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

Omolola E Fayemi^{1,2}, Abolanle S Adekunle^{1,2,3} and Eno E Ebenso^{1,2*}

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/Fe₂O₂). All electrodes were conditioned at potential of 0.2V (vs Ag/AgCI, sat'd KCI) in DA solution for EIS experiment. It was found that the multi- walled carbon nanotubes improve remarkably the reactivity of NiO, ZnO and Fe₂O₄ for dopamine oxidation. The GCE/MWCNT/NiO, GCE/MWCNT/ZnO, GCE/MWCNT/Fe₂O₄ electrodes exhibited good linear properties in the concentration range from 4 × 10⁻⁵ µM 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^{-7} M and 1.386×10^{-6} 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 chemiluminesence [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

*Corresponding author: Eno E Ebenso, Department 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, Tel: +27183892050/2051; Fax: +27183892052; E-mail: Eno.Ebenso@nwu.ac.za

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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 H_2O_2 iodate dopamine (DA), organic small molecules, inorganic ion and even widely used as catalytic electrodes of fuel cells [16-25]. Multiwalled 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 carbohydrates, 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 graphite modified electrode and detect DA successfully in the presence of AA [30]. Chuan-yin Liu et al. fabricated Cu-Ni(OH),/N-GR/Nafion/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 aluminum electrode modified with nickel pentacyanonitrosylferrate (NiPCNF) film was studied by Razmi et al. [32]. The NiPCNF films, formed on the Al 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 polyaminobenzene sulphonated single- walled carbon nanotubes (SWCNTPABS) 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 Fe₂O₄) 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 Fe₂O₄) 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- Fe_3O_4 electrodes respectively. The fabrication of this electrode is simple and, more importantly, provides welldefined voltammograms 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(NO₂)₂.6H₂O); iron (III) chloride FeCl₃, zinc nitrate hexahydrate Zn(NO)₂.6H₂O were obtained from Sigma-Aldrich. Dopamine-hydrochloride (C,H,,NO,.Hcl) was also obtained from Sigma chemicals. Sodium sulphate (Na₂SO₃); sodium hydroxide (NaOH); hydrated potassium hexacyano ferrate (II) (K₄[Fe(CN)₄].6H₂O); potassium hexacyano ferrate(III) (K₂Fe(CN)₄); dimethylformamide (CH₂)₂NC(O)H); acetone (C₂H₂O); ethanol (C₂H₅OH); ammonia solution (NH₂.H₂O); and other reagent were of analytical grade and were obtained from Sigma-Aldrich and Merck chemicals respectively. Dopamine drug (Dopamine HCl- Fresenius* (200 mg/5 ml) product of Bodene (pty) Ltd South Africa, was obtained from a local pharmacy stored for life sample analysis. Ultra-pure water of resistivity 18.2 MΩcm was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used throughout for the preparation of solutions. 0.1 M phosphate buffer solutions of pH 7 was prepared using sodium hydrogen phosphate di-hydrate (NaH,PO, 2H,O) and di-sodium hydrogen phosphate di-hydrate (Na,HPO, 2H,O) or their potassium salts. The pH was adjusted with 0.1 M H, PO, or NaOH. All solutions were prepared using double distilled deionised water and purged with pure nitrogen to eliminate oxygen 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 $(NO_3)_2.6H_2O$ 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 $Zn(NO_3)_2$.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 $0.5 \text{ M Zn} (\text{NO}_3)2.6\text{H}_2\text{O}$ 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 FeCl₃ stock solutions, 20 ml of 1 mol dm⁻³ Na₂SO₃ stock solution, and 50.8 ml of concentrated ammonia diluted to a total volume of 800 ml were used. Just after the mixing of FeCl₃ and Na₂SO₃, 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; this procedure was repeated several times until most of the ions in the suspension were 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 μ m and 0.05 μ m 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 μ L drop of MO (MO=NiO, Fe₃O₄, 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-ZnO, GCE-Fe₃O₄, GCE-MWCNT, and GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ 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 scanning 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 Ka 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 K₄Fe(CN)₆ and a 5 mM K₃Fe(CN)₆ (1:1) mixture in phosphate buffer solution (PBS) of pH 7.0 and at the E1/2 of the Page 3 of 14

 $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ (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 deaerated 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 1Hz 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 approximately 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- Fe₂O₄ in pH 7.0 PBS containing 10⁻² 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[®]) 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 disperse 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 Fe₃O₄ particles have an average diameter of 10 nm. The sizes of ZnO NP were 50 \pm 15 nm. (Figure 1)

The SEM images of MWCNT and the synthesised metal oxide nanoparticles were represented in Figure 1b (i-iv). Figure 1b (i)

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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



Figure 1a: Typical TEM images of (i) MWCNT (ii) NiO (iii) $\rm Fe_3O_4$ and (iv) ZnO nanoparticles.



Figure 1b: Typical SEM images of (i) MWCNT (ii) MWCNT-NiO (iii) MWCNT-ZnO and (iv) MWCNT-Fe $_{3}O_{4}$ nanoparticles.



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 Fe₂O₄ at 350 nm to 280 nm, plus reduction in the Fe₂O₄ band intensity further confirm the transformation of Fe₂O₄ 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

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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 Fe₃O₄ showed a strong band at 667 cm⁻¹ which is characteristic of Fe₃O₄ 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 ZnO peaks, and formation of a well-defined and prominent peak at around 2800 – 3000 cm⁻¹ confirming the successful formation of a new compound due to the interaction between the MO NPs and MWCNT. The Raman spectrum of MWCNT- Fe₃O₄ on the other hand showed the disappearance of the Fe₃O₄ peaks, a shift and drastic reduction in the intensity of the G and the D bands of the pure MWCNT, and an appearance of a new peak at around 500 cm⁻¹ indicating the formation of the MWCNT- Fe_3O_4 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;



Figure 3a: The Raman Spectra of MWCNT, MO metal oxide nanoparticles, and MWCNT-MO nanocomposite.



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 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 Fe₃O₄

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Figure 4: The typical XRD spectra of: (a) MWCNT-NiO (b) MWCNT-ZnO and (c) MWCNT- Fe₃O₄ nanocomposites.

(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 $2\theta=26.3^{\circ}$ and 43.2° corresponding to reflections of (002) and (100) crystallographic plates 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 MWCNTZnO 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 anoparticles. 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).]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 $Fe(CN)_{c}$]⁴⁻ /[Fe(CN)_{c}]³⁻ redox process ($E1/2 \approx 0.2$ V and $\Delta Ep \approx 0.1$ 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 Fe₂O₄ nanoparticles, we performed the cyclic voltammetry experiment for the modified electrodes in 5 mM Fe(CN)_{ϵ}]⁴⁻ /[Fe(CN)_{ϵ}]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 overllap between the $Fe(CN)_6^{]4-} / [Fe(CN)_6^{]3-}$ peaks and the Fe_3O_4 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



Scheme 1: Schematic diagram showing electrode modification procedure, the electron transport and electrocatalytic behaviour of the GCE-MWCNT-MO electrodes towards oxidation of dopamine.



Figure 5: Cyclic Voltammograms of Bare GCE in (a) 0.1 M PBS (pH 7) and (b) 5 mM $Fe(CN)_{a}$]⁴⁻/[Fe(CN)_b]³⁻ solution prepared in 0.1M PBS (scan rate: 25-1000 mVs⁻¹; inner to outer).

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 nanopartilses 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 [57-60]. 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 pproximately unity, indicative of reversible electrochemical process, while that of GCE-MWCNT-ZnO



Figure 6: Cyclic Voltammograms of (1) GCE-MWCNT-MO, (2) GCE-MWCNT, (3) GCE- MO and (4) GCE in 5mM $Fe(CN)_{e_{1}}J^{4-}/[Fe(CN)_{e_{3}}J^{3-}$ solution prepared in 0.1M PBS at scan rate 25 mVs⁻¹. (MO: (a) NiO, (b) $Fe_{3}O_{4}$, and (c) ZnO nanoparticles).

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and GCE-MWCNT- Fe_3O_4 are less than unity suggesting a quasireversible electron transfer process at these electrodes. Using the Randles-Sevcik equation below:

$$I_{n=}(2.99 \times 10^5) \alpha^{0.5} n^{1.5} ACD^{0.5} v^{0.5}$$

Where n is the number of electron transfer, a is the electron transfer coefficient, A is the electroactive surface area, C is bulk concentration (5 mM) of $Fe(CN)_{\ell}^{4-}/[Fe(CN)_{\ell}]^{3-}$ and D is the diffusion coefficient. The electroactive surface area for the electrodes GCE-MWCNT- NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe₂O₄ 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 $Fe(CN)_{\epsilon}$ ⁴⁻ /[Fe(CN)_{\epsilon}]³⁻ redox probe follows the order: GCE-MWCNT- Fe₃O₄ (1800 µAcm⁻²) > GCE-MWCNT-ZnO (366.7 μAcm⁻²) > GCE-MWCNT-NiO (211.9 μAcm⁻²). Therefore GCE-MWCNT- Fe₂O₄ 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)₆]⁴⁻/[Fe(CN)₆]³⁻ 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.

$$\begin{split} &I_{p} (\mu A) = 8 \times 10^{-4} v^{1/2} - 3 \times 10^{-5} ; r^{2} = 0.9931 (\text{GCE-MWCNT-NiO}) \\ &I_{p} (\mu A) = 2.1 \times 10^{-3} v^{1/2} - 5 \times 10^{-4} ; r^{2} = 0.9671 (\text{GCE-MWCNT-ZnO}) \\ &I_{p} (\mu A) = 5.2 \times 10^{-3} v^{1/2} - 6 \times 10^{-4} ; r^{2} = 0.9980 (\text{GCE-MWCNT-Fe}_{3}O_{4}) \end{split}$$

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 *E*pa shifted to more positive values with increasing the scan rate (ν). 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 *E*pa versus log (ν), (1- α) *n* α 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 cms⁻¹ for electrodes GCE- MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively using equation (2).

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

$$i_p = \frac{n^2 F^2 A \Gamma v}{4RT}$$

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



Figure 7: Cyclic Voltammograms obtained for (a) GCE-MWCNT-NiO, (b) GCE-MWCNT-ZnO and (c) GCE-MWCNT-Fe₃O₄ in 5 mM Fe(CN)₆J^{a-}/[Fe(CN)₆J^{a-} solution prepared in 0.1 M PBS (scan rate: 25-1000 mVs⁻¹; inner to outer).



Figure 8: Typical Nyquist plots obtained for the electrodes in 5 mM [Fe(CN)₆]⁴⁻⁷ [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 used in the fitting of the EIS data for bare GCE and GCE-MWCNT, GCE-MWCNT-MO, and MO respectively.

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.

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 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). where circuit 8di represent the EIS data fitting for bare GCE and 8dii represent that of the NiO, ZnO, Fe₃O₄, MWCNT, MWCNT-NiO, MWCNT-ZnO and MWCNT- Fe₃O₄ modified GCE electrodes. In this circuit model, *Rs* is the solution resistance, *Cdl* 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.

From the *R*ct values, the electron transport is faster for the GCE– MWCNT–MO electrode compared to others. The bare GCE exhibited a larger semicircle with an Rct value of 1.572 k Ω when compared with MWCNT-ZnO, MWCNT-NiO and MWCNT- Fe₃O₄ modified GCE (38.2, 6.86 and 5.26 Ω) respectively, revealing the fast electron transfer at MWCNT-MO modified electrode. The rapid electron transfer at the nanocomposite can be ascribed to the excellent conductivity of MWCNT, which acts as a good electron conducting wire between MO and the electrode surface. The *n* values are less than the ideal 1.0 expected from an ideal capacitive behaviour, thus suggesting pseudocapacitive properties for these electrodes.

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

Electrodes	Electrochemical impedance spectroscopy data				
	R _s (Ω)	Q (x 10 ⁶ nF)	R _{ct} (Ω)	C _{dl} (u F)	
GCE	126.60 (0.04)	8.44 (1.19)	1237.00 (0.44)	2.13 (2.25)	
GCE-NiO	104.60 (1.62)	940.00 (3.95)	442.00 (2.14)	22.63 (2.42)	
GCE-ZnO	70.80 (1.10)	3200.00 (1.38)	38.20 (3.34)	83.30 (4.94)	
GCE-Fe ₃ O ₄	55.80 (8.93)	334.00 (9.50)	1915.00 (4.37)	10.61 (3.84)	
GCE-MWCNT-NiO	66.60 (2.17)	1410.00 (4.05)	6.86 (23.39)	10.90 (3.81)	
GCE-MWCNT-ZnO	53.90 (1.39)	5800.00(1.89)	5.33 (13.23)	4.06 (30.17)	
GCE-MWCNT-Fe ₃ O ₄	60.30 (0.59)	8270.00 (1.99)	5.26 (8.75)	18.12 (17.60)	
GCE-MWCNT	85.30 (0.59)	7770.00 (5.94)	73.10 (7.551)	1.73 (7.71)	

Table 1: Impedance data obtained for the bare GCE and the modified electrodes in 5 mM $Fe(CN)_{e}^{J^{*}}/[Fe(CN)_{e}^{J^{*}}$ solution at 0.2 V (vs. Ag/AgCl saturated KCl). All values were obtained from the fitted impedance spectra. The values in parentheses are percent errors of data fitting.



Figure 9: Cyclic voltammograms of 1×10^4 M DA on different electrodes (a) GCE-MWCNT-NiO, (b) GCE-MWCNT-ZnO and (c) GCE-MWCNT-Fe_3O_4 and (d) background subtracted CVs.



Figure 10: Cyclic voltammograms scan rate study of modified electrodes (a) GCE-MWCNT- NiO, (b) GCE-MWCNT-ZnO and (c) GCE-MWCNT-Fe₃O₄ in 1 \times 10⁴ M DA at various scan rates: 25-1000 mVs⁻¹ (e-g are the linear plots of current versus square root of scan rate for GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe₃O₄ respectively.

the GCE-MWCNT-MO electrodes follow the order: GCE-MWCNT-NiO (145 μ A) > GCE-MWCNT-ZnO (76 μ A) and GCE-MWCNT-



Fe₃O₄ (72 μ A). In terms of current density, the DA oxidation current at the electrode follows the order: GCE-MWCNT-NiO (1557 μ Acm⁻²) > GCE-MWCNT-ZnO (1085.7 μ Acm⁻²) and > GCE-MWCNT-Fe3O4 (1028.6 μ Acm⁻²) thus suggesting GCE-MWCNT-NiO electrode as the best electrode for DA oxidation in this study. The higher DA oxidation current at these electrodes indicates that the MWCNT has provided large surface area for effective diffusion of more DA molecules in and out of the electrode surface for maximum electrocatalytic oxidation by the MO nanoparticles compared with the bare GCE and other electrodes investigated. Similar results have been reported for DA oxidation on modified electrodes [63-65].

Effect of varying scan rate

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–Sev^{*}cik equation for an anodic oxidation process Equation (1), the plot of the peak currents (Ip) against the square root of scan rate ($v^{1/2}$) (Figure 10) for scan rate ranging from 25 to 1000 mVs⁻², gave a linear relationship with equations;

$$\begin{split} &I_{pa} = 2697.1 \ v^{1/2} - 467.92; \ R^2 = 0.992, I_{pa} = -2572.4 \ v^{1/2} + 551.82; R^2 = 0.991 \\ &I_{pa} = 2719.2 \ v^{1/2} - 487.96; \ R^2 = 0.9931, I_{pa} = -2574.4 \ v^{1/2} + 553.96; \ R^2 = 0.9931 \\ &I_{pa} = 3004.8 \ v^{1/2} - 656.35; \ R^2 = 0.9931, I_{pa} = -2454.5 \ v^{1/2} + 545.33; R^2 = 0.9931 \end{split}$$

(Figure 10) and approximately zero intercept, confirming a diffusioncontrolled process but with some levels of adsorbed reaction intermediates. The linear relationship of the plot confirmed that the nano composites were electroactive, conducting and confined to the surface. This was further confirmed by the plots of log of peak current against log of scan rate (graphs not shown) which gave a slope of 1 as expected for the electrochemistry of surface-absorbed species as shown by relationship below [66].

GCE-MWCNT-NiO:	I_{pa} =1.0544 log v+ 2.5007;	R ² =0.9907
GCE-MWCNT-ZnO:	I_{pa} =1.0827 log v+ 2.7936;	R ² =0.9651
GCE-MWCNT- Fe ₃ O ₄ :	I_{pa} =1.0721 log v+ 2.7727;	R ² =0.9987

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 *E*pa with log (ν), (1- α) $n\alpha$ 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 Vdec⁻¹. These values are higher than the theoretical 0.118 V dec⁻¹for 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 a was assumed equal to 0.5, na 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-a) na=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^{-2} cm/s, the electron transfer process is very fast, and the electrode reaction is reversible, and when 10^{-4} <ks < 10^{-2} cm/s, the electrode

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 of DA at pH=7.0 phosphate buffer solution between -0.2 to 0.8V (scan rate: 25 mVs⁻¹) (graph not shown). The anodic peak current decrease for about 7, 8 and 4% at electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe₃O₄ respectively after twenty cyclic voltammogram in the supporting electrolyte. However, on rinsing the electrode in a fresh PBS (pH 7.0) solution, the electrode surface was renewed and more than 95% of the initial catalytic current was obtained, indicating the electrode was also used for the analysis of DA after storage in a refrigerator for up to two weeks without a significant change in its response.

Impedance studies were also carried out to monitor the mechanism of the electron transfer process during the electrocatalytic oxidation of 10⁻⁴ M DA at fixed potential 0.2 V and frequencies between 10 kHz and 1.0 Hz. the impedance spectra (Nyquist plots) obtained for the electrodes are presented in Figure 11a, while Figure 11b shows the equivalent circuits used in the fitting of the impedance data. (Figure 11)

However the GCE-electrodes were successfully fitted with minimum error values especially for the Rct data using circuit model RQ(RC) (Figure 11). The charge transfer resistance Rct is lower at GCE MWCNT-MO compared with the bare GCE, GCE-MWCNT and GCE-MO. The finding further confirms the CV data and also indicates that the electron transfer process is faster at GCE-MWCNT-MO electrodes with GCE-MWCNT-NiO > GCE-MWCNT-ZnO and >



Figure 11: Typical Nyquist plots obtained for the electrodes in 1×10^4 M DA 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. (d) Represent the circuit used in the fitting of the EIS data in (a-c).

Electrodes	Electrochemical impedance spectroscopy data			
	Rs (Ω)	Q (x 106 nF)	Rct (Ω)	Cdl (u F)
GCE	54.70 (9.05)	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 (8.53)	2.65 (1.31)	104.80 (4.72)	152.30 (10.72)
GCE-ZnO	81.20 (7.95)	80.30 (3.04)	80.40 (7.47)	180.90 (16.73)
GCE-Fe ₃ O ₄	134.60 (3.18)	80.30 (3.04)	319.00 (2.586)	8.66 (3.54)
GCE-MWCNT-NiO	74.60 (0.57)	350.00 (3.80)	9.50 (7.18)	63.00 (14.82)
GCE-MWCNT-ZnO	80.10 (0.49)	332.00 (3.45)	10.48 (6.59)	72.49 (12.74)
GCE-MWCNT-Fe ₃ O ₄	78.90 (0.65)	235.00 (6.64)	33.30 (5.19)	93.30 (5.15)

Table 2: Impedance data obtained electrodes in 1×10^4 M DA solution in pH 7.0 PBS (at 0.2 V vs. Ag/AgCl saturated KCl). The values in parentheses are percent errors of data fitting.

GCE-MWCNT- Fe_3O_4 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).

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 voltemmetry (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^{-6} 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 thesame line to be 7.99 × 10⁻¹², 3.74 × 10⁻⁷, and 1.389 × 10⁻⁶ mol/L=3) for electrodes GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe₃O₄ respectively. The nano molar limit of detection obtained for GCE-

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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- Fe_3O_4 in 0.1 M pH 7.0 PBS containing mixture of 10^{-2} 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

Electrode material	Techniques	Interference	Detection Limit (molL-1)	References
SWNT/Ppy,Surf.cov.bend	SWV	AA	$5.00 imes 10^{-6}$	[60]
MWCNT/B-CD modified	GCE SWV	AA	6.70 × 10 ⁻⁶	[61]
Fe₃O₄/rGO/GO	SWV	AA	1.20 × 10 ⁻⁷	[62]
GCE/MWCNT-NiO	SWV	AA	$7.99\times10^{\text{-12}}$	This work
GCE/MWCNT-ZnO	SWV	AA	3.74 × 10 ⁻⁷	This work
GCE/MWCNT-Fe ₃ O ₄	SWV	AA	1.39 × 10 ⁻⁶	This work

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



Figure 12: SWV of GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT-Fe $_3O_4$ in 1 × 10⁻⁴ M DA (inset is the graph of current vs concentration of DA).



7.0), 10^2 M AA alone and 10^2 M AA + different volume of 10^4 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/9.09 µM DA, (iv) mixture of 8.33 mM AA/16.7 µM DA (v) mixture of 7.69 mM AA/23.0 DA µM (vi) 7.14 mM AA/28.6 µM DA (vii) 6.67 mM AA/33.0 µM DA (viii) 6.25 mM AA/37.5 µM DA (ix) 5.88 mM AA/41.2 µM DA (x) 5.56 mM AA/44.0 µM DA (xi) 5.2 mM AA/47.0 µM DA and (xii) 5 mM AA/50 µM DA concentrations.

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- Fe_3O_4 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).



Figure 14: DPV profiles of (a) GCE-MWCNT-NiO, (b) GCE-MWCNT-ZnO and (c) GCE- MWCNT-Fe₃O₄ in pH 7.0 PBS containing 10^{-2} M AA and 10^{-4} M DA solutions respectively.



Analytical performance of the proposed sensors for determination of DA in pharmaceutical sample

The proposed sensors were tested for determination of DA in dopamine hydrochloride injection samples. The SWV method was used for the determination of DA in Pharmaceutical samples. The samples were prepared and adjusted to 3.5×10^{-4} M DA in 0.1 M PBS (pH 7.0), by dilution of DA ampoule contents (2.5 ml of 40 mg/ml DA hydrochloride injection solution). The standard addition experiment was carried out by addition of different concentrations of DA to the drug sample and its DA concentration evaluated using SWV. The obtained equations for the plot of peak current versus concentration of



Figure 16: Chronoamperometric curves of (a) GCE-MWCNT-NiO, (b) GCE-MWCNT-ZnO and (c) GCE-MWCNT-Fe₃O₄ in pH 7.0 PBS containing 10⁻⁴ M DA and different concentration of AA (approx. 1000 times DA concentration).

Electrode	Added (mg/ml)	Detected (mg/ml)	Recovery (%)	RSD %
GCE-MWCNT-NiO	40	44.9	112.4	0.1
GCE-MWCNT-ZnO	40	39.1	97.8	0.13
GCE-MWCNT-Fe ₃ O ₄	40	36.1	90.3	0.3

Table 4: Results of detection of DA in dopamine hydrochloride injection (n=5).

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 Fe₂O₄) 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 giving the best peak separation of 400 mV, 300 mV and 600 mV at GCE-MWCNT-NiO, GCE-MWCNT-ZnO and GCE-MWCNT- Fe₂O₄ electrodes respectively. Electrocatalysis of DA on the GCE-MWCNT-MO electrodes was through diffusion and surface-confined electrode process. The study also showed that the GCE/MWCNT/NiO modified electrode can be successfully used for the assay of dopamine in DA real life samples.

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