Novel nanostructured electrodes

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University of Wollongong


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NOVEL NANOSTRUCTURED ELECTRODES

A thesis submitted in fulfillment of the requirements
for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

YONG LIU, B.Sc

Department of Chemistry

August 2007
To my affectionate parents for their self-giving assistance and persistent encouragement.

To my deeply beloved wife Junjun Wei for her continued support and love.
CERTIFICATION

I, Yong Liu, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Yong Liu

August 2007
ACKNOWLEDGEMENTS

I would like to greatly thank my supervisors, Professor Gordon G. Wallace, Dr. Jun Chen and Dr. Violeta Misoska for their enthusiastic supervision, technical advice, persistent support and kind encouragement throughout the course of my study.

The continued assistance and valuable suggestions from Associate Professor Chee O. Too is deeply appreciated.

I am also grateful to all staff and students in the Intelligent Polymer Research Institute, especially Dr. Caiyun Wang, Dr. Binbin Xi, Adrian Gestos and Weimin Zhang for their help in the laboratory; Dr. Kerry Gilmore and Xiao Liu for cell culturing; Dr. Simon Moulton and Dr. Peter Innis for Raman characterisation; Dr. Vahid Mottaghtalab for viscosity measurements; and Jenny Halldorsson for help in surface tension testing. Much appreciation also goes to Dr. Jian Wu, Dr. Philip Whitten, Dr. Syed Ashraf, Dr. Orawan Ngamna, Dr. Fatemeh Masdar, Dr. George Tsekouras, Mehrdad Samani, Phil Smugreski, Rebecca Potter, Scott McGovern and Jakub Mazurkiewicz for their kind assistance.

The continued financial support of the Australian Research Council is gratefully acknowledged.


ABSTRACT

Nanotechnology provides an effective and direct way to create novel properties and phenomena through the reduction in material sizes without changing the materials’ chemical composition. A number of routes to the preparation of novel nanostructured electrodes were investigated in this thesis. These involve the formation of nanoporous opaline electrodes, three dimensional nanofibrous networks and the synthesis of flexible nanoelectrodes based on highly dense ordered aligned carbon nanotubes and conducting polymers. Excellent improvements with the use of nanostructures in a wide range of application areas such as methanol oxidation, photoelectrochemical cells, enzyme biosensors, cell culturing and energy storage are presented in this research work.

Nanoporous opaline structures including inverse opals and opals were prepared by either electrodepositing Pt or sputter coating ITO onto self-assembled polystyrene (PS) synthetic opals, followed by the removal of the PS opal templates. A highly ordered dense nanoporous structure with the porous structure on the top (so-called Pt inverse opal) or with the porous structure on the bottom (so-called ITO opal) was consequently obtained after the removal of PS templates. The improvement in electrochemical area with the use of nanostructures was observed during electrochemical characterisation. The resultant nanostructured Pt inverse opal
electrodes were employed in electro-oxidation of methanol. Compared with the Pt film electrode, the nanostructured Pt inverse opal electrode showed a higher catalytic performance and good stability with a 100 mV negative shift of the potential of methanol oxidation. The mesoporous ITO opal electrode was used as the substrate for the electrodeposition of polyterthiophene and the resultant structure was subsequently utilized in photoelectrochemical cells. An excellent power-conversion efficiency of 0.109\% and an outstanding short circuit current density of 1470 μA•cm⁻² for polyterthiophene deposited at room temperature were obtained; dramatically improved from the previous published work.

Nanofibrous electrodes were fabricated from biomaterials (such as DNA and poly(styrene-β-isobutylene-β-styrene) (SIBS)) and single-walled carbon nanotubes (SWNTs) using the electrospinning technique. Initial studies quantitatively determined the influence of solution properties (such as the solution ionic conductivity, surface tension and viscosity) and process parameters (e.g. tip-to-collector distance, applied potential and the feed rate) on the electrospinning results. Results showed that good electrospun fibrous networks could be obtained from the solution with comparatively high conductivity and viscosity with low surface tension. It was also found that the average diameter of the electrospun fibers decreased with decreased feed rates, increased tip-to-collector distance and increase in the potential employed. With the addition of SWNT, both biomaterial nanofiber electrodes exhibited enhanced electrochemical properties. The resulting DNA based
electrospun fiber electrode showed a broad linearity range and high sensitivity in enzyme biosensors. The SIBS/SWNT nanofibrous electrode demonstrated excellent biocompatibility and suitability for the growth of L-929 cells.

Flexible, light and highly conductive nanostructured electrodes were prepared from aligned carbon nanotubes (ACNTs) and conducting polymers by coating with Pt coated poly(vinylidene fluoride) (PVDF) or poly(3,4-ethylenedioxythiophene) (PEDOT)/PVDF. Pt nanoparticles were subsequently electrodeposited on the ACNT/Pt/PVDF structure. The utilization of the nanostructured ACNT/conducting polymer electrodes in anodic methanol oxidation and as anodic materials in Lithium-ion batteries was demonstrated. Pt nanoparticles coated ACNT/Pt/PVDF electrode exhibited an outstanding electrochemical capacity (133 Fg$^{-1}$) and amazing electrochemical surface area (143 m$^2$g$^{-1}$ for Pt nanoparticles). The Pt nanoparticles-ACNT/Pt/PVDF electrode also showed a 2.5 times higher steady current density for methanol oxidation when compared with the ACNT/Pt/PVDF electrode. A stable current density over a long period (more than 12 hours) was obtained. A 50% improvement in capacity during Lithium-ion battery tests when compared with a SWNT paper was obtained with the ACNT/PEDOT/PVDF electrode.

Nanostructured flexible and conductive electrodes were also obtained from ACNTs and biomaterials (such as SIBS and poly(lactide-co-glycolide)). SWNTs or Pt were
introduced to improve the conductivity. A significant improvement in electrochemical
dproperties with the addition of Pt or SWNT was obtained. The biocompatibility of
ACNTs, SWNTs and Pt was confirmed during cell culturing experiments.
# ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>2D</td>
<td>two dimension</td>
</tr>
<tr>
<td>3D</td>
<td>three dimension</td>
</tr>
<tr>
<td>ACNT</td>
<td>aligned carbon nanotube(s)</td>
</tr>
<tr>
<td>Ag/Ag⁺</td>
<td>silver/silver ion reference electrode</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>silver/silver chloride reference electrode</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube(s)</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammogram</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>D</td>
<td>dye</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>ΔE</td>
<td>separation of anodic and cathodic peak potentials</td>
</tr>
<tr>
<td>Eₚᵢ</td>
<td>final potential value</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>initial potential value</td>
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<tr>
<td>Eₚₐ</td>
<td>peak anodic potential</td>
</tr>
<tr>
<td>Eₚₑ</td>
<td>peak cathodic potential</td>
</tr>
<tr>
<td>Eₛ</td>
<td>switching potential value</td>
</tr>
<tr>
<td>EAS</td>
<td>electrochemical active surface</td>
</tr>
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EC  ethylene carbonate
EM  electromagnetic
El_{ox}  the oxidized phase of the redox mediator
El_{red}  the reduced phase of the redox mediator
eV  electron-volt
Fe (III) tosylate  ferric p-toluenesulfonate
FePc  iron (II) phthalocyanine
FF  fill factor
GOx  glucose oxidase
g  gram
hr  hour
I_1  light intensity
i_{pa}  peak anodic current
i_{pc}  peak cathodic current
I_{sc}  short circuit current
ICP  inherently conducting polymer
IOp  inverse opal
ITO  indium tin oxide
kHZ  kilohertz
kV  kilovolt
LSV  linear sweep voltammetry
m  meter
M  molar
mA  milliampere
MeOH  methanol
mg  milligram
min  minute
mL  milliliter
mm  millimeter
mN  millinewton
mPa  millipascal
MWNT  multi-walled carbon nanotube(s)
n  number of electron
nm  nanometer
NMP  n-methyl-2-pyrrolidinone
$P_{ph}$  incident photon power
PBG  photonic band gaps
PBS  phosphate buffer solution
PC  propylene carbonate
PCE  power-conversion efficiency
PEC  photoelectrochemical cell
PEDOT  poly(3,4-ethylenedioxythiophene)
PEO  poly(ethylene oxide)
PLGA  poly(lactide-co-glycolide)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>PP</td>
<td>peak power</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PTTh</td>
<td>poly(terthiophene)</td>
</tr>
<tr>
<td>PVDF</td>
<td>poly(vinylidene fluoride)</td>
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<tr>
<td>RBM</td>
<td>radial breathing mode</td>
</tr>
<tr>
<td>RE</td>
<td>reference electrode</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>S</td>
<td>siemens</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SIBS</td>
<td>poly(styrene-β-isobutylene-β-styrene)</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled carbon nanotube(s)</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>TBAP</td>
<td>tertrabutylammonium perchlorate</td>
</tr>
<tr>
<td>TPAI</td>
<td>tertrapropylammonium iodide</td>
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<td>μL</td>
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<td>micrometer</td>
</tr>
<tr>
<td>μS</td>
<td>microsiemens</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>v</td>
<td>scan rate</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>WE</td>
<td>working electrode</td>
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1. FIGURES

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\[ E_{\text{app}} = +0.7 \text{ V vs. } \text{Ag/AgCl} \]

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FIGURE 4.9. Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

FIGURE 4.10. Radial breathing mode Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

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**FIGURE 4.15.** Raman spectra obtained for (a) nanofibers electrospun from 13% (w/v) SIBS/0.3% (w/v) SWNTs and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

**FIGURE 4.16.** Radial breathing mode Raman spectra obtained for nanofibers electrospun from (a) 13% (w/v) SIBS/0.3% (w/v) SWNT blend fibers and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

**FIGURE 4.17.** Cyclic voltammograms obtained in 0.01 M K$_3$Fe(CN)$_6$/phosphate buffer solution using (a) the electrospun fibers from 13% (w/v) SIBS/0.3% (w/v) SWNT on ITO glass or (b) the bare ITO coated glass slide as the working electrode (scan rate = 0.05 Vs$^{-1}$).

**FIGURE 4.18.** Fluorescence microscope images of L-929 cells growing on electrospun fibers from 13% (w/v) SIBS/0.3% (w/v) SWNTs. Figure 4.18(a) shows calcein-stained cells using fluorescence detection only. Figure 4.18(b) shows the same field with the addition of transmission (white light) imaging to show the position of SWNT/SIBS fibers (dark regions).
FIGURE 5.1. (a) Schematic representation of the procedures for the synthesis of the ACNT/Pt/PVDF membrane electrode. SEM micrographs of ACNT on (b) the quartz plate and (c) the Pt/PVDF polymer electrode. And (d) digital photograph illustrating the highly flexible ACNT/Pt/PVDF membrane electrode.

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FIGURE 5.9. Chronoamperogram of methanol oxidation at (a) the ACNT/Pt/PVDF electrode and (b) the Pt nanoparticle-ACNT/Pt/PVDF electrode by constant potential at +0.7 V vs. Ag/AgCl (3 M NaCl).

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GENERAL INTRODUCTION
1.1 Introduction to Nanotechnology

Nanotechnology is the ability to control or manipulate materials, devices, and systems at the nanometer scale to create structures with novel properties and functions developed at that length level [1]. Nanostructures are normally less than 100 nanometers in size. A nanometer is one billionth of a meter, which is about 100,000 times smaller than the width of a human hair and is up to 100 times smaller than geometrics typically used in commercial semiconductor manufacturing today. By organizing atoms into structures of different shapes and sizes on a nanoscale, the wavelike properties of electron inside matter and atomic interactions are influenced. Important properties including electrical, optical, physical and magnetic can be fundamentally different because of the significantly reduced size of these structures [2]. A dramatic improvement in chemical properties of nanostructures is also achievable due to the high surface-to-volume ratio of nanometer-sized materials [2]. New phenomena, such as the confinement-induced quantization effect, is also observed at nanoscale where the size of materials becomes comparable to the deBroglie wavelength of the charge carriers inside [2]. As a consequence, it is possible to control the important properties of materials even without changing the chemical composition of materials by preparing nanoscaled structures. It is consequently possible to develop a wide range of new materials and devices of novel properties for numerous applications.
The ability to prepare nanostructures is essential to modern science and technology. There are numerous methods to achieve this via synthesizing novel types of nanomaterials, or simply by down-sizing existing microstructures into the nanoscaled regime. The earlier nanotechnology involves filling materials with nanosized particles including filling rubbers with carbon black or investigation on silicate nanocomposites in 1950s [3]. This technology was developed to prepare a large amount of inverse opals using self-assembled nanostructures-synthetic opals as templates [4-8]. This method provides a simple way to synthesis 3D nanostructures. To date, 2D nanostructures (or quantum wells) [9] have been prepared using techniques such as molecular beam epitaxy by semiconductor community [10]. 0D nanostructures (or quantum dots) [11] have also been obtained using various chemical methods [12]. In the quest for mesoscopic physics and fabrication of nanoscale devices, 1D nanostructures such as fibers, wires, rods, belts, rings and tubes have been attracted great attention. Compared with quantum dots and wells, 1D nanostructures demonstrate advantages in well controlled dimensions, morphology, phase purity, and chemical composition. Nowadays, 1D nanostructures can be fabricated using a number of approaches such as electron-beam or focused-ion-beam writing [13], proximal probe patterning [14], X-ray or extreme-UV lithography [15] and electrospinning [16]. Among these methods, electrospinning provides a simple approach to nanofibers with both solid and hollow interiors that are exceptionally long in length, uniform in diameter, and diversified in composition. Even though technologies for the production of nanomaterials and nanoparticle-filled materials...
have been known for some time, the discovery of carbon nanotubes in 1991 [17] greatly accelerated progress in the field. Nanotubes are interesting due to their unique mechanical, electrical and chemical properties. The alignment of carbon nanotubes offers extra advantages in getting easy access to individual nanotubes and effectively incorporating them into devices [18]. Of great interest are aligned carbon nanotube-polymer nanocomposites which exhibit additional advantages with the combination of unique properties of carbon nanotubes and polymer materials [19].

This project will investigate a number of routes to the fabrication of novel nanostructured materials. These include the use of Inverse Opals and Aligned Carbon Nanotubes as templates and the synthesis of novel nanofibers by electrospinning techniques. Novel properties and functions of the resulting nanomaterials due to the reduction in size are also demonstrated in this research work.

### 1.2 Inverse Opals

#### 1.2.1 Natural Opals and Synthetic Opals

Opals, known for their characteristic iridescence, are composed of a regular array of amorphous silica spheres each with a diameter of approximately 200 nm [20, 21]. Natural opals are formed in nature by sedimentation of colloidal SiO₂ particles [22]. It was proved that there were long range attractive interactions between like charged
colloidal SiO$_2$ that favored the formation of ordered structures such as opals rather than disordered materials [23]. In such three dimensional crystals, the electromagnetic (EM) radiation undergoes Bragg’s diffraction, forming a stop band for all modes propagation in a given direction [24-26]. The absence of the propagating EM radiation inside photonic band gaps (PBG) gives rise to opals’ characteristic iridescence. The differences in refractive indexes between silica spheres and the voids surrounding the spheres are responsible for their ability to diffract white light [27].

Opals are particularly attractive for applications such as optical switches, optical filters [28, 29] or photonic band gap (PBG) materials [30, 31]. PBG materials exhibit three dimensional, highly ordered structure with interesting diameter size comparable to the optical wavelength. However, a shortcoming to using natural opals in industry is their high cost, low availability, and structure defects inside. As a result, synthetic opals were artificially produced to take the place of natural opals in industrialization.

Synthetic opals are normally prepared from silica [32, 33] or polystyrene [34] suspensions containing nano/micro spheres with a high degree of monodispersity. Three basic steps are involved in the preparation of synthetic opals. The first step involves the synthesis of highly monodispersed colloids. A large number of techniques are developed to prepare a highly monodispersed silica or polystyrene colloidal solution [34, 35]. The second step involves a highly ordered crystalline structure. This normally consists of two simultaneous processes i.e. sedimentation and
evaporation. Synthetic opals are generally prepared by evaporation [35, 36] or the spin coating [37] technique. A thin layer of monodispersion is placed or spin coated onto a flat substrate and left at room temperature to allow the evaporation of solvent at a slow evaporation rate. Figure 1.1 shows the schematic of the slow sedimentation of the colloidal particles which direct the sedimented particles into an ordered pattern. This provides a simple and effective way to prepare synthetic opals. The size of opals can be changed using different monodispersed colloids of various sizes. But one significant deficiency is that it is hard to control the opal film thickness, resulting in three-dimensional periodic structures of opals. The last but not the least step concerns the annealing the resulting crystalline structure to improve the mechanical properties of opals by forming intersphere connections.

Figure 1.1. Schematic of formation of synthetic opals.
1.2.2 Inverse Opals

3D patterning of materials at micro/nano the scale has attracted great interest in areas such as catalysis, photonic crystals and separations technology. Synthetic opals exhibit well defined three-dimensional structures on the scale of optical wavelengths. Many applications of opals, however, were deeply limited by its high resistance (resistivities are normally more than $10^{11} \, \Omega$ [38]). One possible way to improve this is incorporating an opal template with conducting/semiconducting materials. The opal template can be subsequently removed, leaving a highly ordered porous structure known as inverse opal. The opal template can be removed either by chemical etching [39] or gasifying and combustion [40]. The work concerning inverse opals was first reported by Zakhidov et al [6]. Carbon or a carbon precursor was infiltrated into silica opals and porous inverse opal films were obtained after chemical removal of the opal template. Ever since, a wide range of materials including conducting polymers [4, 41, 42], graphite and diamond [6, 43], cadmium selenium [5, 44], titanic oxide [7], and metals [8, 45] were used to fill the void spaces between opal particles using various routes such as sol-gel chemistry, chemical vapor deposition, liquid-phase reactions, deposition of small solid particles, or precipitation from a saturated solution. Subsequently a large amount of inverse opals were obtained after removal of the template.
1.2.3 Metal Inverse Opals

There are several routes reported to deposit metals into colloid templates such as depositing metals into liquid crystal [46] and anodic alumina [47] templates to catalyze metal formation. However these templates are quite fragile and easily disrupted during deposition due to the poor accessibility of metals into the interstitial regions of the colloids. Jiang et al. reported the generation of metal inverse opals using a metal nanocrystal catalyzed electroless deposition technique [8]. One drawback of this work is that the thickness of the metal inverse opal film can not be controlled. More recently electrodeposition of metals into opal templates as a new technique for preparing metal inverse opals was developed by Wijnhoven et al. [40]. They demonstrated that electrodeposited gold film, with thickness control, worked as a good replica of silica opal templates; leaving a well defined gold inverse opal structure. In the present work, as shown in Figure 1.2, a synthetic opal template was prepared on an indium tin oxide (ITO) coated glass slide from monodisperse polystyrene (PS) beads with diameters of 200nm to 900nm using the evaporation technique [35, 36]. Platinum was then electrodeposited through the interstitial space of the opal matrix and the template subsequently removed; producing a highly ordered, mesoporous inverse opal structure with essentially the same optical properties as those of the original host.
Figure 1.2. Schematic of synthesis of Pt inverse opals.

Transition metal nano/micro structures are attracting intense scientific interest due to their potential application in catalysis and electronic materials [48]. The supported transition metal nano/micro structured materials also exhibit high electrocatalytic performance in applications related to fuel cells, such as methanol oxidation [49]. To increase the catalytic activity of methanol oxidation, an enormous effort has been devoted towards the development of catalysts, especially in platinum-based nano/micro materials [50, 51]. For example, Kulesza reported that Pt microparticles showed electrocatalytic activity toward reduction of hydronium ions [52]. Platinum microelectrodes were found to be excellent sensors for the amperometric detection of hydrogen peroxide by Evans et al. [53]. Hrapovic et al. have prepared electrochemical biosensors with significantly improved sensitivity toward hydrogen peroxide from Pt nanoparticles incorporating single-wall carbon nanotubes [54].
In this work, we demonstrate the generation of Pt inverse opals using electrochemical deposition of Pt into the void space of PS particles, followed by the removal of the opal template. The resulting Pt inverse opals exhibit a highly ordered structure with a formation of air spheres in the Pt film. Characterisation was subsequently carried out on Pt inverse opals. Results show that Pt inverse opals have a high surface area and interesting electrochemical properties, allowing for their potential applications in areas such as catalysis (methanol oxidation, bio-fuel cells), photovoltaic cells, sensors and energy-harvesting coatings. Also nanostructured Pt inverse opals showing excellent electrocatalytic performance for methanol oxidation will be described.

1.2.4 Photoelectrochemical Cells

There is a rapid growing demand for energy with the fast development of industry and increasing population nowadays. Most energy requirements are currently met by the use of fossil fuels. It is known that the formation of fossil fuels took a long historical period and there are finite resources of fossil fuels present on the earth. For example, oil, one of the major fossil fuel; is estimated to be exhausted around 2050 [55]. In addition, the combustion of fossil fuels have brought lots of environmental problems such as climatic consequences of the greenhouse effect, poor air quality and associated health problems. There is consequently an increasing demand for developing novel environmentally friendly, sustainable and renewable energy sources.
Renewable energy, defined as energy harvested from a source that will never run out, typically originates from solar, thermal, wind, geothermal, hydroelectric or photoelectric sources. One key index called ‘energy payback’ is normally used to evaluate the performance of a renewable energy system. The ‘energy payback’ refers to the operational time required for producing a renewable energy system. For instance, photoelectric systems generally have ‘energy payback’ periods of 3-4 years compared with their normal lifetimes of 30 years [56]; suggesting these systems create much more energy than energy consumed during their fabrication. The development of renewable energy systems provides great opportunities not only for resolving the energy crisis and environmental problems but also for economic gains. In Europe, for example, wind power and photoelectric energy increased by 35% and 33% annually respectively between 1996 and 2003. The renewable energy industry in Europe currently has a turnover of € 10 billion per year [57]. In the United States of America, the total revenue from the photoelectric energy industry exceeded SUS 1.1 billion in 2000 [58]. Comparing with other renewable energy systems, photovoltaic energy systems exhibit many unique advantages such as more convenience in the urban context, zero noise emissions [59] and unobtrusive buildings-integrated products [60, 61].

Commercial photoelectric conversion devices (solar cells) are made mostly from inorganic semiconductors especially crystalline or amorphous silicon. The idea of solar cells is to capture the free sunlight energy and convert it to electrical power or
use it to generate chemical fuels such as hydrogen. In a typical solar cell, electron-hole pairs are produced when photons fall on a semiconductor and an electric potential difference occurs at a junction between two different materials. About 95% of commercial solar cells are prepared from single or multi crystalline silicon wafers [62]. Recently many inorganic solid-state junction devices have also been made from the III/V compounds and the copper-indium-sulphide/selenide materials. However, the main drawback to utilizing inorganic semiconductor-based devices is their high cost. For example, a purity of 99.9999% is normally required for the silicon to fabricate a solar cell [61]. High temperatures are therefore employed to melt the silicon, leading to the high cost of products. A common silicon solar cell for a residential home costs around AUD 20,000 which is quite higher than what the public can afford [59]. In addition, the widespread application of inorganic semiconductor-based solar cells is also inhibited by poor availability and the toxicity of the compounds.

In the last two decades, solar cells based on polymeric and organic materials have attracted much attention [63, 64]. These photoactive materials exhibit improvements in many areas such as mechanical flexibility, readily controllable properties, the possibility of mass production and economic advantages compared with the inorganic equivalents. The classical solid-state junction devices are recently being replaced by devices that consist of a semiconductor in contact with an electrolyte (liquid, gel or organic solid), known as a photoelectrochemical cell (PEC). The earliest work
concerning on light-driven redox reactions was reported by Becquerel in 1839 [65]. In his work, a current between two platinum electrodes was produced by illuminating solutions containing a metal halide salt. Vogel extended the photosensitivity of photographic film to longer wavelengths (longer than 460nm) by adding a dye into silver halide emulsions [66]. Later work by Moser confirmed the dye enhancement from photograph to PECs using the dye erythrosine on silver halide electrodes [67]. New progress on PECs was achieved by Nelson who found that maximum efficiency could be obtained by adsorption of the dye on semiconductor electrodes in a closely packed monolayer [68]. Subsequent discoveries about electron transfer being the prevalent mechanism advanced the photographic and photoelectrochemical sensitization theory [69, 70]. Brattain et al’s [71] and subsequently Gerischer’s [72] works on electrochemical and photoelectrochemical studies of the semiconductor-electrolyte interface separated photoelectrochemistry from photography and founded the modern photoelectrochemical research. There are two basic types of PECs which were intensively investigated. Figure 1.3 and 1.4 describe the schematic representation of these two cells. As shown in Figure 1.3, the first type, which is called the regenerative cell, converts sunlight to electric power leaving no net chemical change behind. Electron-hole pairs are generated when photons of energy exceed that of the band gap. Electron-hole pairs are subsequently separated by the electric field present in the space-charge layer. The negative charged electrons move through the semiconductor electrode to the external circuit while the positive holes accumulate at the surface and are absorbed by the reduced phase of the redox
mediator (El_{red}). The absorption of the holes as well as the oxidation of El_{red} can be demonstrated by the equation below:

\[ \text{h}^+ + \text{El}_{\text{red}} \rightarrow \text{El}_{\text{ox}} \]  

(1.1)

\[ \text{El}_{\text{ox}} \text{ is then reduced back to El}_{\text{red}} \text{ by the electrons that re-enter the system from the external circuit as the equation (1.2):} \]

\[ \text{El}_{\text{ox}} + e^- \rightarrow \text{El}_{\text{red}} \]  

(1.2)

Many researchers who are working on the regenerative cells have paid much attention to electron-doped (n-type) II/VI or (III/V) semiconductor substrates with the use of redox couples such as sulphide/polysulphide, vanadium (II)/vanadium (III) or I\textsubscript{2}/I\textsubscript{−}. The best conversion efficiency for regenerative cells has been obtained as 19.6% to date [73].
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The second type of PECs is known as photosynthetic cells. Different from the first type, there are two redox systems present in this cell. As shown in Figure 1.4, water is oxidized to oxygen by the holes at the surface of the semiconductor and reduced to hydrogen by the electrons re-entering the counter-electrode. The overall reaction is the cleavage of water by sunlight. Fujishima et al firstly utilize titanium dioxide as the semiconductor for water photolysis [74]. Since then, hundreds of studies have been focused on the employment of titanium oxide as the semiconductor substrates. However, conversion efficiencies of TiO$_2$ semiconductor are very low due to its large band gap (3-3.2 eV) which leads to the absorption of photons at TiO$_2$ only occurring at the ultraviolet part of sunlight. Much effort in trying to improve the absorption of

![Figure 1.3. Schematic representation of a regenerative photoelectrochemical cell.](image-url)
photons at TiO₂ in the visible part of the spectrum or replacement of TiO₂ by other oxides has been made. But no successful case is found to date.

Figure 1.4. Schematic representation of a photosynthetic photoelectrochemical cell.

1.2.5 Nanostructures Used in Photoelectrochemical Cells

The development of mesoscopic $n$-type semiconductor substrates with high-surface-area has attracted much attention during recent years [75]. Mesoporous oxide films containing TiO₂, ZnO, SnO₂ and Nb₂O₅ or chalcogenides such as CdSe are normally made up of thin arrays of nanocrystals. Nanostructured pores in the films can subsequently be filled with a semiconducting or a conducting medium such as a $p$-type semiconductor, a polymer, a hole transmitter or an electrolyte. The contact area
between the two interpenetrating phases is therefore very large. In addition, the oxide particles are interconnected that allow electronic conduction to take place. A large electronic internal surface area is thus obtained when charge carriers infiltrate into the mesoporous nanostructures.

Numerous studies on developing nanostructured mesoporous semiconductors to absorb more of the incident light for dye-sensitized solar cells are reported in the recent decade [76, 77]. Most researchers agree that the charge transport in mesoporous systems can be described by a random walk model [78]. Grätzel developed a specific PEC with high efficiency based on dye-sensitized nanostructured TiO$_2$ [79]. In a typical Grätzel photoelectrochemical cell, as shown in Figure 1.5, nanostructured TiO$_2$ coated with dye (D) molecules on an electrode such as glass coated with SnO$_2$:F was used as the anode, with a redox couple in the form of liquid electrolyte and a platinized cathode. The excited state dye (D*) provides an electron to the TiO$_2$ when irradiated and meanwhile, obtains an electron from the reduced form of the redox mediator (E$_{\text{red}}$) at the electrode-electrolyte interface. This kind of solar cell exhibits excellent photovoltaic conversion efficiencies of up to 10.6%. Compared with the traditional PECs, the Grätzel cell shows numerous improvements. First and most particularly, the nanostructured mesoporous TiO$_2$ film (5~20 μm thickness) provides over one thousand times higher surface area for dye chemisorption than traditional flat electrodes, resulting in more than 80% improvement in the incident photon-to-current conversion efficiency. The mesoporous nanostructures also enable
holes to transfer to the redox mediator efficiently since the electrolyte can penetrate all the way to the back of the film. Second, the employment of dye enables photon collection within a wide range of the solar spectrum.

The main issue for the high power-conversion efficiency of mesoporous structures is due to the excellent interconnection of nanoparticles, allowing electronic conduction to take place. Normally the nanoparticles are produced by annealing the nanoparticulate oxide at high temperature (typically more than 500°C), which requires the films to be prepared on particular substrates (such as quartz plates or metal foils) that can withstand the high temperature. One disadvantage of the Grätzel cell is its limited choice of substrates.

Figure 1.5. Schematic representation of a Grätzel photoelectrochemical cell.
1.2.6 The Use of Nanostructured Conducting Polymers in Photoelectrochemical Cells

The use of organic conductors in PECs offers additional advantages in a wider variety of applications such as different substrates (e.g. plastic). The discovery and development of inherently conducting polymers (ICPs) provide opportunity to make photoelectrochemical energy systems more affordable in the future. Since the first preparation of ICPs in 1977 [80, 81], hundreds of researchers have turned their attention to the synthesis and characterization of ICP components including MacDiarmid, Shirakawa and Heeger who were awarded the Noble Prize in Chemistry in 2000 because of their efforts in the discovery and development of ICPs. ICPs combine the electronic and optical properties of semiconductor with the mechanical and physical properties of polymers. A large number of works has focused on making thin-film photovoltaic devices from ICPs since these structures show advantages in low weight, low cost and high flexibility. These include the use of polyaniline [82], poly(p-phenylene vinylene)/perylene heterojunction [83], poly(2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene composite [84, 85], poly(3-methylthiophene) [86] and polythiophene [87]. Recently polythiophene has attracted much interest as an ideal candidate for use in photoelectrochemical devices since it is easier for a wide variety of substituents to be covalently attached to the polymer backbone providing capability for enhanced light absorption and exciton dissociation. Various types of polythiophene (PTTh) have been investigated in PECs. For example, Chen et al made photoelectrochemical devices based on bisterthiophene [88] and
porphyrin-functionalised bisterthiophene [89], and obtained good power-conversion efficiencies (0.069% for bisterthiophene and 0.116% for the latter). Tsekouras et al. [90] quantitatively analyzed the conditions for the electrodeposition of PTTh, such as the solvent used, the upper potential limit used and electropolymerisation temperature, and a best photoelectrochemical efficiency of 0.101% was obtained from PTTh electrodeposited at 60°C under the optimum conditions.

ITO has attracted much interest in many application areas particularly in opto-electronics due to its high transparency in the visible light region, low electric resistivity, and good chemical stability [91, 92]. In this study, mesoporous structured ITO film was introduced as a substrate for the growth of ICPs into the photoelectrochemical system. As shown in Figure 1.6, synthetic opal templates were prepared on ITO coated glass slides from monodisperse polystyrene (PS) beads as described above. A thin layer of ITO film was subsequently sputter coated onto the PS opal template. The thickness of ITO film was controlled to shape the ITO film to the original PS film. The opal template was subsequently removed, leaving a highly ordered, mesoporous nanostructured ITO film with porous structures on the bottom (so-called ITO opals). Conducting polymers such as PTTh (see Figure 1.7 for the structure) were subsequently deposited onto the mesoporous ITO opal film along the edge of the nanostructured ITO film. A mesoporous conducting polymer film with high surface area was thus obtained. PTTh exhibits potential predominance for the use in photoelectrochemical cells considering its wide variety of substituents which an be
easily attached to the polymer backbone providing polymers with various electronic states, conductivities, stabilities and other useful physical properties [93]. The application of the resulting nanostructures in our study as photoelectrochemical conversion devices was investigated in this research work.

![Figure 1.6. Schematic of synthesis of conducting polymers coated mesoporous ITO opal on ITO coated glass slide.](image1)

![Figure 1.7. Chemical structure of polyterthiophene.](image2)
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1.3 Electrospinning

1.3.1 Historical Review of Electrospinning Development

Nanofibers have attracted a lot of interest due to their unique properties such as very large surface area-to-volume ratio and high porosity with very small pore size. Electrospinning provides a simple, rapid, inexpensive and non-mechanical way to produce nano/micro-scaled polymer fibers using electrostatic forces. The first electrospinning apparatus was reported by Formhals in 1934, when Formhals synthesized polymer filaments by taking advantage of the electrostatic repulsions between surfaces charges [16]. Whereafter fabrication of ultrafine fibers with the use of electrostatic force has attracted a large amount of interest, however, there are few publications regarding fiber fabrication using electrospinning. Up until the 1980s, this technique was formally considered as electrostatic spinning and employed in fiber preparation by Baumgaren’s [94] and Larrondo’s research groups [95-97]. A milestone of the electrospinning technique development was reported by Reneker and Chun from the University of Akron, who revived interest in the electrospinning technique and demonstrated the possibility of producing a wide range of organic polymers using electrospinning in 1996 [98]. Since then, there are exponentially increasing numbers of publications and applications concerning the electrospinning technique with the use of a number of conventional polymers including poly(ethylene oxide) (PEO), polystyrene, polyacrylonitrile and polyvinyl chloride/polyurethane with
or without the addition of other conducting polymers. To date, more than 50 different types of organic polymers have already been processed as fibers with diameters ranging from a few micrometers to several nanometers. Electrospun products have been employed in a wide range of areas such as high performance filters, high surface area electrodes and fiber templates.

1.3.2 Electrospinning Setups and Mechanisms

More recently, the electrospinning mechanism has become clearer and clearer with the efforts of numerous researchers’ prestigious work. For example, Doshi and Reneker have reported the electrospinning process with fiber morphology and advocated that the most efficient geometry for fiber collection was curved while electrospun fibers could be collected as different sizes and shapes such as flat, curved, cylindrical, cubic etc. Moreover, Reneker et al. have used a mathematical model to analyse and explain the reasons for the bending instability of electrically charged jets of polymer solutions. Meanwhile, Shin and co-workers have found a stable jet can be extended from the tip to the target at low electric field.

Figure 1.8 shows a schematic illustration of a typical electrospinning setup which contains three major components: A high voltage power supply, a spinneret (typically a metallic needle) and a grounded target such as aluminum foil. The polymer feed
solution is provided via a needle using a syringe pump that provides a constant or controllable feed rate. A high electric field is generated between the needle tip and an electrically grounded target. This results in free charges on the surface or inside the polymer solution. The Coulombic repulsion force between charges of the same polarity produced in the solution destabilizes the hemi-spherical droplet of the polymer solution at the tip of the needle to finally form a droplet with a conical shape i.e. the Taylor cone [112]. When the voltage reaches a critical value (normally 5 to 25 kV), the increased electrostatic force becomes strong enough to overcome the surface tension of the polymer solution at the tip and an electrically charged jet is ejected [113].

Figure 1.8. Schematic of set-up of the electrospinning process.

Six main forces are acting on the charged jet: (1) Gravitational forces, (2) electrostatic forces which drive the jet to the grounded target between the charged jet and the
target, (3) Coulombic repulsion forces between charged polymer molecules which try to push apart adjacent charged molecules and stretch the charged jet, (4) viscoelastic forces which prevent the charged jet from being stretched, (5) surface tension which work the same as viscoelastic forces, and (6) friction drag forces between the charged jet and the surrounding air [103]. As this jet travels towards the target, it begins to elongate by rapidly rotating in a spiral path [114] and thins down. The solvent evaporates and deposits a non-woven mat of nanometer to micrometer diameter fibers onto the target [115].

The electrospinning mechanism is more complicated than the electrospinning setup. A photograph of a typical electrospinning jet is shown in Figure 1.9. The picture shows that the jet is initially a straight line and then becomes unstable. A stable electrospinning jet is composed of four distinct regions: the base region, the jet region, the splaying region and the collection region.

Figure 1.9. Photograph illustrating the typical electrospinning jet.
The base (as shown in Figure 1.10) is the region where the jet emerges from the charged surface of the polymer. In this region, the axial velocity of the polymer is increased by feeding forces resulting in the formation of a conical jet. The liquid surface is quite flat before the employment of high voltage. The jet can be ejected from the surface by the electrostatic forces when an electric field is produced. The charge density in the jet is equal to the charge that flows onto a conducting sphere with the same diameter as the jet, divided by the volume of the sphere. The charge flows only a little distance through the polymer due to the low mobility of the charge carriers.

![Figure 1.10](image)

Figure 1.10. Photograph illustrating the base region of the electrospinning jet.

The jet (Figure 1.11) is the region beyond the base where the polymer is pushed and the jet is stretched by the electrostatic forces. The diameter of the jet decreases and the length increases axially in this region. A stable electrospinning jet is driven by the high electrical forces from a polymer solution to a grounded collector. Electrical charges usually move along the electrostatic field. The drift velocities of the charges
through the polymer solution are much smaller than that of the jet along its axis that the forces transfer from the electric field to the polymer mass. As a result, the electrical forces are resisted by the elongational viscosity of the jet. The acceleration of the polymer in the jet is determined by the transfer of the forces through the viscoelastic jet under various influential factors; such as the evaporation speed of the solvent and the temperature. The charges in the jet carry the polymer liquid and transport along the direction of the electrostatic field. This clearly describes the mechanism of how charges move from the polymer solution to the collector and the formation of an electrical circuit within which the polymer can be accelerated and the surface area of the polymer can also be increased, the flow is driven and the polymer liquid is changed into the jet. The taper of the jet is also influenced by the solvent evaporation due to the changes on the viscoelasticity of the liquid polymer as the solvent is lost.

Figure 1.11. Photograph illustrating the jet region of the electrospinning jet.
Splaying (see Figure 1.12) occurs when the electrostatic forces of the charges carried by the jet is exceeds the cohesive forces within the jet. In this region, the single charged jet divides into multiple jets with similar diameters and charge per unit length. The diameter of the jet thins down quickly due to the combined effect of the jet stretching and the solvent evaporation. When the diameter of the jet becomes small enough, the radial forces from the charges become larger than the cohesive forces of the jet and favor it to split into many sub-jets. The sub-jets are subsequently separated by the repulsion forces between the individual sub-jets and form a bush-like appearance. Meanwhile, ultrafine fibers can also be produced with an elongation of a single jet without splaying. In many cases, splaying and elongation occur simultaneously.

![Figure 1.12. Photograph illustrating the splaying region of the electrospinning jet.](image)

The collection region (Figure 1.13) is the region in which the jet stops and the fibers are collected after the evaporation of the solvent. On a stationary collector, the jet
tends to coil or fold since the arrival velocity of the jet is so high. The electrically charged fiber that arrives at the target earlier seems to repel the other fibers that reach it later. The amount of charge can be affected by ions present in a corona discharge and carried to the collection region by air current. The charge of the fiber can also be transferred to the conducting grounded collector.

More recent experimental observations show that the formation of ultrafine fibers is caused not only by the splaying of the electrically charged jet but by the bending instability associated with the electrically charged jet. For instance, Reneker et al. demonstrated the formation of bending instability in details [110, 116]. They considered the charged jet as a system that consists of interconnected, viscoelastic dumbbells and calculated the three-dimensional trajectory for the jet using a linear Maxwell equation. Rutledge et al. reported a different explanation for the electrospinning process by treating the jet as a long, slender system [113, 117-119].

Figure 1.13. Photograph illustrating the collection region of the electrospinning jet.
They found that the electrospinning process is mainly caused by whipping which comes from the electrostatic interaction between the external electric field and the surface charges on the jet. The resulting ultrafine fibers were created by the stretching and acceleration of the fluid filament in the instability region. Feng also developed another model to demonstrate the transportation of the charged jet and the role of nonlinear rheology during stretching of the jet [120, 121].

**1.3.3. Control of the Electrospun Nanofibers**

The morphology and diameter of the electrospun fibers can be controlled by changing a number of parameters that include: (1) solution properties such as the type of the polymer, the conformation of polymer chain, concentration, viscosity, surface tension, elasticity, ionic conductivity and the polarity of the solvent; (2) process parameters including applied electrostatic potential, tip-to-collector distance and feed rate; and (3) ambient parameters e.g. humidity, temperature and velocity of the surrounding air in the spinning chamber [109, 122].

It was Baumgarten who firstly paid attention to the influence of these parameters on the fiber morphology [94]. He observed that the average diameter of the electrospun fibers increased with increasing the solution viscosity during electrospinning of an acrylic solution. Fong et al. found that the density of beads decreased with decreasing surface tension and increasing net charge density and viscosity in the electrospinning
of poly(ethylene oxide) [123]. Surface tension tends to convert the liquid jet into one or many spherical droplets to minimize the surface area [124] while the electrostatic repulsion between charges on the jet surface tends to increase the surface area and facilitates the formation of a thin jet. Viscoelastic forces prevent the shape from rapid change and favor the formation of fibers. The elimination of beads can thus be achieved if the influence of surface tension could be suppressed by the other two forces. Buchko and co-workers investigated the influences of solution distance, applied potential, collection distance and collection time on the morphology of electrospun protein non-woven webs [125]. Demir et al. found that the electrospun fiber diameter of polyurethane-urea copolymer increased with the third power of the solution concentration [126]. Zong’s group discovered that the morphology of electrospun fibers from poly(D,L-lactic acid) and poly(L-lactic acid) is more dependent on the solution concentration and addition of ionic salts than other parameters [127]. In addition, the type of the solvent or the combination of the solvent also play a significant role in determining the morphology of the electrospun fibers [103, 128, 129].

1.3.4. The Application of Electrospinning in Biology

Recently, electrospinning of nanofibrous polymer scaffolds for tissue engineering applications has attracted considerable attention. Martin and Cockshott first reported the use of electrospinning to produce biomaterials [130] and numerous such studies
have subsequently been reported. A biodegradable poly (lactic-co-glycolic acid) material containing chitin was electrospun from solutions based on hexafluoro propanal and formic acid [131]. Others have electrospun chitosan fibres from trifluoroacetic acid solutions [132] and aliphatic polyesters (such as poly (ε-caprolactone)) from methylene chloride and dimethyl formamide [129]. In the quest for biocompatible/bioresorbable materials, electrospinning has been used to produce nanostructured dextran membranes [133].

In our work, the electrospinning technique was used to prepare nanofibers from biomaterials or biocompatible materials such as deoxyribonucleic acid (DNA) and poly(styrene-β-isobutylene-β-styrene) (SIBS). We have quantitatively analysed the key factors: solution conductivity, surface tension and viscosity that affect the formation of the jet and determine the success of electrospinning. The influence of process parameters such as tip-to-collector distance, applied potential between the needle and the target and feed rate on fiber morphology and diameter distribution has also been determined. In addition, the application of the resulting nanofibers in areas such as biosensors, cell culture and electrochemical devices has been investigated.
1.4 Aligned Carbon Nanotubes

1.4.1 Introduction to Carbon Nanotubes

Carbon nanotubes have attracted much interest since Iijima first reported High-Resolution Transmission Electron Microscopy (HRTEM) studies in 1991 [17]. Since that time, a large number of carbon nanotubes including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have been synthesized by arc-discharge, chemical vapor deposition (CVD), or laser ablation [134-137]. As shown in Figure 1.14, CNT may be considered as a piece of rolled graphite sheet (SWNT) or with additional sheets around the core of SWNT (MWNT) [134-137]. CNT with a diameter ranging from several angstroms to tens of nanometers typically consist of carbon hexagons in the centre and fullerene-like structures containing pentagons at both ends. There are various chiral structures of CNT since the graphene sheet can be rolled up with different degrees of twist along its length [134-137]. CNT can show semiconducting or metallic behavior depending on their diameter and helicity of the arrangement of graphite rings. Due to their interesting properties, CNTs are potentially employed in many areas such as novel single-molecule transistors [138-140], new electron field emitters in panel displays [141], energy storage [142-144], artificial muscles [145], molecular filtration membranes [146], molecular computing [147] and sensors [148]. For most of these
applications, it is highly desirable to prepare the CNT in the form of alignment to get easy access to individual nanotubes and effectively incorporate into devices.

Figure 1.14. Schematic illustrating (a) the formation of single-/multi-walled carbon nanotubes by rolling up graphene sheet(s) and (b) the formation of carbon nanotubes based on a 2D graphene sheet of lattice vector $a_1$ and $a_2$, the roll-up chiral vector $C_h = na_1 + ma_2$, and the chiral angle $\theta$ between $C_h$ and $a_1$. The cylindrical part of the carbon nanotubes is formed by rolling up the graphene sheet while the circumference of nanotube’s circular cross-section is formed by the chiral vector’s ends meeting each other. The chiral vector $(n,m)$ defines the tube helicity.
1.4.2 Literature Review of Aligned Carbon Nanotubes

Carbon nanotubes can be prepared in a form of horizontal alignment or perpendicular alignment. Both aligned carbon nanotubes (ACNT) have been prepared either by post-synthesis manipulation or by synthesis-induced alignment.

Horizontally aligned carbon nanotubes are normally prepared either by slicing a nanotube-dispersed polymer composite or by rubbing a nanotube-dispersed plastic surface with a thin sheet of Teflon or aluminum foil. The first horizontally aligned carbon nanotubes were synthesized by Ajayan in 1994 [18]. In that work, carbon nanotubes were mixed with epoxy-based resin, hardened, and cut into slices. The resulting slices exhibit the presence of preferentially oriented carbon nanotubes. Two years later, De Heer and co-workers developed a novel method called filtering-pressing to prepare aligned carbon nanotubes [149]. The CNT suspension was drawn through a 0.2 μm-pore ceramic filter, leaving a uniform black deposit with nanotubes aligned either parallel or perpendicular to the surface of the film. Zhou et al. immersed a substrate into an aqueous solution of acid-oxidized short SWNT to self-assemble the preformed carbon nanotubes on the substrate and obtained highly ordered carbon nanotubes [150]. Recently Dai and co-workers grew SWNT wires between controlled surface sites by catalyst patterning, developing various interconnecting SWNT architectures including a suspended SWNT power line and a square of suspended SWNT bridges [151]. More recently vectorial growth of SWNT
was achieved with the use of patterned catalyst nanoparticles and a local electric field parallel to the substrate [152].

Perpendicularly aligned carbon nanotubes offer special advantages for many applications especially in the areas such as electron emitters and molecular membranes. It was De Heer et al. who first prepared the carbon nanotubes perpendicularly aligned onto the substrate using a filtering-pressing method as described above [149]. Since then, a technique known as the template synthesis was developed to produce perpendicularly aligned carbon nanotubes with the use of porous membranes such as mesoporous silica and alumina nanoholes [153, 154]. Xie et al. firstly demonstrated the preparation of large-scale growth of ACNTs using CVD from a mesoporous silica template with embedded iron nanoparticles [155]. Xu et al.’s research group prepared ACNT by embedding a nickel catalyst in a porous silicon substrate, followed by the pyrolysis of hydrocarbon [153]. All of these methods involve the use of porous substrates which were prepared, in most cases, by electrochemically etching the crystalline silicon wafer (the anode) in an aqueous HF solution using a Pt wire cathode. Recently Li et al. have reported the preparation of Y-shaped CNT by the pyrolysis of methane over cobalt-covered magnesium oxide on branched nanochannel alumina templates [156]. There is no publication on preparing ACNT without using porous templates until 1998 when Rao and co-workers obtained ACNT by the pyrolysis of ferrocence at 900°C on a pristine quartz substrate [157]. The ferrocence was chosen for both containing the metal catalyst and the carbon
source required for nanotube growth. Meanwhile, Ren et al. reported the preparation of ACNT by plasma-enhanced hot filament CVD of acetylene under ammonia gas below 660°C using a display glass radio-frequency sputter-coated with nickel [158]. Thereafter, numerous plasma techniques such as radiofrequency [159], direct-current [160] and microwave plasma [161-163] were used to improve the preparation of ACNT. Furthermore Avigal et al. designed a system containing a regular cold-wall CVD reactor under an electric field to produce ACNT on Co covered Si by the pyrolysis of methane in the presence of argon at 800°C [164]. Recently Kamalakaran et al. have prepared ACNT from a jet solution of ferrocene and benzene [165].

In this project, we prepared large-scale, perpendicularly aligned carbon nanotubes by the pyrolysis of iron phthalocyanine (FePc) under Ar/H₂ at 800-1000°C following Dai et al.’s method [166, 167]. The presence of FePc which contains both a metal catalyst and a carbon source for the growth of nanotubes, enables the one-step growth of ACNT and favors the formation of ACNT patterns for further applications. Moreover, large-area substrate-free carbon nanotube films and micropatterned vertically aligned carbon nanotubes were also produced.

1.4.3 Aligned Carbon Nanotube/Polymer Composites

Carbon nanotube-polymer composites have attracted great interest in many application areas such as electronic, optical and mechanical with the combination of
unique properties of carbon nanotubes and polymer materials. Recently Dai and co-workers have prepared novel conducting polymer–carbon nanotube coaxial nanowires by electrochemically depositing a suitable layer of polypyrrole onto each of the constituent aligned nanotubes [19, 168]. Good electrochemical active properties with the addition of conducting polymer on the resulting coaxial nanowires were also obtained. More recently, Dai and co-workers also developed a novel type of chemical vapor sensor with high sensitivity, low consumption and excellent stability based on ACNT and poly(vinyl acetate) polymer [169]. In a separate work, Jung et al. fabricated a flexible device from ACNT and poly(dimethylsiloxane) composites. The resulting devices had good electrical conductivity and have the potential applications as flexible emission devices and strain and gas sensors [170].

In our work, we present a novel way to incorporate aligned carbon nanotubes (ACNT) into a series of polymers with various properties such as SIBS (biocompatible), poly(3,4-ethylenedioxythiophene) (conductive) and Pt/poly(vinylidene fluoride) (mechanically robust and highly conductive). The resulting ACNT-polymer membranes exhibit flexibility coupled with a large well-defined surface area and capacity of ACNT. These materials can be used directly as flexible field-emitters, gas sensors and/or anode materials in Lithium-ion batteries without the need for direct manipulation of individual nanotubes.
1.5 Aims of Study

The following chapters will consider the fabrication methods of novel nanostructured materials with the use of inverse opal templates, electrospinning technique and the aligned carbon nanotube substrates. The summary of the work presented in this thesis is shown in Figure 1.15. Novel properties due to the presence of nanostructures will be described. The application of the resulting Pt inverse opals in methanol oxidation, ITO opals in photoelectrochemical cells, biocompatible electrospun fibers used as platforms for cell culturing, and flexible ACNT/polymer electrodes in methanol oxidation and Lithium-ion battery will be investigated in this work.

Figure 1.15. Project aims.
Chapter 2 will describe the general experimental techniques and instruments used in this thesis.

The synthesis of nanostructured Pt inverse opals and ITO opals with the use of synthetic opal templates as well as the application of the products in methanol oxidation and photoelectrochemical cells will be investigated in Chapter 3.

Chapter 4 will consider electrospinning biomaterials (such DNA and poly (styrene-β-isobutylene-β-styrene) (SIBS)) with or without the addition of single-walled carbon nanotubes. The system parameters (e.g. ionic conductivity, viscosity and surface tension) and the process parameters (such as the applied potential, tip-to-collector distance and feed rate) that determine the results of electrospinning will be quantitatively analysed. The utilization of the resulting fibers in areas such as biosensors and cell culture will be demonstrated.

Chapter 5 will demonstrate the preparation of aligned carbon nanotubes incorporated into a flexible and conductive polymer substrate such as Pt/poly(vinylidene fluoride) (PVDF) or poly(3,4-ethylenedioxythiophene)/PVDF. The improved properties with the combination of unique properties both from ACNT and conductive polymers, as well as applications in many areas such as anodic oxidation of methanol and as anode materials in Lithium-ion batteries will be presented.
The fabrication of conducting biomaterial (Pt/poly(lactide-co-glycolide) (PLGA)) or biocompatible (SIBS) material -ACNT composite electrodes will be investigated in Chapter 6. The biocompatibility and application in cell culturing of the resulting electrodes will be described.

Chapter 7 will summarize the work presented in this thesis.
1.6 References


Chapter 1: General Introduction


Chapter 1: General Introduction

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CHAPTER 2:

GENERAL EXPERIMENTAL
21. Introduction

The experimental techniques and instruments used in this thesis are briefly described in this chapter, including the techniques for the preparation, characterisation and application of the resulting nanostructures fabricated in this thesis. Details of specific procedures will be given in the experimental part of each corresponding chapter.

2.2 Preparation of Nanostructures

2.2.1 Electrochemical Deposition

The electrochemical system used in this thesis is shown in Figure 2.1. This comprised of a model 363 Potentiostat/Galvanostat (Princeton Applied Research), a MacLab 400 with Chart (v 3.5.7) and EChem (v 1.3.2) software (ADInstruments) and a computer.
All electrochemical reactions including electrochemical deposition and electrochemical characterisation were carried out in a divided three-electrode electrochemical cell with a Pt mesh auxiliary electrode and a Ag/AgCl (3M NaCl, for aqueous solvent) or Ag/Ag⁺ (for organic solvent) reference electrode, as shown in Figure 2.2.
The electrochemical deposition was achieved using cyclic voltammetry. The process involves imposing on an electrode (the working electrode) a cyclic linear potential sweep and outputting the resulting current-potential curve, called a cyclic voltammogram (CV). In CV, the current is monitored while the potential sweeps from an initial value \( E_i \) to a switching value \( E_s \) and then to the final values \( E_f \) at various scan rates \( v \). The potential as a function of time is:

\[
E = E_i + vt \quad \text{(forward sweep)} \\
E = E_s - vt \quad \text{(reverse sweep)}
\]
The triangular potential waveform is shown in Figure 2.3. Electrical current at the working electrode (WE) due to electron transfer is termed faradic current. A counter electrode (CE) is driven by the potentiostatic circuit to balance the faradic process at the WE with an electron transfer of opposite direction (e.g., if reduction takes place at the WE, oxidation takes place at the CE). The faradic current at the WE is transduced to a potential output at a selected sensitivity, expressed in amperes per volt, and recorded in a digital or analog form. The CV response is plotted as current versus potential. Figure 2.4 shows the shape of a CV current response for a typical redox process. During the forward sweep the oxidized form is reduced, while on the reverse sweep the reduced form near the electrode is reoxidized.

Figure 2.3. The triangular potential waveform and resultant current in a cyclic voltammetric experiment.
Figure 2.4. A typical cyclic voltammogram obtained from a redox process.

2.2.2 Sonication

The dispersion of carbon nanotubes into biopolymer solutions (such as DNA and poly(styrene-β-isobutylene-β-styrene)) was carried out in a Model 102C Branson Digital Sonifier (Figure 2.5) at 30% power (150 Watts, 20 kHz, Pulse: 2sec on/1sec off).
2.2.3 Sputter Coating

The Pt or indium tin oxide (ITO) film was formed using the sputter coating technique.

The sputter coating was conducted in a SC100MS Dynavac Magnetron Sputter Coater (Figure 2.6). ITO was sputter coated onto nanostructured polystyrene opals at 30 mA for 10 minutes. Pt was sputter coated onto aligned carbon nanotubes at 30 mA for 30 minutes.
2.2.4 Electrospinning

Electrospinning is a simple and fast way to prepare nano/micro fibers using electrostatic force (see Chapter 1, Section 1.3.2 for details). In this work, the electrospinning set up consisted of a Gamma High Voltage Power Supply (ES50P-10W/DAM), a 5 mL glass syringe with a NE-1000 syringe pump (New Era Pump Systems Inc.) and a PrecisionGlide™ 19G needle (1.1 mm diameter).

The electrospinning of solutions containing DNA was conducted at various tip-to-collector distances (10 ~ 25 cm), applied potentials between the needle and collector (5 ~ 20 kV) and feed rates (50 ~ 200 μL/min) respectively. Electrospun fibers were collected onto Pt coated glass slides. Pt was sputter coated onto glass
slides for 10 minutes at 30 mA.

The formation of SIBS/SWNT nanofibers using electrospinning was conducted at 15 cm tip-to-collector distance, 20 kV applied potentials between the needle and collector and 100 μL/min feed rates. The resultant fibers were collected on either gold-coated mylar or ITO coated glass slides.

### 2.2.5 Synthesis of Aligned Carbon Nanotubes

Vertically aligned carbon nanotubes were prepared on a quartz plate (2×4 cm²) using thermal chemical vapor deposition (CVD) and the pyrolysis of iron (II) phthalocyanine (designated as FePc) under Ar/H₂ as described elsewhere [1, 2]. As shown in Figure 2.7, a suitable amount of FePc was placed in the 1st zone while clean quartz plates were placed in the 2nd zone. The 2nd zone was heated to 800-1100°C and subsequently the temperature of the 1st zone was increased to 500-600°C for 2-15 minutes. Thereafter, the 1st zone was also heated to 800-1100°C and both zones were maintained at that temperature for 10-20 minutes. A HTF-9012 furnace (LABEC Laboratory Equipment Pty Ltd., Figure 2.8) was used in the experiment.
Figure 2.7. Apparatus for the preparation of aligned carbon nanotubes by pyrolysis of FePc.

Figure 2.8. Photograph of the thermal chemical vapor deposition system for the synthesis of aligned carbon nanotubes.
2.3 Characterisation of Nanostructures

2.3.1 Scanning Electron Microscopy

The morphologies of the resulting nanostructured electrodes were determined using a Leica Cambridge 440 stereoscan scanning electron microscope (SEM). A typical SEM scanning process includes scanning of an electron beam across a sample surface and secondary electrons are ejected from the surface. Secondary electron images are generated when interacting with a solid by synchronizing the optical output of the detector system with the raster of the electron probe across the solid surface. The average sizes of the resulting nanostructures were measured from SEM micrographs using Video Pro 32 (Leading Edge Pty. Ltd.).

2.3.2 Solution Properties

Solution properties such as ionic conductivity, surface tension and viscosity were determined in this project. The conductivity of each solution was measured using a Model 20 pH/Conductivity Meter (Denver Instrument). The surface tension of solutions was determined using KSV contact angle analyzer (goniometer, KSV Instruments Ltd) and the viscosity of solutions was tested using a DV-II viscometer (Brookfield Engineering Lab Inc).
2.3.3 Electronic Conductivity

The electronic conductivity of the nanostructures was determined using a Four-Point Probe (Model RM2, Jandel Engineering Ltd.) as shown in Figure 2.9. It involves using the four-point probe technique and four electrodes patterned as shown in Figure 2.10.

Figure 2.9. Photograph of the Four-Point Probe.

Figure 2.10. Top view of the Four-Point Probe used for conductivity measurement.
2.3.4 UV-vis Spectroscopy

The removal of the synthetic opal template in the resulting opaline nanostructures was confirmed by ultraviolet-visible (UV-vis) absorption spectral measurements using a Shimadzu UV-1601 spectrophotometer as shown in Figure 2.11. Samples were scanned from 300 to 900 nm at a 10 nm/s scan rate.

![Figure 2.11. Photograph of the UV-vis spectrophotometer system.](image)

2.3.5 Raman Spectroscopy

The presence of CNTs in the resulting nanostructures was confirmed using Raman spectroscopy (JYHR800) with a 632.8 nm diode laser excitation with a 300 lines/mm grating at room temperature.
2.3.6 Electrochemical Characterisation.

The electrochemical characterisation was carried in a divided three-electrode electrochemical cell using an electrochemical system as demonstrated in Figure 2.1 and Figure 2.2. The cell was used for cyclic voltammetry. Cyclic voltammetry provides a rapid determination of chemical/electrochemical transitions occurring, the potentials at which these occur, and the rate of these transitions. It is the most effective and versatile method for the study of redox reactions.

A typical cyclic voltammogram for a redox process is shown in Figure 2.12. The voltammogram is characterised by a peak anodic potential $E_{pa}$ and peak cathodic potential $E_{pc}$, where the peak anodic current $i_{pa}$ and peak cathodic current $i_{pc}$ can be obtained respectively. The difference between $E_{pa}$ and $E_{pc}$ determines the reversibility of system according to equation 2.3 [3]:

$$\Delta E = E_{pa} - E_{pc} \sim 0.059/n \text{ (V) at 25ºC}$$  \hspace{1cm} (2.3)

where $n$ is the number of electrons transferred in the redox reaction. A reversible system is obtained when $\Delta E$ equals to 0.059/n (V). If $\Delta E$ is greater than 0.059/n (V), the system is called a quasi-reversible system. In the case as shown in Figure 2.12, a broad separation of anodic and cathodic peaks ($\Delta E > 0.059/n$ V), indicating a slow charge transfer rate and the redox process is considered quasi-reversible. A complete
separation of anodic and cathodic peaks would be found in an irreversible system.

Figure 2.12. Cyclic voltammogram of 0.01 M K₄Fe(CN)₆/0.1 M NaNO₃ (aq) at a scan rate of 0.05 Vs⁻¹. The electrode was ITO coated glass.

2.4 Application of Nanostructures

2.4.1 Oxidation of Methanol

The overall reaction mechanism for electrochemical oxidation of methanol is given by Equation 2.4 [4, 5].

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{E}^\circ = 0.046\text{V} \quad (2.4)$$
Actually this reaction is a multistep reaction. Normally, for simplification, the mechanism has been divided into two steps (Equation 2.5) [6].

$$\text{CH}_3\text{OH} \xrightarrow{k_1} \text{CO} \xrightarrow{k_2} \text{CO}_2$$

In this thesis, electrocatalytic performance of nanostructured electrodes at room temperature for methanol oxidation was evaluated by cyclic voltammetry in the divided three-electrode cell (Figure 2.2). The catalytic activity of the nanostructures was also investigated by the potentiostatic method.

### 2.4.2 Photoelectrochemical Testing

Photoelectrochemical testing was carried out in a black box with a 500 Wm$^{-2}$ halogen lamp (Solux MR-16, Wiko Ltd.) and the electrochemical hardware system described in Figure 2.1. The photoelectrochemical cell (PEC) was set up as illustrated in Figure 2.13. The PTTh coated ITO opal electrode was placed facing the light source. Pt sputter coated ITO coated glass (50 mA, 5 seconds, ca. 10 Å thickness) was employed as the counter electrode. A drop of liquid electrolyte ($\text{I}_3^-/\text{I}^-$), prepared by dissolving appropriate masses of $\text{I}_2$ and terrapropylammonium iodide (TPAI) in a 1:1 (w/w) mixture of ethylene carbonate (EC) and propylene carbonate (PC) to give concentrations of 0.06 M $\text{I}_2$, 0.5 M TPAI) was placed between the two electrodes. A parafilm gasket was then applied, leaving an area of polymer 4 mm$^2$ exposed. The two
electrodes were firmly held together using alligator clips (photographically shown in Figure 2.14). The cell was tested using linear sweep voltammetry (LSV).

Figure 2.13. Schematic of set-up of the photoelectrochemical cell.

Figure 2.14. Digital photograph illustrating the process of photoelectrochemical testing.
An idealized current-potential curve is shown in Figure 2.15. The open circuit voltage ($V_{oc}$) is measured under illumination where the current is zero and the short circuit current ($I_{sc}$) where the voltage is zero. The peak power (PP) is the maximum product of V and I. The incident photon power ($P_{ph}$) can be obtained from the product of the window size (A) and the light intensity ($I_1$). The key properties of a photovoltaic cell such as the fill factor (FF, a measure of the internal resistance) and power-conversion efficiency (PCE) was calculated using equation (2.6) and (2.7) [7].

\[
FF = \frac{V_{pp} \cdot I_{pp}}{V_{oc} \cdot I_{sc}} \quad (2.6)
\]

\[
PCE = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{ph}} \quad (2.7)
\]

Figure 2.15. Characteristics of an idealized current-potential curve under illumination during photovoltaic testing.
2.4.3 Enzyme Biosensors

Glucose oxidase (GOx), the most popular oxidase enzyme, was entrapped in electrospun nanofibers in this work. Glucose oxidase can be employed in the enzymatic determination of D-glucose in solution through the following manner [8]:

\[
\text{Glucose} + \text{GOx (ox)} \rightarrow \text{Gluconolactone} + \text{GOx (red)} \quad (2.8)
\]
\[
\text{GOx(red)} + \text{O}_2 \rightarrow \text{GOx(ox)} + \text{H}_2\text{O}_2 \quad (2.9)
\]

The resulting nanofibers were soaked in a glutaraldehyde solution (2.5% (w/w) in 0.4 M PBS, and 0.05 M KCl, pH 6.4) at 4°C overnight. The electrodes were subsequently washed and soaked in a glucose oxidase (GOx) solution (5 mg/ml GOx in PBS, pH 6.4) at 4°C overnight. After a further washing, the enzyme electrode was ready for use.

A constant anodic potential was applied, at which potential, hydrogen peroxide produced in the enzyme reaction is oxidized, to detect hydrogen peroxide produced in the enzyme reaction. The current was monitored continuously until a steady state value was reached.
2.4.4 Cell Culturing

L-929 is a mouse fibroblast line that is commonly used to assess the cytotoxicity of potential substrates for cell growth. In this work, the resulting nanostructured substrate were washed twice in culture media (soaked overnight), then rinsed in water and dried from 70% ethanol. They were sterilized under UV light for 20 minutes. Nanostructures were placed into 96-well Greiner polystyrene tissue culture plate (Interpath, Sydney) and seeded with $5 \times 10^3$ L-929 cells. Cells were cultured for 72 hours in DMEM:F12 media containing 5% FBS and penicillin/streptomycin in a 5% CO$_2$ humidified incubator. Metabolically active cells were then stained using 5 $\mu$M Calcein AM (Molecular Probes) for 15 minutes at 37 °C, washed in PBS and imaged using a Leica DMIL inverted fluorescence microscope fitted with a Leica DC500 camera.

2.4.5 Lithium-ion Battery Testing

The resulting nanostructured electrode was assembled into a lithium-ion battery for testing (Neware, Electronic Co.) using methods described elsewhere [9]. The Lithium-ion testing cell was assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the nanostructured electrode and a lithium foil counter electrode. The electrolyte used was 1.0 M LiPF$_6$ in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate supplied by Merck KgaA, Germany.
2.5 References


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3.1 Introduction

Three dimensional (3D) patterned materials such as colloidal crystals, opals and inverse opals have been investigated for use in a wide range of areas such as photonic crystals, optical devices, catalysis and nano-electronics [1, 2]. Synthetic opals are normally prepared from nano/micro sized monodisperse particles of silica [3] or polystyrene [4]. Self-assembly of polystyrene or silica on a flat substrate [5, 6] is seen as an effective method to fabricate patterned structures on a large scale [7, 8]. A range of materials can then be used to fill the void spaces between the particles using various routes such as sol-gel chemistry, chemical vapor deposition, liquid-phase reactions, deposition of small solid particles, or precipitation from a saturated solution [9-15]. Removal of the synthetic opal template gives rise to an inverse opal structure.

Nano/micro structured transition metals are also of interest in areas such as catalysis, electronic materials and fuel cells [16, 17]. In the present study, synthetic opals were prepared on indium tin oxide (ITO) glass substrates using highly monodispersed polystyrene (PS) beads with diameters of 220 nm and 800 nm. Metals, such as platinum or gold, were electrodeposited through the interstitial space of the synthetic opal matrix. The metal inverse opals (IOp) were subsequently obtained by the removal of the polystyrene templates, leaving a highly ordered three dimensional structure. The morphologies of both the opal template and the inverse opal were determined by scanning electron microscopy. The results indicated that well-defined, microporous Pt-IOp can be synthesized using the method but this approach was unsuccessful in attempts
to fabricate Au-IOP. The removal of PS in the resulting Pt-IOP was confirmed by UV-visible spectroscopy. Electrochemical characterisation demonstrates that the Pt inverse opal electrode has a high surface area and exhibits excellent redox behavior. The electrocatalytic application of the resulting nanostructured Pt inverse opal electrodes for methanol oxidation was also investigated. The nanostructured Pt-IOP electrode shows a clear catalytic activity and high stable electrocatalytic performance for methanol oxidation.

In addition, nanostructured opaline template has already proven useful in catalytic application and may well find use in other areas such as photoelectrochemical cells based electrodes of appropriate composition. Recently, conducting polymers (polyterthiophene (PTTh)) based photoelectrochemical cells (PEC) have been attracting wide interest due to their readily controlled structures and properties, and economic advantages. Rapid progress with excellent power-conversion efficiencies (PCE) (e.g. 0.116% for porphyrin-functionalised bisterthiophene coated on ITO coated glass [18] and 0.101% for PTTh electrodeposited at 60°C on ITO coated glass [19]) has been achieved. Furthermore, numerous studies have successfully introduced nanostructures into TiO₂ based PEC and as a result, enhanced absorption of incident light was obtained [20, 21]. To date, however, there has been no published work on the application of nanostructures in PTTh based PEC. ITO is seen as an ideal candidate in a wide variety of application areas such as anti-static coatings, heat mirrors, solar cells [22, 23], flat panel displays [24], sensors [25] and organic light emitting diodes [26-28] since its high transparency, good conductivity and good chemical stability. More recently, nanostructured ITO has
attracted great interest in many application areas. For example, Fallah and coworkers demonstrated the synthesis of nanostructured ITO films and quantitatively analyzed the electrical properties and the optical transmittance of the films [29]. Nanostructured ITO films based metal nanoparticles were employed as nitric oxide sensors [30, 31]. The potential applications in photocatalytic areas of nanostructured ITO and TiO$_2$ composite films have also been published [32].

In this chapter, initial studies of the synthesis of nanostructured PTTh inverse opals for PEC are reported. The resulting PTTh, however was not robust enough to support the formation of air-holes. Nanostructured ITO opal template was consequently introduced to PTTh based PEC. Enhanced photovoltaic performances of PEC based on PTTh were obtained due to the dramatic increase in the surface area of the photoanode and counter electrode. Particularly, such improvements were observed through increases in short-circuit-current ($I_{sc}$) and power-conversion-efficiency (PCE). The basis of the improved photovoltaic performance of PTTh-based PEC was attributed to the increase in surface area at the ITO/PTTh interfaces and the corresponding increased rate of charge transfer across these interfaces.
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3.2 Experimental

3.2.1 Reagents and Materials

Monodispersed polystyrene beads (diameter of 220 nm ± 12 nm or 800 nm ± 70 nm) were provided by Polysciences. HAuCl₄, hexachloroplatinic (IV) acid (containing nitric acid, hydrochloric acid and platinic acid), iodine (I₂), tertrapropylammonium iodide (TPAI), ethylene carbonate (EC), propylene carbonate (PC) and 2,2’:5’2”-terthiophene were all purchased from Sigma-Aldrich. NaNO₃ was obtained from Chem-Supply. K₄Fe(CN)₆ was from Asia Pacific Specialty Chemicals. Tertrabutylammonium perchlorate (TBAP) was obtained from Fluka. HCl, methanol and acetonitrile were purchased from Ajax. ITO coated glass slides were obtained from Delta Technologies Limited. Before use, the ITO coated glass was washed in detergent, rinsed and then soaked in acetone for one hour, followed by UV-ozone treatment for 15 minutes to remove any grease or oil.

3.2.2 Preparation of the Opal Templates

Opal templates were prepared using monodisperse polystyrene beads (diameter of 220 nm ± 12 nm or 800 nm ± 70 nm) in water (1 g/10 mL). ITO coated glass slides were used as the substrate for the formation of ordered opals. The ITO coated glass slide was covered with an insulating tape in which a 6 mm-diameter circle was left exposed. A drop of polystyrene colloidal suspension was placed into the circle on the ITO coated glass slide and allowed to evenly spread within the hole. The formation of the opal template
then occurred at room temperature over 24 hours with the slow evaporation of the water [4].

3.2.3 Synthesis of the Metal Inverse Opals

Au or Pt was filled into the interstitial space of the opal matrix using electrochemical deposition. In all cases, a Pt mesh was employed as a counter electrode and Ag/AgCl (3M NaCl) was used as a reference electrode.

Gold was electrodeposited by cyclic voltammetry from 0.1 M HAuCl₄/1 M HCl (aq). The potential was cycled between -0.2 and 1.7 V (vs. Ag/AgCl) at a scan rate of 0.1 Vs⁻¹ (electrode size = 0.2826 cm²).

Pt was deposited onto the PS opal by cyclic voltammetry growth. Deposition was from a solution of 10% (w/w) hexachloroplatinic (IV) acid. The potential was cycled between -0.1 and +0.7 V (vs. Ag/AgCl) for 1 to 15 cycles at a scan rate of 0.05 Vs⁻¹ (electrode size = 0.2826 cm²).

The metal inverse opals were obtained after the removal of the opal template by placing the metal/PS composite in a furnace at 450°C for 90 minutes.
3.2.4 Preparation of the Nanostructured PTTh Inverse Opals and ITO Opals

PTTh was electropolymerised into the PS template from 0.01 M 2,2’:5’2’’-terthiophene/0.1 M TBAP/acetonitrile solution using cyclic voltammetry with potential cycling between -0.4 and +0.9 V vs. Ag/Ag⁺ at 0.1 V s⁻¹ scan rate (electrode size = 0.6 cm²).

ITO was sputter coated onto the PS opal template using an indium oxide/tin oxide target (IN519300, Goodfellow Cambridge Ltd.) at 30 mA for 10 minutes.

The PS template was removed by heating at 450°C for 90 minutes and the composites were further treated by an annealing process (550°C for 30 minutes).

3.2.5 Electrodeposition of PTTh onto ITO Opals

PTTh was subsequently electrodeposited into ITO opal coated slides by cyclic voltammetry. The polymerisation solution consisted of 0.01 M 2,2’:5’2’’-terthiophene/0.1 M TBAP in acetonitrile. The potential was cycled between -0.4 and +0.9 V vs. Ag/Ag⁺ for 1 to 7 cycles at 0.1 V s⁻¹ scan rate (electrode size = 0.6 cm²).

PTTh was also electropolymerised on the pure ITO coated glass slide under the same reaction condition for comparison.
3.2.6 Characterisation

The morphology of the PS opal template and resulting nanostructured opaline materials were observed using a scanning electron microscope (SEM). The removal of PS in the resulting nanostructure was confirmed by UV-vis absorption spectral measurements. An inverse opal or opal sample was placed in one sample holder and the other one had a blank ITO coated glass slide as a reference placed in it. Both inverse opal and opal are transparent and allow the light to pass through.

During the electrochemical characterisation, samples of the Pt-IOp and Pt film were investigated using cyclic voltammetry. Pt mesh was used as the auxiliary electrode and the potential was cycled from -1.0 V to +1.0 V (vs. Ag/AgCl) at a scan rate of 0.05 Vs\(^{-1}\) in 0.01 M potassium ferrocyanide (K\(_4\)Fe(CN)\(_6\)) /0.1 M NaNO\(_3\) (aq) (electrode size = 0.2826 cm\(^2\)).

The electrochemical properties of the ITO opal electrodes were studied using cyclic voltammetry in 0.01 M K\(_4\)Fe(CN)\(_6\)/0.1 M NaNO\(_3\) (aq) (electrode size = 0.6 cm\(^2\)). The potential was cycled between -0.3 and +0.8 V vs. Ag/AgCl. PTTh coated ITO opals were characterized in 0.1 M TBAP/acetonitrile using cyclic voltammetry between -0.4 and +0.9 V vs. Ag/Ag\(^+\). In all cases, Pt mesh was used as an auxiliary electrode.
3.2.7 Electro-oxidation of Methanol

Electrocatalytic performance at room temperature for methanol oxidation was evaluated by cyclic voltammetry in the divided three-electrode cell, with the Pt-IOP modified ITO coated glass electrode as working electrode. The catalytic activity of the nanostructured Pt-IOP electrode was also investigated by the potentiostatic method at +0.70 V.

3.2.8 Photoelectrochemical Testing

PTTh coated ITO opal electrode was measured in photoelectrochemical cell as described in Figure 2.1 and Figure 2.14, Chapter 2. The cell was controlled by linear sweep voltammetry (LSV) and the potential swept from – 0.05 V to +0.2 V at a 100 mVs⁻¹ scan rate.

3.3 Results and Discussion

3.3.1 Scanning Electron Microscopy

3.3.1.1 Polystyrene Opals

A drop of monodispersed PS solution was placed onto ITO coated glass and allowed to evaporate to dryness at room temperature. Capillary forces caused the PS beads to pack into a crystalline structure on the ITO slide [33], forming a highly ordered dense
hexagonal packing [34, 35]. An iridescent sheen was observed after drying. This comes from the Bragg diffraction of light [36] from the opal crystals. Figure 3.1 shows SEM micrographs of the self-assembled PS opal templates. A highly ordered dense hexagonal packing arrangement of the PS colloidal template was observed. Some void space coming from shrinkage during drying is observed between the PS spheres. Several well-ordered layers of beads are observed, indicating that the structure obtained was three dimensional.
Figure 3.1. SEM micrographs of the polystyrene opal templates prepared from (a) 800 nm diameter polystyrene spheres and (b) 220 nm diameter polystyrene spheres.

### 3.3.1.2 Gold Inverse Opals

Initial work involved attempts to synthesize Au inverse opals (IOp) by electrodepositing gold through the polystyrene opal template using cyclic voltammetry. The cyclic voltammogram during the electrodeposition of Au is shown in Figure 3.2. Two oxidation peaks were observed at +1.05 V vs. Ag/AgCl (I) and +1.20 V vs. Ag/AgCl (II), arising from the oxidation of Au and oxygen. The reduction peak (III) observed at +0.58 V can be attributed to the deposition of gold.
Figure 3.2. Cyclic voltammogram obtained during electrodeposition of Au into the polystyrene opal template on an ITO substrate from 0.1 M HAuCl$_4$/1 M HCl$_{\text{aq}}$ at a scan rate of 0.1 Vs$^{-1}$.

The resulting structure after the removal of the PS template was examined using SEM (Figure 3.3). A microporous structure was observed when gold was electrodeposited onto 800nm-PS opals, followed by the removal of PS opals at high temperature. However, a poorly interconnected network with many unstructured areas was obtained (Figure 3.3a). Using a 220 nm-PS opal template, a more highly interconnected network with a structure more closely resembling an inverse opal was obtained (Figure 3.3b). Despite adjusting several electrochemical deposition variables including deposition time, cycled potential ranges and deposition rate etc., it was, however, hard to maintain the nanoporous structure over a reasonable surface area using electrochemical deposition.
Figure 3.3. SEM micrographs of the Au inverse opals prepared from (a) 800 nm diameter and (b) 220 nm diameter polystyrene microspheres using cyclic voltammetry by cycling the potential between -0.2 V and +1.7 V vs. Ag/AgCl (3 M NaCl) for 1 cycle at 0.1 Vs⁻¹.
3.3.1.3 Pt Inverse Opals

Potentiodynamic growth was used to electrodeposit Pt onto the PS opal template or ITO coated glass slide. The cyclic voltammogram is shown in Figure 3.4. Three reactions may be involved in the electrodeposition of Pt.

\[
\begin{align*}
[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-} + 2e^- &\rightleftharpoons [\text{Pt}^{\text{II}}\text{Cl}_4]^{2-} + 2\text{Cl}^- \quad (3.1) \\
[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-} + 2e^- &\rightleftharpoons \text{Pt} + 4\text{Cl}^- \quad (3.2) \\
[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-} + 4e^- &\rightleftharpoons \text{Pt} + 6\text{Cl}^- \quad (3.3)
\end{align*}
\]

In hexachloroplatinic (IV) acid, the major species present is \(\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}\) due to the presence of HCl in the solution [37]. The electrode process can thus be simply described as equation (3.3). As shown in Figure 3.4, one oxidation peak (I) was observed at +0.53 V, originating from the oxidation of Pt. Two reduction peaks observed at +0.49 V (II) and +0.05 V (III) may be due to the reduction of \([\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}\) and \([\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}\), giving rise to the deposition of Pt. It was also found that the currents increased with increasing amount of cycle numbers, suggesting the successful deposition of Pt.
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Figure 3.4. Cyclic voltammogram obtained during electrodeposition of Pt into the polystyrene opal template on an ITO substrate from 10% (w/w) hexachloroplatinic (IV) acid at a scan rate of 0.05 Vs\(^{-1}\).

Figure 3.5 exhibits various structures of resulting inverse opals obtained from 800 nm-diameter PS microspheres after different deposition time. As shown in Figure 3.5(a), the Pt film structure was too fragile to maintain the inverse opal structure when the potential was cycled between -0.1 V and +0.7 V at 0.05 V s\(^{-1}\) for 5 cycles during electrodeposition. When the potential cycle number was increased to 10 cycles, a highly ordered nanostructure was maintained (Figure 3.5b). This structure presents long range area and a highly interconnected porous Pt film. The average diameter of the voids in the Pt inverse opal structure was estimated at around 500 nm. The porous structure was still visible
when the potential was cycled for 15 cycles. However some parts of the voids were covered by a layer of Pt (Figure 3.5c).
Figure 3.5. SEM micrograph of the Pt inverse opal prepared from 800 nm diameter polystyrene microspheres using cyclic voltammetry by cycling the potential between -0.1 V and +0.7 V vs. Ag/AgCl (3 M NaCl) for (a) 5 cycles, (b) 10 cycles and (c) 15 cycles at 0.05 Vs⁻¹.

Figure 3.6 shows the best inner structure of the Pt inverse opal obtained from 220 nm diameter PS microspheres by cyclic voltammetry. It was found that the Pt film successfully filled the void space between PS beads and a nanoporous structure was observed after the removal of the PS template. The application of the resulting film, however, was limited by a lack of uniformity and a poorly interconnected structure over reasonable dimensions. This may be attributed to the small size of void space between the PS beads which prevented the Pt from depositing uniformly.
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Figure 3.6. SEM micrograph of the Pt inverse opal prepared from 220 nm diameter polystyrene microspheres using cyclic voltammetry by cycling potential between -0.1 V and +0.7 V vs. Ag/AgCl (3 M NaCl) for 10 cycles at 0.05 V s\(^{-1}\).

The optimum deposition conditions for preparing Pt IOps was thus obtained as follows: Pt was electrodeposited onto 800 nm diameter PS microspheres using cyclic voltammetry with potential cycling between -0.1 V and +0.7 V at 0.05 V s\(^{-1}\) for 10 cycles. Highly ordered, nanoporous Pt inverse opals were subsequently obtained after the removal of PS templates by annealing the Pt/PS composites at high temperature.

3.3.1.4 Nanostructured Mesoporous ITO Opals

ITO was deposited onto the opaline structure using sputter coating. SEM was obtained after the removal of PS opal template. The right hand side of Figure 3.7 exhibits some inverted part of resulting ITO opals, clearly illustrating the porous bottom of the ITO opal
film. The highly ordered, half ball shaped, mesoporous surface of the ITO opals offers a much larger surface area to the resulting electrode.

Figure 3.7. SEM micrograph of the ITO opals.

3.3.1.5 Polyterthiophene Inverse Opals

Polyterthiophene was grown into the void space between PS beads using cyclic voltammetry with potential cycling between -0.4 and +0.9 V (vs. Ag/Ag+) at 0.1 Vs⁻¹. SEM micrographs were obtained after the removal of the PS. As shown in Figure 3.8(a), PTTh films electrodeposited from 2 cycles by cyclic voltammetry was not strong enough to hold the porous structure after the removal of the PS. Upon increasing the deposition time to 5 cycles, PTTh film became thicker and the porous structure could be found (Figure 3.8b). But PTTh also accumulated together in some parts of the opal indicating less uniform growth (Figure 3.8b). When PTTh was deposited onto PS for 10 cycles, a
thicker film covered the whole opal structure (Figure 3.8c). No well defined inverse opal structure could be found on the resulting PTTh film after soaking PTTh/PS composites in toluene. Electrodeposition of PTTh through the PS opal proved not to be a good way to fabricate PTTh inverse opals probably due to the fragility of the resulting PTTh film. Consequently, ITO opals were considered in further work.
Figure 3.8. SEM micrographs of polyterthiophene inverse opals prepared using cyclic voltammetry with potential cycling between -0.4 and +0.9 V vs. Ag/Ag⁺ at 0.1 V s⁻¹ for (a) 2 cycles; (b) 5 cycles and (c) 10 cycles at (i) low resolution and (ii) high resolution.

3.3.1.6 Electropolymerisation of Polyterthiophene onto ITO Opals

A typical cyclic voltammogram (CV) during the electrodeposition of PTTh onto ITO opals is shown in Figure 3.9. An oxidation onset at +0.65 V was observed. With an increasing number of the potential cycles, a fall in oxidation onset and an increase in the current were observed, indicating the growth of PTTh onto the substrate.
Figure 3.9. Cyclic voltammograms observed during the growth of polyterthiophene from 0.01 M 2,2':5,5':2''-terthiophene/0.1 M tertrabutylammonium perchlorate/acetonitrile to 5 cycles at 0.1 Vs⁻¹ on ITO opals.

Figure 3.10(a) shows the result of PTTh coated ITO opals from 1 cycle. A fairly thin layer of PTTh was electrodeposited on the top of ITO opals. This layer of PTTh film deposited along the half-bowl shape of the original opals very well. When more PTTh was deposited, some opal parts were covered by PTTh significantly while some parts were still exposed (Figure 3.10b), forming a nice 3D structure of PTTh film. A much higher surface area of PTTh film was produced both due to the opaline shape of the film and from the various thickness of the film. This result also indicated that the electrodeposition of PTTh was not uniform and simultaneous on the whole electrode.
When the cycle number for the deposition of PTTh was increased to 5 cycles, all the ITO opaline shell was covered by the polymer film while different thicknesses of the PTTh film still visible (Figure 3.10c). This kind of interesting 3D structure is expected to enhance the photoelectrochemical properties of the product. The opaline structure was not visible again when the PTTh was deposited for 7 cycles (Figure 3.10d) while a nice 3D porous structure was observed, offering a high surface area.

Figure 3.10. SEM micrographs of polyterthiophene electrodeposited on ITO opals using cyclic voltammetry for (a) 1 cycle, (b) 3 cycles, (c) 5 cycles and (d) 7 cycles at 0.1 Vs⁻¹.
3.3.2 UV-vis Absorption Spectroscopy

The UV-vis absorption spectrum of the PS opal is shown in Figure 3.11(a). The small peak (I) observed at 390 nm can be attributed to a photonic band gap (PBG) or pseudogap [38]. Two peaks (II and III) found between 500 nm and 700 nm may arise from the dye molecules present in the PS beads, incorporated during the PS opal preparation process by the supporter (Polysciences). These two peaks can be used as the indicator of the presence or the absence of the PS opal template.

UV-vis spectrum of the resulting Pt inverse opal is illustrated in Figure 3.11(b). Two peaks present in the spectrum of PS opals (II and III, Figure 3.11a) are absent here. This confirms the removal of the PS opal template during annealing. The absorption at 400 nm may be due to the PBG, suggesting a highly ordered 3D of Pt inverse opal with diameter at optical wavelength was obtained.

Figure 3.11(c) shows the UV-vis absorption spectrum obtained for the mesoporous ITO opal structure. The two typical peaks due to the presence of PS microbeads observed in Figure 3.11(a) at 500 nm and 700 nm respectively [38, 39] were absent in the spectrum of the ITO opal (Figure 3.11c); indicating the removal of the PS opal structure. The structured surface observed in the SEM (Figure 3.7) was thus attributed to the ITO film not the PS film. The peak found at 430 nm may be attributed to the PBG, indicating the well-ordered structure of the ITO opal.
Figure 3.11. UV-visible spectra of (a) the polystyrene opal on ITO coated glass, (b) the Pt inverse opal on ITO coated glass and (c) the ITO opal structure on ITO coated glass.

### 3.3.3 Electrochemical Characterisation

Figure 3.12 illustrates cyclic voltammograms obtained using a Pt inverse opal or a Pt film, with the same geometric area. The voltammograms exhibit well defined response assigned to the \([\text{Fe(CN)}_6]^{4-}/[\text{Fe(CN)}_6]^{3-}\) redox pair. One stable redox couple was observed in Figure 3.12(a) at +0.64 V and -0.12 V for the Pt inverse opal electrode, while the redox peaks were found at +0.30 V and +0.11 V for the Pt film electrode (Figure 3.12b). The intensity of the peak currents increased from 0.65 to 2.68 mA cm\(^{-2}\) for the oxidation and
shifted from -0.44 to -1.98 mA•cm$^{-2}$ for the reduction of the electrolytes. The higher currents observed at the Pt inverse opal indicate that it has a higher electroactive surface area than the Pt film.

Figure 3.12. Cyclic voltammograms of (a) a Pt inverse opal (Pt-IOp) and (b) a Pt film in 0.01 M $\text{K}_4\text{Fe(CN)}_6$/0.1 M $\text{NaNO}_3$(aq) (scan rate = 0.05 Vs$^{-1}$).

Redox pairs are normally used to probe the quality of the electrode by cyclic voltammetry [40-42]. In this work, $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$ was chosen as redox pairs for their voltammetric responses in order to investigate the electronic transfer properties of the Pt inverse opal electrode. The peak currents increase with an increase in scan rate (Figure 3.13a). Both anodic peak current ($i_{pa}$) and cathodic peak current ($i_{pc}$) are found to be proportional to the square root of the scan rate ($\nu$) (Figure 3.13b), $i_{pa} = 0.4543 +\ldots$
9.7602v^{1/2}, r = 0.9955, and \( i_{pc} = -0.0549 + 8.8906v^{1/2}, r = 0.9990 \). The electron transfer rate at the interface between the electrode and the solution is faster than diffusion of the reactant. It can thus be concluded that the redox reaction of \( \text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-} \) in 0.1 M NaNO\(_3\) at the Pt inverse opal electrode is a quasi-reversible reaction as the peak potential separation between the anodic and cathodic peaks is greater than 59 mV (for a reversible one electron transfer at 25°C) [43].
Figure 3.13. (a) Cyclic voltammograms of the Pt inverse opal electrode in 0.01 M K₄Fe(CN)₆/0.1 M NaNO₃ (aq) at various scan rates of 0.1 to 0.01 Vs⁻¹ ranges and (b) redox peak currents proportional to square roots of the scan rates for 0.01 M K₄Fe(CN)₆ in 0.1 M NaNO₃ (aq).

Cyclic voltammograms were obtained in 0.01 M K₄Fe(CN)₆/0.1 M NaNO₃ (aq). Two well-defined redox peaks were observed at +0.46 and 0.00 V vs. Ag/AgCl respectively in the cyclic voltammogram of the ITO opal electrode as shown in Figure 3.14b. Compared with the CV of the pristine ITO coated glass slide (Figure 3.14a), the oxidation peak potential was shifted from +0.31 to +0.46 V vs. Ag/AgCl while that of the reduction peak shifted from +0.13 to 0.00 V vs. Ag/AgCl, indicating changes in the electrode structure after the incorporation of nanostructured ITO films. The intensity of the peak currents increased from 1.56 to 1.88 mA•cm⁻² for the oxidation and from -1.20 to -1.58 mA•cm⁻² for the
reduction of the electrolyte. The changes in electroactive surface area from the ITO electrode to the ITO opal electrode can be determined according to the Randles-Sevcik equation [43]:

$$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \nu^{1/2} C$$  \hspace{1cm} (3.4)

where A is the area of the electrode (cm$^2$), D is the diffusion coefficient of the molecule in solution (cm$^2$s$^{-1}$), n is the number of electrons participating in the redox reaction, \( \nu \) is the scan rate of the potential (Vs$^{-1}$), and C is the concentration of the probe molecule in the bulk solution (mol•cm$^{-3}$).

Figure 3.14. Cyclic voltammograms in 0.01 M K$_4$Fe(CN)$_6$/0.1 M NaNO$_3$ (aq) at a scan rate of 0.05 Vs$^{-1}$ of (a) the pristine ITO coated glass, and (b) the ITO nanostructured electrode.
The Fe(CN)$_6^{4-/3-}$ redox system is one of the most extensively studied redox couples in electrochemistry and exhibits a heterogeneous one-electron transfer (n = 1). C is equal to 0.01 M and the diffusion coefficient of Fe(CN)$_6^{4-}$ was taken as 6.3×10$^{-6}$ cm$^2$s$^{-1}$ [44]. The average value of the electroactive surface area for the ITO opal was therefore estimated as 1.14 cm$^2$, compared with that of the pristine ITO coated glass which was 0.91 cm$^2$. A higher surface area due to the mesoporous structure was obtained in the ITO opal electrode than the ITO electrode.

Figure 3.15(a) shows that the peak currents increase with an increase in scan rate. Both anodic peak current ($i_{pa}$) and cathodic peak current ($i_{pc}$) are found to be proportional to the square root of the scan rate ($v$) (Figure 3.15b), $i_{pa} = 0.4315 + 6.355v^{1/2}$, $r = 0.9991$, and $i_{pc} = 0.154 + 6.1678v^{1/2}$, $r = 0.9970$. The electron transfer is fast and the reaction at the ITO opal electrode is diffusion-controlled.
Chapter 3: Opaline Nanostructures

Figure 3.15. (a) Cyclic voltammograms of the ITO opals coated ITO coated glass in 0.01 M $\text{K}_4\text{Fe(CN)}_6$/0.1 M $\text{NaNO}_3$ (aq) at various scan rates of 0.1 to 0.01 Vs$^{-1}$ and (b) redox peak currents proportional to square roots of the scan rates for 0.01 M $\text{K}_4\text{Fe(CN)}_6$ in 0.1 M $\text{NaNO}_3$ (aq).

![Graph showing cyclic voltammograms and redox peak currents](image)

Figure 3.16 exhibits the post-growth CV of PTTh coated ITO opals. A significant cathodic peak was observed at $+0.5\text{V}$ while no anodic peak was found. Little change in current response was observed during 10 consecutive cycles, suggesting that the electrochemical active property of the sample was quite stable.
3.3.4 Methanol Oxidation

Using the Pt-IOp electrode, methanol oxidation was investigated using cyclic voltammetry (Figure 3.17a). A well defined oxidation peak (A) was observed using the Pt-IOp electrode. On the reverse sweep, another oxidation peak (B) was obtained indicating that intermediate oxidation products (e.g. CO) are adsorbed onto the Pt inverse opal structure and continue to be oxidised to CO₂. The peak current for methanol oxidation observed using Pt-IOp was 59.45 μA•cm⁻², which is ca. ten times that (6.05 μA•cm⁻²) observed at a Pt film electrode (Figure 3.17b). The onset of methanol oxidation...
at the Pt-IOp electrode is +0.30 V, which is 100 mV less positive than that observed (+0.40 V) with the Pt film electrode (the insert in Figure 3.17).

Figure 3.17. Cyclic voltammograms at (a) the Pt inverse opal, and (b) the Pt film electrode in 1 M MeOH/1 M H₂SO₄ (aq) (scan rate = 0.05 V s⁻¹). The insert is the zoom of curve b.

The peak current observed for methanol oxidation increased with increasing scan rate (Figure 3.18), however, the peak potential did not change. The peak currents observed are linearly proportional to the square root of scan rate (shown in Figure 3.19), which suggests that the electrocatalytic oxidation of methanol at the Pt-IOp electrode is a
diffusion-controlled process. Similar results were reported by Che et al using a platinised carbon nanotube membrane electrode [45].

Figure 3.18. Cyclic voltammograms of the Pt inverse opal electrode at different scan rates in 1 M MeOH/1 M H₂SO₄(aq).
Figure 3.19. Dependence of the peak current for methanol oxidation at a Pt inverse opal electrode on the square root of scan rate.

Methanol oxidation was also investigated at a constant potential (+0.70 V) to investigate the catalytic activity of the nanostructured Pt-IOp electrode. After the initial drop in current over the first few minutes, a steady current (4 mA•cm⁻²) for methanol oxidation was observed after 1 hr (Figure 3.20a). The current observed at the corresponding Pt disc electrode was approximately 0.2 mA•cm⁻² (Figure 3.20b). This suggests that nanostructured Pt-IOp electrode significantly improves the catalytic activity for methanol oxidation.
Figure 3.20. Chronoamperogram obtained during methanol oxidation at (a) the Pt-IOP and (b) the Pt film electrode in 1 M MeOH/1 M H₂SO₄(aq). E_{app} = +0.7 V vs. Ag/AgCl.
3.3.5 Photoelectrochemical Performance

The photoelectrochemical properties of the resulting the PTTh/ITO opal electrode were probed in a typical PEC. Table 3.1 summarizes the data obtained from tests during the illumination phase. As shown in No.1 Table 3.1, power-conversion efficiency (PCE) was quite low (0.0041%) when 1 cycle was used to deposit PTTh. The small amount of PTTh results in the poor contact area between the polymer and the electrolytes ($I_3^-/I^-$). A significant improvement of PCE was found when the cycle number was increased to 3 cycles (No.2, Table 3.1). The suitable amount of PTTh with the presence of mesoporous substrate and the interesting 3D film structure extend the polymer surface area dramatically. As a result, a larger contact area between PTTh and electrolytes was obtained, leading to a high performance in the PV cell. When the PTTh was electrodeposited for 5 cycles, a higher PTTh surface area was obtained with the mesoporous structure visible, which provided a much higher contact area between the electrolytes and PTTh film. A considerable value (0.109%) for PCE was thus obtained (No.3, Table 3.1), compared with that of PTTh coated pristine ITO coated glass (0.035%, No.5 Table 3.1). When further PTTh was electrodeposited, the opaline substrate was all covered by the polymer film, resulting in a decrease in PCE. However considering that the 3D film structure was still observed, the contact area between the polymer and the liquid electrolytes was still large (No. 4, Table 3.1). The resulting PCE was therefore much higher than the PTTh coated ITO coated glass. Therefore, the best photovoltaic performance was obtained from the device of PTTh coated ITO opals for 5 cycles ($I_{sc} = 1470 \, \mu A \cdot \text{cm}^{-2}$, $V_{oc} = 120 \, \text{mV}$, $FF = 30.8\%$, $PCE = 0.109\%$).
Table 3.1. Photovoltaic performance of PTTh electrodeposited onto ITO opals or ITO coated glass under various conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Substrates</th>
<th>No. of cycles used</th>
<th>$I_{sc}$ (uA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>ITO opals</td>
<td>1</td>
<td>67</td>
<td>113</td>
<td>27.3</td>
<td>0.0041</td>
</tr>
<tr>
<td>2</td>
<td>ITO opals</td>
<td>3</td>
<td>863</td>
<td>110</td>
<td>31.7</td>
<td>0.060</td>
</tr>
<tr>
<td>3</td>
<td>ITO opals</td>
<td>5</td>
<td>1470</td>
<td>120</td>
<td>30.8</td>
<td>0.109</td>
</tr>
<tr>
<td>4</td>
<td>ITO opals</td>
<td>7</td>
<td>954</td>
<td>136</td>
<td>31.5</td>
<td>0.081</td>
</tr>
<tr>
<td>5</td>
<td>ITO coated glass</td>
<td>5</td>
<td>459</td>
<td>131</td>
<td>28.8</td>
<td>0.035</td>
</tr>
</tbody>
</table>

The I-V curve during PV testing of this device in the dark and under illumination using a 500 Wm$^{-2}$ halogen lamp is shown in Figure 3.21. The best PCE of 0.109% obtained is a significant improvement at the literature values of 0.021% [46] and 0.015% [47] for PCE based on electrodeposited PTTh at room temperature and 0.101% [19] for PTTh electrodeposited at 60ºC. The best $I_{sc}$ of 1470 μA cm$^{-2}$ obtained in this study was also a dramatic improvement on previously published work.
Figure 3.21. Current-potential curve obtained during photoelectrochemical testing of polyterthiophene electrodeposited onto ITO opals with 5 cycles (scan rate = 0.1 Vs\(^{-1}\)).
3.4 Conclusions

Nanostructured inverse opals of Pt can be obtained using polystyrene opal templates prepared from 800 nm-diameter polystyrene microspheres, by filling the void space between the polystyrene beads with metals via electrochemical deposition, and then removing the PS opal template by annealing the nanocomposite at 450°C for 90 min. SEM micrographs show that the PS opal template forms a highly ordered dense hexagonal packing structure which is retained following the furnace treatment. This leaves a highly ordered, high surface area nanoporous structure. UV-visible absorption spectra confirm the complete removal of PS and the deposition of Pt in the resulting Pt inverse opal. The high surface area inherent in the inverse opal structure is confirmed by electrochemical characterization when compared to a Pt film of the same geometric size.

The nanostructured Pt-IOp electrode shows excellent electrocatalytic performance for methanol oxidation. When compared with a Pt film, it has extraordinarily higher catalytic performance and stability with a 100 mV negative shift of the potential for methanol oxidation. These features indicate that the nanostructure has a great influence on methanol oxidation which may be useful for other catalytic applications.

Transparent, mesoporous nanostructured ITO opals were also synthesized on the ITO coated glass slide. The resulting opals exhibit a half-ball opaline surface with microporous structure on the bottom. UV-vis spectra confirmed the formation of the ITO opal film and the removal of the host PS opal template. The ITO opal electrode
demonstrates a much higher electroactive surface area than the pristine ITO coated glass during electrochemical characterisation. PTTh was subsequently electrodeposited onto the ITO opals and a nice 3D mesoporous PTTh coated ITO opal film was prepared. The resulting device shows an excellent performance during PV testing with a best PCE of 0.109% and $I_{sc}$ of 1470 $\mu$A$\cdot$cm$^{-2}$ by electrodepositing PTTh at room temperature, suggesting a dramatic improvement in polymer surface area due to the presence of a mesoporous structure.
3.5 References


CHAPTER 4:

FABRICATION OF NANOFIBERS
FROM BIOMATERIALS AND
CARBON NANOTUBES
4.1 Introduction

In this chapter, electrospinning was used to prepare nanofibers based on DNA and poly(styrene-β-isobutylene-β-styrene) (SIBS) with/without the addition of carbon nanotubes (CNTs). The effect of solution properties such as solution conductivity, surface tension and viscosity on the electrospinning process was investigated. The influence of process parameters including the tip-to-collector distance, the applied potential between needle and target and the polymer solution feed rate on fiber diameter and morphology was determined. Application of the resulting nanofibers in areas such as biosensors and cell culturing were considered.

DNA is a nucleic acid that contains the genetic instructions specifying the biological development of all cellular forms of life (and many viruses). There has been much work investigating techniques to prepare novel structures and/or devices by the modification of DNA chains through the sequence-specific pairing interactions [1, 2]. Applications of DNA-based polymers have been investigated in many areas such as ionic liquid DNA [3, 4], semiconductor [5] and non-linear optics [6]. On the other hand, poly(ethylene oxide) (PEO) is known as a highly conductive polymer due to its ability to dissociate salts into ions and stabilizing them with relatively large dipole moment on its ether oxygen. PEO was previously reported as a host polymer to improve processability and biocompatibility of solutions of natural proteins and conducting polymers without the use of organic solvents [7-9], since it is known to be biocompatible [10]. Nishimura et al. have reported
that the ionic conductivity of DNA was improved by introducing PEO onto DNA chains through a covalent bond [11]. To date, no work has been published concerning electrospinning DNA/PEO blends; especially from aqueous solution. In our work, nanofibers were electrospun both from DNA/PEO blended solution and from DNA/PEO/single-walled CNT (SWNT) dispersion. The enhanced electro-conductivity, electrochemical properties and application in biosensors of the resulting fibers with the addition of SWNTs will be described.

Carbon nanotubes (CNTs), first discovered by Iijima in 1991 [12], possess a fascinating combination of electronic and mechanical properties and their potential application as components of novel biomaterials has not gone unnoticed [13, 14]. Numerous techniques have been used to prepare CNTs in various types of configuration; e.g. CNT papers [15], CNT spun fibers [16] and CNT carpets [17]. A further approach to incorporating CNTs into practical devices is the use of electrospinning, a technique known since the early 1930s [18]. The electrospun fiber webs consisted of an interconnected microporous structure. These structures have potential advantages of enhanced mass transport and provision of interpenetrating 3D networks for cell attachment and proliferation.

The combination of DNA with SWNTs has been of interest due to the ability of the biomolecule to self-assemble CNTs to form molecular-scale electronic systems [19, 20]. The noncovalent binding of DNA to the side walls of SWNTs has been reported [21]. Zheng et al. have recently dispersed CNTs using single-stranded DNA [21-23].
Glucose oxidase (GOx) has been immobilised onto CNTs by electrodeposition within a conductive polymer [24, 25], through CNT-based screen-printed electrodes [26] and CNT paper [27]. GOx has been attached to CNTs through covalent binding carbodiimide between amine groups of GOx and the carboxylic acid groups of chemically functionalized CNTs. In this research work, DNA was utilized to favour dispersion and separation of carbon nanotubes [23] and also increase the effective surface in contact between the CNTs coated electrode and enzyme (increased the amount of immobilized enzyme). The resulting biosensor in our work showed wide linearity range and good sensitivity.

Recently the cytocompatibility of both single- and multi-walled carbon nanotubes (SWNTs and MWNTs) was proven using two standard assays (neutral red assay for the cell viability and MTT assay (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenytertrazolium bromide)-tetrazolinium salt-for the cell metabolic activity) [28]. MTT assay is a laboratory test and a standard colorimetric assay for measuring cellular proliferation (cell growth) [29]. The surface morphologies were modified by incorporating CNTs, giving rise to advantages for other implantable devices via selectively growing preferred cell types at the expense of undesirable cell types. CNT platforms have been successfully used for the growth of the mouse fibroblast line L-929 [30] as well as neuronal cells [31, 32], smooth muscle cells [33] and in bone cell proliferation [34]. The inherent electrical conductivity of CNTs also opens up the possibility of using these conductive materials as substrates for studies of the effects of electrical stimulation on cell growth. Various
studies have demonstrated the influence of electric field on cell growth; For example, the growth of nerve cells has found to be enhanced and directed by the application of electric fields [35, 36]. A recent study showed that osteoblast growth on composites of MWNTs and polylactic acid was stimulated to cell proliferate and function by applying alternating currents [37].

In this work, fibrous nanowebs containing SWNTs integrated throughout biocompatible polymers such as SIBS have been produced. SIBS is a block copolymer first reported by Kennedy [38, 39] that exhibits different microphase morphologies depending on the ratio of styrene to isobutylene units in the copolymer (see Figure 4.1 for structure). Compositions that result in SIBS structures consisting of a continuous polyisobutylene phase and discontinuous polystyrene phases provide a material that exhibits mechanical properties similar to an elastomer [40]. SIBS is biostable [41-43] and has been used as a biocompatible drug-eluting coating for cardiac stents [44-47]. The resulting SIBS/SWNT nanofibrous webs consist of an interconnected microporous structure with a high surface area, suggesting potential applications in areas requiring good mass transport and rapid charge/discharge such as biosensors, batteries, super-capacitors and as platforms for cell cultures.
Chapter 4: Fabrication of Nanofibers from Biomaterials and Carbon Nanotubes

Figure 4.1. Chemical structure of poly(styrene-β-isobutylene-β-styrene) (SIBS).

4.2 Experimental

4.2.1 Reagents and Materials

PEO (Mw 300,000), glutaraldehyde, glucose oxidase and glucose were all purchased from Sigma-Aldrich. K₃Fe(CN)₆, Na₂HPO₄, NaH₂PO₄, NaCl and KCl were from Asia Pacific Specialty Chemicals. DNA-Na (Mw 3,000,000) was supplied by Nippon Chemical Feed Co. Ltd. SWNT was obtained from Carbon Nanotechnologies (CNI lot # P0275). Toluene was obtained from Ajax. Poly(styrene-β-isobutylene-β-styrene) (SIBS) (Mw 182,139) was supplied by Boston Scientific Inc. L929 (mouse fibroblast) cells were obtained from Prof. Mark Wilson (Department of Biological Sciences, University of Wollongong). Gold-coated mylar and indium-tin-oxide (ITO) coated glass slides were obtained from CP Films Inc. and Delta Technologies Limited respectively. All chemicals were used without further purification.
4.2.2 Solution Preparation

**Pure DNA aqueous solution:** 2% DNA, 4% DNA, 6% DNA, 8% DNA and 10% (w/w) DNA were prepared by dissolving DNA in Milli-Q water.

**Pure PEO aqueous solution:** 2% PEO, 4% PEO and 6% (w/w) PEO were also dissolved in Milli-Q water.

**DNA/PEO blend solution:** 6%, 8% and 10% (w/w) DNA/PEO solutions with a 1:1 mass ratio of DNA to PEO were prepared by dissolving DNA/PEO in Milli-Q water. In addition, 10% (w/w) DNA/PEO solutions with different mass ratio (3:7, 4:6, 6:4, and 7:3) of DNA to PEO were prepared in Milli-Q water.

**DNA/PEO/SWNT blend dispersion:** 4% (w/w) DNA was dissolved in Milli-Q water by magnetic stirring over 60 minutes and heated at 90°C for 30 minutes to break the double chains of DNA [21-23]. 0.3% (w/w) SWNTs were then added into the DNA solution and sonicated for 1 hour. Subsequently, 6% (w/w), 8% (w/w), 10% (w/w) and 12% (w/w) PEO were added into the dispersions and these were stirred overnight.

**SWNT/SIBS in toluene:** SIBS at concentrations ranging from 4% (w/v) to 15% (w/v) was dissolved in toluene using magnetic stirring for 90 minutes. 0.3% (w/v) SWNT was added to the SIBS solution and this was sonicated for 45 minutes.
4.2.3 Electrospinning

The electrospinning setup and conditions for preparation of nanofibers containing DNA or SIBS were described in Chapter 2, Section 2.2.4.

4.2.4 Characterisation

The solution properties such as conductivity, surface tension and viscosity were determined (Chapter 2, Section 2.3.2). The resulting mat morphology was determined using a scanning electron microscope (SEM). The average diameter of the electrospun fibers was measured from SEM micrographs using Video Pro 32. Samples were sputter coated with gold prior to SEM imaging. The presence of CNTs in the composite fibres was confirmed using Raman spectroscopy (Chapter 2, Section 2.3.5).

The electrochemical properties of the fibers were measured by cyclic voltammetry in a divided three-electrode cell (electrode size: 1×1 cm²). Cyclic voltammograms (CVs) for DNA/SWNT/PEO nanofibers on Pt/glass slide were obtained in 0.15 M NaCl/phosphate buffer solution (PBS, containing 0.2 M Na₂HPO₄ and 0.2 M NaH₂PO₄, pH 7.4). CVs for the SWNT/SIBS fibers on ITO glass were obtained in 0.01 M K₃Fe(CN)₆/phosphate buffer solution (PBS, containing 0.2 M Na₂HPO₄, 0.2 M NaH₂PO₄ and 0.15 M NaCl, pH 7.4). In all cases, a Ag/AgCl (3M NaCl) reference and a Pt mesh auxiliary electrode were employed.
4.2.5 Enzyme Biosensors Based on DNA/SWNT/PEO Electrospun Fibers

DNA/SWNT/PEO electrospun fibers coated onto the Pt/glass slides were soaked in a glutaraldehyde solution (2.5% (w/w) in 0.4 M PBS, and 0.05 M KCl, pH 7.4) at 4°C overnight. The electrodes were subsequently washed and soaked in a glucose oxidase (GOx) solution (5 mg/ml GOx in PBS, pH 7.4) at 4°C overnight. After a further washing, the enzyme electrode was ready for use.

Using this enzyme electrode, amperometry [48] was used to detect glucose in solution. A constant anodic potential (+0.5 V) was applied to detect hydrogen peroxide produced in the enzyme reaction. The current was monitored continuously until a steady state value was reached. The enzyme electrode was measured in 0.4 M PBS (pH 7.4) (electrode size: 1×1 cm²). Glucose was added gradually (5 mM each time) into the working solution.

4.2.6 Cell Culturing

L-929 cells were cultured onto SWNT/SIBS electrospun nanofiber mats/gold mylar as described in Chapter 2, Section 2.4.4. The cells were then stained using Calcein AM and imaged using fluorescence microscope.
4.3 Results and Discussion

4.3.1 Nanofibers Containing DNA

Solution conductivity, surface tension and viscosity have been shown to be key parameters in determining the suitability of polymer solutions for electrospinning [49]. Surface tension changes the jets into spheres in order to decrease the surface area while electrical force tries to increase the surface area by maintaining a thinner jet. Viscosity tends to counteract the Coulombic force and prevents the break-up of the jet. These properties of DNA, PEO and DNA/PEO containing solutions were determined (Table 4.1).
Table 4.1. Properties of aqueous solutions (100 mL) containing DNA/PEO.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>DNA (g)</th>
<th>PEO (g)</th>
<th>Amount of water (g)</th>
<th>Conductivity (μS/cm) (1)</th>
<th>Surface tension (mN/m) (2)</th>
<th>Viscosity (mPa·s) (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>98</td>
<td>32.2</td>
<td>64.21</td>
<td>28.2</td>
</tr>
<tr>
<td>2</td>
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<td>70.15</td>
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</tr>
<tr>
<td>3</td>
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<td>74.1</td>
<td>74.51</td>
<td>369.6</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0</td>
<td>92</td>
<td>79.1</td>
<td>77.79</td>
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</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0</td>
<td>90</td>
<td>104.0</td>
<td>74.26</td>
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</tr>
<tr>
<td>6</td>
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</tr>
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<td>3</td>
<td>90</td>
<td>80.4</td>
<td>61.14</td>
<td>8899.07</td>
</tr>
</tbody>
</table>

(1) Determined by a Model 20 pH/Conductivity Meter (Denver Instrument).

(2) Determined by a KSV contact angle analyser (goniometer, KSV instruments Ltd).

(3) Determined by a DV-II viscometer (Brookfield Engineering Lab Inc.), shear rate using 20s⁻¹ for viscosity testing.
For lower concentrations of DNA solution (less than 2% (w/w)), the viscosity was very low and thus the viscoelastistic force was not large enough to counteract the higher Coulombic force. The charged jet broke up into droplets as a result of surface tension [50] and limited polymer deposited on the target; no nanofiber formation was observed. With increased concentrations of DNA, the viscosity and conductivity increased significantly. Using these higher concentrations, the increase in viscosity was sufficient to prevent the break-up of the jet and resulted in mere polymer deposition on the target [51]. The higher solution conductivity resulted in enough electrical force to overcome the surface tension of the solution. However, if ionic conductivity was too high, the formation of polymer beads and not nanofibers was favored due to the increased elongation force and instability of the charged jet [52]. Consequently none of the conditions used with DNA solutions resulted in nanofiber formation.

With PEO containing solutions, the conductivity remains low (1.67 ~ 1.79 µS/cm) increasing only slightly with increasing PEO concentration (Table 4.1 Solution No. 6 ~ 8). A significant difference was observed in the conductivity of PEO and DNA solutions. The surface tension of pure PEO solutions decreased slowly with increased PEO concentration [53]. Sharply increased viscosity was obtained with increasing concentration of PEO. As with DNA, these solutions only produced beads on the target when electrospinning was attempted. Similar results have also been observed by Son et al. [54]. They found that no fibers could be obtained from pure PEO in water when the concentration of PEO was less than 7% (w/w). The failure to successfully electrospin
pure PEO at these lower concentrations may be attributed to the low ionic conductivity of the solutions.

The properties of 6%, 8% and 10% (w/w) DNA/PEO containing aqueous solutions are summarised in Table 4.1 Solution No. 9-11. Comparing the pure DNA solution with DNA/PEO solutions, the latter had lower conductivity and surface tension and both of these favour the formation of fibers without beads [52]. These mixtures resulted in solutions with the ionic conductivity, surface tension and viscosity in the range required for successful electrospinning. The formation of the Taylor cone was observed during electrospinning and a nanofibrous mat was obtained on the collector electrode (Figure 4.2).

Excellent nanofibrous mats were obtained when using the feed solution containing 5% DNA and 5% PEO (Figure 4.2c). The increased conductivity and decreased surface tension combined with appropriate viscosity results in the formation of beautiful nanofibers with the beaded products that were observed at lower polymer concentrations (Figure 4.2a and 4.2b) eliminated.
Figure 4.2. SEM micrographs of the electrospun fibers from (a) 3% (w/w) DNA/3% (w/w) PEO, (b) 4% (w/w) DNA/4% (w/w) PEO, and (c) 5% (w/w) DNA/5% (w/w) PEO in Milli-Q water.

The ratio of DNA and PEO was then varied while keeping the overall concentration of solids at 10% (w/w). The properties of these solutions are outlined in Table 4.1 Solution No.12 ~ 15.

The conductivity, viscosity and low surface tension values obtained for solutions numbered 12 and 13 make them amenable to electrospinning. With both solutions, well defined Taylor cones [55] were observed during electrospinning and a continuous
nanofibrous mat was obtained. The deposits were examined using SEM (Figure 4.3a and 4.3b) and the ability to form long nanofibers was confirmed.

With Solution No. 14 and 15 containing higher concentrations of DNA more beads were obtained (Figure 4.3c and 4.3d). This may be attributed to the rapid increase in conductivity of the solution [52] with increasing DNA percentage in the blends.

Figure 4.3. SEM micrographs of the electrospun fibers from (a) 3% (w/w) DNA/7% (w/w) PEO, (b) 4% (w/w) DNA/6% (w/w) PEO, (c) 6% (w/w) DNA/4% (w/w) PEO, and (d) 7% (w/w) DNA/3% (w/w) PEO in Milli-Q water.
4.3.1.1 Influence of Process Parameters on Fiber Diameter Distribution

The effect of tip to collector distance, applied potential and the solution feed rate on the morphology and diameter of the fibers obtained was examined using SEM. The solution composition was held constant at 4% (w/w) DNA/ 6% (w/w) PEO.

Influence of Tip-to-collector Distance (D)

Electrospun fibers were obtained using different tip-to-collector distances, while the feed rate (R) and applied potential between the needle and collector (ΔE) remained constant at 100 μL/min and 15 kV respectively. The average diameter of electrospun fibers decreased significantly with increasing tip-to-collector distance (Figure 4.4 and Figure 4.5). This is similar to behaviour observed previously with electrospinning of PEO [54].
Figure 4.4. SEM micrographs of the electrospun fibers from 4% (w/w) DNA/ 6% (w/w) PEO obtained using a range of tip-to-collector distance: (a) 10 cm, (b) 15 cm, (c) 20 cm, and (d) 25 cm.

Figure 4.5. Relationship between average diameter of fibers and tip-to-collector distance during electrospinning.
Influence of Applied Potential (ΔE)

The influence of the applied potential between the needle and collector (ΔE) on the average diameter of electrospun fibers was investigated (Figure 4.6). Fibers were collected at different ΔE while the feed rate and tip to collector distance were kept at 100 μL/min and 15 cm respectively. The average diameter of the fibers obtained decreased as the potential was increased (Figure 4.6). The electrostatic force increased with increasing ΔE, which helps to further dissipate the polymer containing drop during spinning [56] with a concomitant decrease in fiber diameter. This is similar to results observed in previous work on electrospinning chitosan [57].

Figure 4.6. Relationship between average diameter of fibers and applied potential during electrospinning.
Influence of Solution Feed Rate (R)

The feed rate of the polymer solution was controlled by the syringe pump. This was varied from 50 μL/min to 200 μL/min while the tip to collector distance and the applied potential were maintained at 15 cm and 15 kV respectively. The average diameter of the fibers increased rapidly with increasing feed rate (Figure 4.7). An increase in the feed rate results in increased bead area and fiber diameter as observed previously by others when electrospinning polystyrene [58].

![Graph showing the relationship between average diameter of fibers and feed rate during electrospinning.](image)

Figure 4.7. Relationship between average diameter of fibers and feed rate during electrospinning.

4.3.1.2 DNA/SWNT/PEO Electrospun Fibers

A number of solution properties such as solution conductivity, surface tension and viscosity have been shown to be key parameters in determining the morphology of the
electrospun mats [49]. These properties of the resulting DNA/SWNT/PEO dispersions are summarized in Table 4.2.

Table 4.2. Properties of aqueous dispersions containing DNA/SWNT/PEO.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>DNA (%)</th>
<th>PEO (%)</th>
<th>SWNT (%)</th>
<th>Conductivity (μS/cm) (1)</th>
<th>Surface tension (mN/m) (2)</th>
<th>Viscosity (mPas) (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>6</td>
<td>0.3</td>
<td>68.6</td>
<td>67.28</td>
<td>563.2</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>8</td>
<td>0.3</td>
<td>65.3</td>
<td>66.18</td>
<td>1105.3</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>10</td>
<td>0.3</td>
<td>52.5</td>
<td>65.32</td>
<td>2537.6</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>12</td>
<td>0.3</td>
<td>41.8</td>
<td>64.99</td>
<td>9128.0</td>
</tr>
</tbody>
</table>

(1) Determined by a Model 20 pH/Conductivity Meter (Denver Instrument).
(2) Determined by a KSV contact angle analyser (goniometer, KSV instruments Ltd).
(3) Determined by a DV-II viscometer (Brookfield Engineering Lab Inc.), shear rate using 20s⁻¹ for viscosity testing.

The production of nanofibers using electrospinning with 4% (w/w) DNA/0.3% (w/w) SWNT dispersions with the addition of PEO was successful. Compared with Solution No. 13 in Table 4.1, the conductivity of 4% (w/w) DNA/6% (w/w) PEO solution increased from 41.9 μS/cm to 68.6 μS/cm with the addition of 0.3% (w/w) SWNTs (Table 4.2 Solution No. 1) while the viscosity decreased significantly since the double chains of DNA were broken at high temperature (90ºC). A slight increase in surface tension was observed with the addition of SWNTs. Continuous jets were observed during
Electrospinning and non-woven mats were collected on the Pt coated glass slides. SEMs (Figure 4.8a and 4.8b) showed that beads were deposited when the percentage of PEO in the dispersion was less than 10% (w/w). This may be attributed to the low viscosity and high conductivity of the dispersion (Table 4.2 Solution No.1 and 2). The low viscosity resulted in small viscoelastic forces which was not large enough to counter the higher Coulombic forces. The charged jet broke up into droplets as a result of surface tension [50]. At the same time, too high a conductivity of the solution enabled the formation of beads during electrospinning [52]. With the addition of PEO, ionic conductivity decreased due to the decreased comparative concentration of SWNTs. A slight decrease in surface tension and a dramatic increase in viscosity were also observed with increasing concentration of PEO (Table 4.2). A small number of nanofibers were obtained when the concentration of PEO was increased to 10% (w/w) (Figure 4.8c). However large beads were still present. As shown in Figure 4.8(d), a well-defined electrospun fibrillar network was obtained when the PEO was added at 12% (w/w). These well interconnected, rope-like bundles of fibers exhibited various degrees of porosity and were quite uniform in diameter (50-300 nm). The average diameter of SWNT/DNA/PEO electrospun fibers was estimated at 150 nm.
Figure 4.8. SEM micrographs of the electrospun fibers from 4% (w/w) DNA/0.3% (w/w) SWNT dispersions with the addition of (a) 6% (w/w), (b) 8% (w/w), (c) 10% (w/w), and 12% (w/w) PEO at (i) low resolution and (ii) high resolution.
4.3.1.3 Raman Spectroscopy

Raman spectra of electrospun fibers obtained from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO dispersion were obtained (Figure 4.9 and 4.10). As shown in Figure 4.9, three bands were found in the Raman spectra of DNA/SWNT/PEO composite fibers in the 1200 cm\(^{-1}\)-1600 cm\(^{-1}\) range that could be attributed to the G-band of SWNTs: 1590 cm\(^{-1}\) (from the graphitic sheets), 1561 cm\(^{-1}\) (stretching mode of SWNTs) and 1308 cm\(^{-1}\) (defects in SWNTs) [59, 60]. This result confirmed the presence of SWNTs in the electrospun fibers. There were also four bands observed in both spectra of electrospun fibers and raw SWNTs in the 150-300 cm\(^{-1}\) range (Figure 4.10). These peaks originate from the radial breathing mode (RBM) of SWNTs [59, 60]. The shifts observed in RBM peaks (Table 4.3) indicate interactions between DNA/PEO and SWNTs. Furthermore, the diameter of a SWNT is inversely proportional to the RBM frequency [59, 61], according the equation:

\[
\omega_R = 224 \text{ cm}^{-1}/d
\]  

(4.1)

where \(d\) represents the diameter of tube in nanometers and \(\omega_R\) is the RBM frequency. According to Equation 4.1, the up-shift in RBM frequency in the Raman spectra of electrospun fibers correlated to a decrease in tube diameter, indicating that SWNTs were well dispersed in the DNA solutions. Raman spectra were consistent across the electrospun mats over the glass slide, suggesting that SWNTs were well dispersed through the composite fibers.
Figure 4.9. Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

Figure 4.10. Radial breathing mode Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.
Table 4.3. Peak positions observed in RBM peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RBM peak A</th>
<th>RBM peak B</th>
<th>RBM peak C</th>
<th>RBM peak C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNTs</td>
<td>192 cm$^{-1}$</td>
<td>217 cm$^{-1}$</td>
<td>255 cm$^{-1}$</td>
<td>283 cm$^{-1}$</td>
</tr>
<tr>
<td>Electrospun fibres</td>
<td>198 cm$^{-1}$</td>
<td>223 cm$^{-1}$</td>
<td>259 cm$^{-1}$</td>
<td>286 cm$^{-1}$</td>
</tr>
</tbody>
</table>

4.3.1.4 Cyclic Voltammetry

Cyclic voltammograms (CVs) were obtained using mats spun onto the Pt/glass (Figure 4.11). The CV of electrospun fibers before the adsorption of GOx was quite flat and exhibited a rectangular shape (Figure 4.11a), indicating the highly capacitive nature of fibers [62]. The small responses observed at 0.32 V and 0.18 V respectively are probably due to a trace of residual iron in the SWNTs (used as a catalyst in the preparation of carbon nanotubes). Only minimal changes in peak currents were observed during 20 potential cycles indicating that the electrospun fibers are quite stable. After immobilization of GOx into electrospun fibers, a steady state current due to the oxidation of hydrogen peroxide was found at 0.5 V (Figure 4.11b).
4.3.1.5 Glucose Biosensors

Glucose oxidase (GOx) was entrapped in DNA/SWNT/PEO electrospun fibers in this work. Responses of currents with increasing glucose concentration were recorded. No oxidant current was observed in DNA/SWNT/PEO fiber electrodes without GOx after the addition of glucose. A current response, however, was found after the immobilisation of GOx in electrospun fibers. The current response of the fiber electrode with GOx to glucose was recorded in Figure 4.12. These results proved that the current response was
due to the oxidation of hydrogen peroxide produced by the oxidation of glucose by the enzyme rather than direct oxidation of glucose on the electrode.

Figure 4.12. Typical current-time curve as a function of glucose concentration: 1-7 represents the successive injection of 0, 5, 10, 15, 20, 25 and 30 mM glucose into phosphate buffer solution (0.4 M, pH 7.4). Electrode: 4%(w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO with immobilised GOx. E_{app} = + 0.5 V vs. Ag/AgCl (3 M NaCl).

The calibration curve for the response of glucose at the GOx-DNA/SWNT/PEO fiber electrode is shown in Figure 4.13, which is linear up to 20 mM glucose. The sensitivity of the biosensor is determined by the slope of the calibration curve. This biosensor had a sensitivity of 2.4 mAcm^{-2}M^{-1}, compared with previous reported sensitivities of 2-5 mAcm^{-2}M^{-1} range but that were for GOx-conducting polymer biosensors [63]. The resulting biosensor exhibits wide linearity range and good sensitivity, suggesting the
potential application in analysing clinical samples over a wide range of physiological conditions.

![Figure 4.13. Analytical curve obtained for glucose determination at 0.5V vs. Ag/AgCl (3M NaCl) in 0.4 M PBS (pH 7.4) with a SWNT/DNA/PEO electrospun fiber electrode.](image)

4.3.2 Nanofibers Containing SIBS

Solution conductivity, surface tension and viscosity of the SIBS/SWNT dispersions were investigated and listed in Table 4.4.
Chapter 4: Fabrication of Nanofibers from Biomaterials and Carbon Nanotubes

Table 4.4. Properties of SIBS/SWNT dispersions.

<table>
<thead>
<tr>
<th>Solution or dispersion</th>
<th>Conductivity (μS/cm) (^{(1)})</th>
<th>Surface tension (mN/m) (^{(2)})</th>
<th>Viscosity (mPas.s) (^{(3)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>13wt% SIBS</td>
<td>0</td>
<td>34.46</td>
<td>2855.71</td>
</tr>
<tr>
<td>5wt% SIBS / 0.3% SWNT</td>
<td>77.1</td>
<td>31.11</td>
<td>99.15</td>
</tr>
<tr>
<td>9wt% SIBS / 0.3% SWNT</td>
<td>86.1</td>
<td>24.00</td>
<td>193.58</td>
</tr>
<tr>
<td>13wt% SIBS / 0.3 %SWNT</td>
<td>94.7</td>
<td>23.32</td>
<td>385.58</td>
</tr>
</tbody>
</table>

(1) Determined by a Model 20 pH/Conductivity Meter (Denver Instrument).

(2) Determined by a KSV contact angle analyser (goniometer, KSV instruments Ltd).

(3) Determined by a DV-II viscometer (Brookfield Engineering Lab Lnc.), shear rate using 20s\(^{-1}\) for viscosity testing.

Pure SIBS is highly resistant, however the conductivity of the dispersions improved significantly with addition of SWNTs. The surface tension of dispersions decreased and the viscosity increased with increasing concentration of SIBS.

Nanofibers could not be electrospun from SIBS alone, however with the addition of SWNT non-woven mats were collected on the gold coated mylar collector. SEM images showed that few fibers were obtained when the concentration of SIBS was less than 7% (w/v) in the dispersion (Figure 4.14a), perhaps because of the low viscosity of these solutions which was not large enough to counter the higher Coulombic force under the electric field [51]. The fibrous structure of the mats improved significantly when the...
concentration of SIBS was increased from 7% (w/v) to 11% (w/v) (Figure 4.14b) and at concentrations above 12% (w/v) SIBS, non-woven mats of composite fibers could be obtained with a well-interconnected structure (Figure 4.14c). The composite fibers ranged from 30 nm to 350 nm in diameter.

Figure 4.14. SEM micrographs of electrospun fibers obtained from toluene dispersions containing (a) 5% (w/v) SIBS/0.3% (w/v) SWNT, (b) 9% (w/v) SIBS/0.3% (w/v) SWNT, and (c) 13% (w/v) SIBS/0.3% (w/v) SWNT.
4.3.2.1 Raman Spectroscopy

Raman spectra were obtained for electrospun composite nanofibers (Figures 4.15 and 4.16). Well defined G-bands as well as radial breathing mode (RBM) bands were observed in the electrospun fibers corresponding to those observed with SWNTs. According to Rao et al. [59], peaks in the 100-275 cm\(^{-1}\) range (RBM) and in the 1500-1600 cm\(^{-1}\) range (tangential (stretching) modes) should be prominent in Raman spectra of SWNTs. Figure 4.15(a) shows three classical peaks that could be attributed to SWNTs: 1588 cm\(^{-1}\) (from the graphitic sheets), 1556 cm\(^{-1}\) (stretching mode of SWNTs) and 1311 cm\(^{-1}\) (defects in SWNTs) [64]. The observed shifts in RBM (Figure 4.16 and so mentioned in Table 4.5) indicate interactions between the SIBS and the SWNTs. The up-shifts in RBM frequency of the electrospun fibers suggest a decreased diameter of the SWNTs in the blended fibers due to the inversely proportional relationship between the diameter of the tube and RBM frequency [59, 61]. Raman spectra were consistent across the electrospun mats indicating that the SWNTs were well dispersed throughout the fibers.
Figure 4.15. Raman spectra obtained for (a) nanofibers electrospun from 13% (w/v) SIBS/0.3% (w/v) SWNTs and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

Figure 4.16. Radial breathing mode Raman spectra obtained for nanofibers electrospun from (a) 13% (w/v) SIBS/0.3% (w/v) SWNT blend fibers and (b) SWNTs. Laser excitation wavelength was 632.8 nm.
Cyclic voltammograms were obtained using the electrospun SIBS/SWNT mats on ITO coated glass (Figure 4.17). This indicates that electrospun fibers have a much higher charge capacity and higher surface area than the pristine ITO coated glass. A redox couple observed at +0.48 V and -0.05 V (vs. Ag/AgCl (3M NaCl)) indicated an electroactivity for the composite fibers, which is attributed to the presence of SWNTs.
Figure 4.17. Cyclic voltammograms obtained in 0.01 M K₃Fe(CN)₆/phosphate buffer solution using (a) the electrospun fibers from 13% (w/v) SIBS/0.3% (w/v) SWNT on ITO glass or (b) the bare ITO coated glass slide as the working electrode (scan rate = 0.05 Vs⁻¹).

4.3.2.3 Cell Culturing

L929 is a mouse fibroblast line that is commonly used to assess the cytotoxicity of potential substrates for cell growth. Calcein AM is a dye that diffuses across the plasma membrane and is cleaved by intracellular esterases to yield a membrane impermeant, fluorescent Calcein product. Calcein AM therefore may be used as a cell viability dye, staining metabolically active cells bright green. L929 cells were seen to adhere to and grow on electrospun fibers such that clusters of viable cells could be visualised by 72 h of
culture (Figure 4.18a). The cells grew as well on SWNT/SIBS electrospun fibers as on the gold-mylar substrate, as shown using a combination of transmission and fluorescence microscopy (Figure 4.18b), the rate of growth on the electrospun fibers being similar to that on polystyrene tissue culture plastic (not shown). These results suggest that SWNT/SIBS electrospun fibers are biocompatible substrates.

![Image](a)

![Image](b)

Figure 4.18. Fluorescence microscope images of L-929 cells growing on electrospun fibers from 13% (w/v) SIBS/0.3% (w/v) SWNTs. Figure 4.18(a) shows calcein-stained cells using fluorescence detection only. Figure 4.18(b) shows the same field with the addition of transmission (white light) imaging to show the position of SWNT/SIBS fibers (dark regions).
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4.4 Conclusions

DNA/PEO nanofibers with diameters between 50-250 nm were successfully prepared from aqueous solution using an electrospinning technique. Three key solution properties: conductivity, surface tension and viscosity were determined and it was found that nano fibrous mats were obtained from DNA/PEO solutions with suitable combination of conductivity, surface tension and viscosity. It was found that the average diameter of electrospun fibers decreased with increased potential applied between the positive and negative electrodes, decreased feed rate or increased tip-to-collector distance employed during electrospinning.

Novel ultrafine fibers with an average diameter of 150 nm were electrospun from DNA/SWNT/PEO dispersions. Suitable solution properties for good electrospinning DNA/SWNT/PEO blends were found to be similar to those of DNA/PEO solutions. The successful introduction of SWNTs into DNA/PEO composite fibers was confirmed by Raman spectroscopy. Raman spectra also indicated a good dispersion of SWNTs throughout the electrospun fibers. DNA/SWNT/PEO electrospun fibers exhibited electroactive behaviours during electrochemical characterisation, indicating improved electrochemical properties with the addition of SWNTs. Glucose oxidase was immobilised in DNA/SWNT/PEO fibers and a current response was observed with the addition of glucose. The biosensor showed broad linearity range and high sensitivity.
We have also shown that fibrous nanowebs containing carbon nanotubes can be obtained with the presence of biocompatible polymers such as SIBS by electrospinning. The resulting fibers have high surface area and well interconnected microporous structure, indicating potential applications in areas requiring good mass transport. The presence of SWNTs throughout the electrospun fibres rendered the composite fibers conductive and electroactive. The useful combination of properties combined with the compatibility of the SIBS/SWNT fibers with L-929 cells opens up the possibility of using these conductive materials as substrates for studies on the effects of electrical stimulation on cell growth and suggests possible applications in biomedical fields such as in tissue engineering.
4.5 References


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CHAPTER 5:

FLEXIBLE ALIGNED CARBON
NANOTUBE/CONDUCTING POLYMER ELECTRODES
5.1 Introduction

Carbon nanotubes (CNTs) present a new material for the construction of electrodes. The use of perpendicularly aligned carbon nanotubes (ACNTs) has been shown to provide an opportunity to fabricate electrodes with highly ordered, high surface area and the capacity for modifying the carbon nanotube surface with various transduction materials [1, 2]. Although high conductivity and mechanical integrity is realized in the vertical direction, it is highly desirable to develop simple methods of making ACNT composites that are mechanically robust and with sufficient conductivity in the horizontal direction because there is a lack of good electrical connectivity between the aligned tubes. Such interconnects would give rise to a practically useful electrode structure for use in applications such as electron-emitting flat-panel displays [3], electrochemical sensors [1, 4] and energy storage [5].

Growth of ACNTs on conducting substrates which would provide this electrical connection has met with limited success because of the high temperature required for the synthesis of the ACNT. Recently, the growth of ACNTs on a metallic alloy, Inconel 600 (Inconel) using vapor-phase catalyst delivery has been reported [6]. Depositing metals selectively on top of CNT arrays to achieve this electrical connection [7] is fraught with difficulties. Some approaches involve removal of the CNT array from the growth surfaces but result this can in physical damage to the array.
Chapter 5: Flexible Aligned Carbon Nanotube/Conducting Polymer Electrodes

To realize a robust electrical connection between aligned nanotubes, we present here a direct and effective way to incorporate them into a flexible and conductive polymer substrate. In the novel nanostructure created here, the ACNT arrays are held together by a conducting polymer composite layer such as Pt/poly(vinylidene fluoride) (PVDF) or poly(3,4-ethylenedioxythiophene) (PEDOT)/PVDF. The highly flexible nature and electronic conductivity attainable with these materials present some exciting new electrode properties. The resulting nanostructured ACNT/polymer electrode is a flexible, highly conductive and mechanically robust structure with nanotubes vertically oriented and protruding from the conducting polymer layer (80% of the tube length is exposed). The use of these electrode materials for the anodic oxidation of methanol and as anode materials in a Lithium-ion battery are explored here.

5.2 Experimental

5.2.1 Reagents and Materials

Iron (II) phthalocyanine (designated as FePc hereafter), PVDF, chloroplatinic (IV) acid (H$_2$PtCl$_6$), ferric $p$-toluenesulfonate (Fe (III) tosylate) and 3,4-ethylenedioxythiophene (EDOT) were all obtained from Sigma-Aldrich. Sodium nitrate was purchased from Chem-Supply. Potassium ferrocyanide was supplied by Asia Pacific Specialty Chemicals. Methanol, ethanol, n-methyl-2-pyrrolidinone (NMP) and sulfuric acid were all from Ajax. All chemicals were used without further purification.
5.2.2 Synthesis of the ACNT/Pt/PVDF Structure

Aligned carbon nanotubes were prepared on the quartz plate (2×4 cm²) using thermal chemical vapor deposition (CVD) and the pyrolysis of FePc under Ar/H₂ at 800-1100°C as described in Chapter 2, Section 2.2.5. As schematically illustrated in Figure 5.1(a), a suitable layer of Pt was sputter coated onto the ACNT/quartz plate at 30 mA for 30 minutes (Figure 5.1a(i)). It was difficult to remove the Pt/ACNT film from the quartz plate as a free-standing film due to a lack of mechanical integrity. A second polymer layer of PVDF was subsequently cast onto the top of the Pt/ACNT arrays from a 10% (w/w) PVDF/NMP solution (Figure 5.1a(ii)). The sample was maintained at room temperature over 3 hours, allowing the infiltration of PVDF through the Pt. After complete drying of the PVDF, the resulting PVDF/Pt/ACNT structure can be peeled off from the quartz plate and inverted for further characterizations and applications (Figure 5.1a(iii)). For the purpose of comparison, Pt was also sputter coated onto the glass slide with the same geometric size of the ACNT/quartz plate at 30 mA for 30 minutes.
Figure 5.1. (a) Schematic representation of the procedures for the synthesis of the ACNT/Pt/PVDF membrane electrode. SEM micrographs of ACNT on (b) the quartz plate and (c) the Pt/PVDF polymer electrode. And (d) digital photograph illustrating the highly flexible ACNT/Pt/PVDF membrane electrode.
5.2.3 Incorporation of Pt Nanoparticles into the ACNT/Pt/PVDF Structure

The freestanding Pt/ACNT/PVDF electrode was further modified by the electrodeposition of Pt nanoparticles (Figure 5.2a) from 0.01 M H₂PtCl₆/0.5M NaNO₃ (aq) using cyclic voltammetry. The potential was cycled between 0 and +0.6 V (vs. Ag/AgCl) for 2 cycles at 0.05 V s⁻¹ scan rate with the presence of Pt mesh auxiliary electrode.

Figure 5.2. (a) Schematic of electrodeposition of Pt nanoparticles onto the ACNT/Pt/PVDF electrode, (b) SEM micrograph of the Pt nanoparticles coated ACNT/Pt/PVDF, and (c) energy dispersive X-ray analysis of the Pt nanoparticles coated ACNT.
5.2.4 Fabrication of the ACNT/PEDOT/PVDF Structure

The procedure used to form the nanostructured ACNT/PEDOT/PVDF electrode from a quartz plate is summarized in Figure 5.3(a). Following preparation of ACNT on a quartz plate, a thin film of Fe(III) tosylate was coated onto the ACNT array using a spin coater (Laurell Tech. Co.) at a speed of 1000 rpm for 60 seconds. A 10% (w/w) Fe(III) tosylate solution in ethanol was used and the coated structure then placed into an oven at 80ºC for 180 seconds to quickly evaporate the solvent (Figure 5.3a(i)). A thin layer of PEDOT was then formed on the ACNT by exposing the sample to EDOT monomer vapor in the polymerization chamber at 60ºC for 30 minutes (Figure 5.3a(ii)). The sample was dried in air for 60 minutes prior to being washed in ethanol to remove unreacted EDOT as well as Fe ions. Similar to the Pt/ACNT composite, the PEDOT film did not have sufficient mechanical integrity to support the ACNT structure. A thin PVDF (10% (w/w) dissolved in NMP) film was subsequently cast onto the PEDOT/ACNT film (Figure 5.3a(iii)). A highly robust ACNT/PEDOT/PVDF membrane can be peeled off from the quartz plate upon the complete drying of the PVDF film (Figure 5.3a(iv)).
Figure 5.3. (a) Schematic representation of the procedure for the synthesis of the ACNT/PEDOT/PVDF membrane electrode, (b) SEM micrograph of ACNT on the PEDOT/PVDF polymer membrane, and (c) digital photograph illustrating the highly flexible ACNT/PEDOT/PVDF membrane electrode.
5.2.5 Characterisation

The electronic conductivity of the nanostructures was determined using a Four Point Probe. Scanning electron microscope was employed with an Energy Dispersive X-ray Analyzer (EDX, Oxford Instruments) to confirm Pt deposition. The presence of the multi-walled carbon nanotubes in the composite membrane was confirmed using Raman spectra.

Solutions were deoxygenated by argon for 15 minutes prior to all electrochemical reactions. Subsequently all working electrodes were cleaned in 1 M H$_2$SO$_4$ (aq) using 100 consecutive cycles (scan rate 0.1 V s$^{-1}$) within the potential range of -0.2 and 1.2 V (vs. Ag/AgCl, 3M NaCl) before being employed in the electrochemical cells.

The electrochemical characterisation of the resulting membrane electrodes was carried out using cyclic voltammetry in 1 M NaNO$_3$ (aq) solution. The total mass of Pt and ACNTs was used to calculate the capacitance of the Pt nanoparticles coated Pt/ACNT/PVDF membrane (Pt-ACNT/Pt/PVDF) electrode. The mass was measured using a Model ME5 Premium Microbalance (readability (d) = 0.001 mg, Sartorius Mechatronics). An average mass value from three-time measurement was utilized. Cyclic voltammograms (CVs) at various scan rates in 0.01 M K$_4$Fe(CN)$_6$/0.1 M NaNO$_3$ (aq) solution were also used to investigate the quality of the resulting electrode. The electrochemical active surface (EAS) of the Pt-ACNT/Pt/PVDF membrane was measured using cyclic voltammetry with potential ranging from -0.2 to 1.2 V (vs. Ag/AgCl, 3M NaCl) in 1 M H$_2$SO$_4$ (aq) (the electrode size: 0.4 $\times$ 0.5 cm$^2$).
5.2.6 Methanol Electro-oxidation

The electrocatalytic performances of the Pt-ACNT/Pt/PVDF electrode (the electrode size: 0.4 ×0.5 cm$^2$) at room temperature for the electro-oxidation of methanol were evaluated using both cyclic voltammetry with potential range 0 ~ 1.2 V and constant potential at 0.7 V (vs. Ag/AgCl, NaCl) in 1 M MeOH/1 M H$_2$SO$_4$ (aq) solution respectively. The current densities were calculated using the Pt loading mass.

5.2.7 Lithium-ion Battery Testing

A 1×1 cm$^2$ nanostructured ACNT/PEDOT/PVDF electrode was assembled into a Lithium-ion battery for testing. The cell was cycled between 0 and 2 V (vs. Li/Li$^+$) at a constant current density of 0.1 mA•cm$^2$. See details in Chapter 2, Section 2.4.5.
5.3 Results and Discussion

5.3.1 The Pt nanoparticles-ACNT/Pt/PVDF Electrode

5.3.1.1 Morphology and Conductivity Measurement

The electrode structures shown schematically in Figure 5.1(a) show that the ACNT/Pt/PVDF electrodes were successfully configured using the procedures described in the Experimental section. As shown in Figure 5.1(b), the SEM image of ACNTs shows that large scaled carbon nanotubes (CNTs) densely packed with a fairly uniform tubular length of ca. 5 μm were well aligned on the quartz plate. The presence of the well defined ACNT forest into the PVDF layer was also confirmed by SEM (Figure 5.1c). The average tubular length of ACNT was reduced to ca. 4 μm from 5 μm due to the presence of the Pt/PVDF polymer. The addition of Pt film significantly improved the conductivity of the electrode (the electronic conductivity was improved from 6 S•cm⁻¹ for the ACNT/PVDF structure to 600 S•cm⁻¹ for the ACNT/Pt/PVDF structure), suggesting a strong connection between the CNT layer and the Pt/PVDF layer. This result is an average of 10 measurements across the sample, with less than 10% deviation between each measurement, which demonstrates the uniformity of the film structure. The resulting electrode is robust and flexible (Figure 5.1d, obtained for 30% strain stretched electrode).
Electrodeposition of Pt nanoparticles onto the ACNT/Pt/PVDF membrane was schematically carried out as shown in Figure 5.2(a). Nanoparticles with size of ca. 5 ~ 10 nm were obtained on the ACNT structure (Figure 5.2b). EDX analysis confirmed a 95.2% Pt and 4.8% Fe (residual iron during the preparation of ACNT) content for these particles (Figure 5.2c), confirming the successful deposition of Pt onto the ACNT/Pt/PVDF structure.

### 5.3.1.2 Raman Spectroscopy

Raman spectra of the Pt nanoparticles-ACNT/Pt/PVDF electrode and the ACNT powder were obtained (Figure 5.4). Two typical bands which can be attributed to the presence of multi-walled carbon nanotubes (MWNTs) were observed at 1593 cm\(^{-1}\) (graphite vibration G-line) and 1340 cm\(^{-1}\) (disordered carbon mode D-line) (Figure 5.4b) [17]. This result also confirms that the ACNTs we synthesized are multi-walled carbon nanotubes. In the Polymer containing structure, two normal bands occur at 1583 cm\(^{-1}\) and 1333 cm\(^{-1}\) (Figure 5.4a). The shift in wavenumber suggests some interactions between the ACNTs and the PVDF polymer.
Figure 5.4. Raman spectra obtained for (a) the Pt nanoparticle-ACNT/Pt/PVDF structure and (b) the ACNT powders. Laser excitation wavelength was 632.8 nm.

### 5.3.1.3 Electrochemical Characterisation

Cyclic voltammograms were obtained using the Pt nanoparticle-ACNT/Pt/PVDF electrode in 0.1 M NaNO₃ (aq) (Figure 5.5a). The CV shows reversible capacitive behaviour. The anodic and cathodic charging currents were symmetrical around zero. The currents decreased with decreased scan rate. The capacitance value (C) of the electrode was obtained from the CV curve according to the equation:

\[
C = \frac{i}{v}
\]  
(5.1)
where $i$ is the average current and $v$ is the potential scan rate. Normally, the double layer capacitance was measured using CV over narrow potential ranges essentially free of faradaic process [8]. Therefore the capacitance of the Pt nanoparticle-ACNT/Pt/PVDF electrode can be calculated from various potential scan rates over the range from 0.1 to 0.01 Vs$^{-1}$. In order to eliminate most of the error due to the faradic reaction in the calculation of $C$, the specific current ($\Delta i$) was defined as:

$$\Delta i = \frac{(i_a - i_c)}{2}$$ \hspace{1cm} (5.2)

At 0.3 V, the plot of $\Delta i$ versus scan rate ($v$) can be obtained from voltammograms of different potential scan rates. The capacitance of the resulting membrane (at 0.3 V) was determined by the slope of the line in Figure 5.5(b). Thus the capacitance of the Pt nanoparticle-ACNT/Pt/PVDF electrode was determined to be 133 F/g, compared with reported capacitance values of multi-walled CNT composites (102 F/g) and single-walled CNT blends (180 F/g) [9, 10].
Figure 5.5. (a) Cyclic voltammogram at the Pt nanoparticle-ACNT/Pt/PVDF electrode in 1 M NaNO$_3$ (aq) (scan rate = 0.1 Vs$^{-1}$), and (b) specific current ($\Delta i$) determined at 0.3 V vs. scan rate ($\nu$) plot obtained at various scan rates ranging from 0.1 Vs$^{-1}$ to 0.01 Vs$^{-1}$.

\[ y = 133.01x - 0.3515 \]
\[ R^2 = 0.9988 \]
Upon the addition of 0.01 M K₄Fe(CN)₆ into the electrolyte, a well-defined redox couple was observed at potentials with an anodic peak potential of 0.32 and cathodic peak potential of 0.18 V respectively as shown in Figure 5.6(a). Different scan rates were employed to determine what factor limits the rate of the redox reaction. As found in Figure 5.6(b), both anodic peak current ($i_{pa}$) and cathodic peak current ($i_{pc}$) are proportional to the square root of the scan rate ($\nu$); $i_{pa} = -1.5703 + 51.174\nu^{1/2}$, $r = 0.9997$, and $i_{pc} = -0.8306 + 53.039\nu^{1/2}$, $r = 0.9991$, suggesting the redox reaction at the Pt-ACNT/Pt/PVDF electrode is a diffusion-controlled process [11].

(a)
Figure 5.6. (a) Cyclic voltammograms of the Pt nanoparticle-ACNT/Pt/PVDF electrode in 0.01 M $K_4Fe(CN)_6/0.1$ M NaNO$_3$ (aq) at various scan rates of 0.2 ~ 0.01 Vs$^{-1}$, and (b) dependence of redox peak currents proportional to square roots of the scan rates for 0.01 M $K_4Fe(CN)_6$ in 0.1 M NaNO$_3$ (aq).

### 5.3.1.4 Electroactive Surface

To measure the electrochemical activity of catalysts (Pt), the active surface areas of Pt was determined by calculating the charge transfer for the hydrogen adsorption and desorption of the catalysts from the cyclic voltammograms. The specific charge transfer ($Q_H$) due to hydrogen adsorption and desorption can be calculated as follows [12]:

$$Q_H = \frac{\int i dt}{n F A}$$
where $Q_T$ is the expression of the total amount of charge during electro-adsorption and desorption of $H_2$ on Pt sites, and $Q_{DL}$ represents the capacitive current due to the double layer capacitance. $Q_T$ can be obtained by integration of the CV curves in the relevant potential region while $Q_{DL}$ can be similarly obtained by integrating the double layer charging region. The electrochemical active surface (EAS) was determined by dividing $Q_H$ by the product of the deposited Pt mass $[Pt]$ and a conversion factor of 0.21 mC$\cdot$cm$^{-2}$ (the normally electrical charge associated with a monolayer adsorption of hydrogen on bright Pt [13]) following the equation below [14]:

$$EAS = \frac{Q_H}{[Pt] \times 0.21} \quad (5.4)$$

Figure 5.7 shows the CV results of (a) the ACNT/Pt/PVDF electrode and (b) the Pt nanoparticle-ACNT/Pt/PVDF electrode in 1 M $H_2SO_4$. Two typical couple of peaks (see labeled peaks in Figure 5.7) related to the adsorption and desorption of hydrogen were observed both from sputter coated Pt and electrodeposited Pt nanoparticles during cyclic voltammetry. The calculations of EAS for both sputter coated Pt and the electrodeposited Pt nanoparticles are summarized in Table 5.1. The sputter coated Pt exhibits an EAS of 9 m$^2$g$^{-1}$, compared with that of platinum black (20 $\sim$ 26 m$^2$g$^{-1}$) and reported EAS of platinized platinum films (2 $\sim$ 30 m$^2$g$^{-1}$). Considering that sputter coated Pt was partially covered by the PVDF film, the real EAS of the sputter coated Pt, though hard to be
calculated, should be much higher than this value (9 m²g⁻¹). After the electrodeposition of Pt nanoparticles, \( Q_H \) dramatically increased from 6 mC·cm⁻² to 12 mC·cm⁻² though there was only 0.02 mg·cm⁻² Pt electrodeposited. The electrodeposited Pt nanoparticles therefore demonstrate an amazing electrochemical active surface of 143 m²g⁻¹. This value is much higher than literature values of nanostructured Pt film (38 m²g⁻¹) [15], mesoporous platinum powders (60 m²g⁻¹) [16, 17] and Pt/C (14 ~ 87 m²g⁻¹) [18]. The presence of the ACNT template significantly increased the EAS of electrodeposited Pt.

Figure 5.7. Cyclic voltammograms in 1 M H₂SO₄ (aq) of (a) the ACNT/Pt/PVDF electrode, and (b) the Pt nanoparticle-ACNT/Pt/PVDF electrode (scan rate = 0.2 V·s⁻¹).
Table 5.1. Hydrogen adsorption and desorption charges and electroactive surface values.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[Pt] (mg•cm⁻²)</th>
<th>Q_T (mC•cm⁻²)</th>
<th>Q_DL (mC•cm⁻²)</th>
<th>Q_H (mC•cm⁻²)</th>
<th>EAS (m²•g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter coated Pt</td>
<td>0.32</td>
<td>14.1</td>
<td>2.1</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Sputter coated Pt + electrodeposited Pt nanoparticles</td>
<td>0.34</td>
<td>26.6</td>
<td>2.6</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>Electrodeposited Pt nanoparticles</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>143</td>
</tr>
</tbody>
</table>

### 5.3.1.5 Oxidation of Methanol

The catalytic performance at the membrane electrode for methanol oxidation was determined using cyclic voltammetry in an aqueous solution containing 1 M methanol and 1 M H₂SO₄. The peak current densities at 0.02 Vs⁻¹ for Pt coated glass, the ACNT/Pt/PVDF electrode and the Pt nanoparticle-ACNT/Pt/PVDF electrode are 2.56, 2.84 and 4.84 mA•mg⁻¹ respectively (Figure 5.8). The activity of the electrode after electrodepositing 0.02 mg•cm⁻² Pt nanoparticles shows about 1.7 times higher than that of the ACNT/Pt/PVDF electrode and 1.9 times higher than that of the Pt coated glass slide. Significant catalytic performance of the Pt nanoparticles is observed.
Figure 5.8. Cyclic voltammograms of methanol oxidation at (a) the Pt coated glass slide, (b) the ACNT/Pt/PVDF electrode, and (c) the Pt-ACNT/Pt/PVDF electrode in 1 M CH$_3$OH/1 M H$_2$SO$_4$ (aq) (scan rate = 0.02 Vs$^{-1}$).

Constant potential (+0.7 V) was also used to investigate the catalytic activity of the resulting membrane for anodic oxidation of methanol. As shown in Figure 5.9(a), the current density at the ACNT/Pt/PVDF electrode gradually reduced from 32.5 mA•mg$^{-1}$ to 29 mA•mg$^{-1}$ within 12 hours prior to reaching a constant current of 29 mA•mg$^{-1}$ reached. This current density remained stable within the following 12 hours. It took more time (19 hours) for the current density at the Pt nanoparticle-ACNT/Pt/PVDF for methanol oxidation to reach a steady value (73 mA•mg$^{-1}$, Figure 5.9b). The current density remained around 73 mA•mg$^{-1}$ constantly for another 12 hours (not shown here). A stable
current density over a long period (more than 12 hours) can be obtained both from the ACNT/Pt/PVDF electrode and the Pt nanoparticle-ACNT/Pt/PVDF electrode, suggesting the facile removal of poisonous intermediates such as CO with the presence of ACNTs with/without the addition of Pt nanoparticles. The observed steady current density for the Pt nanoparticle-ACNT/Pt/PVDF electrode is 2.5 times higher than that of the ACNT/Pt/PVDF electrode while the increased amount of Pt was only 0.02 mg•cm$^{-2}$, indicating the excellent catalytic activity of the electrodeposited Pt nanoparticles.

Figure 5.9. Chronoamperogram of methanol oxidation at (a) the ACNT/Pt/PVDF electrode and (b) the Pt nanoparticle-ACNT/Pt/PVDF electrode by constant potential at +0.7 V vs. Ag/AgCl (3 M NaCl).
5.3.2 The ACNT/PEDOT/PVDF Electrode

5.3.2.1 Morphology and Conductivity Measurement

The SEM image (Figure 5.3b) of the ACNT/PEDOT/PVDF electrode shows a clear array structure supported by a PEDOT/PVDF composite film. The roots of the carbon nanotubes are held tightly by the underlying PEDOT/PVDF layer. Even upon straining, the ACNT/PEDOT/PVDF structure remains intact, highlighting the robustness of the composite electrode. The aligned carbon nanotube layer was found to be adherent and was not removed by rubbing or abrasion on a hard surface. The composite film could be rolled up without any visual signs of degradation (Figure 5.3c, obtained for a 15% strain stretched electrode).

The ACNT/PEDOT/PVDF electrode had an electronic conductivity over 200 S•cm⁻¹, which is significantly higher than that measured for an ACNT/PVDF electrode (between 2 to 20 S•cm⁻¹) prepared under identical conditions without the conductive PEDOT layer in the middle. The PEDOT layer is obviously critical in producing interconnectivity between the aligned parallel tubes.

5.3.2.2 Electrochemical Characterisation

The CV at the ACNT/PEDOT/PVDF electrode in 1 M NaNO₃ (aq) (Figure 5.10a) shows a rectangular shape, indicative of the highly capacitive nature of the ACNT/PEDOT/PVDF
electrode with rapid charge/discharge characteristics [19] when compared with PEDOT/PVDF (Figure 5.10b). This electrode was cycled for 50 cycles and no obvious degradation was observed.

Figure 5.10. Cyclic voltammograms of (a) the ACNT/PEDOT/PVDF electrode, and (b) the PEDOT/PVDF electrode in 1 M NaNO₃(aq) (scan rate = 0.02 Vs⁻¹).

5.3.2.3 Lithium-ion Battery Testing

The typical charge-discharge (Inset (a) in Figure 5.11) profiles display stable charge-discharge curves during cycling; indicative of stable electrochemical performance by this free-standing ACNT/PEDOT/PVDF membrane electrode. The discharge capacity versus the cycle number for the above cell is shown in Figure 5.11. The first cycle of this electrode exhibits an enormous irreversible capacity, which can be attributed to the
formation of a solid electrolyte interface (SEI) layer on the surface of the electrodes [20]. However, a highly stable discharge capacity of 265 mA\text{g}^{-1} is observed after 50 cycles. This is significantly higher than the value obtained previously for SWNT paper (173 mA\text{g}^{-1}) under identical working conditions [21]. This is attributed to the high accessible surface area of the aligned carbon nanotubes which, coupled with the robust polymer layer, provides a mechanically stable array. The CNTs in the ACNT/PEDOT/PVDF electrode keep their nanostructured architecture, while the CNTs in SWNT paper prepared via vacuum filtration aggregate to form bundle of CNTs and thereby decrease the electroactive surface area of the electrode. This is reflected in the stable long-term electrochemical performance of these electrodes in a Lithium-ion battery. No degradation was observed over 50 charge-discharge cycles.

![Figure 5.11. Discharge capacity vs. the cycle number of ACNT/PEDOT/PVDF electrode in a Lithium-ion testing cell under a constant current density of 0.1 mA•cm$^2$.](image_url)
Another significant improvement is that this free-standing ACNT/PEDOT/PVDF electrode with excellent electronic and mechanical properties does not require a metal substrate (copper foil) as is normally employed to support the active materials in a Lithium-ion battery [22]. For a typical anode (1 cm²) this equates to 14 mg of copper compared to 2 mg of PVDF, which still could be decreased by optimizing the process. This would significantly decrease the weight of the anode in a lithium-ion battery, or allow more active material per unit mass to increase the capacity per battery unit. The other advantage of this copper-free electrode is that it may contribute to the improvement of the long-term battery performance; without copper dissolution caused by impurities in the electrolyte. Due to the chemical and electrochemical stability of PEDOT and PVDF, the impurities in the electrolyte would not cause the same problem as that for copper foil during the long-term battery performance. This may explain the stable electrochemical performance observed when used in a Lithium-ion battery.
5.4 Conclusions

A light, flexible, mechanically robust and highly conductive electrochemical material was prepared from Pt nanoparticles coated ACNT/Pt/PVDF or ACNT/PEDOT/PVDF composites. The Pt-ACNT/Pt/PVDF electrode exhibits an excellent capacitance with high quality of the electrode. An amazing electrochemical active surface was obtained from the electrodeposited nanoparticles on the ACNT based membrane. The resulting membrane also shows a dramatic improvement in catalytic activity for the anodic oxidation of methanol with the presence of nanostructured ACNT and Pt particles.

The resulting ACNT/PEDOT/PVDF electrode can be easily fabricated into a rechargeable battery without using a metal substrate or binder. In this Lithium-ion battery, the weight of the electrode is reduced significantly compared with a conventional electrode made by coating a mixture containing an active material onto the metal substrate. The results also show that the capacity of the ACNT/PEDOT/PVDF electrode is 50% higher than that observed for free-standing SWNT paper.

This study has important implications for the use of aligned carbon nanotube/conductive polymer composites as a new class of electrode materials in developing flexible fuel cells and rechargeable lithium-ion batteries, and may lead to other applications of carbon nanotubes in flexible electronic devices.
5.5 References


Chapter 5: Flexible Aligned Carbon Nanotube/Conducting Polymer Electrodes


CHAPTER 6: FLEXIBLE NANOSTRUCTURES CONTAINING ALIGNED CARBON NANOTUBES AS PLATFORMS FOR CELL CULTURING
6.1 Introduction

The application of flexible aligned carbon nanotubes (ACNT) based nanostructures as electrochemical devices was presented in Chapter 5. Besides the unique electronic and mechanical properties, carbon nanotubes (CNT) have attracted attention for use in the area of biology especially as novel platforms to support mammalian cell growth [1, 2]. Various kinds of cells including mouse fibroblasts [3], neuronal cells [4, 5] and smooth muscle cells [6] have been successfully cultured on CNT based substrates. Poly(styrene-β-isobutylene-β-styrene) (SIBS) is an excellent biostable [7-9] and biocompatible [10-13] polymer used previously for biological applications (see Chapter 4). Poly(lactide-co-glycolide) (PLGA), a random copolymer of poly(lactide) and poly(glycolide) (see Figure 6.1 for structure), is a hydrophobic biodegradable and biocompatible polymer which has been widely investigated for a range of applications such as surgical sutures [14], substrates for tissue regeneration [15], and as a carrier for drug and gene delivery [16]. The degradation rate and mechanical properties of PLGA can be readily tailored for different targeted applications.

(a)  
\[ (-O-\text{CH}_2-\text{C}-)_n \]  
(b)  
\[ (-O-\text{CH}_2-\text{C}-)_n \]

Figure 6.1. Structural formulae of (a) poly(lactic acid) and (b) poly(glycolic acid).
In this work, we demonstrate a direct and effective way to prepare flexible and mechanical robust electrode structures from ACNT and biomaterials including SIBS or PLGA. The application of ACNT/biomaterial structures in cell growth experiments has been investigated.

### 6.2 Experimental

#### 6.2.1 Reagents and Materials

SIBS ($M_w 182,139$) was supplied by Boston Scientific. PLGA (ratio: lactide/glycolide = 75/25) and Iron (II) phthalocyanine (designated as FePc hereafter) were both from Sigma-Aldrich. SWNT was purchased from Carbon Nanotechnologies (CNI lot # P0275). 

$\text{Na}_2\text{HPO}_4$, $\text{NaH}_2\text{PO}_4$ and $\text{NaCl}$ were all obtained from Asia Pacific Specialty Chemicals. Toluene, acetone and ethanol were purchased from Ajax. L-929 (mouse fibroblast) cells were obtained from Prof. Mark Wilson (Department of Biological Sciences, University of Wollongong). Gold-coated mylar was purchased from CP Films. All chemicals were used without further purification.

#### 6.2.2 Synthesis of the Composite Structures

The procedures of preparing ACNT/biomaterial electrodes were the same as the preparation of ACNT/PVDF or ACNT/Pt/PVDF electrodes described in Chapter 5. Similar as schematically shown in Figure 5.1(a), ACNT were prepared on a $2\times4 \text{ cm}^2$
quartz plate by the pyrolysis of FePc as described elsewhere [17, 18]. To improve the
electrochemical properties of the resulting electrode, a suitable layer of Pt was introduced
onto the top of ACNT by sputter coating for 30 minutes at 30 mA. A layer of SIBS (20% w/w in toluene), or PLGA (15% w/w in acetone) was subsequently placed onto the top of Pt/ACNT. On the other hand, ACNT on the quartz plate was directly covered by SIBS/SWNT dispersion (0.3% w/w SWNT sonicated in 15% w/w SIBS in toluene for 45 minutes at 30% power (150 watts, 20 kHz. Pulse: 2sec on/1sec off)). The samples were stored at room temperature for over 3 hours prior to the removal of composite structures from the quartz plate after the complete drying of the solvent. To confirm the effect of sputter coated Pt on the cell culture, Pt was also sputter coated onto the gold mylar with the same geometric size as the ACNT/quartz plate at 30 mA for 30 minutes.

6.2.3 Characterisation

The morphologies of the resulting electrodes were determined by scanning electron microscopy (SEM). A Four Point Probe was used to measure the conductivity of the electrodes.

The electrochemical characterizations were carried out by cyclic voltammetry (CV) in phosphate buffer solution (PBS, containing 0.2M Na₂HPO₄, 0.2M NaH₂PO₄ and 0.15M NaCl, pH 7.4). Solutions were deoxygenated by argon for 15 minutes prior to all electrochemical analyse. In all cases, Ag/AgCl reference and Pt mesh auxiliary electrodes were employed throughout.
6.2.4 Cell Culturing

L-929 cells were cultured onto the nanoelectrodes as described in Chapter 2, Section 2.4.4.

6.3 Results and discussion

6.3.1 The ACNT/Pt/SIBS Structure

The resulting ACNT/Pt/SIBS as well as the ACNT/SIBS electrodes remained intact even under a 40% strain stretch, indicating a much higher elasticity than ACNT/PVDF (30% strain) based electrodes. This may be attributed to elasticity of SIBS. SEM images are shown for the ACNT/Pt/SIBS electrode in Figure 6.2. The carbon nanotube forest retained alignment and was well integrated into the soft Pt/SIBS substrate. It was also observed that more than 80% of the length of carbon nanotubes (normally ca. 5 μm in length) was exposed.

The presence of the Pt layer significantly improved the electronic conductivity from ca. 1 S•cm⁻¹ for the ACNT/SIBS electrode to ca. 100 S•cm⁻¹ for the ACNT/Pt/SIBS structure.
6.3.1.1 Electrochemical Characterisation

Cyclic Voltammograms were obtained for the ACNT/SIBS and ACNT/Pt/SIBS electrodes in PBS solution (Figure 6.3). In both cases, only capacitive currents were observed. The anodic and cathodic charging currents were symmetrical around zero. A higher capacitive current was obtained at the ACNT/Pt/SIBS electrode than the ACNT/SIBS electrode, suggesting more rapid charge/discharge characteristics for the ACNT/Pt/SIBS [19]. Little change was found during 50 consecutive cycles, indicating electrode stability.
Figure 6.3. Cyclic voltammograms obtained using (a) the ACNT/SIBS electrode or (b) the ACNT/Pt/SIBS electrode as working electrode (scan rate = 0.02 Vs\(^{-1}\)). Electrolyte was phosphate buffer solution (pH = 7.4).

### 6.3.1.2 Cell Culturing

To determine the influence of the Pt layer on the ability to sustain cell growth, L-929 cells were cultured onto Pt sputter coated gold mylar. Calcein AM was used as a cell viability dye to stain metabolically active cells bright green. As shown in Figure 6.4, L-929 cells adhered and grew well on Pt coated Au mylar, suggesting the sputter coated platinum was biocompatible.
Figure 6.4. Fluorescence microscope images of L-929 cells growing on Pt coated gold mylar.

When the ACNT/SIBS structure was used as the substrate for the growth of L-929 cells, cell adhesion and growth was found both on the SIBS side (Figure 6.5a) and ACNT side (Figure 6.5b). More cells were observed on ACNT side of the electrode structure, suggesting the excellent biocompatible properties of ACNT.

Figure 6.5. Fluorescence microscope images of L-929 cells growing on (a) SIBS side and (b) ACNT side of the ACNT/SIBS electrode.
Using the ACNT/Pt/SIBS structure, prolific cell growth was still obtained on the SIBS side (Figure 6.6a). However fewer cells were observed on the ACNT/Pt side (Figure 6.6b). The addition of Pt significantly improved the electrochemical activity of the electrode but compromised the ability to sustain cell growth.

![Figure 6.6](image)

(a)                                    (b)

Figure 6.6. Fluorescence microscope images of L-929 cells growing on (a) SIBS side and (b) ACNT/Pt side of the ACNT/Pt/SIBS electrode.

### 6.3.2 The ACNT/SWNT/SIBS Structure

In attempts to improve the conductivity of the SIBS layer while maintaining cell growth, SWNTs were added to this layer.

SEM images (Figure 6.7) of the ACNT/SWNT/SIBS electrode shows the aligned carbon nanotube structure integrated into the SWNT/SIBS layer. The roots of the carbon nanotubes are held tightly by the underlying polymer layer. The electrode exhibits the
Chapter 6: Flexible Nanostructures Containing Aligned Carbon Nanotubes as Platforms for Cell Culturing

best mechanical properties and highest flexibility of all the ACNT based structures investigated in this work. The ACNT structure remains intact even after being exposed to 45% stain, indicating the high robustness of the composite film. More than 80% of the carbon nanotube length (typically ca. 5 μm in total) remained exposed (Figure 6.7).

Conductivity measurements show that the ACNT/SWNT/SIBS electrode had an electronic conductivity ca. 50 S•cm⁻¹, a significant improvement over the ACNT/SIBS electrode (ca. 1 S•cm⁻¹). The incorporation of SWNT obviously provides better interconnectivity between the aligned parallel tubes.

Figure 6.7. SEM micrograph of ACNT on the SWNT/SIBS electrode.
6.3.2.1 Electrochemical Characterisation

Cyclic voltammograms were obtained using the ACNT/SIBS and the ACNT/SWNT/SIBS structures as the working electrode (Figure 6.8). Much higher capacitive currents were found using the ACNT/SWNT/SIBS electrode than those obtained without SWNTs present in the SIBS layer. No degradation was observed after 50 consecutive cycles.

Figure 6.8. Cyclic voltammograms obtained using (a) the ACNT/SIBS electrode or (b) the ACNT/SWNT/SIBS structure as working electrode (scan rate = 0.02 Vs⁻¹). Electrolyte was phosphate buffer solution (pH = 7.4).
6.3.2.2 Cell Culturing

L-929 cells were seeded onto the ACNT/SWNT/SIBS structure using methods as described above. Excellent cell growth and adhesion were observed on both sides of the electrode (Figure 6.9a and b). The addition of SWNT increased the electrochemical activity of the structure without compromising the biocompatibility of the electrode.

(a)                                     (b)

Figure 6.9. Fluorescence microscope images of L-929 cells growing on (a) the SWNT/SIBS side and (b) the ACNT side of the ACNT/SWNT/SIBS electrode.

6.3.3 The ACNT/Pt/PLGA Structure

Using PLGA as the supporting polymer, structures were prepared with or without a sputter coated Pt layer.
Chapter 6: Flexible Nanostructures Containing Aligned Carbon Nanotubes as Platforms for Cell Culturing

SEMs show that the ACNT structure was retained even after sputter coating (Figure 6.10). The resulting ACNT/Pt/PLGA structure remains intact after being stretched under 15% strain, suggesting good mechanical properties and flexibility of the electrode. Compared with the other ACNT/polymer structure, however, the ACNT/Pt/PLGA was more prone to be stiff and folded. This may be attributed to the brittle nature of PLGA. More than 80% of the length of the carbon nanotubes remains exposed after introduction of the Pt and polymer layer.

The electronic conductivity of the ACNT/Pt/PLGA structure was as high as 450 S\( \cdot \)cm\(^{-1} \), distinctly higher than \textit{ca.} 45 S\( \cdot \)cm\(^{-1} \) for the ACNT/PLGA composite.

Figure 6.10. SEM micrograph of ACNT on the Pt/PLGA electrode.
6.3.3.1 Electrochemical Characterisation

Cyclic voltammograms were obtained using the ACNT/PLGA electrode (Figure 6.11a). Only low capacitive currents were observed. The capacitive current was enhanced dramatically after the addition of the Pt layer (Figure 6.11b), and suggesting the highly capacitive nature of the ACNT/Pt/PLGA electrode with rapid charge/discharge characteristics [19]. No obvious degradation was observed after 50 consecutive cycles.

Figure 6.11. Cyclic voltammograms obtained using (a) the ACNT/PLGA electrode and (b) the ACNT/Pt/PLGA electrode (scan rate = 0.02 Vs\(^{-1}\)). Electrolyte was phosphate buffer solution (pH = 7.4).
6.3.3.2 Cell Culturing

Confluent cells were found to grow on both the PLGA side and the ACNT side of the PLGA/ACNT structure (Figure 6.12). A higher fluorescence intensity was observed on the ACNT side.

![Fluorescence microscope images of L-929 cells growing on (a) PLGA side and (b) ACNT side of the ACNT/PLGA electrode.](image)

Figure 6.12. Fluorescence microscope images of L-929 cells growing on (a) PLGA side and (b) ACNT side of the ACNT/PLGA electrode.

After the incorporation of the Pt layer, prolific cell growth was found on both the PLGA side and the ACNT/Pt side (Figure 6.13). More cells were clearly found on the PLGA side (Figure 6.13a) than the ACNT/Pt side (Figure 6.13b). It has been shown to be non-toxic to cell growth. The improved mechanical properties of the ACNT/Pt/PLGA electrode was obtained after the addition of Pt. But the electrode was still quite brittle and folded up after 3 days of cell culture. To sum up, the addition of Pt increased the mechanical properties and electrochemical activity of the ACNT/PLGA electrode while
the cell density decreased when this structure was used as a platform for L-929 cell growth.

Figure 6.13. Fluorescence microscope images of L-929 cells growing on (a) the PLGA side and (b) the ACNT/Pt side of the ACNT/Pt/PLGA electrode.
6.4 Conclusions

The flexible and mechanically robust nano bio-electrodes were fabricated from ACNT, SIBS and PLGA. Pt or SWNT was introduced into the structures to improve the electrochemical activity while maintaining the flexible mechanical properties. The incorporation of Pt significantly improved the electrochemical properties of ACNT/SIBS electrodes. Cell culture results showed that L-929 cells could be grown and adhere well on the electrode. In addition, Pt was proved to be non-poisonous to the L-929 cells while the counteractive influence of Pt on the cell growth was found. The electrode electrochemical and mechanical properties could be amazingly improved with the addition of SWNT into the structure while no adverse effect on the biocompatibility was found.

The biodegradable PLGA/ACNT electrodes were brittle and easy to be folded up. The mechanical and electrochemical properties were improved by sandwiching a Pt layer. Confluent cell growth was found on both sides of the electrode, suggesting excellent biocompatibility of PLGA, ACNT and Pt. Similarly, less cell density was obtained on the ACNT/Pt side.

In summary, flexible, conductive and robust biocompatible nano-electrodes were synthesized successfully; and are the excellent candidates for potential biomaterials which need electrochemical stimulation.
6.5 References


CHAPTER 7:

GENERAL CONCLUSIONS
Chapter 7: General Conclusions

The synthesis and optimisation of novel nanostructured electrode devices through various ways including the use of inverse opal templates, electrospun fiber targets and aligned carbon nanotube forest substrates were demonstrated in this project. We also presented the outstanding improvements with the use of nanostructured materials in a wide variety of application areas including fuel cells, photoelectrochemical cells, biosensors, cell culture, electrochemical capacitor and energy storage in this work.

The fabrication of nanostructured porous Pt inverse opals from self-assembled polystyrene opal templates by filling the void space between the opal beads with electrochemically deposited Pt was illustrated in Chapter 3. A highly ordered dense hexagonal packing structure of Pt film was obtained after the removal of the host template. The high large electrochemical area inherent in the inverse opals was confirmed by electrochemical characterisation. The resulting inverse opal electrode exhibits a much higher catalytic performance in methanol oxidation and excellent stability with a 100 mV negative shift of the potential of methanol oxidation when compared with the Pt film. Another kind of mesoporous nanostructured opals based on the highly conductive and transparent ITO film was prepared. The enhanced electrochemical active surface area was obtained with the use of nanostructured ITO opals when compared with the pristine ITO coated glass. The resulting opal template was used as the substrate to electrodeposit photoelectrochemically active polyterthiophene (PTTh). The PTTh covered nanostructured electrode shows extraordinary performance in photoelectrochemical cells. A best power-conversion efficiency of 0.109% and short circuit current density of 1470 μA•cm⁻² were obtained; which are both better than previously published values.
Chapter 7: General Conclusions

Nanofibers of biomaterials such as DNA and poly(styrene-β-isobutylene-β-styrene) (SIBS) were synthesized using the electrospinning technique in Chapter 4. Attempts were made to well control the electrospinning process and the morphologies of resulting fibers by quantitatively analyzing solution properties including the solution conductivity, surface tension and viscosity, and process parameters e.g. tip-to-collector distance, applied potential and the feed rate. To improve the electrochemical activity of the resulting bio-nanofibers, the biocompatible single wall carbon nanotubes (SWNTs) were introduced into the electrospun fibers. Raman spectra confirmed good interaction between SWNTs and the biomaterial fibers. The improved electrochemical properties with the addition of SWNTs into DNA and poly(ethylene oxide) composite fibers were observed using cyclic voltammetry. The resulting nanofiber electrode demonstrates a broad linearity range and high sensitivity in enzyme biosensors. The presence of SWNT throughout the electrospun SIBS fibers favors mass transport and electroactivity. SIBS/SWNT composite fibers exhibit excellent biocompatibility and suitability for the growth and adhesion of L-929 cells as well as good electrochemical activity, leading to potential applications in electrical stimulation on cell culture and biomedical fields.

The flexible, mechanically robust and highly conductive electrochemical devices were prepared from highly ordered aligned carbon nanotube (ACNT) forest, and flexible and conductive polymer films such as Pt/poly(vinylidene fluoride) (PVDF) or poly(3,4-ethylenedioxythiophene) (PEDOT)/PVDF in Chapter 5. Pt nanoparticles were also fabricated on ACNT/Pt/PVDF structures using electrochemical deposition. An excellent electrochemical capacitance and amazing electrochemical surface area was
were obtained from the resulting Pt nanoparticles coated on the ACNT/Pt/PVDF electrode. The Pt-ACNT/Pt/PVDF electrode also exhibits a dramatic catalytic activity in the anodic electro-oxidation of methanol with the presence of highly ordered nanostructures. The ACNT/PEDOT/PVDF electrode shows 50% improvement in capacity during Li-ion battery tests when compared with a free-standing SWNT paper. The light weight and high flexibility of the electrode also provide advantages in assembling the device for practical applications.

In Chapter 6, flexible and mechanically robust biocompatible nanostructures were synthesized from ACNT and biomaterials such as SIBS and poly(lactide-co-glycolide) (PLGA). The highly ordered ACNT structures were transferred into the flexible biocompatible substrate intact. The conductive Pt or SWNT was incorporated into the ACNT/biomaterial structure to improve the conductivity for the purpose of electrical stimulation in cell culture or tissue engineering. The significant improvements in electrochemical activity were observed during electrochemical characterisation. ACNT and Pt were proved to be biocompatible during cell culture. Confluent cells were obtained in all ACNT and biomaterials composite structures. These studies open up the possibility to prepare flexible cell growth substrates which require electrochemical stimulation, mechanical robustness and good mass transport.

In conclusion, novel properties are expected to be obtained by physically reducing the size of conventional materials to nanoscale. In this project, a wide range of nanostructures were prepared using various routes. These nanomaterials exhibit
extraordinary enhancement in a wide variety of properties including electrochemical, photoelectrochemical, biological and mechanical.