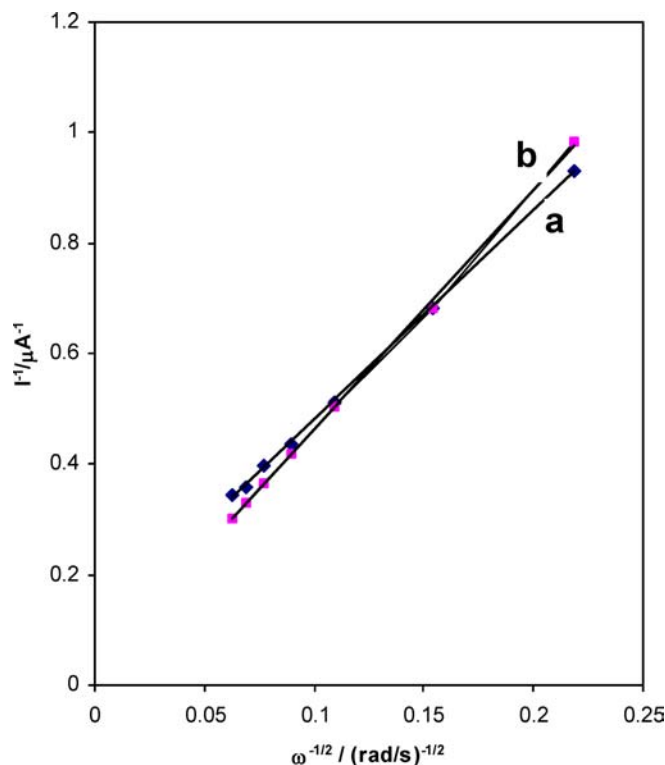


Fig. 7 Koutecky-Levich plot derived from the data of the RDE voltammograms **a** for 1 mM DA and **b** for 1 mM DA in the presence of 1 mM AA

the interference due to the charging current generated by the polymer film, square wave voltammetric technique is resorted to in this study in order to increase sensitivity [10].

Square wave voltammetry

Figure 8 represents the square wave voltammograms at different concentrations of DA where the concentration of AA was kept constant. The peak current of DA increased linearly (Fig. 9) with increasing DA concentration, with a correlation coefficient of 0.981 and a sensitivity of 0.27 $\mu\text{A}/\mu\text{M}$ with an intercept of 1.86 μA . The latter is likely a result of the effect of AA on the electrode kinetics of DA oxidation especially at lower relative concentration of DA (Sect. 3.3). AA was oxidized at a 0.25 V less positive potential than DA and the oxidation peak currents for DA in the absence and presence of AA were found to be almost the same. This suggests that the oxidation of AA does not affect that of DA at the PEDOT modified GC electrode under the experimental conditions of square wave voltammetry.

Hence, the selective detection of DA in the presence of AA by the PEDOT film coated GC electrode can be explained as follows: the oxidation potential of AA is more negative by 0.2 V than that of DA and the fouling effect, that is the adsorption of the oxidized product of AA on the electrode surface, could be successfully

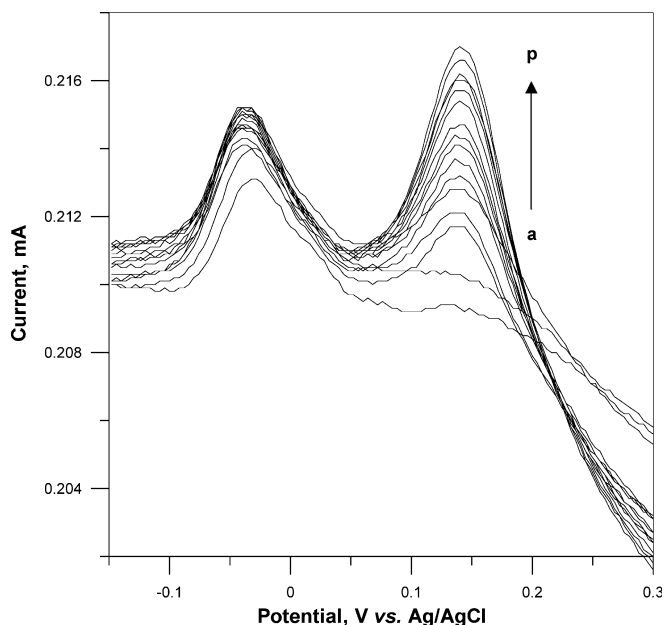


Fig. 8 Square wave Voltammogram of AA (1 mM) at PEDOT coated GC electrode in the presence of different concentrations of DA ($a - p = 1-30 \mu\text{M}$)

removed by introducing the PEDOT film on the electrode surface, and consequently the reproducible response for AA and DA could be observed at the modified GC electrode. Also, the modified electrode can sense the low concentration level of DA ($1 \mu\text{M}$) in the presence of a high concentration of AA (1 mM), that is 1,000 times difference in both concentrations which is much larger than the concentration difference of DA

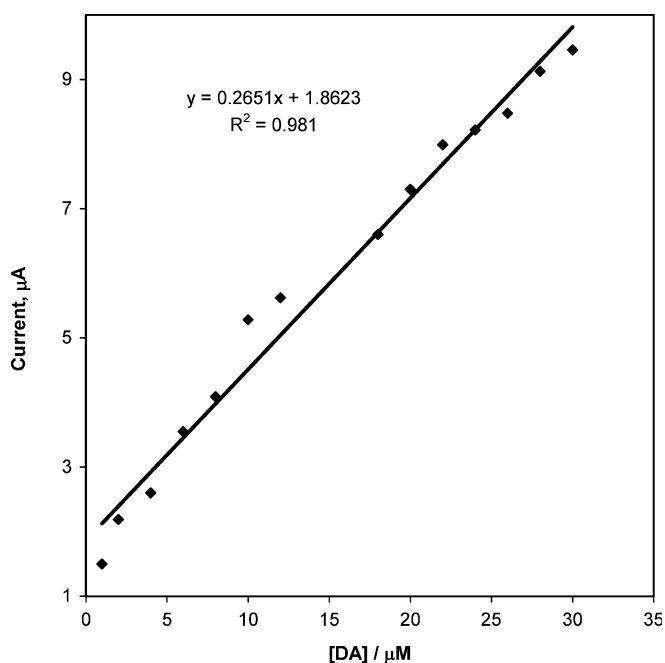


Fig. 9 Plot of DA oxidation peak current and concentration of DA

and AA under physiological conditions [10]. Thus the selective and sensitive detection of DA in the presence of a high concentration of AA was achieved at the PEDOT modified electrode. As this electrode shows a reproducible response to AA without fouling, it can also be used for the simultaneous determination of DA and AA in the biological systems.

It is well understood that the PEDOT film can strongly attach to the electrode surface and to be insoluble in aqueous and non-aqueous solutions [9, 22]. The electrode stability was checked by immersing the electrode in a phosphate buffer solution for 3–4 days and then measuring its response for both DA and AA. The oxidation potentials and peak currents for DA and AA were found to be the same as those obtained at the freshly prepared polymer film coated electrode and thus the electrode showed a stable response.

Conclusions

In this work, we have demonstrated that the PEDOT polymeric film favors peak separation of DA and AA voltammetric signals. Unlike the bare glassy carbon electrode, the PEDOT coated GC electrode showed a separation of $\sim 0.2 \text{ V}$ in the peak potentials of DA and AA simultaneously present in the solution. This peak separation can be explained based on a combination of effects such as electrostatic interactions responsible for the negative shift of peak potential of oxidation of AA and weak hydrophobic interactions of DA with the polymer matrix. DA interacts with the 'reduced' regions of PEDOT through hydrophobic–hydrophobic interactions that influence the selectivity process. The large shift in ascorbic acid oxidation has been analyzed to be primarily due to (a) a possible pre-concentration of the negatively charged ascorbate anion in the CP matrix (electrostatic); and (b) electron transfer mediation by the PEDOT redox. The results of the RDE studies revealed that the presence of AA slightly affects the catalytic oxidation of DA at the PEDOT films. In effect, the PEDOT modified GC electrode could detect DA at $1 \mu\text{M}$ even in the presence of AA in concentrations as high as 1 mM, that is 1:1,000 ratio, which reflects the difference in their concentration under physiological conditions. The modified electrodes also showed excellent sensitivity, selectivity and anti-fouling property. However, it now remains to elucidate the interaction of various analytes with the conducting polymer matrices of different chemical nature and this forms part of our current ongoing investigations.

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