

Full Paper

Electrocatalysis of SDS Surfactant Modified Carbon Paste Electrode for the Simultaneous Determination of Ascorbic Acid, Norepinephrine and Folic Acid

Bananakere Nanjegowda Chandrashekar^{1,2} and Bahaddurghatta E. Kumara Swamy^{2,*}

¹*Center for Materials Science and Technology, Vijnana Bhavan, University of Mysore, Manasagangothri, Mysuru-570006, India*

²*Department of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, Shankaraghatta -577 451, Shimoga, Karnataka, India*

*Corresponding Author, Tel.: +91 8282 256225; Fax: +91 8282 256255

E-Mail: kumaraswamy21@yahoo.com

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Abstract- A carbon paste electrode was modified with anionic surfactant sodium dodecyl sulphate (SDS) solution by immobilization method; surfactant solution was strongly adsorbed on the carbon paste electrode (CPE) and applied to the simultaneous detection of norepinephrine (NE) in the presence of ascorbic acid (AA) and folic acid (FA). The electrochemical response of the SDS modified CPE (SDS/CPE) was evaluated with respect to pH, preconcentration time, scan rate and other variables by cyclic voltammetric technique. The concentration variation of SDS (modifier) results in optimization of the modified electrode and also the good electrocatalytic performance of the SDS/CPE were tested on the redox behavior of the potassium ferricyanide. The present method provided a simple method for the detection of NE in biological samples. Electron transfer of NE redox at bare carbon paste electrode was too slow as compared at SDS/CPE. The SDS/CPE showed reversible electrochemical behavior of NE with a formal potential of 0.065 V versus SCE. The interfacial process between the SDS/CPE and NE in 0.2 M PBS (pH 7.0) was investigated with their electrochemical reaction and the results indicated that the two electron two proton transfer was involved in the electrode reaction process. Under optimal conditions a detection limit of 1 μ M was obtained.

Keywords- Electrocatalysis, Sodium dodecyl sulphate, Carbon paste electrode, Norepinephrine, Cyclic voltammetry

1. INTRODUCTION

Norepinephrine (NE) is an important catecholamine neurotransmitter and plays an important physiological role in the central nervous system [1]. NE functions as a neurotransmitter, which is secreted and released by the adrenal glands and the noradrenergic neurons during synaptic transmission. It can be used for treating myocardial infarction, hypertension, bronchial asthma and organic heart disease [2]. NE has been strongly implicated in the physiological conditions such as stress, anxiety, sleep, memory and learning [3,4]. Extreme abnormalities of NE concentration levels may lead to the occurrence of many diseases, such as ganglia neuroblastoma, ganglion neuronal, paraganglioma, Parkinson' disease etc. So it is very necessary to develop fast, accurate and sensitive methods for the direct detection of NE. Many methods, such as high-performance liquid chromatography [5], spectrophotometry [6], ion chromatography [7] and fluorometry [8] were employed for the determination of NE. However, most of these methods have their shortcomings, such as comparatively low detection limit, time-consuming, low sensitivity and complicated process. Consequently, the electrochemical method [9] has attracted much attention because of its quick response, relatively high sensitivity and the ability to be miniaturized.

However, it is almost impossible to detect this component electrochemically by direct oxidation on a conventional electrode (i.e., glassy carbon, graphite, Au, Pt) because of its high overpotential and because of electrode fouling, poor reproducibility and poor sensitivity. Moreover the direct redox reactions of these species at the bare electrodes often suffer from pronounced fouling effect, which results in rather poor reproducibility. The high overpotential and the poor reproducibility usually limit the use of the bare electrodes for the direct determination and detection of these species in biological matrices. Therefore, there have been numerous attempts to enhance the electrode kinetics using various carbon paste modified electrodes [10-14]. However, these methods needs lot of improvements to developing simple, selective and sensitive methods that can simultaneously detect NE in the presence of other interference like ascorbic acid and folic acid is urgently needed.

Thus, the development of NE sensor has been a major electroanalytical research goal for in vivo and in vitro monitoring in the interference of ascorbic acid and folic acid. The chemical modification of electrodes using electron transfer mediators is an interesting field in analytical chemistry. One of the most important objectives of the mediator is a reduction of the overpotential required for electrochemical reaction, which enhances the sensitivity and selectivity of the method [15]. Therefore, some chemically modified electrodes with various active mediators immobilized at the electrode surface have been used for the catalysis of electrooxidation of NE [16,17]. A surfactant is a linear molecule with a hydrophilic head and a hydrophobic end. Due to their unique molecular structure, surfactants have been extensively used in the fields of electrochemistry and electro analytical chemistry for various purposes. Surfactants, containing hydrophobic and hydrophilic groups, can change the properties of the

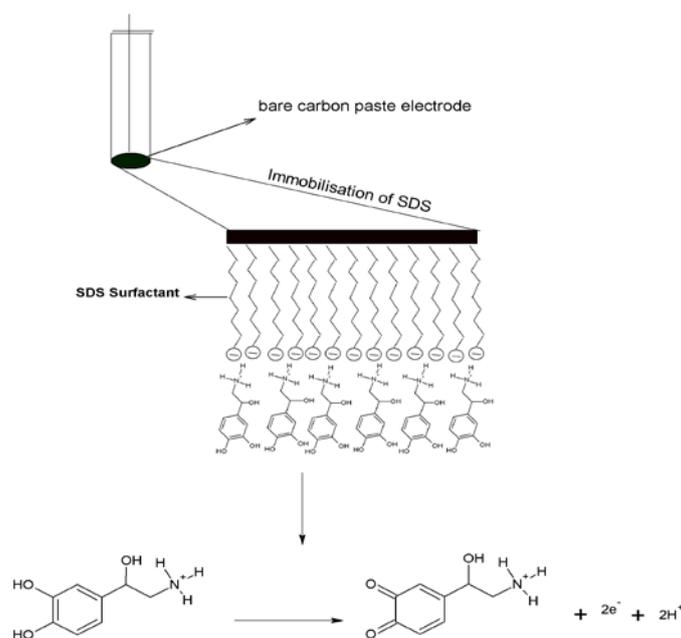
electrode-solution interface and subsequently influence the electrochemical processes of other substances. The importance of surfactant as a modifier of electrodes in the field of electrochemistry has been reported [18-20].

In this report, the modification of CPE is introduced by hydrophobic adsorption of SDS on the surface of CPE. This electrode has a high density of negative charges covered on the electrode surface. The process for the fabrication of modified electrode is comparatively smaller time duration than any method previously reported. A modification made by surfactant solution improved the sensitivity and selectivity of the voltammetric measurements of the NE in the presence of high concentration of AA and FA. The simplicity, high sensitivity and selectivity of the SDS/CPE made the method very highly convenient and satisfactory results were obtained.

2. MATERIALS AND METHODS

2.1. Apparatus

Electrochemical measurements were carried out with a Model CHI-660c electrochemical work station in a conventional three-electrode system. The working electrode was a carbon paste electrode, having cavity of 3 mm diameter. The counter electrode was a bright platinum wire with a saturated calomel electrode (SCE). Digital pH meter MK VII from systronics was used for the adjustment of buffer solution pH.



Scheme 1. Schematic mechanism of NE reaction at the surface of SDS/CPE

2.2. Reagents

NE, AA and FA were obtained from Himedia chemicals. All other chemicals were of analytical grades. A phosphate buffer solution (PBS- 0.2 M) was prepared by mixing standard stock solutions of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 . Freshly prepared analyte solutions of NE, AA and FA were used in all experiments. NE was dissolved in 0.1 M perchloric acid and all other solutions were prepared with double distilled water.

2.3. Preparation of SDS/CPE

A 70:30 ratio mixture of graphite powder and silicon oil was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted into the bottom of the teflon tube. The internal radius of teflon tube was 0.3 mm. The electrical connection was implemented by a copper wire fitted into the teflon tube. 30 μL SDS was immobilized on the bare carbon paste electrode, left for few minutes and washed with PBS.

3. RESULTS AND DISCUSSION

3.1. Optimal working conditions and electrochemical characterization of SDS/CPE

Cyclic voltammetric measurements of the SDS/CPE were conducted in 1 M KCl containing 1 mM K_3FeCN_6 . The current at unmodified electrode exhibited a low response for K_3FeCN_6 but at the SDS film coated CPE (SDS/CPE) current was increased and also potential was shifted to negative side with the peak potential difference of 24 mV, which confirmed that the SDS/CPE acts as an excellent electrocatalytic activity which reduced the over potential of K_3FeCN_6 . Although the SDS surfactant showed an enhanced effect on the oxidation of NE, the highest oxidation peak current with the less capacitance current was optimized by varying the concentration and the accumulation of SDS over the CPE at different time. Fig. 1A shows the cyclic voltammograms of NE responses at different amount of 10 mM SDS modifier. As the concentration of SDS was increased from 10-60 μL of 10 mM, the peak current also increased and above that the peak currents could not be properly identified due to the high capacitance current. Hence the anodic peak current due to 30 μL SDS was optimized and used. Fig. 1B demonstrated that the time variation for the accumulation of SDS to form uniform layer on the CPE. The peak current of NE was increased as the accumulation time of SDS surfactant increased from 5 to 20 minutes. Hence the determination of NE was carried out at 5 minutes of accumulation time for all types of parameter. The surface active morphology of the SDS modified carbon paste electrode was also characterized by scanning electron microscope. Fig. 1C shows the SEM image of the bare carbon paste electrode (a) and SDS/CPE (b). The immobilized SDS solution was

distributed over the carbon paste electrode and formed the smooth surface as compared to the bare carbon paste electrode.

3.2. Oxidation behavior of ascorbic acid at SDS modified carbon paste electrode

Fig. 2A depicts cyclic voltammograms for the oxidation of AA at bare carbon paste electrode (curve a) and at SDS/CPE (curve c) in 0.2 M phosphate buffer (pH 7.0). The voltammogram (curve b) reveals that the SDS/CPE has not shown any characteristic peak in blank solution. Immobilization of SDS formed the negative charge over the carbon paste electrode leads to the electrostatic repulsion between the anionic charged AA and the SDS/CPE. This is very remarkable because, such a catalytic activity is shown in Fig. 2A, the peak current recorded for AA oxidation at SDS/CPE was clearly increased compared to that of bare carbon paste electrode with the large peak potential shifted towards negative side.

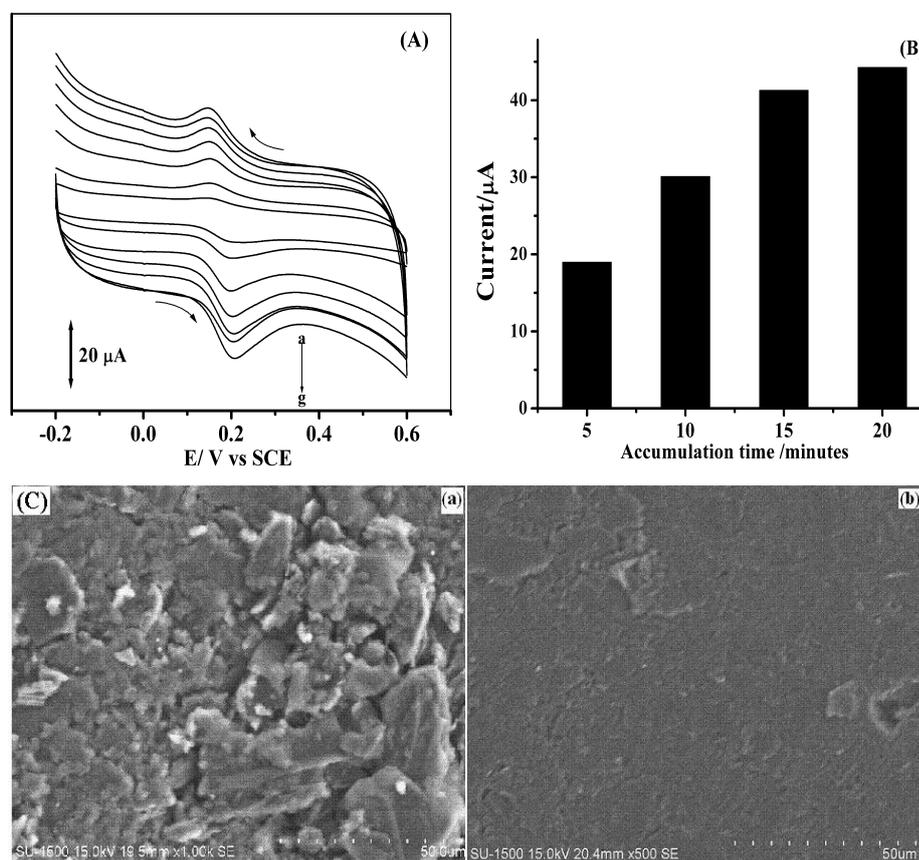


Fig. 1. (A) Cyclic voltammograms of 1×10^{-4} M NE responses at different amount of 10 mM SDS modifier (a to g: 0 to 60 μ L). Sweep rate: 50 mVs^{-1} ; (B) Plot of anodic peak current of NE versus SDS accumulation time of the TX-100/CPE; (C) Scanning electron microscopic image of (a) bare carbon paste electrode and (b) SDS/CPE

Interestingly, the recorded anodic peak potential difference between the bare and SDS modified carbon paste electrode was 216 mV which revealed that the SDS/CPE acts as good electrocatalytic biosensor.

Fig. 2B demonstrates the cyclic voltammograms of SDS/CPE at different scan rates, as scan rate increased the anodic peak current increased without altering its peak potential. The plot of anodic peak current versus square root of scan rate of ascorbic acid is shown that the I_{pa} is proportional to the square root of scan rate over the range of 50 to 300 mVs^{-1} . The linear regression equation was $I_{pa} (10^{-4}\text{A}) = -1.1581(10^{-4}\text{A}) + 0.39 (v^{1/2}/(\text{Vs}^{-1})^{1/2})$, with a correlation coefficient of $r^2 = 0.9939$, therefore, the anodic peak current was controlled by the mass diffusion, showing a diffusion-controlled process in the solution.

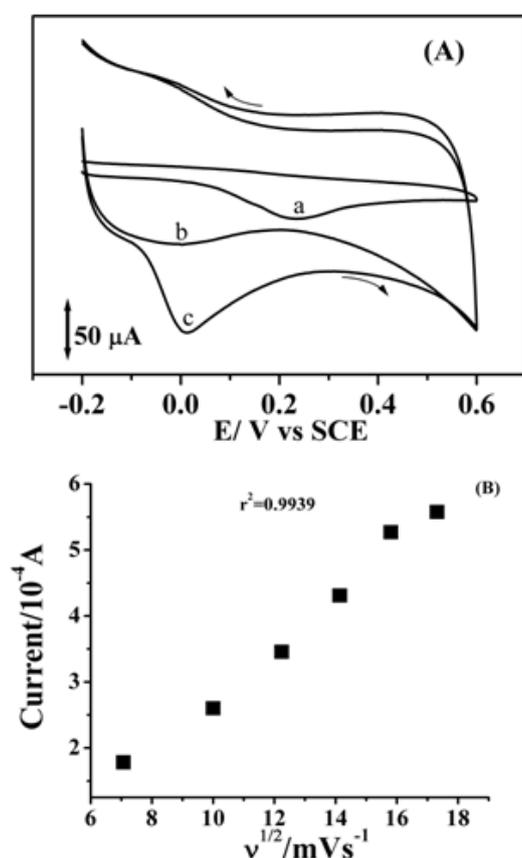


Fig. 2. (A) Cyclic voltammograms at a bare carbon paste electrode (curve a) and SDS modified carbon paste electrode (curve b and c) in the presence of 1×10^{-3} M AA (curve a and c) and in the absence of AA (curve b) in 0.2 M PBS of pH 7. Scan rate: 50 mVs^{-1} ; (B) Graph of anodic peak current versus square root of scan rate

3.3. Electrochemical studies of NE at SDS/CPE

It is well known that NE has electrochemical responses on unmodified carbon paste electrode. In this experiment, after immobilization of negative charged SDS, the anodic peak current signal was increased due to the electrostatic attraction between the NE and the

SDS/CPE is shown in the scheme. 1. Fig. 3A shows the cyclic voltammograms of 0.1 mM NE in 0.2 M PBS at unmodified CPE (curve a) and SDS/CPE (curve b). At the bare CPE a broad anodic peak was recorded at 253 mV which demonstrating slow electron transfers kinetics. While at the modified electrode a sharp oxidation peak was appeared at 191 mV. The reduction of over potential from 253 mV to 191mV and enhanced anodic peak current showed that the electrocatalytic oxidation tendency of SDS/CPE on NE. The electron transfer kinetics of SDS modified electrodes is significantly improved and its electrochemical impedance spectra were clearly demonstrated [21]. CV curves were recorded (Figure is not shown) for the SDS/CPE after addition of different concentrations of NE in 0.2 M PBS solution (pH 7.0). The CV curves show a redox couple occurred at -200 mV to 600 mV (versus SCE). Fig. 2B shows the plot of anodic peak current against NE concentration and were found to be linear with NE concentration from 0.5×10^{-4} M to 4×10^{-4} M, $I_{pa}/\mu A = 35.67/\mu A + 19.44 (10^{-4} \text{ M})$, $r^2 = 0.9908$). The detection limit was calculated to be 1 μ M.

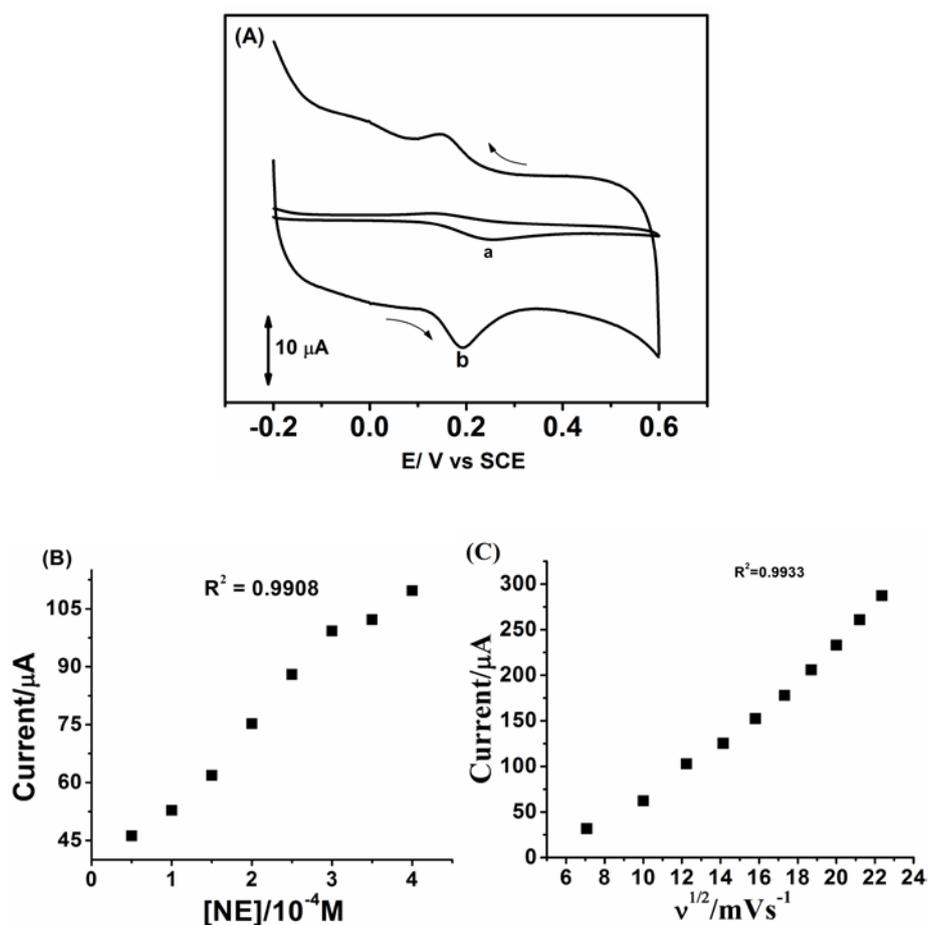


Fig. 3. (A) Cyclic voltammograms of 1×10^{-4} M NE in 0.2 M PBS of pH 7 at bare CPE (curve a) and SDS film coated CPE (curve b); (B) Plot of anodic peak current versus concentration of NE; (C) Graph of anodic peak current versus square root of scan rate

The effect of scan rate on the peak current of NE at the SDS/CPE was investigated by cyclic voltammetry. As shown in the Fig. 3C the anodic peak currents (I_{pa}) of NE were linearly proportional to the square root of scan rate from 50 to 500 mVs^{-1} , $I_{pa}/\mu\text{A}=102.84/\mu\text{A}+16.79$ ($\text{v}^{1/2}(\text{Vs}^{-1})$, $r^2=0.9933$), which is expected that the redox reaction on the electrode surface is diffusion controlled process and the ratio of I_{pa}/I_{pc} remains stable.

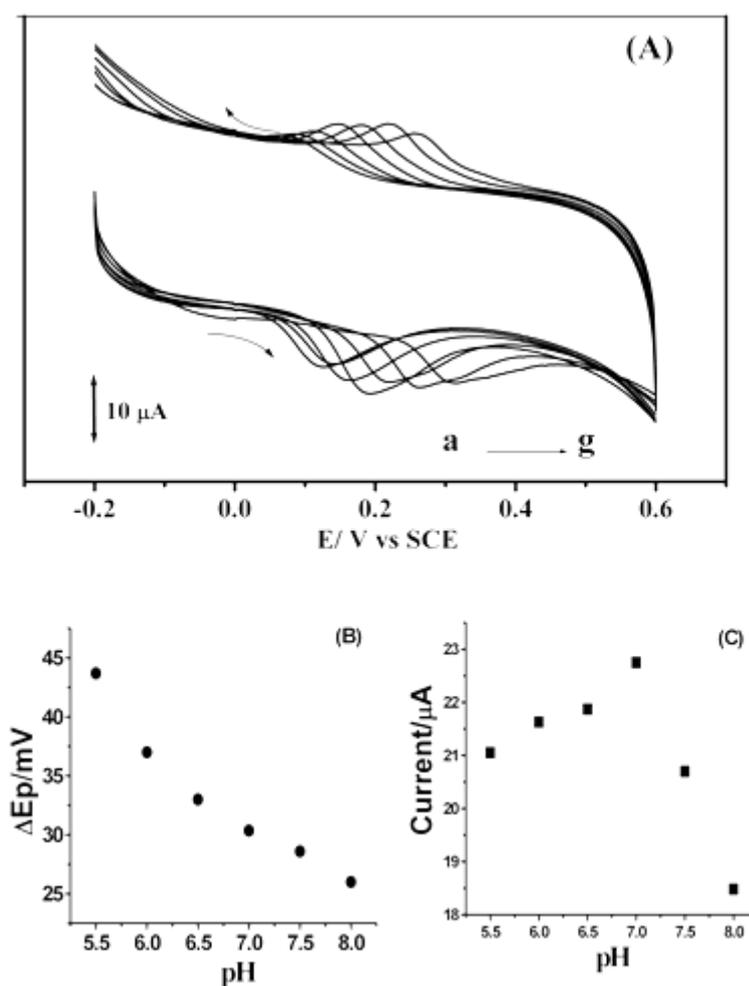


Fig. 4. (A) Variation of pH for oxidation of NE at SDS film coated CPE (a- g; 5.5 to 8); (B) Plot of peak potential difference (ΔE_p) versus different pH solution; (C) Graph of NE oxidation peak current versus different pH

3.4. Effect of pH variation on the NE redox activity

The electrochemical behavior of NE is dependent on the pH of the solution. Fig. 4A shows the electrochemical responses of NE in different pH varied from 5.5 to 8.5 PBS at SDS/CPE. The peak current is increased with increased pH from 5.5 to 7.0 and above that the peak current decreased. Under identical conditions, SDS/CPE produced significantly

increased peak current at pH-7.0 (Fig. 4C). As the pH increased, the ΔE_p value decreased with slight negative shift in peak potentials and the plot of ΔE_p versus pH is shown in the Fig. 4B and the obtained experimental slope 0.069 V is very close to the theoretical value of 0.059 V for the one electron transfer process.

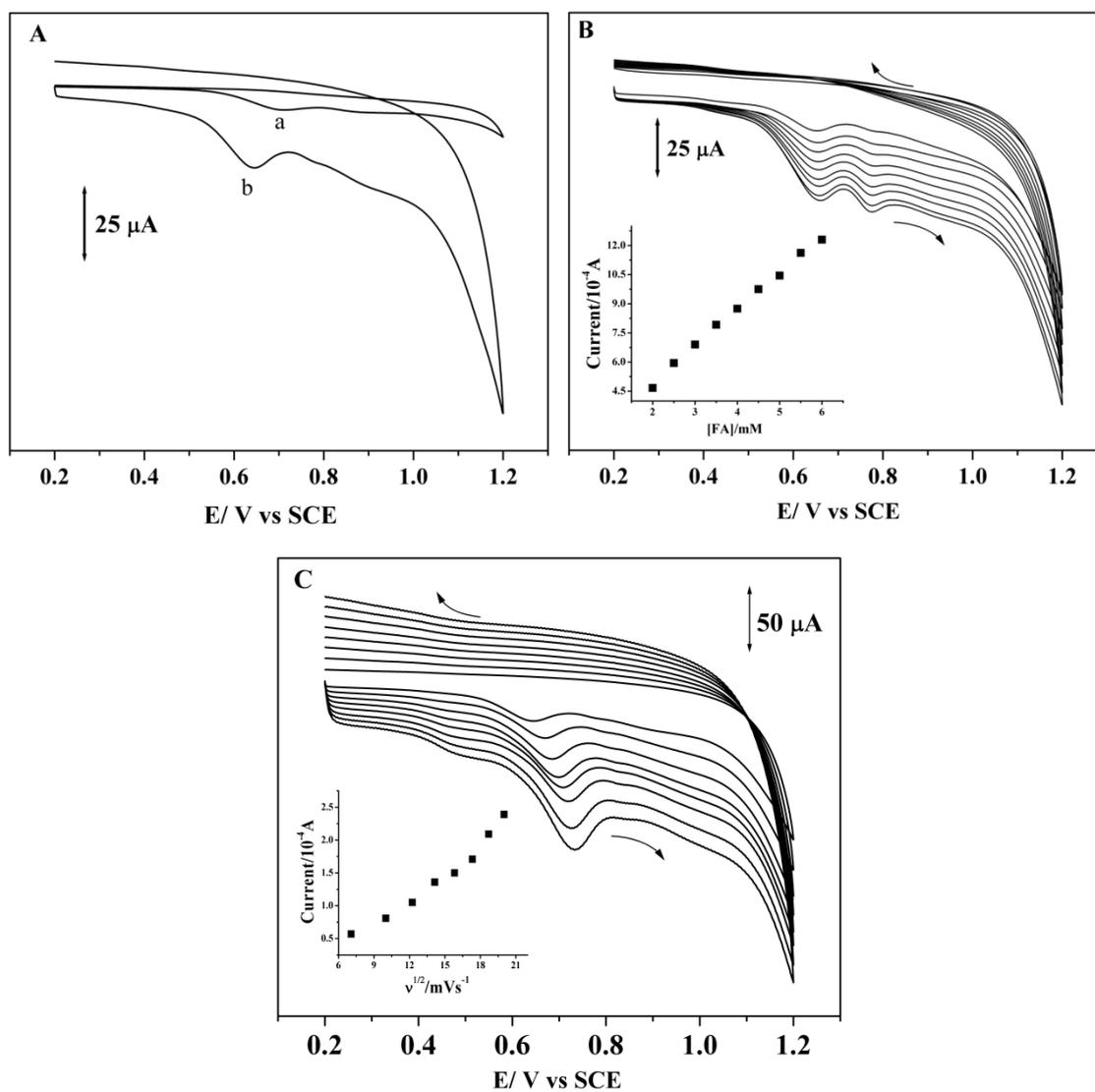


Fig. 5. (A) Cyclic voltammograms at a bare carbon paste electrode (curve a) and SDS modified carbon paste electrode (curve b) in the presence of 1×10^{-3} M FA in 0.2 M PBS of pH 7. Scan rate: 50 mVs^{-1} ; (B) CV's of SDS/CPE in different concentrations, a-f; 2 to 4 mM, at 50 mVs^{-1} . (C) CV's of SDS/CPE in 1mM FA at different scan rate (a - h: 50 to 400 mVs^{-1}). Inset shows the Graph of anodic peak current versus square root of scan rate

Hence, the electrode reaction involves two-electron process which is accompanied by a transfer of two protons, forming NE o-Quinone. In acid media, the well-defined peak was obtained on the cathodic scan as a result of the reduction of NE o-Quinone.

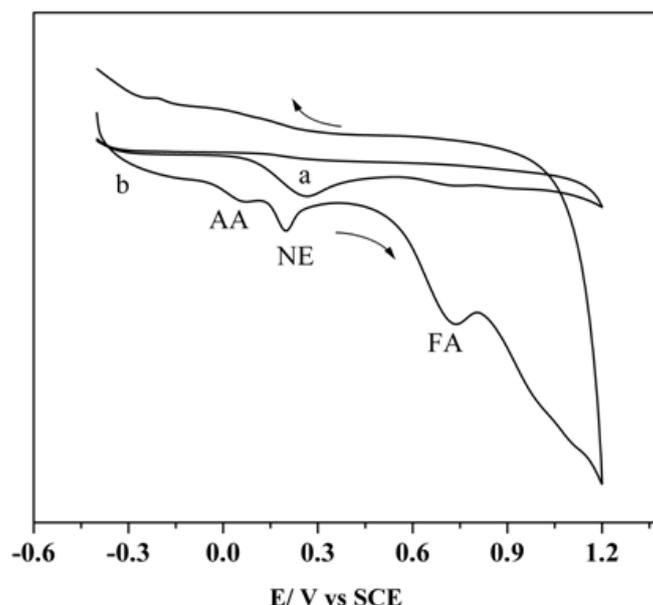


Fig. 6. CV's of simultaneous determination of 0.1 mM NE, 2 mM AA and 2 mM FA at bare CPE (curve a) and at SDS film coated CPE (curve b). Sweep rate: 0.05 Vs^{-1}

3.5. Cyclic voltammetric behavior of folic acid at SDS/CPE

The catalytic oxidation of folic acid was studied by cyclic voltammetric technique was used in the determination of FA concentration at SDS/CPE (Fig. 5A). The oxidation peak current of FA was measured at pH 7.0 PBS. The anodic peak current obtained at SDS/CPE (dashed curve) is three times much greater than that of the unmodified electrode (solid line) at peak 0.6428 V versus SCE. Cyclic voltammetric measurements of different concentration were done by setting the sweep rate at 50 mVs^{-1} . As shown in the Fig. 5B inset the FA oxidation peak current increases linearly with the concentration between 2 mM to 6mM of 0.5 mM increments. SDS/CPE has an excellent reproducibility over the determination of FA. The oxidation peak currents of 2 mM FA at SDS/CPE under different scan rates from 50 to 400 mVs^{-1} were measured (Fig. 5C). It is found that the oxidation peak current is proportional to the square root of scan rate which suggesting that the oxidation of FA at SDS/CPE is diffusion-controlled process.

3.6. Simultaneous determination of AA, NE and FA

In order to assess the applicability of the proposed electrode and the utilization of the selectivity of the SDS/CPE for the simultaneous determination of AA, NE and FA was demonstrated by cyclic voltammetric method. The cyclic voltammetric results show three-well-defined anodic peaks at SDS/CPE. It can be recorded when AA, NE and FA coexist in the same sample, two broad and small anodic peak current was observed at about 0.2628 V and 0.7616 V at unmodified CPE (curve a) (Fig. 6), the peak potentials for AA, NE and FA

are indistinguishable. Thus, the determination of NE in the presence of high concentration of AA and FA are very important. In this perspective, we have studied the determination of NE in the presence of higher concentration of AA and FA. The SDS/CPE resolved the overlapped voltammetric waves of AA, NE and FA into three well-defined voltammetric peaks at 0.102 V, 0.2142 V and 0.7392 V, corresponding to the oxidation of AA, NE and FA respectively (curve b). The separation between three peak potentials such as AA-NE, NE-FA and AA-FA are 0.1122 V, 0.525 V and 0.6372 V respectively which are large enough for the selective determination of NE in the excess presence of AA and FA. These indicated that the selective determination of NE at the SDS/CPE was good.

3.7. Real Sample analysis

The NE injection solution was diluted to 100 ml with water. 10 μ M of the diluted injection solution was added to a series of 10 ml measuring flasks and made up to volume with 0.2 M PBS (pH 7.0).

Table 1. Analysis of NE in norepinephrine hydrochloride injection sample at SDS/CPE

	Sample 1	Sample 2	Sample 3
NE found in the matrix (μ M)	25	50	75
Spiked NE (μ M)	10	10	10
Detected NE (μ M)	34	58	83
Recovery (%)	97.14	96.66	96.74

An aliquot of 10 ml of the solution was placed into the electrochemical cell and then the concentration of NE was determined by calibration method which is shown in the Table 1. The good agreement with the standard content is a promising feature for the applicability of the modified electrode for the simultaneous determination of NE injection sample. The content of NE was also determined by the standard addition method. The results obtained by this method are in good agreement with the declared content. Furthermore, in order to establish the suitability of this proposed method, known amounts of standard NE injection were added into the analytical solution, and the same procedure was applied. The recovery is between 98.4 and 99.2%, indicating that the accuracy and repeatability of this method are very good. From above experimental results, it is very clear that this novel method has great potential for practical sample analysis.

4. CONCLUSION

SDS/CPE can be easily fabricated by immobilization method. SDS was adsorbed on carbon paste electrode surface via strong hydrophobic interaction, altered the structure and property of the electrode/solution interface. Therefore, the electrochemical response of NE at SDS/CPE shows a great difference in the presence of excess concentration of ascorbic acid and folic acid. Under the consistency studies of SDS/CPE both the oxidation peak current and the determining sensitivities of AA, NE and FA are significantly improved.

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