



Electrochemical selective determination of ascorbic acid at redox active polymer modified electrode derived from direct blue 71

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ABSTRACT

A simple selective method for determination of ascorbic acid using polymerized direct blue 71 (DB71) is described. Anodic polymerization of the azo dye DB71 on glassy carbon (GC) electrode in 0.1 M H₂SO₄ acidic medium was found to yield thin and stable polymeric films. The poly(DB71) films were electroactive in wide pH range (1–13). A pair of symmetrical redox peaks at a formal redox potential, $E^0 = -0.02$ V vs. Ag/AgCl (pH 7.0) was observed with a Nernstian slope -0.058 V, is attributed to a 1:1 proton + electron involving polymer redox reactions at the modified electrode. Scanning electron microscope (SEM), atomic force microscope (AFM) and electrochemical impedance spectroscopy (EIS) measurements were used for surface studies of polymer modified electrode. Poly(DB71) modified GC electrode showed excellent electrocatalytic activity towards ascorbic acid in neutral buffer solution. Using amperometric method, linear range (1×10^{-6} – 2×10^{-3} M), dynamic range (1×10^{-6} –0.01 M) and detection limit (1×10^{-6} M, S/N=3) were estimated for measurement of ascorbic acid in pH 7.0 buffer solution. Major interferences such as dopamine and uric acid are tested at this modified electrode and found that selective detection of ascorbic acid can be achieved. This new method successfully applied for determination of ascorbic acid in commercial tablets with satisfactory results.

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1. Introduction

L-Ascorbic acid (vitamin C, AsA) is used in large scale as an antioxidant in food, animal feed, beverages, pharmaceutical formulations and cosmetic applications. AsA is the major soluble antioxidant found in plants and is also an essential component of human nutrition (Zhang et al., 2007; Chen et al., 2003). Due to the above importance of AsA, its determination in their solution is more important. Traditional procedures for AsA determination are generally based on enzymatic methods (Marchesini et al., 1974), on titration with oxidizing agent, like iodine or 2,6-dichlorophenolindophenol (Kirk and Sawyer, 1991) and HPLC analysis with fluorimetric (Kirk and Sawyer, 1991) or UV–vis detection (Wagner et al., 1979; Finley and Duang, 1981). Electroanalytical techniques have also been frequently used for this purpose. Electrochemical oxidation reactions of AsA using various electrodes (unmodified) has been examined (Dominguez et al., 1976; Rueda et al., 1978; Karabinas and Jannakoudakis, 1984), direct oxidation of AsA at con-

ventional electrodes occurred via first a one-electron transfer leads to the dehydroascorbic acid anion radical that is adsorbed on the electrode surface, where it is further oxidized to adsorbed dehydroascorbic acid (DHA). DHA further undergoes slow desorption by hydrolysis to the final dihydrate species (Hammerich and Svensmark, 1991). Electrode fouling by the intermediate adsorbed species takes place and the relevant voltammetric response was poorly reproducible. The requirement of higher overvoltage for oxidation of AsA at naked electrodes limits its direct application in real-world samples because co-existence of easily oxidizable biochemical's such as dopamine, uric acid, etc. To overcome the above problems various electrocatalyst modified electrodes were proposed for determination of AsA (Lupu et al., 2002; Khoo and Chen, 2002; Pournaghi-Azar et al., 2002; Zhang and Sun, 2001; Lu et al., 2002). Polymer modified electrodes are more attractive and possess several advantages for the detection of biomolecules (Kumar and Chen, 2008). Using, electrochemically generated polymer modified electrodes and their applications in determination of AsA were reviewed in detail (Malinauskas et al., 2004). Chitosan incorporating cetyltrimethylammonium bromide modified GC electrode (Zou et al., 2007), citrate capped gold nanoparticles on 1,6-hexanedithiol modified Au electrode (Sivanesan et al., 2007), poly(eriochrome black T) modified GC electrode (Yao et al., 2007), the $[\text{Fe}(\text{CN})_6]^{3-}$

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ion-confined on multilayer thin films composed of poly(allylamine hydrochloride) and carboxymethyl cellulose modified Au electrode (Wang et al., 2007), ruthenium oxide hexacyanoferrate modified carbon electrodes (Thiago et al., 2008) were proposed for determination of AsA.

Direct blue 71 (DB71) is triazo substance with a big π - π conjugated system with a high photostability (Supplementary Scheme S1). The azo form of the DB71 dye appears to be the predominant species in solution, since the steric effects tend to favor the azo tautomeric form of DB71 (Isak et al., 2000). DB71 has a tendency forming the non-aggregated state due to the four negatively charged sulfonate groups on each monomer act against aggregation of the dye molecules (Rena et al., 2007a, 2007b). DB71 also have been used as a staining agent for proteins bound to blotting membranes (Hong et al., 2000). To the best of our knowledge, for the first time, we report the electrochemical polymerization of DB71 and its electrochemical properties. Using poly(DB71) modified GC electrode, amperometric determination of ascorbic acid is demonstrated here.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade unless otherwise specified. DB71 was purchased from Aldrich (Milwaukee, WI, USA) and used as received. Dopamine hydrochloride and uric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulfuric acid and sodium hydroxide were purchased from Wako pure chemicals (Osaka, Japan). Ascorbic acid, sodium acetate and sodium dihydrogen phosphate were received from E-Merck (Darmstadt, Germany) and were also used without further purification. Water was obtained from a Millipore Alpha-Q Lotun ultrapure water system. Solutions and buffers were prepared employing standard laboratory procedures. Before each experiment the solutions were deoxygenated by purging with pre-purified nitrogen gas. The Vitamin C tablets were purchased from local drug store in Taipei.

2.2. Apparatus

Electrochemical measurements were performed with CH Instruments (TX, USA) Model-400 potentiostat with conventional three-electrode cell. A BAS GC or GC electrode coated with poly(DB71) and platinum wire are used as the working electrode and auxiliary electrode, respectively. All the cell potentials were measured with respect to an Ag/AgCl [KCl (sat)] reference electrode. Chronoamperometric studies were performed on a Bi-potentiostat Model CHI750A (TX, USA) having an analytical rotator model AFMSRK with MSRX speed control (PINE Instruments, USA). Hitachi scientific instruments (London, UK) Model S-3000H scanning electron microscope was used for surface image measurements. The AFM images were recorded with a multimode scanning probe microscope system operated in tapping mode using model CSPM4000 Instruments, Ben Yuan Ltd (Beijing, China). Electrochemical impedance measurements were performed using impedance measurement unit, IM6ex ZAHNER, Messsysteme (Kroanch, Germany). All the pH measurements were performed on Suntex Model SP-701 pH meter (Jiangsu, China). All experiments were carried out at an ambient temperature of $25 \pm 2^\circ\text{C}$.

2.3. Electrode preparation

Prior to use, the working electrode was mechanically polished with alumina powder (Al_2O_3 , $0.05 \mu\text{m}$) up to a mirror finish. Then

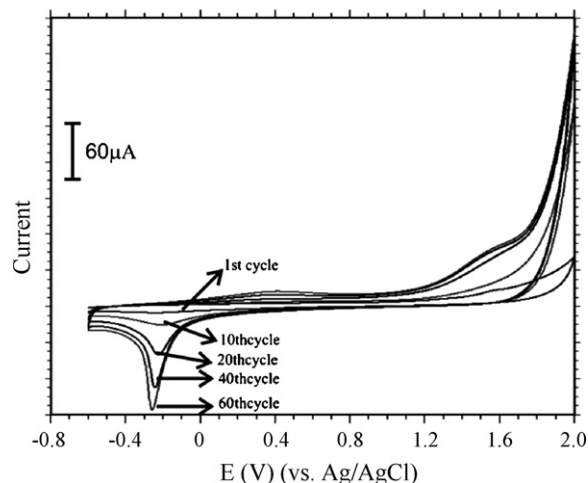


Fig. 1. Cyclic voltammograms (CVs) of the poly(DB71) film growth on GC electrode from the electrolyte $0.1 \text{ M H}_2\text{SO}_4$ solution containing $1 \times 10^{-5} \text{ M}$ DB71 monomers. Scan rate = 0.1 V/s .

the electrode was cycled in 0.1 M sulfuric acid in a potential range from -0.5 to 1 V at a sweep rate of 100 mV s^{-1} until a stable voltammogram obtained. The electrochemical deposition of poly(DB71) film was carried out by cyclic voltammetry (between -0.5 and 2.0 V at 100 mV s^{-1}) for 30 cycles. The electropolymerization was conducted in a three-electrode cell with glassy carbon as the working electrode, Ag/AgCl as the reference electrode and platinum wire as the counter electrode. The electrolyte consisted of $1 \times 10^{-5} \text{ M}$ DB71 monomer in aqueous solution of $0.1 \text{ M H}_2\text{SO}_4$. The resulting polymer film was washed with doubly distilled deionized water before proceed electrochemical measurements. Finally, the modified poly(DB71)/GC electrode was electroactivated by scanning in the potential range between -0.75 and 0.65 V in pH 7.0 buffer solutions using cyclic voltammetry at a scan rate of 100 mV s^{-1} and then electrochemical properties of the poly(DB71)/GC were studied.

3. Results and discussion

3.1. Electrochemical polymerization of DB71

Fig. 1 shows the consecutive cyclic voltammograms (CVs) of GC electrode in $0.1 \text{ M H}_2\text{SO}_4$ solution containing $1 \times 10^{-5} \text{ M}$ DB71 monomers. On the first anodic scan an oxidation peak was observed at $+1.56 \text{ V}$ which corresponds to the oxidation of primary amino group of monomers (Rehan, 2000). Upon scan reversal a cathodic wave with a peak potential centered at -0.24 V was observed. On the second and subsequent potential scans an additional anodic peak was observed at $+0.40 \text{ V}$ with the potential cycle repeating, the peaks start to appear and grow. This behavior is attributed to the deposition and growth of an electroactive layer on the electrode surface. At the same time, it was also observed that polymer film growth was faster for the first twenty cycles than other subsequent cycles. From the 29th cycle on, the film hardly grew, which indicated that polymerization reached saturation (Rehan, 2000). After electropolymerization, a uniform adherent dark blue polymer observed on the GC electrode surface. According to the literature reports of azo dyes (Yao et al., 2007; Rehan, 2000; Eriksson and Nyholm, 1999; Kumar et al., 2008), it was the intermolecular $-\text{NH}_2$ functional group monomers were involved in the polymerization reaction (Supplementary Scheme S2). The oxidation of DB71 via NH_2 moiety leads to dimerization, ultimately to the formation of the polymer through a progressively more facile oxidation of the dimer, trimer, tetramer, etc., and the consequent coupling and deprotonation.

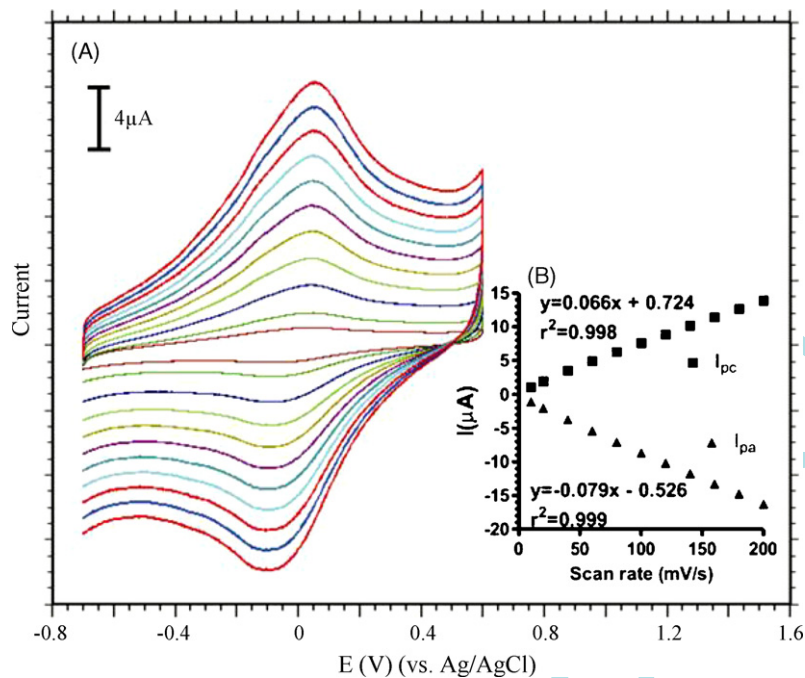


Fig. 2. (A) CVs of Poly(DB71)/GC electrode in 0.1 M PBS (pH 7.0) at different scan rates. The scan rates from inner to outer are 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20 V/s, respectively. (B) Plot of I_{pa} and I_{pc} vs. scan rate.

3.2. Electroactivity of poly(DB71) films

After polymer formation, the modified electrode was transferred into a test buffer solution to investigate the electroactivity using cyclic voltammetry. The poly(DB71)-covered GC electrode showed a pair of redox peaks in the various pH buffer solutions (1–13). The dependence of the redox processes on pH is shown in Supplementary Fig. S1. It is clear that the magnitude and the position of the redox peak depend on pH. As pH increases, the magnitude of the peak slowly diminishes and the peak potential, E_p , shifts to less anodic values. The increase in redox peak currents (i_p) were observed with the decrease of pH indicates that the kinetics of the oxidation and reduction processes depend on the concentration of H^+ ions in solution. In other words, the transport of protons is involved in the rate-determining step of the redox processes. As can be seen in Supplementary Fig. S1, formal potential E^0 decreases linearly with respect to the pH of the buffer solution, with a slope of -0.058 V. This indicates that the electroactivity of poly(DB71) involves a proton + electron elimination in the oxidation processes and a proton + electron addition in the reduction process. This situation is usually met in the examination of the electroactivity of aromatic amine-based conducting polymers such as polyanilines (Inzelt and Horanyi, 1990; Barbero et al., 1991; Kumar and Chen, 2007). This behavior is attributed to the transformation of the protonated amino linkages into protonated imino linkages on oxidizing the polymer and vice versa on reducing the polymer. A formal redox potential (E^0) for the redox processes of poly(DB71) in acidic solution was estimated as ($E^0 = E_{pa} + E_{pc}/2$) 0.32 V vs. Ag/AgCl, this value is very close to E^0 of poly(4-amino-1-1'-azobenzene-3,4'-disulfonic acid) (Kumar et al., 2008) and 4(5-chloro-2-pyridylazo) 1,3-diaminobenzene (Abd El-Rahman and Rehan, 1993) in the same solution were 0.31 and 0.30 V, respectively. Fig. 2 shows the effect of scan rate on the redox peaks of poly(DB71) films in 0.1 M phosphate buffer solution (PBS). It is clear that the peak current increases as the scan rate, ν , increases, while the peak potential is practically insensitive to the change in ν and the peak separation (ΔE_p) is nearly 0.06 V. Within the tested ν range (10–200 mV/s), i_p varies

linearly with ν as can be seen in Fig. 2. This indicates that the electroactivity of poly (DB71) film in 0.1 M PBS is similar to that of surface-attached electroactive sites (Murray, 1984; Laviron, 1982). Similar behavior was reported for many electroactive polymer films (Yao et al., 2007; Rehan, 2000; Kumar et al., 2008; Kumar and Chen, 2007). It should be mentioned that the electroactivity of poly(DB71) films in neutral solutions is quite stable, in the potential range -0.7 to 0.6 V, against repetitive cycling the films do not suffered from degradation.

Fig. 3a shows the SEM images of poly(DB71) coated electrode which indicated that a thin film layer was covered the surface and the thickness of the film was found to be 38.65 nm using AFM measurements (see Supplementary Fig. S2). Fig. 3b illustrates the results of electrochemical impedance spectroscopy on bare GC electrode (curve a) and poly(DB71)/GC electrode (curve b) in the presence of equivalent 5 mM $[Fe(CN)_6]^{3-/4-} + 0.1$ M KCl. It can be seen at the bare GC electrode, a semicircle of about 80Ω diameter with an almost straight tail line present. However, the diameter of the high frequency semicircle was obviously reduced to 60Ω by the surface modification of the poly(DB71) film (curve b), suggesting that a significant acceleration of the $[Fe(CN)_6]^{3-/4-}$ redox reaction occurred due to the presence of polymer film. The decreasing of charge transfer resistance value for poly(DB71)/GC electrode is because that polymer film can act as a electron transfer medium and enhanced electron transfer and also indicated that poly(DB71) had been attached to the GC electrode surface.

3.3. Electrocatalytic oxidation of ascorbic acid

Fig. 4A shows the cyclic voltammograms of 0.5 mM AsA in pH 7.0 phosphate buffer solution at a bare GC electrode and a poly(DB71) modified GC electrode. At a bare GC, an irreversible oxidation peak was observed at 0.35 V. Under identical conditions, the poly(DB71) modified GC electrode gave significantly increased peak currents and a fast electron transfer process to AsA. A well-defined oxidation wave of AsA was observed, with the anodic peak potential at 0.0 V. The remarkable enhancement in the peak currents and the lowering

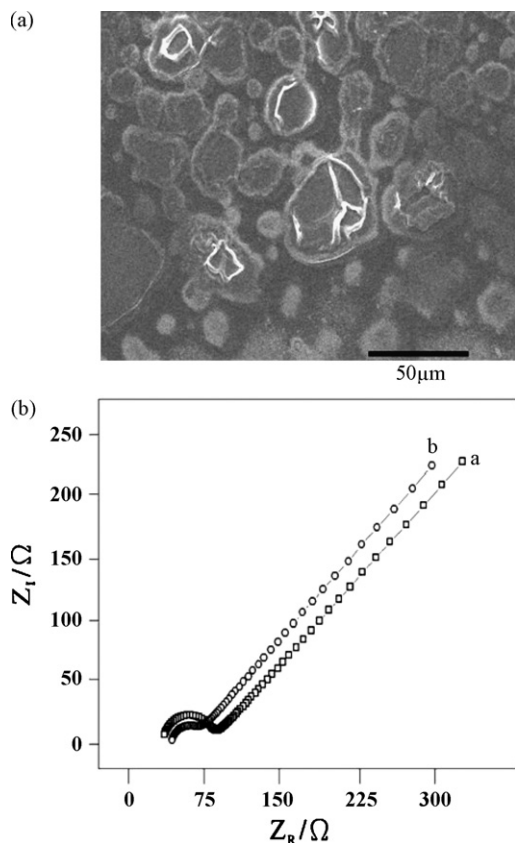


Fig. 3. (a) SEM image of poly(DB71) film modified electrode and (b) EIS obtained for bare GC (curve a) and poly(DB71)/GC (curve b) electrodes in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M KCl solutions.

of overpotential provided clear evidence of the catalytic effect of poly(DB71) film toward AsA.

3.4. Effect of scan rate and pH

The effect of scan rate on the anodic peak current of AsA was studied. As the scan rate increased, the oxidation peak current (I_{pa}) increased. The I_{pa} was proportional to the square root of scan rate over the range of 10–200 mV s^{-1} which suggested a diffusion-controlled irreversible oxidation process of AsA at the poly(DB71)-coated electrode. This behavior is observed for AsA oxidation on some polymer modified electrodes (Chen et al., 2005; Roy et al., 2004).

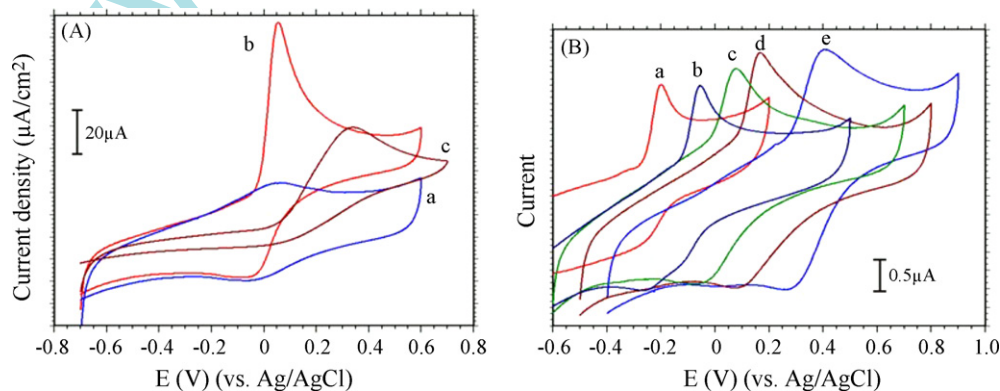


Fig. 4. (A) CVs of poly(DB71)/GC modified electrodes in pH 7.0 PBS: AsA = (a) 0.0 mM, (b) 0.5 mM and (c) bare GC electrode with 0.5 mM AsA; scan rate 10 mV/s . (B) CVs were recorded using poly(DB71)/GC electrode in various pH solutions containing 100 μM AsA, pH (a) 13.0, (b) 10.0, (c) 7.0, (d) 4.0 and (e) 1.0.

The effect of pH on the anodic peak current was investigated by cyclic voltammetry in the solution containing 100 μM AsA. The values of catalytic current, which were dependent on the pH value of the buffer solution, show that the oxidation of the AsA includes some proton transfer processes (Fig. 4B). According to the Nernst equation, the slope of -50.0 mV pH^{-1} reveals that the proportion of the electron and proton involved in the reactions is 1: 1. As AsA oxidation is a two-electron process, the number of protons involved is also predicted to be two. Therefore, a mechanism for the AsA oxidation can be proposed in Scheme 1. Fig. 4B shows the effect of solution pH on the anodic peak current of AsA. In the range of 1–13, the anodic peak current of AsA is influenced by the solution pH and the catalytic current decreases significantly in higher pH value. So we have selected the physiological pH 7.0 and the optimum operating potential 0.1 V for further investigation of AsA oxidation at poly(DB71) modified electrode.

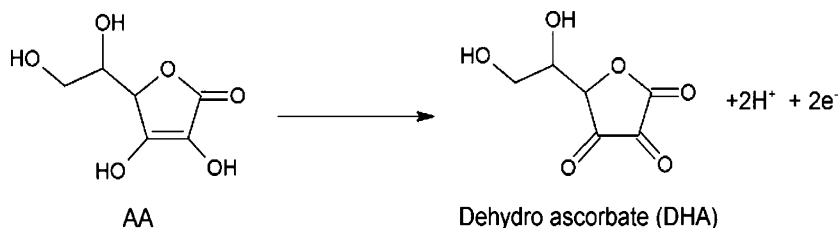
3.5. Amperometric determination of AsA

The determination of AsA concentration using poly(DB71) modified electrode was performed with amperometry. The oxidation peak currents of AsA were measured in 0.1 M PBS (pH 7.0) at 0.1 V and plotted against the bulk concentration of AsA after background subtraction (Fig. 5a and b). The dependence of peak currents on the concentration of AsA is a linear relationship in the range of 1×10^{-6} – 2×10^{-3} M. The linear regression equation is expressed as $i_p (\mu\text{A}) = -0.06 \times -1.0$, $r^2 = 0.996$. The detection limit ($S/N = 3$) is 1×10^{-6} M. The relative standard deviation of 10 successive scans is 2.4% for 1×10^{-4} M AsA, indicating that the poly(DB71) modified electrode had an excellent reproducibility. Poly(DB71) modified electrodes responds with the each addition of AsA concentration, at higher concentrations (up to 0.01 M) poly(DB71) modified electrode showed saturation plateau (Fig. 5b). According to the literature reports (Brazdžiuvienė et al., 2007), a hyperbolic dependence of oxidation current on ascorbate concentration can be explained by the interaction between poly(DB71) film and AsA. The formation of a complex of ascorbate (Asc) with the oxidized active site of poly(DB71)(AS_{ox}) is expected followed by spontaneous fast electron transfer from Asc to AS_{ox} and dissociation of the resulting complex (Bartlett and Wallace, 2001).



where DAsc and AS_{red} represent dehydroascorbate and a reduced form of poly(DB71) active site, respectively.

Using the proposed method described above, the Vitamin C tablets were analyzed. The recovery was studied for the corre-



Scheme 1. Electrochemical oxidation reaction of AsA at poly(DB71) film.

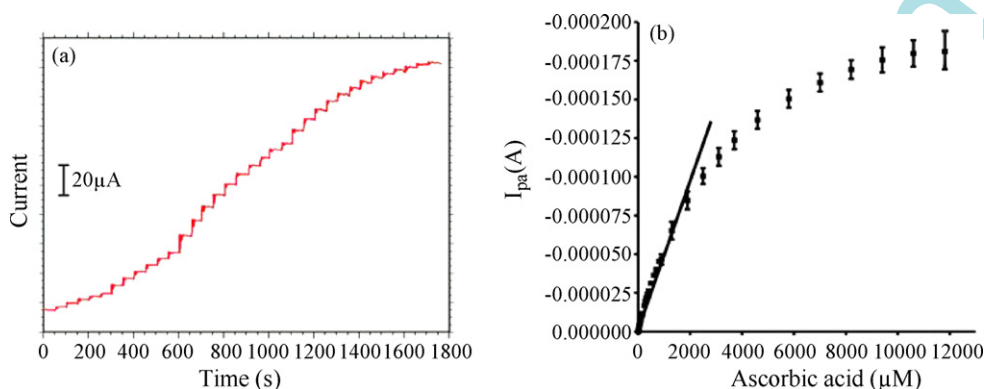


Fig. 5. Typical amperometric curve obtained with a poly(DB71)/GC electrode in 0.1 M PBS (pH 7.0) at an applied potential of 0.1 V vs. Ag/AgCl, stirring rate \sim 1000 rpm. (a) Successive additions of AsA in the range from 1×10^{-6} to 2×10^{-3} M and (b) the corresponding standard addition plots. Each point refers to the mean of triplicate measurements.

sponding tablets added with certain value of standard solution of AsA. The results are shown in Table 1A. The recovery and RSD were acceptable, showing that the proposed methods could be used efficiently for the determination of AsA in tablets.

3.6. Interferences on analytical response

In view of the fact that normally it is difficult to obtain the well-separated voltammetric waves for dopamine and AsA in the presence of each other, the ability of the modified electrode to promote the voltammetric resolution of dopamine and AsA was investigated. To ascertain the dopamine and uric acid interference at this modified electrode under identical condition used for determination of AsA, we have performed amperometry, in this experiment the potential was kept at 0.1 V, the amperometric response for the successive additions of 15 mM DA and 15 mM UA at poly(DB71)/GC modified electrode was recorded, it was observed that these interferences not shown considerable response at poly(DB71)/GC modified electrode. However, further addition of 1 mM AsA into the same buffer solution results oxidation current of AsA (Supplementary Fig. S3). This result clearly indicated that dopamine and uric acid did not interfere in the steady state current of AsA at 0.1 V.

The linear range, pH, oxidation potential and detection limits of proposed method was compared with the earlier reports in Table 1B. From the data shown in Table 1B, proposed method has lower detection limit, lower oxidation potential and wide linear range than earlier reports (Roy et al., 2004; Kumar and

Narayanan, 2006; Sivanesan et al., 2007) and proposed method also has wide linear range and wide dynamic range of detection of AsA than previous reports (Liu et al., 2008; Thiago et al., 2008). In addition, the important biochemical's such as dopamine and uric acid are not interfered in the steady state current of AsA at poly(DB71) modified electrode. Thus, the proposed method provides a possibility for selective detection of AsA in the presence of interferences such as dopamine and uric acid in real-world samples.

In order to study the reproducibility of the sensor and reliability of fabrication procedure, five GC electrodes were modified with poly(DB71) film independently. CVs of sensors were recorded in buffer solution. The relative standard deviation (R.S.D.) value of measured anodic peak currents was 1.8%. Furthermore, the five electrodes showed acceptable reproducibility with R.S.D. of about 2.4% for the current determination of 50 μM AsA. Using, poly(DB71) modified GC electrode, the R.S.D. was determined by twelve successive detection of a 50 μM AsA which was 3.2%. Good reproducibility and stability of the sensor can be attributed to the irreversible deposition and the strong adherent of poly(DB71) onto GC electrode. Since the protocol for the fabrication of modified electrode is easy, the long-term stability of the electrode is not so important. However, we checked the stability of the electrode upon repeated use. A series of 50 repetitive measurements of sample solutions containing 50 μM AsA was used to evaluate the stability of the electrode. The coefficient of variation was found to be 2.5%, showing that the modified electrode is stable and is not subject to surface fouling by the oxidation products. As the electrode fabrication is very easy

Table 1A
Determination of AsA in vitamin C tablets

Sample	Labeled amount (mg)	Found (mg) (n = 5)	R.S.D. (%)	Added (μM)	Found (μM)	Recovery (%)
1	600	594.2	1.58	10	10.58	105.8
2	600	595.8	2.39	10	9.71	97.08
3	600	602.9	2.16	10	9.85	98.52

Table 1B

Comparison of the analytical data's obtained by some modified electrodes proposed for the determination of ascorbic acid

Electrode material	Modifier	pH	E_{pa} (V)	Linear range	Detection limit (μM)	References
GC electrode	Poly <i>N,N</i> -dimethylaniline	7.0	0.37	25 μM –1.65 mM	–	Roy et al. (2004)
GC electrode	Polycalconcarboxylic acid	6.0	0.093	1.0–500.0 μM	0.5	Liu et al. (2008)
GC electrode	Ruthenium oxide hexacyanoferrate modified electrode	6.9	0.0	100–1000 μM	2.2	Thiago et al. (2008)
Au electrode	1,6-Hexanedithiol modified gold electrode	7.0	0.27	1–110 μM	1	Sivanesan et al. (2007)
Graphite rod	Cobalt hexacyano ferrate	–	0.38	55.2 μM –3.23 $\times 10^{-2}$ M	33.3	Kumar and Narayanan (2006)
GC electrode	Poly(direct blue 71) modified electrode	7.0	0.1	1 μM –0.01 M	1	Proposed method

and low cost, the present modified electrode seems to be of great utility for making voltammetric sensor for the detection of ascorbic acid.

4. Conclusions

This study has indicated that poly(DB71) film modified GC electrode exhibits higher electrocatalytic activity towards AsA oxidation. The obtained results revealed that determination of AsA can be easily performed using the poly(DB71) films and the modified electrode had dramatically enhanced electrocatalytic activity towards AsA with good electrode stability in the solution. The applicability of the method to the determination of AsA in a commercial vitamin C tablets were demonstrated. This new poly(DB71) film modified electrode can provide a good electrochemical sensing platform for AsA and thus it is expected to have widely potential applications in real sample analysis. Dopamine and uric acid are not interferences in the study state current measurement of AsA at this modified electrode. Poly(DB71) modified electrode also had good stability and easily can be prepared.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2008.05.007.

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