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Full Paper

Cationic Surfactants–Assisted Synthesis of ZnO Nanoparticles and Their Modified Carbon Paste Electrode for Electrochemical Investigation of Dopamine

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Abstract- ZnO nanoparticles were synthesized using zinc nitrate, cetyltrimethyl ammonium bromide and sodium hydroxide in co-precipitation method. The obtained particles were characterized using X-ray diffractometer (XRD), UV-Vis absorption spectroscopy (UV-Vis), Infrared absorption spectroscopy (IR) and Scanning electron microscopy (SEM). The ZnO nanoparticles are used for the preparation of modified carbon paste electrode (MCPE). The MCPE was applied for electrochemical investigation of dopamine (DA) which exhibits enhancement of current response with reduction of over potential for investigation of DA at pH.7.0. The effect of pH range from 5.5 to 8.0 was studied and the redox peak was pH dependent with a slope of 53 mV/pH. The effect of scan rate shows adsorption controlling process and the electrocatalytic currents increases linearly with increase in DA concentrations in the ranges of 0.1-20 μM. The detection limit was found to be 0.3×10^{-7} M.

Keywords- ZnO Nanoparticles, Carbon Paste Electrode, Dopamine Cyclic Voltammetry, Differential Pulse Voltammetry

1. INTRODUCTION

As a key semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has been widely used in broad areas such as photo-emitters, transducers, actuators, varistors, sensors and catalysis [1,2,3].

Dopamine (DA) is one of the most important catecholamine neurotransmitters in mammals that play crucial roles in the functioning of cardiovascular, renal, hormonal and central nervous system [4]. Loss of DA is associated with neurological disorders such as Parkinson's disease [5]. DA acts like a brain chemical to transmit messages to parts of the brain for coordination of body movement. Thus monitoring the DA levels can be an important marker for biomedical diagnosis. Among other methods which are based on spectroscopy and chromatography [6,7]. DA concentration is very low (0.01–1 μM) in the extracellular fluid of the central nervous system [8]. Electrochemical method is one of the most favorable techniques for the determination of dopamine because of its low cost, high sensitivity and easy operation [9] and nanometal oxide MCPE [3, 10-12] shows good sensors for detection of DA was studied.

In this work, very simple co-precipitation method was adopted for preparation of ZnO nanoparticles using CTAB as surfactant. The ZnO nanoparticles modified carbon paste electrode exhibits enhancement of current response with reduction of over potential for the investigation of dopamine at pH.7.0. in 0.2 M phosphate buffer solution and electrocatalytic currents increases linearly with increase of DA concentrations and the detection limit was found to be 0.3×10^{-7} M.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The ZnO nanoparticles were characterized by various techniques such as Powder XRD patterns are recorded for using Cu-Kα radiation (λ=1.5438 Å) as sources in Philips XRD 'X' PERT PRO diffractometer, IR absorption spectra are recorded in FT-IR SPECTRUM 1000 PERKIN ELMER spectrometer on thoroughly dried samples using KBr pellets as dilutants, UV-Vis spectra were obtained by using Perkin Elmer UV-Vis Spectrophotometer by dispersing and sonicated ZnO nanoparticles in the ethanol. Structural morphology of the synthesis nanoparticles is studied using a JEOL JSM-848 scanning electron microscope (SEM). All the electrochemical experiments were carried using a single compartment, three-electrode cell with above the bare CPE and ZnO nanoparticles MCPE was used as a working electrode, an aqueous saturated calomel electrode (SCE) as reference electrode, and a Pt wire as auxiliary electrode. All potentials were measured and reported *vs*. the SCE. The cyclic

voltammetric measurements (CV) and differential pulse voltammetry techniques (DPV) were performed on a Model 660c (CH Instruments) Potentialstat/Galvanostat.

2.2. Materials

Zinc nitrate [$Zn(NO_3)_2.6H_2O$] and perchloric acid ($HClO_4$) were purchased from sd. Fine chemicals. Dopamine hydrochloride, Sodium dihydrogen ortho phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), silicon oil from Hi Media chemicals. Absolute ethanol (99.9%), sodium hydroxide (NaOH), and graphite powder were from Merck and all chemicals are of analytical grade quality. A dopamine stock solution (25 mM) was prepared by adding dopamine to 0.1 M perchloric acid. Phosphate buffer solution was prepared by adjusting the pH with 0.2 M NaH_2PO_4 and Na_2HPO_4 solution and all the aqueous solutions was prepared by using double distilled water.

2.3. Preparation of ZnO nanoparticles

In a typical experiment, the first solution contains 0.01 M $Zn(NO_3)_2.6H_2O$, 0.02 M CTAB and the second solution contains 0.02 M NaOH was prepared by using distilled water. The first solution is added to second solution with continues stirring. The obtained white precipitate was filtered by using Whatmann filter paper (grade-41) and dried at 80 ^oC in hot air oven about 1 h. The dried precipitate was transferred to silica crucible and ignited at 400 ^oC for about 3 h. Then obtained powder was washed with ethanol three to four times to remove impurities present in ZnO nanoparticles.

2.4. Preparation of bare carbon paste electrode and modified carbon paste electrode

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar for about 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a weighing paper. The modified carbon paste electrode (MCPE) was prepared by adding 10 mg, 20 mg, 30 mg and 40 mg ZnO nanoparticles to above mentioned graphite powder and silicon oil mixture.

3. RESULTS AND DISCUSSION

3.1. Characterization

The XRD pattern of the as-obtained ZnO nanoparticles was shown in Fig. 1. All the peaks can be well indexed to the Hexagonal structure of Zinc Oxide (JCPDS PDF, no. 89-0510) with high crystallinity. No impurity peaks present of other Zinc Oxide were observed, indicating the high purity of the products and by using Debye Scherrer's formula, the crystallite sizes of ZnO nanoparticles can be determined. The obtained average crystallite size of the particles was found to be 62 nm.

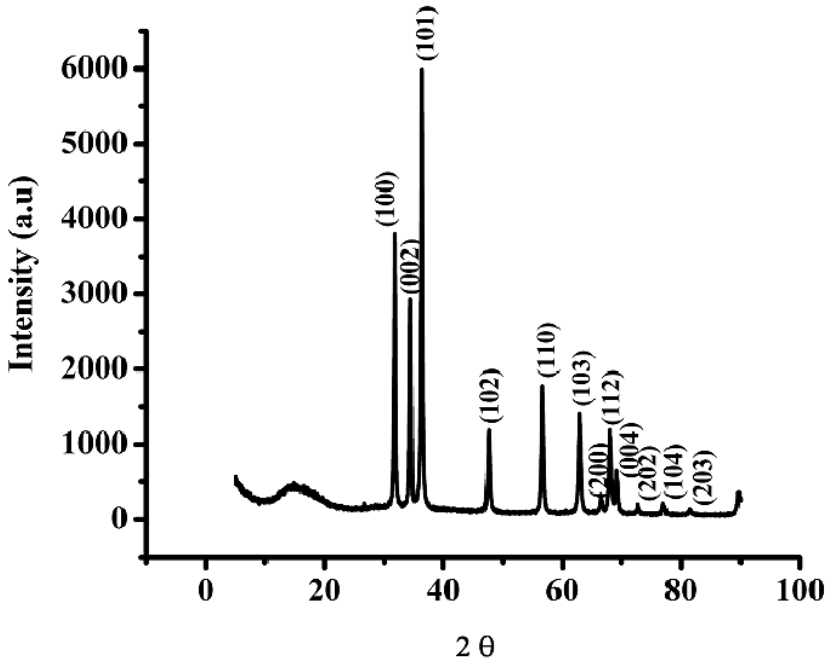

Fig. 1. XRD patterns for ZnO nanoparticles

The IR transmittance spectrum for the ZnO nanoparticles synthesized by using CTAB was displayed in Fig. 3. (B) some bands are observed in the region 2800–3000 $cm^{-1}$and attributed to CTAB surfactants [13-15]. CTAB IR spectra show two intense bands, assigned to asymmetric (2924 cm^{-1}) and symmetric (2852 cm^{-1}) stretching vibrations of C-CH_2 in the methylene chains. The sharp bands in the region of 1439 cm^{-1} are attributed to the deformation of –CH_2– and –CH_3[14] of the incorporated surfactants. The weak band detected in the region of 2924 and 2852 cm^{-1} was assigned to C-CH_3 asymmetric stretching and N-CH_3 symmetric stretching vibrations of solid and a surfactant. These band vibrations provide evidence for the incorporation of CTAB into the Zinc Oxide. The sharp peak 420 cm^{-1} is attributed to the framework vibrations of zinc oxide [16].

UV–Vis absorption spectrum of the as-prepared ZnO nanoparticles dispersed in ethanol solution shows a broad absorption peak whose center was at about 355 nm shown in the Fig. 3A. The results of UV–Vis absorption spectra for ZnO nanoparticles shows good blue shift with enhanced band gap 3.49 eV.

The morphology of ZnO nanoparticles shows the flower-like with 4 to 5 petals were grown, each petals have tip ~50-60 nm, tapering width ~100 nm, width ~160 nm and length is ~200 nm structures and non-uniformly distributed is shown in Fig. 3B.

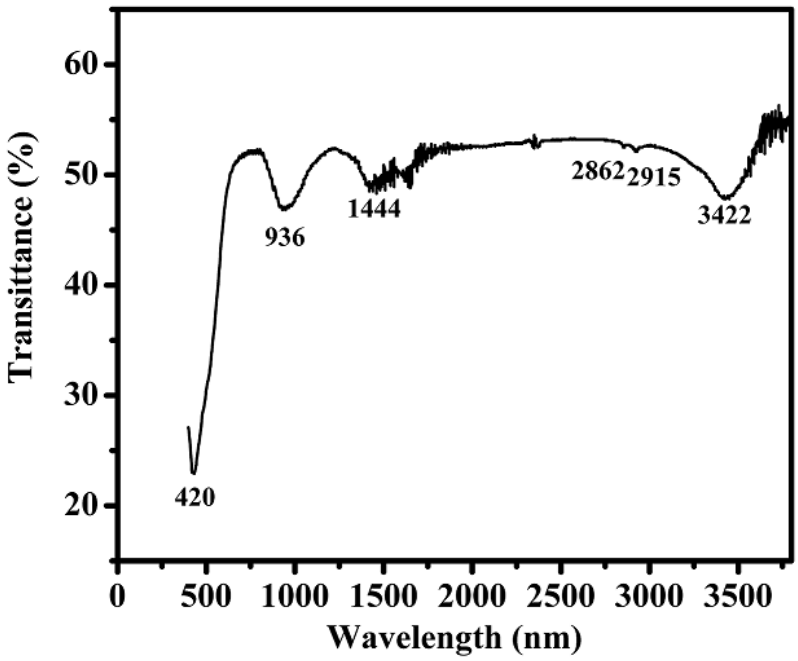

Fig. 2. IR Spectra of ZnO nanoparticles

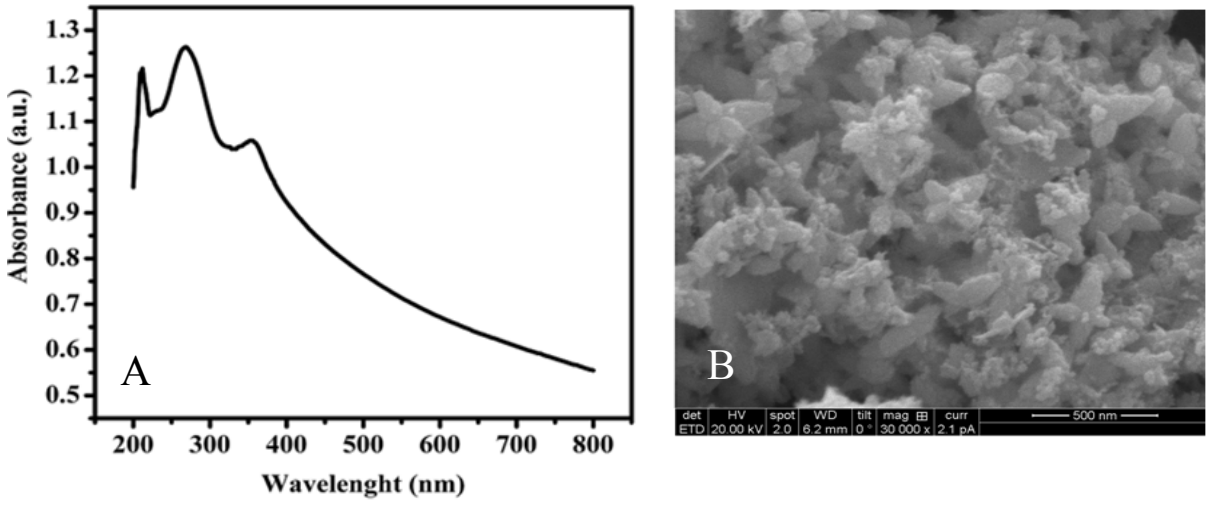

Fig. 3. A) UV-Vis absorption spectra and B) SEM image for ZnO nanoparticles

3.2. Effect of ZnO nanoparticles concentration in CPE on DA

The effect of ZnO nanoparticles concentration in the carbon paste electrode (CPE) on the peak current for the investigation of 1×10^{-5} M DA in 0.2 M phosphate buffer solution of pH 7.0 was studied by CV method. The modified carbon paste electrode with 30 mg of ZnO

nanoparticles enhanced high anodic peak current as compared with the bare CPE, 10, 20, 30 and 40 mg of ZnO nanoparticles as shown in Fig. 4.

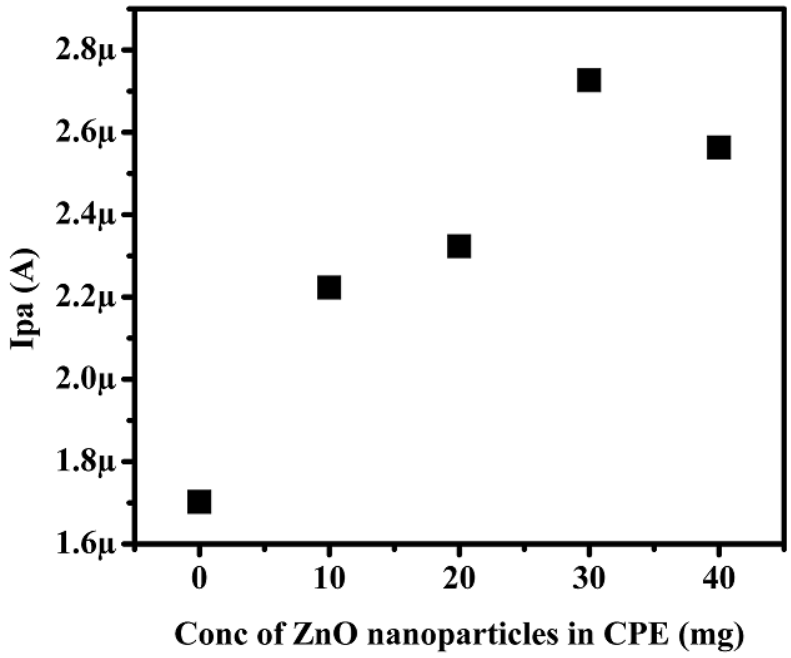

Fig. 4. Shows the graph between anodic peak current (I_{pa}) *vs*. different concentration of ZnO nanoparticles in CPE

3.3. The response of DA at the bare CPE, and ZnO nanoparticles MCPE

Fig.5. shows the electrochemical responses of 1×10^{-5} M DA in 0.2 M phosphate buffer solution of pH 7.0 at the bare CPE and the ZnO nanoparticles MCPE with scan rate 100 mV/s. Compared with the bare CPE the remarkable enhancement in the peak currents with reduction of over potential showed electrocatalytic effects of the ZnO nanoparticles. The mechanism could be as follows; under the condition, ZnO nanoparticles may be combined with the hydrogen bond of the hydroxyl of DA, which activated hydroxyl, weakened the bond energy of O-H and improved the electron transfer rate. At the same time, high surface area of the ZnO nanoparticles improved the electrode contacting area of DA.

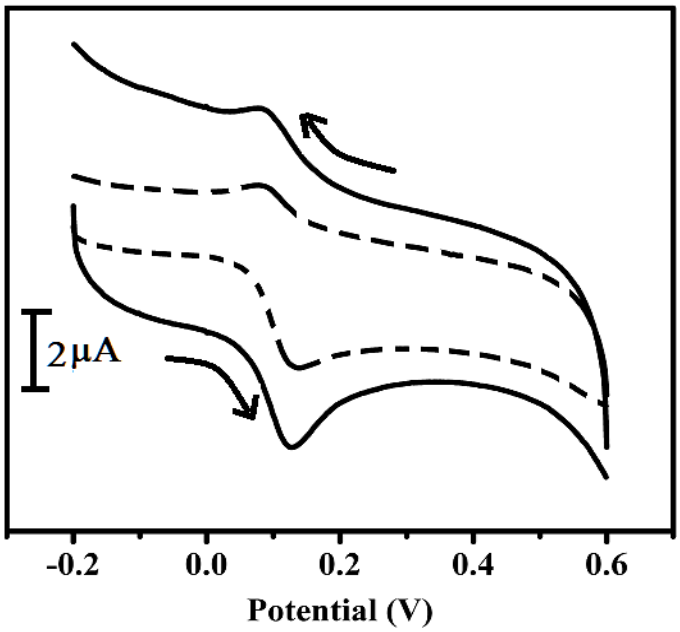

Fig. 5. Cyclic voltammogram of 1×10^{-5} M DA in PBS at pH 7.0 at dashed line for bare CPE and solid line for ZnO nanoparticles MCPE

3.4. Effect of pH

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the ZnO nanoparticles MCPE by affecting both peak currents and peak potentials. The effect of pH value on the determination of DA in PBS solution at ZnO nanoparticles MCPE was carefully investigated in a wider pH range of 5.5–7.5. Fig.6. Illustrates the dependences of the DA anodic peak current and formal potential [E^o (V)] on the buffer solution pH. It can be seen that the anodic peak current of DA increases with increasing pH value until it reaches 7.0, then decrease the peak current of DA until it reaches 7.5. The formal potential of DA shifts towards lower potential with the increase of the pH value of solution, and depends linearly on the pH value in the range of 5.5–7.5 with a slop of 53.3 mV/pH. It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which was consistent with that reported in literature [3].

3.5. Effect of scan rate

The effect of scan rate for 1×10^{-5} M DA in 0.2 M PBS at pH 7.0 was studied by CV at ZnO nanoparticles MCPE. ZnO nanoparticles MCPE showed increase in the redox peak currents with increase in scan rate (10 to 800 mVs^{-1}). The graph of current (i) *vs.* scan rate (ν) was plotted. The graph obtained was good linearity between scan rates and peak current shown in Fig.7, in the range from 10–800 mVs^{-1}. The correlation coefficient (r^2) was 0.99915, which indicate the electrode reaction was adsorption controlled process.

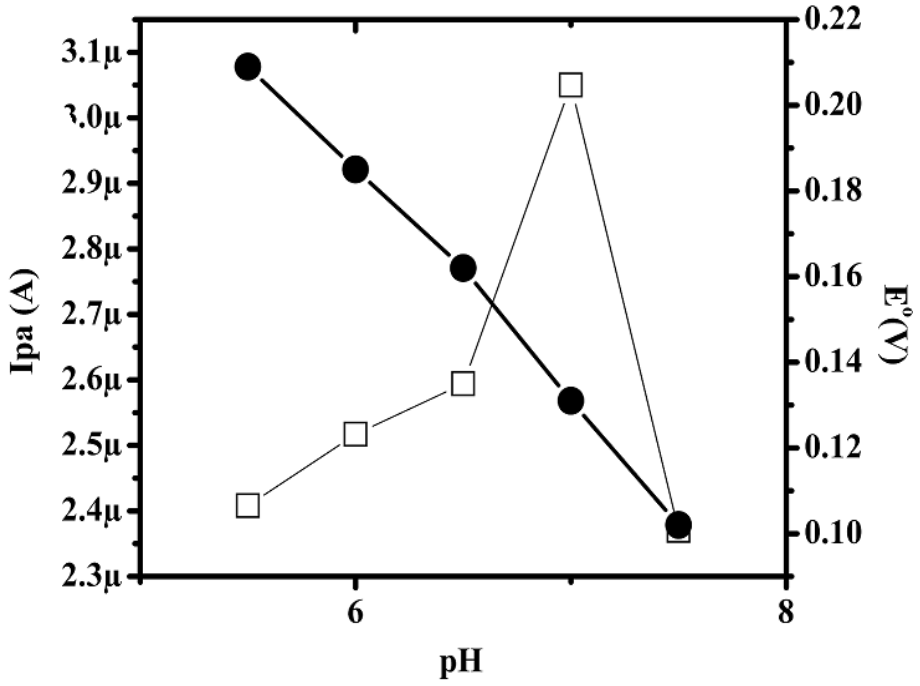

Fig.6. Graph shows the dependences of the DA oxidation peak current (-□-) and for formal redox potential (-●-) on the PBS solution pH with a scanning rate of 100 mVs^{-1}

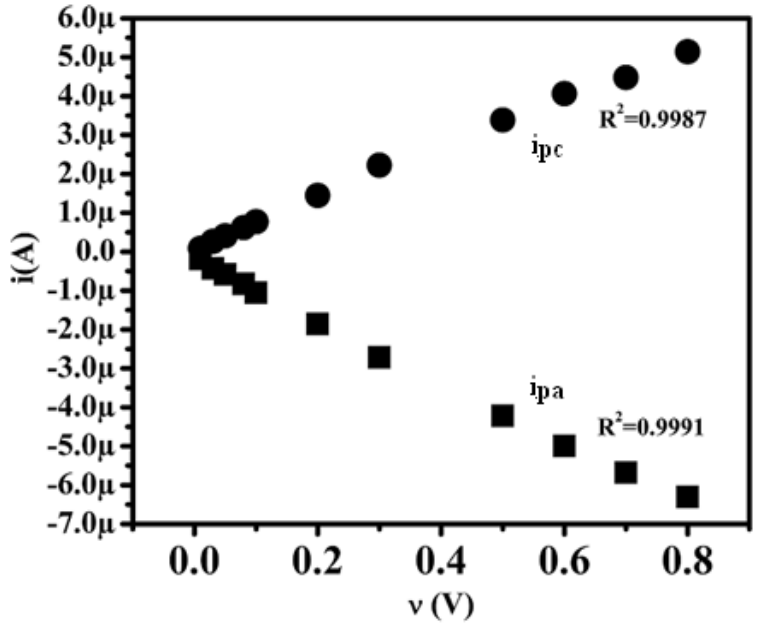

Fig. 7. Graph the linear relationship between the peak current *vs.* the different scan rate (10–800 mVs^{-1}) in 0.2 M PBS solutions at pH 7.0

3.6. Concentration effect of DA

The differential pulse voltammetric technique was used for the analysis DA concentration which varied from 0.1 to 20 μM shown in Fig. 8, for the ZnO nanoparticles MCPE. By increasing the concentration of DA from 0.1 to 20 μM. The graph of I_{pa} *vs*. concentration of DA showed increase in anodic peak current as shown in Fig. 9. The linear relationship ranges 0.3–22 μM with the linear regression equation as I_{pa} (μA)=3.5396 C μM/L+7.865×10^{-7}. The correlation coefficient for the linearity was 0.998 and the detection limit for DA in the linear range region was found to be 0.3×10^{-7} M for ZnO nanoparticles MCPE and which was calculated according recent reported [17] and calculated by using same formula.

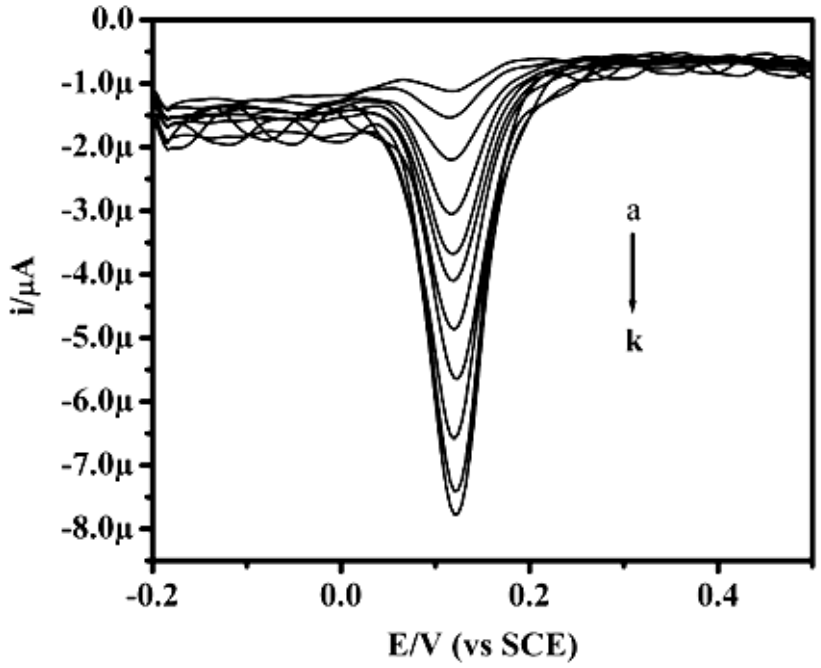

Fig. 8. Differential pulse voltammogram of (a) 1.0×10^{-7} M, (b) 2×10^{-7} M, (c) 4×10^{-7} M, (d) 6×10^{-7} M , (e) 8×10^{-7} M, (f) 10.0×10^{-7} M, (g) 12.0×10^{-7} M, (h) 14.0×10^{-7} M, (i) 16.0×10^{-7} M, (j) 18.0×10^{-7} M and (k) 20.0×10^{-7} M DA in 0.2 M phosphate buffer solution of pH 7.0 at ZnO nanoparticles MCPE

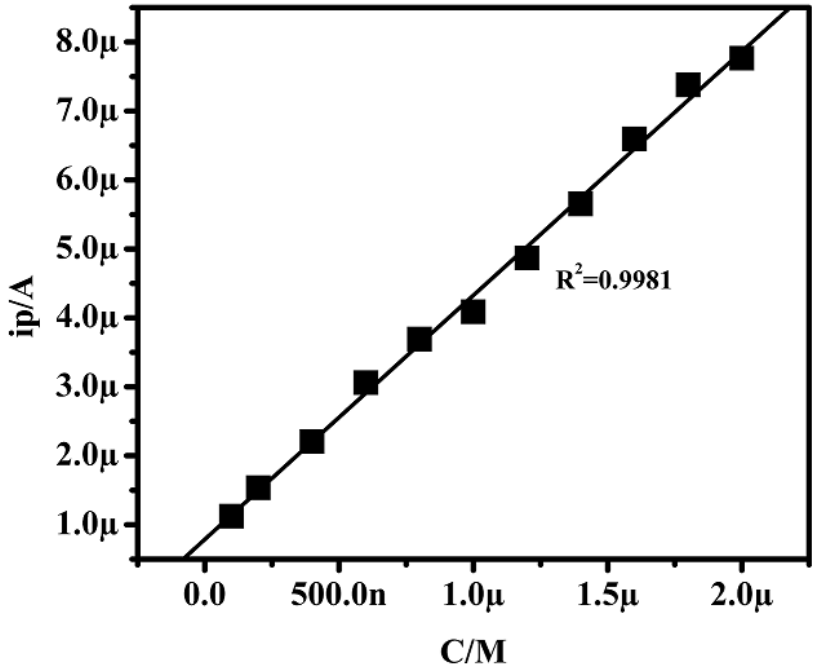

Fig. 9. Graph of I_{pa} *vs.* concentration of DA (0.1–20 µM)

4. CONCLUSIONS

ZnO nanoparticles with average crystalline size 62 nm with significant blue shift of band gap 3.49 eV having flower like morphology have been synthesized by coprecipitation method and their modified carbon paste electrode shows good electrocatalytic activity and enhanced current sensing with low detection limit (0.3×10^{-7}M).

Hence this present synthetic method extended too many metal oxides, ferrites for synthesis and their modified electrode used as sensor for application of determination of some biological active compounds and other neurotransmitters.

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