PART-A

SYNTHESIS OF MgFe₂O₄ NANOPARTICLES AND MgFe₂O₄ NANOPARTICLES/CPE FOR ELECTROCHEMICAL INVESTIGATION OF DOPAMINE


*Analytical Methods, 2 (2011) 2792-96*
4.1. Introduction

Magnesium ferrite nanoparticles (MgFe$_2$O$_4$ NPs) were prepared by a solution based method using magnesium sulphate (MgSO$_4$), ferrous sulphate (FeSO$_4$), dl serine and NaOH as a precipitant and the obtained precipitation was calcinated under 500°C for 4 h. The resulting material was characterized by using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The MgFe$_2$O$_4$ NPs were used for preparation of MgFe$_2$O$_4$ NPs/carbon paste electrode (MgFe$_2$O$_4$NPs/CPE) and applied for electrochemical investigation of dopamine (DA) which exhibits good electrocatalytic activity for investigation of DA at physiological pH 7.4. The effect of pH range from 5.5 to 8.0 was studied and the result shows that the redox peak current was maxima at pH 7.5 and the redox peak was pH dependent with a slope of 0.061 V/pH. The scan rate effect was found to be an adsorption-controlling electrode process. The electrocatalytic currents increased linearly with an increase in DA concentration in the range 0.1–1.2 μM and the detection limit was found to be 7.7 x 10$^{-8}$ M. The proposed method was successfully applied to the determination of DA in injection samples.

4.2. Chemistry and Biological Relevance of Dopamine

The chemistry and biological relevance of dopamine has been explained in details in chapter 2 section 2.2 to 2.2.3.

4.3. Review of Magnesium ferrite, Magnesium ferrite nanoparticles, Cyclic Voltammetry of Dopamine

Magnesium ferrite, MgFe$_2$O$_4$, as a soft magnetic n-type semiconducting material, is an important member of the spinel family. Apart from the applications of its magnetic properties[1–3] it can be used as a heterogeneous catalyst [2], adsorption and humidity sensor [4,5], oxygen sensor [1], sensor technology [6,7] and it has been demonstrated that this material can be used for thermal coagulation therapy, in which tumors are locally heated by an application of alternating magnetic fields [8–10].
It is well known that properties of ferrite materials strongly depend on the preparation conditions [11]. At present, chemical methods, including coprecipitation method have been reported [12–14] and recently the synthesis of leaf-like CuO nanoparticles and a Nafion/GOD/CuO modified electrode was used for detection of glucose [15], the synthesis of CuO nanoparticles and their modified gold electrode was used for investigation of rutin [16], NiFe$_2$O$_4$/MWCNTS/GCE was used for electrochemical investigation of hydrazine [17], silver pentacyanonitrosylferrate films modified electrode was used for investigation of L-cysteine [18], gold nanoparticles modified carbon paste electrode was used for determination of acetaminophen and atenolol [19]. Quantitative determination of dopamine (DA) in human physiological fluids is of considerable significance in both biochemical and clinical diagnosis. Methods for the detection of DA include chemiluminescence [20], fluorimetry [21], ultraviolet visible spectrometry [22], capillary electrophoresis (CE-luminescence) [23] and electrochemical methods. The electrochemical method detection is a simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples. Particularly the development of voltammetric sensors for the determination of secretion neurotransmitters, such as dopamine (DA) and other catecholamine, that exist in the mammalian central nervous system has received a lot of interest. Among the catecholamines, DA has attracted much interest because the change in DA levels has proved to be a very effective route towards understanding brain functions, such as learning and memory formation and the physiological and pathological process of Parkinson’s disease. Electrochemical detection of DA and AA by using LaFe$_3$O$_4$ nanoparticles, CdO nanoparticles, chemically modified carbon paste electrode [24–29], poly (Naphthol Green B) film graphite pencil electrode [30] and gold nanoparticles modified ITO electrode [31] has been reported.

4.4. Experimental

4.4.1. Apparatus

Cyclic voltammetric experiments were performed with a Model 660c (CH Instruments) Potentialstat/Galvanostat. A conventional three electrode cell is employed
and the bare or MgFe$_2$O$_4$ NPs/CPE (3.0 mm diameter) as a working electrode, a saturated calomel electrode as a reference electrode and a platinum electrode as a counter electrode. XRD studies using a Phillips (with X'lerator detector) X-ray diffractometer. Structural morphology of the synthesis NPs was studied using a JEOL JSM-848 scanning electron microscope (SEM).

4.4.2. Chemicals and solutions

Magnesium sulphate (MgSO$_4$), ferrous sulphate (FeSO$_4$) and perchloric acid (HClO$_4$) were purchased from sd. fine chemicals. Dopamine hydrochloride, sodium dihydrogen orthophosphate (NaH$_2$PO$_4$), disodium hydrogen phosphate (Na$_2$HPO$_4$) and silicon oil from Hi Media chemicals, dl-Serine, absolute ethanol (99.9%), sodium hydroxide (NaOH) and graphite powder was from Merck chemicals and all chemicals are of analytical grade quality. DA stock solutions (25 mM) were prepared by adding DA to 0.1 M perchloric acid. Phosphate buffer is prepared by adjusting the pH 7.4 with 0.2 M NaH$_2$PO$_4$ and Na$_2$HPO$_4$ solution. All the aqueous solution was prepared by using double distilled water.

4.4.3. Preparation of MgFe$_2$O$_4$ NPs

In a typical experiment, the first solution 0.2 M MgSO$_4$, 0.4 M FeSO$_4$ and 1.2 M dl serine was dissolved in 250 ml of deionized water and the second solution was prepared by 3 M NaOH pallets in 250 ml of deionized water and the first solution was added to second solution with continuous stirring. The obtained precipitate solution was taken in the condenser and boiled at 100°C temperature for about 2 h then the hot solution was filtered by using Whatmann filter paper (grade-41) and dried at 80°C in a hot air oven for about 1 h. The dried precipitate was transferred to a silica crucible and ignited at 500°C for about 4 h. Then the obtained powder was washed with ethanol three to four times to remove impurities present in MgFe$_2$O$_4$ NPs.
4.4.4. Preparation of bare CPE and modified CPE

The bare CPE (BCPE) was prepared by hand mixing of 80% graphite powder with 20% 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 weighing paper. The MgFe$_2$O$_4$ NPs/CPE was prepared by adding 10, 20, 30 and 40 mg MgFe$_2$O$_4$ NPs to the above mentioned graphite powder and silicon oil mixture.

4.5. Results and Discussion

4.5.1. Characterization

X-ray diffraction patterns were recorded using Cu-Ka ($\lambda = 1.54056$ Å) radiation sources for identification of the crystalline structure and average crystalline size of MgFe$_2$O$_4$ NPs. Fig.4.1 shows that the obtained diffraction pattern reflects (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes belonging to a cubic spinel structure which are in good agreement with the standard pattern (JCPDS 17-0465). The average crystallite diameter can be determined from the full-width at half-maximum (FWHM) of the (311) diffraction peak by using the Scherrer formula [33]. $D = \frac{K\lambda}{(\beta \cos \theta)}$, where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg diffraction angle, and $\beta$ is the full-width at half-maximum. The calculated value is 15 nm. SEM observations reveal that all the products consist of a large quantity of small nanograins with average size around 20–50 ± 1 nm, as shown in Fig.4.2.

4.5.2. Effect of MgFe$_2$O$_4$ NPs in CPE for investigation of DA

The effect of MgFe$_2$O$_4$ NPs in the CPE on the peak current for the investigation of $1 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution at pH 7.4 was studied by cyclic voltammetry technique. The modified CPE with 20 mg of MgFe$_2$O$_4$ NPs enhanced high anodic peak current as compared with the BCPE, 10, 30 and 40 mg of MgFe$_2$O$_4$ NPs as shown in Fig.4.3.
4.5.3. The response of DA at the bare CPE, and MgFe$_2$O$_4$ NPs/ CPE

Fig. 4.4 shows the electrochemical responses of $1 \times 10^{-5}$ MDA in 0.2 M phosphate buffer solution of pH 7.4 at the BCPE and the MgFe$_2$O$_4$ NPs/CPE with scan rate 0.1 V s$^{-1}$. At the BCPE, the difference between the anodic peak potential ($E_{pa}$) 0.136 V and the cathodic peak potential ($E_{pc}$) 0.085 V is reversible wave with $\Delta E_p$ 0.051 V. However, DA peak currents significantly increased at the MgFe$_2$O$_4$ NPs/CPE, with the anodic peak potential is 0.124 V and the corresponding cathodic peak potential is 0.087 V and corresponding $\Delta E_p$ 0.037 V. Compared with BCPE the remarkable enhancement in the peak currents with reduction of over potential showed catalytic effects of the MgFe$_2$O$_4$ NPs. The mechanism may be MgFe$_2$O$_4$ NPs 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 MgFe$_2$O$_4$ NPs improved the electrode contact area of DA.

4.5.4. Effect of pH value on the determination of DA at the MgFe$_2$O$_4$ NPs modified CPE

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the MgFe$_2$O$_4$ NPs/CPE by affecting both peak current and peak potential. The effect of pH value on the determination of DA in PBS solution at MgFe$_2$O$_4$ NPs/CPE was carefully investigated in a wider pH range of 5.3–7.7 of $1 \times 10^{-5}$ M DA in the different pH solutions. The cyclic voltammograms in Fig. 4.5 and Fig. 4.6, illustrate the dependency of the DA anodic peak current and formal potential ($E^\circ$ (V)) on the buffer solution pH. It can be seen that the peak current of DA increases with increasing pH value until it reaches 7.5 [shown with closed circles (●)]. The formal potential of DA shifts negatively with the increase of the pH value of solution and depends linearly on the pH value in the range of 5.3–7.7 with a slope of 0.061 V/pH ($R^2 = 0.991$) (shown with line (0-)). It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which is consistent with that reported in literature [34–37].

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4.5.5. Effect of scan rate on the peak currents

The effect of scan rate for 1 \times 10^{-5} \text{ M} \text{MDA} in 0.2\text{M} \text{PBS at pH 7.4} was studied by cyclic voltammetry at MgFe_2O_4 NPs/CPE as shown in Fig. 4.7. MgFe_2O_4 NPs/CPE showed an increase in the redox peak current with increasing scan rate (0.05 to 0.45 \text{Vs}^{-1}). The graph of redox peak current \( (i_{pa}) \) vs. scan rate \((v)\) was plotted. The graph obtained has good linearity between the scan rate and redox peak current (Fig. 4.8). In the range from 0.05–0.45 \text{Vs}^{-1} the redox peak currents were proportional to \(v\). The correlation coefficient \( (R^2) \) was 0.9993, which indicates the electrode reaction was adsorption controlled which was supported by previously reported literatures [38–40].

4.5.6. Concentration effect of DA

The differential pulse voltammetric technique was used for analysis of DA concentration which was varied from 0.1 to 12 \text{µM} as shown in Fig. 4.9. For the MgFe_2O_4 NPs/CPE, the corresponding graphs of anodic peak current versus concentration of DA shows two linear relationship ranges 0.1 to 0.6 \text{mM} and 0.8 to 12 \text{µM} with the linear regression equations as \( i_{pa} \) (A) = 15.28 \text{CµM L}^{-1} + 4.628 \times 10^{-5} and \( i_{pa} \) (A) = 4.776 \text{CµM L}^{-1} + 5.696 \times 10^{-5}, respectively. The correlation coefficient for the first linearity was 0.987 and for the second linearity it was found to be 0.993 for the MgFe_2O_4 NPs/CPE shown in Fig. 4.10. The correlation coefficient for the first linearity was 0.987, the detection limit for DA in the linear range region was found to be 7.7 \times 10^{-6} \text{M} for MgFe_2O_4 NPs/CPE which was calculated according to the equation of LOD = K S^0/S, and K was a constant related to the confidence level. According to the suggestion of the IUPAC, the value of K is 3 at the 99% confidence level, \( S^0 \) is the standard deviation of ten blank-solution measurements (no added DA) and S is the slope of the calibration graph, the proposed electrode showed relatively lower detection limit than the recent reported [38] and calculated by using same formula. The sensitivity from the slope of first linear calibration plot is found to be 509.33\mu \text{A/µM.cm}^2.
4.5.7. Analytical application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from Sterile Specialities India Private Ltd had a specified content of DA 40.0 mg mL\(^{-1}\) and the sample was used after suitable dilution. The results are shown in Table 4 and the recovery relative standard deviation (RSD) were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in injections with recovery in the range 97.00 and 99.1%.

4.6. Conclusions

- MgFe\(_2\)O\(_4\) nanoparticles (NPs) with average crystalline size 15nm have been synthesized by solution based method.

- SEM image shows products consist of a large quantity of small nanograins with average size around 20–50 ± 1 nm,

- MgFe\(_2\)O\(_4\) nanoparticles modified carbon paste electrode shows good sensor application for electrochemical investigation of DA with detection limit 7.7 \(\times\) 10\(^{-8}\) M and sensitivity is 509.33\(\mu\)A/\(\mu\)M cm\(^2\).

- The proposed methods can be applied to the detection of DA in injections.

- Hence this current synthetic method extended to many metal oxides, ferrites for synthesis and their modified electrode used as sensor for application of determination of biological active compounds, injection sample and other neurotransmitters.
Fig. 4.1. XRD pattern for MgFe$_2$O$_4$ NPs

Fig. 4.2. SEM image for MgFe$_2$O$_4$ NPs
Fig. 4.3. Graph between anodic peak current ($i_{pa}$) versus different concentration of MgFe$_2$O$_4$ NPs in CPE.

Fig. 4.4. Cyclic voltammograms of $1 \times 10^{-5}$ M DA for MgFe$_2$O$_4$ NPs/ CPE (---), and for BCPE (—).
Fig. 4.5. Cyclic voltammograms of $1 \times 10^{-5}$MDA in different pH 5.3–7.7 solutions at the MgFe$_2$O$_4$ NPs/CPE (from right to left).

Fig. 4.6. Dependence of the DA oxidation peak current in closed circles (●) and with line (-O-) for formal redox potential versus pH with the scan rate of 0.1 V s$^{-1}$.
Fig. 4.7. Cyclic voltammograms of MgFe$_2$O$_4$ NPs/CPE in 0.2 M PBS solutions containing $1 \times 10^{-5}$ M DA at different scan rates (0.05–0.45 V s$^{-1}$)

Fig. 4.8. Graph of the linear relationship between the peak current and the scan rate
Fig. 4.9. Differential pulse voltammograms of (a) $1.0 \times 10^{-7}$ M, (b) $2 \times 10^{-7}$ M, (c) $3 \times 10^{-7}$ M, (d) $4 \times 10^{-7}$ M, (e) $6 \times 10^{-7}$ M, (f) $8 \times 10^{-7}$ M, (g) $1 \times 10^{-6}$ M, (h) $2 \times 10^{-6}$ M, (i) $3 \times 10^{-6}$ M, (j) $4 \times 10^{-6}$ M, (k) $5 \times 10^{-6}$, (l) $6 \times 10^{-6}$, (m) $8 \times 10^{-6}$, (n) $1.0 \times 10^{-5}$ and (o) $1.2 \times 10^{-5}$ M DA in 0.2M phosphate buffer solution of pH 7.4 at MgFe$_2$O$_4$ NPs/CPE

Fig. 4.10. Graph of $i_{pa}$ vs. concentration of DA (0.1–1.2 mM)
Table 4.1. Detection of DA in injection samples (n = 5)

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<th>Tested Sample</th>
<th>Added (µg/ml)</th>
<th>Found (µg/ml)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
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<td>1.87</td>
<td>97.2</td>
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<td>1.57</td>
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<td>99.1</td>
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</table>
4.7. References


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PART-B

ANIONIC SURFACTANTS-ASSITED SYNTHESIS OF ZnO NANOPARTICLES AND THEIR MODIFIED CARBON PASTE ELECTRODE FOR ELECTROCHEMICAL INVESTIGATION OF DOPAMINE


Communicated to International Journal of Science Research
4.8. Introduction

A ZnO nanoparticle (Nps) was synthesized by using zinc nitrate, sodium dodecyl sulphate (SDS) and sodium hydroxide by co-precipitation method. The obtained particles were characterized by using X-ray diffractometer (XRD), UV-visible absorption spectroscopy (UV), Infrared absorption spectroscopy (IR) and Scanning electron microscopy (SEM). The ZnO Nps are used for the preparation of ZnO Nps/carbon paste electrode (ZnO Nps/CPE). The ZnO Nps/CPE was applied for electrochemical investigation of dopamine (DA) which exhibits enhancement of current response for investigation of DA at pH.7.4. The effect of pH range from 5.5 to 8.0 was studied and the redox peak was pH dependent with a slope of 50 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 0.2 μM -1.3 mM. The detection limit was found to be 0.8X10^-7 M and the ZnO Nps/CPE was also used for the detection of DA in injection samples.

4.9. Chemistry and Biological Relevance of Dopamine

The chemistry and biological relevance of dopamine has been explained in details in chapter 2 section 2.2 to 2.2.3.

4.10. Review of ZnO nanoparticles, preparation and Cyclic Voltammetry of Dopamine

Over the past few years, the synthesis and functionalism of nanostructures have attracted great interest due to their significant potential application. ZnO, as an important semiconducting material has a wide range of applications in optics, optoelectronics, sensors, actuators, energy and biomedical sciences [1–3]. Because of its direct wide band gap of 3.37 eV, large exciton energy of 60 meV and exhibit the most splendid and abundant configuration of nanostructure that one material can form. 1D ZnO nanocrystals are considered to be the most promising highly sensing materials of sensors due to the slower electron/hole recombine rate, as well as their higher surface-to-volume ratio than the conventional sensing materials [4].
Dopamine (DA) is a well-known biogenic amine acting as a neurotransmitter in the brain. It has received considerable attention because of its suspected role in a variety of neuropsychiatric disorders such as Parkinson’s disease and Schizophrenia [5, 6]. DA concentration is very low (0.01–1μM) in the extracellular fluid of the central nervous system [7]. Methods for the detection of DA include flow-injection analysis and high-performance liquid chromatography with chemiluminescence [8], high-performance liquid chromatography with fluorescence detection [9]. The electrochemical method is a simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples [10]. Particularly the development of voltammetric sensors for the determination of dopamine (DA) and other catecholamine that exist in the mammalian central nervous system has received a lot of interest.

Electrochemical detection of DA by using some modified electrode are recently reported such as CdO Nps, Banana-MWCNTs, Poly(glycine) and Poly(maleic acid) modified Carbon Paste Electrode [11,12,6,13], single-walled carbon nanotubes–iron (III) oxide NPs [14] and ZnO Nps /GCE [15].

There are several literatures previously reported on the synthesis of ZnO nanoparticles by using sodium dodecyl sulphate as a surfactant by different methods in different environments such as; laser ablation in a liquid environment in different surfactant (cationic, anionic(SDS), amphoteric and nonionic) solutions [16], pulsed laser ablation of a piece of zinc metal in an aqueous media of anionic SDS, C_{12}H_{25}SO_4Na (Glaxo Smith Kline) with simultaneous flow of pure oxygen [17], precipitation-thermal decomposition route using ZnSO_4 and Na_2CO_3 as the reactants and sodium dodecyl sulfate (SDS) as the surface modification agent [18], the precipitation process using Zn(CH_3COO)_2·2H_2O in mixed 1-propanol-water solvent. Sodium dodecyl sulfate (SDS) as the anionic surfactant was added to control the morphology [19], a simple and novel method of preparing stabilized laminated SDS/ZnO QDs/SDS 2D superlattices in colloidal solution [20], Zinc oxide ‘nanoleaf’ structures have been synthesized at room temperature and pressure using the novel technique of pulsed laser ablation (Nd:YAG 532 nm) of a zinc target in an aqueous solution of sodium dodecyl sulfate (SDS) [21], the experimentally demonstrated controlled synthesis of ZnO-ZnOOH nanocomposite material by pulsed laser ablation of zinc metal plate in aqueous solution of SDS [22].
4.11. Experimental

4.11.1. Apparatus

The ZnO Nps 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-visible spectra were obtained by using Perkin Elmer UV-VIS Spectrophotometer by dispersing and sonicated ZnO nanoparticles in the ethanol. All the electrochemical experiments were carried using a single compartment, three-electrode cell with above the bare CPE and ZnO Nps /CPE was used as a working electrode, an aqueous saturated calomel electrode (SCE) as reference electrode, and a Pt wire as auxiliary electrode and 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.

4.11.2. Materials

Zinc nitrate (ZnNO₃) and perchloric acid (HClO₄) were purchased from sd. Fine chemicals. Dopamine hydrochloride, sodium dihydrogen ortho phosphate (NaH₂PO₄), disodium hydrogen phosphate (Na₂HPO₄), silicon oil and sodium dodecyl sulphate (SDS) 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 NaH₂PO₄ and Na₂HPO₄ solution and all the aqueous solutions was prepared by using double distilled water.

4.11.3. Preparation of ZnO Nps

In a typical experiment, the first solution contains 0.01M ZnNO₃, 0.02M SDS and the second solution contains 0.02M 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°C in hot air oven about 1 hour. The dried precipitate was transferred to silica crucible and ignited at 400°C for about 3 hours. Then obtained powder was washed with ethanol three to four times to remove impurities present in ZnO Nps.

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

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar for about 30 minutes to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a weighing paper. The ZnO Nps/ carbon paste electrode (ZnO Nps/CPE) was prepared by adding 30mg ZnO Nps to above mentioned graphite powder and silicon oil mixture.

4.12. Results and Discussion

4.12.1. Characterization

The XRD pattern of the as-obtained ZnO Nps was shown in Fig. 4.11. 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 were observed other than Zinc Oxide, indicating the high purity of the products and by using Debye Scherrer's formula, the crystallite sizes of ZnO Nps can be determined. The obtained average particle size of the particles was found to be 45nm.

The IR transmittance spectrum for the ZnO Nps synthesized by using SDS was displayed in Fig.4.12. The peaks at around 2933, 2871, 1587 and 1124 cm\(^{-1}\) are due to C–H stretching and bending. These band vibrations provide evidence for the incorporation of SDS into the zinc oxide. A broadening peak at around 3441 and 1658 cm\(^{-1}\) was proposed to be due to H–OH stretching and small peak around 2371 cm\(^{-1}\) stretching for O=C=O. The peak at 446 cm\(^{-1}\) was a characteristic peak of Zn–O stretching [23-24].
UV–Visible absorption spectrum of the as-prepared ZnO Nps dispersed in ethanol solution shows a broad absorption peak whose center was at about 376 nm shown in the Fig.4.13. The result of UV–visible absorption spectra for ZnO Nps shows good blue shift compared with the bulk particles reported [25].

The morphological of ZnO nanoparticles shows the irregular rod-like were grown, each rod have tip ~40-50nm, tapering width ~60-70nm, width ~100nm and length is ~130nm structures are non-uniformly distributed as shown in Fig. 4.14.

4.12.2. The response of DA at the bare CPE and ZnO Nps /CPE

Fig.4.15 shows the electrochemical responses of 1X10^-5 M DA in 0.2M phosphate buffer solution of pH 7.4 at the bare CPE and the ZnO Nps /CPE with scan rate 100 mV/s. Compared with that at bare CPE the enhancement in the peak currents showed electrochemical sensing effects of the ZnO Nps /CPE.

4.12.3. Effect of pH

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the ZnO Nps /CPE by affecting both peak currents and peak potentials. The effect of pH value on the determination of DA in PBS solution at ZnO Nps /CPE was carefully investigated in a wider pH range of 5.5–8.0 from the Fig.4.16 the dependences of the DA anodic peak current and formal potential [E° (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 7.5 then decreases the peak current of DA until it reaches 8.0 (shown in solid circle with line). 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 5.5–8.0 with a slope of 50mV/pH (shown in square dots with line). It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which was consistent with that reported in literature [15] and pH 7.4 was chosen for use in all experiments.

4.12.4. Effect of scan rate

The effect of scan rate for 1X10^-5 M DA in 0.2 M PBS at pH 7.4 was studied by CV at ZnO Nps /CPE shown in Fig.4.17. ZnO Nps /CPE showed increase in the redox peak currents with increase in scan rate (50 to 600mVs^-1). The graph of current (i) vs scan
rate (v) was plotted and the graph obtained was good linearity between scan rate and peak currents shown in Fig. 4.18 in the range from 50– 600 mVs⁻¹. The correlation coefficient (r²) was 0.9998, which indicate the electrode reaction was adsorption controlled process.

4.12.5. Concentration effect of DA

The differential pulse voltammetric technique was used for the analysis DA concentration which varied from 0.2 μM -1.3 mM shown in Fig. 4.19 for the ZnO Nps/CPE. By increasing the concentration of DA from 0.2 μM -1.3 mM. The graph of Ipa vs concentration of DA showed increase in anodic peak current as shown three linear ranges are in Fig. 4.20. The first linear relationship ranges 0.2–2 μM with the linear regression equation as i_{pa} (μA) = 4.0101 CμM/L+3.1668 x10⁻⁷ (r²=0.993, n=8), the second linear relationship ranges 2.8–24 μM with linear regression equation as I_{pa} (μA) = 0.1320CμM/L+1.3035 x10⁻⁵ (r²=0.983, n=4) and the third linear relationship ranges 33 μM -1.2 mM with linear regression equation as i_{pa} (μA) = 0.0180CμM/L+4.043 x10⁻⁵ (r²=1, n=3) and the detection limit for DA in the lower concentration linear range region was found to be 0.8 x10⁻⁷ M for ZnO Nps/CPE and which was calculated according recent reported [26] and compared with previous reported literatures[26,12,27,6] (Table-4.2). From the table-4.2 it was clearly shows that ZnO Nps/CPE exhibits low detection limit and higher linear range for detection of DA. The of sensitivity is found to be 133.66 μA/μM.cm² from the slope of the first calibration plot.

4.12.6. Analytical application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from Sterile Specialties India Private Ltd had a specified content of DA 40.0 mg mL⁻¹ and the sample was used after suitable dilution. The results are shown in Table.4.3 and the recovery, Relative Standard Deviation (R.S.D.) were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in injections with recovery in the range 99.00 to 99.9%.
4.13. Conclusions

1. ZnO Nps with average crystalline size 45nm have been synthesized by Co-precipitation method.

2. The SEM image morphological of ZnO nanoparticles shows the rod-like were grown, each rod have tip ~40-50nm, tapering width ~60-70nm, width ~100nm and length is ~130nm structures are non-uniformly distributed.

3. ZnO Nps modified carbon paste electrode shows good enhanced current sensing effect for DA with low detection limit (0.8X10⁻⁷M), sensitivity is 133.66μA/μM.cm², good linear range (0.2 μM -1.3mM) and successfully analyses DA concentration in injection sample.

4. Hence this present synthetic method extended to 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.
Fig. 4.11. XRD patterns for ZnO Nps

Fig. 4.12. IR Spectra of ZnO Nps
Fig. 4.13. UV-Visible absorption Spectra of ZnO Nps

Fig. 4.14. SEM image of ZnO nanoparticles
Fig. 4.15. Cyclic voltammogram of $1 \times 10^{-5}$ M DA in PBS at pH 7.4 at dashed line for bare CPE and solid line for ZnO Nps/CPE.

Fig. 4.16. The dependence of the DA oxidation peak current in closed circles with line (-•) and square with line (○-) for formal redox potential versus pH with the scan rate of 100 mV s$^{-1}$. 
Fig. 4.17. Cyclic voltammograms of ZnO nanoparticles MCPE in 0.2M PBS solutions containing $1 \times 10^{-5}$ M DA at different scan rates (50–600 mVs$^{-1}$).

Fig. 4.18. Graph the linear relationship between the peak current versus the different scan rate (50–600 mVs$^{-1}$) in 0.2M PBS solutions at pH 7.4.
Fig. 4.19. Differential pulse voltammogram of (a) $2 \times 10^{-7}$ M, (b) $6 \times 10^{-7}$ M, (c) $8 \times 10^{-7}$ M, (d) $1.0 \times 10^{-6}$ M, (e) $1.2 \times 10^{-6}$ M, (f) $1.6 \times 10^{-6}$ M, (g) $1.8 \times 10^{-6}$ M, (h) $2.0 \times 10^{-6}$ M, (i) $2.8 \times 10^{-6}$ M, (j) $3.8 \times 10^{-6}$ M, (k) $7.0 \times 10^{-5}$ M, (l) $1.6 \times 10^{-4}$ M, (m) $3.0 \times 10^{-4}$ M, (n) $6.0 \times 10^{-4}$ M, and (o) $1.2 \times 10^{-3}$ M DA in 0.2M phosphate buffer solution of pH 7.4 at ZnO nanoparticles MCPE.

Fig. 4.20. Graph of $i_{pa}$ vs concentration of DA (0.2 μM - 1.3 mM)
Table 4.2. Comparison of the analytical performances of different modified electrodes

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<th>Techniques</th>
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<td>DPV</td>
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Table 4.3. Detection of DA in injection samples (n =5)

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<th>Recovery (%)</th>
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4.14. References


PART-C

SYNTHESIS OF NiO NANOPARTICLES AND THEIR MODIFIED CARBON PASTE ELECTRODE FOR ELECTROCHEMICAL INVESTIGATION OF DOPAMINE

Sathish Reddy, B.E. Kumaraswamy, Ongera Gilbert and H. Jayadevappa

Communicated to Sensor and Actuator B, Chemical
4.15. Introduction

NiO nanoparticles were synthesized using nickel sulphate, acetic acid, ethanol and sodium hydroxide by co-precipitation method. The particles were characterized by using X-ray diffractometer (XRD), UV-visible absorption spectroscopy (UV-vis), Infrared absorption spectroscopy (IR) and Scanning electron microscopy (SEM). The NiO nanoparticles are used for the preparation of modified carbon paste electrode (MCPE). This MCPE was applied for electrochemical investigation of dopamine (DA) which exhibit enhancement of current response for investigation of DA at pH 7.0. The effect of pH range from 5.5 to 8.0 was studied the redox peak was pH dependent with a slope of 51 mV/pH. The effect of scan rate shows diffusion controlling process with higher surface area of electrode and enhanced heterogeneous rate constants and the electrocatalytic currents increases linearly with increase in DA concentrations in the ranges of 3-22 μM. The detection limit was found to be 3.8X10⁻⁷ M and the modified electrode was also used for the detection of DA in injection samples.

4.16. Chemistry and Biological Relevance of Dopamine

The chemistry and biological relevance of dopamine has been explained in details in chapter 2 section 2.2 to 2.2.3.

4.17. Review of NiO, NiO nanoparticles and Cyclic Voltammetric Studies of Dopamine

Nickel oxide (NiO) has been under extensive investigations for decades as a kind of important functional material. It is regarded as a very prosperous material and can be used as battery cathodes, catalysts, gas sensors, electrochromic films, and in magnetic materials [1-4]. Because of the volume effect, the quantum size effect and the surface effect, nanocrystalline NiO is expected to possess many improved properties than those of micro-sized NiO particles [5].

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The NiO nanomaterials promising for the development of effective electrochemical sensors for a wide range of potential applications in medicine, biotechnology and environmental chemistry [6]. Dopamine (DA) is one of the most significant catecholamine, belongs to the family of excitatory chemical neurotransmitter [7,8] and plays a very important role in the function of central nervous, renal, hormonal and cardiovascular system [9,10], which is related with several diseases such as schizophrenia and Parkinsonism and to HIV infection [11,12]. DA concentration is very low (0.01–1[^1]M) in the extracellular fluid of the central nervous system [13,14]. Electrochemical method is one of the most favorable techniques for the determination of dopamine because of its low cost, high sensitivity and easy operation [15] and at chemically MCPE [16-18] and nanometaloxide MCPE [19-21] shows good sensors for detection of DA was studied.

4.18. Experimental Methods

4.18.1. Apparatus

The NiO 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-visible spectra were obtained in using Perkin Elmer UV-VIS Spectrophotometer by dispersing and sonicated NiO nanoparticles in the ethanol, structural morphology of the NiO nanoparticles the sample was 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 NiO 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.
4.18.2. Materials

Nickel sulphate (NiSO₄) and perchloric acid (HClO₄) were purchased from sd. Fine chemicals. Dopamine hydrochloride, Sodium dihydrogen ortho phosphate (NaH₂PO₄), disodium hydrogen phosphate (Na₂HPO₄), silicon oil from Hi Media chemicals. Absolute ethanol (99.9%), sodium hydroxide (NaOH), acetic acid and graphite powder were from Merck and all chemicals are of analytical grade quality. Dopamine stock solutions (25 mM) were prepared by adding dopamine to 0.1M perchloric acid. Phosphate buffer solution was prepared by adjusting the pH with 0.2 M NaH₂PO₄ and Na₂HPO₄ solution. All the aqueous solution were prepared by using double distilled water.

4.18.3. Preparation of NiO nanoparticles

In a typical experiment, the first solution contains 0.06M NiSO₄·6H₂O, 0.12M acetic acid and the second solution contains 0.18M NaOH pallets, 100 ml absolute ethanol was prepared by using distilled water, the first solution was added to second solution with continues stirring. The obtained precipitate was filtered by using Whatmann filter paper (grade-41) and dried at 80°C in hot air oven about 1 hour. The dried precipitate was transferred to silica crucible and ignited at 400°C for about 3 hours. Then obtained powder was washed with ethanol three to four times to remove impurities present in NiO nanoparticles.

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

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar for about 30 minutes 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 10mg, 20mg and 30mg NiO nanoparticles to above mentioned graphite powder and silicon oil mixture.
4.19. Results and Discussion

4.19.1. Characterization

The XRD pattern of the as-obtained NiO nanoparticles was shown in Fig.4.21. All the peaks can be well indexed to the face center cubic structure of nickel oxide (JCPDS PDF, no. 780429) with high crystallinity. No impurity peaks present of other nickel oxide were observed, indicating the high purity of the products and by using Debye Scherrer’s formula, the crystallite sizes of NiO nanoparticles can be determined. The obtained average particle size of the particles was 11nm which was less than reported in the literature [22].

The IR transmittance spectrum for the NiO nanoparticles was displayed in Fig.4.22. A broadening peak at around 3404 and 1632 cm\textsuperscript{-1} was proposed to be due to H–OH stretching and peaks at 1108, 420 cm\textsuperscript{-1} was a characteristic peak of Ni–O stretching [22, 23].

UV–Visible absorption spectrum of the as-prepared NiO nanoparticles dispersed in ethanol solution shows a broad absorption peak whose center was at about 306 nm shown in the Fig.4.23. The results of UV–visible absorption spectra for NiO nanoparticles shows good blue shift compared with reported [22,24].

The surface morphology of the samples obtained was examined by SEM was shown in the Fig.4.24. The SEM micrographs clearly show irregular shaped having 50-60% of 50-60 nm, 15-20 % of 100nm, 10-15% of 200nm and 10% of 300-400nm NiO nanoparticles irregularly and non uniformly distributed have been observed.

4.19.2. Effect of NiO nanoparticles concentration in CPE on DA

The effect of NiO nanoparticles concentration in the carbon paste electrode (CPE) on the anodic peak current for the investigation of 40X10\textsuperscript{-5} M DA in 0.2M phosphate buffer solution of pH 6.0 was studied by CV technique. The MCPE with 10mg of NiO nanoparticles shows well defined redox peak current compared the 20 and 30 mg of NiO nanoparticles MCPE. But the 20 and 30 mg of NiO nanoparticles MCPE shows enhancement in background current and the redox peaks was not clearly appear for DA which was shown in Fig.4.25.
4.19.3. The response of DA at the bare CPE, and NiO nanoparticles MCPE

Fig.4.26 shows the electrochemical responses of 100μM DA in 0.2M phosphate buffer solution of pH 7.0 at the bare CPE and the NiO nanoparticles MCPE with scan rate 100 mV/s. At the bare CPE, the difference between the anodic peak potential ($E_{pa}$) 0.19 V and the cathodic peak potential ($E_{pc}$) 0.12 V, however DA peak currents significantly increased at the NiO nanoparticles MCPE, with the anodic peak 0.18 V and the corresponding cathodic peak potential is 0.12 V and corresponding ΔEp 0.06V shows catalytic activity compare with reported literature [19].

Compared with that at bare CPE the remarkable enhancement in the peak currents with reduction of over potential showed catalytic effects of the NiO nanoparticles. The mechanism could be as follows; under the condition, NiO 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 NiO nanoparticles improved the electrode contacting area of DA.

4.19.4. Effect of pH value on the determination of dopamine at the NiO nanoparticles MCPE

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the NiO nanoparticles MCPE by affecting both peak current and peak potential. The effect of pH value on the determination of DA in PBS solution at NiO nanoparticles MCPE was carefully investigated in a wider pH range of 5.5–8.0. Fig.4.27 shows CVs of 40μM DA in the different pH solutions. Fig.4.28 illustrates the dependences of the DA anodic peak current and formal potential ($E^0 (V)$) on the buffer solution pH. It can be seen that the peak current of DA increases with increasing pH value until it reaches 6.0, then decrease the peak current of DA until it reaches 8.0. The formal potential of DA shifts negatively with the increase of the pH value of solution, and depends linearly on the pH value in the range of 5.5–8.0 with a slop of 51.3mV/pH. It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which was consistent with that reported in literatures [20,25,26]. The effect of pH on peak DA current may have resulted from its ion-pair with DA and adsorption on the NiO nanoparticles MCPE [27].
4.19.5. Effect of scan rate

The effect of scan rate for 10μM DA in 0.2 M PBS at pH 7.0 was studied by CV at NiO nanoparticles MCPE shown in Fig.4.29. NiO nanoparticles MCPE showed increase in the redox peak currents with increase in scan rate (10 to 800mVs⁻¹). The graph of current (ip) vs square root of scan rate (v¹/²) was plotted. The graph obtained was good linearity between the square root of scan rate and peak current shown in Fig.4.30 in the range from 10 – 800 mVs⁻¹. The correlation coefficient (r²) was 0.995, which indicate the electrode reaction was diffusion controlled. The surface area available for the electron transfer to species in solution can be estimated by the Randles–Sevcik equation (1) [28, 29]. This equation relates the peak current for an electron transfer-controlled process with the square root of the scan rate, as follows:

\[
    i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}
\]  

where \(i_p\) is the peak current (A), \(A\) is the electroactive area (cm²), \(C\) is the concentration of the electroactive species (mol cm⁻³), \(n\) is the number of exchanged electrons, \(D\) is the diffusion coefficient(cm² s⁻¹) and \(v\) is the scan rate (V s⁻¹). The values of the diffusion coefficients were obtained from the slopes of \(i_p\) vs \(v^{1/2}\) and by using equation (1) the surface area electrode for NiO nanoparticles MCPE are calculated and the obtained surface area of NiO nanoparticles MCPE at 0.1V s⁻¹ was 0.05277 cm².

The values of the diffusion coefficients were obtained from the both slopes of \(i_p\) vs \(v^{1/2}\) and \(i_c\) vs \(v^{1/2}\) are nearly same this indicates that the diffusion coefficients for the oxidized and reduced species are the same (D) and balanced anodic and cathodic charge transfer coefficient (\(\alpha=0.5\)) [30], \(k^o\) can be determined from the following expression:

\[
    K^o = (nFRT/k)_{1/2} \Psi
\]  

where \(n\) is the number of electrons transferred, \(F\) is the faraday constant, \(R\) is the gas constant, \(T\) is the temperature and \(\Psi\) is dimensionless charge transfer parameter that depends on the peak separation. The values of \(\Psi\) can be found tabulated in the original Nicholson’s paper [30] for values of \((nAEp)\) ranging from 61 to 212mV and the obtained heterogeneous rate constant (\(k^o\)) for NiO nanoparticles MCPE at 0.1Vs⁻¹ is 0.006895 cms⁻¹ greater than the recent reported [29].
4.19.6. Concentration effect of DA

The differential pulse voltammetric technique was used for analysis DA concentration which was varied from 3 to 22 μM shown in Fig. 4.31 for the NiO nanoparticles MCPE with increasing the concentration of DA from 3–22 μM. The graph of \(i_{pa}\) vs concentration of DA showed increase in anodic peak current shown in Fig. 4.32. The linear relationships ranges 0.3–22 μM with the linear regression equations as \(i_{pa} (A) = 0.9615C_{\mu M/L} + 3.586 \times 10^{-5}\). The correlation coefficient for the first linearity was 0.997 the detection limit for DA in the linear range region was found to be \(3.841 \times 10^{-7}M\) for NiO nanoparticles MCPE and which was calculated according to the equation of LOD = \(K S^0/S\), and \(K\) was a constant related to the confidence level. According to the suggestion of the IUPAC, the value of \(K\) was 3 at the 99% confidence level, \(S^0\) was the standard deviation of ten blank-solution measurements (no added DA) and \(S\) was the slope of the calibration graph, the proposed electrode showed relatively lower detection limit than the recent reported [31] and calculated by using same formula. The sensitivity is found to be \(32.05 \mu A/\mu M.cm^2\) from the slope of the calibration plot.

4.19.7. Analytical application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from Sterile Specialties India Private Ltd had a specified content of DA 40.0 mg mL\(^{-1}\) and the sample was used after suitable dilution. The results are shown in Table. 4.3. and the recovery R.S.D. were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in injections with recovery in the range 98.5%.
4.20. Conclusions

1. NiO nanoparticles is synthesized using co-precipitation method.

2. The average crystalline size is found to be 11nm.

3. UV-Visible spectra shows significant blue shift as compared with bulk NiO particles.

4. The SEM micrographs clearly shows irregular shaped NiO nanoparticles, non uniformly distributed and particles size is 50-300 nm.

5. Advantage of this method is convenient for synthesis of NiO nanoparticles in normal laboratory conditions, in low cost.

6. NiO nanoparticles modified carbon paste electrode shows high surface area of electrode, enhanced current sensing, sensitivity 32.05 μA/μM.cm² and higher heterogeneous rate constants (k°) with low detection limit (3.8X10⁻⁷M) as compared with recent related literature.

7. The proposed methods can be applied to the detection of DA in injections. Hence this present synthetic method extended to many metal oxides, ferrites for synthesis and their modified electrode used as sensor for application of determination of biological active compounds, injection sample and other neurotransmitters.
Fig. 4.21. XRD patterns for NiO nanoparticles

Fig. 4.22. IR Spectra of NiO nanoparticles
Fig. 4.23. UV-Visible absorption Spectra of NiO nanoparticles

Fig. 4.24. SEM images of NiO nanoparticles
Fig. 4.25. Cyclic voltammogram of $4 \times 10^{-5}$ M DA in PBS at pH 6.0 at (a) 10 mg of NiO nanoparticles MCPE, (b) 20 mg of NiO nanoparticles MCPE and (c) 30 mg of NiO nanoparticles MCPE

Fig. 4.26. Cyclic voltammogram of $1 \times 10^{-5}$ M DA in PBS at pH 7.0 at solid line for bare CPE and dashed line for NiO nanoparticles MCPE
Fig. 4.27. Cyclic voltammograms of $1 \times 10^{-5}$ M DA in different pH 5.3-7.7 solutions at the NiO nanoparticles MCPE (from right to left).

Fig. 4.28. Graph shows the dependences of the DA oxidation peak current (□) and redox potential (●) on the PBS solution pH with a scanning rate of 100mVs$^{-1}$.
Fig. 4.29. Cyclic voltammograms of NiO nanoparticles MCPE in 0.2M PBS solutions containing 1X10^-5 M DA at different scan rates (10–800 mVs^-1)

Fig. 4.30. Graph the linear relationship between the peak current and the square root of scan rate
Fig. 4.31. DPVs for DA 0.3–22 μM at the NiO nanoparticles MCPE in 0.2M PBS solution at pH of 7.0

![Graph showing DPVs for DA](image)

Fig. 4.32. Graph of $i_{pa}$ vs concentration of DA (0.1–22 μM)

Table 4.3. Detection of DA in injection samples (n = 5)

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<tr>
<th>Sl.No</th>
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4.21. References


