2012

Functionalized carbon nanotubes as the platforms in the dopamine and ascorbic acid biosensors

Jie Zhao
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Recommended Citation
UNIVERSITY OF WOLLONGONG

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Functionalized Carbon Nanotubes as the Platforms in the Dopamine and Ascorbic Acid Biosensors

A thesis submitted in (partial) fulfillment of the requirements for the award of the degree

Master by Research

From

UNIVERSITY OF WOLLONGONG

By

Jie Zhao, BEng

Intelligent Polymer Research Institute, Department of Chemistry

2012
CERTIFICATION

I, Jie Zhao, declare that this thesis, submitted in fulfilment of the requirements for the award of Master by Research, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Jie Zhao

February, 2012
ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisors Dr. Jun Chen and Professor Xu-Feng Huang for their excellent supervision and great support throughout the project. I really appreciate the guidance Jun and Xu-Feng have provided on all the matters about my research, as well as encouragement throughout my time in UoW. I would also like to thank Dr Joselito M. Razal, and Associate Professor Andrew Minett for their contribution throughout my master study.

A special thanks to Dr Weimin Zhang whose enthusiasm and attitude for science and research encourage me to pursue high degree research. His advice and patience over my master study is gratefully acknowledged. I would like to thank Mr Ali Jalili and Mr Peter Sherrell for their support on my preparation of materials and data analysis for my project.

In addition, I am very grateful to all the friends and colleagues at Intelligent Polymer Research Centre who have helped and supported me during the master study I have been with the group. Thanks to Mr Tony Romeo, Associate Professor Peter Innis and Dr Sanjeev Gambhir for all their help on SEM, FTIR, Raman and Zeta Potential measurement. Thanks to Dr Caiyun Wang, Dr Zhilian Yue, Mr Meng Wang, Miss Kanlaya Pingmuang, Mr Mark Romano and Mr Dennis Antiohos for their support over the last year.

Finally and most importantly, I would like to thank my parents for giving me life, as well as unconditional and endless love and support in all my life.
PUBLICATIONS


CONFERENCE PRESENTATION

ABSTRACT

The main goal of this study was to design and develop novel carbon nanotube (CNT) based platforms as biosensors for simultaneous voltammetric detecting dopamine (DA) and ascorbic acid (AA). The use of such novel nanostructured electrode platforms will enable the development of affinity-based biosensors for disease diagnostics and therapy monitoring. Such bio-sensing systems will perform sensitively and selectively for detection of the neurotransmitters/neurochemicals by utilizing certain CNT material structure and introducing various functional groups, thus enhance response to the specific bioanalytes. The electrical devices are extremely useful for delivering the diagnostic information in a fast and simple way.

A highly sensitive and selective dopamine sensor was fabricated with a unique 3D CNTs nanoweb electrode. The as-synthesised CNT nanoweb was modified by oxygen plasma to graft functional groups in order to increase selective and electroactive sites at the CNT sidewalls. This electrode was characterized physically and electrochemically using HRSEM, Raman, FT-IR and cyclic voltammetry (CV), respectively. Our investigations indicated that the O₂-plasma treated CNT nanoweb electrode could serve as a highly sensitive biosensor for the selective sensing of dopamine (1 µM to 20 µM) in the presence of ascorbic acid (1000 µM).

Polymer adsorbed multiwalled CNTs (MWCNTs), such as Nafion/MWCNTs and poly (diallyldimethylammonium chloride)/MWCNTs (PDDA/MWCNTs), were prepared to selectively sensing DA and AA, respectively. Compared with the as
synthesized CNT nanoweb, the composite materials showed enhanced sensitivity towards oxidation of DA and AA. The MWCNTs composites were characterized using thermogravimetric analysis (TGA), zeta potential, HRSEM, Raman and CV. In addition, differential pulse voltammetry (DPV) was conducted to determine DA (0.1 μM to 10 μM) and/or AA (10 μM to 200 μM) in the DA and AA mixture solution.
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>SWCNT</td>
<td>singlewall carbon nanotube</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multiwall carbon nanotube</td>
</tr>
<tr>
<td>DA</td>
<td>dopamine</td>
</tr>
<tr>
<td>AA</td>
<td>ascorbic acid</td>
</tr>
<tr>
<td>r</td>
<td>radius</td>
</tr>
<tr>
<td>Φ</td>
<td>wrapping angle</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>wt</td>
<td>weight</td>
</tr>
<tr>
<td>PD</td>
<td>Parkinson Disease</td>
</tr>
<tr>
<td>mdDA</td>
<td>mesodiencephalic dopamine</td>
</tr>
<tr>
<td>SPET</td>
<td>single photon emission tomography</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
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</table>
$E_{\text{ox}}$ oxidation potential

CV cyclic voltammetry

DPV differential pulse voltammetry

SEM scanning electron microscopy

FTIR fourier transform infrared spectroscopy

TGA thermogravimetric analysis

PBS phosphate buffer saline

$I_{pa}$ anodic current

$I_{pc}$ cathodic current

$v$ scan rate

rpm revolutions per minute

$\text{cm}^{-1}$ wavenumber

$\Omega$ Ohms

$\mu$ micro

$^\circ\text{C}$ degree celsius
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>litre</td>
</tr>
<tr>
<td>M</td>
<td>moles per litre</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<td>cm</td>
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Chapter 1:

General Introduction
1. General Introduction

1.1 Overview

The unique structure and morphology of carbon nanotubes (CNTs) keep attracting a great number of researchers to explore the novel properties and applications of these materials since the discovery by Iijima in 1991 [1]. CNTs are considered as coaxial cylinders of graphic sheet with a hexagonal lattice, either single-wall CNTs (SWCNTs) or multi-wall CNTs (MWCNTs) [2]. Due to their strong mechanical properties, excellent thermal and electronic behaviour [3–6], CNTs and CNT hybrids have found their applications in many areas including energy storage and energy devices [7, 8], sensors [9], field emission devices [10, 11], hydrogen storage [12, 13], and probes [14], etc. Currently CNTs entered the domain of biological research because their biocompatibility, bio-electrocatalytic properties, chemical functionalities, and physical stability can be quite easily tailored [15]. CNTs can accumulate important bio-information (e.g. dopamine (DA), ascorbic acid (AA) and proteins) and enhance electrochemical reactivity and promote the electron-transfer reaction of biomolecules in electrochemical detection devices [9]. The remarkable properties of CNTs present themselves promising candidates as electrochemical platforms in biosensing. For example, such electrochemical devices physiologically monitoring the concentration change of DA could benefit the diagnosis of DA system diseases, design of therapeutics and evaluation of their therapeutic efficacy.
1.2 Carbon Nanotubes

1.2.1 Types of Carbon Nanotubes

SWCNTs and MWCNTs are two main types of carbon nanotubes that have high structural perfection. The two types of CNTs, both graphite-related systems, exhibit similar physical properties. SWCNTs (Figure 1.1a-c) are comprised of a single graphite sheet seamlessly wrapped into a cylindrical tube [16]. SWNTs, depending on wrapping vector angles, are divided into armchair, zigzag and chiral form (Figure 1.1d) [17]. The diameter and helicity of a defect-free SWNT are uniquely characterized by the vector \( c_h = n a_1 + m a_2 \) that connects crystallographically equivalent sites on a two-dimensional graphene sheet, where \( a_1 \) and \( a_2 \) are the graphene lattice vectors and \( n \) and \( m \) are integers [18]. SWCNTs are called ‘armchair’ if \( n \) equals \( m \), and ‘zigzag’ in the case \( m = 0 \). All other tubes are of the ‘chiral’ type and have a finite wrapping angle \( \Phi \) with \( 0^\circ < \Phi < 8^\circ \). These three types of SWCNTs have varying vector angles and show differing metallic or semiconducting properties, confirming the strong influence of wrapping angle to CNT properties [5]. MWCNTs consist of an array of such nanotubes that are concentrically nested like rings of a tree trunk (Figure 1.1e) [19]. Nanotube diameters range from \( \sim 0.4 \) to \( \sim 3 \) nm for SWCNTs and from \( \sim 1.4 \) to more than 100 nm for MWCNTs, which turns out to be the one of the main causes of differences in nanotubes properties [20, 21]. The number of nanotubes in a MWCNT can vary from \( N = 2 \) to \( \sim 100 \). The MWCNTs have been reported with the largest outer radius of around \( r \sim 300 \) Å and smallest inner radius of about \( r \sim 5 \) Å, while SWCNTs show a small radius \( r \sim 3.5–20 \) Å [22].
Figure 1.1: The structures of (A) armchair, (B) zigzag, (C) chiral SWNTs [16], (D) the construction of a carbon nanotube from a single graphene sheet [17], and (E) MWNTs [19].

1.2.2 Electrical Properties of Carbon Nanotubes

Among the attractive properties, it is mainly the electrical behaviour of CNTs that stimulates the continuous research and application of CNT based materials. Nanotubes synthesised by different methods show completely different electrical
conductivities, metallic, quasi-metallic and semiconducting. Such properties are reported to be sensitive to the nanotubes’ diameter, wrapping vector angle as well as defects [23]. In other words, even slight differences in these parameters can turn quite similar carbon materials from metallic to semiconducting states. Each carbon atom in the graphite structure carbon has two $1s$ electrons, three $2sp^2$ electrons and one $2p$ electron [24]. The three $2sp^2$ electrons form the three bonds in the plane of the graphene sheet, leaving an unsaturated π orbital. This π orbital, perpendicular to the graphene sheet and thus the nanotube surface, forms a delocalized π network across the nanotube, responsible for its electronic properties. Armchair CNTs should show metallic behaviour which have a band degeneracy between the highest π valence band and the lowest π conduction band, where these bands meet the Fermi level, and another kind of CNTs with $n-m=3i$ ($i$ is an integer) are metallic [25]. The conduction in metallic CNTs is ballistic, $4e^2/h$ quantum conduction observed as long as 4 m at low temperature. This metallic nanotube is least sensitive to gate voltages and rarest in CNT synthesis among all type of CNTs. The rest ones, also the major part of CNTs, are semiconducting in nature and have a smaller band gap [26, 27]. They exhibit field effect transistor (FET) behaviour and are applied in many devices like transistors and sensors [24, 28, 29].

1.2.3 Synthesis of Carbon Nanotubes

CNTs are usually synthesised by carbon arc discharge, laser vaporization and chemical vapour deposition (CVD) [30–32]. As the earliest method of CNTs synthesis, carbon arc discharge is the simplest technique compared with the others.
The laser vaporization was developed for much longer CNTs with controlled diameters. However, the two methods are only limited for obtaining small quantities of CNTs but cannot scale up the production to industrial level. Another shortage related to the methods was found to result in the components of highly tangled CNTs, randomly mixed with other forms of carbon and metal species [33]. Compared to arc discharge and laser methods, CVD is a new, controllable and economic technique to obtain the potential structures and architectures. It also shows a considerably higher proportion of CNTs in yield (around 2 to 3 times) as well as purity than those synthesised by the other two methods.

1.2.3.1 Carbon Arc Discharge

The carbon arc discharge method reported in Iijima’s discovery of CNTs is one of the most common and earliest way to synthesize CNTs [1]. It is similar to the procedure used for fullerene synthesis. C$_{60}$ deposits on the negative end of the carbon electrode at a low insert gas atmosphere (100 torr Argon-filled vessel) and form nanotubes ranging from 4 to 30 nm in diameter and up to 1 µm in length. Later investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen [34, 35]. This method uses a direct current of 50 to 100 A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of a carbon electrode, and forms a small rod-shaped deposit on the other electrode. For this method, producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode [33]. The method
is rather simple and has been widely used to produce small scale CNTs. However, the yield typically contains 30 wt% of CNTs products and the production is a complex mixture of components that requires further purification [36].

1.2.3.2 Laser Vaporization

The laser vaporization method was developed for the synthesis CNTs in 1995 by Smalley’s group [30]. In a typical synthesis process, a pulsed or continuous laser is employed to vaporize a graphite target in an oven at 1200°C filled with inert gas. To vaporize the target more uniformly, a second laser vaporization pulse follows the initial one. The second laser pulse breaks up larger catalyst particles ablated by the first one, and feeds them into the growing nanotube structure. The amount of carbon deposited impurities is successively minimized and the yield is greater than that synthesized by the arc discharge method, due to the use of two laser pulses [37]. The material produced by this method appears as an aligned carbon nanotube bundle, 10–20 nm in diameter and up to 100 μm or more in length [38]. By varying the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution could be controlled toward desirable dimension.

1.2.3.3 Chemical Vapour Deposition

CVD is probably the most popular and widely used method for synthesis of CNTs nowadays and it is a straightforward way to scale-up production to industrial levels
[39]. During a CVD process, large quantities of CNTs are produced by CVD of carbon-rich gas over cobalt or iron catalysts supported on substrates like silica, zeolite or quartz. It has been known that the CVD method can control over the types of nanotubes by setting up various parameter of gas, catalysts, temperature and reacting time. Mostly defect-free CNTs are obtained by this method, which can be used in the fundamental study of the physics and chemistry of nanotubes and CNT functionalization [40].

The theory of the CVD process is shown in Figure 1.2. The hydrocarbon vapour pass through a tubular reactor present with a transition-metal catalyst-contained substrate at a high temperature to decompose the hydrocarbon [41]. At 600–1200°C, the hydrocarbon vapour crack to provide carbon atoms and the catalysts placed in the tube are pyrolysed to liberate metal nanoparticles in situ. CNTs grow on the substrate by the catalysation which can be collected after cooling down to the room temperature. The common carbon feedstock utilizes includes ethylene, carbon monoxide, benzene, and alcohol, etc. [39]. The hydrocarbon gas can be purged directly through the tube, while the liquid hydrocarbon should be heated and then purge the vapour to carry the gasified hydrocarbon to the reacting zone. The mechanism of CNTs synthesis by CVD is controversial and several possibilities have been reported depending on the reaction conditions and materials analysis [41–43]. The most accepted one is outlined as follows. Hydrocarbon vapor decomposes into carbon and hydrogen species are catalysed by metal nanoparticles in the high temperature. The carbon dissolves into the metal and crystallizes in the form of a
cylindrical network when reaching its solubility limit, whilst the hydrogen is depleted. Hydrocarbon decomposition releases some heat to the metal, while carbon crystallization absorbs some heat from the metal’s precipitation zone, which is as thermal gradient to keep the process on.

![Schematic diagram of CVD process](image)

Figure 1.2: Schematic diagram of CVD process [41].

1.2.4 Functionalization of Carbon Nanotubes

CNT based electronics and techniques have been simultaneously developed in recent researches and applications [7, 8, 10–14, 16]. However, the inherent properties of CNTs do not satisfy the rapid growth of such development. Generally, raw CNTs have inert surface properties and are insoluble in all solvents due to strong van der Waals interactions that tightly hold them together, forming bundles. Therefore, in many applications, especially in the biological fields, modification of their surfaces and interfacial engineering are quite essential to activate the CNTs surface and increase their solubility in solvents [44]. Typically, the modification or
functionalization of CNTs can be grouped into two categories (Figure 1.3): (1) covalent attaching chemical groups through chemical reactions on the π-conjugated skeleton of CNTs, and (2) noncovalent adsorption or wrapping of functional molecules onto the tubes [45, 46].

1.2.4.1 Covalent Methods

The covalent modification is the most common used method for the functionalization of CNTs which involves the addition of carbonyl and carboxyl groups via an aggressive treatment with a mixture of HNO₃/H₂SO₄ or plasma etching. The solubility and reactivity of carbon nanotubes could be significantly improved via introducing these functional groups [47]. Acid-oxidized CNTs proved versatile for further elaboration, because the end caps of the nanotubes are opened and acidic functionalities in the oxidation, which is suitable for further derivatization by fluoroalkanes, silanes and polymers to CNTs [48]. However, it also introduces additional structural defects and disrupts the delocalized electron system in the CNT surface, and leads to change of the electric and mechanical properties to some extend that may significantly influence the performance [49].

1.2.4.2 Noncovalent Methods

The synthesis of CNT composites may be covalent or noncovalent [50]. More attraction is focused on the noncovalent absorption of polymer (Figure 1.3c) because of the possibility of introducing various groups on CNT surface without disturbing the π system of the graphite sheets [51, 52]. It is the weak inter-planar interaction of graphite sheet that provides the solid lubricant quality and resistance to polymer
adhesion. There is a lack of interfacial bonding in the type of CNT-polymer composite. Noncovalent absorption of polymer has been indicated as one of the most effective treatments for functionalization of CNTs without detrimental effect on the original CNT structure, maintaining and reinforcing their electronic properties.

Figure 1.3: Schemes of functionalization of carbon nanotubes: (a) HNO₃, (b) O₂ plasma, (c) polymer adorption.

1.3 Electrochemical Biosensors

A biosensor is defined as a “device that uses specific biochemical reactions mediated by isolated enzymes, immunosystems, tissues, organelles, or whole cells to detect chemical compounds usually by electrical, thermal, or optical signals” [53]. A typical biosensor is based on a two-component system: a biological recognition element (ligand) that facilitates specific binding to or biochemical reaction with a
target material, and signal conversion unit (transducer) which is used to monitor the response from the reaction. Compared with other methods of biodetection, biosensors have many advantages such as increased assay speed, flexibility, and immediate interactive information to users. These merits will present the biosensors ideal for the applications in medical, environmental, public security and food safety areas [44, 54, 55].

In recent years, numerous types of biosensors, all combining a biological recognition element and a transducer have been developed and applied in a wide variety of analytical settings [9, 56, 57]. However, our research interest has been focusing on the biosensors for some important neurotransmitter/neurochemicals such as dopamine (DA) and ascorbic acid (AA). Thus, our research content is mainly about the application of functionalized CNTs for DA or AA biosensors.

1.3.1 Detection for DA and AA

DA is an important neurotransmitter that releases a variety of downstream signals in the nervous system of mammals including humans. As the chemical messenger, DA plays a critical role in the cardiovascular, renal, hormonal and central nervous system. It extends into various regions of the brain, producing effects on emotion, movement, heart rate and blood pressure. Dopamine biochemistry is believed to be related to several diseases such as schizophrenia and Parkinsonism (Figure 1.4) [58, 59].
There are several different experimental methods used in detecting the level of DA released in the intact brain [51]. Intracerebral dialysis has been a widely used method, combining with high performance liquid chromatography (HPLC) and electrochemical detection [60]. This method transversally inserts a dialysis tube in the striatum of living rats to extract the substances from the surrounding tissue and
quantitatively estimate the HPLC purified sample by oxidative electrochemical detection. The radiolabel approach was developed by Glowing group which is the first detection dendritic release of DA in the basal ganglia [61]. The radiolabelled precursor went to substantia nigra through the stereotactically placed and push-pull cannulae and synthesis and transport of DA in the nervous system was studied in the group. Some techniques, like single photon emission computed tomography (SPECT) scans and radioimmunoassay, have been well developed and provide new way to assess the DA in the human brain [62, 63]. As a well-established functional imaging technique, SPECT is the common clinic supports in diagnosis of DA system diseases, focusing on precise noninvasive localization of functional state.

However, these traditional methods, though very sensitive and specific, are generally limited by the high cost, time-consumption and the prerequisite of trained operators. Researchers had paid considerable attention on the interest of an electrochemical approach which show highly specific recognition to detect the target analytes and give an electronic signal directly [57]. Compared with other methods, DA bio-electrochemical sensors show many advantages: an extremely small electrode can be made to conveniently implant in vivo or directly test serum samples with minor tissue damage and, because the response is fast, the neurotransmitter can be monitored in real time [9].

In the 1970s, Adams firstly use the simple electroanalytical techniques with micro graphite electrode to detect brain chemistry including DA in vivo [64]. The brain tissue is highly conductive and the initial results were satisfying, supporting that
voltammetry is a potential way and motivating electrochemical analysis of DA in the
next decades. DA can be easily oxidized electrochemically at conventional electrodes,
which have been used to detect the neurotransmitter in both in vitro and in vivo
environments. However, a critical issue that needs to be overcome is the selectivity
of the electrode due to the overlapping oxidation potential ($E_{ox}$) of DA with other
chemicals, in particular, AA present in the nervous system being the major
interfering species due to its abundance in serum samples (up to 100 µM is much
higher than that of DA ~0.01–1 µM) and having a close $E_{ox}$ to that of DA [65]. In
order to selectively detect DA, novel electrode materials including polymer-based
films [66–68] and metal nanoparticles have been developed, however there are still
barriers that need to be overcome, such as inference from AA and low DA oxidation
signals [69–71]. Recently, carbon nanomaterials [56, 72–76] are proving to be
among the outstanding candidates as novel platforms for sensing because their bio-
electrocatalytic properties, chemical functionalities, and physical stability can be
quite easily tailored. Among the carbon nanomaterials, carbon nanotube [77] has
been particularly attractive as novel platform for DA sensing. CNTs are proving to
be outstanding candidates for sensing because their biocompatibility, bio-
electrocatalytic properties, chemical functionalities, and physical stability can be
quite easily tailored. Recent studies showed that the utilization of CNT-based
electrodes is conducive to obtain a significant separation of $E_{ox}$ for both DA and AA,
which could improve the selective sensing of DA against up to 200 µM AA with
improved sensitivity (increased voltametric current signals) [15]. Electrochemical
detection devices show the highly enhanced electrochemical reactivity and promoted
the electron-transfer reaction of biomolecules when accumulating the important bio-
information [9]. The advantages of these remarkable properties are perhaps attributed
to the highly electroractive surface area and the fast electron-transfer properties of
CNT-based electrodes and make the CNTs promising candidates as electrochemical
platforms in DA biosensor [20, 21]. Such CNT-based electrical devices
physiologically monitoring the concentration change of DA could benefit the
diagnosis of DA system diseases, design of therapeutics and evaluation of their
therapeutic efficacy.

1.3.2 Electrochemical Sensors Based on Carbon Nanotubes

For the fabrication of an efficient and sensitive biosensor, the election of substrate
for dispersing the sensing materials proved critical to obtain high sensing
performance. Various kinds of nanostructured materials such as metal nanoparticles,
magnetic nanoparticles, quantum dots, and nanostructured carbon materials have
been widely investigated to incorporate in electrochemical sensors to decrease
overpotential and improve sensitivity and selectivity [66–71, 78].

Especially, CNTs offer unique properties such as enhanced electronic properties, a
large edge/basal plane ratio, and rapid electrode kinetic which provide higher
sensitive, lower limits of detection, and faster electron transfer kinetics than
conventional carbon electrodes [15, 77]. As probes for molecular functiona,
functionalized CNTs based biosensors are certainly of extreme interest. For example,
Liu and co-workers investigated the poly (PAA) functionalized MWCNTs composite
as electrode for sensing physiological level dopamine and uric acid in the presence of
an excess of ascorbic acid in a pH 7.4 phosphate-buffered solution. They found the PAA-MWCNTs electrode can depress the voltammetric peak of AA and showed excellent selectivity for DA and UA determination. Also, they observed that the presence of functional groups in the biosensor system help achieve an improved electron-transfer rate for AA and DA at the electrode [79]. Alwarappan and co-workers attempted to use electrochemically functionalized CNTs for simultaneous detection of DA, AA, and UA. They obtained a selective and enhanced electroanalytical response at the electrode with minimal electrode fouling toward the detection of DA compared with the un-functionalized CNTs electrode [80]. In addition, there are numerous CNT-polymer composite electrodes such as ssDNA/SWCNTs/poly(3-aminophenylboronic acid)/Nafion composite electrode, Nafion/SWCNT/poly(3-methylthiophene) hybrids electrode, and MWCNTs/Nafion/PtAu electrode have been successfully developed for simultaneous determination of neurotransmitters/neurochemicals [81]. In summary, the functionalization of CNTs by various approaches is an extremely effective to develop novel biosensors with highly selective and sensitive activity.
1.4 Project Aims

The main purpose of this project is to develop new selective and sensitive CNT-based electrodes in bio-electrochemical sensor for delivering the DA information. The research contents include synthesis and functionalization of CNT materials, characterization, device design and fabrication, and DA detecting, etc.

Chapter 3 will discuss the high selective CNT nanoweb electrode before and after O₂ plasma treatment for determination of DA in presence of AA in PBS using differential pulse voltammetry (DPV). This chapter will evaluate the effect of plasma functionalization of the CNT nanoweb electrode on the electrochemical sensitivity and selectivity for DA determination.

Chapter 4 will compare the selectivity and sensitivity of the electrodes with Nafion/MWCNT or PDDA/MWCNT composites toward sensing DA or AA. This chapter will focus on influences of surface charge of MWCNTs on DA and AA sensing.

1.5 References


4. Dresselhaus, M.S., et al., *Electronic, thermal and mechanical properties of carbon nanotubes*. Philosophical Transactions of the Royal Society of


Chapter 2:

General Experimental
2. General Experimental

2.1 Reagents and Materials

<table>
<thead>
<tr>
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<td>Sigma</td>
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<tr>
<td>Butanol</td>
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<tr>
<td>Carbon nanotubes (MWCNT)</td>
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<tr>
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<td>Ajax Finechem</td>
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<tr>
<td>Hydrochloric acid (HCl)</td>
<td>Sigma-Aldrich</td>
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<td>Sodium hydroxide (NaOH)</td>
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2.2 Material Preparation Methods

2.2.1 Chemical Vapour Deposition (CVD) Growth of Nanoweb

In this project, the carbon nanotube nanoweb was synthesized using a chemical vapour deposition process. The nanoweb grew on the catalyst-coating substrate in a Thermal CVD System (Atomate) that was completely automated allowing computer control over the growth conditions (Figure 2.1). According to the types of catalysts and substrate, the software can adjust the deposition time, gas flow and furnace temperature, producing a variety of CNT materials. The whole growth process was in the argon atmosphere and hydrogen flow was added at a particular high temperature reducing Fe (III) to Fe (0) nanoparticles which catalytic crack acetylene and grow CNT nanoweb.

![Figure 2.1: Thermal CVD system for CNT nanoweb growth.](image)

2.2.2 Plasma Treatment

Plasma treatment of electrode material was carried out with a radio-frequency-generated plasma under vacuum using a Harrick Plasma system (model PDC-002) combined with a XDS-10 dry vacuum (BOC-Edwards) (Figure 2.2). High purity
oxygen was used in the plasma to introduce hydroxyl and carboxyl functional groups to the CNT material. For improving hydrophicity of material, air plasma was used at room temperature and 1 torr O₂ pressure for several minutes.

Figure 2.2: Image of the plasma system.

2.2.3 Ultrasonication of CNTs

The dispersion of carbon nanotube in ethanol or water was carried out using a Branson Digital Sonifier Model 102C (Figure 2.3) at 30W and 20Hz in the pulse method of 1 second on/1 second off for 1 hour. The dispersion of functionalized CNT was ultrasonicated with the same procedure for 30 minutes.
Chapter 2

2.3 Characterisation Techniques

2.3.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is used for morphological analysis of the nanostructured materials. The images obtained are created through the focusing of a high energy beam of electrons via a thermionic, Schottky or field emission cathode onto a sample. In this study, a JEOL JSM7500FA cold-field-gun (CFG-SEM) field emission scanning electron microscope (FE-SEM) (JEOL Ltd., Japan) (Figure 2.4) was used to monitor the electrode materials. CNT nonaweb was placed into the vacuum system, attached on a stage using adhesive carbon tape and conductive silver paint. Functionalized MWCNTs (Nafion-MWCNTs or PDDA-MWCNTs) solution was dropped on the glassy carbon and ready to be analysed after dried in the oven.

Figure 2.3: Images of (A) Branson Digital Sonifier, and (B) the samples before and after ultrasonication.
Figure 2.4: (A) Cold-field-gun Field Emission Scanning Electron Microscope, and (B) a typical SEM image of CNTs.

2.3.2 Raman Spectroscopy

Raman spectra of CNT materials were recorded using a Jobin-Yvon Horbia 800 with 632.8 nm HeNe laser excitation (Horiba Ltd., France) on a 1800 lines-mm\(^{-1}\) grating at room temperature (Figure 2.5). The laser traverses on the CNT materials and photons were scattered by samples, leading to energy lose or gain during the procedure. The change of energy and shifted scattered light is relative to the wavelength of irradiating photo and molecular vibrations of particular species.
2.3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is a technique used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. In this study, FT-IR spectra of samples were obtained with AIM-8800 automatic infrared microscope (Shimadzu Corporation, Japan) at room temperature (Figure 2.6). FT-IR was employed to determine and/or confirm the functional groups introduced by Plasma or polymer adsorption treatments of CNT materials throughout this thesis.
2.3.4 Zeta Potential

Zeta potential is the interfacial double layer potential between the samples’ slipping plane and a point in the fluid around the interface. The measurement of zeta potential brings detailed insight into the dispersion mechanism and the electrostatic dispersion control and indicates the degree of repulsion and attraction of particles in a solution or colloid. A high zeta potential will confer stable dispersion, while excessive repulsion and poor dispersion is related to a low zeta potential even an unmeasured one. Here a Zetasizer Nano ZS (Malvern Instruments, UK) (Figure 2.7) was used to measure the zeta potential of Nafion/MWCNT and PDDA/MWCNT colloid. CNT-Nafion was characterized directly after mixing without treatment, while
PDDA/MWCNT powder obtained from vacuum filter was dispersed in Milli Q water and measured using a clear disposable zeta cell (DTS1060C).

![Figure 2.7: Zetasizer Nano ZS.](image)

2.3.5 Contact Angle Measurement

DataPhysics OCA20 goniometer was used to carry out the contact angles in air under ambient laboratory condition (Figure 2.8). The contact angle is the angle at which a liquid interface meets a solid surface, measured using a contact angle goniometer. A 2 µL droplet of water was dispensed on the sample surface and at least 5 measurements in different positions for each sample were required for final result calculation. The shape of the droplet, combined with the contact angle, shows
the wettability in the boundary condition. The lower the contact angle of water, the more hydrophilic the surface is.

![Figure 2.8: (A) DataPhysics OCA20 goniometer, and (B) a typical image of contact angle.](image)

2.3.6 Thermogravimetric Analysis

The determination of PDDA loading on CNTs was carried out by the thermogravimetric analysis technique on a Q500 TGA analyzer (TA Instruments, UK) (Figure 2.9). For a typical measurement, a sample (around 4 mg) was weighed for the analysis and heated in a platinum pan. Samples were heated in Nitrogen from room temperature to 900°C at a heating rate of 5°C·min⁻¹. In the process, heat and stoichiometry ratios are utilized to determine the percent by mass ration of a sample. According to the relationship among weight, derivative weight and temperature,
exact points of inflection can be drawn and used to calculate the mass percent of the compounds in a sample.

Figure 2.9: Q500 TGA analyzer.

### 2.4 Electrochemical Techniques

#### 2.4.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most utilised electroanalytical techniques for the analysis of electron transfer process at an electrode surface. This measurement obtains the current-potential dependence in a three-electrode system consisted of a working electrode, reference electrode and counter electrode. A triangle waveform (Figure 2.10) is employed in electrodes, swept at a constant rate
from the initial potential to vertex potential, and back to initial one. Repeating the
triangle waveform for multi-times, the current between the working electrode and the
counter electrode is recorded and plotted versus the applied voltage to perform the
CV cycles. This technique can be used to investigate the mechanism, thermodynamical and kinetics of electrochemical reactions. In this study, CV was
mainly used to investigate the electrochemical behaviours of CNT-based electrode in
a three-electrode cell with a platinum mesh counter electrode and Ag/AgCl reference
electrode. The measurements were recorded using a CHI 720C biopotentiostat (CH
Instruments Inc., USA).

![Triangle waveform used in Cyclic Voltammetry.](image)

Figure 2.10: Triangle waveform used in Cyclic Voltammetry.

A typical CV experiment of 20 μM DA was performed in a N<sub>2</sub> saturated 0.1 M
PBS solution (Figure 2.11) on the glassy carbon (GC) electrode. In this curve, the
potential was swept at a scan rate of 10 V·s\(^{-1}\) between an initial potential limit (-0.2 V) and second potential limit (0.6 V) and anodic current and cathodic current (\(I_{pa}\) and \(I_{pc}\)) responses were obtained. Once the potential reached the second limit, the curve swept back to the initial point and became a cycle. As can be seen in the CV curve, transient and non-Faradaic currents flow at the low potential which is more negative than the redox potential of the DA. Then oxidation occurs on the electrode Faradaic current is produced when sweeping potential reaches the formal potential of the redox species. Upon reaching a certain anodic potential (\(E_{pa}\)), an \(I_{pa}\) peak is observed in the CV curve where redox species are instantaneously oxidised and the transport of redox species reach a limitation. Similarly, a mass transfer limitation is also shown during reducing of the oxidised species, presenting an \(I_{pc}\) peak at a sufficiently cathodic potential (\(E_{pc}\)).

![Figure 2.11: Cyclic voltammogram obtained from a glassy carbon electrode in a PBS solution with 20 µM DA.](image-url)
The $E_{pa}$ and $E_{pc}$ peaks in the CV curve is separated by a value ($\Delta E_{pc}$). When the obtained data satisfy the equation 1.1 and 1.2, the electrochemical system is of ideal reversibility.

Equation 1.1: \( n \times \Delta E_p = 59 \text{mV} \)

Equation 1.2: \( n = \frac{I_{pa}}{I_{pc}} \)

2.4.2 Differential Pulse Voltammetry

Differential pulse voltammetry (DPV) is an electrochemical measurement of redox properties of electroactive conducting samples. The pulse width can be set up for how long an interlevel potential remains from an initial potential and to final one.

Figure 2.12: CHI 720C biopotentiostat.
As the pulse repeats, the potential between the working electrode and the reference electrode changes at a constant difference which is plotted to the current between the working electrode and the counter electrode. Due to the minor change in potential and current, this measurement is highly sensitive to the concentration of materials. So DPV can be used to detect the sample of low concentration that is proportional the peak current. In this study, CHI 720C biopotentiostat (CH Instruments Inc., USA) (Figure 2.12) was carried out for determination of DA concentration using CNT-based electrodes.

Figure 2.13: (A) a typical differential pulse voltammetry curve of a glassy carbon electrode in a PBS solution with DA; (B) potential wave form for differential pulse voltammetry.
The voltammetry curve obtained when a DPV experiment is performed in a PBS solution containing DA on a GC electrode is shown in Figure 2.13A. After a quiet time, a series of regular voltage pulses superimposed on stair steps begin to sweep (Figure 2.13B). An initial potential increase a certain value (amplitude) to an intermediate potential and remains at the potential for several milliseconds (pulse width); then it changes to the final potential. The pulse is repeated, changing the final potential, and a constant difference is kept between the initial and the intermediate potential. During the changing of potential, the current is immediately measured before increasing and decreasing potentials. When the applied potential is close to the DA oxidation potential, a Faradaic current begin to flow and the current peak ($I_p$) is measure at $E_p$. The $I_p$ is proportional to the concentration of redox couples. By measuring the the $I_p$ of a particular analyte, the concentration can be calculated compared to standard samples.
Chapter 3:
Highly Selective Dopamine Sensor Platform:
Carbon Nanotube Nanoweb
3. Highly Selective Dopamine Sensor Platform: Carbon Nanotube Nanoweb

3.1 Introduction

Dopamine (DA) is one of most important neurotransmitters across all animals, including humans. Alterations in DA contribute to the development of a number of severe mental illnesses, such as Parkinson’s disease, Schizophrenia and depression [1–3]. Clearly, an early detection of alteration of DA is important; therefore, detection of DA using voltametric methods has been widely investigated [4], because electrochemical measurements require simple equipment and provide fast detection. In order to sensitively and selectively detect DA, novel electrode materials including polymer-based films and metal nanoparticles have been developed [5–9]. However, there are still barriers that need to be overcome, such as low DA oxidation signals [10, 11]. Recently, carbon nanomaterials [12–17] proved active and efficient for sensing DA because their bio-electrocatalytic properties, chemical functionalities, and physical stability can be quite easily tailored. Among the carbon nanomaterials, carbon nanotube [18] has been particularly attractive as novel platform in the DA sensor. Recent studies showed that the utilization of CNT-based electrodes is conducive to obtain an enhanced current leading to a significantly better sensitivity than conventional electrodes in the case of dopamine oxidation [19]. These merits are perhaps attributed to the highly electrochemically active surface area and the fast electron-transfer properties of CNT-based electrodes [20]. However, a critical issue that needs to be overcome is the selectivity of the electrode due to the overlapping oxidation potential ($E_{ox}$) of DA with other chemicals present in the central nervous
system. In particular, ascorbic acid (AA) has been the major interfering species due to its abundance in serum samples and having a close $E_{\text{ox}}$ to that of DA [21]. For the sake of selectivity, CNT functionalization is used to enhance the electrode compatibility with DA and reduce the inference from AA in the aqueous solution by introducing functional groups [22]. Recent studies indicated that hydroxyl and carboxyl can be generated on the CNT in oxygen ($O_2$) plasma treatment without nanotube detriment [23]. In this study, we report a highly efficient 3D carbon nanoweb electrode [24] treated by $O_2$ plasma as a novel platform for the selective detection of DA over AA. The as-synthesized CNT nanoweb electrode consisting of a highly porous tangled CNT top network layer and a dense bottom CNT-carbon composite layer provides an ideal configuration for a highly sensitive (high surface area) and an electrically and mechanically robust electrode (i.e. the active CNT network is intimately connected with the highly conducting support) [25]. Here we demonstrate that after an $O_2$ plasma treatment is employed the CNT nanoweb shows extremely promising results in the selective detection of DA in the presence of AA using DPV measurements.

3.2 Experiments

3.2.1 Reagents and Materials

DA and AA were obtained from Fluka and Sigma, respectively. Both DA and AA solutions were freshly prepared before electrochemical tests. A phosphate buffer saline (PBS) was prepared from $\text{NaH}_2\text{PO}_4$ (Fluka) and $\text{Na}_2\text{HPO}_4$ (Sigma-Aldrich). The pH value of the buffer solution was adjusted to 7.0 with NaOH (Chem-supply).
3.2.2  Electrode Preparation

3.2.2.1 CNT Nanoweb Synthesis

The CNT nanoweb was synthesised by the modified CVD method as described in our previous report [24]. The entangled carbon nanotube/conductive carbon networks were synthesised by the decomposition of acetylene over Fe(III)pTs thin films on the quartz plate in high temperature. As the iron catalyst, thin film of 10% Fe(III)pTs/Butanol was first spin-coated onto the surface of a quartz plate at a speed of 2000 rpm. The Fe(III) apTs film, then, was heated on a hot plate to evaporate the solvent and the colour would turn dark yellow. After that, the piece quartz plate was placed in a CVD furnace at 60°C in an Argon atmosphere for 30 min. Hydrogen was introduced at a flow rate of 20 sccm to reduce the Fe$^{3+}$ to catalytically active Fe$^{0}$ centres at 550°C. Followed with the decomposition of acetylene (with a gas flow of C$_2$H$_2$/H$_2$ at 15/5 sccm) over the Fe$^{0}$ centres to induce the CNT growth at 800°C for 30 min. Finally, the furnace was cooled down to room temperature under an Argon atmosphere.

3.2.2.2 O$_2$ Plasma Treatment

A free standing piece of nanoweb was peeled off from the quartz plate substrate and transferred to ITO-coated glass as the electrode for further investigations. A plasma generator (Harrick Plasma, USA) was used to perform the oxygen (O$_2$) plasma treatment for CNT nanoweb electrode at room temperature and 0.6 torr O$_2$ pressure for 15 minutes.
3.2.3 Physical Characterisation

The scanning electron microscope (SEM) images of the electrode surface were used to monitor the CNT nanoweb morphology taken by a JSM7500FA field emission SEM (JEOL Ltd, Japan)

The Fourier transform infra red (FT-IR) spectra were used for recording the functionalities information on the surface of CNT nanoweb obtained with AIM-8800 automatic infrared microscope (Shimadzu Corporation, Japan). Raman spectra were recorded using a Jobin-Yvon Horbia 800 (Horiba Ltd., France). These measurements were performed with a typical 632.8 nm wavelength HeNe laser excitation utilizing a 1800 line grating. Both Raman and FT-IR were employed to determine and/or confirm the functional groups introduced by O₂ Plasma.

3.2.4 Electrochemical Measurements

CV was carried out to evaluate the electrochemical performance of the CNT nanoweb electrode with or without O₂ plasma treatment. The nanoweb was used as the working electrode in the system and the CVs were recorded at a scan rate range from 20 to 200 mV⋅s⁻¹, respectively. The determination of the DA concentration was obtained from DPV method. The parameters used to record DPV are as follows: 0.05 V for the amplitude, 0.05 s for the pulse width, 0.025 s for the sample width, and 0.2 s for the pulse period, respectively. A CHI720C electrochemical workstation (CH Instruments Inc., USA) was utilized to perform both of CV and DPV experiments. All measurements were conducted at room temperature in a standard three-electrode
cell that consists of the CNT nanoweb working electrode, a Pt mesh counter electrode and an Ag/AgCl reference electrode.

3.3 Results and Discussion

3.3.1 CNT Nanoweb

Figure 3.1: Digital images of (A) CNT nanoweb deposited on the quartz (~3.5cm×3.5cm), and (B) free-standing CNT nanoweb.

Previous studies had reported that CNT nanoweb can be grown on high-temperature proof substrates such as quartz and cooper foil [24]. In this study, the CNT material was synthesised on quartz and showed perfect black network structure completely covering the surface of substrate (Figure 3.1A) after removal from the CVD furnace. These samples used as the electrodes were grown in the fore part of the CVD tube where normally produced darker nanoweb due to adequate hydrocarbon vapour during the deposit procedure. Figure 3.1B shows the photo
images of a small piece of freestanding CNT nanoweb peeled off from quartz plate. This piece of CNT is about 3 centimetres (cm) × 2.5 cm which is big enough to serve as the electrode. This size could be easily obtained, even though there were some difficulties to peel the whole nanoweb in a piece from the substrate.

Figure 3.2: SEM images of (A) cross-sectional area, (B) bottom area, (C) surface morphology, and (D) individual nanotubes of CNT nanoweb.

The SEM images (Figure 3.2) of the CNT nanoweb indicates a unique 3D structure that can be directly used as an electrode maintaining the original porous
structure [25]. As can be seen from the sectional view of the CNT nanoweb shown in Figure 3.2A, part of the tangled porous CNT network is intimately connected to a dense carbon layer (bottom). The followed cross-section SEM image (Figure 3.2B) reveals the bottom layer forms a mechanically robust continuous support layer for the entangled CNT network and simultaneously provides lateral electrical connection with a low surface resistance of 70 Ω-square⁻¹. This top layer (Figure 3.2C) forms a highly porous entangled structure ideal for providing large surface area per unit volume electrodes. In addition, the closer SEM image of the top surface (Figure 3.2D) shows that the CNTs exhibit an open end with an average of ~60 nm diameter.

3.3.2 Plasma Treatment for the Electrode

Figure 3.3: Contact angle analysis by a 2 µL droplet of water on the nanoweb surface before O₂ plasma treatment.

It is commonly believed that as-synthesised CNT nanoweb was highly hydrophobic and chemically inert which impedes electrochemical investigations in
aqueous environments. This is because as-synthesised CNT is comprised of non-polar carbon material and little defects using CVD method. It presented a challenge for the materials to find their application for biosensing, for the pristine CNT nanoweb cannot contact bio-analytes in aqueous media due to the inert property. Therefore, surface treatment or functionalisation has been shown to be necessary and critical for the interaction between the CNTs surface and biomolecules [26]. In order to enhance the hydrophilic property of the electrode surface, here we used O₂ plasma technique to treat the CNT nanoweb electrode. The hydrophobic evaluation of the CNT nanoweb was performed both before and after exposure in O₂ plasma for 15 minutes (min) by contact angle analysis. Untreated CNT nanoweb exhibited a significantly high H₂O contact angle of 147.5° (Figure 3.3, hydrophobic) for the original CNT nanoweb. However, very small contact angle could be observed after plasma treatment (close to 0°, fully hydrophilic) which indicates the CNT nanoweb was completely wettable.

On these occasions the hydrophobicity of the material was overcome by generating oxygen-containing functional groups in the plasma react with the surface of the CNT [27, 28]. The FT-IR analysis (Figure 3.4A) confirm different appended surface species between the as-synthesised and O₂ plasma-treated CNT nanoweb. The as-synthesised CNT nanoweb shows virtually no surface functionality while the plasma-treated CNT nanoweb reveals signature vibration bands for hydroxyl at 914 cm⁻¹ and 1414 cm⁻¹ and carboxyl and carbonyl at 1605 cm⁻¹ and 1722 cm⁻¹, respectively. In addition, Raman spectra (Figure 3.4B) for CNT nanoweb show clear differences in the spectral response after O₂ plasma treatment. The D band peak
position is constant for both samples at approximately 1330 cm$^{-1}$, however after plasma treatment the G peak, at around 1580 cm$^{-1}$ is split into two separate peaks. Previous reports have demonstrated that the higher wavenumber peak arises from defects along the CNT sidewall [29–31]. The increased $I_D/I_G$ (from 1.19 to 1.24) also supports the generation of defect sites after plasma treatment, as suggested by the FT-IR spectra. This kind of improvement could play an important role in sensing performance.

![Figure 3.4: (A) FT-IR spectra and (B) Raman spectra of the pristine and O$_2$ plasma treated CNT nanoweb.](image)

Figure 3.4: (A) FT-IR spectra and (B) Raman spectra of the pristine and O$_2$ plasma treated CNT nanoweb.
3.3.3 Cyclic Voltammograms

Figure 3.5: Cyclic voltammograms obtained from an O\textsubscript{2} plasma treated and untreated CNT nanoweb electrode in PBS (pH 7.0).

CV experiments were conducted to detect the effect of plasma treatment of the nanoweb materials on their electrochemical properties. CV was initially conducted on the untreated electrode and the nanoweb remained unwet after experiments, while the treated one absorbed the buffer and got wet completely. The application of both kinds of CNT nanoweb electrodes did not produce a Faradic response in deaerated 0.1M PBS, only a double layer effect (Figure 3.5). By comparing the use plasma treated and untreated electrode in PBS, electrochemical current output at double-layer region obtained was effectively improved due to the O\textsubscript{2} plasma functionalization of the nanoweb surface. The untreated nanoweb showed a
significant electrical resistance due to the hydrophobic nature of the surface retarding directly contact with the solubilised electroactive species. In contrast, the treated electrode shows much better electrochemical properties owing to the improved hydrophilicity, efficient adsorption of ions in buffer solution on the CNT nanoweb.

As shown in Figure 3.6, CV measurements of the plasma treated CNT nanoweb bioelectrode produced responses of DA. The presence of 20 µM DA in PBS caused the oxidation and reduction at about 0.18 V and 0.2 V, respectively. The CVs clearly show pairs of symmetric redox peaks that can be ascribed to the electron transfer-chemical reaction-electron transfer (ECE) mechanism. The first step of DA oxidation involves the two-electron transfer and generation of dopaminoquinone; then dopaminoquinone transforms to leucodopaminechrome which is further oxidized to dopaminechrome in pH 7 solutions [32]:

\[
\begin{align*}
\text{HO-CH}_2-\text{CH}_2-\text{NH}_2 & \quad \Leftrightarrow \quad \text{O-CH}_2-\text{CH}_2-\text{NH}_2 + 2\text{H}^+ + 2\text{e} \\
\text{O-CH}_2-\text{CH}_2-\text{NH}_2 & \quad \rightarrow \quad \text{HO-}\begin{array}{c}
\text{N} \\
\text{H}
\end{array} \\
\text{HO-}\begin{array}{c}
\text{N} \\
\text{H}
\end{array} & \quad \Leftrightarrow \quad \text{O-}\begin{array}{c}
\text{N} \\
\text{H}
\end{array} + 2\text{H}^+ + 2\text{e}
\end{align*}
\]

In the CVs, the background current was always present and increased as the scan rate rose. It was caused by the mass transport process for the reactive species from the bulk electrolyte to the double layer region, and non-faradic current increase from the
double layer which perform charging and discharging process during the electron and chemical transfer [33]. The anodic and cathodic peak current ($I_{pa}$ and $I_{pc}$, respectively) were shown to increase over the whole ranges the voltammetry. A plot of anodic peak current versus the square root of scan rate in the investigated range (from 20 to 200 mV·s$^{-1}$) is shown in Figure 6 inset and the linear relationship for anodic peak current response is exhibited by $I_{pa} = 9.47v^{1/2} - 42.03$ ($R = 0.992$). This confirmed that the redox process is dominated by a diffusion controlled oxidation of DA and was also indeed attributed to a redox species concentration. These processes signified reversible electron transfer reactions that exhibited close to ideal and reversible kinetic behaviours at the CNT nanoweb electrode [34].

Figure 3.6 : CV of the O$_2$ plasma treated CNT nanoweb electrode in 20 µM DA solution (pH 7.0 PBS) at different scan rates (a-k): 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV·s$^{-1}$; Inset: Calibration plots of peak current to square root of scan rates of scan rates obtained from CV.
3.3.4 Differential Pulse Voltammogram Determination of DA and AA

The determination of DA was investigated using DPV method with O₂ plasma treated CNT nanoweb electrode in the PBS solution (pH=7.0) with DA and AA mixture. Figure 3.7A shows the representative DPV curves of various DA concentrations (0–20 µM) in the presence of 1000 µM AA on the modified electrode. The DPV curve for 1000 µM of AA shows no current response and accordingly, there were no apparent DPV signal of AA presenting in the other curves for AA and DA mixture. In the contrary, DA could be oxidized (at 0.17 V vs. Ag/AgCl) and assigned to the peak currents at approximately 0.17 V. These responses show a linear response with increasing DA concentration represented by $I_{pa} = 14.69C_{DA} - 5.84$ (R=0.996) (Figure 3.7B). This result shows excellent combined selectivity and sensitivity relative to literature reports that utilised other electrodes, 2–70 µM for poly (vinyl alcohol) [35], 2–80 µM for poly-chromotrope [36], 24–384 µM for pyrolytic graphite [37]. Better sensitivity of 0.2–45.8 µM was demonstrated for poly-Tiron film, however, the response of AA is much stronger than that of DA and the correlation coefficient (0.991) is much lower than that in our study [38].
Figure 3.7: DPV of different concentration DA (a) 0, (b) 1, (c) 2, (d) 5, (e) 10, and (f) 20 µM in the presence of 1000 µM AA on the O2 plasma treated CNT nanoweb in pH=7.0 PBS. (B) Calibration plots of peak current (within 5% variable using different electrodes) to the concentration of DA from DPV on the O2 plasma treated CNT nanoweb.

In order to test the effect of plasma treatment of the nanoweb materials on its signals for DA and AA oxidation, a pristine electrode was used to detect the response for both DA and AA under the identical testing conditions. From Figure 3.8A it can be seen that approximate 23 µA·cm\(^{-2}\) and 17 µA·cm\(^{-2}\) current was detected at 0.09 V vs Ag/AgCl for 1000 µM AA and 20 µM DA, respectively, and an overlapping signal was observed when a mixture of DA and AA (at a DA/AA ratio of 20/1000)
was evaluated. This confirms that O₂ plasma treatment is able to effectively improve the selectivity of CNT nanoweb during determination of DA and AA. Furthermore, the plasma treated electrode also showed significantly increased DA signal (i.e. $I_{pa}$) compared with the pristine one. The $I_{pa}$ for a 20 µM DA solution at a plasma treated CNT nanoweb electrode (278 µA·cm⁻²) was 17 times higher than that of pristine electrode under identical testing conditions (16 µA·cm⁻², Figure 3.8B).

Figure 3.8: DPV of (a) 20 µM DA, (b) 1000 µM AA and (c) 20 µM DA and 1000 µM AA on the pristine CNT nanoweb in pH=7.0 PBS. (B) DPV of (a) 20 µM DA on the pristine CNT nanoweb and (b) 20 µM DA and 1000 µM AA on the O₂ plasma treated CNT nanoweb in pH=7.0 PBS.
The above demonstrated selective activity of plasma treated CNT nanoweb electrode towards DA at various DA/AA concentration ratios (from 1:1000 to 20:1000) may be ascribed to four main reasons. The first one is electrostatic interactions. At a solution of pH 7.0, the CNT surface functional groups are predominantly deprotonated while DA and AA are dissociated hence an electrostatic attraction of cationic DA to the surface of nanoweb is preferred over the anionic AA to which electrostatic repulsion is expected to occur. Contrarily, the untreated electrode with little functional groups did not have affinity with the DA or AA and produced similar oxidation current, further confirming that the selectivity improvement should be due to the combination of several positive attributes of the plasma treated CNT nanoweb. Secondly, the high hydrophilicity enhance the contacting of the CNT nanoweb and the analyst, thereby accelerating the chemical and electron transfer on the surface of the electrode. By rendering the CNT surface more hydrophilic, the interaction with polar molecules is significantly enhanced. In addition, the $\pi-\pi$ interactions between CNTs and DA that is absent for AA could be another contributing factor [39]. The unique structure of CNT nanoweb, three-dimensional and highly conductive network, provides a large specific surface area that improves both the ionic and electronic transport capacities as well [40]. There are no detrimental effects on the original structure during the plasma treatment, which maintains the novel electronic [27, 28]. This effect is best displayed by the increased $I_{pa}$ suggesting that higher amounts of DA penetrate into the 3D nanoweb architecture due to the increased hydrophilicity after plasma treatment.
3.4 Conclusion

In this chapter, we discussed the preparation, characterization and application of CNT nanoweb as a biosensor electrode for detecting DA. This study indicated that the O2 plasma treated CNT nanoweb electrode could serve as a highly selective biosensor for the selective sensing of DA in the presence of ascorbic acid.

This novel CNT nanoweb material was successfully prepared via CVD method and used to measure the concentration of DA after O2 plasma treated. HRSEM recorded the unique 3D structure of CNT nanoweb and the treated electrode was further characterized physically by Raman and FT-IR to confirm the functional groups grafted by plasma. Electrochemical characterization was performed using CV to qualitatively study the electrode interface. It showed a mass diffusion control process and significantly reversible electron transfer reactions in the dopamine detection. DPV was used for quantitative analysis on the concentration of DA with the CNT nanoweb electrode. By using DPV method, the linear of anodic current peaks of DA was covered from 1 µM to 20 µM. In spite of the coexistence of AA, there was just a single oxidation curve, corresponding to DA, and no inference towards the peak current of DA. Promised increased selectivity was demonstrated in this study using plasma-treated CNT nanoweb as the electrode, showing insignificant interferences in the presence of AA. Briefly the O2 plasma treated CNT nanoweb electrode has the potential to be used and developed into a truly selective dopamine sensor, while the response from AA is negligible.
3.5 References


Chapter 4:
Highly Sensitive Dopamine and Ascorbic Acid
Sensor Platforms: Nafion and Poly
Diallyldimethylammonium Chloride
Functionalized Multiwall Carbon Nanotubes
4. Highly Sensitive Dopamine and Ascorbic Acid Sensor Platforms: Nafion and Poly Diallyldimethylammonium Chloride Functionalized Multiwall Carbon Nanotubes

4.1 Introduction

Dopamine (DA) and ascorbic acid (AA) biosensors have been receiving increasing attention as they offer a data support for early clinical diagnosis of Parkinson’s disease, schizophrenia, deficit hyperactivity disorder, scurvy, and cardiovascular, etc. [1–5]. The concentration of DA is less than 1µM in serum samples provided by healthy humans where there is abundant amount of AA (up to 114 µM) tested simultaneously [6, 7]. Therefore, the bio-interface used in electrochemical sensors for DA and AA are required to be highly sensitive and selective. One of the most commonly protocols is to use conductive materials which show highly effective to detect the target analytes and give a strong electronic signal. Alternatively, carbon nanotubes (CNTs) are also proved to be exceptional for sensing because of their excellent properties such as biocompatibility, bio-electrocatalytic properties, chemical functionalities, physical stability, and unique structure [8]. However, recent reports about CNT-based electrodes do not shown ideal sensitivity and/or selectivity to respond low concentration DA and AA and provide two separated signals [9–11]. In our previous study, O₂ plasma treated CNT nanoweb was successfully used for DA determination, showing high selectivity by avoiding the inference of AA oxidation [12]. In that case, CNTs turned out to be anionic nanotubes and prefer to electrostatic attract cationic DA due to dissociation of oxygen-containing functional
groups in PBS solution. Therefore, in this study, we attempted to prepare polyelectrolyte functionalized multi-walled carbon nanotubes (MWCNTs) with Nafion and poly diallyldimethylammonium chloride (PDDA), which was expected to form anionic and cationic carbon nanotubes on the interface, respectively. The investigations focus on the effect of anionic and cationic functional groups on the sensitivity and selectivity of DA and AA determination at polyelectrolyte/MWCNT composite electrodes.

4.2 Experiments

4.2.1 Reagents and Materials

Nafion 117 solution (5 wt%, Sigma Aldrich), PDDA solution (20 wt%, Sigma Aldrich) and MWCNTs (Nanocyl) were used as received.

4.2.2 Electrode Preparation

4.2.2.1 Nafion/MWCNT Modified Glassy Carbon Electrode

Nafion/MWCNTs composite was prepared as the following procedures. 2mg CNTs were dispersed in an aqueous solution containing 0.05 wt% Nafion using ultrasonication bath for 30 minutes. Then the suspension was stirring for overnight on a magnetic stirring apparatus until a well dispersed CNTs solution and a complete adsorption of Nafion on the surface of CNTs were obtained. The electrode for electrochemical measurement was prepared by casting 20 µL of the prepared Nafion/MWCNT solution on the surface of the glassy carbon (GC) electrode. The
electrode dried in a vacuum oven at 60°C and thus formed a thin Nafion/MWCNTs film that will serve as an active layer for bio sensing.

4.2.2.2 PDDA/MWCNT Modified Glassy Carbon Electrode

The PDDA/MWCNTs electrode was prepared as the similar procedures as those for Nafion/MWCNTs electrode. Briefly, 4 mg MWCNTs were dispersed in 10 mL aqueous solution containing 0.5 wt% PDDA and 0.5 wt% NaCl using an ultrasonication bath for 1 hour. After stirring for overnight, the solid PDDA/MWCNTs composite was collected by vacuum filtration and washed with Milli-Q water for several times to remove resided PDDA and NaCl. Then the solid composite was re-dispersed in Milli-Q water and formed an ink. The PDDA/MWCNT electrode was prepared by casting appropriate amount of the ink on GC electrode.

4.2.3 Physical Characterisation

4.2.3.1 Scanning Electron Microscopy

The morphological analysis of the Nafion/MWCNT electrode and PDDA/MWCNT electrode were investigated using a JSM7500FA cold field gun scanning electron microscopy (CFG-SEM) (JEOL Ltd, Japan)

4.2.3.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a Q500 thermogravimetric analyzer (TA Instruments, UK). The measurements of PDDA, MWCNTs and PDDA/MWCNTs were used to evaluate the thermal stability and
surfactant loading on MWCNTs. The weight loss was recorded in the range from room temperature to 900°C at a heating rate of 5°C·min⁻¹ in a Nitrogen atmosphere.

4.2.3.3 Zeta Potential Analysis

Zeta potential was performed using a Zetasizer Nano ZS (Malvern Instruments, UK) to analyze the interfacial double layer potential of Nafion/MWCNT and PDDA/MWCNT solution, respectively.

4.2.3.4 Raman Spectroscopy

A Jobin-Yvon Horbia 800 was used to characterize Nafion/MWCNT and PDDA/MWCNT electrodes with a HeNe laser excitation wavelength of 632.8 nm utilizing a 1800 line grating (Horiba Ltd., France).

4.2.4 Electrochemical Measurements

Cyclic voltammetry (CV) was used to test the electrochemical performance of the CNT nanoweb electrode with or without O₂ plasma treatment. The nanoweb was the working electrode in the system and the CVs were recorded at different scan rates range from 20 to 200 mV·s⁻¹, respectively. The determination of the dependence of DA concentration on the electrochemical response was obtained using DPV method. The parameters used to record DPV are as follows: 0.05 V for the amplitude, 0.05 s for the pulse width, 0.025 s for the sample width, and 0.2 s for the pulse period, respectively. A CHI720C electrochemical workstation (CH Instruments Inc., USA) was utilized to perform all the electrochemical measurements. All measurements were conducted at room temperature in a standard three-electrode cell that consists of
a CNT nanoweb working electrode, a Pt mesh counter electrode and an Ag/AgCl reference electrode.

4.3 Results and Discussion

4.3.1 Functionalized MWCNTs Stability

Typically, the as received MWCNTs were highly hydrophobic, due to the non-polar carbon material composition. It is difficult to disperse the MWCNTs well in aqueous media and the materials tend to aggregate immediately after ultrasonication. We used ethanol solvent other than Milli-Q water to disperse the as received MWCNTs. Although aggregation was still observed in the dispersion (Figure 4.1A), MWCNTs remained stable for a short time which was adequate to modify the electrode with a certain amount. Our further investigation indicated that the hydrophobicity and stability issues were able to be overcome by adsorbing surfactants (Nafion or PDDA) on the surface of MWCNTs. The two dispersed suspensions were left at room temperature for overnight or even 3 months and no sign of agglomeration or precipitation was observed (Figure 4.1B&C), illustrating that the presence of Nafion or PDDA acted as an effective surfactant for the MWCNTs to disperse in an aqueous phase. In addition, three different suspensions were employed, which are PDDA/MWCNTs, Nafion/MWCNTs and as received MWCNTs respectively in aqueous media, to make electrodes for electrochemical characterisations. We observed the films with PDDA/MWCNTs and Nafion/MWCNTs were uniform, while pristine MWCNT film showed significant
aggregation after dried in the oven. This was further confirmed the better dispersion of MWCNTs with the presence of PDDA or Nafion in the suspension.

Figure 4.1: Images of pristine and functionalized MWCNTs dispersion after (A) preparation of electrodes, (B) overnight, and (C) 3 months.

4.3.2 MWCNTs Zeta Potential Analysis

The zeta potential is the electrical potential that exits at the shear plane of nanomaterials. It is widely used to quantify the magnitude of the electrical charge at the double layer via the electrophoretic velocity of the particles in an electrical field. In our study, the zeta potential measurements were performed to confirm the successful functionalization of MWCNTs. As can be seen from Figure 4.2A, the Zeta
potential of the as received MWCNTs was very low (±5 mV). As reported elsewhere, electrically stable suspension or colloidal solution can only be obtained when its Zeta potential reach 60 mV or higher [13]. This may address the reason why the as received CNTs cannot disperse well in aqueous solution and form a stable suspension. In comparison, the Zeta potential of PDDA/MWCNTs and Nafion/MWCNTs were measured to be 60.4 mV and -68.6 mV, respectively. (Figure 4.2A) For the Nafion/MWCNTs, the zeta potential changed to a negative value indicated that Nafion was successfully adsorbed on the surface of MWCNTs. During the functionalization process, the MWCNTs generated monolayer of negatively charged ions (-SO$_3^-$) (Figure 4.2B) (Inner Helmholtz layer) and thus lead to a negatively charged surface property. The mechanism corresponded with the measurement of PDDA/MWCNTs, presenting a positive zeta potential due to the positively charged PDDA chon the surface of MWCNT. Therefore, in this measurement the change of the zeta potentials indicates the adsorption and coverage of charged surfactants (Nafion and PDDA) on MWCNT.
Figure 4.2: (A) Zeta potential of MWCNTs, Nafion/MWCNTs and PDDA/MWCNTs, and (B) scheme of surfactants functionalized CNT.

* Reference [13].
4.3.3 Composite Analysis of Functionalized MWCNTs

Figure 4.3: Temperature dependence of weight loss for (a) MWCNTs, (b) PDDA/MWCNTs, and (c) PDDA in a Nitrogen atmosphere.

Figure 4.3 shows the TGA curves of MWCNTs, PDDA/MWCNTs, and PDDA in a N$_2$ atmosphere. For both PDDA and PDDA/MWCNTs curves, a weight loss occurs between room temperature and 150°C. This is attributed to the elimination of absorbed water in the samples. In comparison, no weight loss for the MWCNTs was observed in this temperature range. This is probably due to the MWCNTs were synthesised in the inert gas atmosphere and stored in a dry environment, so no sign of water adsorbed on the surface of MWCNTs. The weight loss for carbon splitting did not occur until the temperature reached approximately 544°C. As shown in
Figure 4.3c, significant weight loss for PDDA occurred in two temperature ranges between around 235°C and 385°C and from 385°C to 472°C, respectively. Further increase in the temperature found there is 0.04 wt% for the residence in the sample pan. Similarly, the greatest decomposition process for the PDDA/MWCNTs composite was found between 181°C and 475°C, with a 17.5% weight loss for PDDA, and the big weight loss after 550°C could be attributed to thermal decomposition of the carbon nanotubes. Calculated based on the results discussed above, the PDDA functionalized MWCNTs had a surfactant/MWCNT ratio of approximate 0.11. Due to simple preparing procedure and little loss of surfactant, a 11.4 times higher ratio (1.25) was obtained in the Nafion/MWCNTs dispersion than that for PDDA/MWCNT aqueous solution.

4.3.4 Raman Spectra of MWCNT Electrodes

Raman spectroscopy was employed to study the surface structure of MWCNTs, PDDA/MWCNTs, and Nafion/MWCNTs, as illustrated in Figure 4.4. The spectrum obtained in each case shows two prominent peaks: D band (crystalline disorder) at 1324, 1327 and 1328 cm⁻¹ and G band (stretch vibration in the basal plane of graphite) at 1577, 1582 and 1582 cm⁻¹ for MWCNTs, Nafion/MWCNTs and PDDA/MWCNTs, respectively (Figure 4.4A). From the Raman spectra comparison in Figure 4.4A, we can see the D band possesses a higher intensity than G band The main reason for this might be the high content of amorphous carbon and graphitic impurities in the materials [14, 15]. In addition, we can observe that the D band and G band peak positions of MWCNTs underwent shift after adsorbing the
polyelectrolyte molecules on the surface. Typically, the D band describes the degree of disorder present along the tube, indicating the presence of pentagons, heptagonal defects, the pentagon-heptagon pairs, or line defects. Therefore, the extent of the modification and associated defects on the CNTs can be evaluated by the ratio of the D-band and G-band. We can see from Figure 4.4, the ratio of D band and G band
increases ($I_D/I_G$ from 1.68 to 1.71 and 1.73 for functionalized MWCNTs), further confirming the generation of defect sites after functionalization. As shown in Figure 4.4B, different MWCNT composite exhibits different Raman spectra characteristic at the wavenumber area from 1500 cm$^{-1}$ to 1700 cm$^{-1}$. The raman curve for pristine MWCNTs increases until reach the G band peak and then went down constantly, whilst the other two curves for Nafion/MWCNTs and PDDA/MWCNTs grow after G band and generate the third peak. Compared with the sample primarily comprised of MWCNTs, functionalized ones present an extra peak (Dx band) at 1607 cm$^{-1}$ that corresponds to sp$^2$ defects on the CNT sidewalls [16]. The introduction of Dx band indicate that defects were generated on the carbon nanotube during the process of adsorption of Nafion or/and PDDA.

4.3.5 Morphology Analysis

SEM images were obtained on the GC electrodes modified by MWCNTs without or with polyelectrolyte in order to confirm the effect of non-covalent adsorption of Nafion or PDDA on the morphologies of MWCNT electrode (Figure 4.5). We can see from Figure 4.5 that the MWCNTs show porous network structure. In comparison with the functionalized MWCNTs, due to the poor dispersion, the as received MWCNTs contain more aggregations with bundles and ropes presented in the SEM images (Figure 4.5A&B). The aggregation problem was greatly overcome by the introduction of PDDA and Nafion in the materials, which can be confirmed by the well distribution of MWCNTs on the substrates for SEM investigation (Figure 4.5C, D, E&F). In addition, no significant disruption was observed in the SEM
images, which indicated that this non-covalent method was straightforward modified the surface of MWCNTs on the premise of maintaining the pristine structure and properties of carbon nanotubes [17, 18].

Figure 4.5: SEM image of (A&B) pristine MWCNT, (C&D) Nafion/MWCNT, and (E&F) PDDA/MWCNT modified GC electrodes.
4.3.6 Cyclic Voltammetry Performance of MWCNT Electrodes

The electroactive surface area and Faradaic-electron transfer are two of the most important properties of electrode materials. Generally, there are many methods for testing the electroactive surface properties of an electrode. Using a redox active compound may be the most common approach, such as ferrocyanide and ferrocene. In this study, we used DA and AA instead of the widely utilized redox, since the electrodes were designed to detect DA and/or AA in the solution. This method is to perform cyclic voltammetry (CV) experiments and compare the CV curves at various scan rates in PBS solution containing DA or AA.

Shown in Figure 4.6 are the CV curves of the Nafion/MWCNT electrode in a solution containing 10 μM DA and 0.1M PBS at various scan rates. The electrochemical redox mechanism of DA is electron transfer-chemical reaction-electron transfer (ECE) process and this is a reversible reaction [19]. The oxidation and reduction peaks of DA appear at approximately 0.19 V and 0.18V (vs Ag/AgCl). Upon accelerating the scan rate, the current produced in the redox reaction of DA increased with a symmetrical shape. The non-Faradic current growth indicates thickening of the double electron layer on the surface of the electrode, caused by adsorbing redox species [20]. The anodic peak current shows a linear relationship ($I_{pa} = 1.31ν^{1/2} - 7.10$, $R = 0.994$) against the square root of scan rate (Figure 4.6 inset), indicating a diffusion controlled process for the DA oxidation and electron transfer procedure [21].
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Figure 4.6: Cyclic voltammetry of the Nafion/MWCNT electrode in 10 µM DA solution (pH 7.0 PBS) at different scan rates (a-i): 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV·s⁻¹; Inset: Calibration plots of oxidation peak current to square root of scan rates obtained from CV.

Cyclic voltammetry of the PDDA/MWCNT electrode in 200 µM AA solution (pH 7.0 PBS) at different scan rates is shown in Figure 4.7. Unlike DA that undergoes a reversible electrochemical reaction, only an oxidation peak was found during a cyclic sweep scan. There is no reduction peak appeared probably due to AA is a reducing agent and ususally used as an antioxidation agent. The kinetic pathways of ascorbic acid can be illustrated as follows [22]:

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AA is oxidized to a deprotonated anion which will turn the radical anion after losing an electron and proton. A subsequent fast one electron irreversible oxidation takes the anion to dehydroascorbic acid (DHAA) that is electro-inactive. DHAA is rapidly protonated and then hydrated to 2, 3-diketogluconic acid. Since the loss of electron in step 3 is an irreversible procedure, 2, 3-diketogluconic acid can not be reduced to AA and reducing current is not produced as well. On the other hand there is the increasing oxidation current observed in the CV curves over the whole scan rate range. These responses show a linear relationship against the scan rates represented by \( I_{pa} = 0.47v^{1/2} - 0.53 \) (\( R = 0.956 \)), confirming that the diffusion controlled is the dominant mechanism in the AA oxidation process.
Figure 4.7: Cyclic voltammetry of the PDDA/MWCNT electrode in 200 µM AA solution (pH 7.0 PBS) at different scan rates (a-i): 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV s\(^{-1}\); Inset: Calibration plots of oxidation peak current to square root of scan rates obtained from CV.

4.3.7 Differential Pulse Voltammetry Determination of DA and AA

The DPV curves recorded in different solutions containing 200 µM AA and DA of various concentrations (0–10 µM) are shown in Figure 4.8A. Two current peaks are quite visible at around -0.02 and 0.17 mV vs. (Ag/AgCl) which correspond to the oxidation of DA and AA, respectively. As can be seen from Figure 4.8A, it is quite clear that the two peaks separate well from each other making it possible to study the DA process and AA process independently. The signal from DA oxidation is much stronger than that from AA oxidation. For example, the DA signal (~54 mV for 10
Figure 4.8: (A) DPV of different concentration DA: (a) 0, (b) 0.1, (c) 0.2, (d) 0.4, (e) 0.6, (f) 0.8, (g) 1, (h) 2, (i) 4, (j) 6, (k) 8, (l) 10 µM in the presence of 200 µM AA on the Nafion/MWCNT electrode in pH=7.0 PBS. (B) Calibration plots of peak current to the concentration of DA from DPV on the Nafion/MWCNT electrode.

µM) is over 19 times stronger than that for AA (~2.8 mV), even though the AA concentration is up to 200 µM, which could depress the interference from AA
oxidation in determination of DA. The voltammetric peak corresponding to the oxidation of AA remained unchanged, while the peak current for the oxidation of DA increases linearly as the bulk concentration of DA in the solution. This further confirms that the DPV responses of DA and AA at the Nafion/MWCNT electrode are independent. The linear relationship of peak current with the DA concentration represented by $I_{pa} = 5.34C_{DA} + 0.29$ (R=0.998) (Figure 4.8B). The Nafion/MWCNT electrode performed an excellent determination limit as low as 0.1 µM DA, indicating an excellent sensitivity toward DA detection.

In addition to the Nafion/MWCNT electrode as a biosensor for DA detection, we also developed the PDDA/MWCNT electrode for AA sensing because of the significance of this compound in biological-biochemical (e.g., Neurochemistry) and electrocatalysis) settings. Figure 4.9 shows the DPV curves obtained for AA in the presence of DA at the PDDA/MWCNT electrode. Similarly, the voltammetric peaks corresponding to the oxidation of DA at the electrode occurred at 0.14 mV, and oxidation peaks of AA at -0.09 mV vs. Ag/AgCl are independently separated in the DPV curves. Therefore, despite the coexisting of AA and DA oxidation in the system, the response from AA oxidation was not interfered by the signal from DA oxidation due to the separation of electrochemical oxidation processes for these two analytes. From Figure 4.9 we can the voltammetric peak corresponding to the AA oxidation increases with its concentration in the solution over the range of 10-200 µM. A plot of the peak current vs. the concentration appeared linear ($I_{pa} = 0.776C_{AA} + 0.534$) with a correlation coefficient ($R^2$) of 0.993. Obviously, the correlation coefficient in this case is not as great as that obtained at Nafion/MWCNT electrode. Compared with the
Figure 4.9: DPV of different concentration AA (a) 10, (b) 20, (c) 30, (d) 40, (e) 60, (f) 80, (g) 100, (h) 120, (i) 140, (j) 160, (k) 180, (l) 200 µM in the presence of 1 µM DA on the PDDA/MWCNT electrode in pH=7.0 PBS. (B) Calibration plots of peak current to the concentration of AA from DPV on the PDDA/MWCNT electrode.

Nafion/MWCNT electrode, the PDDA/MWCNT electrode exhibits inferior durability due to the highly hydrophilic property of PDDA and thus leads to the PDDA/MWCNTs detached from the electrode after the electrode expose to the aqueous electrolyte. This is why we obtained some noise date between 0 to 0.5 V vs.
Ag/AgCl. The further investigation will focus on the improvement of the durability of PDDA/MWCNTs on electrode in aqueous environment.

For reference, we made an electrode modified with pristine MWCNT to detect both DA and AA under the identical testing conditions to further illustrate the effect of charged electrolyte molecules on carbon nanotube on sensing activity for DA and AA oxidation. From Figure 4.10 it can be seen that approximate 2.9 µA and 1.0 µA current is detected at -0.09 and 0.14 V vs. Ag/AgCl for 200 µM AA and 1 µM DA, respectively. The DA response was obtained at Nafion/MWCNT electrode at a high value of 53.5 V vs. Ag/AgCl, while a stronger signal for AA (16.5 V vs. Ag/AgCl) was presented at PDDA/MWCNT electrode compared to that for pristine MWCNT electrode. This shows that the surface adsorbing molecules on MWCNTs play a significant impact on sensing DA and AA. It is commonly believed that Nafion can efficiently improves the interaction between DA and electrode, while PDDA facilitates the attraction of AA to MWCNTs. Typically, protons on the sulfonic acid groups (-SO$_3$H) of Nafion can easily transfer from one acid site to another and thus form negative charge -SO$_3^-$ in PBS solution [23]. Therefore, Nafion is able to act as a modifier to attact positively charged DA molecules while precluding negatively charged AA molecules. In contrary to Nafion functionalization, MWCNTs non-covalently functionalized with PDDA afforded the cationic nanotubes, due to a high charge density cationic polymer PDDA [24]. The PDDA/MWCNT electrode enhanced an electrostastic attraction of anionic AA that is dissociated in the PH=7 solution, obtaining Faradic current as high as 5.7 folds of that at the untreated electrode. Another predominant reason revealing high selectivity should be debundle
nanotube structure by steric or electrostatic repulsions [25]. After ultrasonication and adsorption of surfactant, highly uniform, porous and conductive network formed on the electrodes, providing a large specific surface area that improves both the ionic and electronic transport capacities [26].

Figure 4.10: DPV of 1 µM DA and 200 µM AA on (a) the pristine MWCNT, (b) Nafion/MWCNT, and (c) PDDA/MWCNT electrodes in pH=7.0 PBS.

4.4 Conclusion

In this chapter, we discussed the preparation, characterization and application of Nafion/WMCNTs and PDDA/WMCNTs as biosensor electrodes for detecting DA
and AA. This study indicated that the anionic and cationic surfactants functionalization improved the sensitivity and selectivity of carbon nanotube electrode for sensing of DA and/or AA in the mixture solution.

The excellent polymer-MWCNT composite electrodes were successfully prepared by non-covalent adsorption of Nafion or PDDA on MWCNTs, respectively. The charge change on the surface was studied by zeta potential. Electrochemical analyses were performed by CV to estimate the electrode/analytes interface. Diffusion control has been proven to be the predominant mechanism on the interface, which is precondition to utilize the electrodes to quantitative analysis of the concentration of samples. DPV method was used to determine the DA on the Nafion/MWCNTs and AA on the PDDA/MWCNTs, respectively. A linear relationship of anodic current peaks of DA against the concentration was obtained from 0.1 μM to 10 μM, showing a higher sensitivity than nanoweb electrode used in Chapter 3. The PDDA/WMCNT electrode utilized was able to detect AA of the concentration from 10 to 200 μM with a correlation coefficient of 0.993.

Promised novel sensitivity of DA and AA was demonstrated in this chapter using Nafion/MWCNTs and PDDA/MWCNTs as the electrodes. Briefly the surfactants adsorbed MWCNT electrodes have the potential to be used and developed into a truly selective dopamine and ascorbic acid sensor.
4.5 References


