CHAPTER TWO

EXPERIMENTAL

2.0 EXPERIMENTAL

2.1 Materials and Reagents

The pristine single-walled carbon nanotubes (SWCNTs, 06509HB Aldrich) and multi-walled carbon nanotubes (MWCNTs) were purchased from Aldrich chemicals and digested by subjecting them to harsh acid conditions for -COOH modification following the method already described [1]. Digestion with strong acids serves the purposes of transforming the CNTs into shorter, uncapped nanotubes bearing mainly acidic groups. A single-walled carbon nanotube poly(m-aminobenzene sulphonic acid (SWCNT-PABS) was also purchased from Aldrich chemical and was used directly without further treatment. The nitrate salts of the metals, nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$); iron nitrate nonahydrate ($Fe(NO_3)_2.9H_2O$); cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) are products of Sigma-Aldrich. Dopamine-hydrochloride ($C_8H_{11}NO_2.HCl$); Hydrazine sulphate ($H_6N_2O_4S$); sodium nitrite ($NaNO_2$); diethylaminoethanethiol (DEAET) are bought from Sigma chemicals. Sodium sulphate (Na_2SO_4); sodium hydroxide ($NaOH$); ammonium carbonate ($(NH_4)_2CO_3$); ferric chloride ($FeCl_3$); hydrated potassium hexacyano ferrate(II) ($K_4[Fe(CN)_6].6H_20$); potassium hexacyano ferrate(III) ($K_3Fe(CN)_6$); potassiumchloride(KCl); cetyltrimethylammoniumbromide (CTAB); dimethylformamide ($(CH_3)_2NC(O)H$); acetone (C_3H_3O); ethanol (C_2H_5OH); isopropyl alcohol (C_3H_7OH); ethylene glycol ($C_3H_8O_3$); sulphuric acid (H_2SO_4); phosphoric acid (H_3PO_4); nitric acid (HNO_3); hydrochloric acids (HCl); hydrazinium hydroxide (N_2H_5OH); ammonia solution ($NH_3.H_2O$); sodium borohydride ($NaBH_4$), and other reagent were of analytical grade and 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 supplied by a local pharmacy store. 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 acetate and phosphate buffer solutions of pH 3.0, 4.0, 7.0, 7.4 and 9.4 respectively were prepared using acetic acid (CH_3COOH), sodium acetate (CH_3COONa), sodium hydrogen phosphate di-hydrate ($NaH_2PO_4.2H_2O$) and di-sodium hydrogen phosphate di-hydrate ($Na_2HPO_4.2H_2O$) or their potassium salts. The pH is adjusted with 0.1 M H_3PO_4 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 as received from the suppliers without further purification. All electrochemical experiments were performed with nitrogen-saturated PBS.

2.1.1 Synthesis of funtionalised CNTs

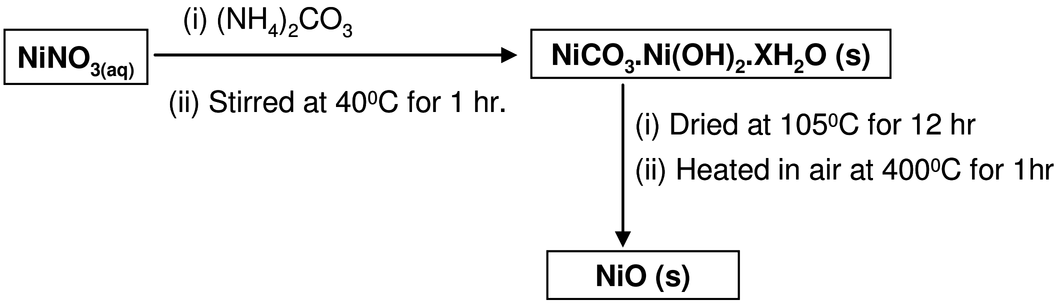
Briefly, the starting material pristine SWCNTs or MWCNTs (Aldrich) was purified and cut into short and uncapped nanotubes bearing acid functional groups (CNT-COOH) according to the multi-step procedures developed [1] (with some little modification) by refluxing a known weight of the SWCNTs in 2.6 M HNO_3 for 48 h. The product was washed with copious amount of water, centrifuged to drive away the water and dried. The residue is ultrasonicated at 40 ^{0}C in a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v) for 24 h. The material was filtered again, washed with copious amount of water and dried. Finally, the suspension was stirred at 70 ^{0}C in a mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2 (4:1, v/v) for 4 h. The product was filtered and washed with copious amount of water until the pH of the filtrate is neutral. The black solid material obtained was dried in an oven over night and characterised using FTIR (to confirm the carbonyl functional group (C=O) of the –COOH), SEM and TEM (to established structural changes after modification). The ash treatment employed cut the nanotubes to smaller sizes that allow for COOH modification.

2.1.2 Synthesis of nickel and nickel oxide nanoparticles

Nickel nanoparticles were synthesised adopting the method described by Wu and Chen, 2003 [2]. An appropriate amount of nickel nitrate (50 mM) was dissolved in ethylene glycol (25 mL). To the solution were added hydrazinium hydroxide (2.0 mL, 1.0 M) and 1.0 M NaOH solution (72 µLmL^{-1}) in sequence. The reaction was maintained at 60 ^{0}C and nickel nanoparticles were formed after about an hour in a capped volumetric flask under stirring. The reduction reaction is shown below.

$$2Ni^{2+}_{(aq)} + N_2H_{4(aq)} + 4OH^{-}_{(aq)} \longrightarrow 2Ni_{(s)} + N_{2(g)} + 4H_2O(l) \qquad (2.1)$$

Nickel oxide (NiO) nanoparticles were prepared using the method described by Xiang et al. [3]. 100 mL of precipitation solution (NH_4HCO_3) was dropped at the rate of 5.0 mL min^{-1} into 50 mL of 0.5 M Ni^{2+} solution. During precipitation, the suspension was kept at constant temperature (40 ^{0}C), and constant stirring (800 rpm) for 1 h. The precipitate formed was washed with distilled water and copious amount of ethanol several times to removed possible adsorbed ions such as Ni^{2+}, NH_4^{+}, Cl^{-}, NO_3^{-}, CO_3^{2-}, and OH^{-}. The precipitate was oven-dried at 105 ^{o}C for 12 h, and later heated in air at 400 ^{o}C for 1 h. The product was pulverised and used for analysis. The procedure is summarised in scheme 2.1 below.



Scheme 2.1: Procedures for the synthesis of NiO nanoparticles.

2.1.3 Synthesis of cobalt and cobalt oxide nanoparticles

Co nanoparticles were synthesized using the method described by Shen et al. [4]. 71.4 mg of $Co(NO_3)_2.6H_2O$ was dissolved in 20 ml ethylene-glycol in 5 mL H_2O. The precursor was reduced by slowly adding solution containing mixture of 0.1 M $NaBH_4$ and 1.0 M NaOH. The mixture was quickly heated to 120 ^{0}C for 2h to reduce the Co completely. Cobalt oxide nanoparticles were prepared using the method described by Yao et al. [5]. A given amount (3.0 g) of $Co(NO_3)_2.6H_2O$ was dissolved into 100 ml of isopropyl alcohol-water (1:1, v/v) solution in a three-necked round-bottom flask. Then appropriate amount (30 - 50 mL) of isopropyl alcohol-ammonia solution was added into the solution and aged for hours to ensure complete precipitation. The precipitate was filtered and dried under vacuum at 70 ^{0}C. The CO_3O_4 was finally obtained by calcining the $Co(OH)_2$ precursor at 500 ^{0}C in Ar for 2h.

2.1.4 Synthesis of iron and iron oxide nanoparticles

Nanoscale zero-valent iron particles were synthesized by the sodium borohydride method [6-8]. The synthesis was conducted in a flask reactor with three open necks. The central neck was housed with a tunable mechanical stirrer at 400 rpm. Through titration at a rate of 0.625 mL/s, 50 mL (0.2 M) $NaBH_4$ was titrated slowly into 50 mL (0.05 M) $Fe(NO_3).9H_2O$ solution. The borohydride was introduced to reduce ferric ion (Fe^{3+}) to zero-valent iron [Fe^0], according to the following reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \longrightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \qquad (2.2)$$

The mixture was vigorously mixed in the flask reactor for additional 30 min after the titration. The generated iron particles were harvested with vacuum filtration and stabilized with a large volume of deionized water (>100 mL/g) to wash, and at the end, with diluted ethanol (~5%).

The maghemite (Fe_2O_3) nanoparticles were synthesized by the method described by Sun et al. [9]. First, Magnetite (Fe_3O_4) nanoparticles were synthesized according to the method proposed by Qu et al. [10] with some modification. Briefly, 9 mL (2 M) $Fe(NO_3).9H_2O$ (dissolved in 2 M HCl) was added to 300 mL double-distilled water, and 10 mL Na_2SO_3 (1 M) was added to the former solution drop wise in 1 min under magnetic stirring. The colour of the solution changed from light yellow to red, indicating complex ions formed between the Fe^{3+} and SO_3^{2-}. When the color of the solution turned black again, the solution was added to 300 mL $NH_3.H_2O$ solution (0.85 M) under vigorous stirring. A black precipitate is formed and allowed to crystallize completely for about an hour under magnetic stirring. The precipitate was washed with copious amount of water to bring the pH of the suspension to less than 7.5. The suspension was dried into black powder at ambient temperature under vacuum. The black precipitate obtained above was diluted to a volume of 300 mL. The suspension temperature was raised to 90 °C in 5 min, and was stirred under aeration for 60 min at about 100 ^{o}C. The colour changed from black to reddish-brown slowly while the suspension became clear and transparent. The reddish-brown solution was washed four times with water by magnetic decantation. It was then dried to powder in the oven at 70 ^{o}C. The morphology of the synthesised M (Ni, Co, Fe) and MO (NiO, Co_3O_4, Fe_2O_3) nanoparticles was investigated with high resolution scanning electron microscopy (HRSEM), transmission electron microscopy (TEM), electron dispersive spectroscopy (EDX) and X-ray Diffractometry (XRD) using CoKα radiation.

2.2 Equipment and Procedure

The edge plane pyrolytic graphite electrode plate (EPPGE) (3.0 and 5.0 mm diameter) or basal plane pyrolytic graphite electrode plate (BPPGE) (5.0 mm diameter) was purchased from Le Carbone, Sussex, UK and was constructed in-house at the University of Pretoria technical workshop by placing it in a teflon tube, extended outside with a copper wire (held in place with conducting silver varnish L 100 (Kemo Electronic, Germany) to make electrical contact with the electrochemical equipment.

Field emission scanning electron microscope (FESEM) images were obtained from JEOL JSM 6000 LV (Japan), high resolution scanning electron microscope (HRSEM) images were obtained using the Zeiss Ultra Plus 55 HRSEM (Germany), while the energy dispersive x-ray spectra (EDX) were obtained from NORAN VANTAGE (USA) at the Microscopy and Microanalysis Laboratory of the University of Pretoria. TEM experiment was performed using a Model JEOL JEM-2100F field emission transmission electron microscope, Tokyo (Japan). AFM experiments were performed with AFM 5100 System (Agilent Technologies, USA) using a contact mode AFM scanner interfaced with a PicoView 1.4.3 controller (scan range 1.25 µm in x–y and 2.322 µm in z). Silicon type PPP-CONT-20 (Nanosensors®) of thickness 2.0±1.0 µm, length 450±10 µm, width 50±7.5 μm, spring constants 0.02-0.77 N m^{-1}, resonant frequencies of 6–21 kHz and tip height of 10-15 μm were used. All images (256 samples/line × 256 lines) were taken in air at room temperature and at scan rates 0.5–0.6 lines s^{-1}. The X-ray photoelectron spectra (XPS) were obtained using a Physical Electronics model 5400 spectrometer system with monochromatic Mg Kα radiation at 1253.6 eV at take-off angles of 45°. 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. UV/Vis experiment was performed with a UV-Visible spectrophotometer, 100 Bio Varian Win UV, Australia. The XRD analysis was done using a back loading preparation method. The sample was analysed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation. The samples are scanned at the required 2θ angle ranges (5^o – 90^o). The phases were identified using X'Pert Highscore plus software.The voltage and current is 35 kV and 50 mA.

Electrochemical experiments (e.g cyclic voltammetry, square wave voltammetry, Linear sweep voltammetry) were carried out using an Autolab Potentiostat PGSTAT 302 (Eco Chemie, Utrecht, and The Netherlands) driven by the GPES software version 4.9. The RDE experiments were performed using AUTOLAB-RDE, (Eco Chemie, Utrecht, The Netherlands) with a locally fabricated RDE EPPGE electrode (5.0 mm in diameter) as the working electrode. Linear sweep voltammetry (LSV) was performed at potential range of 0.0 to 1.0 V (vs Ag|AgCl, sat'd KCl) after 15 min adsorption (by keeping the electrode in a stirred analyte solution). Electrochemical impedance spectroscopy (EIS) measurements were performed with an Autolab Frequency Response Analyser (FRA) software between 100 mHz and 100 kHz using a 5 mV rms sinusoidal modulation in a solution of 5 mM of $K_4Fe(CN)_6$ and a 5 mM $K_3Fe(CN)_6$ (1:1) mixture in phosphate buffer solution (PBS) of pH 7.0 and at the $E_{1/2}$ of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ vs. Ag|AgCl in sat'd KCl. The FRA software allowed the automatic fitting of the raw EIS data to equivalent circuit models using a *non-linear least squares* (CNLS) method based on the EQUIVCRT programme [11], with *Krammers-Kronig rule check*. EIS experiment was also carried out in buffer solution containing different concentrations of the analytes DEAET, hydrazine, dopamine, nitrite and nitric oxide respectively. Bare EPPGE/BPPGE and modified electrodes are used as working electrode. A Ag|AgCl in saturated KCl and platinum wire were used as reference and counter electrodes, respectively. A bench top pH / ISE ORION meter, model 420A, was used for pH measurements. All solutions were de-aerated by bubbling nitrogen prior to each electrochemical experiment. All experiments were performed at 25 ± 1 °C.

All the procedure involves loading (by drop-dry and electrodeposition method) a thin film of the M or MO/CNT nanocomposite on the base electrode (EPPGE or BPPGE), or a conducting carbon electrode (e.g glass carbon plate in cases where the working electrode did not fit into the machine) in preparation for analysis. The detail of the electrode modification process is discussed below.

2.2.1 Assay of dopamine hydrochloride injection

A 2 mL of the dopamine drug (injection), Dopamine HCl-Fresenius®, sample was diluted to 100 mL with distilled de-ionised water. 2 mL of this diluted solution was pipette into each of 50 mL volumetric flask and all except one were spiked with different concentration of standard dopamine solution (standard addition method), 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 5 times for each sample.

2.3 Electrode Modification and Pretreatments

2.3.1 Electrode cleaning

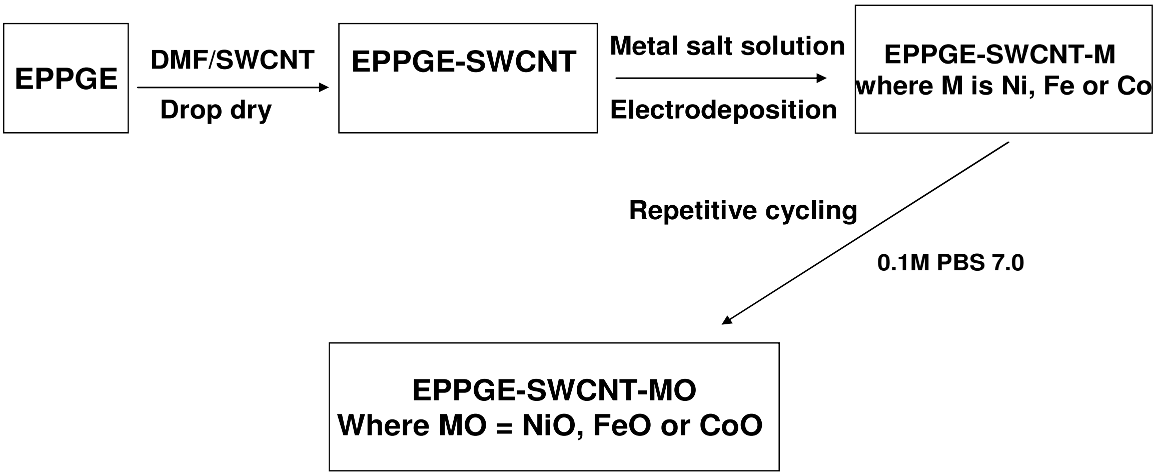
Electrodes were prepared using the following procedures. First, the EPPGE surface was cleaned by gentle polishing in aqueous slurry of alumina oxide nanopowder (Sigma-Aldrich) on a SiC-emery paper and then to a mirror finish on a Buehler felt pad. The electrode was then subjected to ultrasonic vibration in acetone or ethanol to remove residual alumina particles that might be trapped at the surface. On the other hand, BPPGE surface was cleaned by gentle polishing on a carborundum paper and the surface was smoothened by a paper tape. The electrode was then subjected to ultrasonic vibration in absolute ethanol to remove adhesives that might be trapped at the surface.

2.3.2 Electrode modification

2.3.2.1 Drop-dry / electrodeposition techniques

About 20 µL drop of the CNTs/DMF solution (2.5 mg SWCNT-COOH, MWCNT-COOH or SWCNT-PABs in 1 mL DMF) solution was dropped on the bare EPPGE / BPPGE and dried in an oven at 50 ^{o}C for 5 min. The modified electrode obtained is herein denoted as EPPGE-SWCNT, EPPGE-SWCNT-PABs or BPPGE-MWCNT as the case may be. The EPPGE-CNT-M (where M = Fe, Ni or Co) was obtained using similar procedure adopted by others [12-16] for the electrodeposition of metal nanoparticles on carbon electrodes using chronoamperometric strategy. Briefly, EPPGE-CNT was immersed in 5 mM solution of the nitrate salts of the metals ($Ni(NO_3)_2.6H_2O$, $Fe(NO_3)_2.9H_2O$ or $Co(NO_3)_2.6H_2O$, at a fixed potential of -2.0 V (vs

Ag|AgCl, sat'd KCl) for 5 min. A 5 min deposition time as reported by Salimi et al. [12-15] and Giovanelli et al. [16] was chosen for this work. Also the preliminary investigation of the electrochemical response of EPPGE-SWCNT-Ni in 0.1 M NaOH solution obtained at different deposition time's intervals of between 5 - 40 min yielded the highest current response at the lowest deposition time. The resulting electrodes are denoted as, EPPGE-SWCNT-Ni, EPPGE-SWCNT-Co and EPPGE-SWCNT-Fe. EPPGE-Ni, EPPGE-Co and the EPPGE-Fe modified electrodes are obtained through the same procedure but without CNT. The modified electrodes are stored in refrigerator before ready for use. The electrodes, EPPGE-CNT-MO (where M = Fe, Ni or Co) were obtained by immersing the EPPGE-CNT-M in 0.1 M PBS (pH 7.0) and repetitively scanning (20 scans) between 1.5 and -0.8 V potential window at a scan rate of 100 mV/s. The modified electrodes are represented as, EPPGE-SWCNT-NiO, EPPGE-SWCNT-Co_3O_4, EPPGE-SWCNT-Fe_2O_3, EPPGE-NiO, EPPGE-Co_3O_4 EPPGE-Fe_2O_3 respectively. The modification procedure is summarised in scheme 2.2. The electroactive surface coverage area of the electrodes was determined in 5 mM ferri/ferro ($[Fe(CN)_6]^{3-/4-}$) redox probe and estimated by using the relationship; $Q = nFA\Gamma$ [17]).



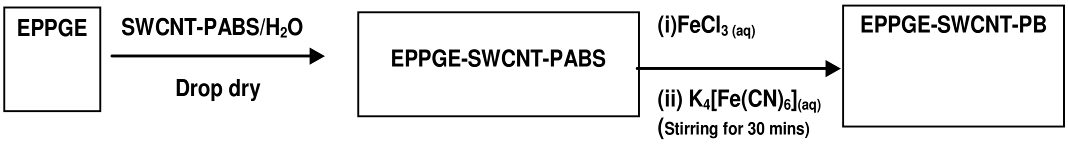
Scheme 2.2: Procedure for the fabrication of metal and metal oxide nanoparticles modified electrodes.

Morphology of the modified electrodes were examined with field emission scanning electron microscopy (FESEM), high resolution scanning electron microscopy (HRSEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), electron dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).

2.3.1.2 Modification with Prussian blue (PB) nanoparticles

The synthesis of Prussian blue (PB) nanoparticles and its integration with the single-walled carbon nanotubes poly(m-aminobenzene sulphonic acid) (SWCNT-PABS) are described below. EPPGE-SWCNT-PABS was prepared by a drop-dry method. About 20 µL drop of the SWCNT-PABS/H_2O or SWCNT-PABS/CTAB solution (0.1 mg SWCNT-PABS in 1 mL H_2O or 1 mL CTAB solution) was dropped on the bare EPPGE and dried in an oven at 50 ^{0}C for 5 min. The electrodes obtained are herein abbreviated as EPPGE-SWCNT-PABS or EPPGE- CTAB-SWCNT-PABS.

The deposition of PB nanoparticles on the EPPGE-SWCNT-PABS modified electrodes follows the procedure described by Han et al. [18] and summarised in scheme 2.3. $FeCl_3$ and $K_4[Fe(CN)_6]$ of the same concentration (e.g. 10^{-4} M) were used for the deposition experiment. The EPPGE-SWCNT-PABS electrode or the EPPGE-CTAB-SWCNT-PABS electrode was immersed in stirred 10^{-4} M $FeCl_3$ solution for 30min. After 30min, the electrode was rinsed, dried and immersed in 10^{-4} M $K_4[Fe(CN)_6]$ for another 30min. It was then rinse and dry again to give the first layer of PB nanoparticles corresponding to the first deposition cycle. The electrode obtained is herein denoted as EPPGE-SWCNT-PB or EPPGE-CTAB-SWCNT-PB electrode. Second and the third layer of PB nanoparticles were obtained on the electrode by systematically repeating the step described above using solutions of $FeCl_3$ and $K_4[Fe(CN)_6]$.



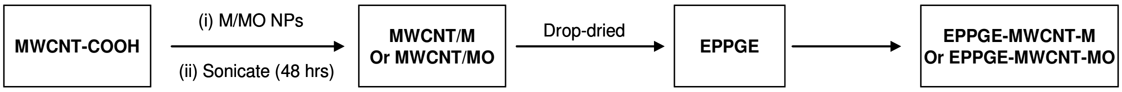
Scheme 2.3: Electrode modification procedure with Prussian blue (PB) nanoparticles.

The modified electrodes morphology were examined with scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), electron dispersive x-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The solid SWCNT-PB nanocomposite film formed on the electrode thorugh several layers was scraped and characterized using UV/Vis, infra-red (IR) spectroscopy and X-ray Diffractometry (XRD) using CoKα radiation.

2.3.1.3 Electrode modification with synthesised M and MO nanoparticles.

For the chemical synthesis experiment, acidified MWCNT was used in place of acidified SWCNTs. The motivation for using MWCNT and employing chemical synthesis procedure are: (i) MWCNT was cheaper and commercially available than SWCNT, (ii) chemical synthesis produces M and MO nanoparticles in commercial quantity compared to electrodeposition method, (iii) the synthesised nanoparticles can easily be used on screen printed electrode (SPE) for disposable experiment, (iv) earlier work using SWCNT and electrodeposition method have been associated with adsorption of the analytes due to large surface area of the SWCNT. Electrode modification follows simple drop-dried procedure (Scheme 2.4). Different weight (2.5 to 10 mg) of the synthesised metal (M) and the metal oxides (MO) nanoparticles were weighed and dissolved in dimethylformamide (1 ml DMF) along with and without 2 mg of the functionalised MWCNT. The mixture was stirred at room temperature for 48 h. About 20 µL of the obtained MWCNT-M was dropped on the EPPGE and left in the oven for 5min. The modified electrode is denoted as EPPGE-MWCNT-M (where M = Ni, Co or Fe). Similar procedure was employed for modifying the EPPG electrode with MO nanoparticles and the resulting electrode is represented as EPPGE-MWCNT-MO (where MO = NiO, Fe_2O_3 or Co_3O_4). Therefore, the modified electrodes obtained are: EPPGE-Ni, EPPGE-Co, EPPGE-Fe, EPPGE-MWCNT, EPPGE-MWCNT-Ni, EPPGE-MWCNT-Co, EPPGE-MWCNT-Fe; EPPGE-NiO, EPPGE-Co_3O_4, EPPGE-Fe_2O_3, EPPGE-MWCNT-NiO, EPPGE-MWCNT-Co_3O_4 and EPPGE-MWCNT-Fe_3O_4.

The electrodes morphology were examined with high resolution scanning electron microscopy (HRSEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), electron dispersive spectroscopy (EDX) and X-ray Diffractometry (XRD) using CoKαradiation.



Scheme 2.4: Procedure for electrode modification with synthesized metal (M) and metal oxides (MO) nanoparticles.

2.4 Electron Transport Experimental Procedure

The electron transport (ET) of the redox-active M, MO and PB nanoparticles integrated with or without CNTs were interrogated in a solution containing an outer-sphere redox probe 5 mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). This usually represents a preliminary experiment conducted to establishing the successful modification and the electrical properties of the redox active nano materials on the modified electrodes. Bare and modified EPPG or BPPG electrodes were used as the working electrode. Ag|AgCl, sat'd KCl and platinum electrodes were employed as reference and counter electrodes respectively. The CV experiment was done by running the bare and the modified electrodes in the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox probe within the potential window of 0.2 to 1.0 V at a scan rate of 50 mVs^{-1}. From the voltammogram obtained, the $E_{1/2}$, ΔE, E_p, I_p, I_c, I_p/I_c for the electrodes were determined and these parameters gave insight into the electron transport properties of the respective electrodes. The EIS experiment is conducted by running the bare and the modified electrodes in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution ($E_{1/2}$ 0.2 or 0.3 V vs. Ag|AgCl in sat'd KCl) between 100 mHz and 10 kHz using a 5 mV rms sinusoidal modulation. The data points generated are fitted with a particular equivalent circuit and the charge transfer resistant (R_{ct}) which controls the electron transfer kinetics of the redox probe at the electrode interface is determined from the EIS fitting.

2.5 Electrocatalytic and Electroanalysis Experiment procedure.

2.5.1 Electrocatalytic procedure

Experiments for electrocatalytic oxidation of the analytes (e.g. DEAET, Hydrazine, Nitrite and Dopamine) were carried out using N_2 purged PBS and Na_2SO_4 solutions at different pH at which the analyte ionizes best unless otherwise stated. For example, 10^{-4} M DEAT was prepared in 0.1 M pH 9.4 PBS, 10^{-3} M nitrite was prepared in 0.1 M pH 7.4 and pH 3.0 PBS, 10^{-3} M hydrazine was prepared in 0.1 M pH 7.0 Na_2SO_4 solution, and 2 x 10^{-4} M dopamine was prepared in 0.1 M pH 7.0 PBS respectively. Generally, the experiment was carried out at scan rate of 25 mVs^{-1} and within the oxidation potential window as wide as -1.3 to 1.3 V. The electrocatalytic experiment was divided into two parts: (i) catalysis using electrode modified by electrodeposition of metal and metal oxide nanoparticles and (ii) catalysis using electrode modified with chemically synthesised metal and metal oxide nanoparticles. In each case, a comparative study of the electrocatalytic behaviour of the modified electrodes towards the analyte was investigated. Preliminary characterisation study showed that DEAET and hydrazine are better catalysed on Ni modified electrode, nitrite on Co modified electrodes and dopamine on Fe modified electrode. Thus in this study, DEAET and hydrazine electrocatalysis was focused on Ni and NiO modified electrode, nitrite on Co and Co_3O_4 modified electrodes and dopamine on Fe and Fe_2O_3 modified electrodes. The interfering effect of ascorbic acid (AA) in a mixture containing dopamine (9.1 µM DA) and 1000 folds AA concentration (9.1 mM AA) was carried out. Dopamine oxidation on PB modified electrodes (described above) was also investgated. Effect of PB concentration (i.e 10^{-4}, 10^{-3} and 10^{-2} M PB) and deposition cycles or layer of PB that is, EPPGE-SWCNT-PB, EPPGE-SWCNT-2PB and EPPGE-SWCNT-3PB towards electrocatalytic oxidation of $2x10^{-4}$ M DA solution was studied. Other electrodes investigated are EPPGE-PB, EPPGE-SWCNT-PABS, EPPGE-CTAB-SWCNT-PABS, EPPGE-SWCNT-PB, EPPGE-CTAB-SWCNT-PB. The effect of stabilising agent such as cetyltrimethylammonium bromide (CTAB) on PB electrocatalytic activities towards DA was studied and compared with electrode modified without CTAB.

Generally, cyclic voltammetry (CV) and electrochemical impedance (EIS) experiments were conducted to investigating the electrocatalytic behaviour of the electrodes towards the analyte. From CVs experiment, electrochemical parameters such as peak current (I_p), peak potential (E_p), ∆E and formal potential ($E_{1/2}$) were measured and discussed. In addition, square wave voltammetry (SWV) and rotating disc electrode (RDE) experiments were carried out for DA to monitoring its kinetic at the electrode, and to monitoring the interfering effect of AA on DA at the electrode. In every case of measurement, the bare or modified electrode is the working electrode while Ag|AgCl, sat'd KCl and platinum electrodes are the reference and counter electrodes respectively. EIS experiment was done by fixing the peak potential (E_p) at which the analyte was best catalyzed (vs Ag|AgCl, sat'd KCl) or its half potential ($E_{1/2}$) especially for a reversible electrocatalytic process.

2.5.2 Electroanalysis procedure

The effect of scan rate (25 to 1000 mVs^{-1}) on the electrode kinetics during analyte oxidation was investigated using the best electrode from the electrocatalytic experiment. Several kinetic parameters such as E_p, I_p, the peak-to-peak separation (ΔE_p) were obtained. The plot of the anodic (I_{pa}) peak current against square root of scan rate ($\nu^{1/2}$) which is an indication of diffusion-controlled reaction was investigated.

As part of the analysis experiment, concentration study on each analyte was carried out using chronoamperometric (CA) experiment. Analysis of the analytes was carried out at their respective peak potential of catalysis. For example, a peak potential of 0.6 V was fixed during DEAET and hydrazine, 0.8 V for nitrite and 0.2 V for dopamine analysis respectively. Different aliquot of the stock analyte solution (corresponding to different concentrations) was injected into 25 or 30 mL of buffer solution and the mixture stirred thoroughly for 5 min. The modified electrode is run in both the buffer and the analyte solutions and the chronoamperogram obtained after 40 to 60 min. From the chronoamperogram, the catalytic current I_{cat} and the buffer current I_{buff} were estimated and recorded. The catalytic rate constant K [19,20] and the diffusion coefficient D [21] of the analyte on the electrode were calculated.

From the plot of peak current response I_p versus different analyte concentration *[analyte]*, sensitivity and the limit of detection (LoD =3.3 s/m [22], where *s* is the relative standard deviation of the intercept and *m*, the slope of the linear current versus the concentration of analyte) were estimated.

To evaluate the extent of adsorption of the analyte at the electrode, linear sweep voltammetry experiment was carried out at different concentration of the analyte. Different aliquot of the sample (corresponding to different concentrations) was injected into 25 or 30 mL of buffer solution and the modified electrode was left in the solution while stirring for 15 min. Thereafter, experiments were carried out using the modified electrodes as the working electrodes in the analyte solution at 25 mVs^{-1} with a potential range of 0.0 to 1.0 V. From the linear sweep voltammogram obtained and applying the Langmuir adsorption isotherm theory (Equation 2.3 [23]), the adsorption equilibrium constant (β) and the standard free energy (ΔG^o) due to adsorption were calculated. The symbols are defined in Chapter 1 and represented on the list of symbols.

$$\frac{[\text{Analyte}]}{I_{cat}} = \frac{I}{\beta I_{max}} + \frac{[\text{Analyte}]}{I_{max}} \qquad (2.3)$$

2.6 Electrochemical supercapacitive procedure

The electrochemical supercapacitive behaviour of the MO or CNT/MO modified electrodes in 1 M Na_2SO_4 (neutral) and 1 M H_2SO_4 (acidic) solutions was studied using cyclic voltammetry (CV), charge discharge (CD) and electrochemical impedance spectroscopy (EIS) experiments. In this experiment, BPPGE was used as the base electrode because of his high capacitive current in 5 mM $Fe(CN)_6]^{4-}$ /$[Fe(CN)_6]^{3-}$ redox probe compared with EPPGE. The supercapacitor experiment was mainly focused on the MO modified electrodes for the following reasons: (i) the CVs for MO or CNT/MO modified electrode gave high charging or capacitive current in most cases in the electrolytes used in this study (see Chapters 3 and 4) (ii) because of the electroactive nature of the material, it is envisaged that the metal nanoparticles (Ni, Fe and Co) will possibly oxidized to their oxide state in the electrolytes used for the supercapacitive study, thus may not give the true picture of their capacitive behaviour.

The supercapacitor experiment is divided into two: (i) using CNT-MO (where M= Ni, Co and Fe) materials made by electrodeposition and (ii) using CNT-MO materials made by chemical synthesis. For the electrodeposition experiment, the electrodes investigated are: BPPGE, BPPGE-NiO, BPPGE-Fe_2O_3, BPPGE-Co_3O_4, BPPGE-SWCNT, BPPGE-SWCNT-NiO, BPPGE-SWCNT-Fe_2O_3, and BPPGE-SWCNT-Co_3O_4. For the chemical synthesis experiment, the electrodes investigated are: BPPGE, BPPGE-NiO, BPPGE-Fe_2O_3, BPPGE-Co_3O_4, BPPGE-MWCNT, BPPGE-MWCNT-NiO, BPPGE-MWCNT-Fe_2O_3, and BPPGE-MWCNT-Co_3O_4. Comparative CV of the electrodes was carried out in 1 M Na_2SO_4 and 1 M H_2SO_4 electrolyte solutions at potential window of 0.2 - 0.8 V (vs Ag|AgCl, sat'd KCl) using three electrode electrochemical system. EIS studies was carried out in 1 M Na_2SO_4 and 1 M H_2SO_4 aqueous electrolytes at a bias potential of 0.3 V (vs Ag|AgCl, sat'd KCl). Charge-discharge (CD) experiment of the electrodes in 1 M Na_2SO_4 and 1 M H_2SO_4 was investigated at different current densities (0.5 to 10 A/g) and potential window of 0.2 - 0.8 V. In the CD experiment, three electrode systems was employed, the modified electrode is the working electrode, Ag|AgCl, sat'd KCl and platinum as the reference and counter electrode respectively. Comparative CD values for the electrodes were estimated at the current density of 0.5 A/g while stability study for the electrode with the highest SC value was carried out at current density of 10 A/g.

The electrochemical performance of the prepared powder of MWCNT-MO nanocomposite made by chemical synthesis was also investigated using two-electrode coin-type cells (CR 2032) with steel foil as reference electrode. The working electrode was assembled by coating the slurry of the MWCNT-MO on an aluminium foil current-collector of 12 mm in diameter. The mixture composed of 71.4 wt. % active material, 14.3 wt. % functionalised MWCNT and 14.3 wt. % binder (polyvinylidene fluoride) in a N-methylpyrrolidione (NMP) solvent. After drying in an oven at 80 ^{0}C for 2 h, the electrodes were pressed under a pressure of 7MPa for 1min. The weight of the active materials was determined by weighing the Al foil before and after pressing the powders. The supercapacitive behaviour was investigated in both acidic (1 M H_2SO_4) and neutral (1 M Na_2SO_4) electrolytes. In each case, both the symmetric (using MWCNT-MO as both anode and cathode material) and asymmetric (using MWCNT-MO as anode and CNT alone as cathode material) assembly are studied. In the asymmetry assembly, the working electrode (MWCNT-MO) was used as the positive electrode while the CNT was used as the negative electrode. The electrodes were soaked in the electrolyte for about 10 min before assembled in the coin cells. A polypropylene (PP) film (Cellgard 2400) was used as the separator.

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SECTION B

RESULT AND DISCUSSION

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*Chapters 3-10 comprise the results and discussion and the publications in peer-reviewed journals that are obtained from this thesis.