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Synthesis and Characterization of ZnO Nanorods for Voltammetric Detection of Dopamine, Folic Acid and Paracetamol

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Abstract: In present global scenario the ability to detect and quantify specific biologically active molecules plays an increasingly important role in our safety and wellbeing. In this regard, the present work involves the synthesis of ZnO nanorods (ZnO) *via* simple hydrothermal method and the nanopowder is used for modification carbon paste electrode (MCPE) and to study voltammetric detection of Dopamine (DA), Folic acid (FA) and paracetamol (PC). The synthesized ZnO nanorods were characterized by X-ray diffraction studies (XRD), Scanning electron microscopy (SEM) and Tunneling electron microscopy (TEM). In this study the ZnOs modified carbon paste electrode was

applied for the electrochemical determination of dopamine at pH 7.2 PBS solution with scan rate 50 mVs^{-1}. The voltammograms obtained during the oxidation studies revealed that ZnO nanorods exhibits better catalytic function towards the oxidation of Dopamine, Folic acid and Paracetamol. The overlapping voltammetric response of the biomolecules at the bare electrode gets resolved into well-defined voltammetric peaks with enhanced oxidation currents. The developed ZnOs /MCPE offered high catalytic activity in sensing the dopamine, paracetamol and Folic acid in the development of biosensors.

Keywords: Dopamine; Paracetamol; Zinc oxide nanoparticles; Modified Carbon Paste Electrode; Cyclic voltammetry.

INTRODUCTION

Recent research has demonstrated that Metal oxide nanomaterials have unique features like high sensitivity and great attention has been paid to the electrochemistry of nanomaterials modified electrodes[1,2]. The applications of the electrode surface with Zinc oxide nanomaterials are an attractive approach for enhancing the power and area of application of electrochemically modified electrodes[3,4]. Among the applications of chemically or electrochemically modified electrodes in electroanalysis offer several advantages and electrochemical biosensors[5]. In recent years, Zinc oxide nanomaterials (ZnO) got much importance because of its extensive important applications in many areas like nanomaterials-based sensors are optical biosensors magnetic and magnetic sensors[6-9].

Recently, different chemicals, physicochemical routines have been utilized to synthesis Zinc oxide and as an ecofriendly material, ZnO is promising biosensor offered high catalytic activity in sensing the Biomolecules[10-12]. In this way, building up a simple method to prepare Zinc oxide nanomaterials electrochemical biosensors is of great importance in the present scenario and hydrothermal method has great circumstances over different method reviewed in the literature[13]. Dopamine (DA) is one of the naturally occurring catechol amines in the mammalian central nervous system and DA functions as a important neurotransmitter in the amygdala, a phylogenetically older structure of the brain, which is thought to play a critical role in neuroendocrine functions[14].

Thus, a loss of Dopamine containing neurons may lead to neurological disorders such as Parkinson, attention deficit hyperactivity disorders (ADHD), DA cannot cross the blood-brain barrier and DA given as a drug does not directly affect the central nervous system[15]. Paracetamol (PC) or acetaminophen (N-acetyl-p-aminophenol or 4-acetamidophenol) is used to reduce pain including, neuralgia, backache, joint pain, toothache and a non-steroidal anti-inflammatory drug that finds widespread application for its strong analgesics action in pharmaceutical formulations[16]. Folic acid (FA) is B vitamin that helps build healthy cells as well as deficiency of FA is a common cause of anemia and many studies suggest that it is a potential agent for cancer prevention by free radical scavenging and antioxidant activity[17].

Herein, the ZnO nanorods were prepared by a hydrothermal method and then used to modify the surface of a carbon paste electrode (CPE). The electrochemical effect of Dopamine on this ZnO nanorods modified CPE (ZnO /CPE) was studied. It was shown that the current peak for the oxidation of Dopamine could be well resolved and is based on different electro-catalytic activities of the modified electrode toward these species; a sensitive and selective method to determine Dopamine was set up for routine analysis.

EXPERIMENTAL

All chemicals were obtained from Sigma Aldrich or Merck with highest grade available and used without further purification. All solutions were prepared using double distilled water. All experiments were carried out at room temperature.

2.1 Reagents and stock solutions: The reactant, Folic acid, triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$), sodium hydroxide, Dopamine hydrochloride (DA), 0.1 mol/L [$Zn(NO)_3.6H_2O$], disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen orthophosphate (NaH_2PO_4), 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 and Folic acid its stock solution was prepared by diluted NaOH aqueous solution prepared in double distilled water.

2.2 Preparation of Zinc oxide (ZnO): ZnO nanorods were synthesized via the hydrothermal method in the presence of Triton X-100. Experimental details are described as in a typical procedure, 20 ml of 0.2 mol/L NaOH solution were slowly added into a 20 ml of 0.1 mol/L [$Zn(NO)_3.6H_2O$] solution containing 0.004 mol/L of Triton X-100, with constant stirring. After vigorous stirring for 3 h, the mixture was autoclaved at 200 °C for 5 h. After the reaction system was naturally cooled to room temperature, the precipitates were separated from the solution and thoroughly washed several times with deionized water and absolute ethanol, and then dried in an oven at 50 °C for 8 h.

2.3 Instrumentation: A CHI 660D electrochemical work station (CH Instruments, Austin, USA) was used for the measurements of cyclic voltammeter. A conventional three electrode system was employed, which consists of a bare carbon paste electrode or modified CPE/ ZnO carbon paste as the working electrode; a saturated calomel electrode (SCE) as the reference electrode to measure cell potentials and a platinum wires an auxiliary electrode to measure current. XRD patterns were obtained on a Bruker D_2Phaser 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, 6, 10 and 8 mg ZnO nanorods to above mentioned graphite powder and silicone oil mixture.

3. RESULT AND DISCUSSION

3.1 Characterization of ZnO nanoparticles: The crystal structure of as-grown ZnO nanorods was investigated using XRD **Fig.1.** All the diffraction peaks in the patterns are exactly indexed as hexagonal wurtzite structures which are in accordance with the values in the standard card (JCPDS 80-0075). The narrower shaped peaks of the samples indicate the higher crystalline and lower surface effects. The lattice parameters and average particle size of the synthesized particles 2θ(deg) 34.40, h k l (002), Size(nm) 21.9.

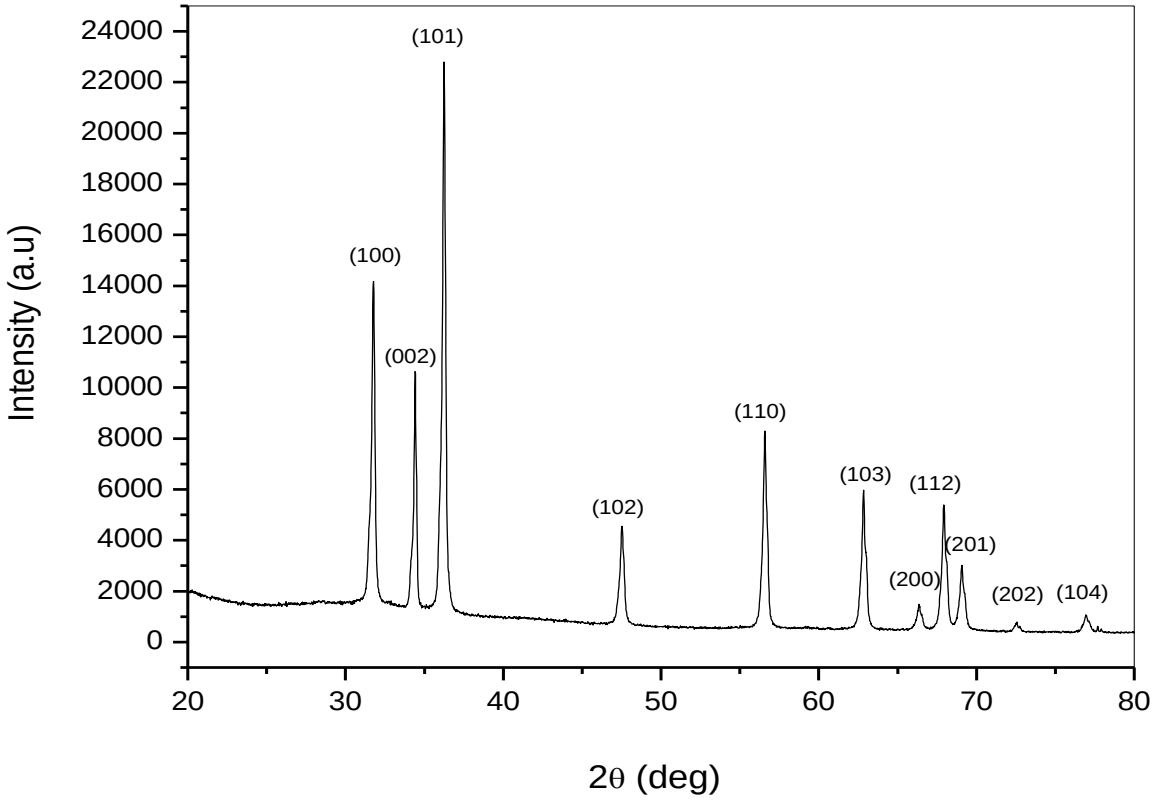

Fig.1. XRD pattern of ZnO nanoparticles.

Fig.2 (a) and (b) shows the typical field emission SEM images of ZnO nanorods grown on nanostructured substrate by the hydrothermal method. It is clear from the images that the straight nanorods can be grown on a substrate at a very high percentage and can highly dispersed in the space without any aggregation are aligned[18]. In addition, their dimensions are very much identical and several nanorods are slanted or tipped over.

TEM image of nanorods shows that the typical diameters and length-to-diameter ratios and to further investigate the microstructure of the synthesized ZnO. Notably, individual nanorod has one hemispherical end and another flat ending.

It revealed the formation of nanorods with hexagonal crystal structure as shown in **Fig.3.** The diffraction pattern of a selected area (SAED) is shown in the inset, confirming their high crystallinity, and that are growing along the 001 plane, which is a common fast growth direction of ZnO, which is similar to the previous reports on the single crystal ZnO whiskers[19].

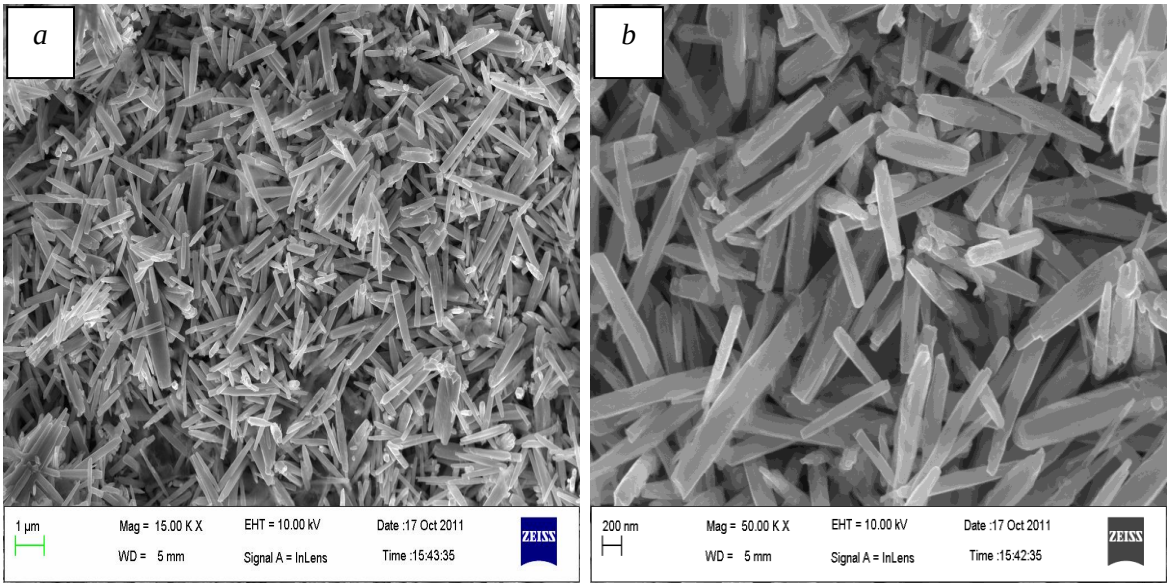

Fig.2. SEM micrographs of ZnO nanoparticles at different magnifications.

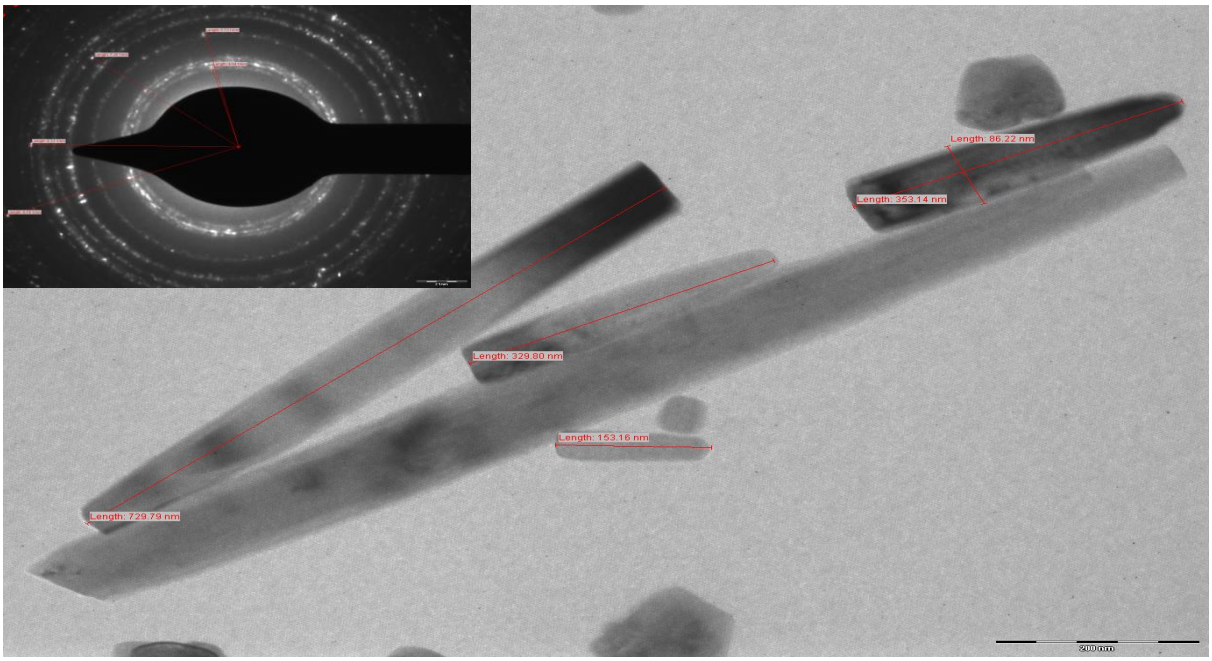

Fig.3. TEM micrograph of ZnO; the inset figure shows the SAED patterns.

3.2. Effect of ZnO nanoparticles on MCPE for investigation of DA, PC and FA: In order to optimize the amount of ZnO /CPE different concentration of the ZnO nanoparticles CPE were used to determine the study of 5×10^{-5} M DA in a 0.2M phosphate buffer (pH 7.2) at a scan rate of 50 mV s^{-1}. The 8 mg ZnO/CPE response to the maximum current as compared with the 2, 4, 6 and 10 mg of ZnO

nanoparticles as shown in **Fig. 4** and this optimized concentration is maintained during further investigation.

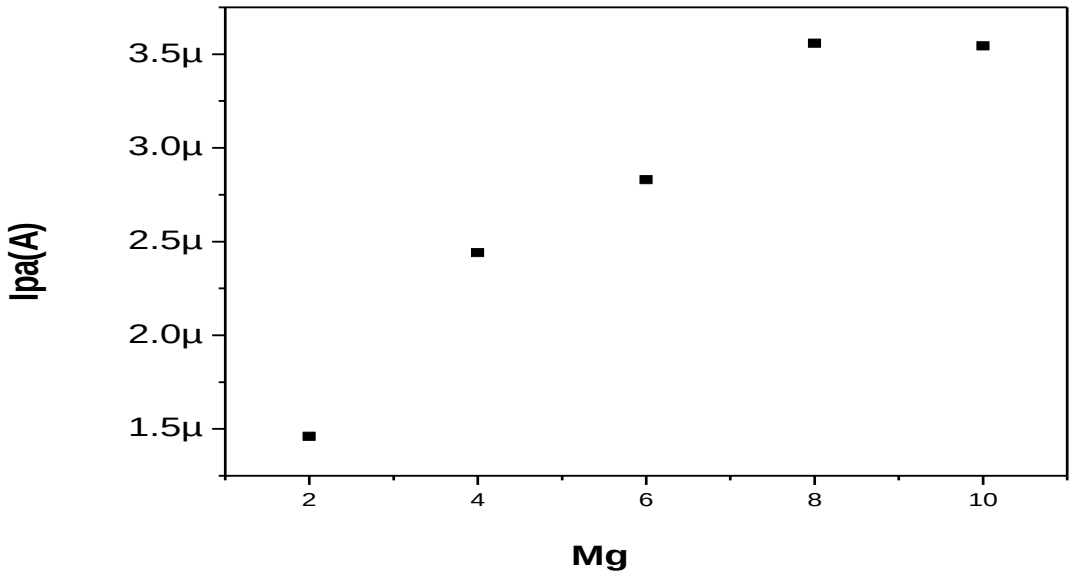

Fig.4. Graph of current versus Different concentration of ZnO nanoparticles /MCPE in 0.2 M phosphate buffer solution containing 5×10^{-5}M DA.

3.3. Electrochemical response of DA, PC and FA at BCPE and ZnO/MCPE.: The electrochemical responses of 5×10^{-5} M DA, 1.0 $\times10^{-6}$ M PC and 5×10^{-5}M FA its voltammogram 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 ZnO nanoparticles were measured at a scan rate of 50 mV s^{-1} by CV technique. The corresponding peak potential differences [ΔEp=0.0816 V] for DA at the ZnO nanoparticles MCPE are shown in **Fig. 5.** At the BCPE the anodic peak potential (Epa) 0.1104 V and the DA peak currents significantly increased at the MCPE with the anodic peak potential 0.1285 V respectively. The oxidation peak potential (Epa) of PC at BCPE and ZnO nanoparticles /MCPE were observed at 0.3257 V and the corresponding cathodic peak potential is 0.1895 V respectively are shown in **Fig. 6.** The cyclic voltammograms obtained for FA at the MCPE the cyclic voltammogram of **FA (Fig. 7)** shows an anodic peak potential 0.7099 V and at the BCPE the anodic peak potential (Epa) 0.6700 V. The result indicates ZnO nanoparticles exhibit good electrocatalytic activity than BCPE and ZnO nanoparticles exhibit enhanced current response with slight reduction of over potential than the BCPE. This shows that the ZnO /MCPE exhibit good electrocatalytic properties and the outcome of the study specifies the better redox kinetics at ZnO Modified carbon past electrode.

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 ZnO 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. 8** show with the increase in the redox peak current at a scan rate from 0.005–0.250 V s^{-1} for ZnO nanoparticles MCPE and the observations was made to investigate the kinetics of the modified

electrode reaction. The graph obtained exhibited good linearity between the scan rate (v) and the redox peak current **(Fig. 9)** for the ZnO nanoparticles MCPE with correlation coefficients of R^2 = 0.96122, which indicates that the electron transfer reaction was adsorption-controlled process.

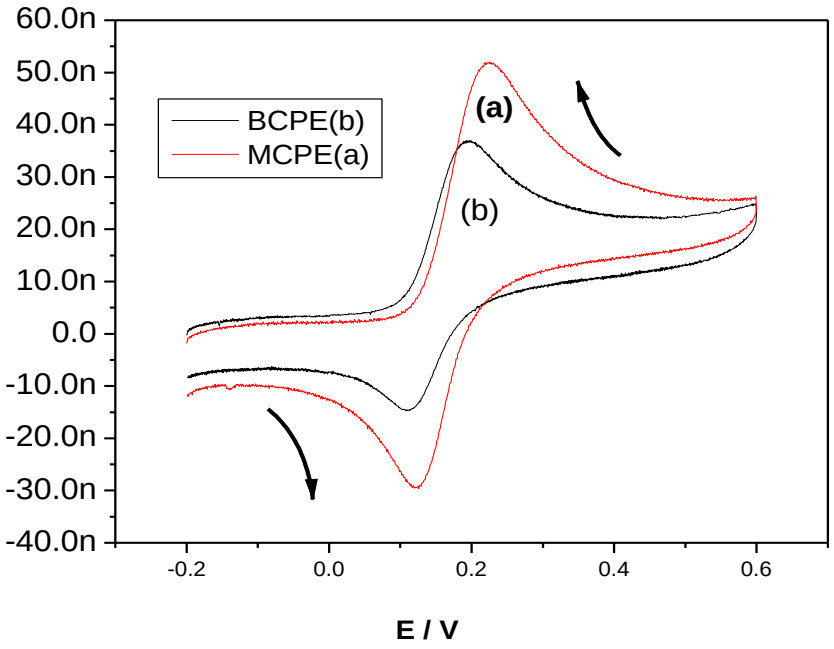

Fig. 5. Cyclic voltmmogram of 1.0 ×10^{-6} M PC in 0.2 M phosphat buffer solution at pH 7.2 using bare CPE and ZnO/MCPE at scan rate 50 mV s^{-1}.

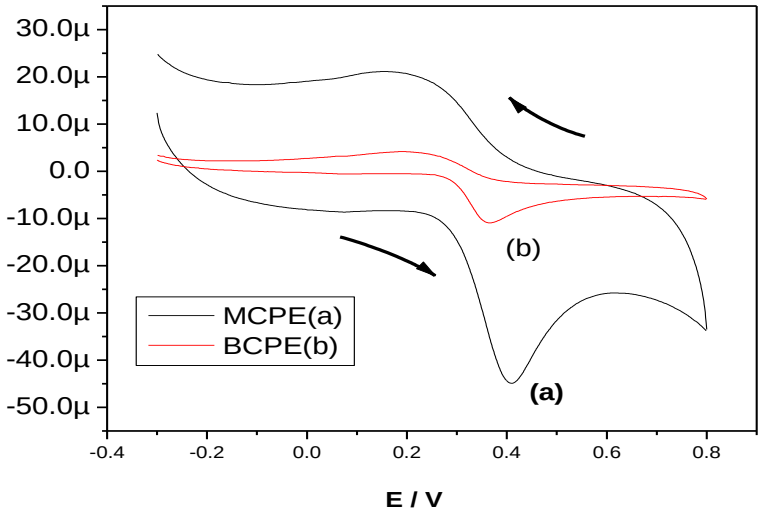

Fig. 6. Cyclic voltmmogram of 5×10^{-5} M FA in 0.2 M phosphate buffer solution using ZnO /MCPE at different scan rates.

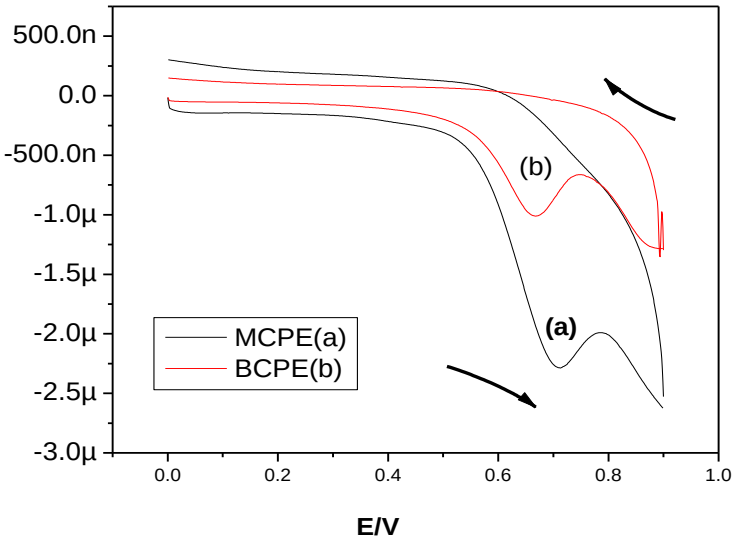

Fig.7. Cyclic voltmmogram in 0.2 M phosphate buffer solution, pH 7.2 at bare CPE and MCPE of 5×10^{-5}M DA with scan rate 50 mV s^{-1}.

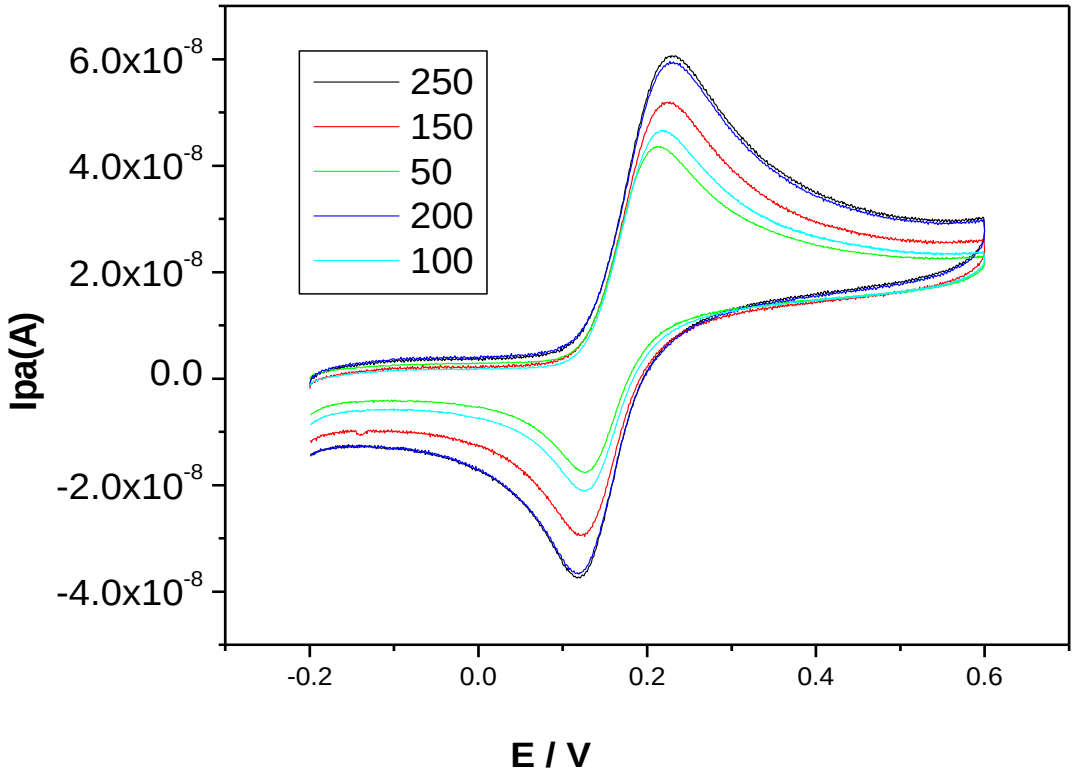

Fig.8. Cyclic voltmmogram of MCPE in 0.2 M phosphate buffer solution containing 5×10^{-5} M DA at different scan rates (0.005 to 0.25 V s^{-1}).

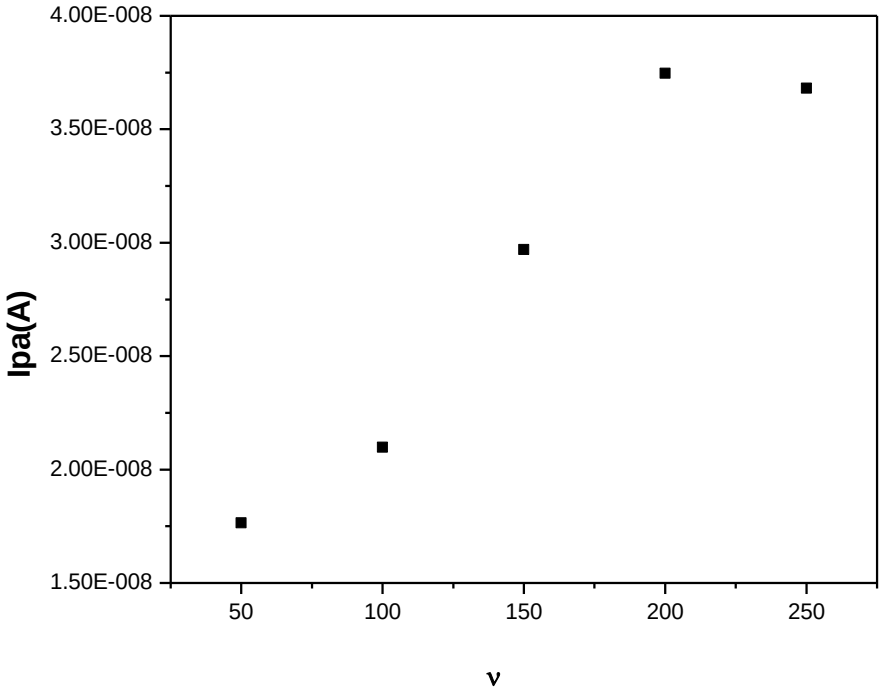

Fig. 9. Graph shows the linear relationship between the anodic peak current and scan rate.

3.6. Real sample analysis and determination of DA in dopamine hydrochloride injections: Five milliliters of dopamine hydrochloride injection solution (40mg/mL) was diluted to 25 mL with double distilled water. Then 0.2 mL of this diluted solution was taken into 10 mL volumetric flask and made up to the volume with the 0.2M phosphate buffer solution of pH 7.2 at the BCPE and the MCPE prepared with ZnO nanoparticles were measured at a scan rate of 50 mV s^{-1} by CV technique.

In **Fig. 10** cyclic voltammogramms for BCPE shows high peak potential differences [ΔEp=0.1472 V] compared to ZnO nanoparticles MCPE, shows low peak potential differences [ΔEp=0.0954 V]. The results are satisfactory; showing that the modified electrode proposed efficiently used for the determination of DA in injections and the projected ZnO based MCPE retained its efficiency for the determination of DA in dopamine hydrochloride injection sample with recovery in the range in the range from 97.5-99.8%.

3.5 Interference Study: The selectivity of the composite sensor was investigated by 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 0.2M 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. After the experiments, we found that no significant interference for the detection of DA was observed from the selected compounds and the results are shown in **Table 1.** Electrochemical response as the peaks remains unchanged after successive 20 cyclic voltammetric scans, confirms ZnO /MCPE has good storage stability and they retained their initial activity for more than one month with a mean loss of its initial activity of about 10–25% was observed.

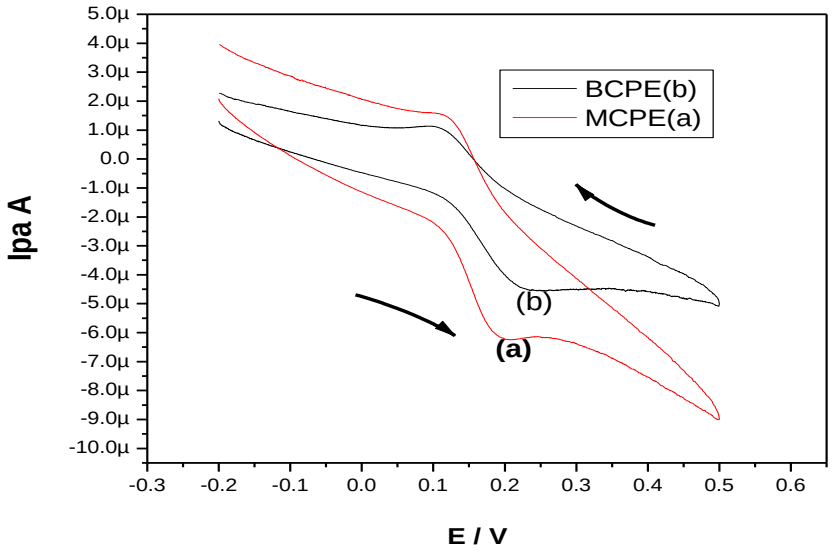

Fig. 10: Cyclic voltmmogram of bare CPE and MCPE in real samples (40 mg/mL DA in injection) at 0.2 M phosphate buffer solution, pH 7.2 with scan rate 50 mV s^{-1}.

Table 1: Interference study for the determination of 40mg/mL DA in pH 7.2 at the ZnO/MCPE.

Selected species for interference study	Tolerant limits ($C_{Species}/C_{DA}$)
Na^+, K^+	300-600
Ascorbic acid, uric acid	50-100

4. CONCLUSION

In the present paper, synthesized ZnO nanoparticles MCPE improved the sensitivity of electrode and acting as a good electrochemical sensor for the detection of Biomolecules. Cyclic voltammetry measurements revealed a reasonably fast electron transfer and a good stability of the electrode in phosphate buffer solution. With its low cost, high selectivity, regeneration of the electrode surface and the good reproducibility of the voltammetric response make the prepared modified system very useful in the construction of simple devices in the medicine field for the diagnosis of DA, PC and FA deficiency. It is expected that its good electro catalytic behavior the ZnO nanoparticles MCPE application in the development of biosensors and Practical utility recommends that the ZnO modified carbon paste electrode is potent promising tool for the determination of other drug. This method can also be applied for other neurotransmitters like practical applications of the ZnO/MCPE are good to determine DA in commercial dopamine hydrochloride injection sample and it has the potential for the future development of nano sensors for clinical research.

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