

Electro Oxidation and Determination of Estriol Using a Surfactant Modified Nanotube Paste Electrode

J.G. Manjunatha, Gururaj Kudur Jayaprakash

Abstract: The electrocatalytic oxidation of Estriol (ET) has been studied by surfactant modified nanotube paste electrode. The sensor was prepared using carbon nanotubes and silicone oil, Carbon nanotube paste electrode (CNTPE) modified with Sodium dodecyl sulfate (SDS) surfactant, the modified electrode highly sensitive for the determination of ET. Cyclic voltammetry (CV) and differential voltammetry (DPV) techniques were used to investigate the ET. A enrich improvement in the microscopic area of the electrode produced in a increase of the peak current of ET oxidation. CV has been used as a electrochemical sensitive analytical method for the detection of small amounts of ET, Two linear ranges have been procured for the ET concentration between the ranges of 6.0×10^{-6} to 2.0×10^{-5} and 2.5×10^{-5} to 1.5×10^{-4} M ET. The detection limit of this electrode is 3.2×10^{-7} M and the quantification limit is 10×10^{-7} M. This sensor has a remarkably good sensitivity for the ET determination in the presence of real samples. The recovery for the ET detection in clinical sample was obtained as 97.2-102 % with a good RSD of 4.2%, (on the basis of 5 repeated determinations). These good qualities make the fabricated sensor suitable for the experiments of the trace amounts of ET in pharmaceutical and clinical preparations.

Keywords: Electrochemical Sensor, Cyclic Voltammetry, Estriol, Detection Limit.

INTRODUCTION

There is an increasing demand for reasonable and wise analytical techniques for the determination of biological active compounds. On the other hand, a major difficulty happening is that biochemical compounds are oxidized less sensitivity at unmodified electrodes. To come out this problem, many modified electrodes have been fabricated such as modified electrodes [1-3], Hydroxylamine Electrochemical sensor based on a modified carbon nanotube paste electrode [4], 2-(4-Oxo-3-phenyl-3,4-dihydro-quinazolinyl)-N-phenyl-hydrazinecarbothioamide modified electrodes [1], electrochemical sensor based on novel hydroquinone and carbon nanotubes [5], modified carbon nanotube paste electrode and its application for simultaneous determination of epinephrine, uric acid and folic acid [6], 2,7-bis (ferrocenyl ethyl) fluoren-9-one and carbon nanotubes [7], surfactant and polymers modified electrodes [8-13].

Estriol (ET) is a main estrogen during gestation and is librated by the placenta [14]. ET tests of placental or feto-placental function are highly used in dangerous pregnancies to describe adverse fetal problem [15]. Oral ET piles have been used with better results, initially for the treatment of local urogenital complaints in postmenopausal women for over 40 years. This can be exhibit by many electrocatalytic studies that have been stated in the literature including HPLC [16], immunoassay [17] and GC-MS [18] in biological samples. Since most chromatographic methods have been fabricated for environmental samples, immunoassay is the preferred techniques for biological samples due to its specificity and sensitivity. Radioimmunoassay (RIA) [19], enzyme immunoassay (EIA) [20] and fluorescence immunoassay (FIA) [21] have been widely applied in screening and determination of ET. However, the major disservice of this methods is that it needs radioisotopes and creates radioactive

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decay. In spite of these techniques are economic, they are labour demanding and not sensitive adequate for determination of ET.

The unique chemical, physical, electronic (metallic or semiconducting) and having a great thermal properties of carbon nanotubes made them curiosity materials for wide application in the fields such as electrochemical sensors [11].

Several utilization of surfactants in analytical electrochemistry are in electroplating [22-23], corrosion [24], fuel cells [25], electrocatalysis [26], and electroanalysis [27-29]. Several analysis of modified electrodes were engaged simply because scientists were interested about new molecules joined to electrode surface behave compared to these species in solution. The area of surface modified electrodes is of particular interest because of its use in biosensors [30-33].

No study has been reported so far presenting the determination of ET by make use of SDS modified carbon nanotube paste electrode. Thus, here we report the preparation and application of surfactant modified carbon nanotube paste electrode (SDSCNTPE) as a new electro-catalyst during the electro-catalytic method and the analysis of ET in a supporting buffer solution. The achievement of the modified electrode has also been tested.

EXPERIMENTAL

Materials

All chemicals were obtained from commercial sources and used without further purification. ET obtained from TCI Co. limited (Japan), Silicone oil, disodium phosphate, monosodium phosphate and SDS was obtained from Himedia chemicals, Bangalore, India. Stock solution of ET (25×10^{-4} M) prepared in ethyl alcohol, SDS (25×10^{-3} M) in twice distilled water. The supporting electrolyte used was pH 7, 0.2 M PBS (phosphate buffer solution) used for all measurements. Spectroscopically pure multiwall carbon nanotubes were obtained from Sigma Aldrich India and Microscopic study did by using FESEM (Field Emission Scanning Electron Microscopy), EDX (Energy-Dispersive X-ray spectroscopy). ET injections containing 10 mg/mL were purchased from the local pharmacy. All experiments were did at approx. 25°C

Atomic coordinates of the all models were constructed using MOLDEN [34] software. Full geometry optimization of the models were carried out using density functional theory (DFT) level of theories in the Gaussian09 program software 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. We have used Sinapsis [40] software for plotting FMO and Fukui results. We used the analytical Fukui function developed using auxiliary density perturbation theory (which is efficient for Fukui analysis of a larger system [41]).

Apparatus

Experimental work was bring out using a model EA-201. All the research tests were carried out in a conventional three electrode electrochemical cell. The electrode system having a working electrode was SDS immobilized modified carbon nanotube paste electrode, a platinum wire as a counter electrode and saturated calomel electrode as reference electrode.

Preparation of SDS Immobilized CNTPE

The CNTPE was prepared as follows; 60% CNT and 40% silicon oil were mixed by hand to get a congruent a homemade CNTPE and smoothed on weighing paper. A SDSMCNTPE was fabricated by immobilizing 10 μ L of SDS on the surface of the CNTPE for 5 min.

RESULTS AND DISCUSSION

FESEM Analysis of BCNTPE and SDSMCNTPE

Fig. 1 explains the surface morphology of BCNTPE and SDSMCNTPE using FESEM. The surface of BCNTPE was conflicting shaped micrometer sized flakes of CNT. However, the SDS film coated CNTPE has typical consistent ordering of SDS on the surface of CNTPE.

This indicates that CNTPE was coated by SDS film. EDX spectrum getting from surface of the modified electrode is also shown in Fig. 2(a). BCNTPE indicates the existence of C, O, and Si and SDSMCNTPE shows the existence of C, O, Na, Si, and S elements in the spectrum (Fig. 2b). This data indicates the presence of SDS thin film on the surface of electrode.

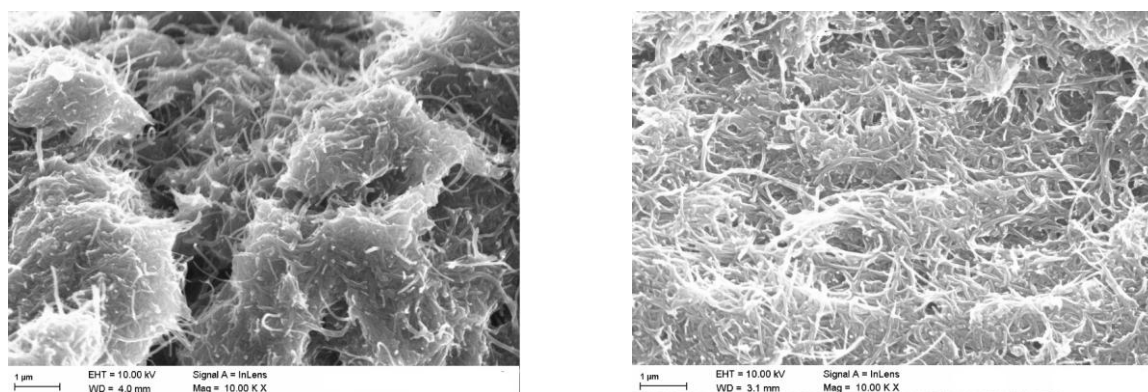


Fig. 1: FESEM images of (a) BCNTPE (b) SDSMCNTPE.

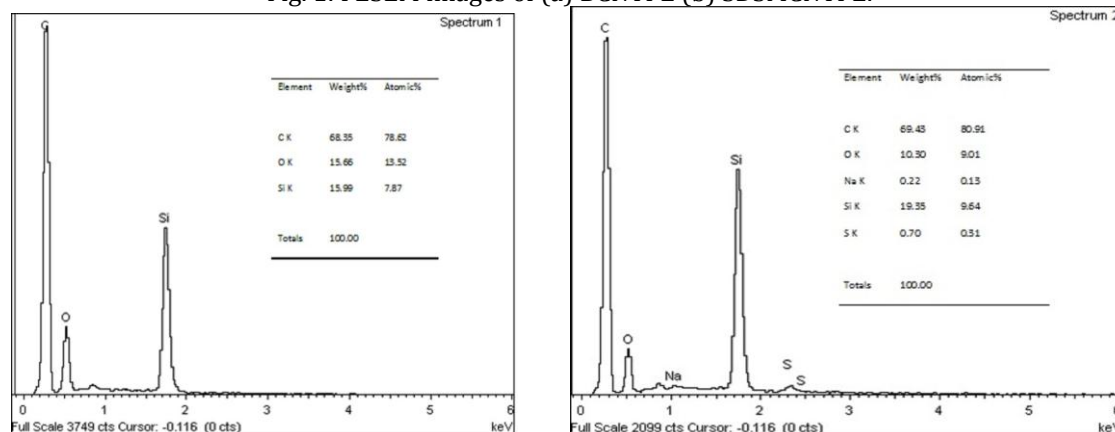


Fig. 2: EDX spectrum of (a) the BCNTPE (b) the SDSMCNTPE

Quantum Chemical Studies of Modifier/SDS

On the surfactant immobilized carbon electrode surface, surfactants acts like a redox mediators [42, 43]. Theoretical models can be beneficial for knowing electron transfer mechanism of redox mediators [44]. In the current work SDS acts as a redox mediator, it will be interesting to know which atoms or functional groups of the SDS are involved in the redox electron transfer reactions. Combination of FMO and Fukui concepts gives the accurate redox electron transfer locations in Electrochemistry [45]. Therefore we have used the FMO and Fukui concept to locate redox electron transfer sites. As we can seen from the Fig.3. HOMO of SDS located near the terminal hydrocarbons of chain and LUMO located on the head group. Therefore oxidation of SDSMCNT electrode via tail of SDS and reduction occurs via head of SDS.

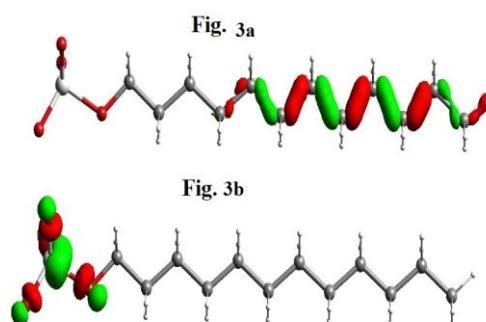


Fig. 3: Frontier molecular orbitals of SDS (a) HOMO orbitals of SDS (b) LUMO orbitals of SDS.

Frontier molecular orbital (FMO) interpretations do not consider the effect of relaxation but Fukui interpretations considers it. Therefore it is necessary to verify FMO results further by Fukui results. Fukui functions can be used to identify local ET reactive sites of modifiers. Fukui function can be defined according to Eq-1 [46-48].

$$f(\mathbf{r}) = (\partial \rho(\mathbf{r}) / \partial N)^{+/-} v(\mathbf{r}) \text{ -----1}$$

Where $\rho(\mathbf{r})$ is the electron density, N is the number of electrons in the system, + and - signs correspond to addition or removal of electrons, respectively. Therefore, Fukui functions can be used to know redox reaction mechanisms in chemistry. As we can see in the Fig. 4. Oxidation sites of the SDS are located on the terminal hydrocarbons of tail and reduction sites of the SDS are located on the oxygen (specially on the oxygen atom which acts as a bridge between tail and head) atoms of the head group. The FMO results are further confirmed by Fukui results, therefore our results (predicted redox electron transfer sites of SDS) are more precise. Thus our quantum chemical calculations are helpful to understand electron transfer reactions of the SDS in molecular level.

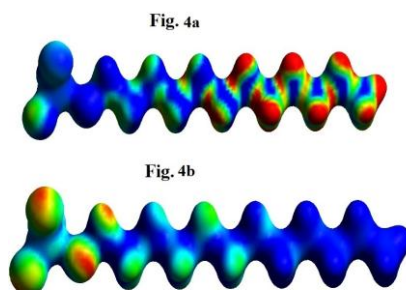


Fig. 4: Fukui results of SDS (a) $f-(r)$ of SDS (b) $f+(r)$ of SDS.

Estimation of the electrode Stability, Repeatability and Reproducibility

The SDSMCNTPE was found to be firmness, even after 40 CV scans. The SDSMCNTPE is quite stable, once prepared it could be used for more than 90 days if preserved in a closed container. Relative standard deviation (RSD) calculated for anodic current and potential after 90 days was found to be 0.01 and 0.003. To investigate the reproducibility of the modified electrode, CV scans were recorded for 10 min intervals. Observed peak height very closely same and its R.S.D. of 2.6% for 5 times analysis, these results shows that this electrode has a better reproducibility

Electrochemical Oxidation of ET at the SDSMCNTPE

One of the targets of this work was the preparation of a modified electrode having the ability of the oxidation of ET. The electrochemical activity of SDS film, the cyclic voltammograms were obtained in the absence and presence of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ET in PBS 0.2 M, and the peaks are shown in Fig. 5. In the absence of ET no peak can be observed (dashed line). When $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ET was added, there was a exciting enhancement of the anodic current, whereas the cathodic current peak was enhanced (solid line), which is very characteristic of an electrochemical oxidation process. Fig.6 depicts the CV reaction for the electrochemical oxidation of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ET at BCNTPE (solid line) and SDSMCNTPE (dashed line) in 0.2 M phosphate buffer solution (pH 7.0) at scan rate of 100 mV s^{-1} . As it is seen, while the anodic peak potential for ET oxidation at the BCNTPE are 620 mV, respectively, the corresponding potential at SDSMCNTPE is 578 mV. This outcome evidenced that the peak potential for ET oxidation at the SDSMCNTPE and BCNTPE electrodes shift by 578 and 620 mV toward negative values compared to SDSMCNTPE and BCNTPE, respectively. The oxidation of ET compared to BCNTPE, showing that the combination of SDS and the BCNTPE has clearly improved the performance of the electrode toward ET oxidation.

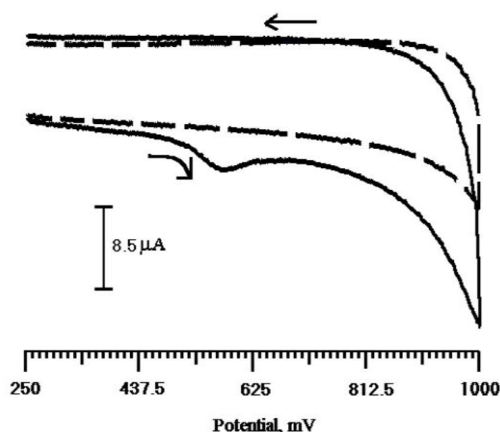


Fig.5. A typical cyclic voltammograms of SDSMCNTPE with ET ($1 \times 10^{-4} \text{ M}$) in pH 6. PBS (solid line) without $1 \times 10^{-4} \text{ M}$ ET and PBS blank (dashed line).

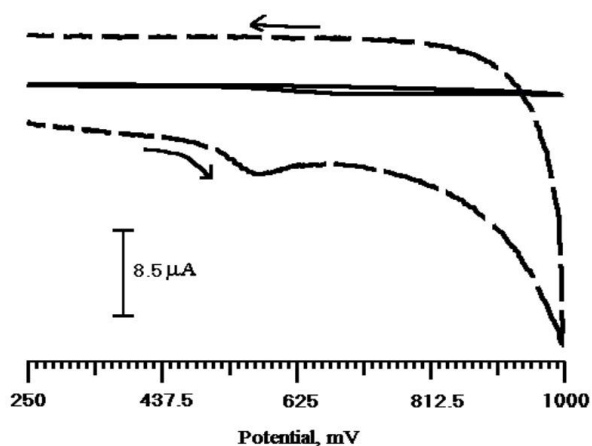


Fig. 6: Cyclic voltammograms of ET ($1 \times 10^{-4} \text{M}$) in 0.2 M phosphate buffer solution of pH 6.0 at BCNTPE (dashed line) and SDSMCNTPE (solid line).

Electro Catalytic Oxidation of ET by DPV

DPV has better current sensitivity and good separation than CV, it was applied in the trace level detection of ET in Fig.7.

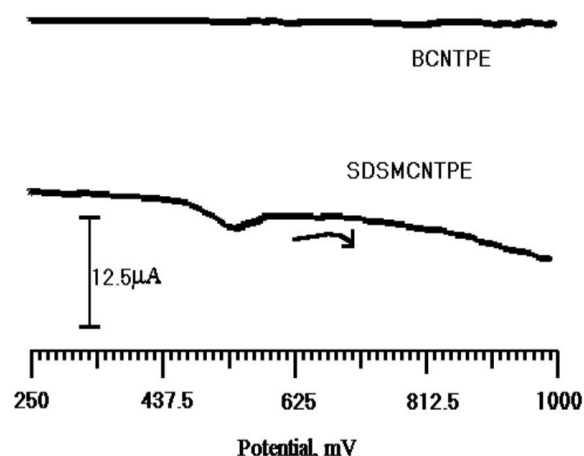


Fig. 7: DPVs of a solution containing ET ($1 \times 10^{-4} \text{M}$) in 0.2 M PBS (pH 6) at the BCNTPE and SDSMCNTPE

In the DPV mode, charging current contribution to background current is negligible leading to more proper assessment. The oxidation peak current of ET at the SDSMCNTPE ($9.02 \mu\text{A}$) is significantly higher than that at the BCNTPE ($1.26 \mu\text{A}$).

These outcome indicated that the presence of SDS in CNTPE matrix improved the sensitivity by increasing peak currents. Likely the large pore volume of SDS contributes a large specific area improving to the enhancement in peak current.

Impact of Scan Rate

Fig. 8a indicates the voltammetric investigation of ET at scan rates ranging from 100 to 250 mV s^{-1} in a solution (pH 6.0) containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ET. We noticed that linear variation of the peaks current with the square root of the scan rate, the linear regression equation was $I_{pa} (\mu\text{A}) = -0.675 + 0.09564 \sqrt{v}$ (mVs^{-1})^{1/2}, with a correlation coefficient of 0.99782 shown in Fig. 8b. This outcome certainly shows a diffusion controlled electro oxidative process. Interesting, the current function plot gave the characteristic shape of a coupled chemical reaction for the ET, clearly confirming electrocatalytic activity. On the basis of the data, we suggest the electrocatalytic mechanism (Scheme 1) (50) for the oxidation of ET. To get the information about the rate-determining step, by this equation $E_{pa} = E^0 + (2.303RT/\alpha nF) \log(RT k^0 / \alpha nF) + (2.303RT/\alpha nF) \log v$ (51), here α is the transfer coefficient and k^0 the standard rate constant of the reaction. n the electron transfer number, v the scan rate, and E^0 the formal potential. Other symbols have their usual significance. The slope is equal to $2.303RT/\alpha nF$, therefore, the plot of E_{pa} versus $\log(v)$ was drawn in Fig. 8c, and the slope of this plot is 120.18 mV, the value of αn calculated was 0.49. Usually, α is taken as 0.5 for the totally irreversible electrode process. The results certainly suggest one-electron ($\alpha n \approx 0.98 \sim 1$).

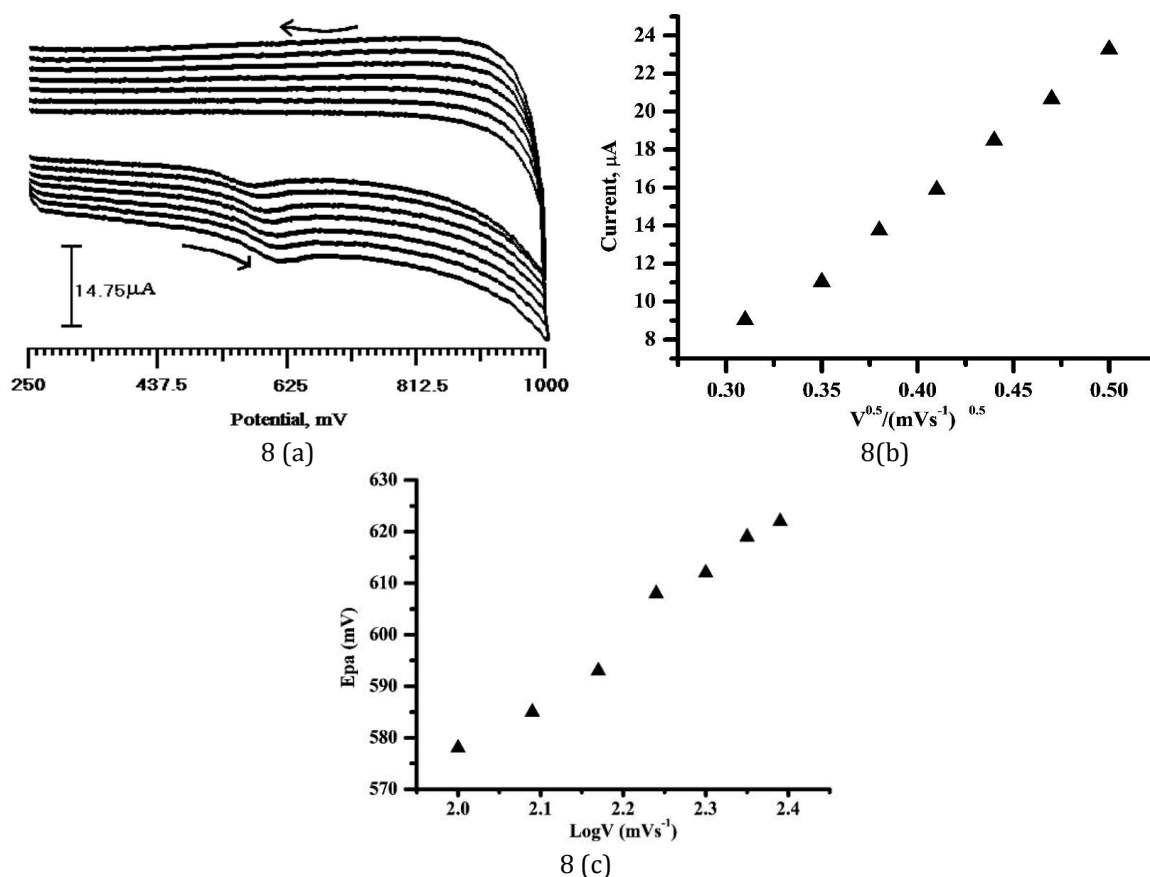


Fig. 8: (a) Cyclic voltammograms of ET (1X10⁻⁴M) at the SDSMCNTPE in pH 6 PBS at various scan rates. From: 100, 125, 150, 175, 200, 225 and 250 mV/s. (b) Plot of the peak current of ET as a function of the square root of scan rate and (c) Plot of the peak potential versus the logarithm of the scan rate (log v)

The Influence of pH on SDSMCNTPE Signal was Investigated by Cyclic Voltammetry

In addition, the consequence of pH on peak potential and peak current of ET (1.0 × 10⁻⁴ mol L⁻¹) was analysed by cyclic voltammetry using 0.2 M buffer solutions at pH levels ranging from 6.0 to 8.0 with a scan rate of 100 mV s⁻¹. It was noticed that peak potential slightly shifted negatively with the increase in pH of the solutions which implies that the electrochemical oxidation of ET at SDSMCNTPE is a pH-dependent reaction shown in Fig.9a. The current response (I_{pa}) observed was maximum at pH 6.0 as shown in Fig. 9b. The results showed that the slope of E_{pa} vs. pH was -61.8 mV pH⁻¹ over a pH range of 6.0 to 8.0, which is adjacent to the anticipated Nernstian value of 59.2 mV pH⁻¹ for a equal number of electron and proton process (Fig. 9c).

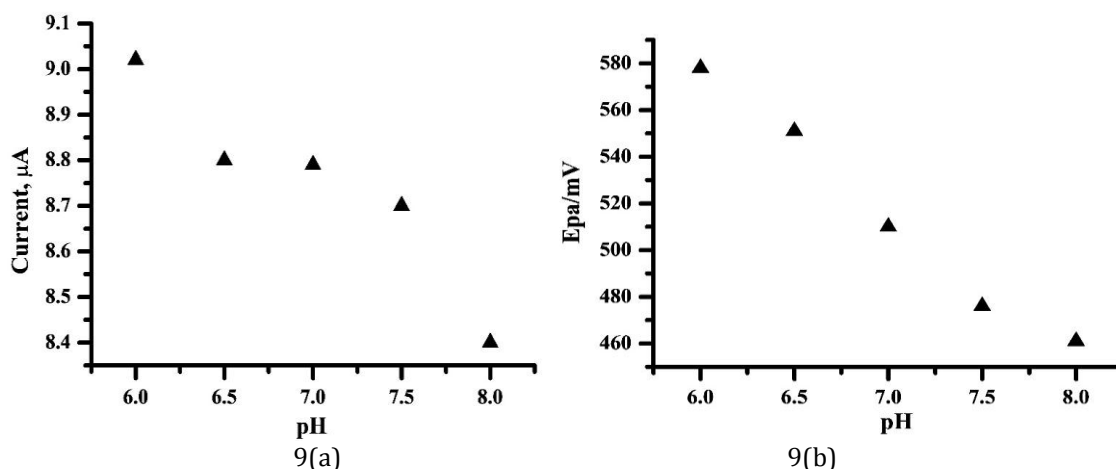


Fig.9. (a) Plot of anodic peak current obtained at the SDSMCNTPE in 0.2 M PBS in pH values, (a) 6 (b) 6.5 (c) 7 (d) 7.5 (e) 8 containing ET (1X10⁻⁴M) vs. pH (6–8.0) of ET (1X10⁻⁴M) at the SDSMCNTPE (b). Plot of E_{pa} vs pH for ET

Analytical Application for Determination of ET

Under the ideal conditions, the calibration curve is plotted by systematically increasing the concentration of ET, from 6×10^{-6} to 1.5×10^{-4} M, in the ET solution and monitoring the response of SDSMCNTPE electrode (Fig. 10). The peak currents are taken and plotted versus concentration. A dynamic calibration curve with two linear ranges, from 6.0×10^{-6} to 2.0×10^{-5} and 2.5×10^{-5} to 1.5×10^{-4} M ET, is observed as [$I_{pa} \text{ (A)} = 6.7093 \times 10^{-6} + 0.0566 C$ $r^2 = 0.9405$] and [$I_{pa} \text{ (A)} = 7.4098 \times 10^{-6} + 0.2115 C$ $r^2 = 0.9951$], respectively (11-13). The limit of detection SDSMCNTPE, calculated from the standard deviation (S) of the background (for signal equals $3S$, where $S = 6.0553 \times 10^{-9}$ A for 5 measurements using equation 3 s/m [10]), is 3.2×10^{-7} M ET, and the limit of quantification is 10×10^{-7} M ET. These results indicate that the SDSMCNTPE is a sensitive sensor for detection of ET at low concentrations. The sensitivity ($0.0566 \mu\text{A}/\mu\text{M}$) and detection limit (3.2×10^{-7} M ET) of this electrode are, respectively. This work showed good advantages like sharp peak with relatively large peak currents and low backgrounds, which can be conducted to enhance the sensitivity and limit of detection in analytical determinations. The detection limit compared with other published reported works [51-56] are mentioned in Table.1.

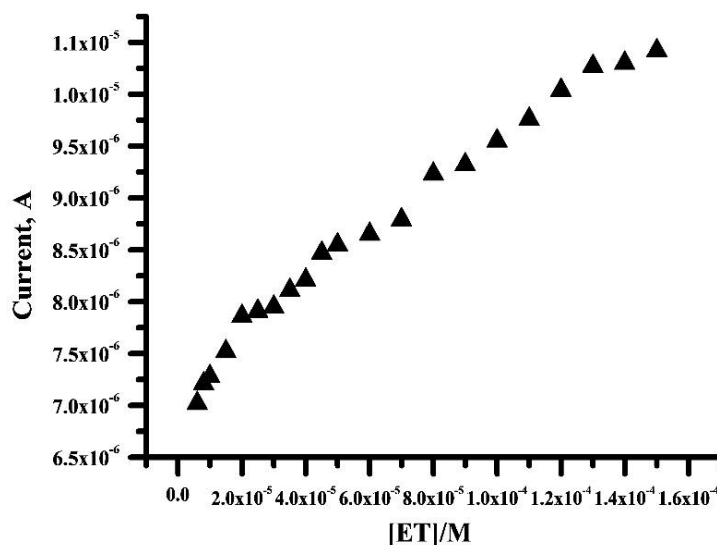
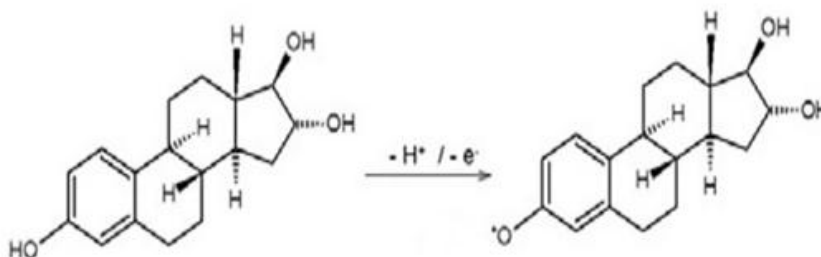


Fig. 10: Calibration plot for the determination of ET at the SDSMCNTPE in pH 6 PBS with the scan rate 100 mV/s.



Scheme 1: Scheme of oxidation mechanism of ET

Table 1: The comparison of SDSMCNTPE with some modified electrodes for the determination of ET

Methods/Electrodes	Linear range (mol/L)	Detection limits (mol/L)	Reference
fluorescence sensor		1.3×10^{-9}	[25]
RGO-GNPs-PS/GCE electrodes	1.5×10^{-6} to 22×10^{-6}	0.48×10^{-6}	[26]
Square-wave voltammetry.	2×10^{-7} to 2×10^{-5}	1.7×10^{-7}	[27]
square-wave voltammetry/ (MWNTs/GCE)	1×10^{-6} to 5×10^{-5}	-	[28]
PGMCPE	2×10^{-6} to 1×10^{-4}	8.7×10^{-7}	[29]
SDSMCNTPE	6.0×10^{-6} to 1.5×10^{-4}	3.2×10^{-7}	This work

Application of SDSMCNTPE for Determination of ET in Pharmaceutical Samples

The applicability and trustworthiness of the proposed modified electrode in real samples with different matrixes were analysed to confirm the effectiveness of SDSMCNTPE. ET injection solution was used as pharmaceutical samples. Preparation of sample was done as standard addition method in PBS and CVs were recorded to estimate the ET concentrations using the calibration curves. The recovery of 97.2 - 102% is obtained in ET injections. Also the RSD% was lower than 4.2%, are acceptable. Thus, SDSMCNTPE can be efficiently used for the determination of ET pharmaceutical samples.

CONCLUSIONS

The modification of the CNTPE electrode surface by SDS enhances the electrochemical catalytic activities toward the oxidation of ET, Comparison between BCNTPE and SDSMCNTPE demonstrates that SDSMCNTPE facilitates the determination of ET with good stability and sensitivity. In comparison with other electroanalytical methods that have been published for the estimation of ET, this method has better figures of merit. The proposed method can be applied to the determination of ET concentrations in real samples with adequate results.

CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

ACKNOWLEDGEMENT

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