Cyclic Voltammetry and Quantum Chemical studies of Poly(methionine) Modified Carbon Paste Electrode for Simultaneous Investigation Dopamine and Uric Acid

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Abstract

Fabrication of biocompatible electrodes for investigation of catecholamines is a known challenge. In this work, methionine was chosen as a modifier for fabrication of a biocompatible carbon paste electrode by electropolymerization through cyclic voltammetry. The electrochemical behavior of the polymethionine modified carbon paste electrode was characterized by cyclic voltammetry for simultaneous determination of dopamine (DA) and uric acid (UA) in a phosphate buffer solution at pH 7.0. In the absence of an amino acid methionine layer, the bare carbon paste electrode exhibits a rather poor voltammetric signals in DA and UA in the binary mixture with oxidation potentials of DA and UA overlapping with each other. The polymethionine modified carbon paste electrode exhibits good catalytic activity with noticeably different oxidation potentials of DA and UA. The experimental results closely agree with the theoretical prediction based on Fukui function complementary to the simulated electrostatic potential maps.

Keywords: Poly(methionine), Dopamine, Cyclic Voltammetry, Fukui functions and Electrostatic potential

1. INTRODUCTION

Neurotransmitters are the chemical messengers that transmit a message from one neuron to another [1]. Dopamine (DA), one of the most significant catecholamine neurotransmitters belonging to the family of excitatory chemical neurotransmitter [2-3], plays an important role in proper functioning of renal, central nervous, hormonal and cardiovascular system [4]. Shortage of DA in the brain is linked to aggregation of symptoms of Parkinson's disease and other

seemingly unrelated diseases including schizophrenia, huntisons diseases as well as drug addiction and HIV infection [5-7]. On the other hand, uric acid (UA), the primary end product of purine metabolism, is an important antioxidant which protects dopaminergic neurons against oxidative damages. Shortage of UA are linked to symptoms of several diseases such as gout, hyperuricemia and leschnyhan diseases [8-10]. In recent years, many studies have been devoted to fabrication of chemically modified electrodes for simultaneous determination of levels of DA and UA in a binary mixture [11-12], with improving selectivity and sensitivity being one of the main objectives of electroanalytical research [11-12].

Polymer modified carbon paste electrodes (PMCPEs) prepared by electropolymerisation methods are believed to be a promising candidate for detection of neurotransmitter in UA. Selectivity and sensitivity of electropolymer modified carbon electrodes are high. Electropolymers forms a homogeneous deposition with strong adherence at carbon paste electrodes [13-14]. Electropolymers formed using essential amino acids have unique advantages over other counterparts in terms of biocompatibility. Several research groups have previously fabricated electrodes modified with carbon coated with essential amino acids for sensing applications. The essential amino acids that have been explored include phenylalanine [15], valine [16], threonine [17], tryptophan [18], methionine [19], leucine [20], isoleucine [21], lysine [22], and histidine [23]. Interestingly, essential amino acid modified electrodes have reportedly displayed above-average sensing capabilities.

Several research groups have reported the benefits of polymethionine on glassy carbon electrode materials for sensing catecholamies and other chemicals of clinical interest [24-25]. Electrodes formed with methionine modified carbon paste have been successfully used in determination of ascorbic acid present in natural fruits in real applications [26]. The use of glassy carbon electrode modified with methionine and graphene in determination of tryptophan in milk has been reported [27]. Glassy carbon electrodes with polymethionine also showed benefits in simultaneous determination of pyrazinamide and amlodipine in urine and blood plasma [28-29]. Methionine modified electrode was found to exhibit an excellent catalytic property towards determination of amlodipine in human biological fluids. The benefits of electrodes chemically modified with methionine in improving their sensing capabilities have generated a lot of research interests, and without any exception, the biocompatibility of methionine warrants further studies. In the present work, the mechanism of the poly(methionine) modified carbon paste electrode in the simultaneous determination of DA and UA is analytically and experimentally explored. Previous studies have demonstrated that layers of the amino acids coating the surface of a carbon electrode acts like an electron transfer mediator which increases the sensing abilities of electrode.[28] Previously, the density functional theory (DFT) based quantum chemical model has been used to explain the mediating behaviors of modifiers [2,22,30–32].

In the present investigation, the conceptual DFT methods based on analytical Fukui functions and electrostatic potential maps are advantageously used for prediction of redox reactive sites of methionine. In this work, the polymethionine modified carbon paste electrode (PMCPE) has been successfully used as a new sensor which simultaneously determines levels of DA and UA in a binary mixture with no loss of selectivity and sensitivity. The detection mechanism involves elimination of the fouling effect of the oxidized products of UA due to the presence of DA. Analytical Fukui function and electrostatic potential maps are found to be highly instrumental in locating the redox electron transfer sites of the methionine molecule.

Unlike other fabric materials, the carbon in the proposed PMCPE can be used as the filler material for a needle or microneedle to realize minimally invasive measurement of the plasma concentration of uric acid and dopamine. The biocompatible nature of the proposed PMCPE permits in-vivo diagnosis of complication of Parkinson's disease and other illnesses associated with the serum levels of uric acid. The experimental results of this work together with the novel prediction methodology using Fukui function and electrostatic potential maps lays a foundation for the future work of nanoelectronics and diagnosing technologies.

2. EXPERIMENTAL METHODS

2.1 Chemicals.

Dopamine and uric acid were purchased from Himidia chemicals and the stock solution of DA was prepared by dissolving in 0.1M perchloric acid and UA in 0.1M sodium hydroxide solution in double distilled water. All chemicals were of analytical grade and were used without further purification. The phosphate buffer solution (PBS) was prepared by standard method. The experiments were performed at room temperature.

2.2 Apparatus and Procedure.

The electrochemical experiments were carried out in a conventional three-electrode system based in a Model CHI-660c Electrochemical workstation. The three-electrode system contained a working carbon paste electrode packed in a home-made cavity of 3mm in diameter, a platinum wire to be used as a counter electrode and saturated calomel electrode to be used as a reference electrode. To prepare the bare carbon paste electrode (BCPE), 70% a finely grinded graphite powder and 30% of silicon oil were hand-mixed in an agate mortar for about 30 minutes into a homogenous solution. The semi-solid paste was then transferred and packed into the cavity of CPE, air-cured and smoothened on a piece of weighing paper.

2.3 Computational methods and model

Atomic coordinates for all models were constructed using MOLDEN [33] software. Full geometry optimization and electrostatic potential computations of the models were carried out using density functional theory (DFT) in the Gaussian09 program [34] with B3LYP [35-36] correlation functions and 6-311G (d, p) [37-38] basis sets. We have used deMon2k [39] for the frontier molecular orbital (FMO) and Fukui functions computations. The FMO and Fukui results were finally plotted using Sinapsis [40] software.

3. RESULTS AND DISCUSSIONS

3.1 Electrochemical modification of poly (methionine) on CPE.

Fig. 1 shows that the poly(methionine) modification has been successfully achieved with $1x10^{-3}$ M L^{-1} methionine in 0.1 M PBS. In the first potential sweep, an oxidation peak was observed by repeated cyclic scanning of potential when the anodic peak potential reaches -0.10 V. During each of the following cycles, the peak was shifted to the positive potential with an increase in current, which corresponds to the time when the poly(methionine) film was formed on the CPE. The results of our experimental investigation suggest that the PMCPE film in the 0.1 M PBS solution is relatively stable. By repeated cyclic scanning of electrode potential from -0.2 to 0.8 V, the peak height and peak potential of the surface of the immobilized film was found to be almost constant.

3.2. Electrochemical oxidation of dopamine.

The results of our experiment suggest that, with a PMCPE, the presence of DA can be easily detected with high sensitivity. As illustrated in Fig. 2, the PMCPE has yielded the clearly distinguishable cyclic voltammograms for detecting the presence or absence of DA. When the bare CPE was used instead, however, the voltammograms for detecting the presence or absence of DA have almost merged with each other with dimly readable peaks.

With the BCPE, a redox peak potential difference was a $\Delta Ep = 90$ mV. But with the PMCPE, the peak current has increased significantly and the peak potential shifted slightly in a positive direction with a peak potential difference 58 mV. At pH 7.0, DA exists as a cation with a positively charged amino group. DA has exhibited a quasi-reversible response at the BCPE. With the PMCPE, however, DA has exhibited a highly noticeable reversible response. The improved sensitivity and selectivity of detection of DA observed in the PMCPE was due to an electrostatic and hydrophobic interaction between polymethionine and DA. The voltammogram *c* in the Fig. 3 shows the blank response of the PMCPE at 0.1 M PBS (pH-7.0). With the PMCPE, DA has exhibited a single oxidation and reduction peak, followed by another oxidation and reduction peak due to the redox reactions of methionine.

The cyclic voltammograms of DA at different scan rates is shown in the Fig. 3a. The plot of scan rate versus current is shown in Fig. 3b, from which it can be seen that, as the scan rate increases, the current also increases. The redox current intensities has increased with an increasing scan rate with a correlation coefficient $r^2 = 0.9995$, suggesting that the electrode reaction was adsorption-controlled. According to Fig. 3b, the current can be linearly regressed in terms of the scan rates using the following equation: $I = 0.0144v - 0.54$ where I is the current in μ A and v is the scan rate in mVs^{-1}.

3.3 Theoretical studies of methionine

Methionine polymer adhered to the surface of electrode increases the electrocatalytic activities of PMCPE towards DA. We have previously reported several polymer modified carbon paste electrodes for the sensitive detection of DA. Based on our previous findings, we have come to conclusion that there exists a mediated electron transfer at the PMCPE [22]. By the same token, a similar mediated electron transfer from the methionine is believed to have occurred on the surface of the PMCPE in this work. Methionine reacts with carbon to form a electropolymer on the surface of the carbon electrode, which may be the dimer or trimer or polymer. For the purpose of mathematical modeling, only a monomer of methionine is considered in the present presentation. In an attempt to determine which atoms of the methionine are involved in the redox electron transfer reactions, we have simulated the electrostatic surface potential, frontier molecular orbitals (FMO) using the Fukui concept to determine the redox electron transfer sites. As a result of this simulation, electrostatic potential energy maps showing the three-dimensional charge distribution of molecules were obtained. These maps allow us to visualize the charged regions of the methionine molecule. Knowledge of the charge distributions can be used to determine how the molecule interacts with one another [41]. Fig. 3c is one of the electrostatic potential energy maps that show the electron distributions obtained using Gaussian09 program. It can be observed from Fig. 3c that high probability of electron distribution was found on the amino group and the sulfur atom, which corresponds to the reduction sites for the DA molecule. The probability of electron distribution is relatively low on the carboxylic acid group, suggesting that the carboxylic acid group is the oxidation site for DA molecule. It can be observed from the Fig. 4 that the highest occupied molecular orbital (HOMO) of methionine is located on the sulfur atom and the lowest occupied molecular orbital (LUMO) located on the carbon and oxygen atoms of the carboxylic acid group of the

methionine. The results of this analysis suggest that oxidation of PMCPE occurs via the sulfur atom in the methionine molecule whilst reduction occurs through the carboxylic acid group of the molecule.

Fukui function is generally used to understand redox reaction mechanisms in Electrochemistry [2,31]. Simulation based on Fukui function can be applied in chemical and electrochemical applications for locating electron transfer sites [5,28,36–38]. Fukui function can be defined according to Eq-1 [42–44].

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]^{+/-}_{v(r)} \quad (1)$$

where $\rho(r)$ is the electron density, N is the number of electrons in the system. + and − signs correspond to addition of electrons or removal of electrons, respectively. The generic form of Fukui function as given in Equation (1) can be further rewritten into $f(r)=f^{+} - f^{-}$, where f^{-} represents electrophilic attack:

$$f^{-} = \rho(N) - \rho(N-1) \quad (2)$$

and f^{+} represents nucleophilic attack:

$$f^{+} = \rho(N+1) - \rho(N) \quad (3)$$

In this work, simulation using Fukui function was done in deMon2k, which further reinforces the hypothesis that HOMO of methionine is located on the sulfur atom and LUMO is located on the carbon and oxygen atoms of the carboxylic acid group of the methionine molecules. The results of simulation using Fukui equation as shown in Fig. 5 consistently suggests that the oxidation site of the methionine is indeed located at the sulfur atom and reduction sites of the methionine is located on the carboxylic acid group. In other words, the sulfur atom of the methionine is responsible for the oxidation of PMCPE whilst the carboxylic acid group is responsible for the reduction of PMCPE. The electron transfer reactions of the PMCPE at a molecular level is further confirmed in this quantum chemical simulation.

3.4 Effect of concentration of DA.

Cyclic voltammogramms of differently concentrated DA (0.1 to 1.9x10−4 M) are shown in the Fig. 6a. The anodic peak currents of DA have been found to increase linearly with the concentration of DA according to Fig. 6b. The current can be expressed by linear regression in terms of the DA concentration using the following equation: I=0.389C+1.8722, where I is the current in μA and C is the DA concentration in 10^{-4}M. Therefore, the proposed PMCPE electrode can be used to detect the different concentrations of DA.

3.5 Effect of pH on the oxidation of DA.

The effect of pH on the electrochemical response of the PMCPE towards the determination of DA has been studied. Fig. 7 shows the variation of peak potential of DA as a function of the change in pH of the electrolyte. As pH increases, the peak potential difference ΔEp decreases. The slope of the pH value was found to be 0.58 mV, suggesting that the proportion of the electron and proton involved in the reaction is 1:1 [28]. Since DA oxidation is a two-electron process, the number of protons involved in the oxidation process is also expected to be two. The peak potential difference can be expressed by linear regression in terms of the pH value using the following equation: ΔEp =-14.25p+166.5, where ΔEp is the peak potential difference in mV and p is the pH value.

3.6 Oxidation of uric acid

The irreversible oxidation voltammogram of UA in pH=7.0 at a BCPE occurs at 0.36 V with respect to the saturated calomel electrode, according to Curve *a* of Fig. 8. According to Curve b of Fig. 8, when the PMCPE was placed into a blank buffer solution, a basis of redox peaks, attributing to oxidation and reduction of methionine occurred. According to Curve *c* of Fig. 8, the redox reaction occurs at approximately 0.41V with a significant increase in current density when the 1 mM UA was added to the 0.1M PBS solution.

Fig. 9a shows the cyclic voltammograms of 1 mM uric acid on poly(methionine)/CPE at different scan rates. When the scan rate was incremented from 70 mVs^{-1} to 150 mVs^{-1}, the peak currents also increase accordingly. The relationship of the anodic peak current with the scan rate was constructed and illustrated in Fig. 9b. Fig. 9b further confirms the fact that the electron transfer reaction was an adsorption-controlled process. According to Fig. 9b, the current can be linearly regressed in terms of the scan rates using the following equation: $I = 0.0163v - 0.7625$ where I is the current in μA and v is the scan rate in mVs^{-1}.

3.7 Simultaneous determination of DA and UA

As shown in Fig. 10, both DA and UA exhibit highly selective and sensitive electrochemical responses at the PMCPE. This performance is due to the electrostatic and hydrophobic interaction of DA and UA with methionine polymer at the PMCPE. In another experiment, the redox reactions of the DA and UA mixtures were studied. It can be observed from the solid line that the voltammetric responses of DA and UA almost overlap with each other at the BCPE immersed in a phosphate buffer solution at pH=7.0. As the dotted line shows, however, two well-defined oxidation peaks with different currents were noticeably observed.

4.0 DISSCUSSION

The results of our Frontier simulation was in complete agreement with the published one [45]. Neither polymethionine nor carbon is toxic to human bodies. With some modification, PMCPE can be easily implemented in micro-needles for in-vivo determination of UA and DA. At the time of this writing, many approaches for simultaneous determination of UA and DA have been attempted (See Table 1). However, most of the published approaches involve the use of chemicals with unknown toxicity that renders in-vivo diagnosis difficult, if not impossible. Some of the known methods have been proven non-toxic but the electric current involved in the analysis is too small to distinguish the UA or DA levels.

Table 1: Previously published approaches for simultaneous determination of UA and DA

Method	Chemical(s)/chemical Modifier(s) involved	Reference(s)
1	Zinc Hexacyanoferrate Clay	46
2	Ribonucleic acid (RNA)	47
3	Poly(l-lysine)/Graphene Oxide	48
4	β-Cyclodextrin	49
5	Exfoliated Graphite Electrodes	50
6	Silver nanoparticle-decorated reduced graphene oxide composite	51
7	Polyadenine	52

5.0 CONCLUSION

In the present study, poly(methionine) modified carbon paste electrode (PMCPE) was used for the simultaneous determination of DA and UA in a phosphate buffer solution at pH 7.0. The PMCPE is carbon paste electrode with a layer of poly(methionine) polymerized on the surface. In repeated cyclic scan of a voltammogram, the modified electrode consistently yields two noticeably different and stable potentials of DA and UA over a long period with a low detection limit. According to the electrostatic electron maps as well as the results of quantum chemical simulation using Fukui equation, the sulfur atom of the poly(methionine) is responsible for the oxidation of PMCPE whilst the carboxylic acid group of the poly(methionine) is responsible for the reduction of PMCPE. The electrocatalytic activity of poly(methionine) improves the reversibility of the cyclic voltammetric analysis and complete resolution of the anodic waves of the DA and UA. The theoretical and experimental approaches of this work point to the feasibility of realistic application of biocompatible electrodes in an in-vivo investigation of clinical interest.

6. Author contributions

B.N.C, B.E.K and C.C designed and set up the experiments, G.K.J performed computational calculations, K.H performed electrostatic potential computations. B.N.C. G.K.J. and L.W.L. wrote the manuscript. All authors have contributed to revising the paper.

7. Conflicts of interest

There are no conflicts to declare

8. Acknowledgements

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Figures:

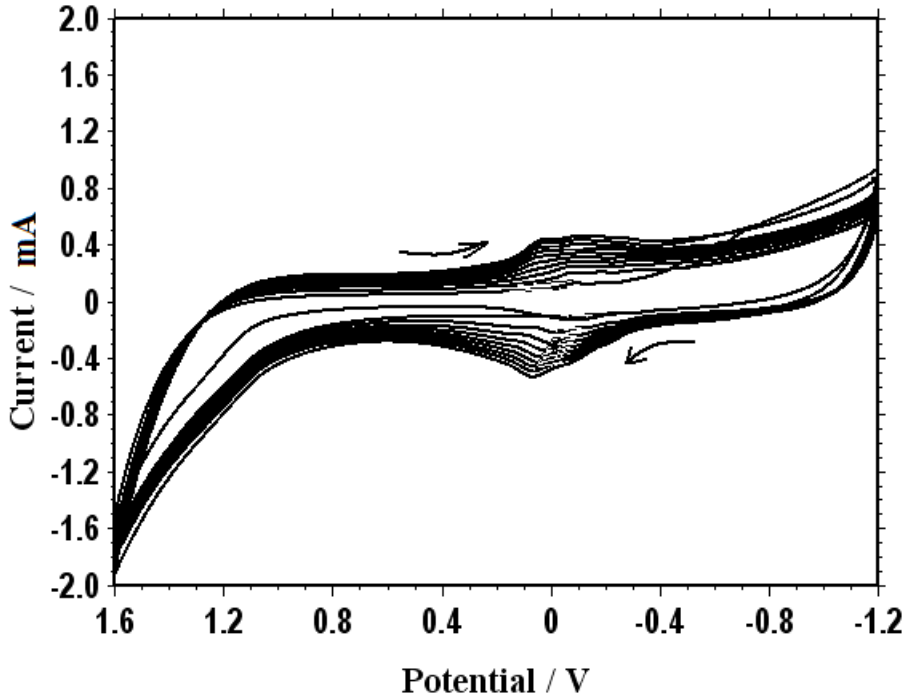


Figure. 1

Fig 1. Cyclic voltammograms for electrochemical polymerisation of methionine on bare carbon paste electrode in 0.1M PBS pH-7.0 by 20 segments. Sweep rate 100 mVs^{-1}

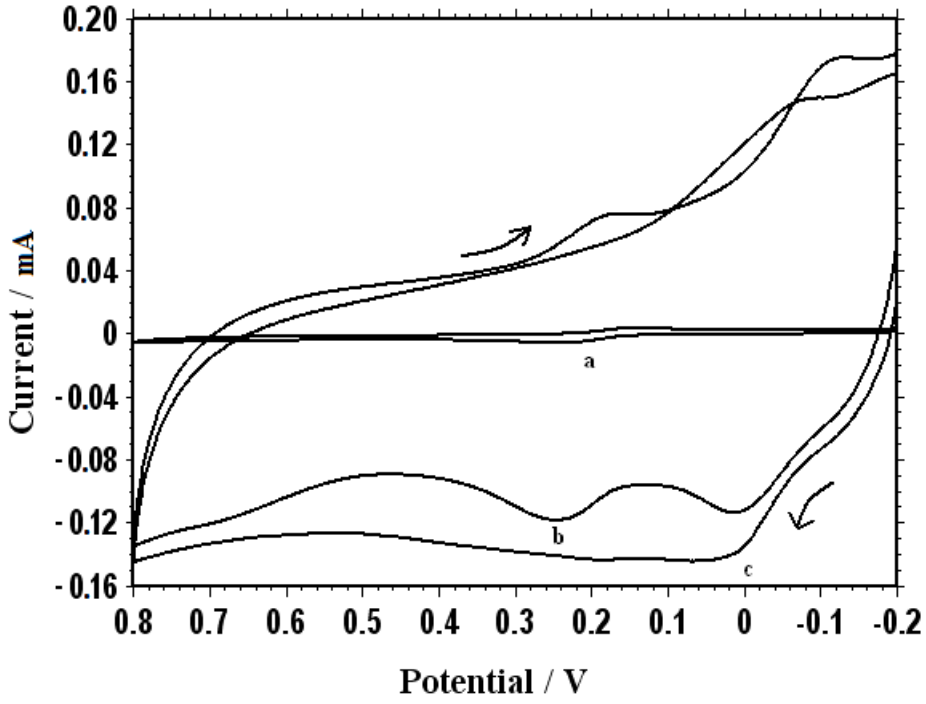
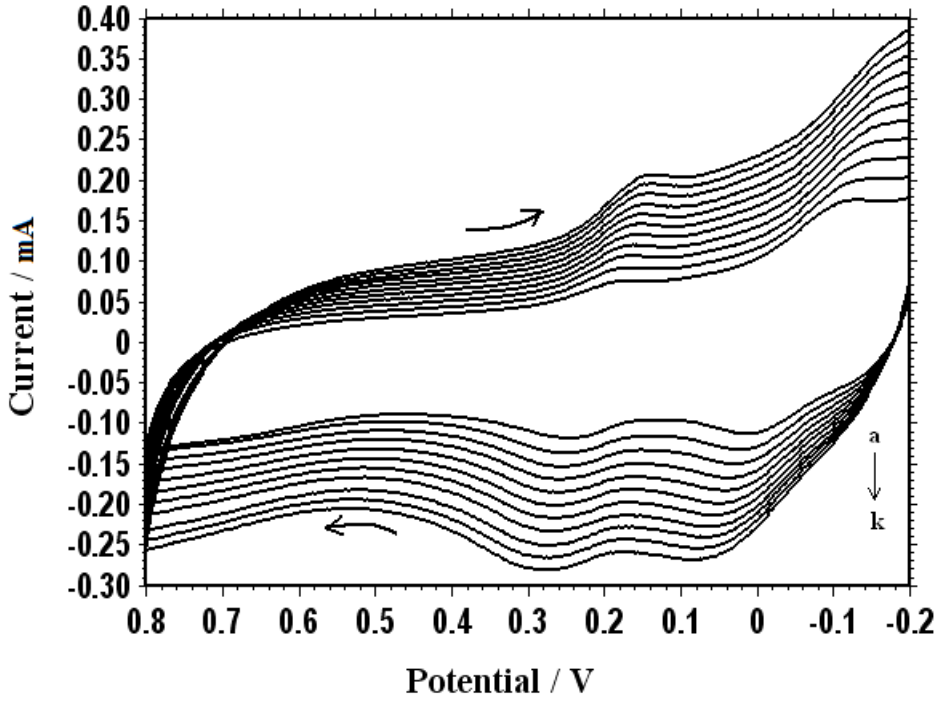
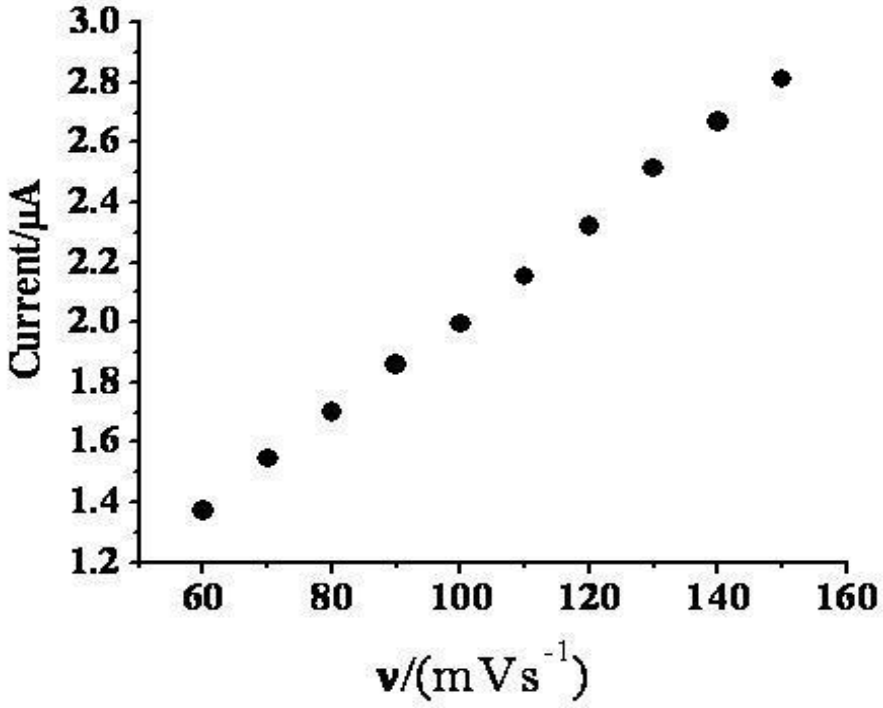


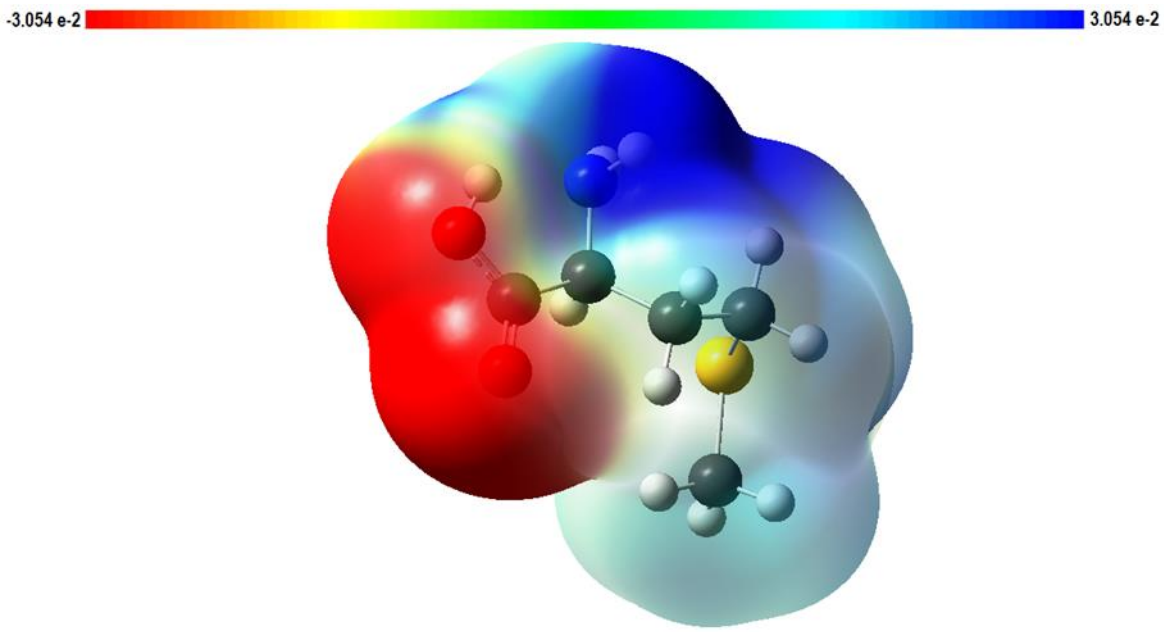
Fig 2. Cyclic voltammograms at a bare CPE (a) and PMCPE (b, c) in presence of 1×10^{-3}M DA (a,b) and in the absence of DA (c) in 0.1 M PBS (pH 7.0): Scan rate 100 mV/s


0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
Current / mA
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
Potential / V
a
k

(a)

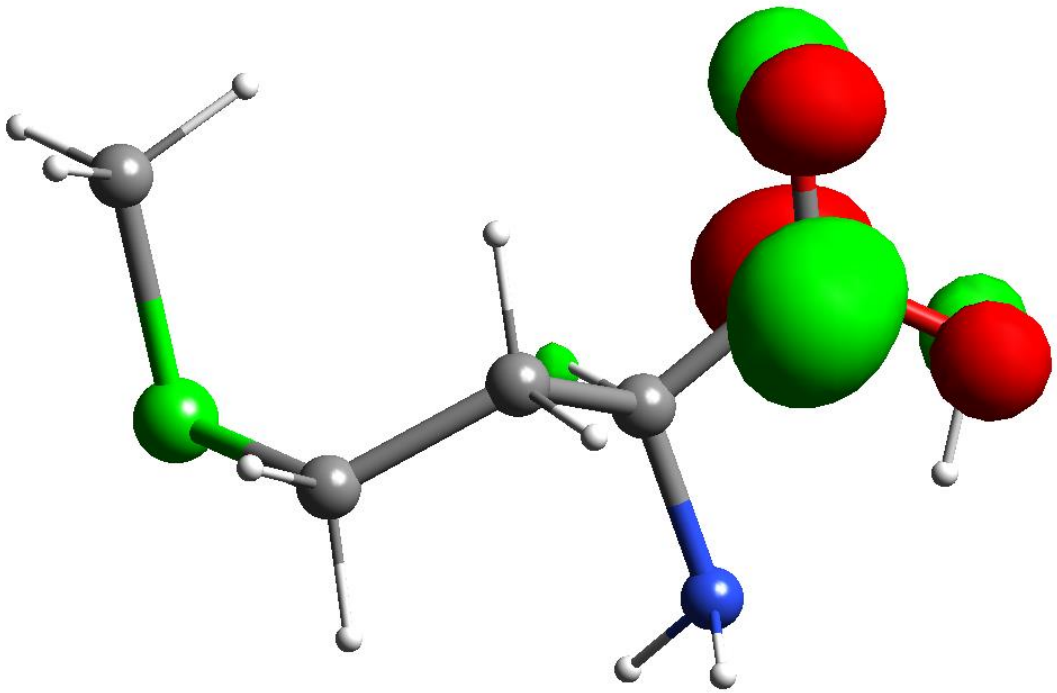

3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
Current/μA
60
80
100
120
140
160
v/(mVs-1)

(b)

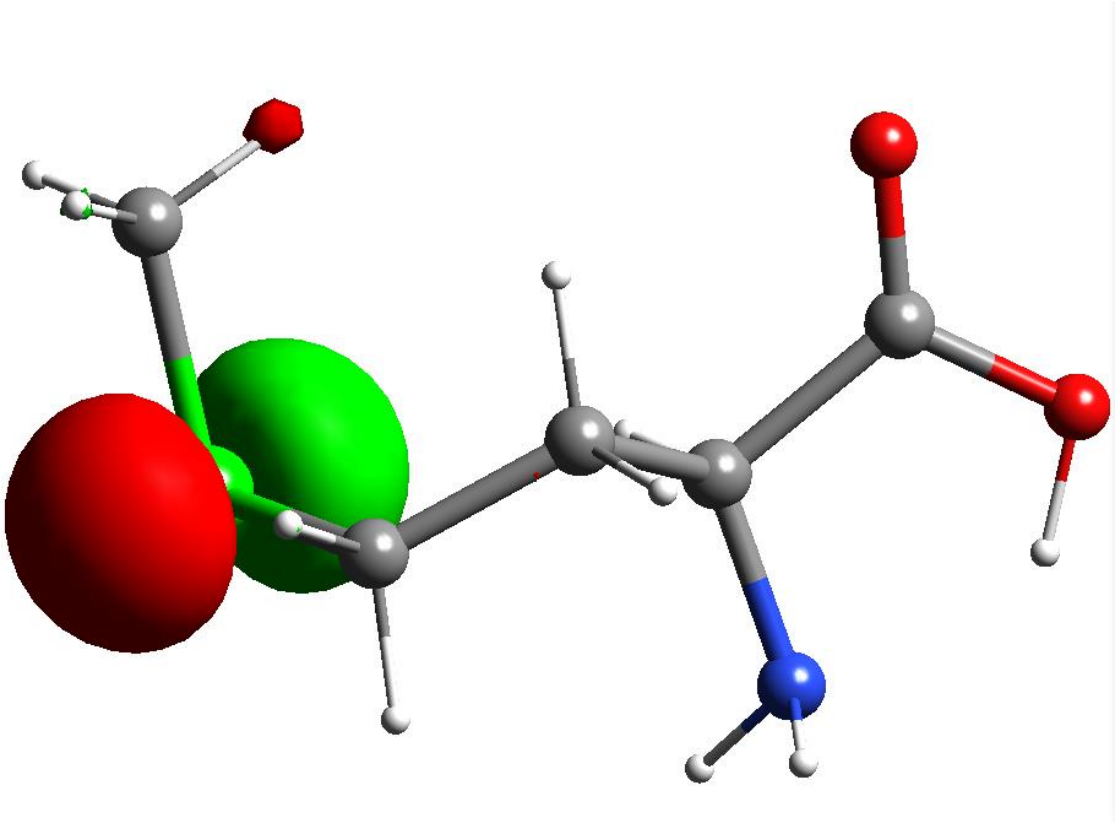


(c)

Fig 3. Effect of different scan rates: a) Cyclic voltammograms of 1 ×10-3 M DA at different scan rates (a-k;50,100,150,200,250,300,350,400 mVs-1) in 0.1 M PBS (pH 7.0); b) Effect of different scan rates on the oxidation peak current of 1 ×10-3 M DA at the PMCPE. c) Electrostatic potential map of methionine.

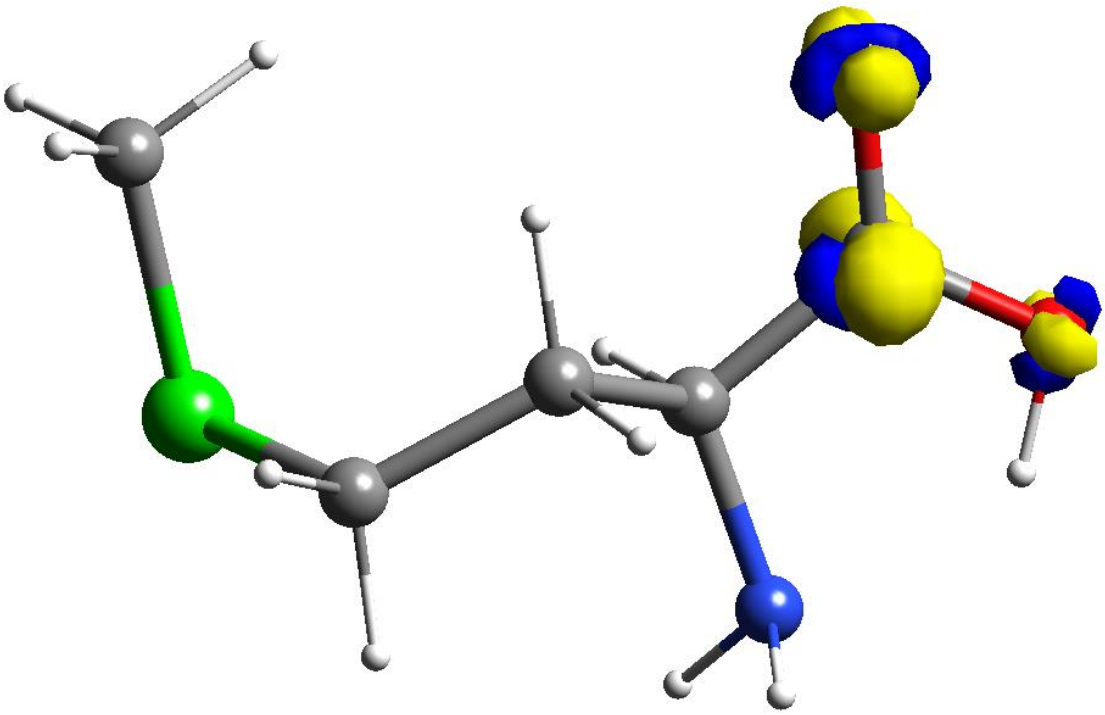


(a)

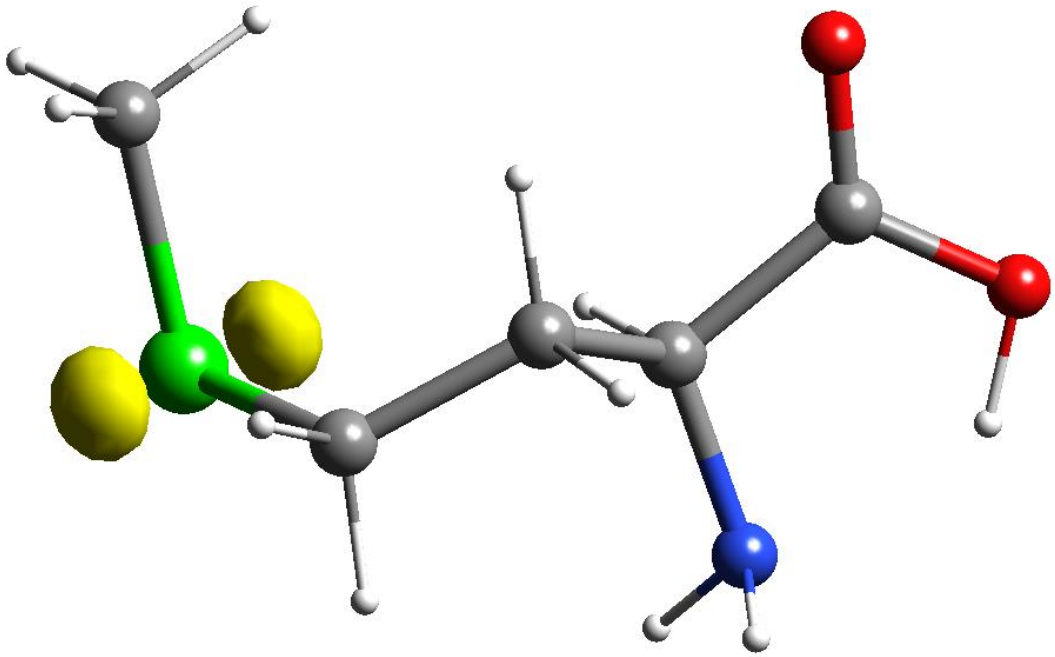


(b)

Fig. 4. Orbital of methionine: a) LUMO orbital of methionine (isosurface value of 0.09); b) HOMO orbital of methionine (isosurface value of 0.09).

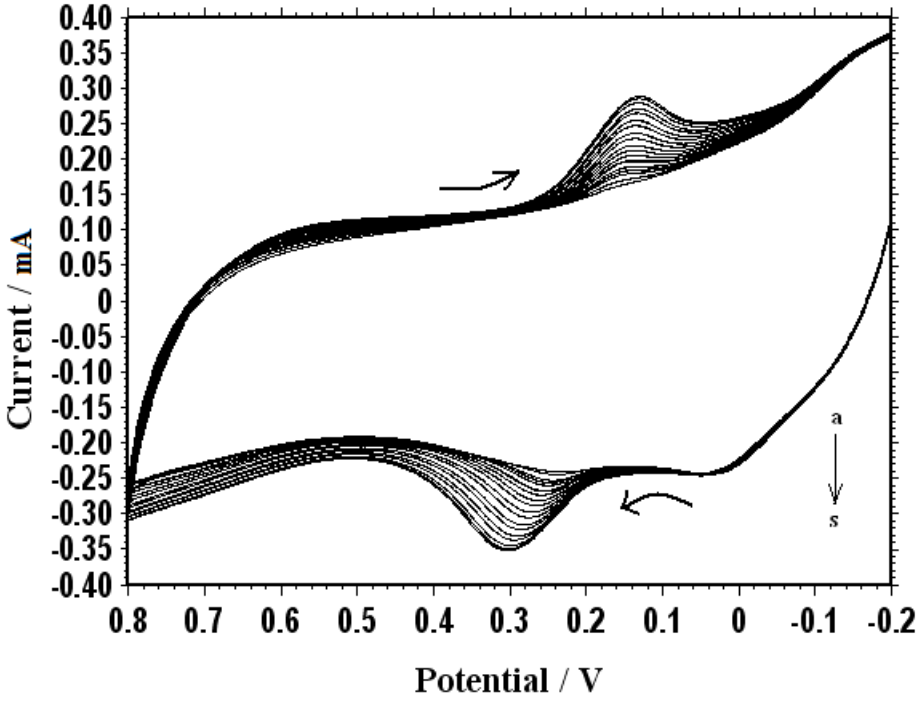


(a)

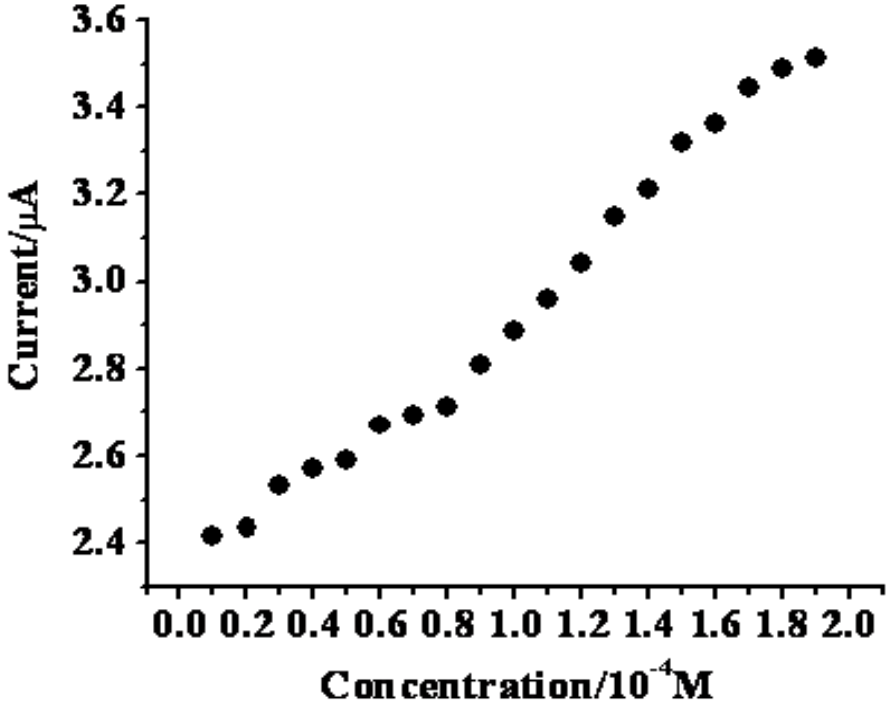


(b)

Fig. 5. Fukui results of methionine: a) Reduction sites of methionine $f^{+}(\mathbf{r})$ of LMCPE (isosurface value of 0.02); b) Oxidation sites of methionine $f^{-}(\mathbf{r})$ of LMCPE (isosurface value of 0.02).


Current / mA
Potential / V
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
a
s

(a)



(b)

Fig. 6. Effects of different concentrations of DA: a) Cyclic voltammograms of DA at different concentration(a-s; 0.1 to 1.9 x 10-4 M) in 0.1 M PBS (pH 7.0): Scan rate 100 mVs-1; b) Effect of different concentrations of DA on the oxidation peak current at PMCPE

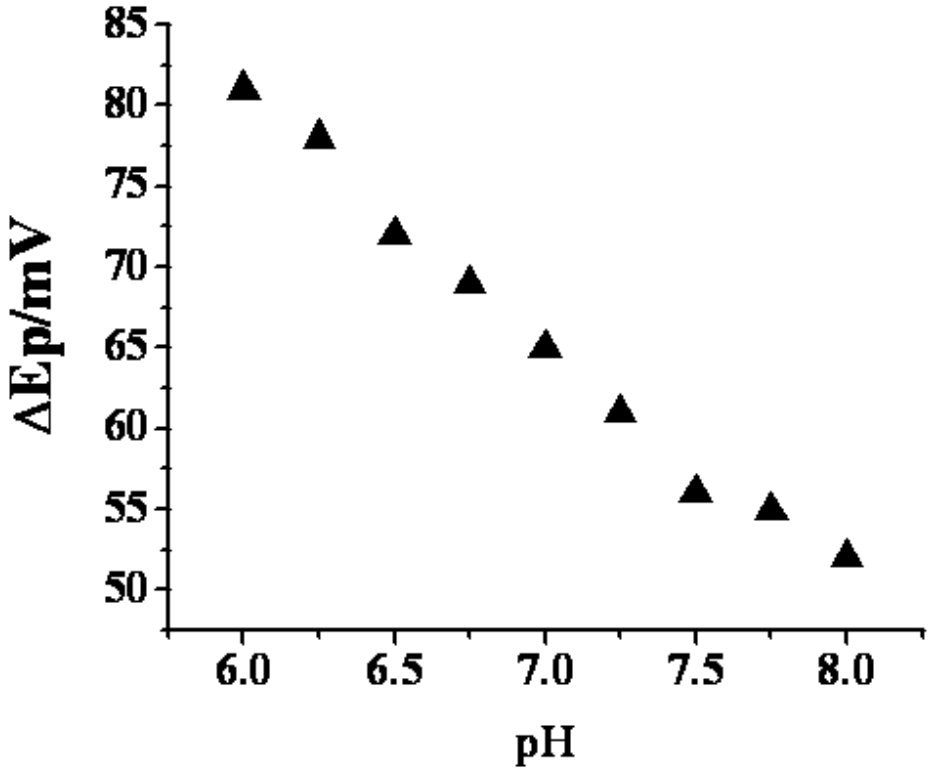


Fig 7. Effect of pH on the oxidation peak potential of 1×10^{-4} M DA at PMCPE.

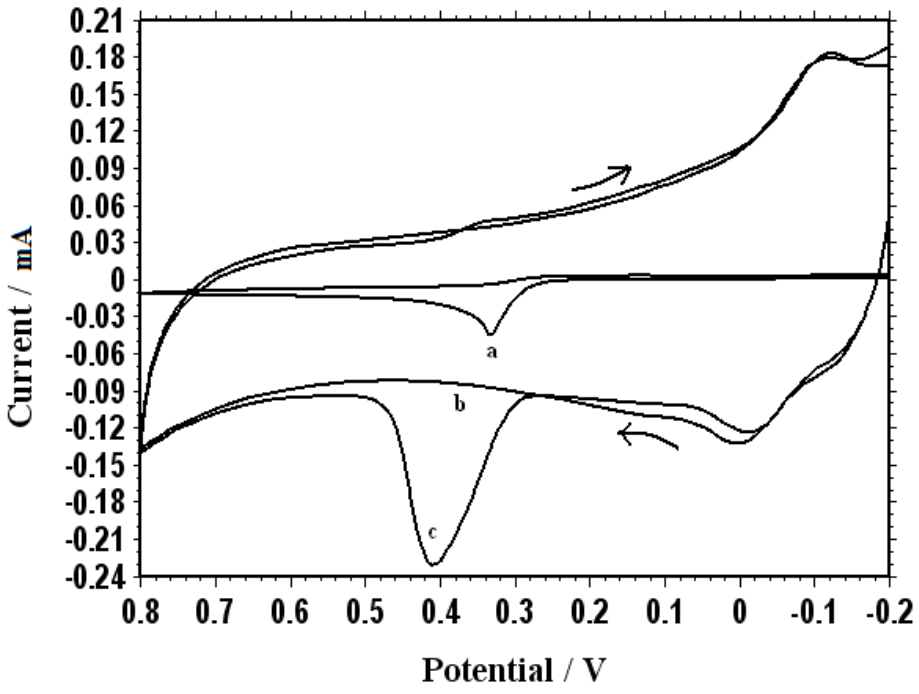
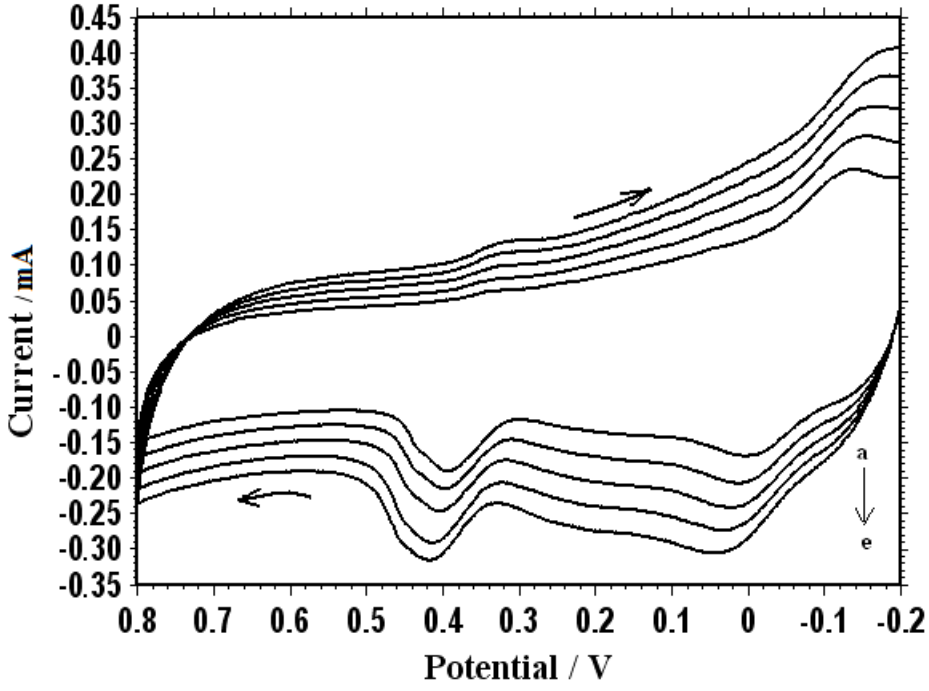
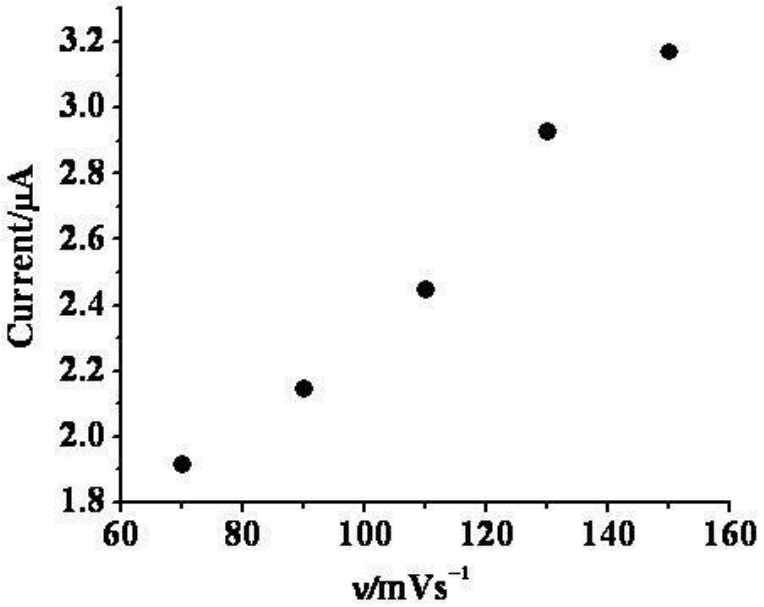


Fig 8. Cyclic voltammogram of the BCPE in 1 mM UA is shown in curve a. Curves b and c respectively shows the cyclic voltammograms of the PMCPE in a blank buffer solution and in 1 mM UA (curve c) at 100 mVs^{-1} in 0.1 M PBS (pH 7.0).


Current / mA
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
Potential / V
a
e

(a)



(b)

Fig 9. a) Cyclic voltammogram of 1×10-4 M UA at different scan rates (70, 90, 110, 130, 150mVs^{-1}) in 0.1 M PBS (pH 7.0); b) Effect of different scan rates on the oxidation peak current of 1×10^{-4} M UA at the PMCPE.

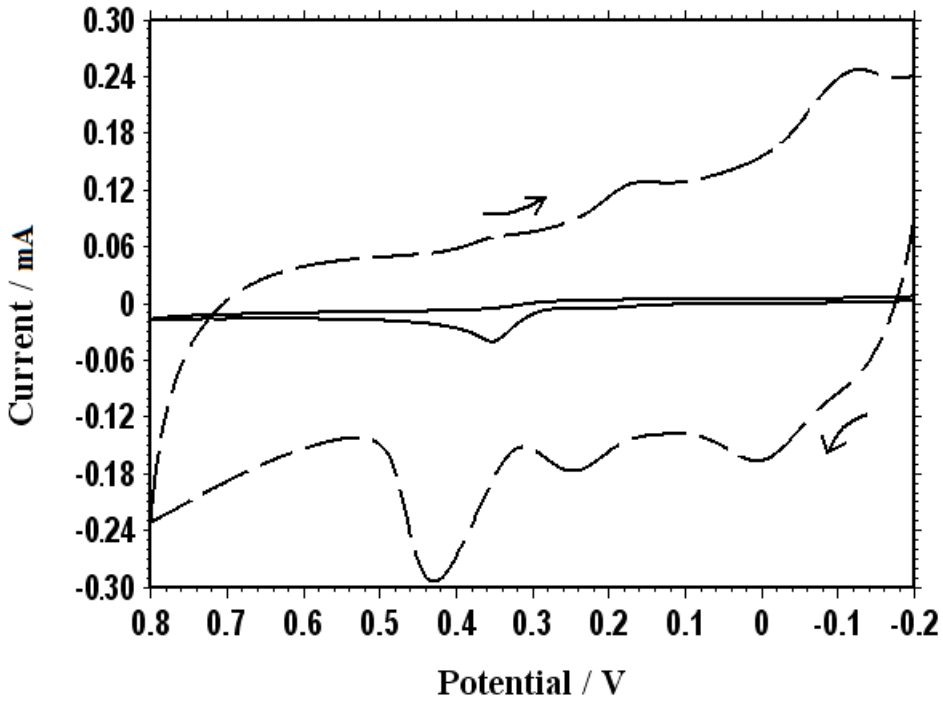


Fig 10. Cyclic voltammogram for simultaneous determination of 1×10^{-4} M DA and 1×10^{-3} M UA in 0.1 M PBS (pH 7.0) at bare(solid line) and PMCPE(dashed line). Scan rate:100 mVs^{-1}