PART-A

SYNTHESIS OF CdO NANOPARTICLES AND THEIR MODIFIED CARBON PASTE ELECTRODE FOR DETERMINATION OF DOPAMINE AND ASCORBIC ACID BY USING CYCLIC VOLTAMMETRY TECHNIQUE

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3.1. Introduction

In this chapter describe, Cadmium oxide (CdO) nanoparticles were prepared using cetyl trimethyl ammonium bromide (CTAB) as surfactant by co-precipitation method, in which cadmium sulphate (CdSO₄) was reacted with sodium hydroxide (NaOH) in the presence of acetic acid, ethanol, CTAB, at room temperature, then thermally treated at 400°C for 4 hours and the obtained product are analyzed by X-ray diffractometer (XRD), the average size of CdO nanoparticles was found to be 47.8nm, UV-visible absorption spectra for CdO nanoparticles shows evidence of quantum size effect, Scanning electron microscopy shows irregular shape having ~50-100nm size. The electrochemical results are compared with bare carbon paste electrode (BCPE) and CdO nanoparticles modified carbon paste electrode (MCPE). The MCPE shows enhanced peak current and exhibited excellent electrocatalytic activity towards detection of dopamine (DA) and ascorbic acid (AA) in acetate buffer solution at pH 6.5.

3.2. Chemistry and Biological Relevance of Dopamine and Ascorbic acid

The chemistry and biological relevance of dopamine and ascorbic acid has been explained in details in chapter 2 section 2.2 to 2.3.2.

3.3. Review of Nanomaterials, Preparation, Dopamine and Ascorbic acid

The science of nanomaterials has created great excitement and expectation in the last decade at the nanoscale fundamental properties changes for example a nanoscale wire or circuit component does not necessarily obey ohm’s law when we reach nanoscale everything will be change, including gold’s color, melting point and chemical properties [1]. Oxide nanomaterials used as catalysts and starting materials for preparing advanced structural ceramics [2-3]. CdO an important n-type semiconductor with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV [4], has promising applications in catalysts [5] sensors [6], nonlinear materials [7], solar cells [8], and other optoelectronic devices etc [9-14]. It has been reported that the physical and chemical properties of CdO are relative to its stoichiometry as well as particle shape and size, which, in turn, depend
on its preparation methods and preparation conditions [9-14]. Recently, hollow nanostructures of inorganic materials have attracted great research attention [14-19] because they exhibit a lower density, higher surface area, and distinct optical property, and in most cases, have improved performances for applications in photonic crystals, fillers, vehicle systems, catalysis, sensing devices. In nanoscience and nanotechnology synthesis forms an essential component. While nanomaterials have been generated by chemical methods have proved to be more effective, as they provide better control as well as enable different sizes, shapes and functionalization than compare with the physical methods such as laser ablation, arc-discharge and evaporation chemical synthesis of nanomaterials has been reviewed by a few authors, (20-26) metal oxide nanoparticles can be produced by soft chemical methods, such as co-precipitation, sol-gel and hydrothermal synthesis [27]. Among these methods co-precipitation has chosen in the present work for synthesis of CdO nanoparticles by using CTAB as surfactant.

AA is one of the most important vitamins, due to its antioxidant and pH regulator properties often being added to various food products and pharmaceuticals [29]. AA exists in mammalian brain in the presence of several other neurotransmitter amines including DA. DA is an important brain neurotransmitter molecule of catecholamine and its deficiency leads to brain disorders such as Parkinson’s disease and Schizophrenia [29-31]. Recently their identification and determination of AA and DA with electrochemical procedures have attracted much attention.

3.4. Experimental

3.4.1. Chemicals and Solutions

Cadmium sulphate, Sodium hydroxide, from S.D fine chemicals. Graphite powder, Acetic acid (99.955%), Ethanol (99.5%), Hydrochloric acid, were from qualigens fine chemicals, CTAB was obtained from Sigma Aldrich Chemicals, Ascorbic acid and Dopamine were purchased from Fluka Chemicals. Acetate buffer was prepared by adjusted the pH with 0.2 M CH₃COONa and CH₃COOH solution. 25mM stock solution of DA was prepared by dissolving in 0.1M perchloric acid solution. 25 mM stock solution of AA was prepared by dissolving in double distilled water.
3.4.2. Apparatus

Cyclic voltammetric experiments were performed with a model EA-201 Electro Analyzer (chemilink systems), equipped with a personal computer was used for electrochemical measurement and treating of data. A conventional three electrode cell was employed throughout the experiments, with bare or CdO nanoparticles modified carbon paste electrode (3.0 mm diameter) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum electrode as a counter electrode.

3.4.3. Preparation of CdO nanoparticles

In a typical experiment first solution prepared using 0.03 M CdSO₄, 0.06 M CH₃COOH and 40 mg CTAB as surfactant in 1 dm³ of double distilled water. The second solution was prepared by 0.09 M NaOH pallets and 25 ml 70% ethanol in 1 dm³ of double distilled water. Then 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. Then dried precipitate was transferred to silica crucible and ignited at 400°C for about 4 hours. Then obtained powder was washed with ethanol three to four times to remove impurities present in the particles.

3.4.4. Characterization

The obtained above nanoparticles were then examined by a Brucker D/MAX 2500 X-ray diffractometer with Cu Kα radiation (λ=1.54056 Å), and the operation voltage and current were maintained at 40 kV and 250 mA, respectively. Samples were measured and recorded using a TU-1901 double-beam UV–visible spectrophotometer were dispersed in toluene solution. Structural morphology of the synthesis NPs was studied using a JEOL JSM-848 scanning electron microscope (SEM).

3.4.5. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (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.
3.4.6. Preparation of CdO nanoparticles modified carbon paste electrode

The CdO nanoparticles modified carbon paste electrode was prepared by hand mixing of 70% graphite powder and 10 mg CdO nanoparticle with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (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.

3.5. Results and Discussion

3.5.1. XRD pattern for CdO nanoparticles

The XRD pattern Fig.3.1 for CdO nanoparticles, the diffraction peaks are absorbed at 20 values. The prominent peaks have been utilized to estimate the grain size of sample with the help of Scherrer equation [32] \[ D = \frac{K\lambda}{\beta \cos \theta} \] where \( K \) is constant (0.9), \( \lambda \) is the wavelength (\( \lambda = 1.5418 \text{ Å} \) (Cu Kα)), \( \beta \) is the full width at the half-maximum of the line and \( \theta \) is the diffraction angle. The grain size estimated using the relative intensity peak (100) for CdO nanoparticles was found to be 47.8 nm and increase in sharpness of XRD peaks indicates that particles are in crystalline nature. The (111), (200), (220), (311) and (222) reflections are clearly seen and closely match the reference patterns for CdO (Joint Committee for Powder Diffraction Studies (JCPDS) File No. 05-0640).

3.5.2. UV–visible absorption spectra for CdO nanoparticles

The UV–visible absorption spectra of CdO nanoparticles are shown in Fig.3.2. although the wavelength of our spectrometer is limited by the light source, the absorption band of the CdO nanoparticles have been shows a blue shift due to the quantum confinement of the excitons present in the sample compare with bulk CdO particles. This optical phenomenon indicates that these nanoparticles show the quantum size effect [33]. Here formation nanoparticle is depend on surfactant and organic solvent because surfactant CTAB helps to bind to the surface of the synthesized nanoparticles, thus acting
as particle stabilizer and tuning the nucleation/growth of particles to achieve a higher
degree of uniformity [34] and acetic acid, ethanol solvent helps to disperse the particle in
uniformly and it help to growth of particles slowly in restricted size and avoid the
aggregation of particles [35].

3.5.3. Scanning electron microscopy (SEM) for CdO nanoparticles

According to the SEM observations reveal that all the products consist of a large
quantity of irregular shape-like structure with size ~50-100 shown in Fig.3.3.

3.5.4. Electrochemical response of dopamine at CdO nanoparticles modified CPE

Electrochemical detection of DA and AA by using carbon paste electrode was
studied by our group (36-39). Fig.3.4. shows the CVs of 1X10^{-5} M DA at bare and CdO
nanoparticles modified CPE at scan rate 100mV/s. The electrochemical response of DA
shows increase in peak current at the CdO nanoparticles modified CPE. At the bare CPE
the cyclic voltammogram of DA (dashed line) shows an oxidation peak potential at
249mV and reduction peak potential at 177 mV. The separation in peak potential (ΔEp) is
72mV which is the characteristic of a quasi-reversible electrode process. At CdO
nanoparticles modified CPE pair of well-defined redox waves of DA was obtained with
an increase of the redox peak current (solid line). The oxidation peak potential occurs at
248mV and reduction peak potential at 172mV respectively, with the peak potential
separation (ΔEp) is 76mV. The negligible shift in the peak potential was observed which
the characteristic of the quasi reversible nature. It was observed that the peak currents
enhanced greatly at CdO nanoparticles modified CPE, which provides high surface area
of the CdO nanoparticles improved the electrode contacting area of DA and its
electrochemistry of reaction product, which increased.

3.5.5. Electrochemical response of Ascorbic acid at CdO nanoparticles modified
CPE

Fig.3.5. shows the CVs of 1X10^{-4} M AA at bare and CdO nanoparticles modified
CPE at scan rate 100mV/s. The electrochemical response of AA shows great increase in
peak current at the CdO nanoparticles modified CPE. At the bare CPE the cyclic
voltammogram of AA (dashed line) shows an oxidation peak potential at 227mV. At CdO nanoparticles modified CPE well defined oxidation wave of AA was obtained with an increase of the oxidation peak current (solid line). The oxidation peak potential occurs at 207mV. It was observed that the peak currents enhanced greatly at CdO nanoparticles modified CPE, which provides evidence for CdO nanoparticles having large surface area possessed highly electrochemical response towards the AA. Thus, we suggest that the mechanism may be as follows: under the condition, CdO nanoparticles may be combined with the hydrogen bond of the hydroxyl of DA and AA, which activated hydroxyl, weakened the bond energy of O-H and improved the electron transfer rate.

3.5.6. The effect of scan rate and concentration of DA on the peak current

The scan rate effect was studied at modified electrode in the range from 50 to 300 mVs$^{-1}$ showed linear response on peak currents with square root of scan rate. The result indicated that the electron transfer reaction was controlled by diffusion shown in Fig.3.6.

3.5.7. Concentration effect of DA and AA on peak current

By increasing the concentration of DA from $1\times10^{-5}$ to $6\times10^{-5}$M and AA from $1\times10^{-4}$ to $6\times10^{-4}$M. The graph obtained linearly increased in peak current with increased in the DA and AA concentration and $i_{pa}$ is proportional to concentration of DA and AA. The correlation coefficient for the linearity was 0.999 shown in Fig.3.7 and Fig.3.8. respectively, from slope of calibration plot the sensitivity and detection limit is calculated using statistical formula found to be $0.47 \mu A/\mu M.cm^{2}$ for DA, $0.0416 \mu A/\mu M.cm^{2}$ for AA and detection limit found to be $5\mu M$ for DA and $50 \mu M$ for AA.
3.6. Conclusions

- This report has shown that synthesis of CdO nanoparticles using CTAB as surfactant by co-precipitation method from XRD data obtained size was 47.8 nm.

- The absorption spectra show evidence quantum confinement effect.

- SEM image shows irregular shapes with ~50-100 nm size.

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

- The synthesized CdO nanoparticles modified CPE act as good electrode for determination of dopamine and ascorbic acid using cyclic voltammetry.

- Sensitivity is found be 0.47 μA/μM.cm² for DA and 0.0416 μA/μM.cm² for AA.

- Detection limit is found to be 5 μM for DA and 50 μM for AA.

- Hence this current synthetic method extended to many metaloxides, ferrites for synthesis and their modified electrode used as sensor application for determination of biological active compounds.
Fig. 3.1. XRD pattern for CdO nanoparticles

Fig. 3.2. UV-Absorption spectra for CdO nanoparticles
Fig. 3.3. SEM image of CdO nanoparticles

Fig. 3.4. Cyclic voltammogram of 1X10^{-5} M DA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line)
Fig. 3.5. Cyclic voltammogram of $1 \times 10^{-4}$M AA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line).

Fig. 3.6. Graph of anodic peak ($i_{pa}$) vs square of scan rate for DA

$R^2 = 0.995$
Fig. 3.7. Graph of anodic peak ($i_{pa}$) vs conc of DA (10 to 60 μM)

Fig. 3.8. Graph of anodic peak ($i_{pa}$) vs conc of AA (100 to 600 μM)
3.7. References


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PART-B

SYNTHESIS OF MgO NANOTHIN FLAKES AND THEIR APPLICATION AS A SENSOR FOR DETERMINATION OF DOPAMINE: A CYCLIC VOLTAMMETRIC STUDY


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3.8. Introduction

This part involves the MgO nanothin flakes has been synthesized by co-precipitation method at room temperature in the presence of cetyltrimethylammonium bromide (CTAB, \( \text{C}_{15}\text{H}_{31}\text{N}^+(\text{CH}_3)_3\text{Br}^- \)) surfactant. The procedure explained in this method gives particles with nanothin flakes. X-ray defraction (XRD) results showed face-centered cubic structures, scanning electron microscopy (SEM) and infrared (IR) spectroscopy were used to characterize MgO particles. The resulting particles were used to modify carbon paste electrode (MCPE) as sensor for determination of dopamine. The result shows very good electrocatalytic activity towards the detection of dopamine and effect of concentration and scan rate was studied.

3.9. Chemistry and Biological Relevance of Dopamine

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

3.10. Review of MgO, MgO nanoparticles, Dopamine and nanoparticle modified electrodes

Magnesium oxide (MgO) is one of the important ceramic materials with different applications like refractory material in industries, paint, catalysis, and superconductors. The different morphologies of MgO, such as nanotube [1], nanoplate [2], flowerlike nano-structures [3] nano-MgO-chit nanocomposite matrix [4], microsphere [5] and Mg (OH)\(_2\), ZnO nanoflakes [6-7] have been prepared and there are few reports [4,8 ]where MgO nanostructures used as biosensors.

Dopamine is an important brain neurotransmitter molecule of catecholamine and its deficiency leads to brain disorders such as Parkinson’s disease and Schizophrenia [9]. Recently, their identification and determination of DA with electrochemical procedures have attracted much attention. Electrochemical detection of DA and AA by using LaFeO\(_3\), CdO nanoparticles and some chemical compounds modified Carbon Paste Electrode was studied [10-15].
3.11. Experimental Part

3.11.1. Apparatus

Cyclic voltammetric experiments were performed with a model EA-201 Electro Analyzer (Chemilink systems). A conventional three electrode cell is employed. The bare or MgO nanothin flakes modified carbon paste electrode (3.0mm diameter) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum electrode as a counter electrode. X-ray diffraction (XRD) studies using a Phillips (with X’lerator detector) X-ray diffractometer. Structural morphology of the synthesis nanoparticles is studied using a JEOL JSM-848 scanning electron microscope (SEM). Structural characterization of the MgO nanothin flakes experimental was carried out by using Perkin Elmer 157 Infrared Spectrometer.

3.11.2. Chemicals and Solutions

Potassium ferrocyanide (K4Fe(CN)6), Magnesium sulphate (MgSO4) and perchloric acid (HClO4) were purchased from sd. Fine chemicals. Dopamine hydrochloride, Potassium chloride (KCl), Sodium dihydrogen orthophosphate (NaH2PO4), disodium hydrogen phosphate (Na2HPO4), silicon oil from Hi Media chemicals. Magnesium Oxide (MgO), CTAB, absolute ethanol (99.9%), Sodium hydroxide (NaOH), acetic acid were from Merck and graphite powder from loba chemicals and all chemicals are of analytical grade quality. Dopamine stock solutions (25 mM) were prepared by adding dopamine to 0.1 M perchloric acid, 25 mM potassium ferrocyanide was prepared in double distilled water and the supporting electrolyte used was 1 M KCl. Phosphate buffer is prepared by adjusted the pH with 0.2 M NaH2PO4 and Na2HPO4 solution. All the aqueous solution were prepared by using double distilled water.

3.11.3. Preparation of MgO nanothin flakes particles

In a typical experiment, the first solution 3.7g MgSO₄·6H₂O, 3ml of concentrated acetic acid and 10mg CTAB as surfactant is dissolved in 250ml of deionised water and the second solution was prepared by 1.8g NaOH pallets, 25 ml absolute alcohol in 250ml
of distilled water. The first solution is added to second solution with continues stirring. The obtained precipitate is filtered by using Whatmann filter paper (grade-41) and dried at 80°C in hot air oven about 1 hour. The dried precipitate is transferred to silica crucible and ignited at 350°C for about 4 hours. Then obtained powder was washed with ethanol three to four times to remove impurities present in MgO nanothin flakes.

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

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 70% graphite powder with 30% 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 MgO nanothin flakes to above mentioned graphite powder and silicon oil mixture and same procedure followed for preparation of commercial MgO MCPE.

3.12. Results and Discussion

3.12.1. Characterization

XRD pattern of the product shows a pure structure with high crystallinity shown in Fig. 3.9 and all diffraction peaks are well indexed to Face centered cubic MgO particles (a = 4.209 Å, JCPDS PDF, no. 77-2364). The crystalline size estimated using the relative intensity peak (100) for MgO nanoparticles was found to be 26 nm and increase in sharpness of XRD peaks indicates that particles are in crystalline nature.

According to the SEM observations reveal that all the products consist of a large quantity of flake-like with typical length in the range of several micrometers with a tendency to form 40-50 nm thin MgO flakes shown in Fig. 3.10.

The IR spectra in the range 4000–400 cm⁻¹ of MgO nanothin flakes are shown in Fig. 3.11. Some bands are observed in the region 2800–3000 cm⁻¹ and attributed to CTAB surfactants [16-18]. CTAB IR spectra show two intense bands, assigned to asymmetric (2924 cm⁻¹) and symmetric (2852 cm⁻¹) stretching vibrations of C-CH₂ in the methylene chains. The sharp bands in the region of 1495 and1426 cm⁻¹ are attributed to the deformation of –CH₂– and –CH₃ [18] of the incorporated surfactants. The weak band detected in the region of 2924 and 2852 cm⁻¹ is assigned to C-CH₃ asymmetric stretching
and N-CH₃ symmetric stretching vibrations of solid surfactant. These band vibrations provide evidence for the incorporation of CTAB into the Magnesium Oxide. The broad band between 3200 and 3600 cm⁻¹ and the band centered at 1630 cm⁻¹ found on all samples are assigned to O–H stretching and deformation vibrations of weak-bound water and furthermore the presence of bands at 1111, 1012, and 861 cm⁻¹ clearly indicate the binding of CTAB molecules to the MgO [19, 20]. The broad band’s 441 cm⁻¹ and small peak 793 cm⁻¹ are attributed to the framework vibrations of Magnesium oxide [20].

The probable mechanism could be as follows, Mg²⁺ ion is precipitate as Mg(OH)₂ which is surrounded by thin layer of CTA⁺ chain in spherical manner. After calcinations at 350°C the water molecule will be eliminated to forms a flake like structure with thin layer of CTA⁺ chain associated with MgO particles. So here thin layer of CTA⁺ chain plays very important role in the formation of shape and avoids aggregations of the particles. It has been reported that acetic acid can be used to reduce the particle size of ZnO and CuO colloids in ethanol by dissolution [21, 22]. Thus we suggested that the addition of acetic acid and ethanol suppressed particle growth.

3.12.2. Electrochemical investigation of potassium ferrocyanide at modified CPE

Ferrocyanide is the name of the anion K₄[Fe(CN)₆]⁺ in aqueous solutions. It is usually available as the potassium salt potassium ferrocyanide, which has the formula K₄Fe(CN)₆. [Fe(CN)₆]⁻ is a diamagnetic species, featuring low-spin iron (II) center in an octahedral ligand environment [23]. Potassium ferrocyanide was selected to evaluate the performance of the proposed electrode. Fig 3.12 shows the electrochemical response of potassium ferrocyanide at the (A) bare, (B) commercial MgO modified CPE and (C) MgO nanothin flakes modified CPE in 1 M KCl containing 1 mM K₄[Fe(CN)₆] at 50 mV/s. A comparison between the anodic and cathodic peaks for ferrocyanide shows that (ΔEp) is 0.061 V for MgO Nanothin flakes modified CPE, 0.077 V for bare CPE and 0.0844V for commercial MgO modified CPE. As ΔEp is a function of the rate of electron transfer, the lower ΔEp, the higher electron transfer rate. The results obtained greatly improved the voltammetric response of potassium ferrocyanide at MgO nanothin flakes modified CPE reflected by the enlargement of peak current and the decline of peak potential (ΔEp = 0.061 V). This indicates that the modified electrode as electrocatalytic activity. Based on the above observations the MgO nanothin flakes modified CPE had favorable and stable electrochemical behavior. It might be used as MgO nanothin flakes modified electrode to explore electroanalytical applications.
3.12.3. Effect of MgO nanothin flakes on peak current

The effect of MgO nanothin flakes concentration in the carbon paste electrode on the peak current for the investigation of 1 mM Ferrocyanide in 1M KCl was studied by CV. The modified carbon paste electrode with 10 mg of MgO nanothin flakes enhanced high anodic peak current as compared with the 2, 4, 6, 8 and 12 mg of MgO nanothin flakes. The graph (Fig.3.13) shown relation between anodic peak current ($i_{pa}$) Vs concentration of MgO nanothin flakes in carbon paste electrode.

3.12.4. Effect of MgO nanothin flakes on potential difference ($\Delta E_p$)

The effect of MgO nanothin flakes concentration in carbon paste electrode on the peak potential difference ($\Delta E_p$) for the investigation of 1 mM Ferrocyanide in 1M KCl was studied by CV technique. The modified carbon paste electrode with 10 mg of MgO nanothin flakes decrease in the peak potential difference ($\Delta E_p$) as compared with the 2, 4, 6, 8 and 12 mg of MgO nanothin flakes. The graph Fig.3.14. shown relation between potential difference ($\Delta E_p$) Vs concentration of MgO nanothin flakes in carbon paste electrode.

From the above results increase in peak current with decrease in peak potential difference ($\Delta E_p$) was observed at 10 mg MgO nanothin flakes MCPE gives good sensitivity and electrocatalytic property. So in this paper we used 10 mg of MgO nanothin flakes to modified carbon paste electrode for electrochemical investigation of dopamine (DA).

3.12.5. The response of DA at the bare, and MgO nanothin flakes modified carbon paste electrode

The electrochemical responses of 1X10^{-5} M DA in 0.2M phosphate buffer solution of pH 7.2 at the bare carbon paste electrode (BCPE) and the MgO nanothin flakes modified carbon paste electrode (MCPE) with scan rate 100 mV/s was shown in Fig.3.15. At the BCPE, the difference between the anodic peak potential (Epa) 0.235 V and the cathodic peak potential (Epc) 0.148 V is quasi reversible wave with $\Delta E_p$ 87 mV, However a well-defined redox wave of DA was observed and the peak currents
significantly increased at the MCPE, with the anodic peak potential shifting negatively to 0.204 V and the corresponding cathodic peak potential is 0.145 V and corresponding $\Delta E_p$ 59 mV.

Compared with that at bare carbon paste electrode the remarkable enhancement in the peak currents and the lowering of over potential showed catalytic effects of the MgO nanothin flakes. The mechanism could be as follows: Under the condition, MgO regular arranged flake-like architecture particles 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 MgO nanothin flakes improved the electrode contacting area of DA.

3.12.6. The effect of scan rate on the peak current

The effect of scan rate for DA in phosphate buffer was studied by CV at MgO nanothin flakes modified CPE. MgO Nano thin flakes modified CPE showed increase in the redox peak current with increase in scan rate (50 to 120 mVs$^{-1}$). The graph of current ($i_{pa}$) vs scan rate (v) was plotted. The graph obtained was good linearity between the scan rate and $i_{pa}$ (Figure 3.16). In the range from 50 – 120 mVs$^{-1}$ the anodic peak currents were proportional to the scan rate (v). The correlation coefficient ($r^2$) was 0.9993, which indicate the electrode reaction was adsorption controlled.

3.12.7. Concentration effect of DA on peak current

By increasing the concentration of DA from $2 \times 10^{-7}$ to $10 \times 10^{-7}$M, The graph of $i_{pa}$ vs concentration of DA showed increase in anodic peak current Fig. 3.17. The graph obtained linearly increased in peak current with increased in the DA concentration and $i_{pa}$ is proportional to concentration of DA. The correlation coefficient for the linearity was 0.99997. From slope of calibration plot the sensitivity and detection limit is calculated using statistical formula was found to be 65 $\mu$A/µM.cm$^2$ sensitivity and detection limit is 0.1 $\mu$M for DA.
3.13. Conclusions

- This report has shown that synthesis of MgO nanothin flakes using CTAB as surfactant by co-precipitation method and XRD data obtained particle size was ~26 nm.

- SEM image shows flakes shapes with 40-50 nm thin size.

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

- The synthesized MgO nanoparticles modified CPE exhibit excellent electrocatalytic activity compared with bare CPE and commercial MgO particle modified CPE for determination of dopamine using cyclic voltammetry.

- The enhanced sensitivity (65 μA/μM.cm²) and low detection limit (0.1 μM) for DA compared with chapter-3A CdO nanoparticles modified carbon paste electrode.

- Hence this current synthetic method extended to many metaloxides, ferrites for synthesis and their modified electrode used as sensor application for determination of biological active compounds
Fig. 3.9. XRD pattern for MgO nanothin flakes
Fig. 3.10. SEM image for MgO nanothin flakes
Fig. 3.11. IR Spectra for MgO nanothin flakes

Fig. 3.12. Cyclic voltammogram of 1X10⁻³ M Ferrocynide at (A) bare CPE (BCPE), (B) Commercial Mgo modified CPE, (C) MgO nanothin flakes modified CPE (MCPE)
Fig. 3.13. Plot of concentration of MgO nanothin flakes in CPE vs anodic peak current

Fig. 3.14. Plot of concentration of MgO nanothin flakes in CPE vs Potential difference $\Delta E_p$ (V)
Fig. 3.15. Cyclic voltammogram of $1 \times 10^{-5}$ M DA at MgO nanothin flakes modified CPE (Solid line) and at bare CPE (dashed line).

Fig. 3.16. Graph of Scan rate vs anodic peak current ($i_{pa}$).
Fig. 3.17. Graph of Concentration of $2 \times 10^{-7}$ M to $10 \times 10^{-7}$ M DA (V) vs anodic peak current ($i_{pa}$)
3.14. References

Chapter - III

PART-C

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

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3.15. Introduction

ZnO nanoparticles was synthesized by using zinc nitrate, cetyltrimethyl ammonium bromide 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 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 0.3X10^-8 M.

3.16. 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.

3.17. Review of ZnO nanoparticles, Cyclic Voltammetry of Dopamine

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 nanometaloxide MCPE [3, 10-12] shows good 
sensors for detection of DA was studied.

3.18. Experimental Methods

3.18.1 Apparatus

The ZnO nanoparticles were characterized by various techniques such as Powder 
XRD patterns are recorded for using Cu-Ka 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. 
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.

3.18.2. 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 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.
3.18.3. Preparation of ZnO nanoparticles

In a typical experiment, the first solution contains 0.01M ZnNO₃, 0.02M CTAB 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 nanoparticles.

3.18.4. 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, 30mg and 40mg ZnO nanoparticles to above mentioned graphite powder and silicon oil mixture.

3.19. Results and Discussion

3.19.1. Characterization

The XRD pattern of the as-obtained ZnO nanoparticles is shown in Fig. 3.18. 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 particle size of the particles was 62 nm.

The IR transmittance spectrum for the ZnO nanoparticles synthesized by using CTAB was displayed in Fig. 3.19. 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-CH₂ in the methylene chains. The sharp bands in the region of 1439 cm⁻¹ are attributed to the deformation of −CH₂− and −CH₃[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–Visible 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.3.20. The results of UV–visible absorption spectra for ZnO nanoparticles shows good blue shift with enhanced band gap 3.49eV.

The morphological of ZnO nanoparticles shows the flower-like with 4 to 5 petals were grown, each petals have tip ~50-60nm, tapering width ~100nm, width ~160nm and length is ~200nm structures and non-uniformly distributed is shown in Fig. 3.21.

### 3.19.2. 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 1X10\(^{-5}\) M DA in 0.2M phosphate buffer solution of pH 7.0 was studied by CV method. The modified carbon paste electrode with 30mg of ZnO nanoparticles enhanced high anodic peak current as compared with the bare CPE, 10, 20, 30 and 40mg of ZnO nanoparticles as shown in Fig.3.22.

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

Fig.3.23 shows the electrochemical responses of 1X10\(^{-5}\) M DA in 0.2M phosphate buffer solution of pH 7.0 at the bare CPE and the ZnO nanoparticles MCPE with scan rate 100 mV/s. Compared with that at 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.
3.19.4. 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. 3.24. 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 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 (shown with closed circles (•)). 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 slope of 53.3mV/pH (shown with line (0)). It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which was consistent with that reported in literature [3].

3.19.5. Effect of scan rate

The effect of scan rate for \(1\times10^{-5}\) 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 800mVs\(^{-1}\)). The graph of current (I) vs scan rate (v) was plotted. The graph obtained was good linearity between scan rate and peak current shown in Fig.3.25 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.

3.19.6. Concentration effect of DA

The differential pulse voltammetric technique was used for the analysis DA concentration which varied from 0.1 to 20 \(\mu\)M shown in Fig. 3.26 for the ZnO nanoparticles MCPE. By increasing the concentration of DA from 0.1 to 20 \(\mu\)M. The graph of \(i_{pa}\) vs concentration of DA showed increase in anodic peak current as shown in Fig. 3.27. The linear relationship ranges 0.3–22 \(\mu\)M with the linear regression equation as 
\[
\text{i}_{pa} (\mu A) = 3.5396C_{\mu M/L}+1.489\times10^{-7}
\]

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^{-8} \text{M} \text{ for ZnO nanoparticles MCPE and which was calculated according recent reported [17] and sensitivity is found to be 117.98 \ \mu \text{A}/\mu \text{M} \cdot \text{cm}^2.}

3.20. Conclusions

- ZnO nanoparticles with average crystalline size 62nm with significant blue shift of band gap 3.49eV have been synthesized by co-precipitation method.

- The IR spectra show surfactant CTAB capped around ZnO nanoparticles.

- The SEM image of ZnO nanoparticles shows flower-like with 4 to 5 petals were grown, each petals have tip ~50-60nm, tapering width ~100nm, width ~160nm and length is ~250nm structures.

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

- The ZnO nanoparticle modified carbon paste electrode shows good electrocatalytic activity and enhanced current sensitivity is 117.98 \ \mu \text{A}/\mu \text{M} \cdot \text{cm}^2 \text{ and low detection limit (0.3X10^{-8} \text{M}) compared with chapter-3A and 3B CdO and MgO nanoparticles modified carbon paste electrode.}

- 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. 3.18. XRD patterns for ZnO nanoparticles

Fig. 3.19. IR Spectra of ZnO nanoparticles
Fig. 3.20. UV-Visible absorption Spectra of ZnO nanoparticles

Fig. 3.21. SEM image of ZnO nanoparticles
Fig. 3.22. Graph between anodic peak current ($i_{pa}$) versus different concentration of ZnO nanoparticles in CPE.

Fig. 3.23. Cyclic voltammogram of 1X10$^{-5}$ M DA in PBS at pH 7.0 at solid line for bare CPE and solid line for ZnO nanoparticles MCPE.
Fig. 3.24. Graph shows the dependences of the DA oxidation peak current in closed circles (●) and redox potential (○) on the PBS solution pH with a scanning rate of 100mVs⁻¹.

Fig. 3.25. Graph the linear relationship between the peak current versus the different scan rate (10–800mVs⁻¹) in 0.2M PBS solutions at pH 7.0.
Fig. 3.26. Differential pulse voltammogram of (a) $1.0 \times 10^{-7}$ M, (b) $2 \times 10^{-7}$ M, (c) $4 \times 10^{-7}$ M, (d) $6 \times 10^{-7}$ M, (e) $8 \times 10^{-7}$ M, (f) $10.0 \times 10^{-7}$ M, (g) $12.0 \times 10^{-7}$ M, (h) $14.0 \times 10^{-7}$ M, (i) $16.0 \times 10^{-7}$ M, (j) $18.0 \times 10^{-7}$ M and (k) $20.0 \times 10^{-7}$ M DA in 0.2M phosphate buffer solution of pH 7.0 at ZnO nanoparticles MCPE.

Fig. 3.27. Graph of $i_{pa}$ vs concentration of DA (0.1–20 μM)
3.21. References


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