

Sodium Dodecyl Sulphate/Poly(Brilliant Blue)/Multi Walled Carbon Nanotube Modified Carbon Paste Electrode for the Voltammetric Resolution of Dopamine in the Presence of Ascorbic Acid and Uric Acid

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Abstract

Sodium dodecyl sulphate/poly(brilliant blue)/multi walled carbon nanotube modified carbon paste electrode was fabricated for the electroanalysis of dopamine in the presence of ascorbic acid and uric acid in phosphate buffer solution of pH 7.4. The key parameters such as sensitivity, selectivity, antifouling property and stability were achieved by the modified electrode. The redox peaks obtained at modified electrode shows good electrocatalytic activity towards the oxidation of dopamine. From the effect of scan rate and concentration the electrode phenomenon was confirmed to be adsorption-controlled process. The lower limit of detection of dopamine was 2.69×10^{-7} M, and the simultaneous analysis shows a good result with peak to peak separation between dopamine and other two analytes ascorbic acid and uric acid by both cyclic voltammetry and differential pulse voltammetric techniques.

Keywords: Electroanalysis; Dopamine; Poly(brilliant blue); Multi walled carbon nanotube; Sodium dodecyl sulphate; Voltammetry

Introduction

In the last few decades the electrochemical methods are most widely studied and accepted for the determination of electroactive compounds in pharmaceutical samples and physiological fluids due to its simple, sensitive, rapid and economical properties [1,2]. Particularly the development of voltammetric sensors for both the analysis and determination of biologically important molecules such as dopamine (DA), ascorbic acid (AA) and uric acid (UA) has been received much more importance for the scientific growth of electroanalytical research [3-6]. DA is one of the naturally occurring neurotransmitter in the human brain belongs to the family of catecholamine and plays a very important role in the normal activity of the central and peripheral nervous systems [7,8]. Extreme abnormalities of DA levels are the major drawbacks of several diseases, such as Parkinsonism and Schizophrenia [9,10]. A patient suffering from this disease shows a low level of DA. UA is the primary product of purine metabolism in the human body and major nitrogenous compound in the urine [11]. Its abnormality in human body leads to many diseases, such as gout, hyperuricaemia and Lesch-Nyan disease [12,13]. Increased urate level also leads to pneumonia and leukaemia [14]. AA is also known as vitamin-c and is water soluble compound that take part in many important life processes, it has been used as a medicament for the treatment of common cold, mental illness and cancer [15]. It can be chemically or electrochemically oxidized to dehydroascorbic acid [16]. Hence monitoring the concentration of these biological compounds is very important in clinical diagnosis. Normally in the electrochemical detection of DA the major problem was the coexistence of the common interference AA and UA. Because of the similar oxidation potential of AA there is an always interference in analysing the DA electrochemically and gives overlapped and broad voltammetric response at bare carbon paste electrode (BCPE). To improve the performance of the BCPE the properties such as sensitivity, selectivity, antifouling property, reproducibility and stability are the key parameters [17-21]. Carbon nanotubes (CNTs) have been one of the most actively studied electrode material due to their unique electronic and mechanical properties and also the availability of high accessible surface area and low resistivity [22-25]. Recently carbon nanotubes modified electrodes were utilised

to investigate the direct electrochemistry of several biomolecules [26-29]. A surfactant is a linear molecule with amphiphilic or amphipathic behaviour and they bear an ionic or non-ionic polar head group and a hydrophobic portion. Due to their unique molecular structure, surfactants have been employed extensively in the field of electroanalytical chemistry for various purposes [30-33]. In the present work the modification of the bare carbon paste electrode was achieved by using different quantity of multi walled carbon nanotube (MWCNT) along with carbon powder and a silicon oil binder by mechanical grinding method. In order to enhance both the sensitivity and selectivity it was further modified by immobilising the sodium dodecyl sulphate (SDS) to the surface of the electrode followed by electropolymerisation brilliant blue [34]. The fabricated electrode was employed for the electroanalysis of dopamine in presence of ascorbic acid and uric acid at physiological pH.

Experimental Section

Reagents

Multi walled carbon nanotube (110-170 nm) are received from Sigma Aldrich. Dopamine hydrochloride (DA), Uric acid (UA), Ascorbic acid (AA) were purchased from Himedia and the stock solutions of 25×10^{-4} M, 25×10^{-3} M and 25×10^{-3} M were prepared in 0.1M perchloric acid, 0.1M NaOH and double distilled water respectively. Buffer used was 0.2M phosphate buffer solution (PBS) of pH 7.4. Graphite powder of 50 μ m particle size was purchased from

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Merck and silicone oil from Himedia was used to prepare carbon paste electrode (CPE). All the chemicals mentioned were all of analytical grade used as received without any further purification.

Apparatus

The electrochemical experiments were performed using a model CHI-660c (CH Instrument-660 electrochemical workstation) at ambient temperature. A traditional three electrode compartment was used with a saturated calomel electrode (SCE) as a reference, a platinum counter electrode, and bare or Sodium dodecyl sulphate/poly(brilliant blue)/multi walled carbon nanotube modified carbon paste electrode (SDS/Poly(brilliant blue)/MWCNT/MCPE) as working electrode.

Preparation of the BCPE and MWCNT/MCPE

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 70% graphite powder and 30% silicone oil in an agate mortar until a homogeneous paste was formed. The paste was then packed into a cavity of PVC tube of 3 mm internal diameter and smoothed on a tissue paper. The electrical contact was provided by a copper wire connected to the end of the tube. MWCNT/MCPE was prepared by homogeneously grinding different amounts of MWCNT in milligrams along with 70% graphite powder and 30% silicone oil.

Preparation of Poly(brilliant blue)/MWCNT/MCPE

The reported procedure was used for the preparation of poly(brilliant blue) film onto the MWCNT/MCPE surface [34]. Electrochemical polymerization of brilliant blue on the surface of MWCNT/MCPE was carried out using cyclic voltammetric method in aqueous solution containing 0.5mM brilliant blue in 0.1M NaOH solution. The electropolymerisation was achieved by the formation of film that grew between -0.5 V to +1.5 V at the scan rate of 0.1 Vs⁻¹ for 10 cycles. After this the electrode was rinsed thoroughly with double distilled water.

Preparation of SDS/poly(brilliant blue)/MWCNT/MCPE

10 μ L of SDS solution (0.1mM) was added by using micropipette on the surface of the poly(brilliant blue)/MWCNT/MCPE and allowed it for about 12 min at room temperature. The electrode was later thoroughly rinsed with double distilled water to remove unadsorbed SDS to get the SDS/poly(brilliant blue)/MWCNT/MCPE.

Results and Discussion

Effect of quantity MWCNT on the peak current of DA

The MWCNT MCPE was prepared by adding different amount of MWCNT to the carbon paste electrode and was employed for the oxidation of 0.1mM DA in 0.2M PBS of pH 7.4 using cyclic voltammetric (CV) technique. By increasing the quantity of MWCNT in the modification, the electrochemical cathodic peak current (I_{pc}) and anodic peak current (I_{pa}) goes on increasing at particular ratio. The modification procedure was calibrated from 2 mg to 14 mg. The redox peak currents were increased up to 8 mg MWCNT in carbon paste electrode. After this, the redox peak current was decreased as shown in Figure 1. Further increase in the quantity of MWCNT both I_{pa} and I_{pc} were decreased. Therefore, 8 mg MWCNT was chosen as optimum for the modification procedure. In order to enhance the sensitivity of detection, the electropolymerisation of brilliant blue on the surface of MWCNT/MCPE was carried out using CV method in an aqueous solution containing 0.5mM brilliant blue in 0.1M NaOH solution. The electropolymerisation was achieved by the formation of

film that grew between -0.5 V to +1.5 V at the scan rate of 0.1 Vs⁻¹ for 10 cycles. After this the poly(brilliant blue)/MWCNT/MCPE electrode was rinsed thoroughly with double distilled water.

Micellar effect on Poly(brilliant blue)/MWCNT/MCPE for the oxidation of DA

Surfactants are proven to enhance the sensitivity of the electrode [35-37]. In the present study 0.1mM sodium dodecyl sulphate (SDS) an anionic, 0.1mM Triton X-100 (TX-100) a non-ionic, 0.1mM cetyl trimethyl ammonium bromide (CTAB) a cationic surfactant solutions of different concentration (5 μ L to 25 μ L) are immobilized on the surface of poly(brilliant blue)/MWCNT/MCPE for about 5 min and it is employed for the oxidation of 0.5mM DA in 0.2M PBS of pH 7.4 at the scan rate 0.05 Vs⁻¹ using CV technique. All three surfactants shows noticeable enhancement in the peak currents of DA as shown in Figure 2(A), 2(B) and 2(C). However, SDS shows remarkable enhancement as compared with other two surfactants namely TX-100 and CTAB. At the concentration of 10 μ L of SDS both anodic and cathodic peak currents was maximum as already illustrated in Figure 2(A). In order to calibrate the sensitivity of the electrode, again the influence of immobilization time was checked in the interval of 2 min each upto 16 min. The I_{pa} and I_{pc} go on increasing upto 12 min and later remains almost constant (Figure 2D). Hence the concentration of 10 μ L SDS and immobilization time of 12 min was fixed as optimum to fabricate a stable working electrode to investigate all other remaining parameters.

Electrocatalytic oxidation of DA at SDS/poly(brilliant blue)/MWCNT/MCPE

DA being an easily oxidizable electroactive catecholamine, its voltammogram was recorded in the potential range from -0.2 to 0.6 V. Figure 3A shows the cyclic voltammograms recorded for 0.1mM DA at BCPE (curve a) MWCNT/MCPE (curve b) poly(brilliant blue)/MWCNT/MCPE (curve c) SDS/poly(brilliant blue)/MWCNT/MCPE (curve d) in 0.2M PBS of pH 7.4 with the scan rate 0.05 Vs⁻¹. At BCPE (curve a) the oxidation potential was occurred at 0.15 V with poor voltammetric response and for the MWCNT/MCPE the oxidation occurred at 0.14 V vs. SCE as shown in inserted Figure 3B. However, at SDS/poly(brilliant blue)/MWCNT/MCPE (curve d) the oxidation potential was observed at 0.180 V with a slight shift in the oxidation potential towards positive side with the significant enhancement in the redox peak current signals. This enhancement of current signal reflects the electrocatalytic activity of SDS/poly(brilliant blue)/MWCNT/MCPE towards the detection of DA.

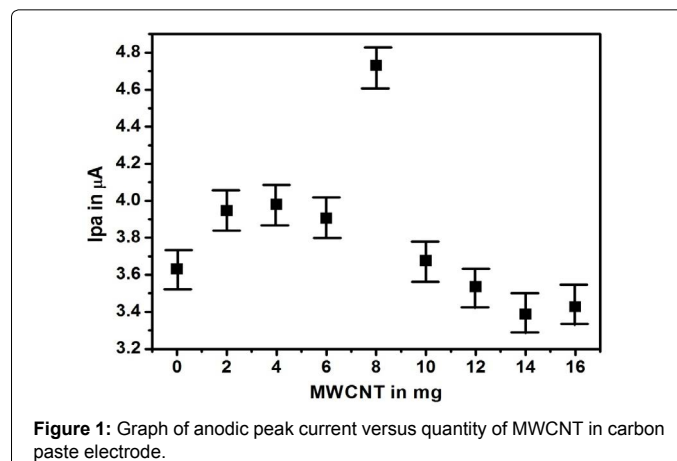


Figure 1: Graph of anodic peak current versus quantity of MWCNT in carbon paste electrode.

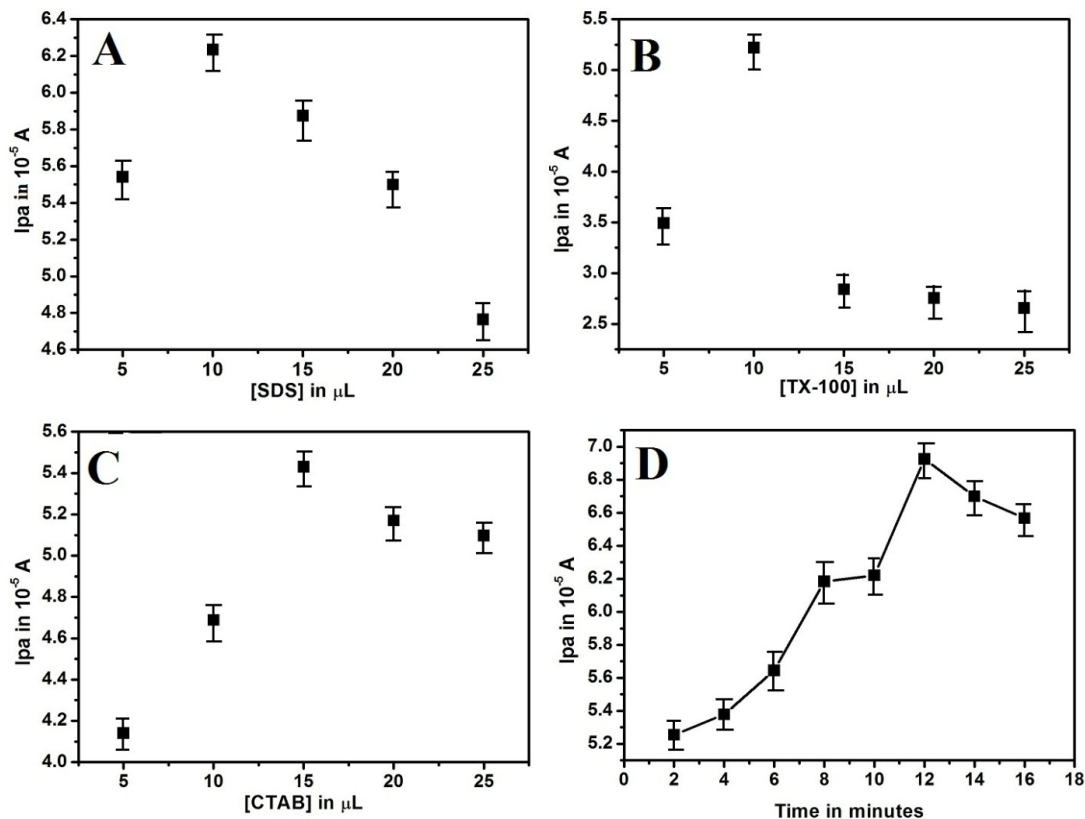


Figure 2: The micellar effect on poly(brilliant blue)/MWCNT MCPE for the oxidation of 0.5mM DA in 0.2M PBS of pH 7.4 (A) SDS (B) TX-100 (C) CTAB (D) Anodic peak current of oxidation of 0.5mM DA in 0.2M PBS of pH 7.4 versus immobilisation time.

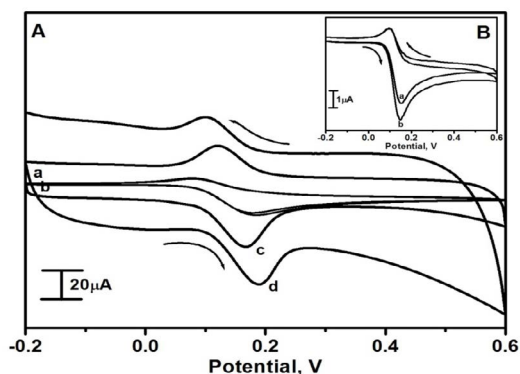


Figure 3: Cyclic voltammograms of 0.1mM DA in 0.2M PBS solution of pH 7.4 at the scan rate 0.05 Vs^{-1} . (A) Shows the results obtained for (a) BCPE (curve a) (b) MWCNT/MCPE (curve b) and (c) poly(brilliant blue)/MWCNT/MCPE (curve c) (d) SDS/Poly(brilliant blue)/MWCNT/MCPE (curve d) (B) Shows the results of (a) BCPE (curve a) (b) MWCNT/MCPE (curve b).

Effect of scan rate

The effect of scan rate for 0.5mM DA in 0.2M PBS of pH 7.4 was studied by CV technique at SDS/poly(brilliant blue)/MWCNT/MCPE as shown in Figure 4A. The modified electrode obeys Randles-Sevcik equation and showed increase in the redox peak currents with increase in the scan rate with the small shifting of the redox peak potential. In order to confirm the electrode process, the graph of peak current (I_p) vs. scan rate (v) was plotted and the obtained graph is a straight line with

good linearity in the range from 0.05-0.5 Vs^{-1} as shown in Figure 4B the correlation coefficient (r^2) was 0.9988 and 0.9984. The I_p vs. square root scan rate ($v^{1/2}$) were plotted as shown in Figure 4C with the correlation coefficient (r^2) 0.9946 and 0.9946 this suggests the electrode process was adsorption controlled and in support to this logarithm of anodic peak current vs. logarithm of scan rate (Figure 5) was plotted and the determined slope was 0.8686 which confirms the electrode process was adsorption controlled process [38]. This was again supported by previously reported literatures [39].

According to an equation previously reported [40] for determining the value of heterogeneous rate constant (k^0) from experimental peak potential difference (ΔE_p) values, equation (1) was used.

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (1)$$

From the experimental ΔE_p values as shown in Table 1 and equation (1) the values of the k^0 for the DA oxidation was determined. The value of k^0 obtained at a scan rate of 0.05 Vs^{-1} for the SDS/poly(brilliant blue)/MWCNT/MCPE exhibits larger heterogeneous rate constant compared with those determined in other scan rate variation studies. All the parameters are tabulated in Table 1.

Effect of DA concentration

The electrocatalytic oxidation of DA was carried out by varying its concentration at SDS/poly(brilliant blue)/MWCNT/MCPE. Figure 6A shows by increasing the concentration of DA from 0.60×10^{-4} M to 1.19×10^{-4} M, the I_{pa} and I_{pc} goes on increasing with shifting E_{pa} towards less positive and E_{pc} towards least negative side. The graph of I_{pa} vs. concentration of DA was plotted as shown in Figure 6B it shows almost

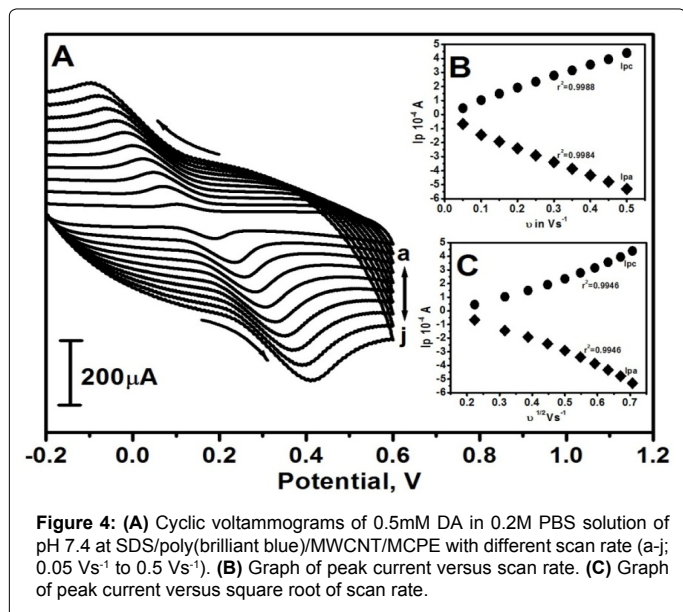


Figure 4: (A) Cyclic voltammograms of 0.5mM DA in 0.2M PBS solution of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE with different scan rate (a-j; 0.05 Vs⁻¹ to 0.5 Vs⁻¹). (B) Graph of peak current versus scan rate. (C) Graph of peak current versus square root of scan rate.

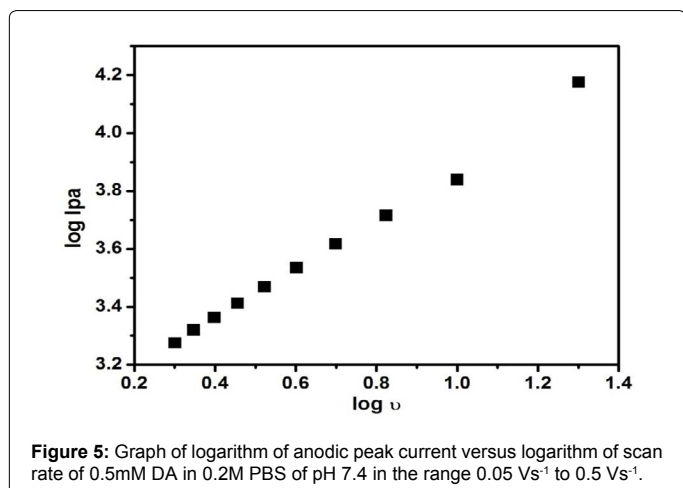


Figure 5: Graph of logarithm of anodic peak current versus logarithm of scan rate of 0.5mM DA in 0.2M PBS of pH 7.4 in the range 0.05 Vs⁻¹ to 0.5 Vs⁻¹.

v/mVs^{-1}	$\Delta E_p/mV$	k^0/s^{-1}
0.05	87.6	0.5827
0.10	165.4	0.4789
0.15	210.6	0.4286
0.20	256.9	0.3365
0.25	302.0	0.2511
0.30	309.2	0.2780
0.35	314.0	0.3069
0.40	311.0	0.3625
0.45	320.8	0.3650
0.50	314.0	0.4385

Table 1: Variation of the voltammetric parameters gathered from the plots shown in Figure 4 as a function of the potential scan rate.

straight line with linear regression equation $I_{pa}(10^{-5}A) = 6.2192(C_0 \cdot 10^{-4}M/L) + 1.6157$, ($r^2 = 0.9975$). The limit of detection was calculated [41,42] and the detection limit on the lower concentration range for DA was $2.69 \times 10^{-7} M$ for the SDS/poly(brilliant blue)/MWCNT/MCPE and limit of quantification was $8.97 \times 10^{-7} M$. The proposed electrode exhibited a relatively lower detection limit than those reported [43-46] as shown in Table 2.

Electrochemical oxidation of AA at SDS/poly(brilliant blue)/MWCNT/MCPE

Figure 7 showed the cyclic voltammograms of 1mM AA at the BCPE (curve a), SDS/poly(brilliant blue)/MWCNT/MCPE (curve b) in 0.2M PBS solution of pH 7.4 with the scan rate 0.05 Vs⁻¹. At the BCPE the oxidation peak occurred at around 0.242 V and generally oxidation of AA at bare electrode was irreversible, seldom broad and required high over potential due to fouling of the electrode surface by the adsorption of oxidized product of AA. However, at the SDS/poly(brilliant blue)/MWCNT/MCPE the oxidation peak potential of AA was obtained at around 0.020 V which shifted to least positive potential and showed faster electron transfer kinetics of AA when compared to that of BCPE, which indicated that the SDS/poly(brilliant blue)/MWCNT/MCPE lowers the over potential and favoured the oxidation process of AA.

Figure 8A shows the cyclic voltammograms of AA at SDS/poly(brilliant blue)/MWCNT/MCPE for 1mM AA in 0.2M PBS of pH 7.4 in the scan rate range of 0.05 Vs⁻¹ to 0.5 Vs⁻¹ by increase the scan rate there was an increase in the anodic peak current (I_{pa}) and the oxidation peak potential was observed to shift positively with the increase in scan rate [47], in addition to this, the graph of I_{pa} versus v and I_{pa} versus v^{1/2} were plotted the graph obtained was linearly straight line shown in Figure 8B and Figure 8C respectively. A good linearity with correlation coefficients 0.9974 and 0.9970 indicated that the electrode transfer reaction was adsorption-controlled process on the SDS/poly(brilliant blue)/MWCNT/MCPE surface.

Effect of AA concentration

The electrochemical oxidation of AA was carried out by varying its concentration at SDS/poly(brilliant blue)/MWCNT/MCPE by using CV technique at scan rate 0.05 Vs⁻¹. Figure 9A shows the voltammograms obtained for AA at different concentrations. By increasing the concentration of AA from $2.77 \times 10^{-3} M$ to $4.31 \times 10^{-3} M$ the I_{pa} was also increased. The graph of I_{pa} vs. different concentration of AA was plotted in Figure 9B the result showed linear increase in peak current with increase in the AA concentration with the linear regression equation $I_{pa}(10^{-5}A) = 1.280(C_0 \cdot 10^{-3}M/L) + 1.938$, ($r^2 = 0.9926$). The LOD and LOQ were 1.31×10^{-6} and 4.36×10^{-6} respectively.

Electrochemical response of UA at SDS/poly(brilliant blue)/MWCNT/MCPE

Figure 10 shows the cyclic voltammograms of 1mM UA for BCPE (curve a) and SDS/poly(brilliant blue)/MWCNT/MCPE (curve b) in 0.2M PBS of pH 7.4 with the scan rate 0.05 Vs⁻¹. It could be noticed that voltammetric peak appeared at about 0.304 V for BCPE, the peak was less sensitive rather broad suggesting slow electron transfer kinetics. However, at SDS/poly(brilliant blue)/MWCNT/MCPE the UA showed a significant increment in oxidation peak current and located at 0.307 V. By this it can be confirmed that there was an occurrence of electrocatalytic reaction between the SDS/poly(brilliant blue)/MWCNT/MCPE and UA.

Figure 11A shows the cyclic voltammograms of UA at SDS/poly(brilliant blue)/MWCNT/MCPE for 1mM UA in 0.2M PBS of pH 7.4 and scan rate from 0.05 to 0.5 Vs⁻¹. The graph of I_{pa} versus v was plotted in the range from 0.05 to 0.5 Vs⁻¹. The graph obtained was linearly straight line shown in Figure 11B with correlation coefficient 0.9976. And a plot of I_{pa} versus v^{1/2} in the same scan rate range showed correlation coefficient of 0.9930 as in Figure 11C. Therefore, it was confirmed that there was an adsorption complications of analytes on the surface of the SDS/poly(brilliant blue)/MWCNT/MCPE.

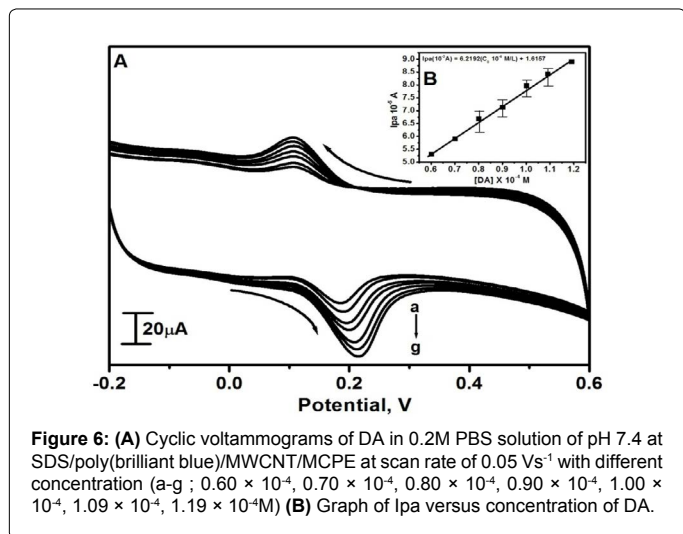


Figure 6: (A) Cyclic voltammograms of DA in 0.2M PBS solution of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE at scan rate of 0.05 Vs⁻¹ with different concentration (a-g ; 0.60×10^{-4} , 0.70×10^{-4} , 0.80×10^{-4} , 0.90×10^{-4} , 1.00×10^{-4} , 1.09×10^{-4} , 1.19×10^{-4} M) (B) Graph of I_{pa} versus concentration of DA.

Working Electrode	Limit of Detection (mol/L)	Method	References
Bicopper complex modified GCE	1.4×10^{-6}	DPV	[43]
CPE modified with SDS micelles at pH 7	3.70×10^{-6}	DPV	[44]
Ionic liquid modified Carbon paste electrode	7.0×10^{-7}	CV	[45]
CTAB/CPE	11×10^{-7}	DPV	[46]
SDS/poly(brilliant blue)/MWCNT/MCPE	2.69×10^{-7}	CV	This work

Table 2: Comparison of detection limits of different modified electrodes.

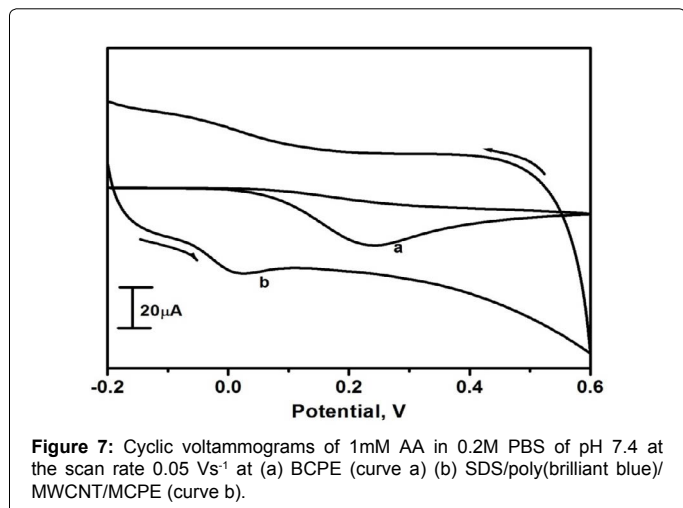


Figure 7: Cyclic voltammograms of 1mM AA in 0.2M PBS of pH 7.4 at the scan rate 0.05 Vs⁻¹ at (a) BCPE (curve a) (b) SDS/poly(brilliant blue)/MWCNT/MCPE (curve b).

Effect of UA concentration

The cyclic voltammograms were recorded for the oxidation of UA with varying concentration in 0.2M PBS of pH 7.4 at scan rate 0.05 Vs⁻¹. The cyclic voltammogram of different concentration of UA (1.65×10^{-3} M to 2.52×10^{-3} M) as shown in the Figure 12A which shows the increase in anodic peak current due to increase in the concentration of UA. The plot shown in the Figure 12B shows the linear relationship between I_{pa} and the concentration of UA with the linear regression equation $I_{pa}(0.1 \text{ mA}) = 0.5045(C_0 \cdot 10^{-3} \text{ M/L}) + 0.4297$, $r^2 = 0.9945$. The detection limit on the lower concentration range for UA was 4.36×10^{-6} M for the SDS/poly(brilliant blue)/MWCNT/MCPE and limit of quantification was 1.10×10^{-5} M.

Simultaneous electroanalysis of DA, AA and UA

In mammalian brain AA and UA were present along with DA. Since the oxidation potential of both AA and UA were nearly same as that of DA results in a broad and overlapped voltammetric response at BCPE. Figure 13 shows CV recorded for 0.5×10^{-4} M DA, 1.0×10^{-3} M AA and 0.5×10^{-3} M UA in 0.2M PBS of pH 7.4 at scan rate 0.05 Vs⁻¹. At BCPE (curve a) the oxidative separation of all the three analytes was impossible due to fouling of the surface and gives poor voltammetric response. However, in the same condition the SDS/poly(brilliant blue)/MWCNT/MCPE (curve b) taken this task and separated all three analytes into well distinguished voltammetric signals, the oxidation potential of AA, DA and UA were located at 0.012 V, 0.173 V and 0.299 V respectively. The peak to peak separation of DA-AA was 0.161 V and that of DA-UA was 0.126 V. This result was sufficient to identify DA in presence of probable interference UA and AA at SDS/poly(brilliant blue)/MWCNT/MCPE.

Differential pulse voltammetry (DPV) was used for the determination of DA, AA and UA at SDS/poly(brilliant blue)/MWCNT/MCPE due to its higher current sensitivity and absence of background current. The simultaneous study was carried out in the potential range from -0.2 to 0.6 V versus SCE. The Figure 14(A) shows the simultaneous determination of 0.61×10^{-4} M DA, 0.51×10^{-3} M AA, 0.21×10^{-3} M UA in 0.2M PBS of pH 7.4 with well separated voltammetric signals corresponding to their oxidation at SDS/poly(brilliant blue)/MWCNT/MCPE. The oxidation potential of DA, AA and UA was located at 0.126 V, -0.048 V and 0.234 V respectively. The peak to peak separation between DA-AA was 0.174 V and that of DA-UA was 0.108 V.

Interference study

The interference study was carried out in the mixture of samples in an electrochemical cell containing DA, AA and UA. In their mixtures DPV was performed at the SDS/poly(brilliant blue)/MWCNT/MCPE when the concentration of one species is changed, whereas the concentration of the other two species was maintained constant. From the Figure 14(B) it can be noticed that the peak current of DA was increased from 0.421×10^{-4} M to 1.02×10^{-4} M by constant keeping of the AA and UA concentration to 0.5×10^{-3} M.

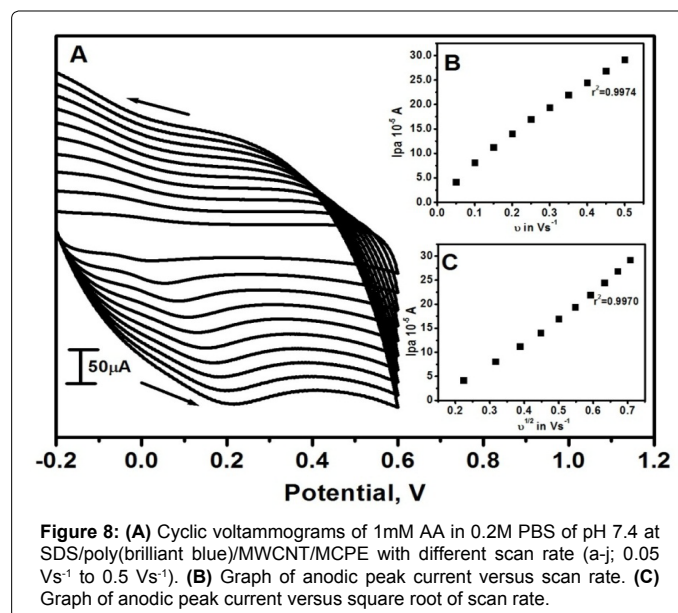


Figure 8: (A) Cyclic voltammograms of 1mM AA in 0.2M PBS of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE with different scan rate (a-j; 0.05 Vs⁻¹ to 0.5 Vs⁻¹). (B) Graph of anodic peak current versus scan rate. (C) Graph of anodic peak current versus square root of scan rate.

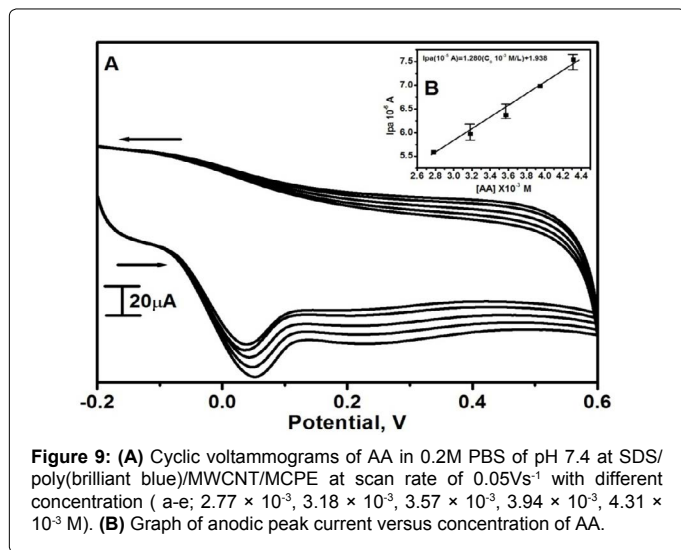


Figure 9: (A) Cyclic voltammograms of AA in 0.2M PBS of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE at scan rate of 0.05Vs⁻¹ with different concentration (a-e; 2.77×10^{-3} , 3.18×10^{-3} , 3.57×10^{-3} , 3.94×10^{-3} , 4.31×10^{-3} M). (B) Graph of anodic peak current versus concentration of AA.

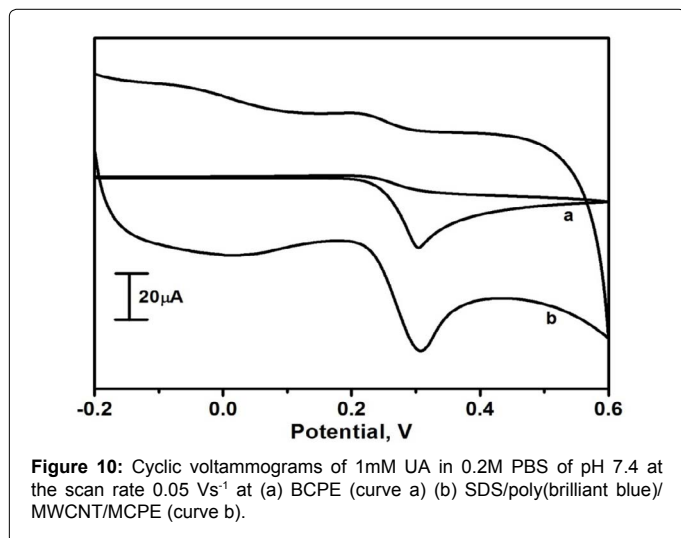


Figure 10: Cyclic voltammograms of 1mM UA in 0.2M PBS of pH 7.4 at the scan rate 0.05 Vs⁻¹ at (a) BCPE (curve a) (b) SDS/poly(brilliant blue)/MWCNT/MCPE (curve b).

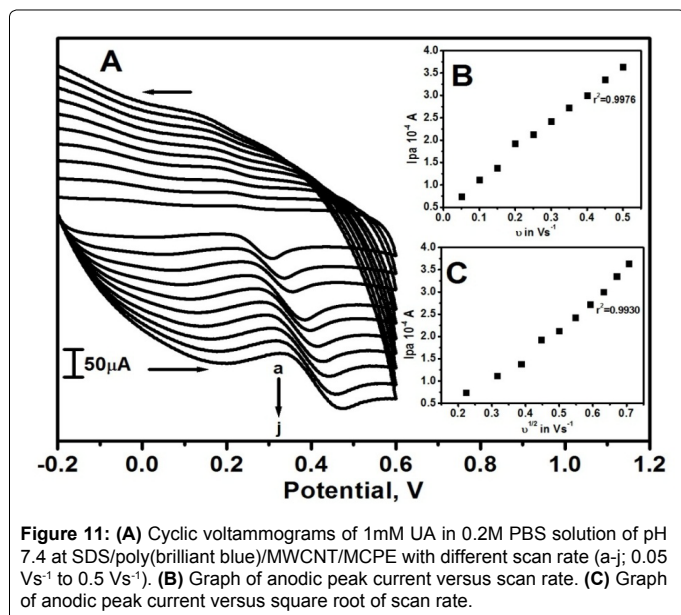


Figure 11: (A) Cyclic voltammograms of 1mM UA in 0.2M PBS solution of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE with different scan rate (a-j; 0.05 Vs⁻¹ to 0.5 Vs⁻¹). (B) Graph of anodic peak current versus scan rate. (C) Graph of anodic peak current versus square root of scan rate.

³M and 0.2×10^{-3} M respectively. From the Figure 14(C) and Figure 14(D) it is seen that by keeping the concentration of other two analytes constant the anodic peak current of AA or UA increased upto a certain concentration range.

Conclusion

A simple and convenient method for the modification of the BCPE was proposed. The prepared SDS/poly(brilliant blue)/MWCNT/MCPE shows excellent sensitivity, reproducibility, antifouling property and electrocatalytic activity towards the electrochemical oxidation of DA in the mixture of solutions contains large excess of AA and UA at physiological pH of 7.4 by using both CV and DPV techniques. Because of the distinguished voltammetric response obtained at SDS/poly(brilliant blue)/MWCNT/MCPE the peak to peak separation of DA-AA was 0.161 V and that of DA-UA was 0.126 V by CV technique. This result was more enough for the electroanalysis of DA in presence of common interferences AA and UA. The proposed method can be used for other neurotransmitters. The modified electrode acts as a very good sensor for the detection of dopamine.

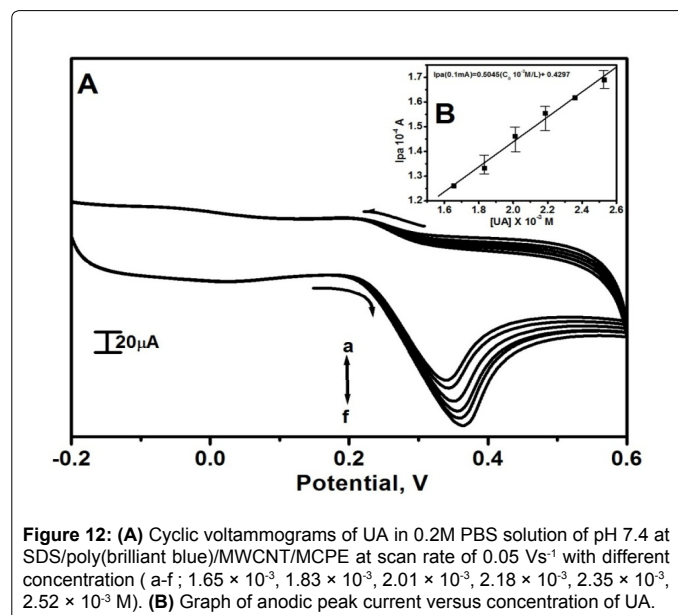


Figure 12: (A) Cyclic voltammograms of UA in 0.2M PBS solution of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE at scan rate of 0.05 Vs⁻¹ with different concentration (a-f; 1.65×10^{-3} , 1.83×10^{-3} , 2.01×10^{-3} , 2.18×10^{-3} , 2.35×10^{-3} , 2.52×10^{-3} M). (B) Graph of anodic peak current versus concentration of UA.

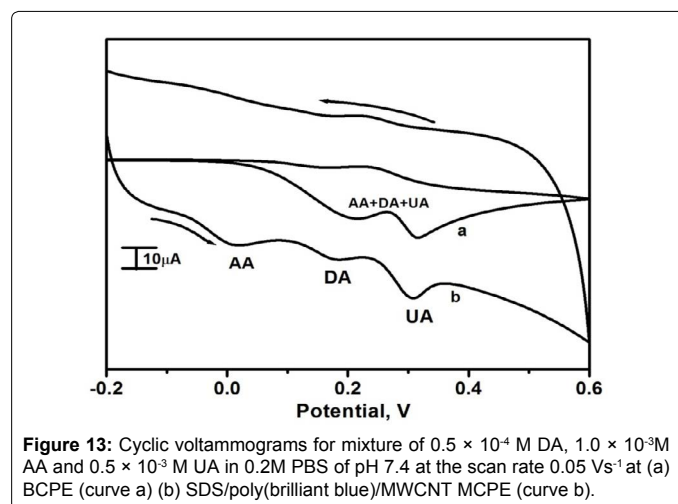


Figure 13: Cyclic voltammograms for mixture of 0.5×10^{-4} M DA, 1.0×10^{-3} M AA and 0.5×10^{-3} M UA in 0.2M PBS of pH 7.4 at the scan rate 0.05 Vs⁻¹ at (a) BCPE (curve a) (b) SDS/poly(brilliant blue)/MWCNT MCPE (curve b).

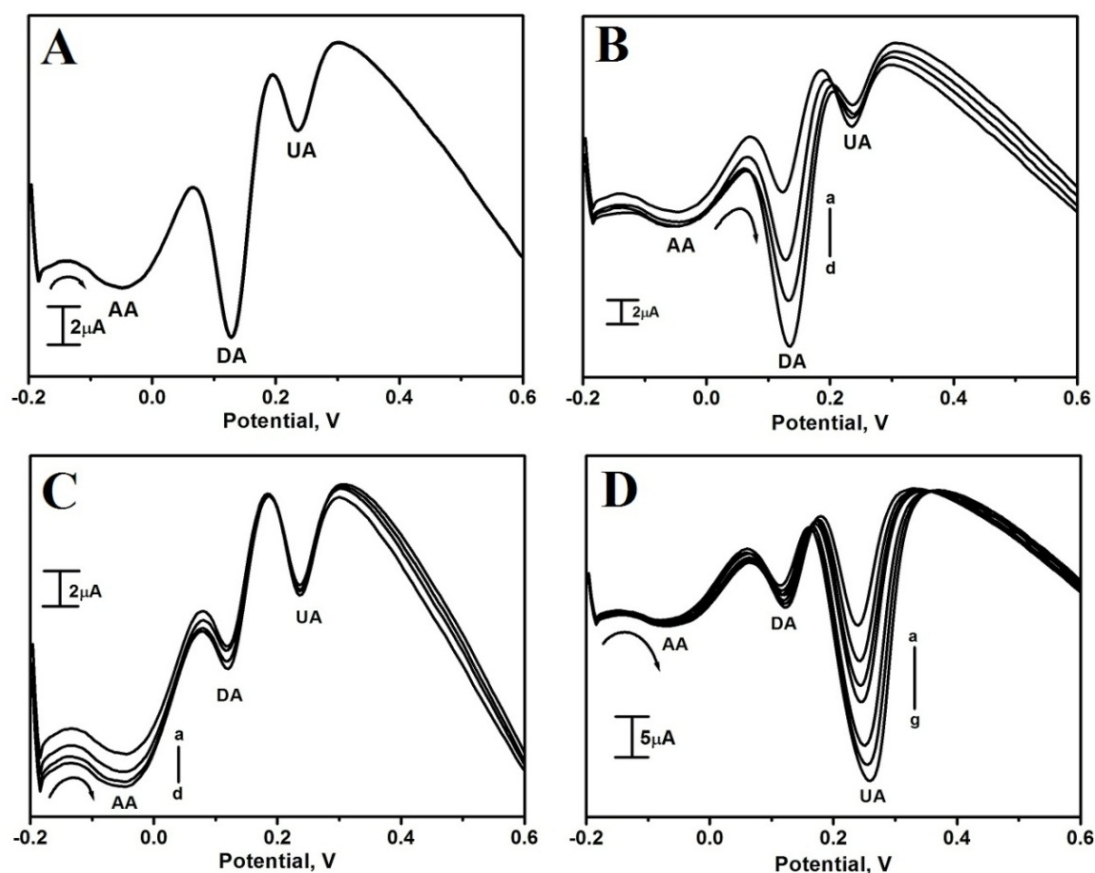


Figure 14: (A) Differential pulse voltammogram obtained for 0.61×10^{-4} M DA, 0.51×10^{-3} M AA and 0.21×10^{-3} M UA in 0.2M PBS solution of pH 7.4 at SDS/poly(brilliant blue)/MWCNT/MCPE (B) Differential pulse voltammograms of (a) 0.421×10^{-4} M (b) 0.627×10^{-4} M (c) 0.823×10^{-4} M (d) 1.02×10^{-4} M DA in 0.2M PBS of pH 7.4 in presence of 0.5×10^{-3} M AA and 0.2×10^{-3} M UA. (C) Differential pulse voltammograms of (a) 0.529×10^{-3} M (b) 0.735×10^{-3} M (c) 0.937×10^{-3} M (d) 1.136×10^{-3} M AA in 0.2M PBS of pH 7.4 in presence of 0.3×10^{-4} M DA and 0.2×10^{-3} M UA (D) Differential pulse voltammograms of (a) 0.630×10^{-3} M (b) 0.833×10^{-3} M (c) 1.033×10^{-3} M (d) 1.229×10^{-3} M (e) 1.422×10^{-3} M (f) 1.612×10^{-3} M (g) 1.800×10^{-3} M UA in 0.2M PBS of pH 7.4 in presence of 0.3×10^{-4} M DA and 0.5×10^{-3} M AA at SDS/poly(brilliant blue)/MWCNT/MCPE.

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