

ELECTROCATALYTIC DETECTION OF DOPAMINE AND URIC ACID AT POLY (BASIC BLUE B) MODIFIED CARBON NANOTUBE PASTE ELECTRODEMANJUNATHA JG^{1,2*}, DERAMAN M², BASRI NH²

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ABSTRACT

Electropolymerization of Basic Blue B by cyclic voltammetry (CV) onto the carbon nanotube (CNT) paste electrode results in the formation of poly (Basic Blue B) film/modified CNT paste electrode (PBBB/MCNTPE). The Modified electrode was used for the electrochemical determination of dopamine (DA) and uric acid. CV results showed that this PBBB/MCNTPE have reversible redox behavior in electrolyte solution. The resulting PBBB/MCNTPE were characterized using field emission scanning electron microscope. The analytical ability was tested with respect to the scan rate, number of cycle, pH of solution, and concentration variation. Measurement of these analytes studied simultaneously by CV and differential pulse voltammetry methods. The analytical curve for DA presented linear dependence over the concentration range from 3×10^{-6} to 1.5×10^{-4} M with a linear correlation coefficient of 0.99036. The detection limit of this method was 5.8×10^{-7} . The method has good selectivity and sensitivity with satisfactory results.

Keywords: Carbon nanotubes paste electrode, Cyclic voltammetry, Poly (Basic Blue B), Dopamine, Uric acid.

INTRODUCTION

In recent years, there has been extensive interest in developing chemically modified electrodes for the electrochemical determination of neurotransmitters. Dihydroxyphenylethylamine, also commonly known as dopamine (DA), is one of the most significant catecholamines and is an important neurotransmitter in the mammalian central nervous system. It has also been suggested that DA plays a role in drug addiction and some manifestations of HIV [1-3]. The end product of purine metabolism in humans is uric acid (UA) [4], is present in blood and urine. Its unusual concentration level in a human body causes several diseases such as gout, renal failure, lactic acidosis, hypothyroidism, chronic kidney disease, parathyroid diseases, and so on are also associated with enhanced urate levels. Therefore, the research of DA determination is of great importance in reality [5] and UA, DA is both present in biological fluids such as blood and urine [6]. Carbon nanotubes (CNTs) have received great interest due to their attractive electronic and mechanical properties [7]. The ultimate features of CNTs make them extremely attractive for biosensor applications [8]. The ability of CNTs electrodes to promote the electron-transfer reactions and resistance to surface fouling and many advantages has been studied using some biologically active molecules [9,10].

Cyclic voltammetric (CV) methods provide a simple, low cost, and fast way of analysing biologically and environmentally important molecules. However, the major problem for voltammetric detection of DA samples is the interference of the existing compounds, such as UA, which generally results in overlapped voltammetric response due to their very similar oxidation peak potentials [11,12] recently electropolymer modified paste electrode surface has been proved to be a successful strategy to circumvent this problem, and various materials and techniques have been used. Manjunatha *et al.* studied the simultaneous determination of DA in the presence of ascorbic acid at electropolymer modified carbon paste electrode [13]. Gabriela *et al.* used poly (neutral red) modified electrode for determination of citrate in soft drinks [14]. Sarah *et al.* studied the electrochemical properties of ascorbic acid and H_2O_2 at poly (*o*-phenylenediamine) film modified platinum-iridium electrodes alloy wires [15]. Among those modified electrodes, electropolymer film coated nanotube paste electrodes have many merits such as good biocompatibility, stability, easiness of

the preparation, control the thickness of the film, and easily available materials [16,17].

In continuation of our studies concerning the preparation of modified electrodes [13,18-29] to the best of our knowledge, no study has reported the simultaneous electrocatalytic determination of DA and UA by using poly (Basic Blue B) film modified CNT paste electrode (PBBB/MCNTPE). Thus, in this paper, we described initially the preparation and suitability of a PBBB/MCNTPE as a new electrode in the electrocatalysis and determination of DA and UA. Using the modified electrode, a sensitive and selective method was established for the simultaneous determination of DA and UA.

EXPERIMENTAL DETAILS**Reagents**

DA, UA, and Basic Blue B were purchased from Sigma Aldrich Malaysia and were of analytical grade. The electropolymerization of Basic Blue B was performed in 0.2 M (phosphate buffered saline [PBS]) buffer solution. PBS (0.2 M, pH 7.0) was prepared from 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 were prepared in distilled water and mixed together for the pH 7.0 aqueous solution. Other chemicals used were of analytical grade spectroscopically pure multiwall CNTs (diameter 50-100 nm, 5-10 μ m length) were obtained from Nanostructured and Amorphous Material Inc., Texas, USA. All solutions were prepared with doubly distilled water.

Apparatus

Electrochemical measurements were carried out with electrochemical analyser (EA-201 Chemilink system) in a conventional three-electrode system. The working electrode was a PBBB/MCNTPE and bare CNT paste electrode (BCNTPE), having a cavity of 3 mm diameter. The counter electrode was a bright platinum wire with saturated calomel electrode (SCE) as reference electrode completing the circuit.

Preparation of bare carbon paste electrode

The BCNTPE was prepared by mixing in mortar multiwall CNTs powder and silicone oil in a ratio 60:40.0% w/w [30]. The paste was then packed into the cavity of a homemade electrode and smoothed out on a weighing paper.

Preparation of the PBBB/MCNTPE

The polymer film-modified electrode was fabricated by the electrochemical polymerization of Basic Blue B by CV in the potential range -400 to 1200 mV at a sweep rate of 100 mV/s in PBS (pH 7). The monomer concentration was usually 1×10^{-4} M. After 30 cycles (Fig. 1a), the surface of the electrode was washed with doubly distilled water to remove the physically adsorbed material and PBBB/MCNTPE film with different thickness was achieved by altering the scan cycles during polymerization process (Fig. 1b).

RESULTS AND DISCUSSION

Morphological characterization of BCNTPE and PBBB/MCNTPE

Fig. 2 explains the surface morphology of BCNTPE and PBBB/MCNTPE using the field emission scanning electron microscope. The surface of BCNTPE (Fig. 2a) was irregularly shaped CNTs. However, the PBBB/MCNTPE (Fig. 2b) has typical uniform arrangement of PBBB molecules on the surface of CNT paste electrode. This confirms the CNT paste electrode was coated by PBBB film.

Electrochemistry of DA at the PBBB/MCNTPE

Fig. 3 shows the cyclic voltammograms of the sensor in the presence and absence of 0.2 mM DA in 0.2 M PBS (pH 7.0) at a scan rate of 100 mV/s. In the absence of DA, PBBB/MCNTPE gave no response and only a small background current was observed (dashed line). When the DA was added to the buffer solution, a relatively larger anodic and cathodic current at potentials of 140 and 111 mV was observed. In the present electrochemical approach, the electrode response was proportional to

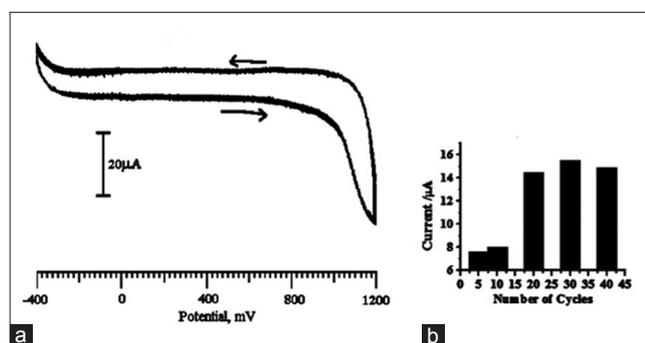


Fig. 1: Continuous cyclic voltammograms for the electrochemical polymerization of 1×10^{-4} M Basic Blue B on a carbon nanotubes paste electrodes in phosphate buffered saline (pH 7) at the scan rate 100 mV/s, (b) dependence of the oxidation peak current of 0.2 mM dopamine on the number of voltammetric scans

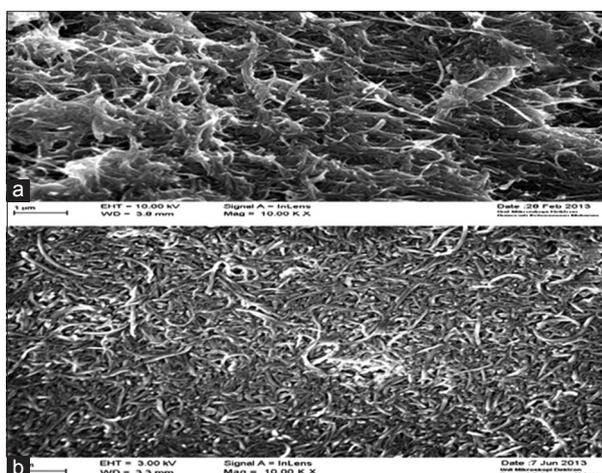
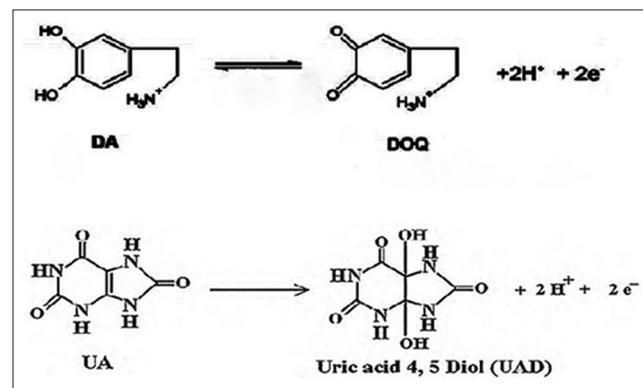


Fig. 2: Field emission scanning electron microscope images of: (a) Bare carbon nanotube paste (CNTPE) electrode, (b) poly (Basic Blue B) film modified CNTPE electrode

the oxidation of an electroactive species produced by the reaction. The mechanism of the reaction are shown in Scheme 1.

Interaction of PBBB/MCNTPE surface with potassium ferrocyanide.

Fig. 4 shows the cyclic voltammograms of 1 mM potassium ferrocyanide at BCNTPE and PBBB/MCNTPE in 1 M potassium chloride and scan rate 100 mV/s. At the BCNTPE the cyclic voltammogram of potassium



Scheme 1: The scheme of oxidation of dopamine and uric acid

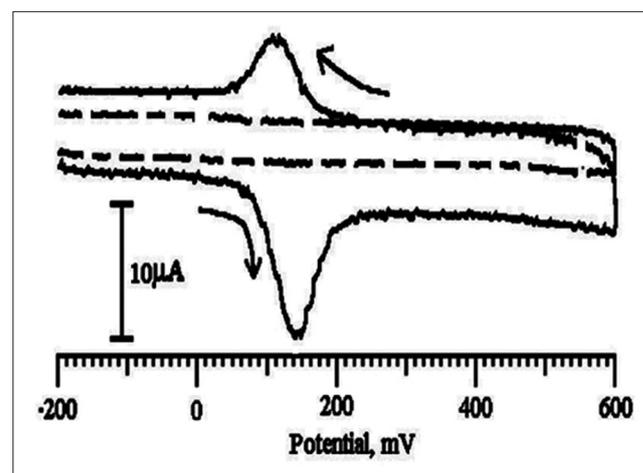


Fig. 3: A typical cyclic voltammogram of poly (Basic Blue B) film modified carbon nanotube paste electrode with 0.2 mM dopamine in pH 7 phosphate buffered saline (PBS) (solid line) without 0.2 mM dopamine in pH 7 PBS blank (dashed line)

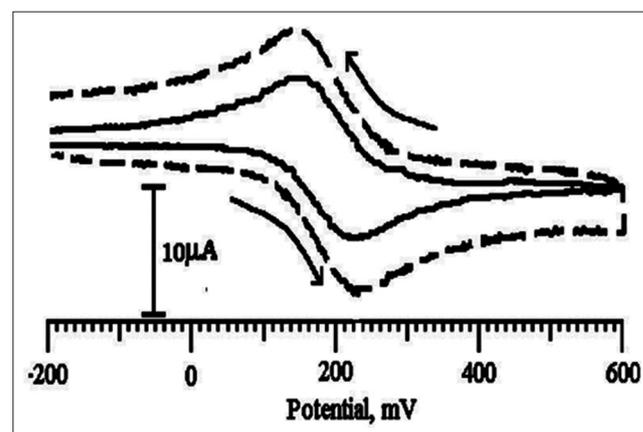


Fig. 4: Cyclic voltammograms of 1 mM potassium ferrocyanide at the bare carbon nanotube paste electrode (CNTPE) (solid line) and at the poly (Basic Blue B) film modified CNTPE (dashed line) in 1 M KCl

ferrocyanide (solid line) shows an oxidation peak potential at 228 mV and reduction peak potential at 148 mV with low current signals. The electrochemical response of potassium ferrocyanide at PBBB/MCNTPE showed well defined redox waves of potassium ferrocyanide with strong increase of the redox peak currents (dashed line). The oxidation peak potential occurs at 229 mV and reduction peak potential at 150 mV, respectively, with the peak potential separation (ΔE_p) 79 mV. The value of i_{pa}/i_{pc} was about 1.38 and negligible shift in the redox peak potentials. The modified electrode exhibited strong promoting effect and high stability toward the electrochemical oxidation of potassium ferrocyanide. It was observed that the peak currents enhanced at the PBBB/MCNTPE, which provides more evidence for asserting that the PBBB in the CNTPE possessed high electrocatalytic activity toward the potassium ferrocyanide detection.

Electrocatalytic response of DA at PBBB/MCNTPE

DA being an easily oxidizable catecholamine, showed quasi-reversible voltammogram with supporting electrolyte 0.2 M PBS of pH 7.0 at 100/mVs scan rate for BCNTPE in the potential range of -200 to 600 mV. Fig. 5 showed a pair of redox peak for BCNTPE (solid line), with E_{pa} 143 mV and E_{pc} 95 mV (vs. SCE). The separation of redox peaks (ΔE_p) was found to be 48 mV and the ratio of redox peak current (i_{pa}/i_{pc}) was 3.41, which were the characteristics of a reversible electrode process. The formal peak potential (E_0), which is the midpoint of E_{pa} and E_{pc} was obtained as 119 mV. However, at the PBBB/MCNTPE a pair of redox peaks are obtained with strong increased in both i_{pa} and i_{pc} (dashed line). The PBBB/MCNTPE reduced the over potential which occurred for BCNTPE. The E_{pa} and E_{pc} were located at 140 mV and 111 mV, respectively. At PBBB/MCNTPE the E_{pa} was shifted negatively upto 3 mV and E_{pc} was positively upto 16 mV. The ΔE_p was found to be 29 mV, which was on accordance with a Nernst reversible behavior and identified that number of electrons involved in the reaction was about equal to two. The ratio (i_{pa}/i_{pc}) was 2.15 and the E_0 was 125.5 mV. The voltammogram obtained for DA at PBBB/MCNTPE was reversible with an excellent enhancement of oxidation and reduction peak currents.

Effect of scan rate on the oxidation of DA

The cyclic voltammogram of PBBB/MCNTPE at various scan rates in the presence of DA (1 mM) was studied (Fig. 6a). It showed that the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming that the electrons transfer slowed down in the film because polymer film got thicker with the increase of scan rate. Also, there is a linear relationship between the reduction peak current (i_{pc}) and square root of the scan rate ($v^{1/2}$) in the scan rates of 100-500 mV/s for DA. The PBBB/MCNTPE exhibited the linear equations of i_{pa} (μA) = $7.14778 - 0.10277 V$ ($r^2=0.99681$) (Fig. 6b) and i_{pc} (μA) = $-2.57925 \times 10^{-5} - 9.94815 \times 10^{-5} V^{1/2}$ ($r^2=0.9925$) (Fig. 6c) respectively, and the rate of redox peak currents was found to be almost unity, indicates the DA oxidation is adsorption-controlled process [21].

Effect of pH

The solution pH is another important factor that affects the electrochemical reactions of DA. Fig. 7a shows the effect of pH on the current response of DA on the PBBB/MCNTPE. As seen, the oxidation peak current of DA increased with increasing pH from 5 to 8 in PBS. From these pH studies, it revealed that in pH 7 PBS, the maximum current response was obtained. Hence, pH 7 phosphate buffer solution was chosen for the electrochemical determination of DA. Our study showed that electrocatalytic oxidation of DA with PBBB/MCNTPE was more favored under the neutral conditions. The electrocatalytic effect appeared as a gradual growth in the anodic peak current and a simultaneous decrease was observed in the cathodic peak current in the PBBB/MCNTPE voltammogram while the peak potential shifted toward the negative values. Based on the results, the anodic peak current for the electrooxidation of DA was high at pH 7.0. Therefore, pH 7.0 was selected as the optimum pH for the electrocatalytic oxidation of DA at the PBBB/MCNTPE. The potential diagram was constructed by plotting the graph of calculated E_0 versus pH of the solution (Fig. 7b). The linear regression equation for the anodic peak is given by $E_{pa}=563.07-58.42$

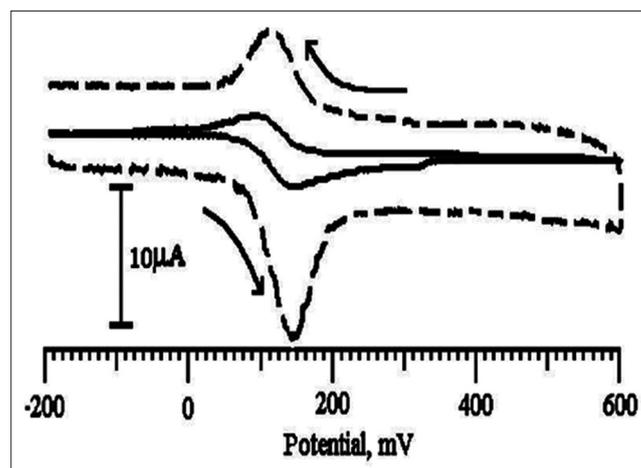


Fig. 5: Cyclic voltammograms of 0.2 mM dopamine in pH 7 phosphate buffered saline at, (a) Bare carbon nanotube paste electrode (CNTPE) (solid line), (b) poly (Basic Blue B) film modified CNTPE (dashed line)

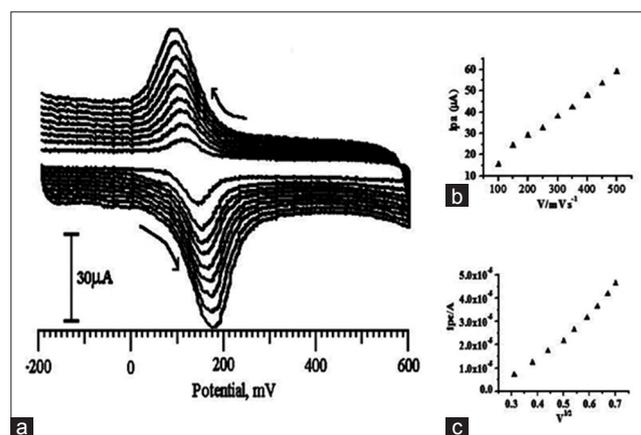


Fig. 6: (a) cyclic voltammograms of 0.2 mM dopamine (DA) at the poly (Basic Blue B) film modified carbon nanotube paste electrode in pH 7 phosphate buffered saline at various scan rates. From: 100 to 500 mV/s, (b) plot of the anodic peak current of DA as a function of the scan rate, (c) effect of variation of square root of scan rate on the cathodic peak current

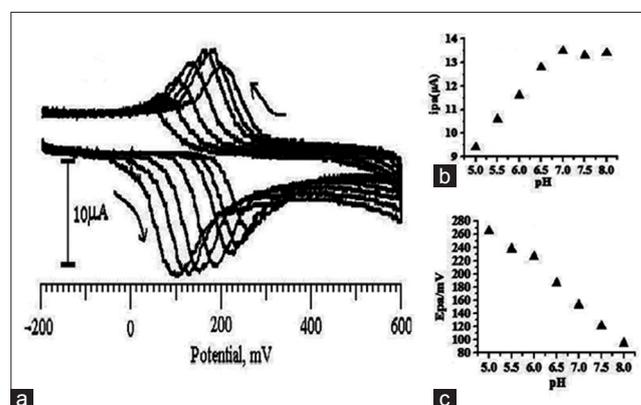


Fig. 7: (a) Cyclic voltammograms obtained at the poly (Basic Blue B) film modified carbon nanotube paste electrode (PBBB/MCNTPE) in 0.2 M phosphate buffered saline in pH values, 5-8 containing 0.2 mM dopamine (DA), (b) plot of anodic peak current versus pH (5.0-8.0) of 0.2 mM DA at the PBBB/MCNTPE, (c) plot of E_{pa} versus pH for DA

pH ($r^2=0.99464$). A slope of 58.42 mV/pH which is close to the theoretical value of 59 mV/pH (Fig. 7c) this behavior obeyed the Nernst equation for the equal number of electron and proton transfer reaction [30-32].

Calibration curve

Under optimized experimental parameters, the calibration curve was obtained in pH 7.0 PBS by CV. Fig. 8 shows the cyclic voltammograms of PBBB/MCNTPE in pH 7.0 PBS containing different concentration of DA. The linear segment increases from its concentration in the range of 3.0×10^{-6} – 1.5×10^{-4} M. The corresponding regression equations can be expressed as $i_{pa} \text{ (A)} = 2.80145 \text{ (M)} + 0.06173$ ($r^2=0.99036$). The detection limit of this method for DA is 5.8×10^{-7} M calculated according to $DL = 3 \text{ sb/m}$ where, sb is the standard deviation of the blank response, m is the slope of the calibration plot and this electrochemical method was compared with other corresponding results were tabulated in Table 1 [33-37].

Electrochemical behavior of UA at PBBB/MCNTPE

Cyclic voltammograms of UA at the BCNTPE and the PBBB/MCNTPE are shown in Fig. 9a which shows that the current response of 0.5 mM of UA at the BCNTPE is weak, $E_{pa}=295$ mV, $i_{pa}=-9.5$ μA and the current response of UA at the PBBB/MCNTPE is much better, $E_{pa}=316$ mV, $E_{pa}=-18.7$ μA . Oxidation peak current of UA at the PBBB/MCNTPE is almost high current response, which indicates that PBBB film can significantly catalyze the UA oxidation process and the electron transfer rate of UA in PBBB film is much faster.

Fig. 9b gives the CV curves of UA at different scan rates, which shows that the oxidation peak potential shift positively with scan rate increasing and the oxidation peak current is proportional to the scan rates when the scan rates are between 100 and 400 mV/s. The linear equation is $i_{pa} \text{ (A)} = -1.1755 \times 10^{-6} - 6.080 \times 10^{-5} v$ (mV/s), $r^2=0.99095$ [20]. This shows that the electrode reaction is controlled by the adsorption process (Fig. 9c).

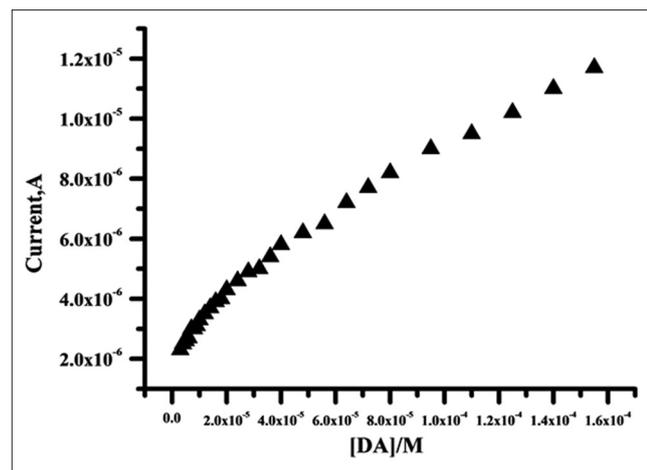


Fig. 8: Calibration plot for the determination of dopamine at the poly (Basic Blue B) film modified carbon nanotube paste electrode in pH 7 phosphate buffered saline with the scan rate 100 mV/s

The effect of solution pH on the response of UA was investigated over the pH range of 5-8. Fig. 9d shows that the anodic peak potential shifted toward the negative direction with the increase of pH, showing that protons had taken part in the electrode process. As can be seen in Fig. 9e, UA oxidation peak potential changes linearly depending on a pH from 5 to 8.0, and the equation is $E_{pa}=559.1071+33.64 \text{ pH}$ ($r^2=0.99086$). And a maximum peak current was obtained at pH 7.0. Thus, a PBS (pH 7) was chosen for supporting the electrolyte for investigation of the oxidation of UA at the PBBB/MCNTPE (Fig. 9f).

Simultaneous determination of DA and UA

The biological compounds such as UA usually present along with DA in human brain and the concentration of this biological compound higher than that of DA. The separation of oxidation peak potentials between DA and UA plays an important role for the analysis of DA [19]. Fig. 10 shows the CV response of DA (0.2 mM) in the presence of UA (0.2 mM) and in

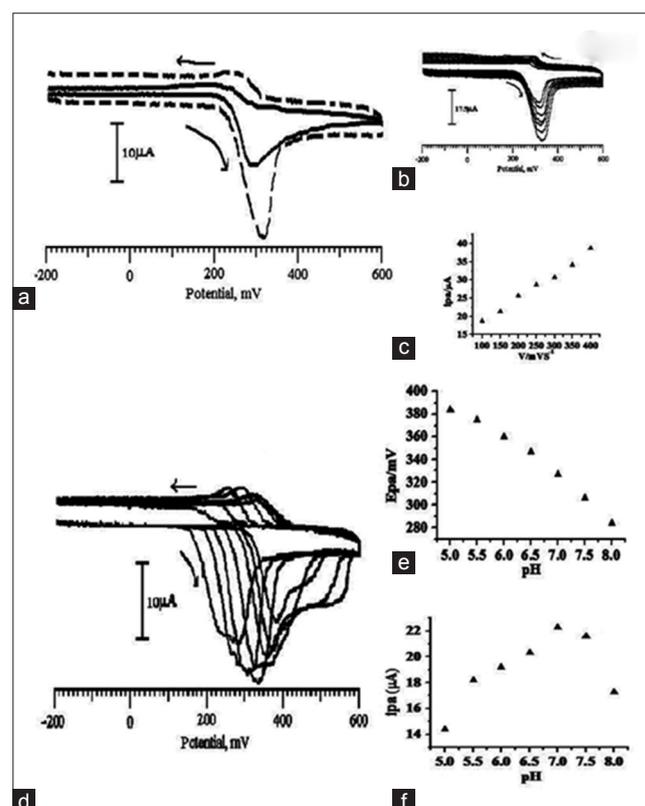


Fig. 9: Cyclic voltammograms obtained for the oxidation of 0.5 mM uric acid (UA) at poly (Basic Blue B) film modified carbon nanotube paste electrode (PBBB/MCNTPE) (dashed line) and bare CNTPE (solid line), (b) the oxidation of 0.5 mM UA at different scan rate 100 to 400 mV/s in 0.2 M phosphate buffered saline (PBS) (pH 7), (c) plot of the anodic peak current of UA as a function of the scan rate, (d) the PBBB/MCNTPE in 0.2 M PBS in pH values, 5-8 containing 0.5 mM UA, (e) plot of anodic peak current versus pH (5.0-8.0) of 0.5 mM UA at the PBBB/MCNTPE, (f) plot of E_{pa} versus pH for UA

Table 1: The comparison of PBBB with some modified electrodes for the determination of DA at different modified electrodes

Electrode	Modifier	Analyte	Detection limit (M)	Method	References
Gold electrode	Metallothioneins self-assembled	DA	6×10^{-6}	CV	[33]
Carbon paste electrode	Ionic liquid	DA	7×10^{-7}	CV	[34]
Glassy carbon electrode	Ionic micelles	DA	3×10^{-6}	CV	[35]
PGE	α -CD/CNT	DA	1×10^{-6}	DPV	[36]
Glassy carbon electrode	Poly (p-toluene sulfonic acid)	DA	6.0×10^{-7}	DPV	[37]
Nanotube paste electrode	PBBB	DA	5.8×10^{-7}	CV	This work

CV: Cyclic voltammetry, DA: Dopamine, DPV: Differential pulse voltammetry, PGE: Pencil graphite electrode, PBBB: Poly (Basic Blue B)

PBS (pH 7.0) solution at both BCNTPE and PBBB/MCNTPE. The CV at PBBB/MCNTPE showed a good separated two well defined peaks for the DA and UA with different oxidation potentials. On the other hand, the poor current response and irreversible electrochemical behaviors at BCNTPE. The oxidation peak potentials of DA and UA on the modified electrode separated completely into two well-defined peaks with 139 mV and 289 mV versus with an increase in current, respectively, at the PBBB/MCNTPE.

Simultaneous detection of DA and UA by differential pulse voltammetry (DPV)

DPV was used for the determination of DA and UA at PBBB/MCNTPE because of its higher current sensitivity and better quality than CV. The simultaneous study was carried out in the potential range from -200 to 600 mV (Fig. 11a). The DPV showed the simultaneous determination of DA and UA with well separated two anodic peaks corresponding to their oxidation could be possible at PBBB/MCNTPE. The 0.2 mM DA showed its Epa at 122 and 0.2 mM UA was at 270 mV.

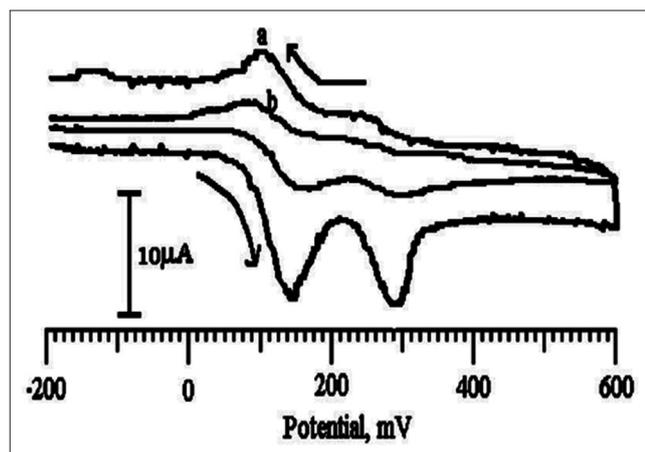


Fig. 10: Cyclic voltammograms obtained at bare carbon nanotube paste electrode (CNTPE) (curve "a") and poly (Basic Blue B) film modified CNTPE (curve "b") containing mixture of both 0.2 mM dopamine and 0.2 mM uric acid in 0.2 M phosphate buffered saline of pH 7

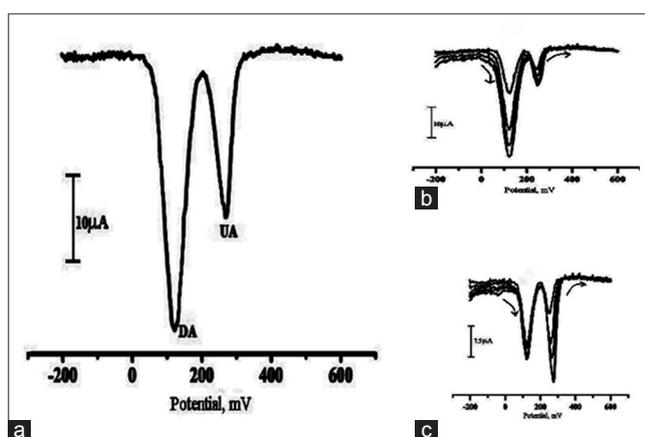


Fig. 11: (a) Differential pulse voltammetry (DPVs) of mixture of 0.2 mM dopamine (DA) and 0.2 mM uric acid (UA) in 0.2 M phosphate buffered saline (PBS) of pH 7. At poly (Basic Blue B) film modified carbon nanotube paste electrode (PBBB/MCNTPE), (b) DPV recordings for DA at PBBB/MCNTPE in the presence of 0.05 mM UA in PBS for different concentration DA pH 7 (0.05-0.2 mM), (c) DPV recordings of 0.05 mM DA in the presence of different concentration of UA (0.05-0.3 mM)

In order to check the intermolecular effects between DA and UA, two different experiments were carried out under the optimum conditions at a pH 7.0. In each experiment, the concentration of one of the two compounds was changed while keeping the concentrations of the other one constant [38-40]. From the Fig. 11b, it can be seen that the peak current of DA was proportional to its concentration, which was increased from 0.05 mM to 0.2 mM when keeping the concentration of UA 0.05 mM. There was no change in the peak current and peak potential occurred for UA. Similarly in the Fig. 11c keeping the concentration of DA constant, the UA concentration was varied from 0.05 mM to 0.3 mM. The oxidation peak current of UA increases with increase in its concentrations exhibit an excellent DPV responses to DA and UA without any obvious intermolecular effects among them.

Analytical application

To verify our results, the modified electrode was applied to the determination of DA hydrochloride injection. The specified content of DA of 40.0 mg/ml. The sample was used after required dilution. Results were obtained with recovery in the range 99.5-102.25%, which indicates that the sensor can be applied for the analysis of these compounds and RSD all so acceptable.

CONCLUSION

The electrochemically manufactured PBBB/MCNTPE exhibited a highly effective, electrocatalytic activity toward the determination of DA and UA in mixture of solution at physiological pH. The proposed chemical sensor has showed excellent sensitivity, selectivity, fast response, good linearity range, low detection limit with satisfactory stability, repeatability, reproducibility, and good potential applications toward the determination of DA and UA. The proposed method can be applied for the detection of DA and UA in the pharmaceutical formulations.

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