DEVELOPING CONDUCTING POLYMER NANOCOMPOSITES
WITH CARBON NANOMATERIALS FOR MOLECULAR
DETECTION AND FUEL CELL APPLICATIONS

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ABSTRACT OF THE THESIS

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Thesis Director: Prof. Huixin He

Conducting polymers are attractive for chemical sensors because their conductivity and electrochemical activity is extremely sensitive to molecular interactions. The inherent specificity of the conducting polymer based sensors stems from the fact that only certain chemicals can trigger a dramatic conductance change. It can be made more specific by further chemical functionalization of the polymer. The use of conducting polymers (CPs) as low-cost electrocatalysts was also investigated in the early history of conducting polymer research and applications. However, their low environmental stability, low conductivity, and electrochemical activity limit their practical industrial applications. Inspired by the remarkable electronic and superior mechanical properties of carbon nanomaterials, especially carbon nanotubes (CNTs) and the relatively new material graphene, tremendous efforts have been made over the past decade to fabricate conducting polymer and CNT composites with an aim of synergistically combining the merits of each individual components. In this thesis, a series of novel conducting polymer
nanocomposites with these remarkable carbon nanomaterials will be designed and
developed with an ultimate goal of sensitive and selective detection of warfare agents for
homeland security and low-cost metal free electrocatalysts for fuel cell applications.
Experimental results demonstrate that the composite shows dramatically improved
performance compared to each of the individual components. The results obtained from
these studies combined with an introduction of the state of the art of the development in
this field and future prospects will be presented through 6 chapters of this thesis.

Chapter 1 will be the general introduction of state of the art of the applications of
conjugated polymer based nanocomposites in sensors and electrocatalysts. Starting with
the summary of state of the art researches on molecular detection of warfare agents and
precious metal free oxygen electrocatalysts, this chapter will introduce the application of
conducting polymers in molecular detection and electrocatalysis and their respective
limitations, followed by the summary of the unique structures, remarkable properties of
carbon nanomateirals, especially carbon nanotubes and single carbon layer graphene.
Another focus of this chapter is to summarize the current state of development of
conducting polymer nanocomposites with these carbon nanomaterials, and their
applications in electrochemical sensors and Oxygen Reduction Reaction catalysis (ORR).

Chapter 2 describes the fabrication of self-doped polyaniline/SWNT based potentiometric
pH detection platform. A copolymer of aniline with o-aminobenzoic acid has been
electrochemically deposited on top of single stranded DNA dispersed single walled
carbon nanotube. This new pH transducer was employed to detect organophosphate
compounds by immobilization of organophosphate hydrolase (OPH) enzyme onto the
nanocomposite film. The attractive performance characteristics superior over those of
existing pH sensors and offer great promise for the development of field deployable sensors for the detection of chemical warfare agents in connection to various defense and environmental scenario.

With the knowledge gained in chapter 2, a potentiometric sensor for fluoride ion (F⁻) detection in aqueous medium is fabricated in chapter 3. Boron-modified polythiophene (PTBM), a luminescent conjugated polymer is used to disperse and functionalize SWNTs and graphene sheets. A detail study of the interactions between PTBM and SWNTs will be discussed. Both SWNT/PTBM nanocomposite and Graphene/PTBM nanocomposites were tested for their potential applications in fluoride detection in aqueous media.

Chapter 4 describes the fabrication of carbon nanotube/poly (3,4-Ethylenedioxythiophene) nanocomposites (SWNT/PEDOT) as a metal free electrocatalyst for oxygen reduction reaction. We started with a bilayer of SWNT/PEDOT synthesized electrochemically as an active layer in the electrode. A detail study to understand the role of carbon nanotubes in nanocomposites, to improve the interfacial electronic properties and their effect in the catalysis of Oxygen Reduction Reaction (ORR) will be discussed in chapter 4.

After a simple modification of the polymerization techniques, the efficiency of PEDOT/nanocomposite towards oxygen reduction reaction was greatly improved. These results obtained by employing Vapor Phase Polymerization (VPP) of PEDOT/SWNT along with the investigations of kinetics and mechanisms of ORR are discussed in chapter 5. Since our approach is completely precious metal free, we believe it has great potential to develop an efficient and affordable electrocatalyst for fuel cells.
A simple and scalable exfoliation approach to produce high quality single layer graphene sheets from graphite powder will be discussed in chapter 6. Also, these graphene nanosheets with high electrical conductivity and optical transparency can be employed as an electrode material either as synthesized form or incorporating with ICPs for various applications. Our preliminary results of chemically functionalized graphene /PEDOT nanocomposites demonstrated the potential applications of such nanomaterials to replace carbon nanotubes in the electrocatalytic reduction of oxygen.
Dedicated to my Late Father

Mr. Gyani R. Parajuli
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aspirations. I know how lucky I am to have gotten this opportunity and have all of you in my life. This work wouldn't have been possible without you all.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>Å</td>
<td>Angstrom</td>
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<tr>
<td>APS</td>
<td>Ammonium persulfate</td>
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<tr>
<td>a.u.</td>
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<tr>
<td>°C</td>
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<td>CHES</td>
<td>Cyclo hexyl amino Ethanesulfonic acid</td>
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<td>cm</td>
<td>centimeter</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>CV</td>
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<td>Chemical Warfare Agents</td>
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<td>Coated wire electrode</td>
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<td>DC</td>
<td>Direct current</td>
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<td>DNA</td>
<td>Deoxyribonucleic acid</td>
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<td>EDOOT</td>
<td>3,4-Ethlenedioxy thiophene</td>
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<td>EIS</td>
<td>Electrochemical Impedance spectroscopy</td>
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<td>F</td>
<td>Faraday</td>
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<td>F</td>
<td>Fluoride</td>
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<td>Field Effect Transistor</td>
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<td>ISE</td>
<td>Ion selective electrode</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
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<td>L</td>
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<tr>
<td>mV</td>
<td>millivolt</td>
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<tr>
<td>MWNT</td>
<td>Multi-walled carbon nanotube</td>
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<td>NIR</td>
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<td>Organophosphate hydrolase</td>
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<td>ORR</td>
<td>Oxygen reduction reaction</td>
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<td>PANI</td>
<td>Polyaniline</td>
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<tr>
<td>PBS</td>
<td>Phosphate buffered saline</td>
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<td>PEDOT</td>
<td>Poly (3,4-ethylene dioxythiophene)</td>
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<td>PEMFC</td>
<td>Polymer exchange membrane fuel cell</td>
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<tr>
<td>PPY</td>
<td>Poly pyrrole</td>
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<td>PSS</td>
<td>Poly styrene sulfonic acid</td>
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<td>PTh</td>
<td>Polythiophene</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
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<tr>
<td>RRDE</td>
<td>Rotating ring disk electrode</td>
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<tr>
<td>S</td>
<td>Siemens</td>
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<td>ss-DNA</td>
<td>single stranded deoxyribonucleic acid</td>
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<tr>
<td>SWNT</td>
<td>single-walled carbon nanotube</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>V</td>
<td>Volt</td>
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<td>VBS</td>
<td>Valence band spectra</td>
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<tr>
<td>VPP</td>
<td>Vapor phase polymerization</td>
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<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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Chapter 1 Introduction

1.1. Nanomaterials

The rise of nanotechnology from a laboratory curiosity to a multibillion dollar industry has been the most remarkable transformation seen by the technology industries in the past few years. There is a general agreement in the field of material science that nanomaterials are defined as such when they exploit characteristics which become manifest only at the nanometer scale and that are not present in the bulk material. Since at this scale the laws of quantum mechanics are very important, most of these peculiar behaviors of nanomaterials originate from quantum phenomena.

One important class of such nanomaterials a nanocomposite, which consists in a large number of nanometric particles such as nanotubes or graphene (sheets) as filler dispersed in a more or less ordered fashion in some sort of matrix mostly constituted by polymers. The goal to fabricate such hybrid materials is to obtain distinct properties evolved from the synergistic effects of the component materials. This may include either new or improved electronic or chemical properties that may be exploited for chemical or biological sensing, or enhanced stabilities in different environments that can be utilized for energy storage and/or conversions.

This thesis is mainly based on the development of the nanocomposites of polymers with carbon nanotube or graphene and on the investigation of their potential applications for molecular detection and fuel cell electrode. In this chapter, the current state of art works will be summarized, which is also the background of this thesis. This chapter is organized
as follows: An introduction to conducting polymers, carbon nanotubes, graphene, and their corresponding composite fabrication, property, and applications in the development of chemical and biochemical sensors and electrocatalyst materials will be discussed. Fundamental working principles of polymeric membrane based potentiometric sensors and the electrochemical techniques used in this thesis will be discussed followed by the objective of this thesis.

1.2 Conducting polymers

During the last few decades, conducting polymers have been gathering a great interest in academia and industry by providing the opportunity of combining the electrical properties of a semiconductor and metals with the traditional advantages of conventional polymers such as easy and low cost preparation and fabrication. After the discovery made by MacDiarmid and co-workers in 1977\(^1\) that polyacetylene can gain the conductivity of a metal by doping with either I\(_2\), Br\(_2\) or AsF\(_5\), many aromatic conjugated polymers were studied. (Fig 1)

Nowadays, most of the researches about conducting polymers are focused on Polyaniline (PANI), Polypyrrole (PPY), Polythiophene (PTh) and Poly (3,4 ethylenedioxythiophene) (PEDOT) as they possess relatively high conductivities and exhibit reasonable air stabilities. The conductivity of such polymers is the result of several processes. For example, in traditional polymers such as polyethylene, the valence electrons are bound in sp\(^3\) hybridized covalent bonds. Such sigma-bonding electrons have low mobility and do not contribute to the electrical conductivity of the material. Conducting polymers on the other hand, have backbones of contiguous sp\(^2\) hybridized carbon centers. One valence electron on each center resides in a p\(_z\) orbital, which is orthogonal to the other three
sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is doped by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied.

Figure 1.1. Chemical structures of major families of conjugated polymers.

The conductivity of conducting polymers can reach as high as $\sim 10^5 \text{ S/m}$ whereas that value for traditional polymers is $\sim 10^{-10} \text{ S/m}$. Since the conducting property originates from the inherent (extended conjugated $\pi$-bond) structure of these polymers, they are called as intrinsically semi-conducting polymers.
1.2.1 Polyaniline (PANI)

Polyaniline (PANI) is one of the most interesting conducting polymers and has been investigated intensively over the past decades due to its ease of synthesis, environmental stability, and striking electronic and optical properties. The existence of nitrogen atoms as imine (in sp²) or amine (in sp³ hybridized state) forms, and their relative proportion in the overall polymer backbone chain determines the resulting structure and the different properties of polyaniline.

![Diagram of Polyaniline Structure]

**Figure 1.2** General chemical structure of polyaniline

The general chemical structure of polyaniline is shown in fig.1.2. It contains \( y \) (reduced) and \( (1-y) \) oxidizing units. The value of \( y \) can vary from 0, (all quinonoid) units to give completely oxidized form (pernigraniline), to one (all benzenoid units) which gives a completely reduced leucoemeraldine. When \( y=0.5 \), i.e. the number of reduced units equals the number of oxidized units, it is known as emeraldine base. It is well known that polyaniline has a wide range of oxidation states which are both pH and potential dependent (fig 1.3). The oxidation of a polyaniline chain occurs with concurrent loss of protons on amine structures, resulting in neutral (quinoid) units. Quinoid units contain imine nitrogen, which can be protonated completely or partially to yield the
corresponding salts. The preferential protonation of imine nitrogen over amine nitrogen is due to their more basic property. The pKa of protonated amine and imine are 2.5 and 5.5 respectively\textsuperscript{2}. Pernigraniline is the fully oxidized state of polyaniline, pink/purple in color. It does not exhibit conducting properties like the other states. Leucoemeraldine, the fully reduced state of polyaniline, has a pale brown color and is also non-conducting. The emeraldine state of polyaniline does not have conducting property either and can be differentiated with its blue color. On the other hand, the only electronic conducting state of polyaniline is the protonated emeraldine form which has partially oxidized/reduced structure. The conductive property of this state originates from the charge carriers that are generated after the acid treatment of the emeraldine form (reversible reaction by base treatment). This state of polyaniline has a dark green color, and a conductivity value between 2-10 S/cm.

To obtain polyaniline from the aniline monomer, the most widely employed synthetic routes are the chemical oxidative polymerization and the electrochemical polymerization. Chemical oxidative polymerization (radical cationic) reaction of aniline is usually conducted in acidic medium with a suitable oxidizing agent such as ammonium persulfate; APS ((NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) and proceeds to form polyaniline. As-produced polyaniline can be rendered electrically conducting by an additional acid treatment (doping) after its polymerization reaction.

Electrochemical synthesis of PANI can be carried out by the oxidation of acidic media on an inert metallic (e.g., Pt, Au) electrode or on a piece of conducting Indium Tin Oxide (ITO) glass, by either constant potential, constant current, or repeatedly cycling the applied voltage between two pre-selected potentials.
Although PANI can be doped oxidatively, the most common method of doping polyaniline is a non-redox doping process using protonic acids. The initial product of imine protonation undergoes an electron rearrangement resulting in an unpaired electron and a positive charge on the imine nitrogen atoms. This charge carrier is called bipolaron, which is relatively unstable and undergoes a redistribution of charge and spin to yield more stable polarons (radical cations). Conversions between neutral, polaronic and bipolaronic species are reversible using either chemical or electrochemical means to oxidize or reduce the polymer. The most conductive state of PANI can be converted to an insulator at pH >4. PANI and other conjugated polymers possessing strongly basic functionalities undergo a more complex chemical doping mechanism (Fig 1.4). While
the leucoemeraldine form can undergo oxidative doping leading to a radical cation (polaron) formation, the emeraldine base of PANI can also undergo protonation by acid base chemistry to yield the emeraldine salt (bipolaron) form. Internal charge distribution in the emeraldine form can also yield the polaron form. Finally, the charge carriers allow electronic transport within these materials. With strong rate of doping, there is a collection of the polaronic and/or bipolaronic states, so that the defect charges can move along the polymeric chains. During non-oxidative doping process the number of electrons associated with the polymer backbone does not change. However, the energy levels are rearranged and a stable poly semiquinone radical cation (a polaron) is produced, leading the polymer into a highly conducting regime. The highly conducting form of polyaniline, which corresponds to a salt, can be reversibly de-doped into its non-conducting base form. During the doping process the conductivity of the polymer increases from $10^{-10}$ S/cm (undoped state) to 10 S/cm (doped state).

The continuously growing interest in the study of polyaniline over the past years is because of diverse but unique properties that allows the potential applications in various fields. The ability of polyaniline to undergo reversible doping/de-doping and charge transfer interactions has resulted in a large number of applications such as gas, chemicals and pH sensors. The unique property of polyaniline to exhibit various oxidation states has been used in corrosion inhibition. Their reversible oxidation/reduction ability has also been utilized in rechargeable batteries.

1.2.1.1 Self-doped Polyaniline

Despite the ease of synthesis, low cost, good stability under ambient conditions, and its response to the immediate environment, the application of native polyaniline is limited
due to its poor solubility in various solvents and electrochemical inactivity in neutral or slightly basic pH. This largely limits its further applications as a sensor for the determination of biomolecules in actual neutral media. Several researches have been carried out during the past two decades to tune this limitation of polyaniline.

Figure 1.4 Schematic of chemical doping routes of polyaniline.³
A major breakthrough in the field was the discovery of self-doped polyaniline due to its desirable properties, including better solubility as well as redox activity and conductivity over a wider pH range.

A self-dopped polyaniline bears ionizable negatively charged functional groups such as boronic, sulfonic, carboxylic and phosphonic acid groups introduced during their synthesis bound on the phenyl ring or nitrogen of imine site of PANI. The structure of a carboxylic acid doped polyaniline used in this work is shown in fig1.5.

Jiang et al. have suggested that the copolymer films prepared electrochemically were partially self-doped and were more rigid than PANI. In these self-doped polymers, high populations of bi-polarons can be expected due to attractive columbic interactions between main chain cations and immobile carboxylate counter anions linked directly to main chain benzene rings. This then decreases the mobility of cations, which makes the dissociation of a bi-polaron into two independent polarons difficult. Therefore, the conductivity depends on the aniline fraction in the copolymer composition. This doping is also expected in the copolymer of aniline, and the carboxylic groups in the backbone of the PANI chain may act as a matrix for immobilization of cationic species in solution, e.g. proteins and enzymes.
Also, the existence of intramolecular interactions between the COO\(^{-}\) group and the cationic radical nitrogen prevent the protons from diffusing away from the ring bound negatively charged polymer chain. This high concentration of protons in the vicinity of polymer backbone has been claimed to be responsible for the retention of doping at neutral pH.\(^{10}\)

1.2.2 Conjugated organoborane polymers

Conjugated polymers in which Lewis acid centers are embedded or attached in the \(\pi\) – conjugated system are interesting materials due to their excellent optical and electronic properties that can be exploited for emission and electron conduction materials in OLED devices, and Lewis base recognition probes for chemical sensors. One class of such compounds is polythiophene based organoborane compounds in which Lewis acidity is due to the empty p- orbital on tri- coordinate boron. Boron can achieve its desired octet configuration either by overlapping with an organic \(\pi\) -system or by formation of Lewis acid- base complexes \(^{22}\) (Fig 1.6). It is this \(\pi\)- interaction that leads to interesting linear and non-linear optical properties as well as favorable electron transport abilities, which allow for
the use of organoboranes as emission and electron conduction materials in OLED devices.\textsuperscript{22}  

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{organoborane.png}
\caption{Schematic of properties of organoborate compounds.\textsuperscript{22}}
\end{figure}

The boron p-orbital is susceptible to nucleophilic attack which can lead to either a cleavage of the B-C bond or formation of a tetra-coordinated boron species in which the extended conjugation is broken. Sterically demanding groups such as mesityl (2,4,6-trimethylphenyl) or tripyl (2,4,6-triisopropylphenyl) groups are used to provide stability to the boron center.\textsuperscript{24} Many researchers have successfully synthesized such boron containing small molecules, one example being the synthesis of 3-boryl-2,2’-bithiophene\textsuperscript{25} by Yamaguchi and co-workers. These bithiophene based \(\pi\)-electron materials show intense solid state emission which can be tuned either by using electron-withdrawing or electron-donating substituents and may be employed for optoelectronic applications. Polymeric compounds present certain advantages over small molecule analogues, such as the possibility of using solution processability (spin casting, roll printing, inkjet printing) for fabrication of devices and in case of sensor materials, the prospect of signal amplification.\textsuperscript{26}
Recently Jäkle et al. reported incorporation of electron deficient boron centers to the side chain of polythiophenes and their photophysical and electrochemical properties.\textsuperscript{27} The polymer named PTBM (fig 1.7) demonstrated selective affinity for different anions as reflected by the change in the polymer photophysical properties upon anion binding in organic medium.

![Polymer structure](image)

In this work, the application of PTBM is extended to disperse and functionalize single walled carbon nanotube. Further application of hence synthesized nanocomposite is demonstrated by the fabrication of a potentiometric sensor to detect fluoride in aqueous medium with improved sensitivity.

1.2.3. Poly (3, 4-ethylenedioxythiophene) (PEDOT)

Poly (3,4-ethylenedioxythiophene) [PEDOT] is a relatively new conducting polymer which was developed by scientists at the Bayer AG research laboratories in Germany in conjunction with AGFA in the late 1980’s.\textsuperscript{28-29} PEDOT possesses the structure shown in Figure 1.8.
Figure 1.7 Structure of a doped conductive poly (3,4-ethylene dioxythiophene).

PEDOT can be synthesized by polymerization of its monomer 3,4-ethylenedioxythiophene (EDOT) through electrochemical or chemical methods. One of the inherent difficulties of polymerizing EDOT is its low solubility in water. Therefore the polymerizations are normally carried out either in non-aqueous solutions or in solutions with ionomers or surfactants. However, such surfactants or polyelectrolytes are difficult to remove completely from the reaction mixtures and their residues may affect the electronic properties of PEDOT. The most successful commercial product Baytron P, which is sold as a stable PEDOT/poly (styrene sulfonic acid) PSS) aqueous suspension can produce films with conductivities up to ~10 S/cm and was developed by Bayer AG for antistatic coating applications. However, even higher conductivity is required for applications in electrical current paths in electronic devices such as anodes on photovoltaic devices, source/drain electrodes in thin film transistors, electrodes in organic light emitting diodes, supercapacitors, sensors and catalyst supports in fuel cells.

In situ polymerization, in which a polymer is deposited directly onto a substrate, has been intensively studied by employing three approaches for achieving high conductivity: (i) liquid-phase polymerization (LPP), which involves spinning a mixture of monomer,
oxidant, and inhibitor directly onto the substrate; (ii) electrochemical polymerization and (iii) vapor-phase polymerization (VPP). de Leeuw\textsuperscript{33} developed a direct oxidative polymerization method suitable for formation of surface films. By an adaptation of this method, conductivities up to 550 S/cm have been reported for PEDOT.\textsuperscript{34} It is, however, not trivial to obtain reproducible, homogeneous films using this method.\textsuperscript{35} In situ formation by electrochemical polymerization can lead to conducting polymers with a high conjugation length, if the synthesis conditions are chosen properly.\textsuperscript{36}

Electrochemical polymerization presents several advantages such as fast, absence of catalyst, controlled thickness by deposition charge and direct deposition of the polymer film in conductive oxidized form. Aleshin et al produced PEDOT-PF\textsubscript{6} by electrochemical polymerization from acetonitrile at -30 °C and obtained conductivities up to 300 S/cm\textsuperscript{37}.

Iron (III) salts have proven to be particularly useful oxidation agents for PEDOT. Iron (III) tosylate (FTS) is the most prominent case, since this salt is well soluble in organic solvents such as alcohols and readily available. Mixtures of (FTS) solutions with EDOT are easily prepared and result in a well-controlled deposition of conductive films. Furthermore, the tosylate ion has proven to promote the chemical reaction of EDOT. Beginning with first attempts by J. Kim et al.\textsuperscript{38}, a new route to highly conductive PEDOT layers by vapor phase polymerization (VPP) was established in 2003 to 2005. In the vapor-phase polymerization of PEDOT, the surface of a solid sample is first coated with an Fe (III) salt and then exposed to an atmosphere of EDOT monomer. This technique results in uniform, relatively thin (submicron) films of PEDOT. Winther-Jensen et al. reported that the use of a FTS oxidant with pyridine as a weak base (to suppress an acid
initiated polymerization) in vapor phase polymerization (VPP) can enhance the electrical conductivity of PEDOT as high as 1000 S/cm.\textsuperscript{39}

Kirchmeyer et al.\textsuperscript{40} proposed the detailed mechanism of oxidative polymerization of EDOT (Figure 1-9). The first step in this reaction is the EDOT oxidation to the corresponding radical cation. This is the slowest and therefore rate-determining step with a rate constant $k_1= 0.16 \text{ L}^3\text{mol}^{-3}\text{h}^{-1}$. The free radical cation then very rapidly dimerizes with $k_2= 10^8 - 10^9 \text{Lmol}^{-1}\text{h}^{-1}$. End group oxidation of EDOT oligomers follows, starting with dimer oxidation, which is remarkably faster than monomer oxidation ($k_5= 3 \times 10^3\text{Lmol}^{-1}\text{h}^{-1}$; the same value as proposed for all chain lengths). Recombination of two radical cationic end groups results in oligomer formation with the same rate constant for recombination as for the monomeric cations ($k_2= 10^9\text{Lmol}^{-1}\text{h}^{-1}$). Finally, oligomers or polymers are doped by further oxidation. The doping process results in charges along the conjugated backbone of the polymer, which enables the flow of current. Therefore, the amount of dopant is directly related to the conductivity of conjugated polymer.\textsuperscript{41} In Figure 1.9 the paramagnetic polaron state as the first step of doping and intermediate to the highly conductive, diamagnetic bipolaron state is shown. This state is stabilized by the charge balancing counter ion.

As shown in Figure 1.10, the type of conjugation may be deformed in the course of doping process\textsuperscript{42}. The two possible types of conjugation are shown in B and Q. Form B is often referred to as benzoid and form Q as quinoid.

PEDOT is at the present time the most successful conducting polymer in commercial applications and is used for various applications. Depending on the extent of doping, oxidation and film thickness, PEDOT films can range in appearance from almost
transparent with a sky-blue tint, to an intense blue-black. As a result, much of the research on PEDOT has centered on its use in low color anti-static coatings and electrochromic devices.\textsuperscript{29,43}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{reaction_mechanism.png}
\caption{Proposed reaction mechanism for EDOT oxidation to conductive PEDOT-tosylate.\textsuperscript{27}}
\end{figure}

Outstanding environmental stability and low band-gap of PEDOT (1.5-1.6eV)\textsuperscript{44} make PEDOT a promising sensing material to detect wide range of chemical and biological species.\textsuperscript{45-46} Moreover, the most promising application of PEDOT as a catalysts support for fuel cell electrodes has been demonstrated recently\textsuperscript{47}. Current research trends to
improve the properties of PEDOT focus on conductivity enhancement, modification of surface properties, work function tuning, water-soluble derivatives, and the synthesis of PEDOT nanoobjects and nanocomposites.\textsuperscript{48-52}

\textbf{Figure 1.9} Chemical structure of Benzoid (B) and Quinoid (Q) type of PEDOT.

\section*{1.3 Carbon Nanomaterials}

The fact that carbon forms many allotropes, compounds, and intricate networks, is essential to the existence of life on earth. There is no surprise, therefore, that carbon compounds and allotropes are the most studied and researched materials in the world. The capability of carbon atoms to from complicated networks\textsuperscript{53} is fundamental to organic chemistry. Even elemental carbon shows complicated bonding, forming a number of allotropic structures. Pure carbon is found in nature both as diamond and graphite. They have very different properties, even though they differ only by the arrangement of the
carbon atoms. While diamond is insulating and very hard, graphite is conducting and lubricant. Recently discovered allotropes like fullerenes and nanotubes are the center of focus for many scientists researching in the fields of chemistry, physics, biology, and material science.\textsuperscript{54} After the discovery of the first artificial pure carbon material, the spherical molecule called fullerene, an intense research on other pure carbon materials had begun. In 1991, carbon was produced in the form of quasi one-dimensional nanotubes. Later, in 2004, a single sheet of carbon, named graphene, has been experimentally discovered\textsuperscript{55}. The strictly two-dimensional graphene can be seen as the basic building block for the other graphite materials, having different dimensionalities. The fullerenes can be seen as zero-dimensional wrapped up graphene, the nanotubes as one-dimensional rolled graphene, and graphite as three-dimensional stacked graphene (see Fig. 1-11).

\textbf{Figure 1.10} Crystal structure of different allotropes of carbon (left to right) three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one-dimensional nanotubes (1D); and zero-dimensional buckyballs (0D).\textsuperscript{56}

\subsection*{1.3.1 Carbon nanotubes}
Ijima discovered carbon nanotubes in 1991\textsuperscript{57} and a method for the large-scale synthesis of nanotubes by Ebbesen and Ajayan was introduced in 1992.\textsuperscript{58} Since then various nanotubes, have been experimentally produced either by the arc-discharge methods or by
chemical vapor deposition of organic chemicals. These elongated tubes consist of carbon hexagons arranged in a concentric manner with both ends of the tubes normally capped by fullerene like structures. They usually have a diameter of the order of tens of Å and lengths of up to several µm and can behave as semiconductors or metals depending on the diameter and helicity of the arrangement of graphitic rings in the walls.

Two distinct types of carbon nanotubes have been recognized. The first is multi-walled carbon nanotubes (MWCNT) that consists of more than one concentric cylindrical shell of graphene sheets (monolayer of sp² bonded carbon atoms), which are coaxially arranged around a central hollow with a constant interlayer separation of 3.4 nm. The second is single-walled carbon nanotubes (SWCNT) that are made of single layer of graphene cylinders. The SWCNT have some distinct advantages over their MWCNT counterparts. For example, SWCNTs are transparent to electromagnetic radiation including lights and they show truly one-dimensional quantum effects.

The various ways of rolling graphene into tubes are described by the tube chirality (or helicity or wrapping) as defined by the circumferential vector, $C_h=n\mathbf{a}_1 + m\mathbf{a}_2$ (Figure 1.12), where the integers $(n, m)$ are the number of steps along the unit vectors ($\mathbf{a}_1$ and $\mathbf{a}_2$) of the hexagonal lattice. Using this $(n, m)$ naming scheme, the three types of orientations of the carbon atoms around the nanotube circumference are specified as armchair $(n, m)$, zigzag $(n =0$ or $m =0)$, or chiral (all others). The chirality of nanotubes has significant impact on its transport properties, particularly the electronic properties. All armchair SWNT are metallic with a band gap of 0 eV. SWNT with $n - m = 3i$ ($i$ being an integer and $\neq 0$) are semi metallic with a band gap on the order of a few meV, while
SWNT with \( n - m \neq 3i \) are semiconductors with a band gap of ca. 0.5-1 eV.\(^{70} \) Each MWNT contains a variety of tube chiralities, so their physical properties are more complicated to predict.

**Figure 1.11** A graphene sheet that can be rolled into a SWNT. \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the unit vectors of the graphene lattice. The dashed lines denote the main symmetry directions in the graphene sheet.

Due to unique electronic properties, high aspect ratio, high chemical stability, extraordinary mechanical properties, and feasibility to attach foreign species or chemical groups, carbon nanotubes have become increasingly focused in many research areas. Their applications ranges from field microelectronic devices,\(^ {71-73} \) catalyst supports,\(^ {74-75} \) sensors,\(^ {76-79} \) hydrogen storage\(^ {80-81} \) and electrocatalysis.\(^ {82-84} \) For sensing applications, SWNTs have some advantages over MWNT such as high surface area to weight ratio, (200-400 \( \text{m}^2\text{g}^{-1} \)), relative chemical inertness; and greatly enhanced electron/ion and mass transfer when used as a support of redox mediators.\(^ {85} \) However, the full exploitation of these properties of carbon nanotubes is impeded by their tendency to form bundles due
to the extraordinary intermolecular cohesive interaction between neighboring nanotubes. Another obstacle for the nanotube in real applications is their poor compatibility to polymer matrices as adding bundles of nanotubes would even weaken the host materials. Several methods have been used to disperse single walled carbon nanotubes to form a stable suspension and therefore to create desirable interfacial contact between the polymer and nanotube additives. Based on the strategies of functionalization, they can be classified into three groups: non-covalent and covalent modifications, and acid oxidation. Among these different methods, functionalization with supramolecules via non-covalent approaches seems striking as the pi-extended graphitic surface of the nanotube is preserved in this approach, and thus the pristine nature is generally retained. The high molecular weight molecules can modify a SWNT surface by either threading or wrapping around its surface. Successful dispersion of SWNT by non-covalent approaches can be achieved by disrupting the van der Waals forces that hold nanotubes together into bundles.

1.3.2 Graphene

Graphene shows a planar hexagonal arrangement of carbon atoms (Fig. 1.11). It is the name given to a flat monolayer of carbon atoms arranged tightly in honeycomb lattice, which is the building block of graphitic materials. Graphene is a conceptually new class of materials that is only one atom thick, and, on this basis, offers new insight into low-dimensional physics. Single-layer graphene might be the thinnest material one can ever discover, since it is only one atomic layer thick.

Graphene is a semiconductor but it has an unusual feature that its band gap is exactly zero. The low scattering rates and the electronic structure of graphene give rise to good
electronic transport that is easy to modify by doping or electrostatic fields. Its high conductivity could allow it to serve as interconnects. It can be gated so it could be used as the channel in novel transistors. Graphene is quite stable and inert, thus it is possible to prepare large areas that have low defect densities and low electronic scattering rates.\textsuperscript{87}

The nanoscale graphene platelets (NGPs) are predicted to have a range of peculiar electronic, optical, magnetic, and mechanical properties.\textsuperscript{55,88} In addition to single graphene sheets, double-layer or multiple-layer graphene sheets also exhibit unique and useful behaviors. Electrons in a single-layer NGP are believed to behave like massless chiral relativistic particles\textsuperscript{55,88-89} as reflected by the anomalous quantization of the Hall conductance. NGP's peculiar properties can result in many applications. One potential application of NGPs is in the field effect transistors. Due to the ultra-high thermal conductivity of NGPs (four times more thermally conductive, yet four times lower in density compared to copper), a nanocomposite thin film, paper, or coating can be used as a thermal management layer in a densely packed microelectronic device. NGP nanocomposites have a good combination of mechanical stiffness, strength, microcracking resistance, electrical and thermal conductivities. NGPs can also be a component material for lithium ion battery electrodes, sensors and fuel cell electrodes.

 Nonetheless, to date the exfoliation of graphite to graphene and its incorporation into polymers have been rarely reported. Low solubility, strong interaction and small spacing between stacked graphene planes make it nearly impossible to achieve a fully separated state of graphene by pure mechanical mixing with solvents/polymers. While deriving graphene from graphite was regarded nearly impossible for decades, recently developed strategies have paved a way for polymer nanocomposites reinforced with graphene.
Novoselov and Geim first demonstrated free-standing single layer carbons from repeated mechanical cleavages of graphite with Scotch tapes. Isolation of graphene was also achieved via liquid-phase exfoliation using surfactants and ionic liquids. Even bottom-up approaches such as chemical vapor deposition and epitaxial graphitization have been also reported. However, difficulties in large-scale production limit their practical applications. Moreover, obtained high-purity graphene layers tend to stack into graphite again or scroll into tubes in order to minimize surface energy. A simple and scalable exfoliation approach to produce high quality single layer graphene sheets from graphite powder is developed in this thesis.

1.4 Composites of conducting polymer with carbon nanomaterials

1.4.1 Carbon nanotube based composites

The combination of carbon nanotubes (CNTs) with insulating or conducting polymers offers an attractive route to reinforce macromolecular compounds, as well as to introduce new electronic properties based on morphological modifications or electronic interactions between the two constituents. The unique properties of these various types of nanomaterials provide novel electrical, catalytic, magnetic, mechanical, thermal, and other features that are desirable for applications in commercial, medical, military, and environmental sectors. Besides the expected improvements in the mechanical and electronic properties of polymers, the preparation of carbon nanotube/polymer composites has been and is still explored for effective incorporation of CNTs into devices. Nevertheless, the use of CNTs as a rough material in different applications has been largely limited by their poor processability, insolubility, and infusibility. To bypass this disadvantage, an efficient key is the functionalization of CNTs with polymers,
leading to soluble composite materials. Researchers have been focusing on two types of materials: on one hand, composites based on insulating polymers (IPs) such as polystyrene (PS) or poly (methyl metacrylate) (PMMA), and on the other hand, those made with conducting polymers (CPs), such as polyaniline (PANI), polypyrrole (PPy), poly (3,4-ethylenedioxy thiophene) (PEDOT), polythiophene (PTh), and 2,2-polybithiophene (PBTh) and polyacetylene (PA).

Usual methods for the preparation of polymer/CNT composites consist of the direct mixing of components in the melt or in solution, in situ polymerization of corresponding monomer solution in the presence of carbon nanotube; by chemical or electrochemical approaches, and by nanotube seeding approaches. The effectiveness of interfacial nanotube-polymer contact depends on the synthetic process. Direct mixing of carbon nanotube with polymer followed by sonication is straightforward; however the nanotube in such composites would easily get damaged, which consequently limits the applications of the resulting composite. In situ polymerization leads to the most effective interfacial contact compared to the direct mixing and the nanotube seeding approach, which has been reported as an efficient way to form conducting polymer nanowire structure.

1.4.2 Composites of graphene

The one-carbon-atom thick graphene can be a very promising reinforcement, providing combined benefits of both layered silicates and CNT. Unlike layered silicates, it has exceptional electrical and thermal transport properties. Unlike CNT, these 2-dimensional carbon layers can reduce gas permeability of hostmembranes, and can be derived from naturally occurring graphite at a fraction of cost. In addition to much lower costs (compared to carbon nanotubes, CNTs), another major advantage of
graphene-based nanocomposites is their capability of forming a thin film or coating for electromagnetic interference (EMI) shielding, and electrostatic charge dissipation (ESD). Moreover, its in-plane mechanical properties are similar to those of CNT. In addition, composites of graphene with conducting polymers will benefit from the surface textures, larger surface area and the geometry of graphene sheets. The rough and wrinkled texture of graphene caused by a high density of surface defects has a tendency to interlock extremely well with the surrounding polymers and helps to boost the interfacial properties of the nanocomposites. As a planar two dimensional sheet, graphene benefits from the stronger contact with the polymer material than the tube shaped carbon nanotubes. All these properties are extremely important to obtain high performance materials in the applications of sensors, catalysis, and other electronic devices.

1.5 Electrocatalysis: History and Development

Electrocatalysis is defined as the heterogeneous catalysis of electrochemical reactions by an electrode material. The demand for clean energy technology is growing worldwide as discussed in a report by the Basic Energy Sciences office of the US Department of Energy. In general, the reliance on polluting, fossil fuel-based technology is unsustainable in respect to both the worldwide economy and environment. While stationary power concerns (e.g. electrical power plants) are invariably responsible for degradation to the environment, it is in transportation applications that a serious effort must be focused. Essentially every automobile on the road is powered by an internal combustion engine utilizing a fuel source derived from oil. The most promising technology for mitigating these concerns, first proposed by William Grove in 1839, is the non-polluting fuel cell technology. Fuel cells are electrochemical cells which converts
chemical energy into electrical energy with a constant supply of fuel. A fuel cell consists of an anode to which a fuel is supplied and a cathode to which an oxidant commonly oxygen is supplied. The oxygen needed by a fuel cell is generally supplied in the form of air. The two electrodes are separated by an ion conducting electrolyte. All fuel cells have similar basic operating principle. The input fuel that passes over the anode is catalytically split into electrons and ions. The electrons from the oxidation reaction at the anode are passed through an external circuit to perform work, and are returned to the cell at the cathode and reduce the oxygen passes over the cathode. The ions which are formed at the anode and transported to the cathode combine with the oxide ions and generate the oxidized product. If the fuel happens to be hydrogen then water is formed. Depending on the input fuel and electrolyte, different chemical reactions will occur. A typical example of a fuel cell, polymer exchange membrane fuel cell (PEMFC) is illustrated in Figure 1.13. ORR in aqueous solutions occurs mainly by two pathways: the direct 4-electron reduction pathway from O₂ to H₂O₂:

\[
2O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_0 = 1.23 \text{ V vs NHE (acid media)}
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4 OH^- \quad E_0 = 0.401 \text{ V (alkaline media)}
\]

The peroxide 2-electron reduction pathway from O₂ to H₂O₂:

\[
O_2 + 2 H^+ + 2e^- \rightarrow H_2O_2 \quad E_0 = 0.67 \text{ V Vs NHE (acidic media)}
\]

Peroxide can undergo further reduction or decomposition

**In acid media**

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2 H_2O \quad E_0 = 1.77 \text{ V}
\]

\[
2 H_2O_2 \rightarrow 2 H_2O + O_2
\]

**In alkaline media**

\[
O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad E_0 = -0.065 \text{ V}
\]
The reaction is followed by further two-electron reduction or by decomposition

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow 3 \text{OH}^- \quad E_0 = 0.867 \text{ V} \]

\[ 2\text{HO}_2^- \rightarrow 2 \text{OH}^- + \text{O}_2 \]

The electronic and morphological properties of the electrode surface (such as electrode material, solution pH and electrode potential) will determine the extent to which the mechanism proceeds through 1-, 2-, and 4-electron reduction pathways. In reality, the power density of an operating fuel cell is constrained by both the cathodic and anodic losses. At both electrodes, ohmic losses reduce the overall cell potential in respect to increasing current density. The ohmic contributions to the non-ideal behavior of the operating fuel cell are inherent to any realistic device, and result from a combination of resistive factors. First, there will forever be an inherent cumulative electrical resistance in the components. In addition, the ionic conductivity of the membrane is not infinite, and is influenced heavily by both temperature and level of hydration. For all intents and purposes, while these losses are inherent, they do not factor in any significant manner. The most significant detriments to performance arise from kinetic losses at the cathode (Figure 1.14a). In particular, the oxygen reduction reaction (ORR) performed at the cathode suffers from sluggish kinetics. Indeed, the majority of research with an aim to making fuel cells a viable energy source has focused on improving the conditions for efficient ORR. The actual mechanism of ORR was first proposed in the late 1960s, by Damjanovic’s group.\textsuperscript{112-113} The complete reaction involves a full 4e\textsuperscript{-} reduction of adsorbed molecular oxygen to water. However, a simultaneous pathway involving a 2e\textsuperscript{-} reduction to hydrogen peroxide is inherently present. In addition to lowering the overall power output of a model PEMFC, hydrogen peroxide is damaging to the polymer
exchange membrane (PEM). Peroxide has a tendency to form free radical species in a true PEMFC operating environment which will attack and degrade the PEM.\textsuperscript{114-115} The overall effect is an increase in resistance within the membrane further lowering the power output of the cell. Building upon the substantial contributions of Damjanovic \textit{et al.}\textsuperscript{112-113} the commonly accepted kinetic pathway for ORR was reported by Wroblowa \textit{et al.}\textsuperscript{116} in mid-1970. This scheme (Figure 1.14b) identifies ORR as a first-order reaction with the adsorption of molecular oxygen as the rate-limiting step. The sluggish kinetics of ORR arises from the initial adsorption step. Research into ORR essentially shifted to a new objective: the identification of electrocatalysts which were predisposed to facilitate the initial adsorption step. For basic research purposes, these studies were centered on the highest-performing electrocatalyst for ORR, platinum. The first high-profile application of Pt as a fuel cell electrocatalyst was developed during the Apollo Lunar mission conducted by NASA during the 1960s (manufactured by United Technologies Corporation.; http://www.utc.com). However, their large-scale commercial application has been precluded by the high cost of the requisite noble metals. Since electrocatalysis is a surface phenomenon,\textsuperscript{117} increasing the concentrations of surface vs. bulk (i.e. unreactive for ORR) atoms was the first step in reducing amount of Pt required for realistic applications (i.e. consumer). Despite the high intrinsic activity for ORR possessed by Pt-based electrocatalysts, there are significant drawbacks. First and foremost, Pt is an expensive, rare metal. Further, while Pt exhibits exceptional activity towards ORR, it also expresses activity for a large variety of other materials. Pt cathodes are substantially depolarized by a vast array of substances such as methanol, halide anions, carbon monoxide, etc. In particular, the extremely low methanol tolerance of Pt renders its
immediate adoption untenable.\textsuperscript{118-119} The best way to avoid the cost of Pt is to eliminate its incorporation into the electrocatalyst altogether. Ideally, Pt should be replaced at both fuel cell electrodes; however, its substitution at the cathode with a non-precious metal catalyst would have comparatively greater impact, because the slow oxygen reduction reaction (ORR) at this electrode requires much more Pt than the much faster hydrogen oxidation reaction at the anode. In this scenario, the utilization of cheap transition metals (e.g. Fe, Co, etc.) would allow for higher loadings to offset their performance lag. Unfortunately, the majority of transition metals are unstable in the corrosive fuel cell operating environments. As such, much research has been directed into identifying stable compounds that exhibit acceptable activity and stability towards ORR. Examples of these include specific metal oxides and carbides, which although exhibiting appreciable activity towards ORR, they are yet to overcome stability requirements.

Conducting polymers with good electrical conductivity and electrocatalytic behavior have aroused wide interest as cathode materials for oxygen reduction reaction.\textsuperscript{120-121} It has been reported earlier that conducting polymers such as polyaniline (PANI), polypyrrole, polythiophene, poly (3-methylthiophene) and poly (3,4-ethylenedioxy thiophene) (PEDOT) in oxygen saturated electrolytes exhibited electrocatalytic activity towards the ORR with the exception of PEDOT.\textsuperscript{122} Later on a highly conductive PEDOT synthesized by VPP techniques is reported to possess electrocatalytic activity towards ORR without CO poisoning.\textsuperscript{47} However, a lack of fully understanding of oxygen reduction pathway of PEDOT catalyst in a fuel cell operating environment hinders further development of their practical applications in fuel cell electrodes.
Figure 1.12 Idealized concept of a polymer exchange membrane fuel cell.\textsuperscript{115}

Figure 1.13 (a) Schematic of the loss in cell voltage experienced by an operating PEM fuel cell and (b) A simplified scheme of ORR pathways.\textsuperscript{116}
1.6 Applications of conducting polymer nano composites in electrocatalysis

From the above discussions, it is clear that electrocatalysis of ORR depends on the adsorption process therefore the electrocatalytic activity depends on the nature and structure of catalytic electrodes. In order to increase the catalytic activity which is proportional to the active surface area of the electrode, the catalyst material is sometimes dispersed on a high surface area, suitable electron conducting substrates. In principle, a nanocomposite of conducting polymer with carbon nanomaterials (carbon nanotubes or graphene) can serve as such a catalyst provided that the nanocomposite meets the following criteria:

- It is sufficiently stable under the experimental condition
- It is sufficiently conductive to avoid an ohmic drop in the film
- It is sufficiently porous to allow the electroactive species to reach the catalytic sites.

Preparation of modified electrodes in which a conducting polymer is present as connecting unit to CNT and their catalytic activity towards ORR has been reported. For example glassy carbon electrode modified with polyaniline grafted multiwall carbon nanotube film has been enhanced electrocatalytic for oxygen reduction. However, the real applications of these nanocomposites are limited due to less-efficient two steps oxygen reduction. Therefore finding a novel nanocomposite for efficient oxygen reduction will be a step forward to solve the problems associated with current ORR electrocatalysts.

Developing a conducting polymer nanocomposite for efficient Oxygen Reduction Reaction (ORR) is one of the main objectives of this thesis.
1.7 Electrochemical Theory

This section describes the theory behind the three major types of measurements investigated in this thesis. Firstly, the relationship between the open circuit potential and the ion concentrations in a polymeric film is discussed, followed by the fundamentals of AC impedance spectroscopy applied to the analysis of an appropriate equivalent circuit describing the nanocomposite. Finally, the fundamentals of voltammetry and its application in the determination of oxygen reduction reaction mechanism will be discussed. The theory and equations derived in this section will be of invaluable use to the analysis of the experimental results in the following chapters of the thesis.

1.7.1 Open Circuit Potential Measurement

Potentiometric measurements are based on monitoring potential values under a zero current flow (open circuit) regime, in order to determine the analytical concentration of desired components in an analyte. In these methods the potential difference between an indicator electrode (ion- selective electrode, redox electrode, metal- metal oxide electrode) and the reference electrode is measured as the analytical potential. The potential of an electrochemical cell is due to the changes in the free energy that occur if the chemical phenomenon reach an equilibrium, which is a concept typically applied in the quantitative analysis in relation to electrochemical cells. Under open circuit potential condition, the potential across the polymeric membrane electrode is

\[
E = E^0 + \frac{RT}{F} \ln \left[ \frac{[poly]^+}{[Poly]} \right] + \Delta \varphi \quad (1.1)
\]
where $E^0$ is the formal potential of the polymer, $\text{[poly]}^+$ and $\text{[poly]}$ are the oxidized and reduced state of the polymer and $\Delta \phi$ is the membrane potential.

If the cell is properly designed, all possible potential contributions can be kept constant except for the membrane potential ($\Delta \phi$). The $\Delta \phi$ can be found using the Nernst equation, which states that $\Delta \phi$ is dependent on the activity of the analyte ion in solution, assuming the activity of the analyte ion $I^+$ in the membrane is constant$^{124}$

$$\Delta \phi = E^0 \pm \frac{RT}{zF} \ln \frac{a_{I,pb}}{[I]_{pb}}$$

(1.2)

where $R$ is the ideal gas constant, $T$ is the temperature, $F$ is the Faraday constant, $z$ is the charge of the analyte ion, $a_{I,pb}$ is the activity in the sample, and $[I]_{pb}$ is the concentration in the membrane phase. In equation 1.2, (+) sign holds for cation analyte and (-) sign for anion analyte. According to above equations, if the activity of a monovalent analyte changes by a factor of 10, a potential change of 59 mV will be observed. This is a general theory of classical potentiometry. However, for trace analysis, higher sensitivity of the potentiometric sensor to detect nanomolar or sub-nanomolar concentration of analyte is required. Previous works showing the detection limit of conventional ISEs can be lowered towards the sub-nanomolar concentration level$^{125}$ has attracted more interest to these devices.

1.7.1.1 Conducting polymer nanocomposites in potentiometric sensors

There is no doubt that our ability to see, hear, taste, smell and feel tactile simulations has a great impact on our lives. However, the smart human sensors created by nature are not enough to cope with the tremendous analytical demands in areas like environmental, industrial process and clinical analysis. It has been estimated that there are total of 100
million known chemicals and biochemical to be monitored quantitatively. Chemical sensing involves both molecular recognition and signal transduction. Therefore, development of novel chemical sensors is closely related to the development of new materials for both molecular recognition and signal transduction.

Potentiometric ion sensors (ISE) are very attractive, especially due to their portability, low cost and easy working principle. However, conventional ISE configurations are inconvenient owing to their large size and internal filling solutions. Therefore miniaturization of ISE has become a growing trend in the field of electrochemical sensors. The disadvantages of conventional type of ISEs can be overcome by the development of all-solid-state ISEs that do not require internal filling solutions termed coated wire electrode (CWEs) or solid state device. In CWEs the organic polymeric ion selective membranes are deposited directly on the conductive electrode material by simple dip coating. Removal of the inner filling solutions brings numerous advantages to the ISEs. Besides their small sizes, low cost in fabricating, mechanical flexibility and simple construction, the CWEs have response characteristic equal or even better than conventional ISEs. In many cases, the limits of detection are significantly improved compared to conventional ISEs with internal filling solutions. This is because the leaching of primary ions from the internal solution is prevented in the CWE configuration.

However, a main disadvantage of the CWEs is the unstable potential that develops at the interface of the organic ion selective sensing membrane and the conducting substrate. The formation of an aqueous layer, which serves as a pseudo internal electrolyte between the polymeric membrane and solid conductor has been considered as one of the possible
reasons for this problem. Since the composition of this aqueous layer is uncontrollable, the cell constant (EMF) changes are in unpredicted manner. Another factor that contributes to the instability of the CWEs is the poorly defined charge transfer at the blocked interface between the ion sensitive membrane with ionic conductivity and the conducting substrate with electronic conductivity (e.g. no defined redox reactions)

A variety of approaches have been reported in attempt to improve the stability of the CWEs. One effective approach is to employ an intermediate layer which translates the ionic response of the sensing membrane into a stable electronic signal better poising the phase boundary potential between the polymeric membrane and solid conductor. The intermediate layers can be hydrogels, redox active monolayers or conducting polymers or three dimensionally ordered macro porous carbon electrodes. Hydrogel-contact ISEs suffer, however, from shortcomings originating from the water uptake/release and the resulting volume changes of the hydrogel layer which is a function of the salt concentration of the hydrogel. Monolayers however, suffer an inherently low frequency redox capacitance to provide stability condition which depends on the low frequency redox capacitance of the conducting polymer. The low-frequency impedance response of conducting polymers is similar to ideal capacitance resulting from reversible oxidation of the polymer bulk connected with ion transport. The small current that passes through the electrode during potentiometric measurements inevitably results in oxidation/reduction of the conducting polymer, i.e. charging/discharging of the bulk capacitance.

Fabrications of conducting polymer-modified electrodes have been one of the most preferred approaches for the preparation of electrochemical sensors since many years.
The combination of the well-known characteristics of conducting polymers (good stability, reproducibility, high number of active sites, strong adherence and homogeneity in electrochemical deposition) with those of CNTs would lead to a largely improved performance of the resulting sensing devices, due to their complementary electrical, electrochemical and mechanical properties, and also to the synergistic effect of the component materials. The advantages of such nanocomposite in potentiometric sensing device can be easily hypothesized as improved sensitivity, fast response, and enhanced stability due to increased surface area, fast signal transduction behavior and facile charge transfer at the interface, respectively. Also, owing to the hydrophobic nature of carbon nanotubes or graphene, the formation of water layer at the interface can be avoided.

1.7.3 AC Impedance Spectroscopy

The ratio of voltage to current V/I for a resistor is defined as its resistance. When voltage and current are in phase, their resistance does not depend on frequency. However, more interest has been directed to the cases where the ratio of voltage to current does depend on the frequency and there is a phase difference. Impedance (Z) is a measure of a circuit’s tendency to resist (or impede) the flow of an alternating electrical current. The equivalent mathematical expression is

$$Z = \frac{V_{ac}}{I_{ac}}$$  \hspace{1cm} (1.3)

The technique where cell or electrode impedance is plotted against frequency is commonly called as electrochemical impedance spectroscopy (EIS). In EIS technique a small perturbation (sinusoidal potential wave form of 5-10 mV) is applied (fig 1.14a) to the electrochemical cell and the electrochemical response is measured and interpreted in
terms of an equivalent circuit (fig 1.14b), a circuit composed of electrical components with the same frequency response as the electrochemical reactions.

A pure sinusoidal voltage excitation signal normally can be expressed as equation:

\[ e = E \sin(\omega t) \quad (1.4) \]

Where \( e \) is the potential of the excitation voltage, \( \omega \) is the angular frequency, \( E \) is the amplitude of AC excitation, and \( t \) is time.

In a linear system, the response signal, \( I_t \), is shifted in phase (\( \Phi \)) and has a different amplitude, \( I_0 \)

\[ I_t = I_0 \sin(\omega t + \Phi) \quad (1.5) \]

\[ Z = \frac{e}{I_t} \quad (1.6) \]

There are many ways to plot impedance data. Since, the function impedance is an AC signal, one can express in terms of complex number

\[ Z = Z_{\text{real}} + j Z_{\text{imag}} \]

and plot the \( Z_{\text{real}} \) vs \( Z_{\text{imag}} \). Such kind of plot is called Nyquist plot and provides visual insight into the system dynamics at the interface.

In electrochemistry, the imaginary impedance is almost always capacitive and therefore negative. A detailed derivation of these equation can be found in Bard’s text book.\textsuperscript{135} In here, the applications of EIS to characterize the polymeric thin films are presented.

An ideal Nyquist plot for a polymer coated metal electrode in an electrolyte solution in a purely charge-transfer control system is shown in fig 1.14c, where the charge transfer resistance can be derived from the diameter of the semicircle. The two semicircles at the highest frequencies induced by the process at the metal/polymer and polymer/solution interfaces are in practice not always detectable.
When both diffusion and kinetic control are involved, a more complex Nyquist plot will occur, which can be illustrated in fig 1.14d. The circular portion corresponds to the charge transfer control and the linear portion corresponds to the diffusion control.

Figure 1.14 Impedance function (a) and typical equivalent circuit (b) at the electrochemical interface (c) Sample of Nyquist plot of a polymer membrane coated electrode and (d) mixed control complex electrochemical system

The EIS spectra of conducting polymers are quite complex and still not well understood because of numerous processes taking place simultaneously during recharge of the polymer layer. However, a number of models, describing the impedance spectra for some particular kind of polymer layers, has been proposed in the literature. In this work a generalized transmission line circuit model, as first proposed by Pick up et al., applied describing the capacitive effects in the low frequency range through chemical
processes\textsuperscript{137}. The transmission line model predicts the impedance features of a polymer system in terms of Nyquist plots based on mathematical approach and yields fairly accurate ionic and electronic conductivities. In a real system, the measured semicircle may have a center below the x-axis determined by the electrolyte/electrode interfacial properties such as the roughness of a polycrystalline electrode, the inhomogeneous reaction rates across the electrode surface or the non-uniformity of current distribution. These depressions in the semicircles can be modeled as a constant phase element (CPE) in the equivalent circuit.\textsuperscript{137-138} Furthermore, they can also overlap to the mid-frequency Warburg impedance quasi with a 45\(^{\circ}\) slope that reflect the diffusion-migration of ions at the boundary surface between solution and polymer. Finally, the 90\(^{\circ}\) trend at the lowest frequency due to capacitive impedance accounts for the charge transport process inside the bulk of the film. A combination of EIS with a commonly used technique like CV thus provides a powerful tool to understand the properties of conducting polymer based nanocomposites and thus to develop such nanomaterials for the specific applications.\textsuperscript{138}

The low frequency capacitances values characterizing the polymer film redox capacitance can be obtained by using the relation,

\[
C_F = \frac{1}{\omega Z''} = \frac{1}{(2\pi f)Z''}
\]

(1.7)

Where ‘\(f\)’ is the lowest frequency used to record the spectra and \(Z''\) is the imaginary part of the impedance at that frequency.

The electronic and ionic resistances of the conducting polymer composite film at different dc potential can be extracted from the Nyquist plots by using the relationship\textsuperscript{139}
\[
\frac{1}{R_\infty} = \frac{1}{R_E} + \frac{1}{R_I} \quad (1.8)
\]

\[
R_\Sigma = R_E + R_I \quad (1.9)
\]

Where \( R_\infty \) is the high frequency intercept of the Warburg-type region in the complex impedance plot (corrected for uncompensated solution resistance (R_s)) and \( R_\Sigma / 3 \) is the theoretically constant real impedance at low frequency corrected for R_s. The ionic and electronic conductivities of the film (\( \sigma \)) can be calculated from the resistance (R), obtained by the simultaneous solutions of equation 1.8 and 1.9 by using the relation.\(^{140}\)

\[
\sigma = \frac{d}{RA} \quad (1.10)
\]

where, A is the geometric area of the electrode and d represents the thickness of the film. The thickness of the film, ‘d’ can be obtained by using the relation proposed by Hoier and Park\(^{141}\) for the conductive polymer.

In this work, we used electrochemical Impedance spectroscopy (EIS) technique to complement and elucidate the voltammetric data. Information such as electrochemical activity due to faradic reactions as well as the ionic conductivity and charge transfer resistance will be obtained using EIS.

### 1.7.4 Rotating Disk Electrode (RDE and RRDE) Voltametry

Tantamount to understanding the ORR activity of materials is the ability to quantitatively deduce their activity and kinetics. All of electrochemistry is governed by, and must conform to, the Nernst equation\(^{135}\):

\[
E = E^o + \frac{RT}{nF} \ln \frac{[n^{a}]^{\frac{1}{n}}}{[O^{2-}]^{\frac{1}{2}}} \quad (1.11)
\]
where \( E \) is the actual potential, \( E^0 \) is the standard potential, \( n \) is number of electrons transferred, \( \frac{RT}{F} \) represents the division of the product of the gas constant and temperature by Faraday’s constant, and \([[]]^a\) are the bulk concentration of the oxidants and reductants in the system.

The Nernst equation related the thermodynamics of an electrochemical system by equating the influences of concentration upon the electrochemical potential via the Gibb’s free energy of a system,

\[
\Delta G = \Delta G^0 + \frac{RT}{nF} \ln \left( \frac{[\text{prod}]^a}{[\text{react}]^a} \right) \tag{1.12}
\]

and can be related to \( E \) by the following relationship:

\[
\Delta G = -nFE \tag{1.13}
\]

Following the confirmation that an electrochemical system adheres to the thermodynamic limits described by the Nernst equation (eq. 1.11), it is possible to pursue a kinetic measurement of the system. The methodology is provided by the well-established rotating disk electrode (RDE, Figure 1.14). This method comprises the utilization of a smooth disk (commonly glassy carbon, or GC) of a known geometric diameter. The disk is spun at a series of known angular rotation rates (\( \omega \)) which results in a laminar flow of the electrolyte to the electrode surface, and a compact diffusion layer of electrolyte which is fully saturated with the reactant. Rotation of the electrode results in near-linear region of current at high overpotentials. This current is limited by the rotation rate; that is, at this point the rotation rate has limited the supply of reactants to the electrode, and is commonly referred to as the limiting current density (\( i_{\text{lim}} \)). The supply of reactants will vary in proportion to the rotation rate, as described by the Levich relationship:
\[ i_{\text{lim}} = B \omega^\frac{1}{2} \]  

(1.14)

Where \( B \) represents the Levich slope and is defined by

\[ B = 0.62nFAD^\frac{2}{3}v^\frac{1}{2}C_o \]  

(1.15)

Where ‘\( D \)’ is the diffusion coefficient, ‘\( v \)’ is the kinematic viscosity (dynamic viscosity divided by density of the medium), and \( C_o \) represents the dissolved concentration of the electrolyte (in the case of PEMFC cathodes, this represents dissolved oxygen), \( A \) is the geometric area of the disc electrode. The value of angular rotation rate of the electrode \( \omega \) in radian per second, can be obtained from the relation,

\[ \omega = \frac{2\pi f}{60} \]  

(1.16)

with \( f \) is the rotation per minute (rpm)

The number of electrons involved in the oxygen reduction reaction can be obtained from equation 1.15. If the limiting current density can be determined to be approximately equal to the diffusion limiting current \( (i_{\text{lim}}) \) this allows the separation of the kinetic current density \( (i_k) \) from the total current density \( (i) \):

\[ \frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{\text{lim}}} \]  

(1.17)

Current is reciprocal (from Ohm’s Law), and it is the rate of an electrochemical reaction \( (\text{Amp} = Q \text{ s}^{-1} = \text{Coloumb s}^{-1}) \), and \( i_k \) can be expressed as,

\[ i_k = nFAK_0C_0\Gamma \]  

(1.18)

Where ‘\( \Gamma \)’ is the surface concentration of the catalyst, or the catalyst loading and can be obtained from the relation,
\[ Q = nF\Delta \]  

Where \( Q \) is the surface charge and can be obtained by integration of the area under the peak in the Cyclic Voltammogram.

To further confirm, number of electron transfer can also be quantitatively deduced via the rotating ring disk electrode (Figure 1.14). In this technique, the \( \text{O}_2 \) reduction reaction occurring on the disk electrode produces intermediates, which can be detected on the ring and are used to deduce the ORR mechanism. The metal ring is polarized at a potential where peroxide from the disk will oxidize. The \( n \) value is calculated by the ratio of faradaic, ring \( (I_R) \) to disc current \( (I_D) \) by using the following equation:

\[ n = \frac{4I_D}{I_D + \frac{I_R}{N}} \]  

Where, \( N \) is the collection efficiency of the ring, and is derived from direct measurement of a known system\textsuperscript{143}.

\textbf{Figure 1.15} Schematic representation of a rotating disk electrode. Laminar flow of the electrolyte at the electrode surface (left) and frontal view of the ring and disk (right).\textsuperscript{115}
1.8 Objective of the Dissertation

This dissertation aims to control, investigate, improve and characterize several properties of conducting polymer based nanocomposites in order to build a substantial background for the future industrial applications. A series of novel conducting polymer nanocomposites with carbon nanomaterials will be designed and developed with an ultimate goal of sensitive and selective detection of warfare agents for homeland security and low-cost metal free electrocatalysts for fuel cell applications. Since polymers themselves are being used in various industrial applications, development of such high performance nanocomposites would represent a step forward in these areas.

1.9 References

(13) Yin, W. S.; Ruckenstein, E. Macromolecules2000, 33, 1129.


(42) Im, S. G.; Gleason, K. K. Macromolecules 2007, 40, 6552.
(115) Zhang, L. *PHD Thesis North Western University (Boston)* **2005**.
Chapter 2 A Sensitive Potentiometric pH Transducer Based on Self-Doped Polyaniline Carbon nanotube Composite for Neurotoxin Detection

2.1 Introduction

Sensitive detection of neurotoxins has become increasingly important for protecting water resources and food supplies in defense against terrorist activity, as well as for monitoring detoxification process. The majority of biosensors to detect neurotoxins are based on the inhibition of acetylcholinesterase enzyme integrated with a sensing element. Such inhibition biosensors are sensitive for single use, but are difficult for field deployable detections and on-line continuous monitoring, mainly due to their lack of selectivity and the multiple step detection process. Some newly developed organophosphate-hydrolyzing enzymes can effectively evade these problems. These enzymes are highly selective for hydrolysis of specific neurotoxins through a reaction in which P-O, P-F bonds are cleaved, producing compounds that can be electrochemically selectively detected. The sensitivity is limited by the electrocatalytic capability of the electrode modification to detect them. On the other hand, the hydrolysis also results in a large change in acidity (pH) of the detection environment. Each neurotoxin molecule releases two protons. The protons released correspond to the quantity of organophosphate hydrolyzed. This stoichiometric relationship has been exploited to develop neurotoxin sensors using a pH-based assay. However, the sensitivity is limited by the currently available pH detection techniques. Diiopropyl fluorophosphate
(DFP), one neurotoxin, can be detected with a detection limit of 25 μM with a pH glass electrode \(^4\) and a detection limit of 20 μM with a pH sensitive field effect transistor as pH transducers. By using a pH sensitive fluorescent dye, the sensitivity was improved to 1.0 μM.\(^9\) Apparently, the ability to efficiently and sensitively monitor pH changes will greatly increase the detection sensitivity for neurotoxin agents. Furthermore, the pH to have the best catalytic activity of the enzymes is around pH 9. Therefore a pH sensor with higher sensitivity in this pH range is required for neurotoxin detection. In this work, we report a rational design for a pH transducer, satisfying all these requirements for sensitive and direct detection of neurotoxins.

By copolymerizing aniline and \(o\)-aminobenzoic acid in the presence of single-stranded DNA dispersed and functionalized single walled carbon nanotubes (ss-DNA/SWNTs), we produced a composite network in which the polyaniline component is functionalized with –COOH groups. Remarkably, the network exhibits extremely high sensitivity to pH changes around pH 9, at which the enzymes have the best catalytic activity. Using paraoxon as a model compound, we demonstrated the application of this pH transducer as a sensor for early detection of chemical warfare agent with a detection limit (defined as the concentration that gives the signal which is 3 times stronger than noise) of 2 nM, which is \(10^3\) times more sensitive than that based on a pH sensitive field effect transistor\(^10\) and CNT based FET.\(^11\)

### 2.2 Experimental

#### 2.2.1 Reagents

Purified single walled-CNTs were purchased from Carbon Nanotechnologies, Inc. Houston, TX. Single-stranded DNA with sequence d \((T)_{30}\) was purchased from Integrated
DNA Technologies, Inc., Coralville, IA. Aniline, O-aminobenzoic acid (O-ABA) and 2 N-cyclohexylaminoethanesulfonic acid (CHES) buffer, sodium hydroxide, hydrochloric acid and sulfuric acid, were purchased from Aldrich Chemicals Inc., Milwaukee, WI. Aniline was doubly distilled prior to use and all other chemicals were used as received. All solutions were prepared using nanopure water (18.2 MΩ) (Barnstead), which was also used to rinse and clean samples after polymerization and before any characterization.

2.2.2 Electrochemical measurements

Electrochemical copolymerization of aniline and o-aminobenzoic acid (4:1 molar ratio) and electrochemical characterization of the resulting films were carried out in a CH Instrument 760C series electrochemical station. Cyclic voltammetry (CV) and open circuit potential (OCP) measurements were conducted using a homemade Teflon cell (with an accessible area of 0.25 cm²) with the modified gold substrate as the working electrode, a platinum wire as a counter electrode, and a Ag wire as a quasi-reference electrode. (The quasi-reference electrode was calibrated against the more widely used Ag/AgCl/saturated KCl reference, and all the potentials quoted in this work are in terms of the Ag/AgCl ). All the pH measurements were carried out using a Fisher AB15 pH meter calibrated with commercially available standard buffer solutions.

2.2.3 Synthesis of Nanocomposite

The copolymer nanocomposite was fabricated on the gold electrode surface by following the procedure described previously. Briefly, 4 µL of the dispersed ss-DNA/SWNT solution with a concentration of 70mg/L, was cast on top of the Au electrode modified with a 2-aminoethanethiol monolayer and allowed to dry at room temperature to form an ss-DNA/SWNT film. Poly (aniline co-o-aminobenzoic acid) (PANI co-O-ABA) was
then deposited onto the modified Au substrate by sweeping the electrochemical potential from –0.34 to 0.65 V (vs Ag/AgCl) with a solution of 0.1 M aniline and 0.025 M O-aminobenzoic acid in 0.05 M H₂SO₄. After the second cycle, the polymerization potential was decreased to 0.60 V to reduce the possibility of over-oxidizing the polymer backbone. Repeated cycling of the potential resulted in continuous deposition of copolymer onto the electrode surface. The resulting PANI co-O-ABA/ss-DNA/SWNT composite on the electrode was first stabilized in 0.05 M H₂SO₄ and then in 0.01 M phosphate-buffered saline (PBS, pH 7.4) by sweeping the potential between -0.3 and 0.65 V (in H₂SO₄) and -0.4 and 0.60 V (in PBS) until the CV curves were stabilized. The nanocomposite film was washed three times before the pH measurements and the pH on the composite film was checked with precise pH paper.

2.2.4 Potentiometric measurements

2.2.4.1 pH calibration

The potentiometric response of the nanocomposite coated gold electrodes was measured within the pH range of 3-9. The buffer solutions of pH 3-9 consisted of 1.0mM CHES. Hydrochloric acid or NaOH was used to adjust the pH of the CHES buffer and the pH of the solution was calibrated by a traditional glass electrode. In-situ titration was performed by adding small volumes of HCl solution or NaOH solution in the CHES buffer solution. The added volume was derived from the solution pH, measured independently by a glass electrode. Calibration solutions with pH 2, 7, and 10 were used as obtained from the supplier. Potentiometric measurements were carried out from pH 9-3. The mean values of the potential readings at the different pH values were used to calculate the slope of the calibration curve.
2.2.4.2 Paraoxon detection

In order to selectively hydrolyze paraoxon, 10 μL of organophosphate hydrolase (OPH) (1.92 mg/mL) was physically immobilized on the nanocomposite film by simply casting the enzyme on top of the composite film and drying under vacuum over ice bath to prevent the enzyme from denaturation. Paraoxon (12.8 mM) was used as a stock solution and diluted to make the required concentrations using deionized water. After the enzyme was dried, various concentrations of paraoxon were added to the electrochemical cell and the open circuit potential (OCP) of the composite modified electrode was measured.

2.3. Results and discussion

2.3.1 Electrochemical synthesis of ss-DNA SWNT/Poly (aniline co- o-aminobenzoic acid) (ss-DNA SWNT/PANI co-O-ABA) nanocomposite

The copolymerization of aniline and o-aminobenzoic acid was carried out on a ss-DNA/SWNT modified gold electrode by electropolymerization in acidic aqueous solutions containing aniline and o-aminobenzoic acid monomers. A typical cyclic voltammogram for electrochemical polymerization is shown in fig 1a. In general, the polymerization of aniline in 0.1 M H₂SO₄ solution exhibited two redox couples corresponding to electrode process of leucoemeraldine/emeraldine and emeraldine/pernigraniline, but for this copolymerization process there is an obvious third redox couple ~0.22V in fig 2.1(a). The third redox couple, which was observed in the aniline polymerization only with a high positive polymerization potential¹³ is ascribed to the formation of phenazine groups resulting from ortho-coupling and cyclization within the polyaniline chains by the space hindrance of o-aminobenzoic acid unit copolymerized in polymer chain. This is similar to the previous report,¹⁴ except the redox peaks are
shifted to more negative potentials which could be due to the electrocatalytic properties of SWNT, which makes copolymerization faster and easier.

Moreover, all peak currents of these electrocouples increased with continuously increasing cyclic sweep numbers, suggesting a polymer formed on the electrode surface.

### 2.3.2 Electroactivity of copolymers nanocomposites in neutral PBS solution

To study the electrochemical activity of poly (aniline co-o ABA)/SWNT nanocomposite, cyclic voltammograms in PBS buffer with pH from 6 to 9 as supporting electrolyte were investigated. The cyclic voltammograms presented in (fig 1b), showed that at all pH values studied a well-defined redox couple is observed which is similar to the one observed for self-doped PANI, at pH>5.8. This observation illustrates that the copolymer nanocomposite shows electrochemical activity in neutral and basic pH solutions. However, the redox peak current of the composite is decreased with the solution pH, suggesting that the electrochemical activity of the composite decreased in alkaline solutions. It has been reported that no electroactivity in neutral pH solution can be found for pure polyaniline.\(^{15}\) However, when polyaniline is copolymerized with o-aminobenzoic acid, the polyaniline backbone can be partially doped with the carboxylic acid functional groups, possibly by forming hydrogen bonding between the imine or amine groups in the polyaniline backbone (scheme 1). Therefore the PANI backbone can remain doped in neutral and even in slightly basic solutions, which is responsible for the extended electrochemical activity in neutral and basic solutions.
Scheme 2.1. Chemical structure of ploy (aniline-co-o-aminobenzoic acid)

Figure 2.1 (a) A typical cyclic voltammogram of ss-DNA SWNT modified gold electrode swept from -0.3 V to 0.6 V at a scan rate of 100 mV/s in 0.05 M H₂SO₄ containing 0.1 M aniline and 0.25 M o-aminobenzoic acid. (b) Cyclic voltammograms of the resulting copolymer nanocomposite modified electrode recorded in different pH PBS buffer solutions (0.1 M).

2.3.3 Optimization of composition of the copolymer/SWNT composites

Six composite films have been fabricated on gold electrodes with different ratios of the composite ingredients as presented in Table 2.1. Since the ultimate aim of this work is to fabricate a pH sensitive material with highest sensitivity around pH 9, the criterion for the optimization was pH sensitivity of the resulting nanocomposite in the pH range of 7-9. The pH dependence of fabricated electrodes was measured by recording the open circuit potential in various pH buffer solutions ranging from pH 9 to 3 in 100 µL of 1.0 mM...
phosphate buffered saline buffer (PBS) solution (fig 2a). Before each measurement, the sensor was immersed into buffer and then into nanopure water in order to ensure the same starting conditions. The stabilized open circuit potential at t = 300 s were used to generate the calibration curve showed in fig 2b.

Initially, the effect of a sensor, with no any conducting polymer and SWNT/polymer composite was coated on the electrode was studied. It showed no response to pH change. Then the ratio of aniline to o-aminobenzoic acid was optimized by fabricating the copolymer composite with SWNT. The ratio of the aniline to o-aminobenzoic acid was found to affect the sensitivity of the sensors. A ratio of 1:4 was found to be the optimum and further addition of o-aminobenzoic acid resulted in a diminished response of the sensors. Since, the degree of self-doping depends on the aniline and o-aminobenzoic acid (o-ABA) monomer ratios, we believe a lower content of o-ABA results in a copolymer with less doping. A high content decreases the yield of copolymer due to the electron withdrawing nature and the steric effect of the carboxylate groups, which largely influence the reactivity of the o-aminobenzoic acid for polymerization. The electron-withdrawing carboxylic acid groups coupled with the steric factors deactivate the aromatic system retarding the polymerization of amino benzoic acid compared to that of aniline.

From table 2.1, it is also obvious that composites of homopolymer of either of the monomers with equal amount of SWNT are less sensitive to pH change as compared to the copolymer nanocomposites. A control experiment was conducted with copolymer synthesized using optimized monomer ratio without carbon nanotubes. In this case the sensitivity observed is better than that of homopolymer nanocomposites, but still lower
than the copolymer nanocomposites. The pure copolymer sensor fabricated without SWNT demonstrated a slope of 134 mV/pH unit in the pH range 7.5 to 9, whereas the copolymer composite with optimized monomer ratio demonstrated pH sensitivity with a slope of 250 mV/pH unit in the same pH range. These results demonstrate that, the sensitivity of the copolymer depends on the ratio of the monomers as well as a synergistic effect of the individual components in the nanocomposite. The pH detection sensitivity in the acidic and alkaline solution can be tuned by careful selection of the components of the composites to modify an electrode surface. The presence of carbon nanotubes in the composite leads an open network structure which allows a fast and complete exchange of ions within the entire sensing surface (which is the composite film) on the electrode.

These results suggest that the best material in terms of its electrochemical properties at high pH can be synthesized by copolymerization of aniline and o-ABA in the ratio of 4:1.
Figure 2.2 (a) A typical open circuit potential of ss-DNA/SWNT poly (aniline-co-o-ABA) nanocomposite modified electrode at different pH (b), (c) and (d), correlation curves obtained from the pH response with pure copolymer and SWNT nanocomposites SWNT nanocomposites with each of the homopolymers and nanocomposites with different ratio of polyaniline and o-ABA, modified electrodes respectively.
Table 1 pH sensitivity of different electrode materials fabricated

<table>
<thead>
<tr>
<th>Electrode composition with ss-DNA/SWNT</th>
<th>Slopes (mV/pH unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH (3-7)</td>
</tr>
<tr>
<td>3:1 (Aniline: o-ABA)</td>
<td>49</td>
</tr>
<tr>
<td>4:1 (Aniline: o-ABA)</td>
<td>38</td>
</tr>
<tr>
<td>5:1 (Aniline: o-ABA)</td>
<td>52</td>
</tr>
<tr>
<td>1:0 (Aniline:o-ABA)</td>
<td>91</td>
</tr>
<tr>
<td>0:1 (Aniline:o-ABA)</td>
<td>50</td>
</tr>
<tr>
<td>4:1(Aniline:o-ABA)*</td>
<td>31</td>
</tr>
</tbody>
</table>

* Copolymer without SWNT

### 2.3.4 Potentiometric pH response

In order to test the potential application of the sensor for field application, the sensory response was investigated by monitoring the change of the open circuit potential with pH employing standard addition technique. A typical potentiometric curve obtained during the acid base titration (addition of acid to a base solution) is given in fig.2. 3a. From fig 2.3a, it can be easily observed that, when the bulk solution is alkaline, the response is fast as manifested by the sharp changes in potential upon addition of small volume of the acid and come back to the starting potential instantly. However, a stable signal is observed when we move towards pH< 7.0. This behavior can be attributed to the diffusion of protons to the bulk alkaline solution. When the bulk solution is more alkaline protons added during the titration are consumed by the hydroxyl ions instantly and the bulk solution pH is higher than the calculated pH, but when the pH changes to more acidic, such a process is less significant and the observed signal is stable. A correlation curve
between OCP and pH is obtained and shown in fig 2.3b. The maximum potential reached after each addition was recorded and used to construct the correlation curve. From the correlation curve two different slopes in the pH range of 3-9 are observed. A slope of 43mV/pH unit and a sub Nernstian slope in the pH range of 3-7 and steeper slope of 217mV/pH unit in the range of pH 7.5-9 with a correlation coefficient of 0.98 and 0.96 respectively, are observed.

![Graph showing the relationship between E/V vs Ag/AgCl and Time/S, and another graph showing the relationship between E/V vs Ag/AgCl and pH.](image)

**Figure 2.3** (a) Potentiometric response of nanocomposite sensor with time during the titration of 0.0004M NaOH by 0.00004M HCl. Final pH of the solution on the electrochemical cell is indicated below the curve. (b) the calibration curve obtained from the potentiometric titration.

### 2.3.5 The Response Mechanism

The open circuit potential of an electrode coated by a conducting polymer layer can be expressed as the sum of two components\(^{18-20}\).

Firstly the redox potential that represents the process:

\[
\text{Poly}^+ + e^- = \text{Poly}
\]

Where ‘Poly\(^+\)’ and ‘Poly’ are the oxidized and the neutral form of the polymer respectively. The redox potential is influenced by pH as H\(^+\) ions as the redox chemistry of
1 (the benzenoid unit in scheme 2) involves both electron and proton transfer.\textsuperscript{21-22} It has been well established that for PANI and self–doped PANI, the redox potential shifted to more positive with increase in H\textsuperscript{+} concentration.\textsuperscript{22-24}

Scheme 2.2. Chemical structure of aniline- anthranilic acid copolymers showing benzenoid and quinoid units

Secondly, it is the membrane potential which is affected by ion exchange processes on the polymer solution interface. The membrane potential arises due to the differences in the distribution of protons in the polymeric membrane and the solution phases, which eventually leads to the formation of pH dependant Nernst phase – boundary potential.

\[
E = E' - \frac{RT}{F} \ln \frac{[H^+]_p}{[H^+]_s}
\]

(2.1)

Where, the subscripts p and s stands for the polymer and solution respectively and E’ represents the standard redox potential. From equation 1, it is clear that the phase boundary potential E increases with H\textsuperscript{+} ion concentration in the solution. Thus equation 1, predicts a positive shift of the open circuit potential with decreasing pH. Therefore the net effect of increasing H\textsuperscript{+} ion concentrations is to shift the open circuit potential more positive.
The reason of the higher sensitivity of the copolymer composite electrode in alkaline pH is not well understood yet. Tarver et al. reported that such a behavior in polymer doped PANI, stems from proton deficiencies in the alkaline environment and attributed the excess potential to the overpotential necessary to strip protons from alkaline buffer solution\textsuperscript{24}. However, in case of other composites such a response in alkaline pH is not observed. Therefore, a greater change in equilibrium potential at pH > 7 cannot be explained by considering solely the overpotential but could be due to the differences in the pKa for the imine protonation de-protonation equilibrium due to the intra-molecular interaction between COO\(^-\) groups and the cationic radical nitrogen atoms of PANI (Scheme 2.3)

\textbf{Scheme 2.3.} Structure of copolymer showing the intramolecular interaction between the carboxylic group and polaronic nitrogen atom.

\textbf{2.3.6. Potentiometric detection of paraoxon}

Organophosphate hydrolase (OPH),\textsuperscript{25} hydrolyzes an organophosphate molecule, the product of which can be monitored electrochemically or spectrophotometrically.\textsuperscript{26-27} The enzymes upon hydrolysis of an organophosphate releases two protons, which decrease the local pH in the environment (Scheme 4). Because organophosphate is a substrate for
OPH, this scheme leads to a direct determination of the analyte as the rate of signal generation is directly proportional to the concentrations of the organophosphate.

\[
\begin{align*}
\text{Scheme 2.4 Hydrolysis of paraoxon by OPH} \\
\end{align*}
\]

It has been reported that OPH has an optimum pH 8.5\textsuperscript{28-29}. An initial pH of 9.0 was chosen because the range of pH values between 7.5 and 9.0 was shown to be optimal for paraoxon hydrolysis by purified OPH.\textsuperscript{25} Also, it would be wiser to use a relatively basic buffer in the solution to provide the enzyme with an optimum microenvironment. So, we used the co-polymer /CNT composite pH sensor for the detection of paraoxon, an organophosphate. We immobilized OPH by simple physical adsorption on the surface of the composite electrode. Since the copolymer nanocomposite contains carboxylic groups in the polymer backbone, which may act as a matrix for immobilization of cationic species like proteins and enzymes, we expected the low molecular weight OPH to be adsorbed by self-doped polyaniline film from the enzyme solution. The sensor was soaked in 1mM CHES buffer and paraoxon was added successively.
Figure 2.4 (a) Potentiometric response of the OPH biosensor to the additions of nanomolar concentrations of paraoxon. (b) Calibration plots showing the absolute potential as a function of paraoxon concentrations. The error bars show the standard deviations of measurements taken from independent experiments with at least three distinct sensors. The inset in fig.b shows the linear portion of the calibration curve.

The potentiometric response of the biosensor to successive additions of paraoxon and the resulting calibration plots is presented in fig 2.4. A control experiment was carried out by successive addition of volume equivalent concentrations of 1mM CHES buffer. As expected, the successive addition of buffer using a pipette did not cause any significant change in OCP of the biosensor Fig 2.5, suggesting that the sensor is not affected by a simple mechanical disturbance during adding an analyte into the electrochemical cell. However, when paraoxon was injected, the sensor shows a rapid response as manifested by an increase in open circuit potential. The response time of the sensor usually did not exceed more than 1-2 minutes. The high sensitivity of the biosensor towards paraoxon additions can be explained by the change in pH in the local environment of the copolymer backbone. The enzymatic hydrolysis of paraoxon by OPH released protons, which decrease the pH of the system. The pH decrease was transduced to the open circuit potential change as the concentration of paraoxon increases.
Figure 2.5 (a) Potentiometric response of the OPH biosensor to the additions of 5, 15, 20, 25, 30 and 50 nM of paraoxon (black curve) and same volume equivalent of 1.0 mM CHES buffer solution (red). Arrows indicate additions of increasing concentrations of paraoxon or buffer. (b) The corresponding calibrations plots extracted from the curves in (a).

2.4 Conclusions

In summary, the pH sensitivity of PANI-based conducting polymer/CNT composites is tuned by co-polymerization with o-aminobenzoic acid. The resulting composite network electrode shows super-Nernstian and highly sensitive potentiometric pH response at alkaline pH (7.0 - 9.0) and a sub-Nernstian slope at pH 3-6. OPH is immobilized on the pH sensitive matrix and paraoxon is detected as a model organophosphate compound with very high sensitivity, fast response and the detection limit of 2nM. This highly sensitive potentiometric pH sensitive matrix might find the applications in both clinical and environmental settings. This approach is expected to be used for direct reagent-less detection of a wide range of compounds without the requirement of any time-consuming conjugation reactions. Also, this sensor concept might open up the possibility for miniaturization and integration using microelectronic fabrication technology to produce inexpensive chips for sensing in real time with a microliter volume of sample.
2.5 References


3.1 Introduction

The development of anion sensors for biologically important anions is an active area of investigation because of their indispensible roles in physiological process\(^1-2\). Among the anions, fluoride ions (F\(^-\)) are most attractive targets because of their considerable significance with respect to health and environmental issues. Main sources of fluoride include drinking water, toothpastes and osteoporosis drugs. Some other sources are UF\(_6\) and organophosphate nerve agents such as sarin and soman, which release fluoride anion upon hydrolysis. Fluoride is an essential ion for the body, but an inappropriate and unnecessary ingestion of this anion can cause several disorders such as fluorosis, urolithiasis or cancer\(^3\). The U.S. Environmental Protection Agency (EPA) gives an enforceable drinking water standard for fluoride of 4 part per million (ppm) (~200\(\mu\)M) to prevent osteofluorosis and a secondary fluoride standard of 2 ppm to protect against dental fluorosis. Therefore, an accurate determination of fluoride in drinking water is necessary not only to provide healthy water supply but also for tracking UF\(_6\) and organophosphate nerve agents introduced for warfare purpose.

A considerable research effort has been undertaken on the development of sensors for fluoride anions encompassing a range of host-guest strategies to bind the target analytes. Most commonly used methods for the quantitative determination of fluoride includes ion chromatography, solid state LaF\(_3\) based ion selective electrode, and fluorescence
chemosensors. Initial efforts focused on receptors that interact with the anionic guest via hydrogen bonds.\textsuperscript{4,5} Unfortunately, such receptors only function in organic solvents and are usually not compatible with water.\textsuperscript{6} Faced with these limitations, several groups have considered Lewis acidic receptors which covalently interact with the fluoride anion.\textsuperscript{7-10} Triarylboranes, for example, complex fluoride anions in organic solvents with binding constants typically in the $10^{-5}$-$10^{-6}$ M$^{-1}$ range.\textsuperscript{9-8} Unfortunately, the resulting anionic complexes dissociate in the presence of water, a process driven by the high hydration enthalpy (-504 kJ/mol)\textsuperscript{11} of the small fluoride anion. Moreover, sensors for biological applications and environmental monitoring as well as tracking fluoride in drinking water are required to function in neutral aqueous solutions.

One approach to overcome this problem is to increase the affinity of the F$^{-}$ binding center by coulombic effect. Kim\textsuperscript{11} et al. demonstrated that F$^{-}$ detection in water can be achieved by incorporating cationic groups and simultaneously increasing the hydrophobicity of the boron center. Using this approach they were able to detect F$^{-}$ in water as low as 4 ppm. However, the sensitivity is still below than FDA secondary fluoride standard. Therefore, it is important to develop highly sensitive, low cost, convenient and rapid fluoride detection sensors that can be employed in water.

Recently, carbon-based nanomaterials such as fullerene C$_{60}$, three dimensionally ordered macroporous (3DOM) carbon, single walled carbon nanotubes (SWNTs), and multiwalled carbon nanotubes (MWNTs) have been used as a solid-contact ion to electron transducer in the fabrication of ion selective electrodes\textsuperscript{12-15}. In a more recent report, Bobacka et al. demonstrated the application of carbon nanotubes composites as an ion to electron transducer.\textsuperscript{16} The electrode fabricated from the dispersions of carbon
nanotubes into an ion selective polymeric material demonstrated a more reproducible response than the pure polymer. However, all these works are focused on the development of cation selective potentiometric sensors. Development of anion sensors is more challenging due to their relatively larger sizes, high hydration enthalpies and their existence in a narrow pH range.\textsuperscript{17}

In this chapter, a new approach to sensing aqueous fluoride ions based on a single walled carbon nanotube-polythiophene nanocomposite is demonstrated. The aim of this chapter is two fold. In the first place, a generic approach to fabricating a nanocomposite of a single walled carbon nanotube-conjugated polymer with desired functionalities will be discussed. We used boron-modified polythiophene (PTBM) as a conjugated polymer to disperse and functionalize single walled carbon nanotube. Secondly, the synergistic properties of this nanocomposite, employed for the selective detection of fluoride anions in aqueous medium will be discussed. Fluoride ion as low as 0.5 µM, which is 10 times lower than the currently available fluoride sensors was easily detected. The application of this novel method to design various carbon nanomaterials- based sensors is extended to disperse and functionalize relatively new and promising material graphene to fabricate a fluoride ion sensor. This has the potential to achieve higher sensitivity, at a reduced cost and without the impurities associated with carbon nanotubes production. This simple and inexpensive approach to detect fluoride in water has the potential for the development of other CNT polymer based ion sensors as well.
3.2 Experimental

3.2.1 Reagents

Purified single walled-CNTs were purchased from Carbon Nanotechnologies, Inc. Houston, TX. Hydrochloric acid, potassium fluoride, tris (hydroxymethyl) aminomethane (Tris), chloroform, and graphite flakes with size > 20 µm were purchased from Aldrich Chemicals Inc., Milwaukee, WI. All these chemicals were used as received. Nanopure water (18.2 MΩ) (Barnstead), was used to clean the apparatus. The Au substrates were prepared by sputtering high-purity Au onto cleaned Si (100) wafers with a Ti adhesion layer (100 nm Au and 10 nm Ti). The resulting gold substrates were cleaned with freshly made piranha solution (98% H₂SO₄: 30% H₂O₂, 3:1 v/v, 90 °C) for 3 minutes (Caution: piranha solution should be handled with extreme care), and rinsed with water and ethanol.

3.2.2 Fabrication of SWNT/PTBM nanocomposite

PTBM was synthesized by Prof. Jäkle’s group (Rutgers, Newark) by a previously reported procedure\(^\text{18}\). Single walled carbon nanotube and PTBM were mixed in the ratio of (polymer SWNT = 0.65 w/w) in chloroform and sonicated for 30 minutes with Sonics VX-130 (130W, 65%) in an ice bath to obtain a PTBM/SWNT nanocomposite. The obtained dark dispersions were then centrifuged at 6000 rpm for 20 mins to remove bundled carbon nanotubes using a Beckman J2-21 centrifuge unit. The supernatant containing dispersed carbon nanotubes was dialyzed 3 times using PTFB (0.2µm) (Millipore) membranes in order to remove unbound polymers. The removal of free polymer was monitored by measuring UV-vis and emission spectra of the solutions after each dialysis. Then the dispersed nanocomposite was characterized by UV-Vis NIR
spectroscopy, fluorescence spectroscopy and Raman spectroscopy. All fluorescence measurements were performed using a Cary-Eclipse fluorescence spectrophotometer (Varian, Inc, Palo Alto, CA) and UV-Vis NIR measurements were performed using a Cary 500 UV-Visible spectrophotometer. Raman spectra were obtained by a Kaiser Optical Systems Raman Microprobe with a 785 nm solid state diode laser on the films obtained by drop casting on gold surface with 100 nm gold layer. Pristine carbon nanotube samples were prepared from the dispersions of SWNT by 0.2 wt % Sodium dodecyl sulfate (SDS). Free SDS was removed by washing the film 5 times with deionized water before being subjected to measurement. Spectra were acquired using a 30 s exposure time and four accumulations. The total concentration of polymer in the solution were estimated to be 7.7 µM from the differences between the concentrations of starting polymer and the separated polymer after SWNT dispersions and dialysis, monitored by UV-vis spectra.

3.2.3 Atomic force microscopy (AFM) and Transmission electron microscopy (TEM)

AFM images were obtained using a Nanoscope IIIa instrument (Digital Instruments, Santa Barbara, CA) in tapping mode operating in ambient air. A 125 um long rectangular silicon cantilever/tip assembly was used with a spring constant of 40N/M, resonance frequency of 315-352 kHz, and tip radius of 5-10 nm. The images were generated by the change in amplitude of the free oscillation of the cantilever as it interacted with the sample. The height differences on the surface are indicated by the color; lighter regions indicate higher regions. Transmission Electron Microscopy (TEM) images were recorded using a JEOL 2010F FEG transmission image microscope at an accelerating voltage of
80 kV. The TEM samples were prepared by drying a droplet of the dispersed suspension on a lacey carbon grid.

3.2.4 Fabrication of potentiometric sensor

The potentiometric sensor was fabricated by drop casting the above synthesized PTBM/SWNT nanocomposite on a gold electrode. The electrode was dried under vacuum for one hour. After stabilization in 10 µM tris-HCl buffer, the sensor performance was evaluated by monitoring the open circuit potential change with fluoride concentration. Open circuit potential (OCP) measurements were conducted using a homemade Teflon cell (Area = 0.25 cm$^2$) containing 100 µL of 10 mM tris buffer solution (pH 8.0) with the PTBM/SWNT nanocomposite modified gold substrate as the working electrode, a platinum wire as a counter electrode, and a Ag wire as a quasi-reference electrode. (The quasi-reference electrode was calibrated against the more widely used Ag/AgCl/saturated KCl reference, and all the potentials quoted in this work are in terms of the Ag/AgCl scale). The pH of tris-HCl buffer was adjusted by HCl. All the pH measurements were carried out using a Fisher AB15 pH meter calibrated with commercial available standard buffer solutions. A CHI 760 C potentiostat (CH Instruments) was used for all electrochemical measurements.

3.3 Results and Discussion

3.3.1 Fabrication of PTBM-SWNT nanocomposite

The hybrid nanocomposite is fabricated as shown in scheme 1 by mixing the PTBM and SWNT in chloroform. The solubility of PTBM/SWNT hybrid in chloroform was observed by visual inspection (fig 1). The color of the PTBM solution in chloroform changed from yellow to brown (fig 1.b) immediately after the SWNT is added because of
the superposition of the optical absorptions of PTBM and SWNTs. The solution color gradually intensifies during the sonication process and, the resultant dark brown solution (fig 1c) is stable for weeks without any precipitation, indicating the uniform dispersions of CNT with the aid of sonication results in a stable solution via non-covalent interactions between CNTs and PTBM. This result is consistent with the solubilization effect of other conjugated polymers.\textsuperscript{19-22}

The solubilization of SWNT can be realized through the following mechanism: the polymer chains are attracted to the CNT shells due to strong electronic interaction between the aromatic units and the CNT surface and the affinity of the polymer chains with the solvent molecule bring the polymer-wrapped or coated CNTs into the liquid media leading to the dissolution of CNTs into chloroform. (Scheme 1)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Scheme 3.1. Schematic of the preparation of PTBM/SWNT nanocomposites}
\end{figure}
3.3.2 Characterizations of Nanocomposite

3.3.2.1 UV-Vis NIR and Fluorescence Spectroscopy

UV-Vis and NIR absorption spectra of PTBM and SWNT-PTBM were compared in fig 3.2a. The absorption spectra of the PTBM/SWNT hybrid solution in chloroform reveal several important features of both PTBM and SWNT. Since the background increases with the increase in SWNT concentration due to the scattering effect of the nanotubes in solution, it is difficult to observe the polymer peaks and the de-bundled carbon nanotube peaks in the same spectrum. In order to take a closer look, UV-Vis-NIR spectrum of the nanocomposite with higher concentrations of carbon nanotube (160 mg/L) was recorded and shown in fig 3.2b. The sharp peaks in the spectrum are due to dispersed and non-bundled SWNTs. These observed peaks are almost the same as those previously reported for surfactant- and DNA-wrapped individual HiPco tubes.
originating from M11, S22, and S11 transitions, indicates the presence of dispersed carbon nanotubes in chloroform by the PTBM.

In UV-Vis spectrum two major absorption bands were observed for PTBM with $\lambda_{\text{max}}$ values of 342 and 438 nm. As compared to pure PTBM, these peaks are blue shifted (by 5-7 nm) with relatively broad absorption peaks in the nanocomposite. It has been established that the interaction between conjugated polymers and CNT take place via polymer wrapping around the CNTs or parallel adhesion of the polymer main chains to the nanotube surfaces. Such $\pi-\pi$ interactions between conjugated polymer and CNTs usually result in band shift or broadening of polymer characteristic absorption peaks due to the change of the effective conjugation length of the conjugated polymer in the presence of nanotubes.$^{20}$
Figure 3.2 (a) and (b) UV-Vis and NIR spectra of PTBM and SWNT/PTBM nanocomposite, (c) UV-Vis spectra of pure PTBM and composite after subtraction of pristine SWNT spectra (d) Fluorescence spectra of PTBM and SWNT/PTBM nanocomposite. The concentration of SWNT in the spectra a, c and d is 70 mg/L and in spectra b is 160 mg/L.

To further confirm, this peak broadening results due to the interaction between PTBM and SWNT, a corrected spectrum for the composite was obtained after subtraction of pristine SWNT spectra and the result is compared with pure PTBM (fig 3.2c). From fig 3.2c, it can be observed that the polymer peaks broadened. The characteristic absorption peaks at 342 nm and 438 nm arising from PTBM are broadened in the spectra of the nanocomposite compared with the spectrum of pure PTBM (fig. 3.2a and 3.2c), consistent with the π-π interaction between the PTBM and SWNT in the nanocomposite.
An additional proof for SWNT PTBM interaction came from emission experiments, which show more than 90% quenching of PTBM fluorescence (fig 3.2d). This fluorescence quenching clearly indicates a strong molecular interaction between PTBM and SWNTs in the nanocomposite.

**3.3.2.2 Raman Spectroscopy**

Raman spectroscopy is a powerful non-destructive tool to study CNT composites to provide unique information about vibrational and electronic properties, and to determine structure. Raman spectroscopy has been used to investigate the interaction between polymers and nanotubes in CNT composites.\(^{26-27}\) In general, a peak shift or a change of a peak width in Raman spectra is observed if there is an interaction between nanotubes and polymer due to the change in the electronic effect. As shown in fig 3.3b, the tangential vibration band (G band) of SWNTs shifts to higher frequency from 1591 to 1596 cm\(^{-1}\) after dispersion with PTBM, while the radial breathing mode (RBM) shifts from 235 cm\(^{-1}\) to 239.0 cm\(^{-1}\). Previous studies showed that the G band and RBM band will shift to higher frequency when SWNTs lose electrons\(^{27}\). The observed band shifts here also suggest that a molecular level interaction occurred between CNTs and PTBM which is consistent with above fluorescence quenching experiment.
3.3.2.3 Transmission Electron Microscopy (TEM) and Atomic Force Microscopy

The dispersions of SWNT and a deposition of PTBM on SWNT surface were examined by AFM and TEM (fig 3.4). A high resolution TEM image of PTBM dispersed SWNT shown in fig 3.4a reveals the presence of a thin layer of amorphous coating of PTBM on the wall of SWNT. A closer look in AFM image (fig3.4b) demonstrates that the SWNTs are not fully coated with PTBM. However, most of them were separated. It is likely that the interaction between PTBM and SWNT via π- stacking overcomes the van der Waals interaction between CNTs, resulting in de-bundling of the CNTs. Thus the SWNTs dispersed by PTBM in chloroform solution exist in very small bundles or even as isolated tubes.

**Figure 3.3** Raman spectra of pristine SWNT and PTBM/SWNT showing, (a) RBM and (b) G-band peaks.
3.3.3 Potentiometric detection of fluoride in aqueous medium

Carbon nanotubes possess extraordinary capability to promote electron transfer between heterogeneous phases due to the presence of mobile electrons on their surfaces. Because of their poor solubility in most of the solvents, the fabrication of CNT based sensors usually involves the dispersions of CNTs with the aid of surfactants or chemical modification on CNT structures. Both of these methods are complicated and introduce unnecessary interferences while used for sensor applications. In this work, for the first time we investigated the compatibility of SWNTs with tri coordinate organoborane polymer (fluoride ion sensing material) in aqueous solution. Fig 3.5a shows a typical potentiometric response of the sensor when different concentrations of fluoride added. As shown in fig.3.5a the open circuit potential of the sensor decreased with increase in fluoride concentration.
Figure 3.5(a) Potentiometric response upon aqueous KF additions to 10mM tris-HCl buffer (pH 8.0) on PTBM/SWNT nanocomposite modified Au electrode. The successive concentrations shown on top of the potentiometric curve are µM of F\textsuperscript{-}, (b) calibration curve resulting from the response of the sensor. The error bars show the standard deviations of measurements taken from independent experiments with at least three distinct sensors. The linear portion of the calibration curve is shown in inset.

A calibration plot obtained from three different sensors is shown in fig 3.5b. From fig 3.5b (inset) it is clear that the sensor shows a linear relationship between the open circuit potential change (ΔE) with F\textsuperscript{-} concentration in the range of 0.5 µM to 10 µM. A control experiment was conducted by adding equal volumes of tris-HCl buffer solution instead of F\textsuperscript{-} anion solution. As expected, the sensor does not show any response to buffer (fig 3.6A). This result confirms that the changes in the open circuit potential were induced by the nanocomposite-fluoride complexation and not to any mechanical or dilution effect.
**Figure 3.6** (A) Potentiometric response of PTBM/SWNT modified electrode towards (a) F\textsuperscript{-} and (b) tris-HCl buffer. The arrows show the addition of F\textsuperscript{-} and same volume of tris-HCl buffer as a control. (B) A comparison of the potentiometric response of (a) PTBM/SWNT and (b) PTBM modified electrode towards same concentrations of aqueous F\textsuperscript{-} ion and (C) Potentiometric response of pristine SWNT modified electrode towards F\textsuperscript{-} ion. (the astrik * in fig (B) and (C) shows a total concentration of 10mM aqueous F\textsuperscript{-} in the electrochemical cell)

### 3.3.5 Mechanism of potentiometric response

A possible mechanism for the potentiometric response for PTBM/SWNT composite electrode towards F\textsuperscript{-} ion is depicted in scheme 2. Like other conducting polymer-based potentiometric sensors, the potentiometric ion sensitivity of PTBM membrane can be hypothesized as the dependence of open circuit potential at equilibrium in the phase boundary (membrane) potential which originated as a result of interfacial ion transfer and complexation of anion with the polymer binding sites. The open circuit potential E can be described by the equation\textsuperscript{28-29}.

$$E = E^0 + \frac{RT}{F} \ln \left[ \frac{[poly]^\dagger}{[poly]} \right] + \Delta \varphi$$  \hspace{1cm} (1)

where $E^0$ is the formal potential of the polymer, $[poly]^\dagger$ and $[poly]$ are the oxidized and reduced state of the polymer $\Delta \varphi$ is the membrane potential related to the concentration of the electrolyte ‘c’ and ionic binding site ‘X’ as:
\[
\Delta \varphi = \pm \frac{RT}{F} \ln \left[ \frac{X}{2c} + \left(1 + \left(\frac{X}{2c}\right)^2\right)^{1/2} \right]
\]

In equation 2, the + sign holds for the anion binding site and – denotes for cationic binding sites. In this case, assuming that the polymer oxidation state remains constant throughout the measurements, when \( F^- \) binds to the polymer binding site (boron atom), the concentration of \( X \) decreased and thus the open circuit potential decreased with increased \( F^- \) ion concentrations. From equation 1, a potential drift should be observed if the oxidation state of the polymer is altered by side reactions such as charging / discharging of the membrane or oxidation due to dissolved oxygen and water layer formed at the membrane-electrode interface. However, such spontaneous reactions are relatively slow compared to interfacial ion transfer and complexation process. Moreover, due to the hydrophobic nature of SWNT, the influence such process are hindered in the absence of water layer at the interface.\(^{14}\)

### 3.3.6 Synergistic effect of PTBM/SWNT nanocomposite in \( F^- \) detection

The synergistic effect of PTBM/SWNT nanocomposite is clearly exhibited, when a potentiometric response of the sensor based on PTBM/SWNT nanocomposite was compared to that fabricated with pure PTBM and pristine SWNT modified electrodes. Figure 3.6 shows the open circuit potential (OCP) changes as a function of fluoride ion concentration by all three different sensors. In contrast to the sensor prepared from PTBM/SWNT nanocomposite, pure PTBM modified sensor shows only an obvious OCP change (~ 40 mV) at higher concentration of fluoride (10mM), not any significant change in the OCP with lower concentrations of fluoride is observed. In case of the sensor prepared with pristine SWNT, the OCP increased slightly with each addition of \( F^- \) ion. However, no trend in OCP increased was observed with \( F^- \) ion concentrations and only ~
15 mV of OCP increased with 10 mM F\textsuperscript{−}. These results clearly demonstrated that the higher sensitivity of the PTBM/SWNT composite sensor as compared to its component materials based sensors is due to the synergistic effect of SWNT and PTBM.

The synergistic effect of the nanocomposite is also manifested by the nanocomposite in the fluorescence spectra upon addition of aqueous F\textsuperscript{−} in the optical sensors fabricated from the composite or PTBM by spin coating on a quartz substrate, PTBM is an emissive polymer with emission maxima at ~614 nm in chloroform solution. In dispersions with SWNT the fluorescence of PTBM is quenched. Spin coated films containing only PTBM prepared in the same fashion as the sensor display an emission maxima at 615 nm. Upon addition of aqueous F\textsuperscript{−} ion on the sensor, the fluorescence signal of PTBM nanocomposite which was initially quenched due to strong interactions between SWNT and PTBM, is enhanced with F\textsuperscript{−} ion concentration, with an emission peak at (~580 nm), which is similar to that of the pure PTBM when titrated with F\textsuperscript{−} in organic solvents.

**Figure 3.7** Emission (\(\lambda = 438\) nm) of (a) PTBM/SWNT and (b) PTBM film on quartz substrate before and after exposure to 200 µM aqueous F\textsuperscript{−}.
In contrast to this, the original fluorescence signal of a PTBM thin film on quartz is diminished upon aqueous fluoride addition (fig 3.7b). This observation further demonstrates that the polymer bound to SWNT is still capable of interacting with $F^-$ and that quenching by SWNTs is attenuated. However, pure PTBM film without SWNT probably degraded due to hydrolysis. Therefore, $F^-$ detection in aqueous medium is not possible with pure PTBM as a sensing layer. Also, this result inspired us to further investigate the dual mode (optical and electrochemical) of aqueous $F^-$ ion detection by employing the PTBM/SWNT nanocomposite as a sensing layer.

**3.3.7 Investigation of optical/electrochemical detection mode**

To utilize SWNT/PTBM nanocomposite as an optical/electrochemical ion selective chemosensor for $F^-$, a transparent, conductive ITO coated glass was used as a conductive substrate. A thin film of composite material spin coated on ITO, was used to monitor the fluorescence before and after fluoride addition as well as potentiometric sensor. The experimental results shown in fig 3.8, are similar to the results observed above from separate experiments conducted for two separate samples for potentiometric and optical measurements.
Figure 3.8(a) Potentiometric response to aqueous F⁻ ion on PTBM/SWNT coated ITO, and (b) emission measurements before (red) and after (blue) F⁻ binding measured on the same electrode on (a).

Even though, the potentiometric sensitivity (fig 3.8a) is lower as compared to PTBM/SWNT coated gold electrode, which could be due to the higher resistance of ITO surface, a higher concentration (200 µM) of F⁻ caused a significant change in open circuit potential. Similar to the above results obtained on quartz substrate the fluorescence signal was enhanced upon fluoride binding and a fluorescence peak at ~ 580 nm is observed. (fig3. 8b) These observations help us to understand that both the optical and the electrochemical changes are induced by the fluoride binding with the nanocomposite and a proper design of a device will allow us to monitor both signals simultaneously.
**Figure 3.9** AFM image of PTBM/SWNT nanocomposite conductive network modified Au electrode used for F- detection.

**Scheme 3.2** Proposed schematic description of F- binding and ion to electron transduction process of the PTBM/SWNT nanocomposite modified electrode.

From the above discussions carbon nanotubes in the nanocomposites play a dual role to improve the sensor performance.
In the first place, carbon nanotubes are very hydrophobic, therefore there is no water layer formed at the interface between the CNTs and the polymer membrane, this causes a fast and stable response.\textsuperscript{14,30} The hydrophobic nature of the carbon nanotubes has been used to improve the hydrophobicity of various polymer materials.\textsuperscript{31-32} It is possible that the ion sensing membranes became more water repellent with the formation of nanotube network. These results are favorable in terms of elimination of undesirable water layer in solid-contact ion selective electrodes (ISEs). In case of pure PTBM, possibly a water layer is formed at the interface between the ion selective electrode and the electrode surface which could be the reason for possible degradation of the polymer membrane.

Secondly, carbon nanotubes function as ion-to-electron transducers. The transduction mechanism of the carbon nanotubes-based potentiometric electrodes is generally thought to rely on the formation of the CNT conductive network (fig 3.9) and its extreme sensitivity of the electrical properties to the change of the local environment. When PTBM/SWNT nanocomposite electrodes were used as a potentiometric fluoride sensor, \( F^- \) binds with electron deficient boron center and forms a charged complex (Scheme 2). These charge species in the membrane are in close contact to the SWNTs thus change the electrostatic properties of the carbon nanotube and thus there is a change in the phase boundary potential (eq.2) and the membrane potential change can modulate the carbon nanotube charge, so that ion to electron transduction occurred. This also explains the high sensitivity of PTBM/SWNT nanocomposite electrodes.

3.3.6 Stability of the PTBM/SWNT sensor

In order to study the stability of the sensor, the nanocomposite sensor was soaked in the working -buffer solution for 36 hours and open circuit measurements were carried out as
a function of fluoride concentrations. After 36 hrs the slope of the linear region in open circuit potential changes by ~5%. (fig 3.10)

Figure 3.10 Plot showing the aqueous F⁻ sensitivity of PTBM/SWNT sensor after 36 hrs of soaking in tris- HCl buffer (10mM; pH 8.0)

From above experimental results it is clear that PTBM/SWNT nanocomposite based fluoride detection platform is suitable to detect F⁻ ion in aqueous media at sub-micromolar range. However, a nanomolar or sub-nanomolar range of F⁻ detection is required for an early detection of neurotoxins to protect water resources and food supplies in the defense against terrorist activity, as well as to monitor the detoxification process. Therefore, a composite of PTBM with a hydrophobic, truly two dimensional transport system with exceptionally high electron mobility, higher surface area and low noise level carbon nanomaterial is more desirable, because higher sensitivity can be achieved. Hoping to validate this new hypothesis we synthesized PTBM-graphene nanocomposite and explored its potential application as F⁻ sensor.
3.4 Fabrication of PTBM - Graphene nanocomposite

Graphene is the basic building block for graphitic materials in all dimensions 0-D fullerene, 1-D carbon nanotube and 3-D graphite.\textsuperscript{33} Studying graphene is expected to provide a fundamental insight into all carbon materials. In comparison with carbon nanotubes, graphene exhibits advantages of low cost, high surface area, ease of processing and safety.\textsuperscript{34} Graphene is expected to compete with carbon nanotubes in many aspects. An excellent electron transfer ability of graphene is already demonstrated as superior in terms of electrocatalytic activity and macroscopic conductivity.\textsuperscript{35-36} In spite of all these advantages, functionalized graphene has never been employed as ion to electron transducer before. In this part, we used our above developed approach to functionalize graphene by PTBM and used PTBM graphene nanocomposite for fluoride detection.

The dispersion of graphene is confirmed by UV-Vis spectroscopy and the interaction was characterized by fluorescence spectroscopy. As shown in fig 3.11a, a typical graphene absorption band at 264 nm as previously observed for DNA stabilized graphene,\textsuperscript{37} was observed and the PTBM absorption bands were broadened, consistent with formation of PTBM/SWNT. Also ~90\% of the emission due to polymer was quenched when the polymer interacts with graphene, indication a strong interaction between the two components. A potentiometric sensor fabricated by drop coating of PTBM-graphene demonstrated a decrease in OCP with fluoride anion which is similar to PTBM/SWNT modified electrode. However, as compared to CNT nanocomposites, graphene nanocomposites have less sensitivity but a broad detection range (fig 3.12). However, further optimization of the experimental conditions for graphene PTBM are required to improve the sensitivity.
Figure 3.11 (a) UV-Vis, and (b) fluorescence spectra of PTBM and PTBM-G in chloroform, and (c) optical photographs of PTBM and PTBM-G in chloroform solution.
Figure 3.12 (a) Potentiometric response of F\(^{-}\) additions on PTBM-G nanocomposite electrode. The successive concentrations shown on the right of the curve are mg/L of F\(^{-}\), (b) the calibration curve obtained from a.

3.5 Conclusions

In summary, a facile method for the fabrication of potentiometric F\(^{-}\) sensor is demonstrated. With tri-coordinate boron functionalized conjugated polymer as a dispersant SWNT can be successfully dispersed and produce sensing membrane in different substrates. The synergistic properties of PTBM/SWNT nanocomposite such as excellent ion-electron transducing capability, hydrophobic property of SWNT and active fluoride binding sites in PTBM demonstrated excellent sensing properties including higher sensitivity, fast response time and stability. Experimental results suggest that this approach may yield anion sensors potentially useful for sensing of anions in the presence of water and electrolytes. An immediate extension of this novel approach is demonstrated to fabricate relatively inexpensive graphene based sensor. The excellent potential stability, general compatibility, ease of fabrication and low costs of these nanocomposites can find a wide range of application for the development of more useful electrochemical
nanosensors, CHEMFETs and BIOFETs for tracking UF₆ and organophosphate nerve agents, which release fluoride anion upon hydrolysis.

3.6 References


Chapter 4 Enhanced electrocatalytic Reduction of Oxygen using In-situ Electrochemical Polymerization of PEDOT CNT/ Composites

4.1 Introduction

Fuel cells are promising alternative energy devices that convert the chemical energy of a fuel directly into electricity without combustion. The advantages of fuel cells rely on their higher fuel efficiencies, fuel flexibilities, non-polluting and simple in designs. Oxygen (O\textsubscript{2}), either pure or as a component of air, is the oxidant used in the cathode compartment of a fuel cell, because it is readily available, a good oxidant and its reduction product (water) is harmless. In addition, oxygen reduction reaction (ORR) is also the most important reaction in life processes such as biological respiration, and several other industrial processes such as corrosion and secondary metal-air batteries.\textsuperscript{1-2} In general, the ORR kinetics is very slow. In order to speed up the kinetics to reach a practical usable level in a fuel cell or metal air batteries, an efficient electrode or supporting catalyst is needed. Such electrodes are usually platinum nanoparticles, embedded in a porous carbon electrode (Pt-C). However, Pt-based electrodes are not stable due to particle agglomeration and deactivation by carbon monoxide that comes from either in air supplies or as a by-product of methanol oxidation in a direct methanol fuel cell. Furthermore, the cost of the platinum catalysts is very high, together with its limited reserves in nature. Therefore, large-scale practical applications of fuel cells would be difficult to realize if the expensive platinum-based electrocatalysts for oxygen reduction reaction (ORR) cannot be replaced by efficient, low-cost, and stable electrodes.
Recent research efforts in reducing/replacing expensive platinum-based electrode in fuel cells have led to the developments of some new ORR electrocatalysts. Among them, PEDOT, has exhibited high electrocatalytic activity, excellent long-term stability, and resistance to crossover effects for the ORR. These properties were superior to those observed for other conducting polymer based electrocatalysts and the commercially available Pt-C catalyst.

Using vapor phase polymerization method to deposit PEDOT onto a nonconductive Goretex membrane pre-coated by a layer of Au as electrodes, Winther-Jensen et al demonstrated tremendous capability of PEDOT to catalytically reduce oxygen, which shows great potential to replace Pt based electrodes in fuel cells and metal/air batteries. However, the maximum current density observed needed an extremely high overpotential (-0.9 V vs. SCE), which largely decreased the output voltage.

Even though, the maximum current density observed at room temperature (6mA/cm²) by Winther-Jensen et al. was sufficient for some metal/air batteries, a higher current density for fuel cell applications of the PEDOT electrocatalyst concept would require extension of the three phase interface into a much thicker three dimensional highly porous and conductive structure, which is hard to achieve by using the nonconductive Goretex membrane reported. The conductivity of PEDOT decreases dramatically with its thickness, and consequently the efficiency for O₂ reduction. Even though multiple layer deposition could increase the conductivity of the PEDOT layer, the ionic conductivity of PEDOT and O₂ transport into the inner layer of PEDOT will be limited.

The mechanism of the efficient electrocatalytic capability was ascribed to the unique electrochemical behavior of the PEDOT. PEDOT, which naturally rests in its oxidized
form, can be momentarily reduced by the action of the electrochemical cell, which is different from traditional solution phase produced PEDOT. Oxygen molecules absorb on the reduced PEDOT surface and rapidly re-oxidize the PEDOT to its preferred oxidized state. Oxygen itself is reduced in the process. Therefore, to develop more efficient PEDOT based fuel cell cathode catalyst, an improved facile redox activity of PEDOT would be beneficial.

Inspired by the remarkable electronic and superior mechanical properties of carbon nanotubes (CNTs), conducting polymer and CNT composites have been fabricated to increase the conductivity and redox activity of such polymers. Fabrication of PEDOT/CNT composites has been reported and high conductivity was observed compared to PEDOT alone, even though the mechanism of the enhanced conductivity is still a hot debate. Most of the composites of PEDOT were fabricated as flexible transparent conductive materials that can be used to replace ITO glass in solar cell and light emitting diode (LED) related researches and super capacitors. Recently, it has been exploited as cathode materials to replace Pt/C nanoparticle based cathode to electrocatalytically reduce I$_3^-$ in solar cell applications. Exploitation of PEDOT/CNT composites for electrocatalytic reduction of O$_2$ for fuel cell applications has not been reported. Composite materials of carbon or carbon nanotube with conducting polymers such as PPY or PANI have been reported for the ORR, but electrocatalytic ability of carbon nanotube PEDOT nanocomposite for oxygen reduction is still a new area to explore. Therefore, this chapter aims to develop an electrochemically synthesized PEDOT/CNT nanocomposite material with improved redox activity and high electronic
and ionic conductivity to reduce oxygen at lower overpotential to obtain maximum output voltage.

4.2. Experimental

4.2.1. Materials
All chemicals except EDOT were used without further purification. 3, 4-Ethylendioxythiophene (EDOT), lithium perchlorate (LiClO₄) were purchased from Sigma-Aldrich Co. Purified HiPco single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. Houston, TX. Single-stranded DNA with sequence d (T)₃₀ was purchased from Integrated DNA Technologies, Inc. Coralville. EDOT was distilled prior to use and stored below 8 °C. All solutions were prepared using deionized water (18.2 MΩ) (Nanopure water, Barnstead), which was also used to rinse and clean.

4.2.2. Preparation of Electrodes
The glassy carbon electrode (GCE) was polished with a 0.05 µm Al₂O₃ particle suspension on a moistened polishing cloth in a “figure eight” pattern for four minutes to mirror finish. The polished electrode was rinsed with nanopure water, sonicated in Branson 2510 ultrasonic cleaner for four minutes in nanopure water to remove adhered alumina powder, and it was rinsed well again and then dried at room temperature in air for 20 minutes before use. A CNT network on the electrode surface was prepared by drop casting 4 µL of ss-DNA dispersed SWNT on the cleaned electrode area and dried under vacuum for 2 hrs.

Aqueous solution of single stranded DNA dispersed carbon nanotubes (ss-DNA/SWNT) were prepared by following the previous method.₁²
4.2.4. **Electrochemical Measurements**

All the electrochemical investigations, including electrochemical polymerization of EDOT, electrochemical characterization of the resulting films were carried out at a CH Instrument 750 series electrochemical station. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted using a glass beaker cell with the modified GCE as the working electrode, a platinum wire as a counter electrode, and a Ag/AgCl (sat.KCl) as a reference electrode. All the potentials quoted in this work are in terms of the Ag/AgCl (sat. KCl) scale.

4.2.5. **Electropolymerization of EDOT**

The polymerization of EDOT was carried out by a cyclic potential-scanning method under the following electrolytic conditions: working electrode, GCE (Bioanalytical lab; area = 0.070 cm²), counter electrode; platinum wire; reference electrode, Ag/AgCl (sat. KCl) electrochemical cell, undivided glass beaker cell; temperature, 25±2ºC; potential scanning range, -0.45 to +0.8 V vs. Ag/AgCl; scanning rate, 100 mV s⁻¹; EDOT monomer, 0.05 M; electrolytes, 0.1 M lithium perchlorate (LiClO₄), in deionized water. PEDOT/CNT composite was fabricated on the GCE surface as follows: 4 µL of ss-DNA dispersed SWNT solution was casted on cleaned GCE and allowed to vacuum dry at room temperature to form an SWNT film. 0.5 M of EDOT was prepared in an aqueous solution containing 0.1 M of LiClO₄ supporting electrolyte in glass beaker cell in a cooling bath and the mixture was sonicated for 60 seconds in a Sonics VX-130 (130W, 30%). PEDOT was then deposited onto the electrode by sweeping the electrochemical potential from -0.45 to 0.80 V (vs Ag/AgCl). After the second cycle, the polymerization potential was decreased to 0.75 V to further reduce the possibility of over-oxidizing the
polymer backbone. Repeated cycling of the potential resulted in continuous deposition of PEDOT onto the electrode surface. The resulting dark blue PEDOT /SWNT composite on the electrode was first washed with acetonitrile and then thoroughly with deionized water to remove free monomer. The composite modified electrode was then characterized in a monomer free electrolyte solution. For control study, pure PEDOT was electrochemically synthesized using the above condition without SWNTs.

4.2.6 Electrochemical characterizations of the nanocomposite

The composite films were characterized by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). A solution of 0.1 M (LiClO$_4$) was used as an electrolyte in a three electrode cell. Cyclic voltammetry was performed in a three-electrode configuration with the polymer composite modified GCE as a working electrode, a Pt wire as a counter electrode and Ag/AgCl (sat. KCl) as reference electrode. A scan rate of 100 mV/s was used and the potential on the working electrode was swept from -0.4 V to -0.65 V. Before each CV was recorded, several cycles were swept to ensure that the conducting polymer nanocomposite had reached a stable state. Electrochemical impedance spectra at different dc potentials were recorded over the frequency range of 1-10$^5$ Hz by applying an AC sinusoidal signal of 10 mV in amplitude. Ionic conductivity, redox capacitance and charge transfer resistances under different potentials were determined from electrochemical impedance spectra.

Tapping mode Atomic force microscopy (AFM) was performed on NanoscopeIIIa atomic force microscope (Veeco instrument, Santa Barbara, CA, USA) in air on the sample polymerized on Au surface with an Au layer of 100 nm as a substrate. During imaging, a 125 µm long rectangular silicon cantilever/tip assembly (Model: MPP-12100, Veeco)
was used with a resonance frequency of approximately 127-170 kHz, a spring constant of approximately 5 N/m, and a tip radius of less than 10 nm.

### 4.2.7 X-Ray Photoelectron Spectroscopy (XPS)

Valence band spectra were extracted from XPS spectra taken with a Perkin-Elmer hemispherical analyzer with a non-monochromatic Mg Kα x-ray source (hν =1253.6 eV). At 17.9 eV pass energy, the full width at half maximum (FWHM) of the Cu 2p 3/2 core level is 1.2 eV. All core level photoemission peaks were referenced to the Au 4f 7/2 peak with a binding energy of 84.0 eV. Corrections due to charging effects were taken care of by using C(1s) as an internal reference and the Fermi edge of a gold sample.

### 4.2.8 Investigation of electrocatalytic activity to oxygen reduction

Cyclic voltammetry and amperometry were used to investigate the electrocatalytic activity of the polymer nanocomposite electrode. The electrolyte solution LiClO$_4$, was purged with pure argon for 25 minutes to remove the gaseous oxygen from the polymer nanocomposite pores as well as the dissolved oxygen in the electrolytes solution. Then cyclic voltammetry was run in the potential range from -0.8 V to 0.0 V to confirm that there is no oxygen remaining. The baseline was obtained by sweeping from -0.8 V to 0.0 V at 10 mV/S in the argon sparged solution. Then the electrolyte solution was saturated with O$_2$ until the consecutive CVs matched and recorded as a oxygen reduction CV. Amperometric spectra were recorded at -0.4 V in 0.1 M LiClO$_4$ as supporting electrolyte solution alternately purged with O$_2$ and Ar gas. The oxygen reduction peak currents in the CVs were measured. In addition, the amperometric O$_2$ reduction current, which is the current difference between the O$_2$ and Ar saturated states in the amperometric spectrum was recorded.
4.3. Results and Discussion

4.3.1 Electrochemical polymerization of EDOT in aqueous medium

Polymerization of EDOT monomer in water is limited due to its lower solubility in water. Several works have been published about the aqueous polymerization of EDOT using some surfactants\textsuperscript{14-15} and polyanions\textsuperscript{16} such as PSS to increase the solubility of EDOT in water and hence made aqueous polymerization possible. However, such surfactants or the polyelectrolytes are difficult to remove from the reaction mixtures thus may alter the electronic properties of the resulted PEDOT. To fabricate SWNT/PEDOT composites which can synergistically combine the merit from both of the components, we first modify a GC electrode with a thin layer of ss-DNA/SWNTs. PEDOT was then deposited onto the modified GC electrode using a slightly modified novel acoustic assisted electrochemical polymerization approach which developed by Asami et al.\textsuperscript{17} Briefly, 0.05 M 3,4-ethylenedioxythiophene (EDOT) monomer in 0.1 M lithium perchlorate (LiClO\textsubscript{4}) in deionized water, was ultrasonicated for 30 min. It was reported that ultrasonic irradiation provides stable emulsions without the need for surfactants simply by mechanical forces which arise at the liquid/liquid phase boundaries. During sonication, EDOT nanoemulsions were formed. Furthermore, due to the relatively higher solubility of LiClO\textsubscript{4} in organic media, it enters inside the EDOT nanoemulsions formed during ultrasonic treatments, and contribute the formation of an electrical double layer inside the nanoemulsions, which in turn facilities the polymerization process. Then PEDOT was polymerized by sweeping the electrochemical potential from -0.45 to +0.8 V (versus Ag/AgCl). This potential is much lower than reported by Asami et al possibly due to the reduced monomer concentrations we used, as the higher amount of EDOT would yield larger droplets during emulsification which requires higher potential to oxidize.
Fig. 4.1a displays the CVs recorded for 13 cycles during the electrochemical polymerization of a solution consisting of EDOT in GC electrodes modified with ss-DNA/SWNT. For comparison, the CVs recorded for the electropolymerization of EDOT without CNTs are shown in fig1b. It can be clearly seen that all CVs showed increased polymer oxidation–reduction peaks with cycles showed similar characteristics other inherently conducting polymers, indicating that the polymerization proceeds easily. The redox characteristic of CVs representing the growth of polymer film on GC electrode with and without CNTs from the monomer solution were compared to obtain information about the deposition of PEDOT on SWNT modified electrodes and shown in fig 4.1.

To clearly read the initial potentials for the polymerization and compare the polymerization current, we illustrate the first cycles for the electrodes with different modifications in Figure 1c. The large irreversible anodic peak observed in the first cycle belongs to the polymerization of EDOT. The CV curve shows an oxidation current starting at ~0.59 V, much lower than that of the polymerization without ss-DNA/SWNT modification, in which the polymerization starts at ~0.73 V. The large negative shift (~140 mV) of the initial polymerization potential (indicated by the arrows in Figure 1c) indicates that the monomer polymerized more readily on the ss-DNA/SWNTs-modified electrode. The maximum current for the polymerization was ten times higher in the presence of ss-DNA/SWNTs, providing further support on this point (Figure 1d).

In subsequent cycles, one pair of broad peaks appeared (Figure 1a and 1b), which corresponds to the redox reactions of the PEDOT backbone. Figure 1e displayed the CV curves for the last (13th) cycles, which clearly shows that the amount of PEDOT deposited on the ss-DNA/SWNTs modified electrodes was significantly larger than the
electrode without ss-DNA/SWNTs modification. Figure 1e shows the current (the 
Faradaic current at ~0.17 V, for the transformation from EDOT to PEDOT as a function 
of the CV cycle numbers for each of the electrodes with and with CNT modifications. At 
the ss-DNA/SWNT modified electrodes, the PEDOT current increased during all cycles, 
with a slower increase rate after the 3rd cycle. From the slopes of the current vs. cycle 
numbers in Figure 1e, we can estimate the current increase speed ~23 µA/cycle which is 
~25 times faster than that at the electrode without ss-DNA/SWNT. After three cycles, the 
current increase rate lowered to ~6 µA per cycle, but it was still ~9 times higher than that 
at the electrode without ss-DNA/ SWNTs, where the rate remained 0.7 µA per cycle 
throughout.

**Figure 4.1** Typical cyclic voltammograms of the electrochemical polymerization of 
PEDOT on (a) ss-DNA SWNT modified GCE and (b) bare GCE. Cyclic voltamgram 
comparing the (c) first and (d) 13th cycles of polymerization and, (e) polymer growth 
curves extracted from a and b.
This improvement in the electrosynthesis of conducting polymer with ss-DNA/SWNT has already observed and stated as a template effect of the carbon nanotubes due to the negatively charged phosphate groups present in the ss-DNA/SWNT and hydrophobic graphene regions both present in the ss-DNA SWNT. In case of EDOT polymerization, the negatively charged groups in the surface of the carbon nanotubes strongly interacts with EDOT$^+$ cation radical forms a pseudo complex (scheme 1) and results in the decrease in the redox potential of EDOT similar as in the case of anionic surfactant.

![Scheme 4.1](image)

**Scheme 4.1.** Schematic illustration of the formation of a ss-DNA/SWNT/PEDOT nanocomposite during electrochemical polymerization.

4.3.2 Characterizations of PEDOT nanocomposites

4.3.2.1 Cyclic voltammetry and electrochemical impedance spectroscopy

The electrochemical behavior of the PEDOT and ss-DNA/SWNT/PEDOT (which will be represented as SWNT/PEDOT from now on) composite deposited was studied with cyclic voltammetry (CV) and AC impedance spectroscopy (Figure 2). Cyclic
voltammograms recorded at GC-PEDOT and GC-ss-DNA/SWNT/PEDOT electrodes are shown in fig 2a. Similar to the literature, both the SWNT/PEDOT composite and PEDOT exhibited pseudo-capacitive behaviors due to the electrochemical redox capability of PEDOT. In this potential range, however, the capacitive current obtained at GC/ss-DNA/SWNT/PEDOT electrode is ca.~10 times higher than that at GC/PEDOT electrode. Since, the current measured by CV contains both Faradaic and non-Faradaic charging current it is still not conclusive that the electrochemical redox activity of PEDOT in the ss-DNA/SWNT/PEDOT composite is higher than PEDOT alone. This is because the contribution of non-Faradaic charging current of ss-DNA/SWNT/PEDOT composite is more significant than PEDOT due to its larger surface area. Compared to CV technique, electrochemical impedance spectroscopy (EIS) is a steady state technique with small perturbation, can be used to study various electrochemical process and measure Faradaic capacitance with minimized non-Faradaic charging effects. The Faradaic capacitance of PEDOT and SWNT/PEDOT composite at different potentials (at intervals of 0.05 V) was calculated using the relation, $C=1/\omega Z''=1/(2\pi f Z'')$, where, ‘f’ is the lowest frequency (1 Hz was used in this study to record the spectra) and $Z''$ is the imaginary part of the impedance at 1 Hz. At higher potential, the capacitance of the composite is much higher than PEDOT alone, consistent with literatures. However, below -0.21 V, the capacitance of the composite sharply decreases and become even lower than that of PEDOT alone. Since the Faradaic capacitance measured by EIS is purely contributed from electrochemical redox reaction of PEDOT, the high Faradaic capacitance in the composite demonstrated the high electrochemical activity of PEDOT in the composite than PEDOT alone. The dramatic decrease in
capacitance at -0.21 V indicated that the PEDOT in the composite switched to the nonconductive reduced states of PEDOT. While the capacitance slowly declined until -0.7 V, which is the most negative potential used for this study, suggesting that PEDOT alone needs much more negative potential to switch to reduced states. It is reported that crystal structure and molecular weight of conducting polymer have narrower potential range for redox switching. These results indicated that PEDOT in the composite may have more narrow molecular weight and better crystalline structures.

The conductivity of counter ions in the films at different potentials has been extracted from the Nyquist plots using the diameter of the impedance arc (the PEDOT thickness was estimated using the relation proposed by Hoier and Park). It is obvious from fig 4.2e, that the ionic conductivity of the composite film is also much higher than that of PEDOT alone over the entire potential range under consideration. Therefore, the ionic transport at the solution PEDOT interface is more facile in the nanocomposite compared to that in the control PEDOT film.

Following the modified transmission line model proposed by Deepa et al., we extracted the charge transfer resistance (R_{ct}) for both PEDOT/SWNT nanocomposite and control PEDOT film (fig 4.2f). It is observed from fig 4.2f that the R_{ct} value is higher for the control PEDOT throughout the whole potential range. The larger value of R_{ct} for pure PEDOT film reiterates that SWNT/PEDOT can be more easily reduced than pure PEDOT, when subjected to the same value of external potential.
Figure 4.2 (a) CV of PEDOT and SWNT/PEDOT, and Nyquist plot of SWNT/PEDOT (b), and PEDOT(c) at different dc potentials at an interval of 50mV from (0.7V to -0.7V, left to right) recorded in 0.1M LiClO4 solution at 10 mV. (d), (e), and (f) capacitance, ionic conductivity and charge transfer resistance, as a function of applied potential, for SWNT/PEDOT (red) and control PEDOT (black) extracted from plots b and c.

4.3.2.2 Morphology of PEDOT and SWNT PEDOT nanocomposite

An evidence for the formation of SWNT/PEDOT nanocomposite network was obtained from Atomic Force Microscopy (AFM) imaging. Fig 4.3 shows AFM images of pure PEDOT and SWNT/PEDOT nanocomposite deposited on Au electrode substrate. A comparison of AFM images of PEDOT and SWNT/PEDOT nanocomposite reveals the formation of a layer of PEDOT on the SWNT network in which PEDOT coated SWNTs are densely packed and well connected with each other (fig 4.3b). This type of nanostructure in which carbon nanotubes are incorporated in the catalyst layer are believed to facilities the electron transfer and oxygen mass transport to the electrode surface to achieve the faster kinetics of ORR.
Figure 4.3 Atomic Force Microscopy images of PEDOT(a) and SWNT/PEDOT nanocomposites (b) deposited electrochemically.

4.3.2.3 Valence Band Spectra of PEDOT and SWNT/PEDOT

X-ray photoelectron spectroscopy (XPS) was used to obtain the information about the band gap difference between PEDOT and SWNT/PEDOT nanocomposite. The density of states close to Fermi level (corresponding to energy zero) can be viewed in Figure 4.4. No abrupt drop was observed in the density of states at zero binding energy, akin to that observed by Greczynski et al.\textsuperscript{25} for PEDOT/PSS films in both of the two films under consideration. The calculated energy difference between the valence band and Fermi level is $\sim 1.00$eV for the SWNT/PEDOT film, which is lower than that of the control PEDOT sample (1.25eV). The lower energy difference between the Fermi level and valence band gives an idea that SWNT/PEDOT film in comparison to that of the control PEDOT film have a lower band gap, demonstrates that a lower potential will suffice to induce electrochemical reduction and oxidation in the nanocomposite. This observation further supports the results obtained from the AC impedance measurements. Furthermore, oxygen reduction reaction requires donation of electrons from the cathode electrode to
oxygen, a lower valance band have improved electron donation capabilities of cathode which is beneficial to ORR.

![Figure 4.4](image)

**Figure 4.4** Valance band spectra of SWNT/PEDOT composite (Black) and control PEDOT (red) films displaying their respective Fermi edges

4.3.3. Electrocatalytic reduction of oxygen at PEDOT composited modified GC electrodes

4.3.3.1 Cyclic Voltammetry

The electrocatalytic activity of ss-DNA/SWNT/PEDOT to ORR is evaluated by CV and compared with PEDOT alone (Figure 4.5a). The cyclic voltammograms (CVs) of oxygen reduction in O$_2$ or Ar saturated electrolyte solutions at different electrodes clearly shows the ORR peaks for all the electrodes in O$_2$ saturated but not in Ar saturated solution. A better electrocatalytic effect of electrodeposited PEDOT nanocomposites to O$_2$ reduction, as compared to pure PEDOT, can be clearly observed in the CVs, reflected by two important catalytic features: (i) a positive shift of the O$_2$ reduction potential and, (ii) a
concurrent increase in the oxygen reduction peak current. A positive oxygen reduction potential and a high oxygen reduction current are two essential requirements an efficient fuel cell.

On PEDOT modified electrodes, the onset potential for O₂ reduction is -0.35 V and the reduction reached a peak current at -0.51 V. It is worthy to mention that PEDOT prepared by chemical polymerization in acetonitrile solution phase does not show this electrocatalytic ability. This is because the PEDOT produced cannot be reduced until negative -0.4 V vs Ag/AgCl reference electrode. It should be noted that hydrogen evolution on the PEDOT takes place at less negative potential than the full reduction of polymer occurred. For SWNT/PEDOT modified electrodes, the ORR onset potential shifted positively to -0.23 V and the peak current also reached at a less negative potential of -0.40 V. Furthermore, the normalized peak current density is much larger (~ 4 times) than that on the PEDOT electrode. It has been reported that carbon nanotubes demonstrated the electrolycatalytic behavior towards oxygen reduction. To understand if this increase in the reduction current was stem from CNTs alone, a control experiment was conducted by modifying the GC electrode with the same amount of CNTs which was used for the SWNT/PEDOT modified electrode. From Figure 4.5a (the blue curve), we can see that O₂ was indeed reduced in the same potential, however the reduction current is smaller by ~1.25 times than that on composites electrode. The O₂ catalytic reduction current on the PEDOT-SWNT modified electrode is much higher than both PEDOT and SWNT alone modified electrodes, indicates that PEDOT-SWNT composite synergistically enhanced O₂ catalytic reduction.
Interestingly, it is very obvious that the onset and the peak potential for the SWNT/PEDOT composite electrode are much closer to the SWNT alone modified electrode compared to the PEDOT modified electrode, indicating a strong electronic interaction between PEDOT and SWNTs in the composites.

Therefore, a part from the increased electrochemical activity, the incorporation of carbon nanotubes in the composite structure also played a crucial role in the ORR process by facilitating the electrolyte diffusion possibly due to the open network structure of the nanocomposite.

**Figure 4.5** Cyclic voltammograms recorded in O₂ saturated 0.1 M LiClO₄ at PEDOT(blue), SWNT/PEDOT(red) and SWNT(black) electrodes, and Ar saturated 0.1M LiClO₄ (green) PEDOT/SWNT electrode. b Amperometric curves for O₂ reduction at SWNT/PEDOT modified GC electrode (red), SWNT modified GC electrode (black), and PEDOT modified GC electrode (blue) in 0.1 M LiClO₄ solution purged with O₂ and Ar alternatively at -0.4 V and (c) showing the response time for oxygen and argon respectively, by GCE modified with different materials with the error bars of 6 purges of oxygen in each case form two independent experiments.

### 4.3.2.3. Amperometry

The synergistic effect of CNT and PEDOT in ORR was also demonstrated in the fast response to O₂, which is related to the mass transport properties of O₂ in the PEDOT
films. Fig 4.5b shows the amperograms recorded at SWNT/PEDOT, PEDOT and SWNT modified GC electrodes, in 0.1 M LiClO₄ solution purged with O₂ and Ar alternatively. From fig 5b, it is clear that under identical experimental conditions, a higher ORR catalytic current is observed at SWNT/PEDOT than PEDOT and SWNT electrode in O₂ purged 0.1 M LiClO₄. The amperometric O₂ reduction current at SWNT/PEDOT is 6 times higher than those of pure PEDOT at the same potential (-400mV). Fig 5c illustrates the response time at different electrodes, which is defined as the time to the maximum current upon the electrolyte solution was purged with O₂. The PEDOT composite not only exhibited higher catalytic current toward reduction of O₂, the response to O₂ is also much faster compared to the control PEDOT and ss-DNA-SWNT only. The fast response was ascribed to the porous structure of the composite because of CNTs, which facilitate O₂ to reach all the active sites of PEDOT, while the pure PEDOT may have more compact structures, which are resistant for O₂ to come inside or out of the film.

4.3.2.4 Oxygen reduction catalysis by a vertically grown carbon nanotube PEDOT coated electrodes

The electrocatalysis of ORR by SWNT/PEDOT nanocomposite is realized from above experimental results. However, the oxygen reduction proceeds at relatively higher negative working potential when such nanocomposites were prepared using dispersed carbon nanotubes. To be an efficient electrocatalyst, the material should be able to reduce oxygen at the potential closer to the standard potential of ORR which is 1.23 V vs NHE (in acid media). One possible reason for the higher overpotential in above experiments could be the contact resistance between the electrode surface and the carbon nanotubes network and the contact resistance between carbon nanotubes in the network which is formed when they were drop-casted from their colloidal dispersions and self-assembled
on the electrode surface. The contact resistance between the carbon nanotubes in a network can be minimized if the polymer coating can be obtained on vertically aligned CNTs. Such vertically aligned CNTs act as molecular wires to allow direct electrical communication between the underlying electrode and a redox active species in the electrolyte, which could facilitates a direct electron transfer between the electrode surface and the electroactive species in the electrolyte. In order to check this hypothesis, we synthesized the PEDOT nanocomposite on a vertically aligned carbon nanotube array following the same procedure as described above and the electrocatalytic efficiency of thus formed nanocomposite (VA-CNT/PEDOT) is compared with the dispersed CNT/PEDOT (D-CNT/PEDOT).

The typical morphology of the well-aligned carbon nanotubes is shown in Fig. 4.6a. To make an electrical connection, a copper ribbon of 5 mm width was attached from the back of the CNT containing Si surface using a conductive silver paint (Structure probe, Inc., USA). The edge of Si substrate and the copper surface which remains in the electrolyte was insulated with commercially available epoxy resin (Loctite from Lowes) (fig 4.6b). These CNTs bound Si surface were used as the working electrode without any further treatment. Before the polymerization, the electrical connection between the copper connector and the CNTS covered area was checked by using a voltmeter.
The electrocatalytic activity of the PEDOT nanocomposite with the vertically aligned carbon nanotube was measured and the result is presented in fig 4.7. In contrast to D-CNT/PEDOT modified electrode where, O$_2$ reduction starts at -0.230 V and reaches a maximum at -0.41 V (fig 4.7a blue line), while the reduction of O$_2$ at VA-CNT/PEDOT nanocomposite electrode starts at -0.060 V and reached a peak current at -0.220 V (Fig. 4.7a green line). This ~0.200 V positive shift in ORR potential reveals that PEDOT/CNT nanocomposite prepared by electrochemical polymerization on VA CNT demonstrated more efficient catalytic ability towards O$_2$ reduction. The O$_2$ reduction potential shifted positively in the presence of VA-CNT/PEDOT is a clear indication of efficient catalysis of ORR. After background corrected, the reduction peak current of the VA-CNT/PEDOT electrode is about 1.5 times of that observed at the electrode modified with D-CNT/PEDOT. The increase of the peak current and the positive shift of the potential clearly indicated the catalytic efficiency of the PEDOT nanocomposite, which is dramatically enhanced when an vertically aligned CNT array on a conductive substrate were employed to prepare the composite.
4.3.5. Determination of catalytic rate constant by double-step Chronoamperometry

Chronoamperometry can be used to evaluate the catalytic rate constant for the ORR occurring at different electrode material using the method described in the literature. Following equation is used to calculate the electrocatalytic rate constant \( k \),

\[
\frac{I_C}{I_L} = (\pi k c t)^{\frac{1}{2}}
\]  

(4.1)

Where \( I_C \) is the catalytic current of ORR at the composite electrode and \( I_L \) is the limiting current in the absence of O\(_2\), ‘c’ is the bulk concentration of O\(_2\)(= 3× 10\(^{-4}\)M).

Fig. 4.7b represents a typical chronoamperogram obtained at VA-CNT/PEDOT composite electrode in 0.1 M LiClO\(_4\) by setting the first and second working electrode potential at 0.mV and -250 mV vs Ag/AgCl, respectively, in the absence and presence of O\(_2\). From the slope of the \( I_C/I_L \) vs (t)\(^{1/2}\) (inset fig 4.7b) the catalytic rate constants for different electrodes are calculated and tabulated in table 4.1. From the results it can be observed that the electrocatalytic rate constant for ORR, at D-SWNT/PEDOT electrode is 6 times higher than that of pure PEDOT electrode. This rate is ~ 10 times larger than reported for PANI MWNT nanocomposite as reported by Gopalan et al.\(^\text{11}\). Furthermore, at VA-CNT/PEDOT the electrocatalytic rate constant calculated is 27×10\(^{-3}\)M\(^1\)s\(^{-1}\), which ~ 2 times more than that at D-CNT/PEDOT and ~ 13 times higher than pure PEDOT.

These results help us to understand that the contact resistance in CNT network plays a significant role in the electrocatalytic performance of the PEDOT nanocomposite
Table 2 Calculated values of k from double step chronoamperometry data for oxygen reduction reaction by different electrode materials in 0.1 M LiClO₄

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>k (×10³ M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT</td>
<td>2.10</td>
</tr>
<tr>
<td>D-CNT/PEDOT</td>
<td>12.10</td>
</tr>
<tr>
<td>VA-CNT/PEDOT</td>
<td>27.05</td>
</tr>
</tbody>
</table>

Figure 4.7 (a) Cyclic Voltammogram recorded for O₂ reduction at D-CNT/PEDOT(A), and VACNT/PEDOT (B) electrodes under identical experimental conditions and (b) double step chronoamperograms obtained at VA-CNT/PEDOT modified electrode in O₂ saturated and de-aerated 0.1 M LiClO₄ electrolyte. Inset plot of I_c/I_L vs t ½.

4.4. Conclusions

In summary, nanocomposite of poly (3, 4ethylenedioxythiophene) with ss-DNA dispersed single –walled carbon nanotubes fabricated by electrochemical polymerization showed superior redox activity, a lower charge transfer resistance and efficient electrocatalytic ability for oxygen reduction reaction in comparison to control PEDOT films. Carbon nanotubes in addition to enhance the polymerization speed are also responsible for the formation of films with interconnected units in the composite
network, which promote ion/electron transfer at the PEDOT-CNT/electrolyte interface.

Owing to the synergistic properties of CNT and PEDOT, the resulting nanocomposite shows improved electrocatalytic properties towards oxygen reduction reaction. Also, a potential application of PEDOT/CNT nanocomposite for the integration to fuel cell devices is demonstrated by VA-CNT/PEDOT, with significantly improved electrocatalytic properties.

4.5. References

Chapter 5 Vapor Phase Polymerized PEDOT/Carbon Nanotube Composite as an Efficient Metal-free Electrocatalyst for Oxygen Reduction

5.1 Introduction

Recently, there has been a growing worldwide interest in the electrocatalytic reduction of oxygen to water at the cathode compartment of low temperature fuel cells. The electrochemical reduction of oxygen is a multi-electron reaction that has two main possible pathways: a direct four electrons pathway to combine oxygen with electrons and protons when coupled with oxidation on the anode to produce water, or a two-step, two electron pathway involving the formation of hydrogen peroxide as an intermediate. To obtain maximum energy capacity, it is highly desirable to reduce $O_2$ via the four-electron pathway. However, the mechanisms of oxygen reduction are critically dependent on the electrode materials, their surface structures and the nature of the electrolyte solutions used in the applications. The development of efficient oxygen reduction reaction (ORR) electrocatalysts is thus of great significance for the commercialization of fuel cells.

Although platinum-based electrocatalysts have been traditionally used to catalyze ORR with a high efficiency,$^{1-2}$ the success of commercialization of Pt-based fuel cell for practical applications is limited by the high cost and limited availability of the most commonly used cathode material, platinum. Furthermore, Pt based electrode materials are found to be easily poisoned by a vast array of substances, such as carbon monoxide, methanol and halide anions.$^{3-4}$ Thus over time, many Pt based electrodes lose their
catalytic activities for ORR under field conditions. These problems drive the search for precious metal free efficient cathode materials that catalyze ORR.

Recently, non-precious metal and metal free catalysts for ORR have attracted interests as an alternative to platinum based catalysts. Amongst a number of electrocatalysts investigated, conducting polymers have been identified as promising candidates due to their stability, ease of fabrication and low cost. However, most of the conducting polymer based ORR electrocatalysts are less efficient. due to their poor conductivity or the limited access of the molecular oxygen to the electrode surface through the polymer films. During the past few years, several approaches have been developed to overcome these limitations, focused including fabrication of highly conductive polymer by modifying the conventional polymerization techniques or by incorporation of conductive fillers such as carbon nanotubes, in the polymer matrix.

The association of conducting polymers with carbon nanotubes is a relatively new strategy to obtain hybrid materials with enhanced functionalities such as high conductivity, thermal stability and reinforcement properties. A composite of multi-walled carbon nanotube (MWNT) and polyaniline (PANI) has been prepared on an electrode surface and its catalytic activity towards ORR has been reported. The incorporation of MWNT in PANI nanostructures facilities the electron transfer and oxygen mass transport to the electrode surface which dramatically enhances the kinetics of ORR as compared to pure PANI in acid environments. However, further development of PANI/MWNT nanocomposite materials for practical applications is impeded by their poor efficiency, as demonstrated by its two steps two electrons ORR pathways. For
practical fuel cell applications, the catalytic system should ideally be able to catalyze oxygen reduction exclusively through a four electron mechanism in fuel cell operating environment.

From previous chapter we understand that the electrochemically fabricated CNTs/poly(3, 4-ethylenedioxythiophene) (PEDOT) composite demonstrated superior redox activity, a lower charge transfer resistance and efficient electrocatalytic ability for oxygen reduction reaction in comparison to the control PEDOT films. Although, electrochemical polymerization presents several advantages such as rapidity, absence of catalyst, controlled thickness by controlling the deposition charges and the direct obtainment of the polymer film in conductive oxidized form, the optimized molecular structure of PEDOT and the highest conductivity of PEDOT film toward efficient ORR is still not reached. Vapor phase polymerization on the other hand has been reported as a relatively new technique to synthesize a highly conductive thin layer of PEDOT on a surface which is pre-coated with oxidant for polymerization of EDOT monomers. Vapor phase polymerization induces molecular ordering in the polymer chain which is responsible for the high conductivity. Winther et al.\textsuperscript{16} reported a thin layer of vapor phase polymerized poly (3,4-ethylenedioxythiophene) PEDOT on a porous membrane can reduce oxygen, which is in highly contrast to the previous report of chemically polymerized PEDOT.\textsuperscript{17} This work opens new possibilities in the potential applications of PEDOT in an oxygen reduction electrocatalyst without CO poisoning or methanol crossover effect. However, lack of fully understanding of oxygen reduction pathway of PEDOT catalyst hinders further development of their practical applications in fuel cell electrodes.
This chapter aims to evaluate the performance of CNT/PEDOT nanocomposite for oxygen reduction catalysis in an alkaline fuel cell operating environment. Single stranded DNA dispersed SWNT (ss-DNA SWNT) mat was used as a conductive matrix to grow PEDOT polymer by modified vapor phase polymerization technique (VPP). The unique features of the resulting nanocomposite, including: high surface area, and ordered polymeric structure with improved conductivity, which leads to high electrocatalytic activity. These properties were superior to those observed for other conducting polymers and their carbon nanotube composites. A detail study to elucidate the oxygen reduction pathways and the rate of ORR on VPP PEDOT/carbon nanotube nanocomposite is performed by electrochemical measurements such as rotating disk electrode (RDE) and the rotating ring disk electrode (RRDE) voltammetry in alkaline media. The results indicated that oxygen reduction on VPP PEDOT nanocomposites takes place by efficient four electron process at more positive potential (-0.15V vs. Ag/AgCl). To the best of our knowledge, such excellent electrochemical performance in the ORR has never been observed for conducting polymer based metal free electrocatalysts.

5.2 Experimental

5.2.1 Materials

3, 4-Ethylendioxythiophene (EDOT), Iron (III) p-touline sulfonate hexahydrate (tech. grade) pyridine, n-butanol, methanol, potassium hydroxide were purchased from Sigma-Aldrich Co. Purified HiPco single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. Houston, TX. Single-stranded DNA with sequence d(T)\textsubscript{30} was purchased from Integrated DNA Technologies, Inc. Coralville. All solutions were prepared using deionized water (18.2 MΩ) (Nanopure water, Barnstead), which was also
used to rinse and clean. Ultra High purity Oxygen UHP 200 and high purity argon (HP 300) were purchased from Airgas.

5.2.2. Dispersions of single walled carbon nanotubes in water

Aqueous solution of Single stranded DNA dispersed carbon nanotubes (ss-DNA-SWNT) were prepared by following the previous method. Free DNA and bundled carbon nanotubes were removed by centrifugation and dialysis.

5.2.3. Preparation of Electrodes

The glassy carbon electrode (GCE) was polished with a 0.05 µm Al₂O₃ particle suspension on a moistened polishing cloth in a “figure eight” pattern for four minutes to mirror finish. The polished electrode was rinsed with nanopure water, sonicated in Branson 2510 ultrasonic cleaner for four minutes in nanopure water to remove adhered alumina powder; it was rinsed well again and then dried at room temperature in air for 20 minutes before use. A CNT mat on the electrode surface was prepared by drop casting 4 µL of ss-DNA dispersed SWNT on the cleaned electrode area and dried under vacuum for 2 hrs.

After drying, the electrode with CNT mats was dipped in the oxidant solution for 1 minute. Excess of the oxidant was gently wiped off with the tissue and the coated electrode was annealed in air at 70⁰C for 5 minutes. The electrode was placed in a glass reactor already charged with the EDOT monomer under vacuum for the desired polymerization time. The monomer vapors placed in a small vial containing the liquid EDOT at the bottom of the reactor, progressively filled the reactor. After polymerization, the electrode was removed out from the reactor, left in ambient atmosphere for 1 hr to
ensure the complete evaporation of EDOT vapors. It was then soaked alternately in methanol and deionized water three times to remove the residual oxidant. Hence fabricated electrode were dried under vacuum at room temperature for 2 hrs and then stored at ambient atmosphere prior to use. A control experiment was performed for PEDOT without CNT in the same way.

5.2.4 Characterizations

Tapping mode Atomic force microscopy (AFM) was performed on Nanoscope IIIa atomic force microscope (Veeco instrument, Santa Barbara, CA, USA) in air on the sample polymerized on SiO₂ with a SiO₂ layer of 300nm as a substrate. During imaging, a 125 µm long rectangular silicon cantilever/tip assembly (Model: MPP-12100, Veeco) was used with a resonance frequency of approximately 127-170 kHz, a spring constant of approximately 5 N/m, and a tip radius of less than 10 nm. UV-Vis-NIR absorption spectroscopy performed on a Cary 500 visible-near-infrared (UV-Vis-NIR) spectrophotometer in double-beam mode.

5.2.5 Electrochemical Measurements

Cyclic Voltammetry (CV) measurements were performed using a computer-controlled potentiostat (CHI 750A, CH Instrument) in a standard three-electrode cell. PEDOT/GC or CNT/PEDOT/GC electrode was used as working electrode, a Pt wire as counter electrode, and an Ag/AgCl (3 M NaCl filled) electrode as reference electrode. Measurements on rotating ring-disk electrode (RRDE) and/or rotating disk electrode (RDE) were carried out on a RRDE 3A electrode rotator (CH Instrument) and the CHI 750A potentiostat using GC disk (diameter 0.5cm) and Pt ring electrode, separated from each other by a thin layer of teflon. For all electrocatalytic experiments (CV and RDE
and RRDE measurements), 0.1M KOH was used as the electrolyte. Ar or O₂ was used to purge the solutions to achieve the oxygen-free or oxygen-saturated electrolyte solution respectively. Potential-sweep electrolysis was performed at the modified GC disk electrode while the Pt ring electrode was polarized at 0.50 V for oxidizing HO₂⁻ intermediate, if any, from the disk electrode. All the experiments were conducted at room temperature (25 ± 1°C)

### 5.3 Results and Discussion

#### 5.3.1 Fabrication of SWNT/PEDOT nanocomposite

The coating process is depicted in fig 5.1. The electrode modified with ss-DNA dispersed SWNT mats was dipped into iron (III) tosylate ((Fe(OTS)₃) solution. The excess of Fe(OTS)₃ solution was gently wiped off with a tissue paper and the coated electrode was annealed in air at 70°C for 5 min. The vaporized EDOT monomers polymerize as they come in contact with Fe(OTS)₃ coated CNTs producing a thin film coating doped with tosylate anions (fig 5.1). In the PEDOT coating procedure, 0.5 mol of pyridine per mole of Fe(OTS)₃ was added to the oxidant solution in order to hinder acidic side reactions during the subsequent polymerization.¹⁸

![Scheme of the two steps vapor phase PEDOT coating process](image)

**Figure 5.1** Scheme of the two steps vapor phase PEDOT coating process
Although Fe (OTs)$_3$ is required for polymerization to occur and to dope the growing polymer chains, an excess amount of it should be avoided to prevent over-doping which decreases the conductivity of the film. While if the stoichiometric ratio between Fe (OTs)$_3$ and the monomers was too low, the slow polymerization kinetics would result in a low molecular weight EDOT oligomers, instead of highly conductive PEDOT.$^{19}$ In this work we optimized the wt% ratio and polymerization time in terms of oxygen reducing efficiencies of the PEDOT nanocomposite by monitoring both the ORR onset potential and peak current (figures 5.2 and 5.3). From the experimental results an optimum polymerization conditions was obtained to be a 20 wt% of Fe (OTs)$_3$ and 8 hrs of polymerization. It was reported that iron (Fe) is detrimental for ORR catalysis.$^{16}$ So we washed the thus obtained PEDOT film thoroughly to remove all the residue of iron in the PEDOT and the SWNT/PEDOT film. We monitored the iron content as a residue in the washed film by UV-Vis spectroscopy and found that no Fe content left after final washing was detected.

![Scheme 5.1](image)

**Scheme 5.1.** Schematic description of oxidative chemical polymerization of EDOT into PEDOT-OTS
Figure 5.2 Oxygen Reduction onset potential (a), and peak current (b), in ss-DNA/SWNT/PEDOT nanocomposite modified GC electrode as a function of Fe (OTS)$_3$wt%.

Figure 5.3 Oxygen Reduction onset potential (a), and peak current (b), of ORR in ss-DNA SWNT/PEDOT nanocomposite electrode as a function of polymerization time.
5.3.2 Characterizations of PEDOT and SWNT PEDOT nanocomposite

5.3.2.1 UV- vis -NIR Spectroscopy

UV-VIS-NIR spectrum was obtained on the rinsed PEDOT and ss-DNA/SWNT/ PEDOT nanocomposite (Fig. 5.4). For comparison, the UV-VIS NIR spectrum of ss- DNA/SWNT used to fabricate the nanocomposite was also recorded and plotted in fig 5.4. As expected from the NIR spectra of individual components, the spectrum of SWNT/PEDOT is clearly a combination of both spectra. In both nanocomposite and pure PEDOT, the characteristic PEDOT spectrum is observed with a low absorption in the visible and an increased absorption after 700 nm, extending in the NIR region. The presence of this broad absorption band at higher wavelengths as seen in fig 5.4, has been shown to correspond to the polymer having longer conjugation length and better molecular order of the PEDOT film. It is well known that a conducting polymer with long conjugation length and good molecular alignment has been demonstrated with greater mobility of charge carriers indicating high level of doping, and doping induced mid gap states. These results clearly demonstrate that the PEDOT and the SWNT PEDOT nanocomposite synthesized by modified vapor phase polymerization of PEDOT results in a highly conductive and structurally ordered film in PEDOT and SWNT/PEDOT composite as reflected by the higher absorption than pure PEDOT.
Figure 5.4 UV-Vis spectra of ss-DNA SWNT, and vapor phase polymerized, PEDOT and SWNT/ PEDOT film on quartz substrate.

Cyclic voltammetry (CV) is a sensitive method to characterize the redox states and thereby the electronic properties of conjugated polymers. The voltammetry current which is proportional to the number of active sites that can be reduced/ oxidized at a given potential, is dependent not only on the chemical composition of the polymer but also on the structural factors such as conjugation length and local order of the polymer chains. Figure 5.5 shows the CV curve of SWNT/PEDOT composite. The CV curve of PEDOT alone is also displayed for comparison. All the CV curves were recorded at a sweep rate of 20mV/s in an aqueous electrolyte solution (0.1 M Lithium perchlorate). From the CV curves, it can be observed that the electrochemical responses of the PEDOT and ss-DNA/SWNT/PEDOT nanocomposites as a function of potential are similar to what has previously been reported for electropolymerized PEDOT and vapor phase polymerized PEDOT.\cite{24,25} However, the ss-DNA/SWNT/PEDOT shows a much larger response,
possibly due to the large surface area of the SWNT provided. It is also possible that the PEDOT in the SWNT/PEDOT composites has higher conductivity/electrochemical activity. We also found that the reduction peak potential of PEDOT in the nanocomposite shifted positively by ~ 100 mV compared to that of pure PEDOT. Since PEDOT reduction is the first step before oxygen re-oxidize it during ORR, a positive reduction potential of PEDOT nanocomposite would significantly increase the efficiency to catalyze ORR. Specifically, a positive reduction potential of PEDOT could lower the overpotential for ORR and then eventually increase the output voltage of a fuel cell when the SWNT/PEDOT composite is used as the cathode materials.

Figure 5.5 Cyclic voltammograms of the PEDOT and ss-DNA/SWNT/PEDOT films deposited on a GCE by VPP in an aqueous solution of 0.1 M LiClO₄, scan rate of 20 mV s⁻¹.
The formation of SWNT/PEDOT nanocomposite network was evidenced from Atomic Force Microscopy (AFM) imaging. Fig 5.6 shows AFM images of pure PEDOT and SWNT/PEDOT nanocomposite deposited on a SiO$_2$ substrate. A comparison of AFM images of PEDOT and SWNT/PEDOT nanocomposite reveals the formation of a layer of PEDOT on the SWNT network in which SWNTs are densely packed and well connected with each other in PEDOT matrix (fig 5.6 b). This type of nanostructure in which carbon nanotubes are incorporated in the catalyst layer are believed to facilities the electron transfer and oxygen mass transport to the electrode surface to achieve a faster kinetics of ORR.

Figure 5.6: Atomic Force Microscopy (AFM) images of PEDOT (a), and ss-DNA SWNT/PEDOT (b), synthesized by vapor phase polymerization on SiO$_2$ surface

5.4. Determination of collection efficiency ‘N’ from RRDE experiments

A fundamental parameter of RRDE experiments, is the electrode collection efficiency N, which takes into account the efficiency of the transport of electrochemical reaction
product from the disc electrode to the ring electrode. This application of RRDE to find an electrochemical reaction pathway is often called a collection experiment.  

For the collection experiments, the electrodes were prepared as described above. The electrolyte was de-aerated 0.1 M KOH with 10mM K$_3$Fe(CN)$_6$, a typical compound for the determination of the collection efficiency. The ring and the disk currents in the positive sweep direction (10 mV s$^{-1}$) at a constant ring potential of 0.6 V are shown in Fig. 5.7. Disk potential was scanned from 0.6 V to -0.2 V vs Ag/AgCl at a scan rate of 10 mV/s. At this ring potential, the oxidation of [Fe(CN)$_6$]$^{4-}$, which is produced at the disk electrode, to [Fe(CN)$_6$]$^{3-}$, proceeds under pure diffusion control, while oxygen evolution currents at the Pt-ring electrode are still negligible. The collection efficiency is then determined from the ring ($I_R$) and disk ($I_D$) currents. 

$$N = -\frac{I_R}{I_D} \quad (5.1)$$

**Figure 5.7** Ring ($\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$) and disk ($\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$) currents for the determination of the collection efficiency on a Pt ring GC disk RRDE in 0.1 M KOH supporting electrolyte with 10 mM K$_3$Fe(CN)$_6$. Positive sweeps at 10 mV s$^{-1}$; $E_{\text{Ring}}$=0.6V)
The collection efficiency of the RRDE used in our study was determined to be 0.35 which is similar the previously reported value for a similar system.\textsuperscript{6}

5.4 Electro catalytic Reduction of Oxygen

5.4.1 Cyclic Voltammetry

The oxygen reduction catalyzed by SWNT/PEDOT nanocomposite was initially conducted in 0.1 M KOH solution mimicking an alkaline fuel cell (AFC) working conditions. Fig 5.8 shows the cyclic voltammograms (CVs) of oxygen reduction in O\textsubscript{2} or Ar-saturated 0.1M KOH solutions at different electrode materials. A large reduction peak was observed in the O\textsubscript{2} the saturated electrolyte solution, but not in the Ar saturated solution, suggesting that O\textsubscript{2} is electrocatalytically reduced at negative potentials. For the electrode modified with SWNT network only and PEDOT only, the onset potentials for ORR is at \(-0.22\) V (versus Ag/AgCl) with a single cathodic peak around \(-0.37\) V and \(-0.35\) V (versus Ag/AgCl figures 5.8a) and c) respectively. In case of SWNT/PEDOT nanocomposite electrode, both the onset potential and the reduction peak potential of ORR, shifted positively to around \(-0.13\) V and \(-0.28\) V respectively with a concomitant increase in the peak current density (fig 5.8b). Compared with the PEDOT only electrode (fig 5.8a), the large positive shift (90 mV) of the onset ORR potential and the largely increased reduction current (~2 times) on the SWNT/PEDOT electrode (fig 5.8b) clearly demonstrate that a significant enhancement in the ORR electrocatalytic activity for the SWNT/PEDOT nanocomposite, possibly due to the same reason as we discussed in the previous chapter (the large surface area of SWNTs, and higher conductivity and electrochemical activity of PEDOT in the composite film). Compared to the SWNT/PEDOT nanocomposite prepared electrochemical polymerization, the onset ORR
potential for the SWNT/PEDOT nanocomposite by vapor phase polymerization (VPP) is ~100 mV more positive, indicating that the PEDOT formed by VPP have even better molecular alignment than that PEDOT formed by electrochemical polymerization approach.

Figure 5.8 Cyclic Voltammetry curves or ORR on, PEDOT (a), ss-DNA SWNT/PEDOT(b), and ss-DNA SWNT(c), in Ar (black curve), and O₂ (red curve)-saturated in 0.1M KOH solutions at a scan rate of 10 mV/s, and the cyclic voltammetry curves for oxygen reduction in the O₂ staurated 0.1M KOH solution at different electrodes (d).
5.4.2 Rotating Disk Electrode (RDE) Voltammetry

To further investigate the ORR performance, we carried out the linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) for each of the electrode materials in O₂ saturated 0.1M KOH at a scan rate of 10 mV/s and a rotation rate of 1600 rpm. As can be seen in fig 5.10 (a), the ORR at the pure PEDOT and SWNT only electrode started at around potential (-0.24 V and -0.22V respectively), followed by the continuous increase in the current density at -0.45 V with current intensity of 0.37mA/cm² and -0.77mA/cm², respectively. The ORR onset potential of the SWNT/PEDOT electrode significantly shifted positively to -0.18 V and the limiting diffusion current at -0.45V is much higher (0.85mA/cm²) with a relatively wide plateau in respect to pure PEDOT. Compared to both SWNT and PEDOT electrodes, the highest limiting diffusion current with a relatively wide plateau was observed for PEDOT/SWNT electrode due most probably, to an efficient four- electron path way. The ORR current density at – 0.45V is 0.85mA/cm² which is ~ 2.3 times and ~1.2 times higher than that at the PEDOT and SWNT respectively, indicating that the synergistic effects of PEDOT and SWNT are responsible for the higher electrocatalytic activity observed for SWNT/PEDOT electrode. Although, the onset potential is still lower that most of the Pt/C catalysts measured, 27 its limiting diffusion current density and onset potentials both are better than the conducting polymer based ORR catalysts reported so far. Thus our results should be sufficiently promising to warrant further research efforts in developing novel metal free catalyst through SWNT based conducting polymer nanocomposites.

To explore a more quantitative evaluation of the ORR electrocatalytic activity for the electrode materials, rotation-rate-dependent RDE measurements were performed. Fig
5.9a shows RDE current potential curves at different rotation rates for SWNT/PEDOT modified electrode. As can be seen, the limiting current density increases with increase in rotation rates for the SWNT/PEDOT nanocomposite electrodes. Similar trend was observed for PEDOT only electrode and SWNT only electrode. Koutecky-Levich equation which relates the measured current density ‘j’ to the rotation rate of the electrode ω, was used to gain further insight on the performance of the PEDOT and SWNT/PEDOT electrodes. This equation is valid for a first-order process with respect to the diffusion of species. The kinetic parameters can be analyzed on the basis of the Koutecky-Levich equations (eqs.2-4)\textsuperscript{26,28},

\[
\frac{1}{j} = \frac{i}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{\frac{1}{2}}} \tag{5.2}
\]

\[
B = 0.62nFAD_2^{\frac{1}{2}}\nu^{-\frac{1}{6}}C_o \tag{5.3}
\]

\[
j_k = nFk\Gamma C_0 \tag{5.4}
\]

in which \(j_k\) and \(j_L\) are the kinetic and diffusion- limiting current densities, \(n\) is the number of electrons transferred in the reduction of one \(O_2\) molecule, \(F\) is the Faraday constant (\(F = 96485 \text{ C/mol}\)), \(D\) is the diffusion coefficient of \(O_2\) in 0.1 M KOH, \((1.9\times10^{-5} \text{ cm}^2 \text{ s}^{-1})\); \(C_0\) is the concentration of \(O_2\) (1.2 mM), \(\nu\) is the kinematic viscosity \((0.01 \text{ cm}^2 \text{ s}^{-1})\), \(\Gamma\) is the surface coverage of the catalyst in mol cm\(^{-2}\) (calculated from integration of the area under the peak in the CV as \(Q = nF\Delta\Gamma\)), \(A\) is the rotating disk area \((0.196 \text{ cm}^2)\).\textsuperscript{28-29} \(k\) is the rate constant for the oxygen reduction.
According to equations (2) and (3) the number of electron transferred (n) and the $j_k$ can be obtained from the slope and the intercept of the Koutecky-Levich plots respectively. The Koutecky-Levich curves plotted at various electrode potentials (Fig 5.9 b) exhibited good linearity with a slope approximately constant over the potential range, which suggests that the electron transfer numbers for oxygen reduction at different electrode potentials are similar. The parallel and straight fitting lines of $1/j$ vs $1/\omega^{1/2}$ imply a first-order reaction toward dissolved oxygen. Table 1 summarizes the results obtained from Koutecky-Levich plots. The number of electrons transferred per O$_2$ molecule was derived and the results suggest a four-electron process for the PEDOT/SWNT modified electrode and PEDOT electrode. While the electron transferred number is 2.10, at the SWNT electrode, which is close to the classical two- electron process as in the case of many other carbon based materials. Since, the number of electrons transferred by pure PEDOT and SWNT PEDOT nanocomposite is almost similar, which suggested that the composite electrocatalyst does not alter the reaction mechanism compared to the pure
PEDOT but enhances the catalytic activity. The kinetic rate constant, k, of SWNT/PEDOT is ~6 times larger than pure PEDOT. Again, it is noteworthy to mention that, oxygen reduction rate constant is one order of magnitude higher than the previously reported value of MWNT/PANI nanostructure. The facile kinetics and virtually complete reduction of oxygen to water can be hypothesized as: the presence of SWNT in SWNT/PEDOT provides high surface area and PEDOT keeps excess electroactive sites for ORR. The shift in the overpotential of O$_2$ is expected to arise from the more facile kinetic and transport environment for ORR at SWNT/PEDOT nanocomposite modified electrodes and the highly conductive PEDOT formed along the carbon nanotube when synthesized by the modified VPP approach.

5.4.3 Rotation Ring Disk Electrode (RRDE) Voltammetry

Although the voltage of oxygen reduction reaction current peak may be an effective way to compare the activities of the samples, it doesn’t necessarily correlate to how a catalyst will perform in an actual fuel cell. In addition to being catalytically active, cathode materials must be conductive for electrons and ions and possess sufficient mass transfer properties to allow O$_2$ to diffuse into the electrode and the water to diffuse out. To prevent corrosion of cell components and achieve better efficiency, ORR catalyst should also be highly selective to the formation of water not peroxide ions. One way to evaluate the selectivity of the catalyst material towards the more efficient 4 electron ORR process can be calculated by using equation

\[
n = \frac{4I_D}{I_D + \frac{i_R}{N}} \quad (5)
\]
Fig 5.10 (b) shows the RRDE polarization curves for O$_2$ reduction on SWNT/PEDOT, PEDOT and SWNT modified electrodes with a rotation rate of 1600 rpm in 0.1 M KOH solution saturated with oxygen. From the polarization curve, it is clear that ORR on both PEDOT and SWNT/PEDOT electrode, no significant solution phase peroxide is observed. However, for SWNT electrode, a significant ring current was detected starting at the ORR onset potential of the disk electrode which corresponds to the oxidation of peroxide. This result corresponds well with the literature reported for dispersed CNT$^6$ which reports a two electron pathway for oxygen reduction reaction. From the ratio of faradic current measured at the disk and the ring electrode, the number of electron transferred per O$_2$ molecule are calculated to be 3.75, 3.53 and 2.12 for SWNT/PEDOT, PEDOT and SWNT, respectively, using equation 5.

![Graph](image.png)

**Figure 5.10** Linear sweep voltammetry curves of ORR in an O$_2$-saturated 0.1M KOH solution at a scan rate of 10 mV/s and the rotation rate of 1600 rpm (a), and RRDE voltammetry curves of ORR at different electrodes (b).
Table 3 Calculated values of n and k for oxygen reduction by different electrode materials in 0.1 M KOH solutions

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>n (Koutecky-Levich plot)</th>
<th>n (RRDE data at 1600 rpm)</th>
<th>k (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT ss-DN A/SWNT/PEDOT</td>
<td>3.63</td>
<td>3.53</td>
<td>0.2×10⁴</td>
</tr>
<tr>
<td>ss-DNA/SWNT</td>
<td>4.02</td>
<td>3.75</td>
<td>1.3×10³</td>
</tr>
<tr>
<td>ss-DNA/SWNT</td>
<td>2.15</td>
<td>2.12</td>
<td>------------</td>
</tr>
</tbody>
</table>

5.5 Conclusions

In this chapter, a detail study of oxygen reduction pathways by a conducting polymer based metal-free electrocatalyst is discussed. Vapor phase polymerizations of PEDOT on SWNT network generate SWNT/PEDOT nanocomposite with high surface area and good electrical conductivity with more catalytically active sites for ORR. Hence, the nanocomposites have significant electrocatalytic activity for the selective one step four-electron reduction of oxygen to water in alkaline fuel cell operating environment. The high efficiency of SWNT/PEDOT modified electrodes to ORR electrocatalysis as compared to pure PEDOT, is reflected by the lower onset potential, higher peak current and faster kinetics. These features combined with the cost and ease of preparation of the electrode, suggest this material as an attractive candidate for metal-free cathodes in a fuel cell.
5.6 References

Chapter 6 Simple Production of Graphene Sheets by Direct Dispersion with Aromatic Healing Agents

6.1 Introduction

Graphene exhibits remarkable properties therefore attractive for various novel applications. One of many appealing applications of graphene would be to fabricate transparent conductive films to replace indium tin oxide (ITO). The use of graphene is promising due to its high optical transmittance, low resistance, high chemical stability, and high mechanical strength.1-2 This as well as other applications require a large quantity of high-quality graphene as the basic component.3 Among the reported methods to prepare graphene, liquid phase methods have drawn tremendous attraction due to their scalability, and ease of functionalization.4 Compared to chemical vapor deposition approaches, which produced graphene films with the highest conductivity yet obtained,5 one advantage of liquid phase methods is that the produced graphene can be conveniently deposited on any substrate with simple processing, such as spin-coating or inkjet-printing on plastic substrates. Therefore, liquid-based techniques have the potential to realize large scale organic devices including photovoltaic cells.

Most of the liquid phase methods involve oxidation of graphite and subsequent exfoliation to form graphene oxide (GO) suspensions. While GO is not very conductive, it must be reduced to graphene by toxic hydrazine and/or by annealing at high temperatures in inert conditions to recover much of its electrical conductivity.6-8 Another significant disadvantage of these methods is that the structural defects formed during the oxidation process, which dramatically degrade the unique electronic properties of
graphene and therefore affect its applications, are virtually impossible to repair completely. Recently, Bao and colleagues found that high temperature annealing is the most effective method to reduce GO to conductive graphene. However, even after annealing at 1100 °C, residual C=O and C-O bonds were still observed by X-ray photoelectron spectroscopy (XPS).\textsuperscript{9-11}

Recently, it was reported that graphite can be directly exfoliated in certain solvents such as hexafluorobenzene to give defect-free monolayer graphene.\textsuperscript{2,12-14} However, these solvents are expensive and require special care when handling. In addition, these solvents tend to have high boiling points, and are difficult to completely remove. The residual solvents result in poor electronic contacts between graphene sheets and therefore lower the overall conductivity of the resulted multi-sheet graphene films. Coleman et al. reported a liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions.\textsuperscript{15} However, the residuals surfactant, similar to the solvents with high boiling points, is difficult to remove.

Here we report a simple and scalable exfoliation approach to produce high quality single layer graphene sheets. In a typical experimental procedure, graphite powders were exfoliated by sonicating in an aqueous solution of pyrene molecules that had been functionalized with different water soluble groups. Highly conductive graphene sheets stabilized in aqueous suspension were directly produced without requiring toxic reducing agents and expensive solvents. Most importantly, different from other surfactants and polymers that have been used to prevent graphene sheets from aggregation in solution, the pyrene molecules also act as nanographene molecules to heal the possible defects in the graphene sheets during annealing.\textsuperscript{16} Remarkably, they also appear to act as electrical
“glue” soldering adjacent graphene sheets such that electric contacts between graphene sheets can be dramatically improved across the film. Graphene films with conductivity of 181,200 S/m (778 Ω/square) with light transmittance greater than 90% in the 400–800 nm wavelength range are reproducibly obtained, which is the highest conductivity values ever achieved for graphene films fabricated by graphite exfoliation approaches (note that graphene films fabricated by chemical vapor deposition (CVD) method can reach 200 Ω/square at 80% optical transparency\(^5\)). Nevertheless, this simple and scalable approach is extremely promising to produce high quality graphene films for a wide range of optoelectronic applications, including photovoltaics. Here, a nanocomposite of PEDOT/PY-SO3-G is synthesized and its electrocatalytic ability to reduce oxygen is demonstrated.

6.2 Experimental Section

6.2.1 Materials and Methods

Synthetic graphite powder (< 20 µm), 1-pyrenemethylamine (Py-NH\(_2\)) hydrochloride from Sigma Aldrich, and 1,3,6,8-pyrenetetrasulfonic acid (Py-SO\(_3\)) tetrasodium salt hydrate from Acros Organic were purchased and used as received. All solutions were prepared using deionized water (18.2 MΩ) (Nanopore water, Barnstead), which was also used to rinse and clean the samples.

6.2.2 Dispersion of graphene with pyrene molecules

Stock solutions of Py-NH2 and Py-SO\(_3\) with a concentration of 0.4 mg/ml were prepared in deionized water by vigorous stirring for 1 hour. Graphite powder was added into the resultant solutions, in which the weight ratio between the pyrene derivatives to the
graphite powder is 4:1. Direct exfoliation of graphite to graphene sheets was performed by sonication of the obtained mixture solution with Sonics VX-130 (130W, 45%) in an ice bath. The exfoliation process was monitored by recording the fluorescence spectra of the suspension at different exfoliation period. All fluorescence measurements were performed using a Cary-Eclipse fluorescence spectrophotometer (Varian, Inc, Palo Alto, CA). The obtained grey dispersion was then centrifuged at 4000 r.p.m. for 20 minutes to remove un-exfoliated graphite using a Beckman J2-21 centrifuge (usually very small amount). The supernatant containing graphene sheets was dialyzed three times with an Amicon YM-50 centrifugal filter unit (Millipore) to remove most of the free pyrene molecules. The removal of free pyrene was monitored by measuring UV-vis and emission spectra of the solution after each dialysis. The yield of graphene sheets was estimated to be 50%. The resulted solution was directly used to prepare graphene films with a vacuum filtration method.

6.2.3 Characterization

The Py-NH₂ and Py-SO₃ exfoliated graphene samples (after being extensively dialyzed, normally 25 times for Py-NH₂ and 10 times for Py-SO₃) were imaged with a tapping mode Nanoscope IIIa atomic force microscope (Veeco instrument, Santa Barbara, CA, USA) in air. In order to image the graphene sheets, 2 μL of the prepared solutions were deposited on freshly cleaved mica. After a 3–5 min incubation, the mica surface was rinsed with 1 drop of DI water and dried in a fume hood for 20-30 mins. During imaging, a 125 μm long rectangular silicon cantilever/tip assembly (Model: MPP-12100, Veeco) was used with a resonance frequency of approximately 127-170 kHz, a spring constant of approximately 5 N/m, and a tip radius of less than 10 nm. The applied frequency was set
on the lower side of the resonance frequency and scan rate was ~1.0 Hz. Height differences were obtained from section analysis of the topographic images. In the figures variations in height are indicated by color coding.

XPS spectra were taken with a Perkin-Elmer hemispherical analyzer with a non-monochromatic Mg Kα x-ray source (hv =1253.6 eV). At 17.9 eV pass energy, the full width at half maximum (FWHM) of the Cu 2p 3/2 core level is 1.2 eV. All core level photoemission peaks were referenced to the Au 4f 7/2 peak with a binding energy of 83.7 eV.

Raman spectra were acquired with a micro-Raman spectroscopy (Renishaw 1000) assembled with a confocal imaging microscope, with an excitation energy of 1.96 eV (632.8 nm) and power around 0.1 W~0.3 W. Spectra are acquired using a 30 s exposure time and two accumulations.

UV-Vis-NIR absorption spectroscopy was used to characterize the electronic states of the exfoliated graphene sheets. All spectra were obtained using a Cary 500 visible-near-infrared (UV-Vis-NIR) spectrophotometer in double-beam mode.

Graphene films with different thickness were prepared from the corresponding suspension by vacuum filtration using Anodisc 47 inorganic membranes with 200 nm pores (Whatman Ltd.). After filtration, the thin films were dried in air for 15-20 min. The sheet resistance of the films was determined by a 302 manual four point resistivity probe (Lucas Laboratories). To study the optical properties, these films were transferred from the anodisc filter membranes onto polydimethylsiloxane (PDMS) sheets and the sheet transmittance was measured using a Cary 500 UV-vis-NIR spectrophotometer in double-beam mode in the wavelength range of 400 – 800 nm. The reported transmittance here
was corrected by subtracting the absorption of the same thickness PDMS sheet at each wavelength from the measured absorption curves.

To make a transparent and highly conductive film, graphene films on quartz were prepared by drop coating. The films were annealed at different temperatures with a Lindberg Blue oven in high purity Ar. Electrical and optical properties of the annealed films were measured after being cooled to room temperatures.

6.3 Results and Discussion

6.3.1 Direct Dispersion of Graphene by Sonication in the Presence of Pyrene Derivatives

Several works have reported that the excimer emission of pyrene was quenched when GO was reduced in the presence of pyrene molecules functionalized with different water soluble groups, which has been ascribed to the effective electron or energy transfer between the reduced conductive graphene and pyrene moiety of the molecules. \(^{17-18}\)

Similar quenching phenomena were observed when pyrene derivatives were used to disperse carbon nanotubes, which was explained by energy transfer from the pyrene moieties to the nanotubes. We hypothesize that similar quenching phenomena would occur during direct exfoliation of graphite and therefore we used fluorescence spectroscopy to monitor the exfoliation process.

Figure 6.1a shows the fluorescence spectra (excited at 340 nm) of 1-pyrenemethylamine hydrochloride (Py-NH\(_2\))/graphene suspension at different sonication period. Prior to sonication, the spectrum shows a big peak at 501 nm which was ascribed to the excimer emission of pyrene derivatives. \(^{18-19}\) We found that the intensity of this peak largely decreased after 2 hours of sonication. At the same time, we observed a dramatic increase in the peak at 400 nm and a new sharp peak at 385 nm. These fluorescence behaviors
were virtually the same as those of the Py-NH$_2$ aqueous solutions alone when the concentration of Py-NH$_2$ is below its critical micelle concentration, suggesting that the fluorescence from the graphene/Py-NH2 solution is derived from the non-bound (free) Py-NH$_2$ monomers in the solution. The obtained solution was deep grey and stable for two days without any observable aggregation and precipitation. To remove the free Py-NH$_2$ molecules, the solution was extensively dialyzed against DI water (25 times) until the monomer fluorescent peak was almost non-observable. After this extensive dialysis, the solution becomes less stable. A small amount of aggregation and precipitation can be seen after 12 hours.

A similar trend was observed when exfoliation of graphite was performed by sonication in the presence of 1,3,6,8-pyrenetetrasulfonic acid (Py-SO$_3$) (Figure 1b). However, compared to the case of Py-NH$_2$, a shorter period of sonication was required to diminish the excimer peak at 501 nm and also fewer times of dialysis were needed to remove the free Py-SO$_3$ monomers. We think these subtle differences may be due to the different solubility of the two pyrene molecules.

It was reported that pyrene molecules with ionic pendant groups easily form micellar architectures of aggregates due to their amphiphilic nature. The critical micelle concentration of pyrene molecules is as low as 10$^{-7}$ M, which may change depending on the functional groups of the pyrene rings.$^{19}$ The intrinsic fluorescence of pyrene derivatives above its critical micellar concentration was ascribed to its excimer emission.$^{20}$ With sonication, the excimer emission gradually disappeared and was replaced with its monomer emission, indicating that some pyrene molecules adsorbed onto the graphene surface and the equilibrium in the solution phase shifted towards
monomers of pyrene (Scheme 1). The large planar aromatic structures of pyrene molecules can strongly anchor themselves onto the hydrophobic surface of graphene sheets via $\pi-\pi$ interactions and yield stable solutions of graphene/pyrene hybrids.\textsuperscript{18,21} The negative and positive charges in both dispersion molecules act as stabilizing species to maintain a strong static repulsion force between the charged graphene sheets in solution, similar to the scenario when SWNTs were dispersed by 1-(trimethylammonium acetyl) pyrene.\textsuperscript{19}

\textbf{Figure 6.1} Fluorescence spectroscopy to monitor the direct exfoliation process in the presence of (a) Py-NH$_2$ and (b) Py-SO. Inset: a picture of the resulting graphene suspension.
Scheme 6.1. Schematic drawing shows that with sonication, graphite was exfoliated to graphene sheets, which dramatically increased the surface area for pyrene molecules adsorption (here using Py-SO$_3$ as an example). Therefore the concentration of free pyrene molecules in the solution was dramatically decreased; consequently, the excimer emission gradually disappeared and was replaced with its monomer emission of Py-SO$_3$.

6.3.2 AFM measurements

We used atomic force microscopy (AFM) to characterize the obtained graphene sheets. Figure 6.2A shows a typical tapping mode AFM image of graphene/Py-NH$_2$ hybrids (Gr-Py-NH$_2$) deposited on a freshly cleaved mica surface. The size of the graphene patches are in the micrometer range. The thickness of a single layer Gr-Py-NH$_2$ ranges from 0.7 to 1.1 nm with an average of 0.9±0.3 nm, measured from cross-section pictures, as shown in Figure 6.2C. The variation of thickness was attributed to the possible inhomogeneous coverage of Py-NH$_2$ molecules on the graphene surface or simply due to the AFM system noises. Figure 2B shows a typical picture of graphene/Py-SO$_3$ hybrids (Gr-Py-SO$_3$). Compared to the Gr-Py-NH$_2$ sheets, there are some holes with diameters ranging from 20 nm to 500 nm randomly arranged on the Gr-Py-SO$_3$ graphene sheets. Single layer graphene shows an average thickness of 1.3 nm (Figure 6.2D). Besides the large quantities of single-layer, double-layer graphene with a thickness of 2.6 nm was also
observed on the surface, corresponding to the tandem sandwich structures of Gr-Py-SO$_3$. It was reported that the interlayer distance between pyrene molecules and graphene sheets is 0.35 nm in the graphene hybrid prepared by reduction of GO in the presence of pyrene-1-sulfonic acid, and the pyrene molecules are mainly arranged face-on on both sides of the graphene sheet in a sandwich-like manner.\textsuperscript{18,21} It is not known yet how Py-SO$_3$ and Py-NH$_2$ are arranged on the graphene sheets in the Gr-Py-SO$_3$ and Gr-Py-NH$_2$ hybrids prepared here, which needs further studies. The slight difference in the thickness of single layer Gr-Py-SO$_3$ and Gr-Py-NH$_2$ may indicate that the density and the arrangement of Py-SO$_3$ and Py-NH$_2$ on the graphene sheets were different. It has been reported that a thickness of more than 1 nm for single layer graphene sheets by reduction of GO are often observed, which is much larger than the theoretical value of 0.34 nm. This difference has been attributed to some unreduced surface oxygen-containing functional groups.\textsuperscript{23} So it is also possible that the graphene sheets in these two hybrids consisted of different amounts of oxygen-containing functional groups. Nevertheless, the thicknesses for both of the graphene-pyrene hybrids are smaller than the hybrids prepared by reduction of GO in the presence of pyrene directives (1.7 nm).\textsuperscript{18,21} This deviation in thickness may indicate that fewer oxygen-containing functional groups, therefore fewer defects were introduced by our simple approach reported here. UV-Vis-Near IR spectroscopy, x-ray photoelectron spectroscopy, and Raman spectroscopy were used to characterize the hybrids.
Figure 6.2 Atomic force microscopic (AFM) images of the graphene sheets on mica substrate (A) Gr-Py-NH$_2$ and (B) Gr-Py-SO$_3$. Panel (C) and (D) are the section analysis of the AFM image (A) and (B) respectively along the black line. The arrows in the pictures help to see the height of the graphene sheet.

6.3.3 UV-Vis-Near IR spectroscopy measurements

UV-Vis-Near IR spectroscopy measurements of the obtained hybrid suspensions demonstrated that graphene sheets were directly produced without the toxic chemical reduction procedure. It is known that the GO solutions, prepared by the commonly used Hummer and modified Hummer methods,$^{24}$ shows two main features in their UV-Vis spectra: (1) a peak at 233 nm, which is due to $\pi$-\(\pi^*\) of C=C, and (2) a shoulder at ~290-300 nm, corresponding to $n$-\(\pi^*\) transition of the C=O bond.$^{25}$ Figure 6.3 shows that after extensive dialysis, the direct exfoliated graphene solutions, both Gr-Py-NH$_2$ and Gr-Py-
SO₃, displayed an absorption maximum at 265 nm with significant tailing in the red region (note before dialysis of the solution, the absorption was dominated by the pyrene derivatives in the UV-Vis spectra). The spectra are similar to that of GO suspension after reduction by NaBH₄ and hydrazine,¹⁷ demonstrating again the π-conjugation of graphene sheets is largely retained during the direct exfoliation process.

![UV-Vis Spectra](image)

**Figure 6.3** UV-Vis Spectra of the Graphene suspension dispersed by Py-NH₂ and Py-SO₃. For comparison, the UV-Vis Spectrum of graphite oxide suspension, prepared by the traditional Hummer’s method was also showed here.

### 6.3.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to characterize the graphene hybrid after deposition from the suspensions onto a gold film (a 100 nm gold layer was sputter-coated on silicon with a 10 nm Ti adhesion layer). The thickness of the graphene hybrids on the gold substrates is roughly 30 nm. The XPS spectra of the two hydrides are shown in Figs.6.4. The C1s signal
consisted of 4 different peaks: C=C/C-C in aromatic rings (284.6 eV); C-O (286.1 eV); C=O (287.5 eV) and C(=O)-OH (289.2 eV), consistent with literature assignments.\textsuperscript{10} If a homogenous distribution of carbon and oxygen throughout the bulk of the sample is assumed, the C/O ratio for Gr-Py-NH$_2$ is \~10.7 and for Gr-Py-SO$_3$ is \~5.3 (after excluding the oxygen contribution from the SO$_3$ groups). This represents \~4 times and \~2 times the C/O ratio (\~2.5) associated with the pristine GO produced by Hummer's method.\textsuperscript{26} The sp$^2$ C-C component in the as-produced Gr-Py-NH$_2$ and Gr-Py-SO$_3$ hybrids is 76\% and 62\%, (sp$^2$ C/total C + O) respectively. The total oxygen component in the as-produced Gr-Py-NH$_2$ and Gr-Py-SO$_3$ hybrids is 8.5\% and 16\%, respectively. This calculation demonstrates that less defects exist in the Gr-Py-NH$_2$produced films made than those made with Gr-Py-SO$_3$ hybrids, consistent with the AFM study described above. Note that the sp$^2$ C-C and oxygen components in both as-produced hybrids are very close to the maximum carbon sp$^2$(80\%) and minimum oxygen fraction (8\%) of reduced GO upon annealing at 1100 °C \textsuperscript{26}, further confirming that we can produce high-quality graphene sheets with less oxidation.
Figure 6.4 C1s XPS spectra collected on 30 nm as produced graphene hybrids deposited on gold substrates: (A) Gr-Py-NH$_2$ film and (B) Gr-Py-SO$_3$ film. The spectra were fit by Doniach-Sunjic function after the substraction of Shirley background.

6.3.5 Raman spectroscopy measurements

Raman spectroscopy was used to characterize the obtained hybrid suspensions after deposition onto a Si substrate with a 300 nm thick SiO$_2$ layer. The typical features of the G band at 1585 cm$^{-1}$ and the D band at 1335 cm$^{-1}$ are shown in the Raman spectra (Figure 6.5), which agrees well with the literatures by direct exfoliation approaches. $^{12,14-15}$ The G band is usually assigned to the $E_{2g}$ phonon of C sp$^2$ atoms, while the D band is a breathing mode of κ-point phonons of $A_{1g}$ symmetry. The $A_{1g}$ mode is attributed to particle size effects due to the existence of specific vibrations at the edges of graphene sheets. The appearance of a prominent D band in the spectrum is also an indication of disorder in graphene originating from the defects associated with vacancies and grain boundaries. $^{27-28}$ It has been well documented that the size of the defect free sp$^3$ cluster regions is the inverse of the ratio of the D and the G band integrated intensities ($I_D/I_G$). $^{29}$ This correlation has been used to determine the size of sp$^2$ domains in various carbon materials including graphene. $^{28-29}$ After baseline correction, the intensity ratio ($I_D/I_G$) of
the D band to the G band of the hybrid suspensions was calculated to be 0.64, which is much lower than those graphene sheets obtained from reduction of GO by hydrazine ((I_D/I_G≈ 1.44)\(^{30}\) and the recently reported sodium hydride reduction process (I_D/I_G≈ 1.08)).\(^{31}\) It is even smaller than that achieved by the supercritical-water-based reduction process (I_D/I_G≈ 0.9),\(^{32}\) and the 180 °C solvothermal reduction process (I_D/I_G≈ 0.9).\(^{33}\) Therefore, similar to the other reported direct exfoliation approaches,\(^{2,12-15}\) the simple exfoliation approach provided in this work can also produce graphene sheets with much less defects.

Using the empirical Tuinstra-Koening relation,\(^{28}\) we found that the size of the ordered crystallite graphitic domain was≈ 7.0 nm in the as-produced Gr-Py-SO\(_3\). It has been demonstrated that large sp\(^2\)domain sizes that are minimally interrupted by defects are essential for obtaining exceptional high conductivity and mobility in reduced GO. The large domain sizes in the as-produced graphene hybrids further demonstrate the high quality of the graphene sheets dispersed by this simple method. Furthermore, after annealing at 1000 °C for 6 mins, the ratio of I_D/I_G further decreased to 0.46, corresponds to an increase in sp\(^2\) domain size to ≈9.6 nm. This suggests that the annealing of the hybrid films can further recover the aromatic structures by repairing defects. This observation is very different from the recent reports by Chhowalla et al. who systematically studied de-oxidation and structural evolution of GO during thermal annealing by XPS and Raman spectroscopy.\(^{10-11}\) They found that annealing GO at different temperatures, even at 1100 °C, did not increase the size of defect-free sp\(^2\)domain significantly, even though the sp\(^3\) carbon–carbon bonds were restored by de-oxidation. They explained this observation as the generation of vacancies in the lattices
and dangling bonds from the detachment of CO groups, especially at high temperatures. However, our result is consistent with the report by Mullen et al.\textsuperscript{21} Pyrene molecules in graphene hybrids can be decomposed under thermal annealing, which induced a thermal reaction between pyrene and graphene sheets and resulted in a better $\pi$-conjugation of graphene basal plane. Therefore, larger defect-free sp$^2$ domain sizes were produced and the conductivity of graphene films was increased dramatically.

![Raman spectra of Gr-Py-SO$_3$ deposited on Si substrate with 300 nm layer of SiO$_2$.](image)

**Figure 6.5** Raman spectra of Gr-Py-SO$_3$ deposited on Si substrate with 300 nm layer of SiO$_2$.

### 6.3.5 Optical and Electrical Properties

We prepared graphene films from the obtained suspensions with different thickness by a vacuum filtration method through an anodisc filter membrane.\textsuperscript{6,34} To understand if the performance of the graphene film can replace ITO in solar cell and other optoelectronic applications, we studied the electrical properties of the graphene sheets by measuring the sheet resistance of the corresponding graphene films with a four-probe approach. To
study the optical properties, these films were transferred from the anodic filter membranes onto polydimethylsiloxane (PDMS) sheets and the sheet transmittance was measured in the wavelength range of 400 – 800 nm. The reported transmittance here was corrected by subtracting the absorption of the same thickness PDMS sheet at each wavelength from the measured absorption curves. As expected, the graphene films show a percolation electronic behavior. The sheet resistance and the transmittance of the graphene film decrease with increasing the amounts of graphene used to prepare the films, as shown in Figure 6.6. Gr-Py-NH$_2$ films reach percolation slightly earlier than the Gr-Py-SO$_3$ films. After reaching the percolation threshold, the sheet resistance of the Gr-Py-NH$_2$ films is 1.3 k$\Omega$/square at a transmittance of 41%, and the sheet resistance of the Gr-Py-SO$_3$ films is 1.1 k$\Omega$/square at a transmittance of 40%. These correspond to a DC conductivity of 1900 S m$^{-1}$ and 2150 S m$^{-1}$ for Gr-Py-NH$_2$ and Gr-Py-SO$_3$, respectively (The thickness of the film was estimated according to the reports by Bao et al.$^9$ and Mullen et al.$^{35}$). Even though these values are slightly better than that of sodium dodecylbenzene sulfonate (SDBS) directly exfoliated graphene films reported by Coleman et al.$^{15}$ (35 S m$^{-1}$ before annealing), they are still much lower than the films prepared from N-methyl-pyrrolidone-based dispersions$^{12}$ (6500 S m$^{-1}$). We believe the low conductivity was due to the presence of residual pyrene molecules on graphene sheets. Similar to the case of SDBS, the nonconductive pyrene molecules largely impede the electrical contact between graphene sheets in the film, which results in the low conductivity of the films.

However, different from SDBS,$^{15}$ which is difficult to be removed completely, the pyrene molecules here can serve as nanographene building blocks to heal defects in the graphene
Therefore, we expect that graphene films with high transparency and high conductivity can be fabricated, which can be used as an ITO replacement material for solar cell and other electro-optical applications. To make a transparent and highly conductive film, we prepared films on quartz by drop coating with a sheet resistance of $1.9 \times 10^8 \ \Omega \cdot m^{-1}$ and transmittance of 90% between a wavelength range of 400-800 nm. The samples were annealed at different temperatures before being cooled to room temperatures for various measurements. As demonstrated in Figure 6.7, the thermal annealing at 400 ºC decreased the sheet resistance to $3.5 \times 10^7 \Omega$/square and $4.5 \times 10^6 \Omega$/square for Gr-Py-NH$_2$ and Gr-Py-SO$_3$, respectively. At 1000 ºC, the sheet resistance was further decreased to $1.7 \times 10^4 \Omega$/square and 778 $\Omega$/square at 90% transmittance (between 400-800 nm wavelength range), which correspond to conductivities of 8400 S m$^{-1}$ and 181,200 S m$^{-1}$ for Gr-Py-NH$_2$ and Gr-Py-SO$_3$, respectively. Note that the conductivity of the graphene prepared from the graphene suspensions with extensive dialysis did not increase significantly. The purity of Ar is also critical for the successful healing of the graphene, otherwise the films can be quickly lost, likely through reactions with residual oxygen in the system. From studies by AFM, UV-Vis-Near IR spectroscopy, X- XPS, and Raman spectroscopy, we understand that more defects existed in Gr-Py-SO$_3$ films compared to those of Gr-Py-NH$_2$, so it is a surprise to us that the conductivity of Gr-Py-SO$_3$ films increased much faster than those of Gr-Py-NH$_2$ upon annealing. Currently we are studying the annealing mechanism by in-situ XPS studies to explain this interesting observation, which will be reported later. Nevertheless, it is worth to mention that films prepared from reduced graphene oxide have displayed conductivities ranging from 7200 S m$^{-1}$ to 10,200 S m$^{-1}$.

In addition, Mullen et al. $^{21}$
reported that high temperature annealing graphene/pyrene composites (at 1100 °C) which were obtained by reduction of GO in the presence of pyrene derivatives led to graphene films with conductivity around 110,000 S m⁻¹. Therefore, the conductivity of the graphene films combined with the high transparency by our approach reached the highest conductivity values ever achieved for graphene films from liquid exfoliation processes, which make our simple and scalable approach extremely attractive to produce high quality graphene films.

We believe that the remarkable high performance of the graphene films is due to our unique fabrication method which dramatically reduced structural defects in individual graphene sheets and also improved the electrical contacts between graphene sheets in the films. First, the direct exfoliation of graphite powder in the presence of pyrene derivatives produced graphene sheets with fewer defects compared to the traditional GO-reduction methods.²,¹²,¹⁵ In addition, the novel reparative thermal annealing of the graphene films, in which the pyrene derivatives acted as healing agents during thermal treatment, further repaired some of the defects.²¹ Most importantly, the electrical contacts between graphene sheets in the film are also dramatically improved. The pyrene molecules which originally adsorbed on both sides of the graphene sheets may chemically graft onto the edge of adjacent graphene sheets and electrically “glue” them together during the thermal annealing process.
Figure 6.6 (a) Sheet resistance of the graphene films as a function the weight of the graphene sheet in solution to prepare the graphene films. (b) Sheet resistance of the graphene films as a function of the transmittance of the corresponding films.

Figure 6.7 (a) The sheet resistance of thin graphene films prepared on quartz substrates by drop coating as function of the annealing temperatures. The concentration of graphene for both of the hybrid suspension is roughly 0.1 mg/L. (b) The corresponding optical transmittance of the films.
6.3.6 Fabrication of graphene PEDOT nanocomposite for Oxygen Reduction Reaction.

As we mentioned in the first chapter, increase in surface area of an electrocatalyst is important for an efficient ORR. Due to high surface area and excellent electron transfer properties of graphene, we assumed that a nanocomposite of PEDOT with graphene would be an efficient electrocatalyst to reduce oxygen. In order to test this hypothesis, a nanocomposite of PY-SO$_3$-G with PEDOT is fabricated by vapor phase polymerization method following the same procedure as described in previous chapter. Hence, fabricated nanocomposite was employed as a catalyst material for oxygen reduction reaction in 0.1M KOH solution. Fig 6.8 shows the cyclic voltammograms recorded in both Ar and O$_2$ saturated 0.1 M KOH. Cyclic voltammograms exhibited that oxygen reduction proceeds at an onset potential of ~ -0.15 V and a peak potential for ORR is observed at ~ -0.32 V. This value of onset potential is comparable to the SWNT/PEDOT nanocomposite modified electrode. This preliminary result demonstrates that graphene we synthesized above, have potential to replace carbon nanotube based electrode and thus to minimize the costs of fuel cell devices by reducing the manufacturing expenses associated with CNT productions. A nanocomposite with highly porous graphene structure containing more graphitic edges can further improve the electrocatalytic ability towards ORR. However, a detail investigation of PEDOT/graphene nanocomposite for oxygen reduction reaction is required, which is an ongoing work in our research group.
6.4 Conclusions

In summary, we developed a simple and scalable exfoliation approach to produce high quality single layer graphene sheets (rather than non-conductive graphene oxide) in one step, which can be used to fabricate transparent conductive films. Compared to the traditional graphene oxide (GO) approach to produce conductive graphene sheets, there is no oxidation and reduction reaction of GO involved. Toxic and expensive solvents are not needed. Our method decreases the number of preparation steps and significantly shortens production time. Compared to other direct exfoliation methods, this method does not require high boiling point solvents. The lack of residual solvents and other impurities results in much better electrical contacts between graphene sheets needed to produce
highly conductive graphene films. In a typical experimental procedure, graphite powders were exfoliated in a water solution of pyrene derivatives with the help of sonication. The pyrene derivatives acted as dispersion agents during the exfoliation process, and also acted as healing agents and electric “glue” during the thermal annealing process. Transparent conductive films fabricated with this approach exhibit a conductivity of 181,200 S/m (sheet resistance of 778 Ω/square with 90% light transmittance in the 400–800 nm wavelength range), the best to date of which we are aware. Transparent conductive graphene films are promising candidates to replace transparent conductive oxides (TCOs) for PV/solar cell applications. nanocomposite of PEDOT/PY-SO$_3$-G demonstrated a potential applications to use as an electrocatalyst for ORR.

6.5 References

(11) Mkhoyan, K. A.; Contrynman, A. W.; Silcox, J.; Stewart, D. A.; Eda, G.; Mattevi, C.; Miller, S.; Chhowalla, M. *Nano Lett.* 2009, 9, ASAP.

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