Full Paper

Electrochemical Studies of Dopamine Using Titanium Dioxide Nanoparticle Modified Carbon Paste Electrode

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Abstract- Titanium Dioxide (TiO_2) nanoparticles were synthesized by the precipitation method. The obtained products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). As synthesized TiO_2 nanoparticles were used for the modification of carbon paste electrode (MCPE). Electrochemical determination of dopamine was carried out using phosphate buffer solution at pH 7.2. MCPE exhibit excellent electrochemical sensor for dopamine having high sensitivity and reproducibility. Potentially interfering compounds did not interfere for determination of DA at a surface of propose sensor in the optimum condition. The proposed sensor was successfully applied for the determination of DA in real samples such as DA in injections.

1. INTRODUCTION

There has been considerable interest in developing methods to measure secretion neurotransmitters. Electrochemical techniques have been proven to be significantly

advantageous to biosciences [1]. Dopamine (DA), as a simple organic chemical in the catecholamine family, is a monoamine neurotransmitter that plays a critical role in the function of the central nervous, hormonal, and cardiovascular systems. The DA biochemistry is believed to be related to several diseases such as Schizophrenia, Parkinsonism and Huntington [2]. The studies on the electrochemistry of DA are helpful for us to well understand its physiological functions and action mechanism in bodies [3]. The development of anorexia nervosa and bulimia nervosa has also been associated with malfunctioning dopaminergic activities. Hence, the development of electrochemical sensors for the determination of neurotransmitters has received great attention in the past [4-6]. Update, many methods such as spectroscopy, chromatography and electrochemistry [7] were introduced to determine DA. Since DA is an oxidizable compound, it can be easily detectable by electrochemistry methods based on anodic oxidation [8]. Carbon paste electrode was very much attracted towards the determination of biologically active molecules because of the easy preparation of modified electrode, renewability, low background current, and fast response [9-11].

The modification can be done by adding different types of modifiers [12-14]. One of the modifiers used for this work, the determination of electrochemical response of DA is metal oxide nanoparticles [15,16]. The oxide nanoparticles synthesized by several methods appears more and more useful because these nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts [17].

Titanium dioxide (TiO_2) nanoparticles are one of the most capable materials, which is of potential interest as a sensor electrode in electrochemistry [18]. There are several factors in determining important properties in the performance of TiO_2 for applications such as particle size, crystallinity and the morphology. There are many methods to synthesise TiO_2, such as the sonochemical method, solvothermal-assisted heat treatment method and electrochemical [19].

Herein, this work includes the preparation of TiO_2 using a simple, cost effective and eco-friendly co-precipitation method. The prepared TiO_2 is characterized by powder XRD and SEM. The TiO_2 modifed electrode shows an increase in sensitivity towards DA. The MCPE was used for an electrochemical investigation of the low concentration of DA in a phosphate buffer at pH 7.2. Thus the present study also presents an excellent method for the selective and sensitive detection of DA.

2. EXPERIMENTAL PART

2.1. Reagents and stock solution

All the reagents were of analytical grade and used as received without further purification. The reactant, Titanium iso-propoxide, ($C_{12}H_{28}O_4Ti$), Dopamine hydrochloride

(DA), disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen orthophosphate (NaH_2PO_4), Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$), silicone oil, graphite powder (mm particle size) were purchased from SD Fine chemicals, Mumbai, India. The stock solution of dopamine (25 mM) was prepared in 0.1 M perchloric acid, phosphate buffer of pH 7.2 prepared in double distilled water.

2.2. Preparation of TiO$_2$ nanoparticles

In a typical route, TiO$_2$ nanoparticles were prepared by adding 100 ml of basic precipitant 0.4 M NaOH solution into a 100 ml of 0.2 M titanium iso-propoxide under constant stirring. About 50 ml/L triton X-100 was added as capping agent which inhibits the anamolous growth of metal hydroxide crystals during the course of precipitation. Then the resulting solution was kept at room temperature for about 3 hrs under constant stirring. The obtained slurry was centrifuged at 1000 rpm and precipitate was washed several times with water and alcohol, dried in an oven for a period of 1-2 hrs at 60^0 C. Then powder is further heated in silica crucible for a period of 6 hrs at 600^0 C. Finally, the resulting nanoparticles were stored in air-tight container for further sensor applications.

2.3. Instruments

The cyclic voltammetric (CV) measurements were performed on a Model 660C (CH Instruments). Electrochemical experiments were carried out in a three electrode cell system, which contained a bare carbon paste electrode (BCPE), CPE/ TiO$_2$, as the working electrode, an aqueous saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the auxiliary electrode. XRD patterns were obtained on a Bruker D$_2$ Phaser XRD system. SEM was studied using scanning electron microscope (JEOL JSM 840).

2.4. Preparation of bare carbon paste electrode (BCPE) and modified carbon paste electrode (MCPE)

The bare carbon paste electrode was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the cavity of CPE of 3 mm in diameter and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube. MCPE was prepared by adding 2, 4 and 6 mg TiO$_2$ nanoparticles to above mentioned graphite powder and silicone oil mixture.

## 3. RESULTS AND DISCUSSION

3.1. Characterization of TiO$_2$

The XRD patterns of the nanoparticles obtained by precipitation route are shown in Fig. 1. Synthesized nanoparticles showed crystalline nature with 2θ peaks lying at $2\theta=25.25^{\circ}$ (101), $2\theta=37.8^{\circ}$ (004), $2\theta=47.9^{\circ}$ (200), $2\theta=53.59^{\circ}$ (105) and $2\theta=62.36^{\circ}$ (204). All the peaks in the XRD patterns can be indexed as anatase phases of TiO_2 and the diffraction data were in good agreement with JCPDS files # 21-1272. Crystallite size was obtained by Debye-Scherrer's formula given by equation

$$D_P = \left(\frac{K\lambda}{\beta_{1/2} cos\theta} \right) \qquad (1)$$

where D is the crystal size and K is a constant equal to 0.89, λ is the X-ray wave length equal to 1.54 A$^{\circ}$, $\beta_{1/2}$ is the full width at half maximum and θ is the half diffraction angle. Table.1 shows that the average crystallite size obtained using this formula is 6.23 nm.
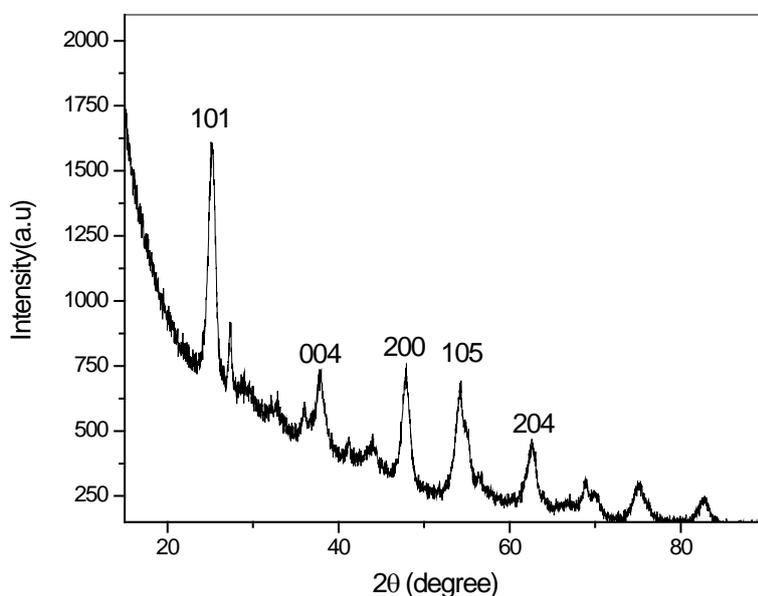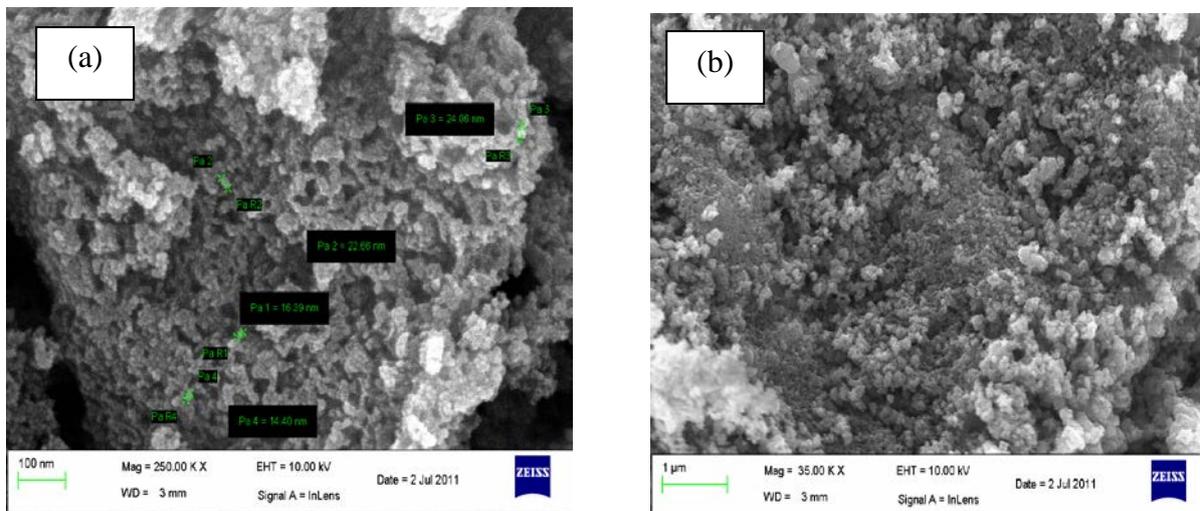

Fig. 1. Typical XRD image of TiO_2 nanoparticles

Table 1. Parameters derived from XRD of TiO_2

Metal Oxide	2θ	h k l	Size	Structure
	25.25	(101)	4.6	
TiO_2	38.00	(004)	6.7	anatase
	48.00	(200)	7.4	

Fig. 2 shows the typical SEM images of TiO_2 nanoparticles. Single-phase primary particles, nearly of spherical shaped nanocrystallites can be clearly seen but it shows the interconnected ultrafine particles with nanosized dimensions forming agglomerates, all the

particles are irregular and some are spherical in nature. Sizes of the particles were also measured by SEM, the average particle size of TiO_2 was found to be 19 nm.

Fig. 2. Typical SEM images of TiO_2 at different magnifications

### 3.2. Effect of TiO₂ nanoparticles on MCPE for investigation of Dopamine

In order to optimize the amount of TiO_2/CPE different concentration of the TiO_2 nanoparticle in a CPE were used to determine the study of 5×10^{-5} M DA in a 0.2 M phosphate buffer (pH 7.2) at a scan rate of 50 mV s^{-1}. The 2 mg TiO_2/CPE response to the maximum current as compared with the 4 and 6 mg of TiO_2 nanoparticles as shown in Fig. 3 and this optimized concentration is maintained during further investigation.
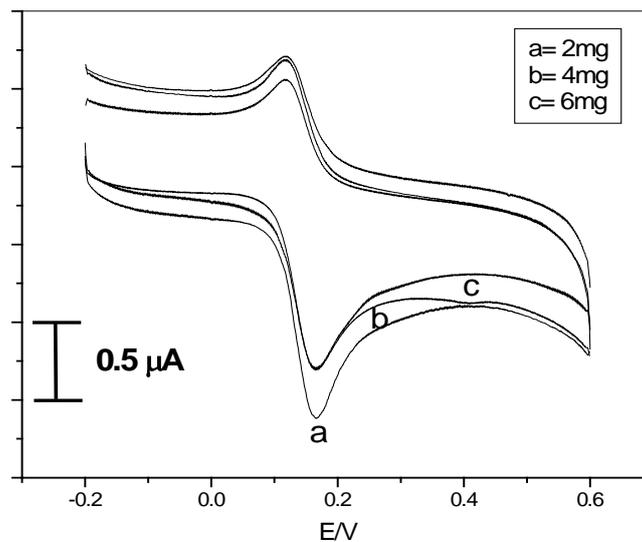
Fig. 3. Cyclic voltmmogram of 5×10^{-5} M DA at different concentration of TiO_2 nanoparticles in MCPE

### 3.3. Electrochemical response of dopamine at the BCPE and MCPE

The electrochemical responses of 5×10^{-5} M DA and its voltammogramm was recorded in the potential range of -0.2 to 0.6 *vs*. SCE in the 0.2 M phosphate buffer solution of pH 7.2 at the BCPE and the MCPE prepared with TiO_2 nanoparticles were measured at a scan rate of 50 mV s^{-1} by CV technique. The corresponding peak potential differences [$\Delta Ep=0.0521$ V] and [$\Delta Ep=0.0487$ V] for the BCPE (solid line) and the TiO_2 nanoparticles MCPE (dotted line) are shown in Fig. 4. At the BCPE the anodic peak potential (Epa) 0.1677 V and the cathodic peak potential (Epc) 0.1156 v. DA peak currents significantly increased at the MCPE with the anodic peak potential 0.1660 V and the corresponding cathodic peak potential is 0.1173 V respectively. The result indicates TiO_2 nanoparticles exhibit good electrocatalytic activity than BCPE and TiO_2 nanoparticles exhibit enhanced current response with slight reduction of over potential than the BCPE. This shows that the MCPE exhibit good electrocatalytic activity.
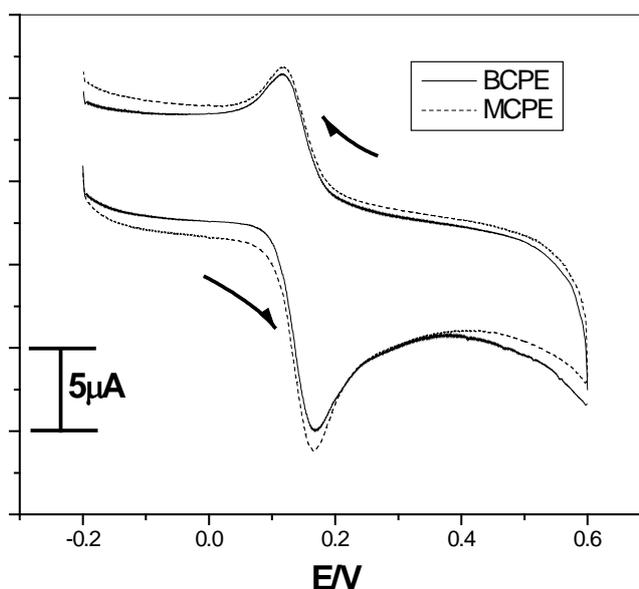

Fig. 4. Cyclic voltmmogram in 0.2 M phosphate buffer solution, pH 7.2 at bare CPE and MCPE of 5×10^{-5} M DA with scan rate 50 mV s^{-1}

3.4. Effect of scan rate on the peak current

The effect of scan rate for DA in phosphate buffer solution at pH 7.2 was studied by CV at MCPE. This was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport or not. The Fig. 5 show an increase in the redox peak current at a scan rate of 0.01–0.800 V s^{-1} for MCPE. The graph obtained exhibited good linearity between the scan rate (v) and the redox peak current (Fig. 6) for the MCPE with correlation coefficients of $R^2=0.99$, which indicates that the electron transfer reaction was diffusion-controlled process.
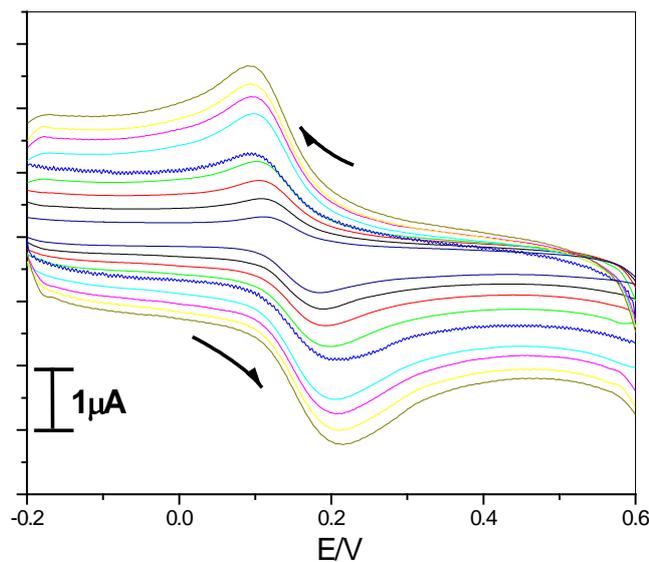
Fig. 5. Cyclic voltmmogram of MCPE in 0.2 M phosphate buffer solution containing 5×10^{-5} M DA at different scan rates (0.01 to 0.8 V s^{-1})
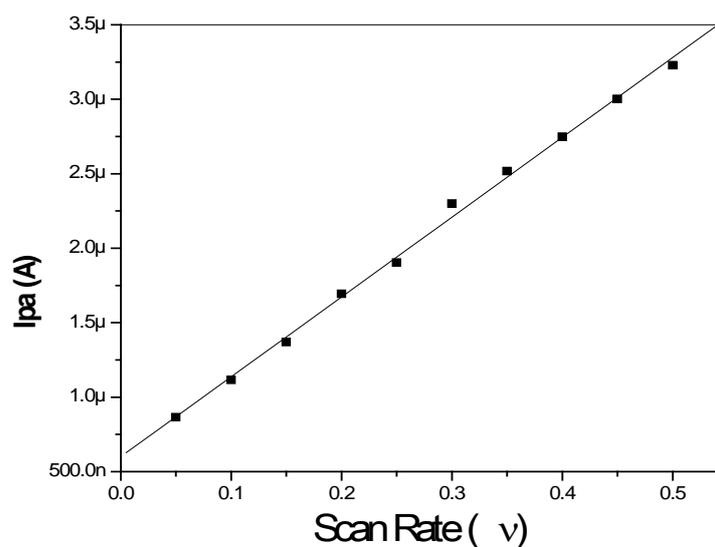
Fig. 6. Graph shows the linear relationship between the anodic peak current and scan rate

3.5. The effect of the concentration of Dopamine

According to electrochemical response, the redox peak current increased with increasing the concentration of analyte. By increasing the concentration of DA (1 mM to 8 mM), both Ipa and Ipc goes on increasing are shown in Fig. 7. At the same time, high surface area of the TiO$_2$ nanoparticles in MCPE improved the electrode contact area of DA.
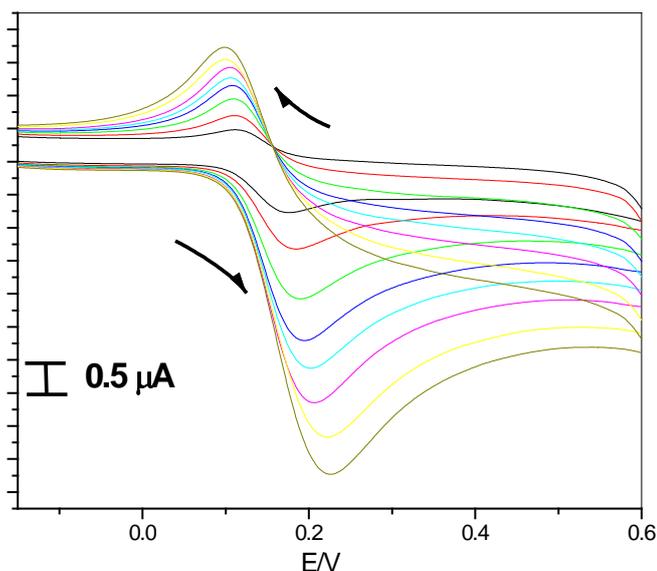
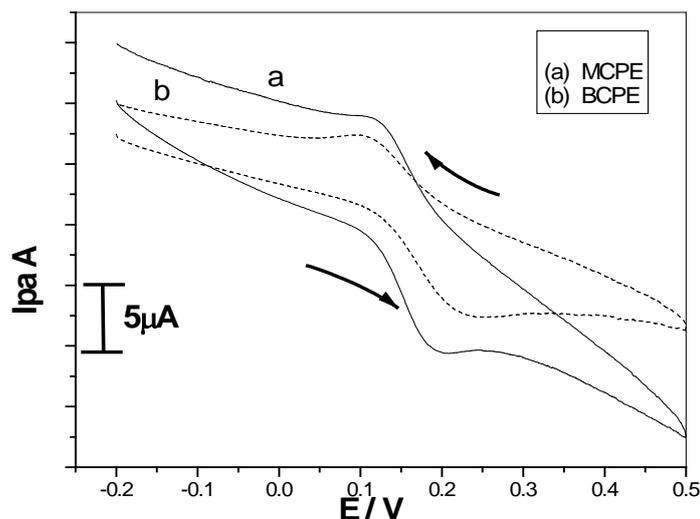**Fig. 7.** Plot of different concentration of DA (1 mM to 8 mM)

3.6. Real sample analysis

3.6.1 .Determination of DA in dopamine hydrochloride injections

Five milliliters of dopamine hydrochloride injection solution (40 mg/mL) was diluted to 25 mL with double distilled water. Then 0.2 mL of this diluted solution was injected into 10 mL volumetric flask and made up to the volume with the 0.2 M phosphate buffer solution of pH 7.2 at the BCPE and the MCPE prepared with TiO_2 nanoparticles were measured at a scan rate of 50 mV s^{-1} by CV technique. In Fig. 8 cyclic voltammogramms for BCPE (dotted line) shows high peak potential differences [$\Delta Ep=0.1553$ V] compared to TiO_2 nanoparticles MCPE, shows low peak potential differences [$\Delta Ep=0.0932$ V]. The results are satisfactory, showing that the modified electrode proposed efficiently used for the determination of DA in injections. The detection limit obtained for the determination DA with the sensor is comparable to or better than those obtained with several other modified electrodes using DPV (Table 2).

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

Electrode	Detection limit (μM)	Techniques	Reference
Banana/MWCNTs/MCPE	2.09	DPV	[20]
CCE/ferrocene carboxylic acid	0.45	SWV	[21]
Polygycine/CPE	0.1	CV	[22]
MEs/SAM-Au electrode	1.1	CV	[23]
LDH/CILE	5	DPV	[24]
TiO_2/ MCPE	2	DPV	Present work

Fig. 8. Cyclic voltmmogram of bare CPE and MCPE in real samples (40 mg/mL DA in injection) at 0.2 M phosphate buffer solution, pH 7.2 with scan rate 50 mV s^{-1}

3.7. Interference study

The influence of various foreign species as potentially interfering compounds with the determination of DA was investigated under the optimum conditions 40 mg/mL at the 0.2 M phosphate buffer solution of pH 7.2. Tolerance limit was defined as the maximum concentration of interfering species that caused an approximate relative error of ±5% for the determination of DA. The results are shown in Table 3. These results demonstrate that the TiO$_2$ nanoparticles MCPE results confirm has a good selectivity for DA analysis in the presence of other interfering substance.

Table 3. Interference study for the determination of DA under the optimized conditions

Selected compounds for interference study	Tolerant limits ($W_{Substance}/W_{DA}$)
Na$^+$, K$^+$	330-630

4. CONCLUSIONS

In the present work, the MCPE was acting as a good sensor for the detection of DA. The MCPE exhibits a higher electrode surface area, a higher electron-transfer rate constant and a lower detection limit. The modified electrode has been able to show high sensitivity for voltammetric detection of DA. With its low cost, high sensitivity and very easy preparation of the modified electrode and the reproducibility of the voltammetric response make the prepared modified system very useful in the construction of simple devices for the determination of DA in clinical and pharmaceutical preparations.

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