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Electrochemical Studies of Dopamine and Epinephrine at a Poly (Tannic Acid) Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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A carbon paste electrode (CPE) modified with poly (tannic acid) was used for the sensitive voltammetric determination of dopamine (DA) and epinephrine (EP). The electrochemical response characteristics of the modified electrode towards determination of EP and DA were investigated by cyclic voltammetric technique (CV). The effect of pH, concentration and potential sweep rate on the mechanism of the electrode process was investigated. The modified electrode exhibits an efficient electron mediating behavior for DA and EP. The modified electrode showed high sensitivity, detection limit, high reproducibility, easy preparation and regeneration of the electrode surface.

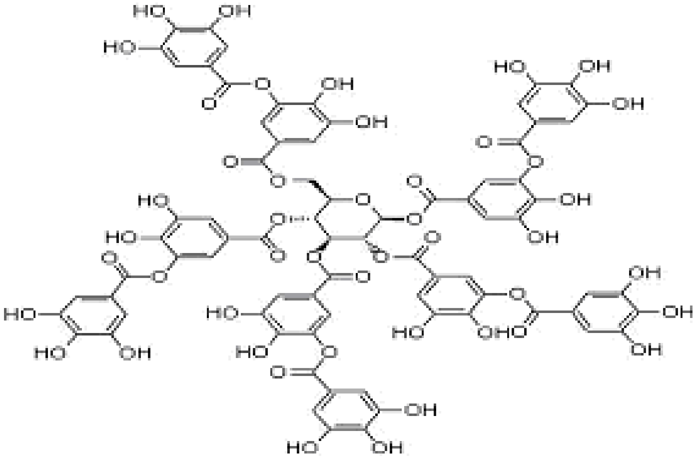
Keywords: Carbon paste modified electrode, Poly(tannic acid), Electropolymerisation, Dopamine, Epinephrine, Cyclic voltammetry.

1. INTRODUCTION

Dopamine and epinephrine are two important catecholamine neurotransmitters, present in the mammalian central nervous system in the presence of several other substances including ascorbic acid (AA), uric acid (UA), which plays an important role in the nervous system. Many diseases are related to the changes of their concentration or extreme abnormalities, such as parkinsonism, schizophrenia, Huntinton's disease as well as drug addiction and HIV infection [1– 6]. However, DA and EP are similar in structure and difficult to differentiate electrochemically. Moreover, DA, EP, UA and AA frequently exist together in biological system at most solid electrodes are oxidized at a close potential resulting in an overlapping voltammetric response. It is always too difficult to selectively determine

DA and EP in presence of high concentrations of UA and AA simultaneously [7–10]. Therefore, it is necessary to accurately determinate each of them for diagnosis purpose and for development of new medicine. Chemical modified electrodes (CME) have been largely used in the area of electrochemical and biological fields [11–16]. An enormous of amount of research has been devoted to the determination of DA and EP using CME, however, many of these works have been limited in single component's determination [17–21]. Amino acids are essential for lives and have been of interest to both chemists and biologists. Efforts have been made on the synthesis and determination of them [22–24]. However, few reports using amino acid as modifier to decorate the electrode have been reported in determining other compounds [25–27].

Tannic acid (TA) is a natural polyphenolic compound, whose structure is as shown in scheme 1. TA is widely used in food and medicine industry.

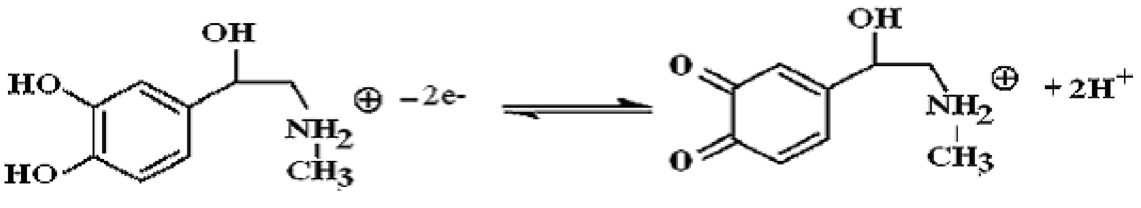


Scheme.1

It can be used as clarifying agent in the brewing and wine industry, and as flavouring agent in baked foods, candy and meat products. It is also used as additive in medicinal products, including those used for treatment of burns, diarrhoea [28]. TA has anti-oxidant antimutagenic and anticarcinogenic activities [29].

Polymer-modified electrodes (PMEs) have shown to be a powerful tool. Because characteristics like film thickness, permeation and charge transport can be controlled by adjusting the electrochemical parameters. Therefore, PMEs have many advantages such as improved electro catalysis, absence of surface fouling and prevention of undesirable reactions competing kinetically with the desired electrode process [30, 31]. The intervention of H^+ in the electrochemical reaction correlates with the mechanism proposed by other authors for the oxidation of EP (scheme.2) [32].

The present work describes an electropolymerized film of tannic acid on the surface of carbon paste electrode by cyclic voltammetric technique. The modified carbon paste electrode shows significant increase in anodic peak current for DA and EP. The mixture of both DA and EP at bare carbon paste electrode shows one oxidation peak two reduction peaks and there is enhancement of DA in presence of EP at poly(tannic acid) modified carbon paste electrode.



Scheme.2

Related works have been done by our research group [34-40]. Poly (taurine) modified glassy carbon electrode for the simultaneous determination of EP and DA was studied by Y.Wang[41]. Thus the present study provides a novel method for sensitive detection of DA in the presence of EP, which has a significant attraction in biological and chemical fields.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Cyclic voltammetry experiments were carried out with a model EA-201 (Electro Analyser) connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or polyTA modified CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE. Dopamine hydrochloride, Tannic acid was obtained from Himedia chemicals and Epinephrine obtained from Sigma Aldrich was used as received. All other chemicals were of analytical grades. Phosphate buffer solutions (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 solutions of DA, EP and TA were used in all experiments. Epinephrine and dopamine were dissolved in 0.1M perchloric acid and all other solutions were prepared with double distilled water.

2.2. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.3. Preparation of pre treated and poly TA modified CPE

The pretreatment of the carbon paste electrode was done by placing the bare cpe in 0.05M H_2SO_4 containing $1x10^{-3}$ M of TA. The CPE was pretreated by scanning from –400 to 1200mV at $100mVs^{-1}$ for 10 times .After this, electropolymerization was enforced under sweeping from –400 to 1200mV at $100mVs^{-1}$ for 10 cycles in 0.01M NaOH containing $1x10^{-3}$MTA as shown in fig.1. The poly (TA) modified CPE was rinsed with water and used for the determination of DA, and EP.

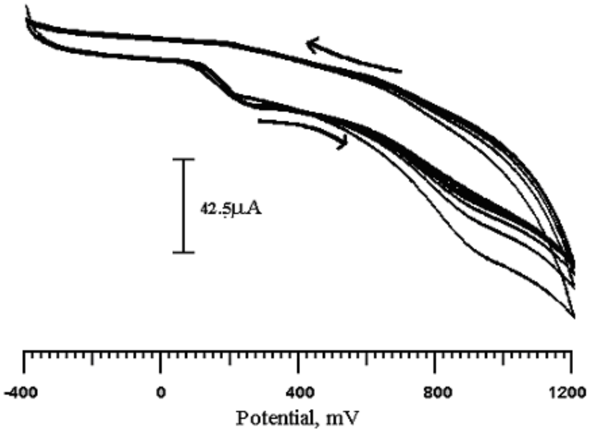


Figure 1. Cyclic voltammogram of poly TA film coated CPE in 0.01M NaOH at 100 cycles with sweep rate of 100 mVs^{-1}

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical investigation of potassium ferrocyanide at polyTA modified CPE

The electrochemical response of K_4 Fe (CN) $_6$ at bare and polyTAMCPE is shown in Fig.2 At bare carbon paste electrode (BCPE) the voltammogram of K_4 Fe $(CN)_6$ showed poor electrochemical response (dashed line) with reversible behavior in 1M KCl as supporting electrolyte. However, the voltammetric response was apparently improved at polyTAMCPE (solid line) with increasing the potential. At BCPE the anodic peak potential (E_{pa}) was found to be 244 mV and cathodic peak potential (E_{pc}) 163 mV (vs. SCE). The separation of redox potential peaks (ΔE_p) 81mV and the ratio of peak currents (I_{pa}/I_{pc}) was 1.51. At polyTAMCPE, a pair of redox peak is obtained with increase in both anodic cathodic peak currents. The E_{pa} was found at 286mV and E_{pc} at 165mV. The separation of redox potential peaks ΔE_p was found to be 121mV and the I_{pa}/I_{pc} was 1.83.

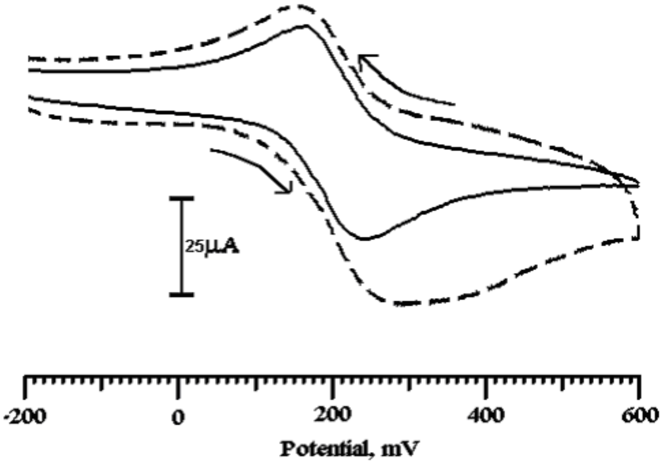


Figure 2. Cyclic voltammograms for the electrochemical responses of K_4 [Fe(CN)$_6$] at bare (solid line) and poly TA modified CPE (dashed line) in 1 M KCl containing 1mM K_4[Fe(CN)$_6$] at scan rate 100 mV/s^{-1}.

3.2. Electrochemical investigation of dopamine at the polyTA modified CPE.

Figure 3 shows the cyclic voltammograms obtained for the electrochemical response of DA at the polytannic acid modified CPE (dashed line) and bare CPE (solid line) in 0.2 M phosphate buffer solution pH 7.0 and 1X10^{-3} M DA.

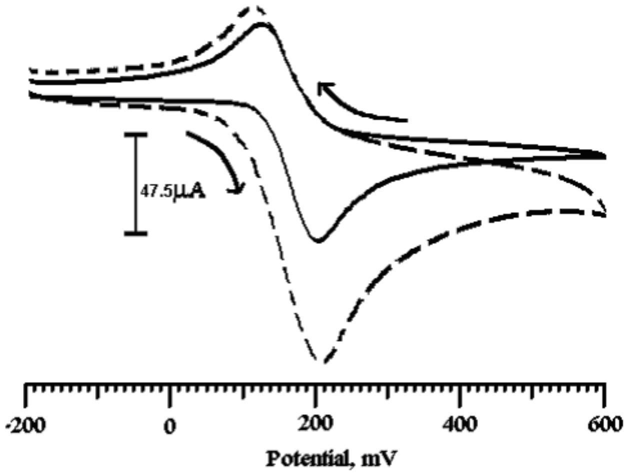
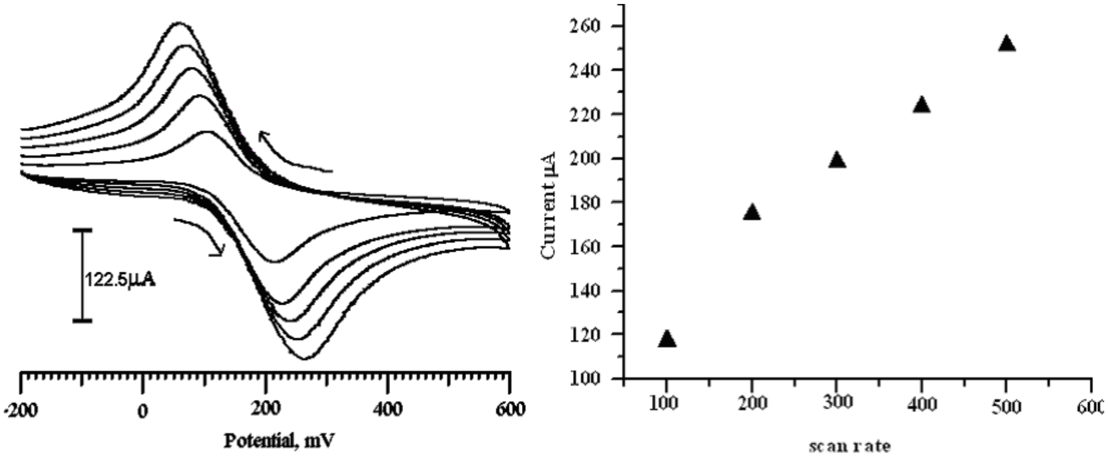


Figure 3. Cyclic voltammogram of 1X10^{-3} M DA in 0.2 M phosphate buffer solution of pH 7 at bare

At bare CPE, the oxidation and reduction peak potentials occur at 203mV and 125mV respectively. The peak potential separation (ΔE_P) was 78 mv and corresponding current ratio's *I*pa/*I*pc=1.84. Under identical conditions, the polyTA modified CPE produces significantly increased peak current and a more qusi-reversible electron process of DA with the oxidation and reduction peak potentials at 216mV and 105mV respectively. So peak potential separation (ΔE_P) was 111 mv with *I*pa/*I*pc=1.85. The remarkable enhancement of peak current provides clear evidence of the catalytic effect of poly (tannic acid) modified CPE.

3.3. Effect of scan rate on the peak currents of dopamine.



(a) **(b)**

Figure 4(a,b). a)Cyclic voltammograms of 1X10^{-3} M DA at the poly TA modified CPE at different scan rates (100, 200, 300,400,500 mV/s^{-1}) in 0.2 M phosphate buffer solution pH 7.0; b) The plot of the anodic peak current versus scan rate.

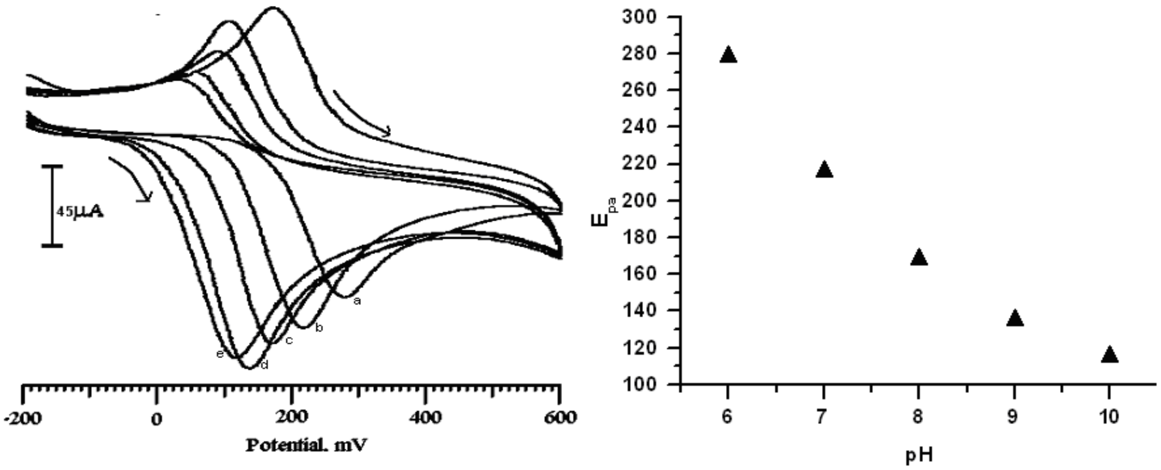
The effect of scan rates on the anodic peak current of DA was studied. As the scan rate increased, the oxidation peak current (Ipa) was also increased. The Ipa was directly proportional to the scan rate *v (*over the range of 100–500mVs^{-1} (Fig.4a) which suggested a surface-controlled process was the adsorption–controlled processes [40] with linear regression 0.98112 (Fig.4b).

3.4. Effects of pH.

To optimize the electrochemical response of modified carbon paste electrode for the oxidation and reduction of DA, the effect of pH on the electrode response was studied. As the pH increases from 6 to 10, the anodic peak current shifted towards the negative side and the well redox peak is arrived at the neutral pH=7.0 (fig.5a) and the value of slope obtained was 40.7 mV/ pH. The *E*pa versus pH graph clearly indicates that the catalytic peak shifts to a more negative potential with increasing the pH.

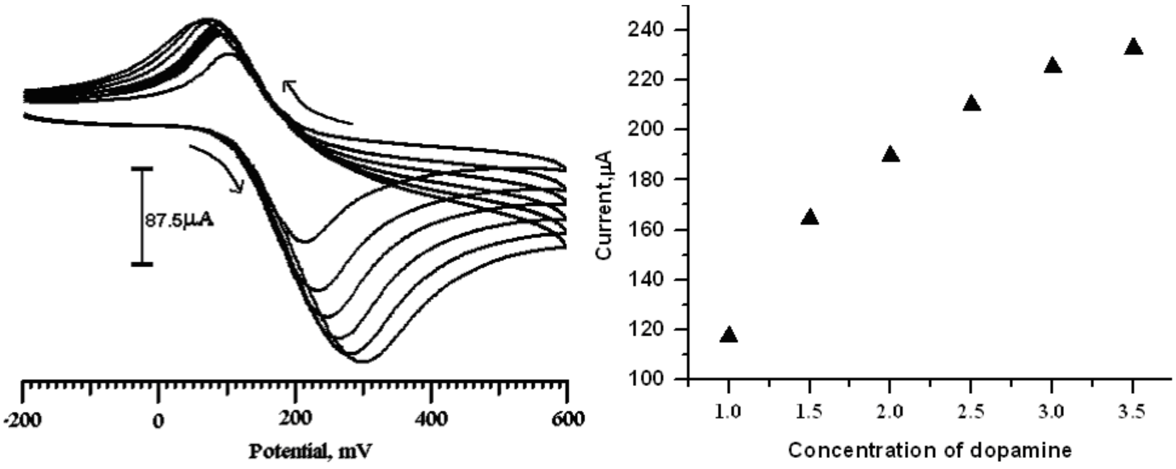
3.5 Effect of dopamine concentration

The effect of concentration of DA was studied at modified CPE in 0.2 M phosphate buffer of pH 7.0, Fig.6a it shows the dependence of the voltammetric response of DA. It clearly indicates that the catalytic peak shifts to a more positive potential with increasing concentration. The CV anodic and cathodic peak current showed a linear relation versus DA concentration in the range of 1 to 3.5 mM with a correlation coefficient $r^2 = 0.9614$ as shown in Fig.6b.



(a) (b)

Figure 5(a,b). a)Cyclic voltammograms obtained at the poly TA modified CPE in 0.2 M phosphate buffer solutions in pH values, (a) 6 (b) 7 (c) 8 (d) 9(e)10 containing $1x10^{-3}$DA M at scan rate of 100 mV/s^{-1}; b)The plot of E_{pa} versus pH values



(a) (b)

Figure 6(a,b) a)Cyclic voltammogram of DA at different concentration ($1X10^{-3}$M, $1.5X10^{-3}$M, $2X10^{-3}$M, $2.5X10^{-3}$M, $3X10^{-3}$, $3.5X10^{-3}$ M) b)Graph of current vs concentration of DA.

3.6. Electrochemical response of Epinephrine at the PolyTA modified CPE

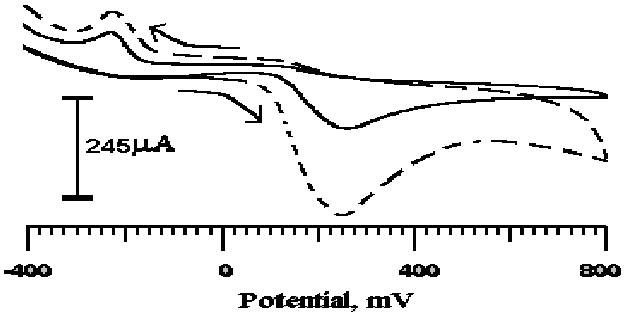


Figure 7. Cyclic voltammograms obtained for the oxidation of 1x10^{-3}EP at poly TA modified CPE(dashed line) and bare CPE (solid line)at scan rate 100 mV/s^{-1}.

The electrochemical behavior of 1.0×10^{-3}M EP at the CPE was investigated using cyclic voltammetric technique and the cyclic voltammograms are shown in Fig.7. At bare CPE, the voltammogram of EP showed poor electrochemical response (solid line). However, the voltammetric response was apparently improved at the modified CPE in PBS at pH 7.0 (dashed line) the results of the enhancement of the peak current showed the excellent catalytic ability of poly TA.

3.7. Effect of scan rate on the peak currents of Epinephrine.

The cyclic voltammograms of the poly(TA) modified electrode at various scan rates obtained in 0.2M^{1} phosphate buffer (pH 7.0) containing 1x10^{-3} M EP. The peak current for the anodic oxidation of EP is proportional to the scan rate in the range of 100-300 mV/s^{-1} with a correlation coefficient of 0.9789(Fig.8), indicating that the catalytic reaction is controlled by adsorption and the anodic potential shifted positively with the increase of scan rate, indicating the quasi-reversible nature of the electrode reaction.

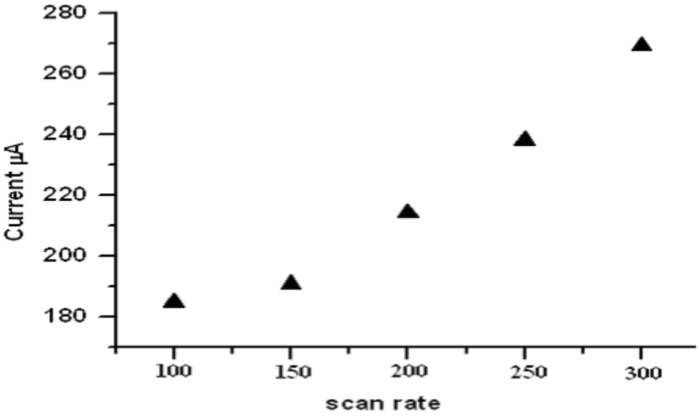


Figure 8. The plot of anodic peak current versus different scan rate 100,150,200,250,300, mV/s^{-1} in 0.2 M phosphate buffer solution (pH 7.0)

3.8. Sensitive detection of EP in the presence of DA at poly TAMCPE

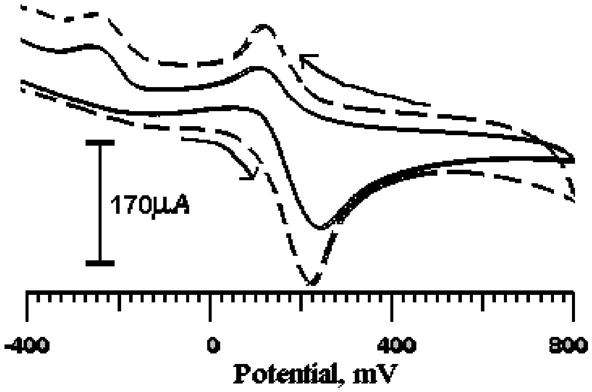


Figure 9. Sensitive determination of 1X10^{-3}M DA, and 1X10^{-3}M EP at bare CPE(solid line) and polyTA film coated CPE(dashed line) .

Fig.9 demonstrated the CVs of the mixture containing EP and DA at bare CPE and modified electrode. At bare CPE exhibited poor current response so that it is difficult to use the bare electrode for sensitive determination of the two species. The modified electrode showed an overlapping of anodic peaks and two separated cathodic peaks at 120 and -238mV with increase in peak currents corresponding to DA and EP respectively with the potential difference of about 358 mV of reduction peak potential. Therefore, very sharp and well defined reduction peaks with significantly enhanced peak currents were selected for sensitive detection of DA and EP in the mixture.

4. CONCLUSION

The poly(Tannic acid) modified electrode was prepared and used for the sensitive determination of EP and DA. The modified electrode showed good stability and sensitivity. The proposed method can be applied for the sensitive determination DA and EP with satisfactory results.

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