SUMMARY OF THE THESIS

The focus of the work covered in this thesis was the preparation of some nanometaloxides (CuO, CdO, NiO, MgO, ZnO and NiO/ZnO) particles using inexpensive methods like co-precipitation, solution and microemulsion method based on a modified version of the reported in the literature. The obtained nanometaloxide particles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared absorption spectroscopy (IR) and UV-visible absorption spectroscopy (UV-vis). The fabrication of nanometaloxide based electrochemical sensor extremely interesting materials for biosensor applications. The different nanometaloxide particles were prepared and carbon paste electrode was chosen for fabrication of nanometaloxide based carbon paste electrochemical sensor. Because controllably alter the properties of carbon surfaces, surface as it is highly conducting with a wide potential window, structurally stable, relatively inexpensive and metal oxide nanoparticles easily and uniformly mixed in carbon paste electrode. The carbon powder was selected and was used to study the structure and electrochemical properties of the neurotransmitters and the process taking place across the interface of the nanometaloxide based electrode surface and the electrolyte. A species capable of undergoing electron transfer process is called an electroactive species. In order to carry out electron transfer process with the electrode, the electroactive species comes from the bulk solution and approaches the electrode surface.

The following aspects like, number of electrons involved in the electrochemical reaction, electrochemical sensing, rate constants, surface area of electrode, nature of intermediates in the electrode reaction, detection limit and nature of electrode process were investigated.
Organization of the Thesis

The work carried out in this thesis is divided and described into seven chapters.

Chapter–1

Introduction, review of nanometaloxide, voltammetry and theoretical considerations

This chapter covers the introduction, preparation of nanometaloxide, characterization and voltammetric techniques and their theoretical aspects have been described. Basic principles, theory theoretical considerations and applications of cyclic voltammetry, solvents, supporting electrolytes and electrodes. Brief literature survey of cyclic voltammetric investigations of dopamine and dopamine in presence of ascorbic acid, uric acid has been reviewed. The electrode processes, objectives and scope of the present work is also included in this chapter.

Chapter - 2

CuO nanoparticle sensor for the electrochemical determination of dopamine

In this chapter, the different shaped CuO nanoparticles were synthesized using cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in a co-precipitation method. The CuO nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared absorption spectroscopy (IR) and UV–visible absorption spectroscopy (UV–vis). The prepared CuO nanoparticles were used for the preparation of modified carbon-paste electrodes (MCPE) for the electrochemical detection of dopamine (DA) at pH 6.0. The MCPE prepared from flake-shaped CuO nanoparticles exhibited an enhanced current response for DA. Electrochemical parameters, such as the surface area of the electrode, the heterogeneous rate constant (ks) and the lower detection limit (5.5 ×10⁻⁸ M), were calculated and compared with those of the MCPE prepared from rod-shaped CuO nanoparticles. The MCPE prepared from SDS/polyglycine/flake-shaped CuO nanoparticles exhibited a further improved current response for DA and a high selectivity (EAA – EDA = 0.28 V) for the simultaneous investigation of DA and ascorbic acid (AA)
Summary of the Thesis

at pH 6.0. The modified carbon-paste electrochemical sensors were compared and the MCPE prepared from SDS/polyglycineflake-shaped CuO nanoparticles exhibited better performance than the MCPE prepared from CTAB/polyglycineflake-shaped CuO nanoparticles.

Chapter - 3

This chapter divided into three parts such as Part-A, Part-B and Part-C

Part - A

Synthesis of CdO nanoparticles and their modified carbon paste electrode for determination of dopamine and ascorbic acid by using cyclic voltammetry technique

Cadmium oxide (CdO) nanoparticles were prepared using cetyltrimethyl 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 diffraction (XRD), the average size of CdO nanoparticles 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). The CdO nanoparticles modified carbon paste electrode (MCPE) shows enhanced peak current and exhibited excellent electrocatalytic activity towards oxidation of dopamine (DA) and ascorbic acid (AA) in acetate buffer solution at pH 6.5.

Part - B

Synthesis of MgO nanothin flakes and their application as a sensor for determination of dopamine: A cyclic voltammetric study

MgO nanothin flakes has been synthesized by co-precipitation method at room temperature in the presence of cetyltrimethylammonium bromide (CTAB, CH₃(CH₂)₁₅ N⁺(CH₃)₃Br⁻) surfactant. The procedure explained in this method gives particles with
Summary of the Thesis

nanothin flakes. X-ray diffraction (XRD) results showed face-centered cubic structures, scanning electron microscopy (SEM) and infrared absorption spectroscopy (IR) were used to characterize MgO nanoparticles. The resulting nanoparticles 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.

Part - C

Cationic surfactants-assisted synthesis of ZnO nanoparticles and their modified carbon paste electrode for electrochemical investigation of dopamine

A ZnO nanoparticle was synthesized using zinc nitrate, cetyltrimethylammonium bromide and sodium hydroxide by co-precipitation method. The particles were characterized by using X-ray diffraction (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). This 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 53mV/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 0.1-20µM. The detection limit was found to be 0.3X10⁻⁸ M.

Chapter - 4

This chapter divided into three parts such as Part-A, Part-B and Part-C.

Part - A

Synthesis of MgFe₂O₄ nanoparticles and MgFe₂O₄ nanoparticles/CPE for electrochemical investigation of dopamine

Magnesium ferrite nanoparticles (MgFe₂O₄ NPs) were prepared by a solution based method using magnesium sulphate (MgSO₄), ferrous sulphate (FeSO₄), 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 diffraction (XRD) and scanning electron microscopy (SEM). The MgFe₂O₄ NPs were used for preparation of
MgFe₂O₄ NPs/carbon paste electrode (MgFe₂O₄ 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.

Part - B

Anionic surfactants-assisted synthesis of ZnO nanoparticles and their modified carbon paste electrode for electrochemical investigation of dopamine

ZnO nanoparticle (Nps) was synthesized 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–vis), 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). This 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. The electrocatalytic currents increase 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. The proposed method was successfully applied to the determination of DA in injection samples.

Part - C

Synthesis of NiO nanoparticles and their modified carbon paste electrode for electrochemical investigation of dopamine

A NiO nanoparticle was synthesized using nickel sulphate, acetic acid, ethanol and sodium hydroxide by co-precipitation method. The particles were characterized 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. The electrocatalytic currents increase linearly with increase in DA concentrations in the ranges of 3-22 μM. The detection limit was found to be 3.8X10^−7M. The proposed method was successfully applied to the determination of DA in injection samples.

Chapter - 5

Electrochemical investigation of dopamine by using different shaped NiO nanoparticles

In the present work, different shaped NiO nanoparticles were synthesized using cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) by co-precipitation method. The NiO nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-visible absorption spectroscopy (UV-Vis). The prepared NiO nanoparticles were used for the preparation of modified carbon-paste electrodes (MCPE) for the electrochemical study of potassium ferrocyanide K₄[Fe(CN)₆] and dopamine (DA). The MCPE prepared from flake-shaped NiO nanoparticles exhibited an enhanced current response for K₄[Fe(CN)₆] and DA. Electrochemical parameters, such as the surface area of the electrode and the heterogeneous rate constant (k°), were calculated and compared with those of the MCPE prepared from irregular-shaped NiO nanoparticles. The MCPE prepared from SDS/polyglycine Flake-shaped NiO nanoparticles exhibited a further improved peak current response and successfully investigated DA in presence of Ascorbic acid (AA), Uric acid (UA) and Bisphenol-A (BPA) at physiological pH 7.4 and results are compared with MCPE prepared from flake-shaped NiO nanoparticles.
Chapter - 6
Screening of ZnO nanoparticles as an electrochemical sensor for bioactive molecules

In this chapter, ZnO nanoparticles (ZnO NPs) were synthesized using anionic, cationic, amphoteric and nonionic types of surfactant in aqueous solution, water and ethanol mixture by solution method. The synthesized products were well characterized using X-ray diffraction (XRD), infrared absorption spectroscopy (IR), thermogravimetric and differential thermal analysis (TGA-DTA), UV-visible absorption spectroscopy (UV-vis), fluorescence spectroscopy and scanning electron microscopy (SEM). The prepared ZnO nanoparticles were used for the preparation of modified carbon-paste electrodes (MCPE) for the electrocatalytic detection of dopamine (DA) at pH 7.4. The MCPE prepared from ZnO nanoparticles exhibited an enhanced redox peak currents response for DA. Electrochemical parameters, such as the surface area of electrode, the heterogeneous rate constant were evaluated and the cationic surfactant (cetriamide, CA) assisted ZnO NPs modified MCPE showed a better performance compared to the rest of the modified electrodes. This MCPE acts as a good electrochemical sensor for the detection of bioactive molecules, such as DA, uric acid (UA), ascorbic acid (AA), tryptophan (Trp) and serotonin (5-HT) in physiological pH. The proposed method was successfully applied for detection of DA in blood serum and injection samples.

Chapter - 7
Preparation of NiO/ZnO hybrid nanoparticles for electrochemical sensing of dopamine and uric acid

The NiO/ZnO hybrid nanoparticles were synthesized using sodium dodecyl sulfate (SDS) in a micro-emulsion method. The NiO/ZnO nanoparticles were characterized using X-ray diffraction, scanning electron microscopy, UV-visible absorption spectroscopy, infrared absorption spectroscopy and energy dispersive X-ray spectrum. The obtained NiO/ZnO hybrid nanoparticles were used for the preparation of modified carbon paste electrode (MCPE) for electrochemical detection of dopamine and uric acid at physiological pH 7.4. The MCPE exhibits enhanced electrochemical parameters such as peak current response, surface area of electrode, electrocatalytic activity, diffusion-coefficient, lower detection limit, sensitivity and higher linear range. The proposed method was successfully applied for the detection of dopamine and uric acid in real samples.