Metal Oxide Nanoparticles/Multi-walled Carbon Nanotube Nanocomposite Modified Electrode for the Detection of Dopamine: Comparative Electrochemical Study

Omolola E Fayemi1,2, Abolanle S Adekunle1,2,3 and Eno E Ebenso1,2*

1Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
2Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
3Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

Abstract

Electrochemical properties and sensor application of multi-walled carbon nanotubes (MWCNTs), doped with metal oxides [(MO=nickel oxide (NiO), zinc oxide (ZnO) and iron oxide (Fe3O4)] nanoparticles was investigated using FTIR, XRD, UV-vis spectroscopy, Raman spectroscopy, TEM, SEM, EDX, and cyclic voltammetry techniques. Electrochemical oxidation of dopamine on a glassy carbon electrode (GCE) modified with multi-walled carbon nanotubes doped with metal oxides (GCE/MWCNT/NiO, GCE/MWCNT/ZnO, GCE/MWCNT/Fe3O4) was examined by cyclic voltammetry, EIS and square wave voltammetry in 0.1 M phosphate buffer solution PBS at pH 7. The results were compared with those obtained on bare GCE, GCE/MWCNT and MO GCE modified electrodes (GCE/NiO, GCE/ZnO, GCE/Fe3O4). All electrodes were conditioned at potential of 0.2 V (vs Ag/AgCl, sat’d KCl) in DA solution for EIS experiment. It was found that the multi-walled carbon nanotubes improve remarkably the reactivity of NiO, ZnO and Fe3O4 for dopamine oxidation. The GCE/MWCNT/NiO, GCE/MWCNT/ZnO, GCE/MWCNT/Fe3O4 electrodes exhibited good linear properties in the concentration range from 4 × 10-5 M to 6.25 μM for the quantitative analysis of dopamine (DA) with a limit of detection of 7.99 × 10-12 M, 3.742 × 10-12 M and 1.386 × 10-10 M respectively. The limit of detection of GCE/MWCNT/NiO was better than the other two nanocomposites modified electrodes. The interference study also revealed no AA interference signal at AA concentration 1000 times that of DA. The DPV techniques give well distinct peaks for the DA and AA and a wider separation potential. The prepared electrode exhibited satisfactory stability and long shelf life when stored at ambient conditions. It has been demonstrated that the GCE/MWCNT/NiO modified electrode can be successfully used for the assay of dopamine in some real samples.

Keywords: Nanoparticles; Nickel oxide; Zinc oxide; Iron oxide; Multi-walled carbon nano-tubes; Glassy carbon electrode; Dopamine; Cyclic voltammetry; Square wave voltammetry

Introduction

There is significant interest in developing electrochemical techniques for determination of neurotransmitters such as dopamine (DA). DA is ever-present neurotransmitter in mammalian brain tissues that plays an important physiological role in the functioning of central nervous, renal, hormonal and cardiovascular systems as an extra cellular chemical messenger [1,2]. DA belongs to the family of inhibitory neurotransmitters; its function is to regulate neural interactions by reducing the permeability of gap junctions between adjacent neurons of the same type. In addition, neuro degeneration of DA-containing neurons contributes to late-onset neurological diseases, including Parkinson’s and Alzheimer’s diseases, and possibly to normal ageing of the brain [3]. Besides, numerous reports have shown its coexistence in biological systems [4,5]. Therefore investigation of neurological behavior and also simultaneous determination of DA is of great importance for the elucidation of its precise physiological functions.

A range of analytical techniques such as chromatographic methods, mass spectroscopy [6], spectrophotometry [7] and chemiluminescence [8] are reported in the literature for detection of DA. However these methods suffer from some disadvantages including long analysis times, high costs, the requirement for sample pretreatment, and in some cases low sensitivity and selectivity. These disadvantages probably make them unsuitable for routine analysis. The advantages of electrochemical methods for determination of DA include low cost, high sensitivity and short measurement time. However, the electrochemical measurement of neurotransmitter concentrations has been mainly unsatisfactory due to the inability of the electrodes employed to separate the potentials of these species sufficiently to allow for accurate detection. Ascorbic acid (AA) is usually present in vivo at concentrations 100-1000 times higher than the neurotransmitters. Obviously, it is necessary to develop selective and sensitive techniques to resolve these problems. Therefore, various electrochemical approaches have been made to overcome these difficulties for the determination of DA [9-14].

The attractive features of the multi-walled carbon nano-tubes (MWCNTs) including their unique mechanical and electrical properties are significant advantages in the design and development of...
The electrochemical sensors [13-15]. Furthermore, MWCNTs modified by the adsorption of small organic molecules or metal nanoparticles via redox or electro-deposition can be used to determine H₂O₂ iodate dopamine (DA), organic small molecules, inorganic ion and even widely used as catalytic electrodes of fuel cells [16-25]. Multilayered carbon nanotubes (MWCNT)-modified glassy carbon electrodes GCEs exhibited signals enhanced by about five-fold in the detection of dopamine in the presence of AA [26], Jacobs et al. [27] reviewed the use of MWCNTs to obtain enhanced signals in the detection of substances such as carboxyhdrates, nucleic acids, glucose, pesticides, and serotonin, with similar reports relating to trace metals [28] and nitroaromatic compounds [29]. There are several literatures on the electro-oxidation of dopamine on modified electrodes [30-34]. For example, Yang-Rae Kim et al. developed a graphene modified electrode (GME) by drop-casting graphene on glassy carbon electrode. The graphene modified electrode showed an increased current intensity compared with glassy carbon electrode and graphene modified electrode and detect DA successfully in the presence of AA [30]. Chuan-yin Liu et al. fabricated Cu-Ni(OH)₂/N-functionalized GCE sensor been prepared by electrodeposition and the proposed modified GCE was used for the determination of DA in simulated samples and DA injections with favourable recoveries [31]. The electrocatalytic oxidation of dopamine (DA) at a home-made aluminium electrode modified with nickel pentacyanonitrosylferrate (NiPCNF) film was studied by Razmi et al. [32]. The NiPCNF films, formed on the Ag electrode show excellent electrocatalytic activity toward the oxidation of DA. Kangbing et al. reported a chemically modified electrode based on the carbon nanotube film–coated glassy carbon electrode (GCE) for the simultaneous determination of dopamine (DA) and serotonin (5-HT) and lowers oxidation overpotentials [33]. Adekunle et al. reported chemical deposition of Prussian blue (PB) nanoparticles and polyanilinebenzene sulfonated single-walled carbon nanotubes (SWCNT-PABS) on edged plane pyrolytic graphite electrode (EPPGE) and used the obtained EPPGE-SWCNT-PB for dopamine sensing. Results showed that EPPGE-SWCNT-PB electrode gave the best dopamine (DA) current response, which increases with increasing PB layers [34].

Despite this huge literature, and to the best of our knowledge this work represent the first time an extensive comparative study on the electrocatalytic properties of oxides of three transition metals nanoparticles (NiO, ZnO and Fe₃O₄) integrated with MWCNTs towards dopamine oxidation will be carried out. In addition, this study also provides report on the extent and mechanism of electron transport of the different metal oxides (NiO, ZnO and Fe₃O₄) nanoparticles and their nanocomposite with MWCNT, and their interaction with dopamine at physiological pH condition. GCE-MWCNT-NiO electrode has proven to be the best electrode in terms of DA oxidation current and nano molar limit of detection. DA and ascorbic acid (AA) signal were well resolved using SWV and DPV techniques compared to CV technique, with DPV giving the best peak separation of 400 mV, 300 mV and 600 mV at GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe₃O₄ electrodes respectively. The fabrication of this electrode is simple and, more importantly, provides well-defined voltamograms for catalytic detection of dopamine, as well as simultaneous detection of dopamine in the presence of ascorbic acid. Dopamine real sample analysis using the developed sensors was also carried out and reported.

### Experimental Details

#### Materials and reagents

The pristine multi-walled carbon nanotubes (MWCNTs), was obtained commercially from Aldrich chemicals. A working Glassy carbon electrode (GCE, 3 mm diameter), Ag/AgCl, sat’d KCl reference electrode and a platinum disk counter electrode (99.999%) were purchased from CH Instrument Inc., US. The salts of the metals, nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O); iron (III) chloride FeCl₃; zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O were obtained from Sigma-Aldrich. Dopamine-hydrochloride (C₆H₉NO₂·HCl) was also obtained from Sigma chemicals. Sodium sulphate (Na₂SO₄); sodium hydroxide (NaOH); potassium hexacyano ferrate (II) (K₃[Fe(CN)₆]·6H₂O); potassium hexacyano ferrate (III) (K₄[Fe(CN)₆]·3H₂O); sodium chloride (NaCl); acetic acid (CH₃COOH); ethanol (C₂H₅OH); ammonia solution (NH₃·H₂O); and acetic acid (C₂H₅OH); alcohol (C₆H₁₂O₆); ammonium solution (NH₄OH) and any form of oxidation during experiment. All other reagents were of analytical grades and were used directly as received from the suppliers without further purification. All electrochemical experiments will be performed with nitrogen.

#### Preparation of metal oxides nanoparticles

**Nickel oxide nanoparticle:** In a typical procedure, 291 mg Ni(NO₃)₂·6H₂O was dissolved in 10 ml water. Then, concentrated ammonia solution was added until formation of Ni(OH)₂. The precipitate colour was light green. Addition of ammonia solution was continued just to dissolve Ni(OH)₂ and form dark blue nickel-ammonia complex with a solution pH of ≈10. This solution was then placed near a baker containing 10 ml concentrated sulphuric acid in a closed polyethylene container for 48 h at room temperature. A light green powder was precipitated. The product was washed with distilled water and ethanol and dried at 40°C to obtain the nickel oxide nanoparticles [35].

**Zinc oxide nanoparticle:** The production unit of ZnO nanostructures consists basically of a jacketed three-neck glass flask and of a magnetic stirrer with temperature control. In the three-neck glass flask, NaOH was dissolved in deionized water to a concentration of 1.0 M and the resulting solution was heated, under constant stirring, to the temperature of 70°C. After achieving this temperature, a solution of 0.5 M Zn(NO₃)₂·6H₂O was added slowly (dripped for 60 minutes) into the three-neck glass flask containing the NaOH aqueous solution under continual stirring. In this procedure the reaction temperature was constantly maintained at 70°C.

The suspension formed with the dropping of 0.5 M Zn(NO₃)₂·6H₂O solution to the alkaline aqueous solution was kept stirred for two hours at the temperature of 70°C. The material formed was filtered and washed several times with deionized water. The washed sample was dried at 65°C in oven for several hours [36].
Iron (III) oxide nanoparticle: 30 ml of 2 mol dm$^{-3}$ FeCl$_3$ stock solutions, 20 ml of 1 mol dm$^{-3}$ Na$_2$SO$_4$ stock solution, and 50.8 ml of concentrated ammonia diluted to a total volume of 800 ml were used. Just after the mixing of FeCl$_3$ and Na$_2$SO$_4$, the color of the solution in the smaller beaker could be seen to alter from light yellow to red, indicating formation of complex ions. This solution was poured quickly into the diluted ammonia solution under vigorous stirring when the color changed from red to yellow again. A black precipitate formed. Stirring was continued for 30 min. After the reaction, the beaker containing the suspension was placed on a permanent magnet. Black powders could be seen to quickly settle on the bottom of the beaker. The supernatant was removed. Dry powders were obtained by filtering and drying at room temperature [37].

Preparation of catalysts

2 mg of MWCNT in 2 ml DMF was weighed and doped with 2.5 mg of metal oxides NiO nanoparticles. The mixture was stirred for 72 hrs at room temperature. The known volume of the putty formed of the MWCNT-NiO nanocomposites was dried at 25°C overnight for the solvent to evaporate.

Preparation of modified GC electrode

The GC electrode was polished with 0.3 µm and 0.05 µm alumina slurries for 3 min each, followed by thorough rinsing with water, and sonicating in turn with distilled water, ethanol and distilled water for 3 min each before modification. The electrodes were prepared by a drop-dry method. About 20 µl drop of MO (MO=NiO, Fe$_3$O$_4$, ZnO), MWCNT and MWCNT-MO (2mg acidified MWCNTs and 2.5 mg MO in 1 ml DMF) were dropped on the bare GCE and dried in an oven at 50°C for about 2min [38,39]. The obtained GCE-NiO, GCE-Fe$_3$O$_4$, GCE-MWCNT, and GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe$_3$O$_4$ were characterised by cyclic voltammetry using 5 mM potassium ferricyanide solution prepared in 0.1 M PBS at pH 7 as a redox probe.

Characterization

Infrared spectroscopy data were obtained with PerkinElmer GX 2000 FT-IR Spectrometer attached to a PerkinElmer Auto Image Microscope System equipped with liquid nitrogen cooled MCT detector. The samples were analyzed using KBr in the transmission mode. Field emission electron microscopy (FESEM) images were obtained from JEOL JSM 5800 LV (Japan) while the energy dispersive x-ray spectra (EDX) were obtained from NORAN VANTAGE EDX (USA). TEM experiments were performed using a Model JEOL JEM-2100F field emission transmission electron microscope, Tokyo (Japan). UV/Vis experiment were performed with a UV-Visible spectrophotometer, 100 Bio Varian Win UV, Australia. Raman measurements were carried out in Renishaw InVia model spectrometer with the laser excitation of 514 nm. Powder X-ray diffraction (XRD) study was performed on XPERT-PRO diffractometer operating at 40 kV and 30 mA, using Cu Kα radiation. Electrochemical experiments were carried out using an AUTOLAB Potentiostat PGSTAT 302 (Eco Chemie, Utrecht, and The Netherlands) driven by the GPES software version 4.9. Electrochemical impedance spectroscopy (EIS) measurements were performed with an AUTOLAB Frequency Response Analyser (FRA) software between 1.0 Hz and 10 kHz using a 5 mV rms sinusoidal modulation with a solution of 5 mM of K$_4$Fe(CN)$_6$ and a 5 mM K$_3$Fe(CN)$_6$ (1:1) mixture in phosphate buffer solution (PBS) of pH 7.0 and at the E1/2 of the [Fe(CN)$_6$$^{3-}$/Fe(CN)$_6$$^{4-}$ (0.3 V vs. Ag|AgCl in sat’d KCl)]. Bare or modified glassy carbon electrode (GCE) disk (d=3.0 mm in Teflon) was used as the working electrode. A bench top pH/ISE ORION meter, model 420 A, was used for pH measurements. All solutions were de-aerated by bubbling nitrogen prior to each electrochemical experiment. Experiments were performed at 25 ± 1°C.

Electrochemical studies

The modified GCE was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 0.1 mol/L PBS containing 5 mM Fe(CN)$_6$$^{3-}$/4$^{-}$- . The potential was set at 0.2 V in the frequency range from 10 kHz to 1 Hz for the EIS study. Electrochemical oxidation of DA was investigated in pH 7.0 PBS using cyclic voltammetry and square wave voltammetry (SWV). The interference studies were carried out by using SWV, DPV and chronoamperometric techniques. Frequencies used for square wave voltammetry typically range from 1 Hz to 120 Hz. DPV provides the necessary resolving power, by suppressing background currents, which give rise to well defined peak separation. The DPV and SWV experiments were carried out using GCE- MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe$_3$O$_4$ in pH 7.0 PBS containing 10$^{-4}$ M AA and 10$^{-4}$ M DA solutions respectively. All the electrochemical experiments were carried out at room temperature and distil-deionised water was used throughout.

Preparation of the dopamine hydrochloride injection solution

A 2 ml of the drug (dopamine hydrochloride injection-Dopamine HCl Fresenius’s) sample was diluted to 100 ml with distilled de-ionised water. 2 ml of the diluted solution was pipette into five 50 ml volumetric flask and all except one were spiked with different concentration of standard dopamine solution, and made to volume with phosphate buffer pH 7.0. The concentration of each test aliquot solution was determined using square wave voltammetry. Four different injections from the same batch were analysed using the same procedure. The experiment was repeated 3 times for each sample.

Results and Discussion

Characterization of the electrodes

Morphological characterization: The surface morphology of the material was examined with SEM and transmission electron microscope (TEM). TEM/SEM samples were prepared for electron microscopy by drop-dried the sample on a glass plate and mounting on the SEM stubs using double-sided graphite tape, and then sputter coated with gold using a Balzers’ union sputtering device. The samples were viewed using a TESCAN Vega TS 5136LM typically at 20 kV at a working distance of 20 mm. Figure 1a (i-iv) shows TEM images of the MWCNT and metal oxides nanoparticles. Unlike the MWCNT with dispersed spiral tubes (Figure 1a (i)), the TEM images of the metal oxide nanoparticles were porous, crystalline and somewhat aggregated, possibly due to ineffective dispersing capability of the solvent. TEM image of ZnO nanoparticles (Figure 1a (iv)) shows dark layers of several nanoparticles on top of one another and they have either spherical or rod-like structure. The average diameter of MWCNT nanoparticles is about 8-11 nm. The relatively mono disperse Fe$_3$O$_4$ particles have an average diameter of 10 nm. The sizes of ZnO NP were 50 ± 15 nm. (Figure 1i)

The SEM images of MWCNT and the synthesised metal oxide nanoparticles were represented in Figure 1b (i-iv). Figure 1b (i)
show the SEM image for the carbon nanotube materials, showing the appearance of loose curly CNTs together with some amorphous-like particles. These nanotubes seemingly have a broad length distribution. The nanotube diameters range from 20 to 60 nm. The SEM image Figure 1b (ii) indicates the formation of a flower-like conglomerate structures nickel oxide nanoparticles. Figure 1b (iii) shows a aggregated ZnO microstructures. It can be clearly seen that the flower is made of taper shape rods that are 400 - 500 nm long and 100 - 150 nm thick. The Fe₃O₄ particle (Figure 1b (iv)) showed an aggregated film probably due to the method of preparation. The average sizes of Fe₃O₄ nanoparticles are estimated to be 40-100 nm.

**UV-vis study:** The optical absorption spectrum of nickel oxide nanoparticle is shown in Figure 2. It can be seen that the strongest absorption peak of the NiO sample appears at around 330 nm, which is closer to 355 and 320 nm reported for NiO nanoparticles [40,41]. The different in absorption bands can be attributed to the different methods of preparation of the nanoparticles. The absorption bands at 330 nm for the NiO shifted to lower absorption band at around 280 nm in the presence of MWCNT suggesting the successful formation of MWCNT-NiO nanocomposite.

The Uv-vis absorption spectrum of ZnO sample shows excitonic peak with absorbance intensity at wavelength of 280 nm. Another absorption peak observed at around 350 nm is characteristic of ZnO nanoparticles [42]. For ZnO of wide band Gap of 3.37 eV, an absorption peak is expected at ~358 nm [43]. In the MWCNT-ZnO nanocomposite, aside the ZnO absorption bands at 350 nm two new absorption bands emerged at around 530 and 650 nm respectively and a reduction in the ZnO band intensity also confirming successful transformation of ZnO to MWCNT-ZnO nanocomposite. The Uv-vis absorption spectrum of Fe₃O₄ sample shows broad absorption peak ranging from 350 to 400 nm and was suggested to originate primarily from the absorption and scattering of light by magnetic nanoparticles. This observed absorption peak is in accordance with the literatures [44]. The high absorption band at 385 nm could indicate the formation of a least agglomerated nanosize particle which was observed at 410 nm in a related study [45]. However in the MWCNT- Fe₃O₄ nanocomposite, a shift in the absorption band of Fe₃O₄ at 350 nm to 280 nm, plus reduction in the Fe₃O₄ band intensity further confirm the transformation of Fe₃O₄ to MWCNT- Fe₃O₄ nanocomposite. From the results, it can be observed that the UV absorption ability of MWCNT-MO nanocomposite decreased as demonstrated by reduction in the band intensity of the MO nanoparticles after incorporated into MWCNT. This behaviour

**Figure 1a:** Typical TEM images of (i) MWCNT (ii) NiO (iii) Fe₃O₄ and (iv) ZnO nanoparticles.

**Figure 1b:** Typical SEM images of (i) MWCNT (ii) MWCNT-NiO (iii) MWCNT-ZnO and (iv) MWCNT-Fe₃O₄ nanoparticles.

**Figure 2:** The UV-vis spectra of metal oxide nanoparticles and MWCNT-MO nanocomposites.
has been described previously by authors as the characteristic of the adsorption of the assembled CNTs [46]. It can also be attributed to the smooth and pure nature of the MWCNTs, with the absence of other light absorbing groups that may lead to an increased absorption band. (Figure 2)

Raman and FTIR spectra: Figure 3a shows the Raman spectra of MWCNT and the metal oxide nanoparticles synthesized in this study. The Raman spectra of MWCNTs showed two charateristics sharp peaks at 1600 and 1380 cm⁻¹ respectively. The sharp band at 1600 cm⁻¹ (G band) is attributed to the in-plane vibration of the C–C bond [47], while the band at 1380 cm⁻¹ (D band) is attributed to activation by the presence of disorder in carbon systems [48]. The Raman spectrum of NiO nanoparticles exhibited a strong, broad peak at 550 to 600 cm⁻¹ which is due to the NiO stretching mode, also reported at 518 cm⁻¹ for NiO in another study [49]. The Raman spectrum of Fe₂O₃ showed a strong band at 667 cm⁻¹ which is characteristic of Fe₂O₃ nanoparticles [50]. The Raman spectrum of ZnO nanoparticles showed ZnO stretching modes at 442, 571 and 1103 cm⁻¹ characteristic of ZnO nanoparticles [51]. The Raman spectra for MWCNT-NiO and MWCNT-ZnO composite mixture show the characteristic bands observed in pure MWCNT (G and D bands), disappearance of NiO and MWCNT-Fe₃O₄ composite. (Figure 3a)

The FTIR spectra showed several significant absorption peaks Figure 3b. The broad absorption band in the region of 500-600 cm⁻¹ is assigned to Ni–O, Zn–O and Fe–O stretching vibration mode; the broadness of the absorption band indicates that the metal oxide powders are nanocrystals [52]. The weak band near 1635 cm⁻¹ is assigned to H–O–H bending vibrations mode due to the adsorption of water in air during FTIR sample preparation. These observations provided the evidence to the effect of hydration in the structure. The serrated absorption bands in the region of 1000-1500 cm⁻¹ are assigned to the O=C=O symmetric and asymmetric stretching vibrations and the C–O stretching vibration, but the intensity of the band has weakened, which indicated that the ultrafine powers tend to strong physically adsorbed H₂O and CO₂ [53]. There are distinct absorption peaks at 1582, 2920, 2850 and 3446 cm⁻¹. The spectra show a band around 3446 cm⁻¹ which can be attributed to the hydroxyl group (vOH) of adsorbed water molecules. The band between 1582-1653 cm⁻¹ can be attributed to H–O–H bending vibrations mode due to the adsorption of water in air during FTIR sample preparation. These observations provided the evidence to the effect of hydration in the structure. The serrated absorption bands in the region of 1000-1500 cm⁻¹ are assigned to the O=C=O symmetric and asymmetric stretching vibrations and the C–O stretching vibration, but the intensity of the band has weakened, which indicated that the ultrafine powers tend to strong physically adsorbed H₂O and CO₂ [53]. There are distinct absorption peaks at 1582, 2920, 2850 and 3446 cm⁻¹. The spectra show a band around 3446 cm⁻¹ which can be attributed to the hydroxyl group (vOH) of adsorbed water molecules. The band between 1582-1653 cm⁻¹ can be attributed to vibration mode of C=C bonds of graphite in MWCNTs, while bands around 2920 and 2850 cm⁻¹ are due to asymmetric and symmetric C–H stretching in the MWCNTs. In the MWCNT-MO spectra, upon modification of the MO nanoparticles with MWCNT, the peaks around 500-600 cm⁻¹ becomes more pronounced due to drastic reduction in the intensities of the MO peaks indicating that the MO have now been transformed to MWCNT-MO. There are also evidences of new peaks around 1200-1600 cm⁻¹ in the MWCNT-MO nanocomposite but absent in MO nanoparticles alone. This is also an evidence of the successful formation of the MWCNT-MO nanocomposite through electrostatic interactions. (Figure 3b)

EDX study: EDX spectra (supplementary Figure S1) show the elemental compositions of the MWCNT (i) and the synthesized metal oxide nanoparticles (ii – iv). The MWCNT spectrum is predominantly characterised with prominent carbon peak (C=92.22%). The prominence of nickel, zinc, iron and oxygen peaks in the EDX spectra of confirm the successful synthesis of NiO (ii), ZnO (iii), and Fe₂O₃.
(iv) nanoparticles. The elemental components for the metal oxides nanoparticles are NiO (Ni=72.98%, O=25.56%), ZnO (Zn=87.34%, O=11.88%) and Fe3O4 (Fe=75.58%, O=21.70%).

**XRD:** XRD analysis was used to determine the crystalline phase and the purity of the metal oxides nanoparticles incorporated into MWCNT (Figure 4). The results revealed that the nanocomposite formed were crystalline. Observed peaks diffraction indicated a high phase purity of metal oxide nanoparticles and also diffraction peaks at 2θ=26.3° and 43.2° corresponding to reflections of (002) and (100) crystallographic planes of MWCNT. In Figure 4, XRD analysis of the nanocomposites indicates that MWCNT is decorated with the metal oxides nanoparticles. The formation of MWCNT-NiO composites are confirmed by the presence of (002) plane of CNTs and 5 planes of NiO in XRD spectra (Figure 4a) [54]. The formation of MWCNT-ZnO composites are characterized by the diffraction peaks situated at 2θ =31.8°, 34.5°, 36.2°, 47.5° and 56.7° corresponding to (100), (002), (101), (102) and (110) orientation planes of ZnO (Figure 4b) [55].

The diffraction lines typical of cubic crystal structures of magnetite are welldefined in the XRD pattern for MWCNT-Fe3O4 (Figure 4c), therefore the formation of the nanocomposite is confirmed by diffraction peaks corresponding to (200), (220), (311), (400), (422), (511), (533) and (622) indicating a cubic crystal structure for the Fe3O4 nanoparticles. These results demonstrate that the product is a mixture of two phases: cubic Fe3O4 and MWCNTs [56] (Figure 4).

**Electrochemical characterization of electrodes**

Scheme 1 is the schematic diagram summarising the electrochemical response of the GCE- MWCNT-MO electrodes in 5 mM Fe(CN)6[4-] / [Fe(CN)6]3- redox probe prepared in 0.1 M PBS at pH 7.0, and in 0.1 mM DA prepared in 0.1 M PBS (pH 7.0). The cyclic voltammograms study (scan rate, 25 – 1000 mVs-1) of the bare GCE electrode in 0.1 M PBS and 5 mM Fe(CN)6[4-] / [Fe(CN)6]3- solution prepared in 0.1M PBS at pH 7 is presented in Figure 5. The bare GCE did not show any peak in PBS (Figure 6a) while it showed a pair of redox peaks AA' in the regions of 0.16 and 0.24 V (attributed to the Fe(CN)6[4-] / [Fe(CN)6]3- redox process (E1/2 = 0.2 V and ΔEp = 0.1 V) as shown in Figures 5b and 6. To evaluate the charge transfer properties of the GCE-MWCNT-MO modified electrodes where MO represents NiO, ZnO and Fe3O4 nanoparticles, we performed the cyclic voltammetry experiment for the modified electrodes in 5 mM Fe(CN)6[4-] / [Fe(CN)6]3- in 0.1 M PBS (scan rate, 25 mVs-1) and the result is presented in Figure 6. Two pairs of redox peaks were observed for the NiO modified electrodes (Figure 6a). The first redox peaks AA' ranging from the regions of 0.0 to 400 mV is attributed to the Fe(CN)6[4-] / [Fe(CN)6]3- redox process. Similar redox peaks was observed in Figures 6b and 6c. Another pair of redox peaks BB' in the regions of 543 and 491 mV is attributed to Ni(II)/Ni(III) redox process. Second redox peaks BB' around 879 mV attributed to Zn(II)/Zn(III) redox process was observed on the ZnO modified electrodes (Figure 6c). There is no observable peaks corresponding to Fe(II)/Fe(III) redox process on the Fe3O4 modified electrodes probably because of the faster electron transfer at the electrode, or overlap between the Fe(CN)6[4-] / [Fe(CN)6]3- peaks and the Fe3O4 redox peaks. Generally, the GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE- MWCNT- Fe3O4 Electrodes gave higher current response compared with bare GCE, GCE-MWCNT and GCE-MO (MO=NiO, ZnO, Fe3O4) modified electrodes electrodes. Thus, the GCE- MWCNT-MO...
electrodes have demonstrated faster charge transport behaviour in this study. (Figures 5 and 6).

The synergy between MWCNT and MO nanoparticles in enhancing the electron transport process obtained at the GCE modified electrodes cannot be over emphasized. The conductive nature of the MO nanoparticles and the MWCNTs due to its facile electronic nature, plus the ionic interaction between the MO nanoparticles and MWCNTs are some of the factors responsible for this significant electron transport at the GCE-MWCNT-MO modified electrodes. Similarly, the large surface area created by the porous MWCNT on the electrode for free flow of electrolytes and charges between the base electrode and the electroactive species at the electrode surface is also another important factor for the great feat at the GCE- MWCNT-MO electrode. Similar results have been reported for modified electrodes in literature [37-60]. The peak-to-peak potential separation (ΔEp) for the three GCE-MWCNT- MO electrodes is ≥100 mV, which is greater than the theoretical 59.8 mV expected for a fast one-electron transport. Also, the ratios of the anodic to the cathodic peak current response (Ipa/Ipc) for GCE-MWCNT-NiO electrode is approximately unity, indicative of reversible electrochemical process, while that of GCE-MWCNT-ZnO and GCE-MWCNT- Fe3O4 are less than unity suggesting a quasi-reversible electron transfer process at these electrodes. Using the Randles-Sevck equation below:

\[ I_p = (2.99 \times 10^4) \, n^{3/2} \, A^{1/2} \, C^{1/2} \, D^{1/2} \, \nu^{1/2} \]  

Where n is the number of electron transfer, A is the electrode surface area, C is bulk concentration, D is the diffusion coefficient. The electroactive surface area for the electrodes GCE-MWCNT- NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 were calculated to be 1.18, 1.50 and 0.5 cm² respectively. Therefore, the anodic current response (in current density) of each electrode in Fe(CN)64-/Fe(CN)63- redox probe follows the order: GCE-MWCNT- Fe3O4 (1800 µAcm²) > GCE-MWCNT-ZnO (366.7 µAcm²) > GCE-MWCNT-NiO (211.9 µAcm²). Therefore GCE-MWCNT- Fe3O4 has demonstrated the best electron transport properties with current density approximately 5 and 9 times current produced at GCE-MWCNT-ZnO and GCE-MWCNT-NiO electrodes respectively. This could be attributed to the presence of four (4) oxygen atoms with lone pair of electrons in Fe3O4 thereby contributing to the net electron cloud and electron transport process at the GCE-MWCNT- Fe3O4 electrode as compared with NiO and ZnO modified electrodes with one oxygen atom each.

The scan rate study (scan rate, 25-1000 mVs⁻¹) of the GCE-MWCNT-MO electrode was carried out in 5 mM Fe(CN)64-/Fe(CN)63- solution prepared in 0.1M PBS (pH 7) using cyclic voltammetry experiment. Both anodic current (Ipa) and cathodic current (Ipc) increase with increase in scan rates (25 to 1000 mVs⁻¹) (Figure 7).

The plot of the anodic peak currents (Ipa) varies linearly with square root of scan rate and the regression equation for the different electrodes is given below.

\[ I_p (\mu A) = 8 \times 10^{-3} \, v^{1/2} - 3 \times 10^{-5} \, r^2 = 0.9931 \quad (GCE-MWCNT-NiO) \]
\[ I_p (\mu A) = 2.1 \times 10^{-3} \, v^{1/2} - 5 \times 10^{-5} \, r^2 = 0.9671 \quad (GCE-MWCNT-ZnO) \]
\[ I_p (\mu A) = 5.2 \times 10^{-4} \, v^{1/2} - 6 \times 10^{-8} \, r^2 = 0.9980 \quad (GCE-MWCNT-Fe3O4) \]

The apparent charge transfer rate constant (ks) and the charge transfer coefficient (α) of a surface-confined redox couple can be evaluated from the cyclic voltammetric experiments by using the variation of anodic and cathodic peak potentials with logarithm of scan rate. The Epa shifted to more positive values with increasing the scan rate (v). The transfer coefficient (i.e., α) and the number of electrons involved in the rate-determining step can be evaluated. Based on the slope of Epa versus log (v), (1-α) na was calculated to be 0.74, 0.34 and 0.33 for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 respectively. The values of ks were evaluated to be 0.12, 0.17 and 0.15 cm²s⁻¹ for electrodes GCE- MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 respectively using equation (2).

\[ \log ks = a \log (1 - a) + (1 - a) \log (RT/nF) - a(1-a) nFE/2.3RT \]  

Furthermore, from the slope of the linear plot of I vs. ν, the surface concentration of the electroactive species (Γ) can be estimated according to the following equation.

\[ i_p = \frac{n^2 F^2 A D \nu}{4 RT} \]

Where (Γ) is the surface coverage, A is the electrode surface area, F is the Faraday constant. The calculated surface coverage was 5.9, 6.7 and 2.2 nmol/cm² for GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 respectively. It should be pointed out that the
the semicircle corresponds to the electron transfer resistance (Rct) of the redox probe at the electrode interface. A smaller Rct value implies that the probe has a higher interfacial electron transfer rate (Figure 8).

The Nyquist plots obtained from the impedance experiment (at fixed potential of 0.2 V vs Ag/AgCl, sat’d KCl) and between 10 kHz and 1 Hz are presented in Figures 8a-8c, while the circuit model used in the fitting of the impedance data is represented in Figure 8d (i and ii). The double layer capacitance, Q or CPE is the constant phase element, and Rct is the charge transfer resistance. The values obtained from the fitting of the raw impedance spectra with this circuit are presented in Table 1.

Table 1: Impedance data obtained for the bare GCE and the modified electrodes in 5 mM Fe(CN)64−/[Fe(CN)6]3− solution at 0.2 V (vs. Ag/AgCl saturated KCl). The data points are experimental while the solid lines in the raw impedance spectra with this circuit are presented in Table 1.

| Electrodes       | Electrochemical impedance spectroscopy data |
|------------------|--------------------------------------------|
|                  | Rct (Ω) | Q (x 10^6 nF) | Rs (Ω) | Cdl (u F) |
| GCE              | 55.80 (8.93) | 334.00 (9.50) | 1915.00 (4.37) | 10.61 (3.84) |
| GCE-NiO          | 66.60 (0.04) | 8.44 (1.19) | 3200.00 (1.38) | 38.20 (3.34) |
| GCE-ZnO          | 70.80 (1.10) | 3200.00 (1.38) | 38.20 (3.34) | 38.30 (4.94) |
| GCE-Fe3O4        | 70.80 (1.10) | 8.44 (1.19) | 3200.00 (1.38) | 38.20 (3.34) |
| GCE-MWCNT-NiO    | 66.60 (0.04) | 8.44 (1.19) | 3200.00 (1.38) | 38.20 (3.34) |
| GCE-MWCNT-ZnO    | 70.80 (1.10) | 3200.00 (1.38) | 38.20 (3.34) | 38.30 (4.94) |
| GCE-MWCNT-Fe3O4  | 70.80 (1.10) | 8.44 (1.19) | 3200.00 (1.38) | 38.20 (3.34) |
| GCE-MWCNT-MO     | 66.60 (0.04) | 8.44 (1.19) | 3200.00 (1.38) | 38.20 (3.34) |
| GCE-MWCNT       | 55.80 (8.93) | 334.00 (9.50) | 1915.00 (4.37) | 10.61 (3.84) |

Figure 8: Typical Nyquist plots obtained for the electrodes in 5 mM Fe(CN)64−/[Fe(CN)6]3− solution (PBS pH 7.0) at a fixed potential of 0.2 V (vs. Ag/AgCl, saturated KCl). The data points are experimental while the solid lines in the spectra represent non-linear squares fits. (di and dii) Represents the circuit model, Rs represents the double layer capacitance, Q or CPE is the constant phase element, and Rct is the charge transfer resistance. The values obtained from the fitting of the raw impedance spectra with this circuit are presented in Table 1.

Electrochemical impedance spectroscopic (EIS) studies: EIS is a complex electrochemical process that gives insightful information about reaction at the electrode-electrolyte interface. The result obtained is presented in Nyquist plot (Figure 8), which includes a semi-circular portion corresponding to the electron-transfer-limited process and a linear part resulting from the diffusion process [61]. The diameter of the calculated surface coverage is an efficient attribute (per cross section of the electrode) and does not reflect the actual amount of MWCNT-MO per area of exposed glassy carbon.

Electrooxidation of DA at the surface of the Electrodes

Figure 9 shows the electrochemical response of dopamine at bare GCE, GCE-MWCNT, GCE-MO and GCE-MWCNT-MO electrodes in 0.1M phosphate buffer solution (pH 7.0). The CV evolution of electrodes in DA is typical for DA oxidation process where the anodic peak corresponds to dopaminoquinone (DA+) (Figure 10 and scheme 2) and the cathodic peak corresponds to reduction of dopaminoquinone to leucodopanoquinone [62]. The results showed that DA was oxidized with well-defined sharp DA oxidation peak at lower potentials and significantly enhanced DA oxidation current at the GCE-MWCNT-MO electrodes compared with other electrodes investigated (Figure 9).

The oxidation peak potentials of DA on the GCE-MWCNT-MO modified electrodes were at around 0.20V vs. Ag/AgCl. On the other hand, the indistinguishable and broad peak at a bare GCE and GCE-MO electrodes indicate a slow electron transfer kinetic at the electrode. In addition, the enhanced DA currents at lower potential at the GCE-MWCNT-MO indicate that the modified electrode plays a catalytic effect on the oxidation of DA. The DA oxidation current at
Cyclic voltammetry experiments were carried out with the GCE-MWCNT-MO to establish the impact of scan rate at constant concentration (10⁻⁴ M) of dopamine in pH 7.0 PBS solutions. In all cases, we observed a shift in potential with increase in scan rate (Figure 10). From the Randles–Sevčík equation for an anodic oxidation process Equation (1), the plot of the peak currents (Ip) against the square root of scan rate (ν₁/₂) (Figure 10) for scan rate ranging from 25 to 1000 mVs⁻¹ gave a linear relationship with equations;

GCE-MWCNT-NiO:  \( I_{pa} = 2697.1 \nu^{1/2} - 467.92; \ R^2 = 0.991 \)
GCE-MWCNT-ZnO:  \( I_{pa} = 2572.4 \nu^{1/2} + 531.8; \ R^2 = 0.993 \)
GCE-MWCNT-Fe₃O₄:  \( I_{pa} = -2454.5 \nu^{1/2} + 545.3; \ R^2 = 0.993 \)

The charge transfer coefficient (α) for the reaction can be evaluated from cyclic voltammetric experiments by using the variation of anodic and cathodic peak potentials with logarithm of scan rate. Based on the slope of Epa with log (ν), (1-α) na was calculated to be 0.86, 0.84 and 0.85 for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively. In order to get information on the rate determining step, the peak potential, Ep, is proportional to log ν (graph not shown). The slopes of Ep vs. log ν for the different electrodes were 0.226, 0.190, and 0.196 V for electrodes GCE-MWCNT-NiO,
GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively. The tafel slopes may be estimated according to the equation (4) for the totally irreversible diffusion controlled process [67]. So, the respective values of b for these electrodes were obtained as 0.452, 0.380 and 0.392 V dec⁻¹. These values are higher than the theoretical 0.118 V dec⁻¹ for a one-electron process involved in the rate-determining step. Therefore the high tafel values suggest adsorption of dopamine or its reaction intermediate at the electrode surface since high tafel values have been attributed to the adsorption of reactants or intermediates on the electrode surfaces and/or reactions occurring within a porous electrode structure [68]. Adsorption process at the electrode can be linked with the porous CNT layer [69].

\[ E_p = \left( \frac{b}{2} \right) \log v + \text{constant} \]

If α was assumed equal to 0.5, nα was 1.7 (approximately 2) for all the electrodes indicating that the redox reaction of DA on the GCE electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ was two protons coupled two electrons process. Also, the electron transfer rate constant for the GCE-MWCNT-MO electrode can be determined using Equation 2 above, and assuming (1-α) nα=0.56 [67] v is the sweep rate and all other symbols having their conventional meanings. The value of ks was evaluated to be equal to 0.65, 0.81 and 0.05 cm s⁻¹ for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively. According to the kinetics of electron process, when the rate constant is larger than 10⁻³ cm/s, the electron transfer process is very fast, and the electrode reaction is reversible, and when 10⁻¹ < ks < 10⁻² cm/s, the electrode reaction is a quasireversible process.

So the electrode reaction of DA on the proposed electrodes is reversible process.

The stability of modified GCE towards oxidation of DA was checked by repetitive scanning (20 scans). The results show that the modified electrode has a good stability in aqueous solution after repeated twenty cyclic voltammogram of modified GCE-MWCNT-MO in 1 × 10⁻⁴ M DA solution at pH 7.0 at a fixed potential of 0.2 V (vs. Ag/AgCl saturated KCl). The data points are experimental while the solid lines in the spectra represent non-linear squares fits. (d) Represent the circuit used in the fitting of the EIS data in (a-c).

Electrochemical impedance spectroscopy data

| Electrodes | Rs (Ω) | Q (x 10⁶ nF) | Rct (Ω) | Cdl (µF) |
|------------|--------|--------------|---------|----------|
| GCE        | 54.70 (0.05) | 2.77 (1.33) | 98.40 (4.63) | 163.70 (10.56) |
| GCE-MWCNT  | 80.40 (0.50) | 307.00 (3.25) | 8.50 (7.77) | 78.50 (15.72) |
| GCE-NiO    | 62.60 (6.53) | 2.65 (1.31) | 104.80 (4.72) | 152.30 (10.72) |
| GCE-ZnO    | 81.20 (7.96) | 80.30 (3.04) | 80.40 (4.77) | 180.90 (16.73) |
| GCE-Fe₃O₄  | 134.60 (3.18) | 80.30 (3.04) | 319.00 (2.566) | 86.8 (3.54) |
| GCE-MWCNT-NiO | 74.60 (0.57) | 350.00 (3.80) | 9.50 (7.18) | 63.00 (14.82) |
| GCE-MWCNT-ZnO | 81.20 (7.96) | 330.00 (4.53) | 10.48 (6.69) | 72.49 (12.74) |
| GCE-MWCNT-Fe₃O₄ | 78.90 (0.65) | 235.00 (6.64) | 33.30 (5.19) | 93.30 (5.15) |

Electroanalysis of dopamine

Since the proposed MWCNT-MO GCE electrodes have demonstrated favourable electrochemical response towards DA, they have been used for determination of DA. To improve the sensitivity of the developed sensors in detection of DA, square wave voltammetry (SWV) technique has been used. Results showed that the electrochemical oxidation current is linearly proportional to its concentration in the range 4.0 × 10⁻¹¹ mol/L to 6.25 × 10⁻⁸ mol/L for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively (Figure 12). The respective detection limit for the electrodes were calculated based on the relationship LoD=3.3 δ/m where δ is the relative standard deviation of the intercept of the y-coordinates from the line of best fit, and m the slope of the same line to be 7.99 × 10⁻¹¹, 3.74 × 10⁻⁸, and 1.389 × 10⁻¹⁰ mol/L for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively. The nano molar limit of detection obtained for GCE-MWCNT-Fe₃O₄ as shown in Table 2. This was achieved because of the presence of MWCNT on the electrode. The MWCNT creates a porous and large surface area that mediates the analyte/catalyst electrocatalytic process (Table 2).

![Figure 11](image-url)
MWCNT-NiO compared favourably and even better that the limit of detection reported for other electrodes in literature (Table 3 and Figure 12).

**Interference study: Detection of DA in the presence of AA**

Figure 13 is the cyclic voltammetric responses of (a) bare GCE (b) GCE-MWCNT-ZnO, (c) GCE-MWCNT-NiO and (d) GCE-MWCNT-Fe3O4 in 0.1 M pH 7.0 PBS containing mixture of 10⁻³ M AA, approximately 1000 times concentration of DA. On the bare electrode, the detection of DA in the presence of AA was not successful (Figure 13a). That is, AA signal interferes with the DA signal thus no signal separation for the two analytes. (Figure 13).

However at the GCE-MWCNT-MO modified electrodes, AA signal which was initially observed at 0.05 V in the absence of DA remained at the same potential after the addition of DA, while the DA signal was observed at 0.25 V. The simultaneous detection of AA and DA even at AA concentration (9.09 mM) which is 1000 times as high as DA concentration (9.09 µM) was successful at the GCE-MWCNT-MO electrodes with potential separation of about 170 mV, 190 mV and 150 mV observed at GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 electrodes respectively. The height and amplitude of the peak corresponding to DA signal increases as the concentration DA increases.

The simultaneous determination of DA in the presence of AA has also been carried out using more sensitive techniques such as differential pulse voltammetry (DPV) (Figure 14), square wave voltammetry (SWV) (Figure 15) and chronoamperometric (CA) techniques (Figure 16). A well resolved signal difference at large enough potential peak separation was observed for the modified electrodes using SWV and DPV respectively as compared to CV. For example using SWV, potential peak separation of about 200 mV, 500 mV and 250 mV observed at GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 electrodes respectively, while DPV gave peak separation of 400 mV, 300 mV and 600 mV observed at GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 electrodes respectively. Figure 16 presents the amperometric measurements recorded at an applied potential of +0.20 V vs Ag/AgCl on MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe3O4 modified electrodes by continuous addition of 1 ml DA and 1 ml AA (approx. 1000x DA concentration) respectively. The DA response was determined before and after 50s injection of AA into the DA solution. From the result obtained, there is no significant decrease in DA current response after addition of different concentration of ascorbic acid (AA) indicating that AA signal did not interfere with DA detection on the developed GCE-MWCNT-MO modified electrodes. GCE-MWCNT-NiO and GCE-MWCNT-ZnO gave comparable DA recovery current compare with GCE-MWCNT-Fe3O4 (Figures 14-16).

### Table 3: Comparison of different electrochemical sensors for the determination of dopamine.

| Electrode material                      | Techniques | Interference | Detection Limit (mM) | References |
|-----------------------------------------|------------|--------------|----------------------|------------|
| SWNT/Ppy,Surf.cov.bend                 | SWV        | AA           | 5.00 × 10⁻⁶          | [60]       |
| MWCNT/B-CD modified                    | GCE SWV    | AA           | 6.70 × 10⁻⁶          | [61]       |
| Fe₃O₄/rGO/GO                           | SWV        | AA           | 1.20 × 10⁻⁶          | [62]       |
| GCE/MWCNT-NiO                          | SWV        | AA           | 7.99 × 10⁻³²         | This work  |
| GCE/MWCNT-ZnO                          | SWV        | AA           | 3.74 × 10⁻⁷          | This work  |
| GCE/MWCNT-Fe₃O₄                       | SWV        | AA           | 1.39 × 10⁻⁶          | This work  |

Figure 12: SWV of GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ in 1 x 10⁻² M DA (inset is the graph of current vs concentration of DA).

Figure 13: Cyclic voltammograms responses of: (a) bare GCE in PBS (pH 7.0), 10⁻³ M AA alone and 10⁻² M AA + different volume of 10⁻³ M DA solutions; (b) GCE-MWCNT-ZnO, and (c) GCE-MWCNT-NiO in (i) 0.1M pH 7.0 PBS (ii) 10⁻² M AA alone, (iii) mixture of 9.09 mM AA and 9.09 µM DA, (iv) mixture of 8.33 mM AA and 16.7 µM DA (v) mixture of 7.69 mM AA and 23.0 µM DA (vi) 7.14 mM AA and 28.6 µM DA (vii) 6.67 mM AA and 33.0 µM DA (viii) 6.25 mM AA and 37.5 µM DA (ix) 5.88 mM AA and 41.2 µM DA (x) 5.56 mM AA and 44.0 µM DA (xi) 5.2 mM AA and 47.0 µM DA and (xii) 5 mM AA and 50 µM DA concentrations.
DA (graph not shown) are:

The analytical results obtained are presented in Table 4. The result clearly indicates that dopamine can be reliably assayed from its drug using the proposed GCE-MWCNT-MO sensor.

**Conclusion**

This work describes the electron transport and electrocatalytic properties of chemically-synthesized metal oxide nanoparticles (NiO, ZnO and Fe3O4) supported on multi-walled carbon nanotubes (MWCNT) platforms on GCE. It is shown that the GCE-MWCNT-MO nanocomposite modified electrode gave better electron transport as well as better DA response compared with other electrodes investigated. GCE-MWCNT-NiO electrode has proven to be the best electrode in terms of DA oxidation current and nano molar limit of detection. DA and ascorbic acid (AA) signal were well resolved using SWV and DPV techniques compared to CV techniques, with DPV electrode in terms of DA oxidation current and nano molar limit of detection. DA and ascorbic acid (AA) signal were well resolved using SWV and DPV techniques compared to CV techniques, with DPV.

**Acknowledgements**

This project was supported by the North-West University (Mafikeng Campus), Material Science Innovation and Modelling (MaSIM) Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus).
ASA thanks the North-West University for post-doctoral fellowship and Obafemi Awolowo University, Nigeria for the research leave visit. EEE acknowledges the National Research Foundation of South Africa for Incentive funding for Rated Researchers.

References
1. Hyman SE, Malenka RC (2001) Addiction and the brain: The neurobiology of compulsion and its persistence. Nat Rev Neurosci 2: 695-703.
2. Nikolaus S, Antike C, Müller HW (2009) In vivo imaging of synaptic function in the central nervous system: II. Mental and affective disorders. Behav Brain Res 204: 32-66.
3. Sardar AM, Czudek C, Reynolds GP (1996) Dopamine deficits in the brain: The neurochemical basis of parkinsonian symptoms in AIDS. Neuroreport 7: 910-912.
4. Perry KW, Fuller RW (1992) Effect of fluoxetine on serotonin and dopamine concentration in microdialysis fluid from rat striatum. Life Sci 50: 1683-1690.
5. Parsons LH, Justice Jr JB, (1993) Per fusate serotonin increases extracellular dopamine in the nucleus accumbens as measured by in vivo microdialysis. Brain Research 606: 195-199.
6. Yoshitake T, Kehr J, Todokori K, Notha H, Yamaguchi M (2006) Derivatization chemistries for determination of serotonin, norepinephrine and dopamine in brain microdialysis samples by liquid chromatography with fluorescence detection. Biomedical Chromatography 20: 267-281.
7. Shafi N, Midgley JM, Watson DG, Small GA, Strang R, et al. (1989) Analysis of biogenic amines in the brain of the American cockroach (Periplaneta Americana) by gas chromatography-negative ion chemical ionisation mass spectrometry. J. Chromatogr B 490: 8-19.
8. Saleen SB, (1987) Electrochromatographic and titrimetric determination of coumaloamines. Talanta 34: 810-812.
9. Zhang L, Teshima N, Hasebe T, Kurihara M, Kawashima T (1999) Flow-injection determination of trace amounts of dopamine by chemiluminescence detection. Talanta 50: 677-683.
10. Wu K, Fei J, Hu S (2003) Simultaneous determination of dopamine and serotonin on a glassy carbon electrode coated with a film of carbon nanotubes. Anal Biochem 318: 100-106.
11. Torabi R, Compton RG (2007) A simple electroanalytical methodology for the simultaneous determination of dopamine, serotonin and ascorbic acid, using an unmodified edge plane pyrolytic graphite electrode. Anal and Bioanal Chem 387: 2793-2800.
12. Sun CL, Lee HH, Yang JM, Wu CC (2011) The simultaneous electrochemical detection of ascorbic acid, dopamine, and uric acid using graphite/size-selected Pt nanocomposites. Biosens Bioelectron 26: 3450-3455.
13. Adekunle AS, Ozoemenia KJ, Agboala BO (2013) MWCNTs/metal (Ni, Co, Fe) oxide nanocomposite as potential material for supercapacitors application in acidic and neutral media. J Electrochem 17: 1311-1320.
14. Selvaraju T, Ramaraj R (2003) Simultaneous determination of ascorbic acid, dopamine and serotonin at poly(phenosafranine) modified electrode. Electrochem. Commun 5: 667-671.
15. Jiang X, Lin X, (2005) Overoxidized polypyrrole film directed DNA immobilization for construction of electrochemical micro-biosensors and simultaneous determination of serotonin and dopamine. Analitica Chimica Acta 537: 145-151.
16. Habib B, Pournaghi-Azar MH (2010) Simultaneous determination of ascorbic acid, dopamine and uric acid by use of a MWNT modified carbon-ceramic electrode and differential pulse voltammetry. Electrochem. Acta 55: 5492-5498.
17. Arvand M, Niazi A, Matoghed Mazhabi R, Biparva P (2012) Direct electrochemistry of adenine on multiwalled carbon nanotube–ionic liquid composite film modified carbon paste electrode and its determination in DNA. J. Mol. Liq 173: 1-7.
18. Prabakar SJ, Salthivel C, Narayanan SS (2011) Hg(ll) immobilized MWNT graphite electrode for the anodic stripping voltammetric determination of lead and cadmium. Talanta 85: 290-297.
19. Esmaeilifar A, Yazdanpour M, Zamir SR, Eikani MH (2011) Hydrothermal synthesis of Pt/MWCNTs nanocomposite electrocatalysts for proton exchange membrane fuel cells. Int J Hydrogen Energy 36: 5500-5511.
20. Zhao Y, E YF, Fan LZ, Qiu YF, Yang SH (2007) A new route for the electrodeposition of platinum–nickel alloy nanoparticles on multi-walled carbon nanotubes. Electrochem Acta 52: 5873-5876.
21. Periasamy AP, Ho YH, Chen SM (2011) Multiwalled carbon nanotubes dispersed in carminic acid for the determination of catalase based biosensor for selective amperometric determination of H2O2(2) and iodate. Biosens Bioelectron 29: 151-158.
22. Kumar AS, Sethwa P (2011) Simple adsorption of anthraquinone on carbon nanotube modified electrode and its efficient electrochemical behaviors. Colloids Surf A 384: 597-604.
23. Kumar SA, Wang SF, Chang YT, Lu HC, Yeh CT (2011) Electrochemical properties of myoglobin deposited on multi-walled carbon nanotube/ ciprofloxacin film. Colloids Surf B Interfaces 82: 526-531.
24. Zhang J, Gao L (2010) Synthesis of Highly Dispersed Platinum Nanoparticles on Multiwalled Carbon Nanotubes and their Electro catalytic Activity towards Hydrogen Peroxide. J Alloys Comp 505: 604-608.
25. Dursun Z, Gelmez B (2009) Simultaneous Determination of Ascorbic Acid, Dopamine and Uric Acid at Pt Nanocomposites Decorated Multwall Carbon Nanotubes Modified GCE. Electroanalysis 22: 1106-1114.
26. Wu K, Hu S (2004) Electrochemical determination of hydrogen sulfide at carbon nanotube modified electrodes. Microchim Acta 144: 131-137.
27. Jacobs CB, Pearjs MJ, Ventura B (2010) Carbon nanotube based electrochemical sensors for biomolecules. J Anal Chimica Acta 662: 105-127.
28. Liu Y, Lan D, Wanzhi W (2009) Layer-by-layer assembled DNA-functionalized single-walled carbon nanotube hybrids-modified electrodes for 2,4,6-trinitrotoluene detection. J Electroanal. Chem 637: 1-5.
29. Kim YR, Bong S, Kang YJ, Yang Y, Mahajan RK, et al. (2010) Electrochemical detection of dopamine in the presence of ascorbic acid using graphene modified electrodes. Biosens Bioelectron 25: 2366-2369.
30. Chuan-yin Liu, Zhong-yong Liu, Rong Peng, Zhi-cheng Zhong, (2014) Quasireversible Process of Dopamine on Copper-Nickel Hydroxide Composite/ Nitrogen Doped Graphene/Nafion Modified GCE and Its Electrochemical Application. Journal of Analytical Methods in Chemistry 2014: Article ID 724538.
31. Razmi H, Agazadeh M, Habib-A B (2003) Electrochemical oxidation of dopamine at aluminum electrode modified with nickel pentacyanonitrosylferrate film, synthesized by electroselect process. Journal of electrochemistry 547: 25-33.
32. Wu K, Fei J, Hu S (2003) Simultaneous determination of dopamine and serotonin on a glassy carbon electrode coated with a film of carbon nanotubes. Anal Biochem 318: 100-106.
33. Adekunle AS, Abdullahi MF, Pillay J, Kenneth IO, Bheki B, et al. (2012) Electro catalytic properties of prussian blue nanobolecules supported on poly(m-aminobenzenesulphonic acid)-functionalised single-walled carbon nanotubes towards the detection of dopamine. Colloids and Surfaces B: Biointerfaces 95: 186-194.
34. Maryam D, Tahoora J, Mojdeh E, Majedeh B, Roya S, et al. (2013) Synthesis and Characterization of NiO Nanoparticle as a High Sensitive Voltammetric Sensor for Vitamin C Determination in Food Samples. Int J Electrochem Sci 8: 8252-8263.
35. Sho KM, Rajneesh KS, Prakash SG (2012) ZnO nanoparticles: Structural, optical and photocatalytic characteristics. Journal of Alloys and Compounds 539: 1-6.
36. Fengdan J (2014) The Preparation of Glucan-Fe3O4 Magnetic Nanoparticles and Its In Vivo Distribution in Mice. J Chem 2014: 1-4.
37. Giovaneli D, Lawerence NS, Wilkins SJ, Jiang L, Jones TG, et al. (2003) Anodic stripping voltammetry of sulphide at a nickel film: Towards the development of a reagentless sensor. Talanta 61: 211-220.
38. Zagal J, Paez M, Tanaka AA, dos Santos Jr. JR, Linkous CA (1992) Electro catalytic activity of metal mithalcoxaines for oxygen reduction. J Electroanal Chem 339: 13-30.
39. Assem B, Al-Noaimi M, Suleiman M, Abdullah SA, Hammout B (2013) One Step Synthesis of NiO Nanoparticles via Solid-State Thermal Decomposition at Low-Temperature of Novel Aqua (2,9-dime thyl-1,10- phenanthroline)NiCl2. Complex. Int J Mol Sci 12: 23941-23954.
40. Dhammaraj N, Prabu P, Nagarajan S, Kimb CH, Park JH, et al. (2006) Synthesis of nickel oxide nanoparticles using nickel acetate and poly(vinyl acetate)
precursor. Materials Science and Engineering B 128: 111-114.

41. Satyanarayana T, Srivinasa RK, Nagarjuna G (2012) Synthesis, Characterization, and Spectroscopic Properties of ZnO Nanoparticles. ISRN Nanotechnology, 2012: 1-6.

42. Awodugba AO, Iyasu Abdul-Majeed O (2013) Synthesis and characterization of ZnO nanoparticles with zinc chloride as zinc source. Asian Journal of Natural & Applied Sciences 2: 41-43.

43. Koutzarova T, Kolev S, Ghelev C, Paneva D, Nedkov I (2006) Microstructural study and size control of iron oxide nanoparticles produced by microemulsion technique. Phys Stat Sol 31: 1302-1307.

44. Sharrif A, Ufana R, Ajeet K, Javed A (2009) Soft Template Synthesis of Super Paramagnetic Fe3O4 Nanoparticles a Novel Technique. J Inorg Organomet Polym.

45. Xu Z, Gao N, Chen H, Dong S (2005) Biopolymer and carbon nanotubes interface prepared by self-assembly for studying the electrochemistry of microperoxidase-11. Langmuir 21: 10808-10813.

46. Bokobza S, Choquet D, Alaf M, Akbulut A (2013) Synthesis and characterization of ZnO nanoparticles doped with Prussian blue (PB) and Fe2O3 nanoparticles. RSC Adv 5: 27759.

47. Wei Lai, Sossina M (2005) Impedance Spectroscopy as a Tool for Chemical and Electrochemical Analysis of Mixed Conductors: A Case Study of Ceria. J Am Ceram Soc 88: 2979-2997.

48. Tovide O, Jaheed N, Mohamed N, Nuxxani E, Sunday CE, et al. (2014) Graphenated polyaniline-doped tungsten oxide nanocomposite sensor for real time determination of phenanthrene. Electrochim Acta 128: 138-148.

49. Min K, Yoo YJ (2009) Amperometric detection of dopamine based on tyrosinase-SWNTs-Psy composite electrode. Talanta 80: 1007-1011.

50. Angeles GA, Lopez BP, Pardave MP, Silva MTR, Alegret S, et al. (2008) Enhanced host-guest electrochemical recognition of dopamine using cyclodextrin in the presence of carbon nanotubes. Carbon 46: 896-906.

51. Teo Peik-See, Alagarsamy P, Nay-Ming H, Hong-Ngee L, Sulaiman Y (2014) Simultaneous Electrochemical Detection of Dopamine and Ascorbic Acid Using an Iron Oxide/Reduced Graphene Oxide Modified Glassy Carbon Electrode. Sensors 14: 15227-15243.

52. Bard AJ, Faulkner LR (2001) Electrochemical methods. John Wiley & Sons, New York.

53. Soderberg JN, Co AC, Sirk AH, Birss VI (2006) Impact of porous electrode properties on the electrochemical transfer coefficient. J Phys Chem B 110: 10401-10410.

54. Hasanazdeh M, Khalizadeh B, Shadzou N, Karim-Nezhad G, Lotfali L, et al. (2010) A New Kinetic-Mechanistic Approach to Elucidate Formaldehyde Electrooxidation on Copper Electrode. Electroanalysis 22: 168.

55. Refat FA, Gehad GM, Hala AM, et al. (2012) Chemically Modified Carbon Paste Electrode for Determination of Cesium Ion by Potentiometric. Method American Journal of Analytical Chemistry 3: 576-586.