

Electrochemical Studies of Carbon-Based Materials



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Abstract

Graphene, as a recently discovered carbon allotrope, possesses with it many outstanding properties ranging from high electrical conductivity to great mechanical strength. Single layer graphene can be prepared by mechanical cleavage of graphite or by a more sophisticated method, CVD. However, the scale-up process for these preparation techniques is still unconvincing. Solution-processed graphene from exfoliation of graphite oxide on the other hand provides an alternative prospect resulting in the formation of graphene nanoplatelets (GNPs), which can be readily manipulated to tailor-suit various application demands. The main aim of the thesis is to explore the possibility and availability of this versatile method to produce graphene nanoplatelet and its composites with good all-round performance in energy and bioanalytical applications. A range of physical and chemical characterisation techniques were utilised including SEM, TEM, AFM, XPS, XRD, DLS, FTIR, Raman and UV-Vis spectroscopy in order to investigate the structural and chemical information of the graphene-based materials prepared.

Functionalisation of graphene oxide with polyelectrolyte polymer could facilitate deposition of platinum nanoparticles in the formation of Pt-GNPs composites. The resultant composite was employed for bioanalytical application in the detection of an important neurotransmitter, glutamate, based on glutamate oxidase enzyme. The performance of Pt-GNPs based

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glutamate sensor exhibited enhanced sensitivity and prolonged stability compared to the sensors based on Pt decorated diamond or glassy carbon electrodes. The significant interfering effect from concomitant electrochemically active biological compounds associated with Pt-GNPs electrode however could be alleviated via opting for Prussian blue deposited GNPs electrode instead. The oppositely charged Pt-GNPs due to different functionalising polymers were also subject to self-assembly, which was enabled by the electrostatic interaction of the opposite charges of Pt-GNPs. The self-assembled film showed enhanced mechanical stability than the conventional drop-casted film and provided reasonably good activity towards oxidation of hydrogen peroxide.

Three-component composite of graphene, nanodiamond and polyaniline was prepared via in-situ polymerisation for usage as an electrode material in electrochemical capacitors (“supercapacitors”). The addition of graphene was shown to significantly enhance specific capacitance while nanodiamond could improve the stability of the electrode by strengthening the polymer core. Another approach to produce a supercapacitor was via electrodeposition of nickel and cobalt hydroxides on graphene oxide film incorporated with bicarbonate salt. The film was then subject to thermal reduction of GO and expansion of graphene layers within the film was observed. This leavening process enhanced the surface area of graphene film and thus the higher specific capacitance was obtained. The decoration of nickel and cobalt hydroxides onto the film also boosted the specific capacitance further however the poor cycling stability of the heated film still remained an issue.

Graphene nanoplatelets were also used as a support for electrodeposition of Pt nanoparticles for methanol oxidation in acidic media. The preferential phase of the Pt deposited and large surface area of graphene in comparison to other carbon supports studied led to good catalytic activity being observed.

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Publications

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Glutamate detection by Prussian blue electrodeposited on reduced graphene oxide nanoplatelets

S. Wisetsuwannaphum and J. S. Foord (*in preparation*)

Electrodeposition of Textured Pt nanoparticles on Graphene for Electrocatalytic Oxidation of Methanol

S. Wisetsuwannaphum, J. Hu and J. S. Foord (*in preparation*)

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List of Abbreviations

Acronym	Definition
AA	Ascorbic acid
AFM	Atomic force microscopy
AP	4-Aminophenol
BDD	Boron doped diamond
bls	Bilayers
CA	Citric acid
CNTs	Carbon nanotubes
Csp	Specific capacitance
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
DLS	Dynamic light scattering
DMFCs	Direct methanol fuel cells
DOE	Department of Energy
EAS	Electrochemical active surface area
ECF	Extracellular fluid
EDLC	Electrochemical Double Layer Capacitor
EIS	Electrochemical impedance spectroscopy
FWHM	Full width at half maximum

List of Abbreviations

GA	Glutaraldehyde
GCD	Galvanostatic Charge Discharge
GCE	Glassy Carbon Electrode
GluOx	Glutamate Oxidase Enzyme
GNPs	Graphene Nanoplatelets
GO	Graphene Oxide
IHP	Inner Helmholtz plane
LbL	Layer-by-Layer
ND	Nanodiamond
OHP	Outer Helmholtz plane
PANI	Polyaniline
PB	Prussian blue
PBS	Phosphate Buffer Saline
PDDA	Poly(diallyldimethylammonium chloride)
PPD	Polyphenylenediamine
PSS	Polystyrene Sulfonate
rGO	Reduced Graphene Oxide
SA	Self-Assembly
SC	Supercapacitor
SEM	Scanning Electron Microscope
TEM	Tunnelling Electron Microscope

List of Abbreviations

UA	Uric Acid
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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Chapter 1 Introduction

1.1 Energy Devices – General Overview

Since the global industrial revolution the world has been concerned with energy demand raising political, economic and environmental issues to name just a few. The perpetual increase of world's population reaching above 7 billions in 2014 [1], the figure which more than doubles the 3 billions seen half a century ago in 1960, does not add to a positive note for the global energy demand. In order to sustain the current standard of life, around 14 TW of energy is required annually [2]. According to the world's energy consumption from 1988 to 2013 reported by BP statistics [3] as shown in **Figure 1.1**, it is likely that the world's consumption will reach 13000 million tonnes of oil equivalent. The only decrease seen in the past decade in 2009 is due to the global economic crisis with the loss of world's GDP of 0.6%. The highest sectors of consumed energy are coal, oil and natural gases. There are thus considerably high amount of concerns over the energy consumption based on fossil fuels and non-renewable energy resources. Consequently for the past few decades, there has been a growing demand for the more sustainable and environmentally friendly alternative energy sources as can be seen in **Figure 1.1** for the upwards trend of the energy consumed from renewable resources.

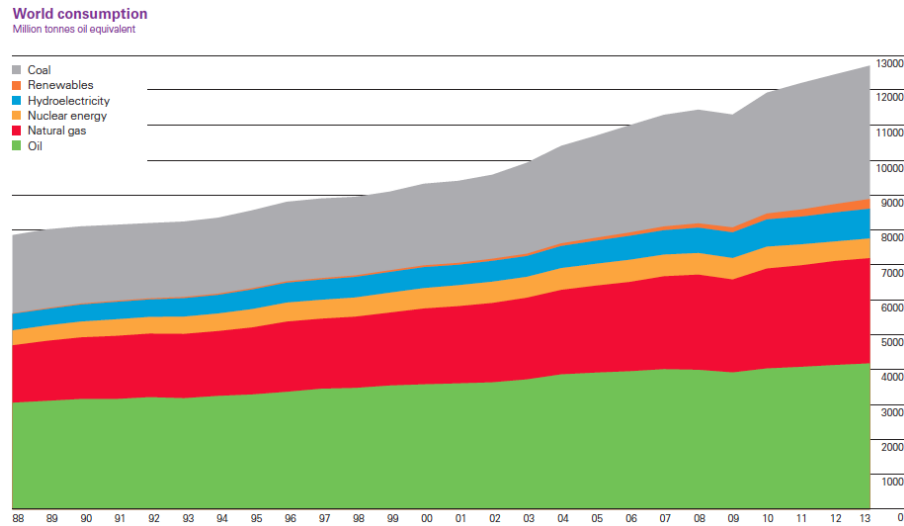


Figure 1.1 World energy consumption from 1988 to 2013 [3]

Environmentally there is a threat posed by the substantial emission of greenhouse gases, which is twice that observed in the pre-industrial period [4]. Even so, to date coal and gasoline are still the major source of energy supply. With the detrimental effect of climate change seen around the world and the fear over the scarcity of energy in the near future, there is a rise in public awareness as well as governmental policies over energy issue. These have caused a real thrust for the search of more sustainable and environmentally benign energy and power sources without resorting to nuclear energy, which still causes many debatable aspects especially regarding problematic waste disposal [5]. As a result, the development in energy storage and conversion technologies has greatly intensified over the recent years. Amidst others lie electrochemical energy storage and conversion systems such as batteries, fuel cells and electrochemical capacitors, which have been regarded as the most feasible and efficient, particularly for portable, stationary, and transportation applications [6].

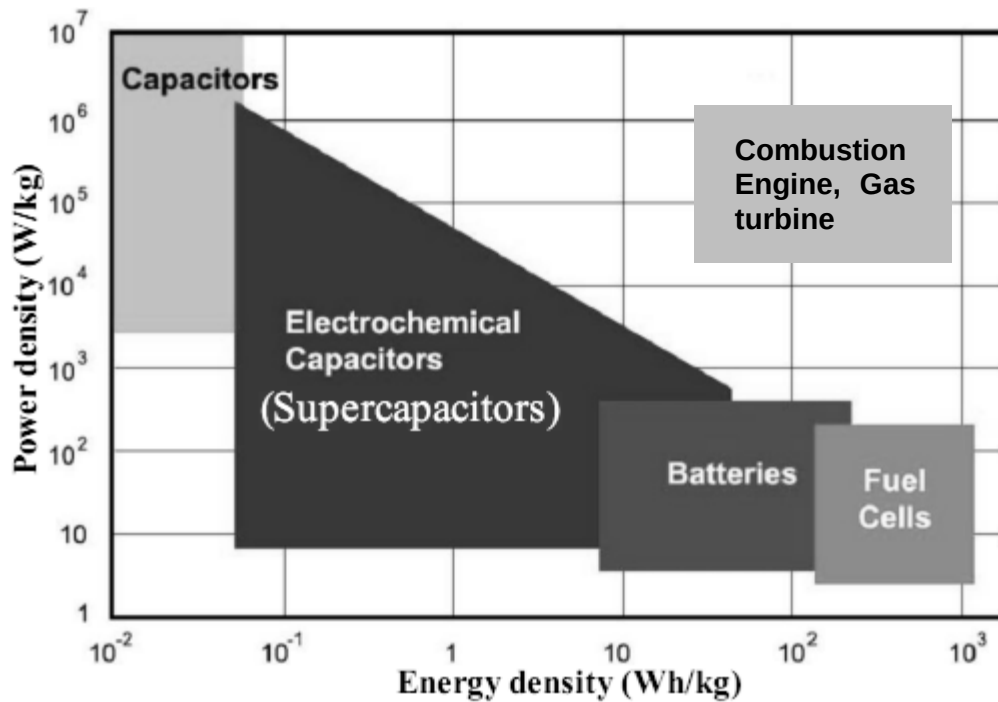


Figure 1.2 A simplified Ragone plot [7, 138]

The three energy systems share common traits among them such that the energy-providing processes take place at the phase boundary of the electrode/electrolyte interface and electron and ion transport are separated [7]. These energy storage and conversion devices can be characterised according to their energy and the power capabilities by a representation known as the Ragone plot or diagram [8] as depicted in **Figure 1.2**. The difference between each device is rather prominent, to take for an example, fuel cells can be considered to be high-energy but low-power systems, whereas supercapacitors are regarded as high-power but low-energy systems. So far no device has yet to overcome the high energy and high power system of combustion engines. However, unlike combustion engines, battery and fuel cells can convert chemical energy directly to electrical energy and therefore are not limited by Carnot cycle thus higher efficiency to reach theoretical values is possible.

1.1.1 Fuel Cells

A fuel cell is an energy conversion device that converts chemical energy stored in fuel such as hydrogen, natural gas, and alcohol into electricity via chemical reaction with an oxidizing agent such as oxygen. The pioneer development of fuel cells can be dated back to the early 18th century by Sir William Grove whose work was on the first gas voltaic batteries [9]. It was however only in 1970 that fuel cells had gained wider attention particularly due to its application and usage for space programme from NASA [10]. Since 2007 fuel cells have become commercially available [11]. To date, according to the market report on fuel cells from the US Department of Energy (DOE), the total shipments of fuel cell of 2012 have rocketed by 321% from 2008. The number of megawatts that were shipped also double that in 2008 to 120 MW. It was projected that by 2030, in UK alone there will be 1.6 million fuel cell electric vehicles (FCEVs) on the road [12].

The increasing trend of fuel cells in the world's market is achieved by no surprise. The higher energy density of fuel cells compared to batteries is the impetus to the development and many applications of fuel cells. Specific energy per unit mass from fuel cells is an evident advantage in comparison to batteries. Fuel cells rather than battery seem set to supersede combustion engines [7]. One of the most advantageous features of fuel cells is their efficiencies in energy conversion and they also provide the cleanest power generation [13]. Applications of fuel cells can be as stationary, portable devices or for transportation, which will depend also on the types of fuel cell being used. As for portable devices such as notebook laptops, mobile phones or tablets, all demand high-energy input to keep up to date with the highly advanced and reviving today's technology. The promising candidate to overcome the systematic limitations of conventional batteries is the direct methanol fuel cell (DMFCs) [7, 14].

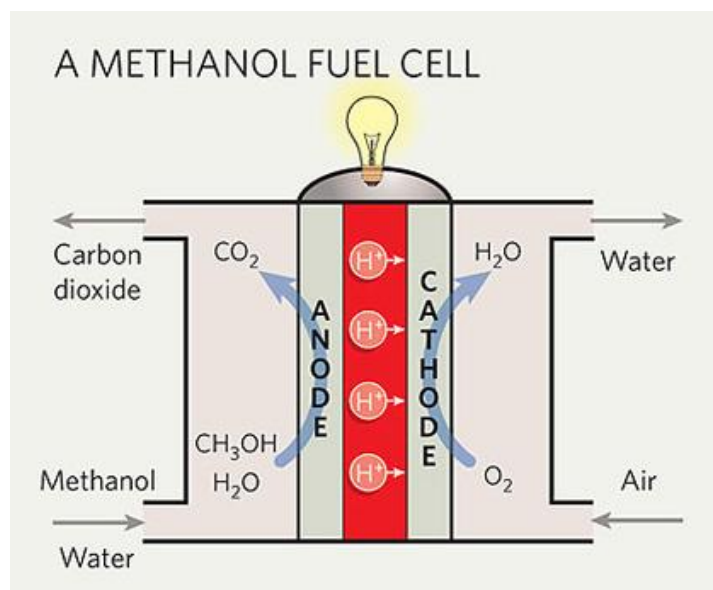
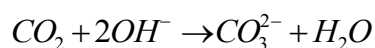


Figure 1.3 Diagram of DMFCs based on a proton exchange membrane [15]

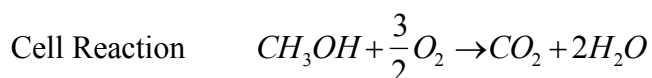
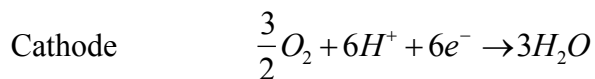
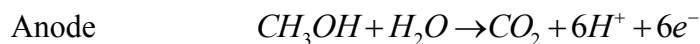
Direct alcohol Fuel cells have received considerable interest for their usage as power sources for portable devices due to the inevitable advantages over the hydrogen-fuelled analogues [16]. Methanol and ethanol, in particular, exhibit much higher volumetric energy density, more reversible efficiency and are more convenient for storage and transport than hydrogen [17, 18]. Although most available DAFCs are based on acidic electrolytes, alkaline fuel cells are actually more mature with initial development dating back in 1960s-1980s [19]. However the main drawback of traditional alkaline fuel cells is the degradation of electrolyte and electrode. This occurs as a result of reaction of CO_2 with hydroxyl ions as:



This results in precipitation of Na_2CO_3 or K_2CO_3 , which subsequently block the pores of the membrane as well as disrupt and destroy the active layers of the electrode [20-22].

Direct methanol fuel cells are the most common type of DAFC. The operational process specific to this type of fuel cells in acidic electrolyte can be illustrated as in **Figure 1.3**. The

half-cell reaction and the overall redox process in DMFCs are described by the following equations.



The main challenges associated with the development of fuel cells are the cost-performance barrier and the durability. In 2012, the cost for 80 kW net Proton Exchange Membrane (PEM) fuel cell systems is still around \$42 and still higher than the criteria set by the DOE to have a cost of only \$30 [23]. In terms of catalyst, much effort has been devoted to replacing Pt-based catalysts in order to reduce the cost and broaden the choice of materials. Nevertheless, at present the state-of-the-art and the most practical electrocatalysts for PEM fuel cells are still carbon-supported Pt catalysts [6]. The aforementioned advantages of DMFCs and its existing challenges had prompted the study on methanol oxidation by electrochemically fabricated Pt nanoparticles on various carbon supports, which features in Chapter 7 of this thesis.

1.1.2 Supercapacitors

Electrochemical capacitor or EC is an energy storage device with substantially higher charge stored than the conventional capacitor. The terms supercapacitor and ultracapacitor are also used interchangeably for electrochemical capacitor referring to a capacitor with ‘enhanced’ performance hence the prefixes, ‘super’ and ‘ultra’. Supercapacitor has currently emerged as

a gap-bridging energy device between conventional capacitors and batteries providing higher energy density than conventional capacitor and higher power density than batteries as evident from the Ragone plot. Supercapacitors have attracted attention recently due to the need for higher-power energy storage systems to replace or combine with batteries in a number of applications such as back-up supplies protecting power disruption [24]. Although supercapacitor generally possesses relatively low energy density (around 5 Wh kg⁻¹), it operates at very fast rate by completing its full charging or discharging process within seconds and can offer high power density in a range of 0.5 to 10 kW kg⁻¹ as shown and compared in **Table 1.1**.

Table 1.1 Comparison between different types of capacitors and batteries [25, 26]

Characteristic	Electrolytic capacitor	Carbon supercapacitor	Battery
Specific energy (Wh kg ⁻¹)	<0.1	1-10	10-100
Specific power (W kg ⁻¹)	≫10000	500-10000	<1000
Discharge time	10 ⁻⁶ to 10 ⁻³ s	s to min	0.3-3 h
Charging time	10 ⁻⁶ to 10 ⁻³ s	s to min	1-5 h
Charge/discharge efficiency (%)	~100	85-98	70-85
Cycle-life (cycles)	Infinite	>500000	~1000

Electrochemical capacitors can be grouped into two main categories according to their charge storage mechanisms. Electrochemical double layer capacitors or EDLCs store charge via the same process as for the conventional electrostatic capacitor. For a conventional capacitor, charge is electrostatically stored in an electric field between two parallel plates or electrodes separated by a non-conducting dielectric medium. When a potential difference is applied, positive charge is accumulated on one plate leaving the opposite plate with the resulting negative charge. The charge storage of a capacitor can be characterised by its capacitance. If the distance between the two plates is D and the area of each plate is A then the capacitance is $C = \epsilon_0 \epsilon_r A / D$ where ϵ is the dielectric constant of the electrical double-layer region. As for the EDLCs, charge is stored in a similar manner via reversible adsorption of ions of the electrolyte, which is sandwiched between the two electrodes.

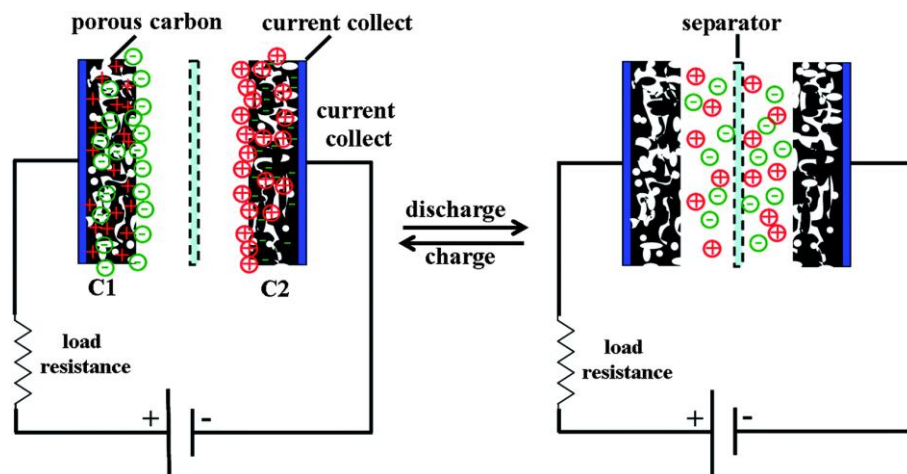


Figure 1.4 Diagram showing charging and discharging mechanism at supercapacitor electrodes [27]

Charge separation also occurs at the electrode electrolyte interface in the form of electrical double layer at the interface upon polarisation [28] giving rise to the double layer capacitance described also by the same equation, $C = \epsilon_0 \epsilon_r A / D$. The combination of high surface-area (A) with extremely small charge separation (D) generally in Angstrom range is responsible for the extremely high capacitance of supercapacitors [29]. EDLCs exhibit a very high degree of

reversibility in repetitive charge–discharge cycling, cycle lives in excess of 100,000 cycles have been demonstrated [28]. This impressive durability also makes the supercapacitors environmentally friendly. EDLCs electrode materials are most commonly based on high surface area carbon materials such as carbon black [30], carbon fibre [31], carbon aerogels [32] and the more recent ones in the form of nanostructured carbon such as carbon nanotubes [33, 34] and graphene [35]. The prototyped supercapacitor was developed by General Electric in 1957 following the double layer model introduced by Helmholtz. The energy storage capability of the device was acknowledged later when the first commercialised supercapacitor was originated from SOHIO [36]. It was only until 1971 that supercapacitors were successfully marketed by yet another company called NEC where the device was primarily used for memory back-up system [37].

Another type of supercapacitors is pseudocapacitor where the word ‘psuedo’ implies a different mechanism of charge storage is taking place. Unlike EDLCs, pseudocapacitors store energy via Faradaic redox reactions, which are fast and reversible, of electrode materials making them battery-like in behaviour for this respect [38]. As for carbon electrodes in EDLCs, they can exhibit partial pseudocapacitance via the redox reactions of the functional groups of the carbon electrode. Most common materials for pseudocapacitors are metal oxides especially transition metals and conducting polymers that have reversible redox reactions such as RuO_2 [39], MnO_2 [40], NiO [41], polyaniline [42], and polypyrrole [33]. However, the pseudocapacitive materials also carry with them some shortcomings for practical applications. These include the low power density due to the lack of good electrical conductivity and the poor cycling stability as the structure of the materials can be deteriorated upon numerous successive redox processes [38]. These problems can be overcome by the use of highly conductive and large surface area carbon as a backbone material in combination

with such pseudocapacitive materials for the hybrid supercapacitor electrodes. This area of interest was realised and featured in the work in Chapter 5 and 6 of this thesis.

1.2 Graphene

Among various forms of carbon allotropes, graphene, a two-dimensional monolayer of carbon atoms [43], has sparked worldwide interest from the scientific and public sectors alike after being discovered by Andre Geim and Konstantin Novoselov to whom Nobel Prize in Physics was awarded in 2010 [44]. Graphene as a layer of sp^2 carbon acts as a basic building block to carbon materials in different dimensionalities. Three-dimensional graphite is formed by stacking of graphene layers. Rolling graphene sheets give rise to the 1D carbon nanotube and graphene can be wrapped to form 0D fullerenes. Owing to its unique properties, graphene has found its versatile applications ranging from electronics to drug-delivery. A surge of research and development regarding this unique material is evident, as the number of patent publications shown in **Figure 1.5** has increased exponentially since 2004, the year marked as its first discovery as a stable isolated form. Despite only being prepared successfully in just a decade, graphene has long been hypothesized since 1947 [45] but was believed to be thermodynamically unstable at finite temperatures as of other two-dimensional crystals [46].

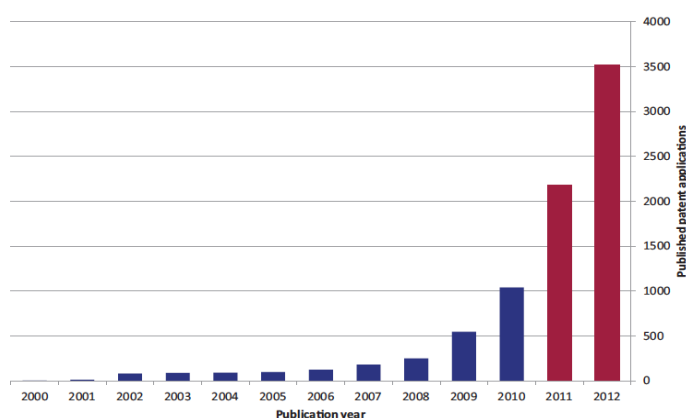


Figure 1.5 Worldwide patent publications related to graphene from 2000-2012 [44]

1.2.1 Structure and Properties

Graphene has a honeycomb lattice with each carbon (sp^2) atom having 3 sigma bonds and 1 pi bond. The delocalisation of pi electrons is key to the unique features surrounding its electrical properties. Ripples of graphene sheet can be observed by TEM and STM with the height of the corrugation estimated to be around 0.7 to 1 nm [47]. The corrugation occurs as a result of thermal fluctuations [48]. It was suggested that the degree of corrugation of a graphene sheet could affect its electrical properties. Being a ‘flat’ 2D sheet, graphene was theoretically predicted to exhibit as large specific surface area (SSA) as $\sim 2600 \text{ m}^2/\text{g}$ [49].

Graphene was first isolated by a technique named ‘micromechanical cleavage’ which is typically peeling off graphite surface with an adhesive tape. Despite being discovered unexpectedly, the rise of graphene comes about due to its extraordinary properties. Intrinsic graphene is a zero-gap semiconductor or a semimetal. Its room-temperature electron mobility as high as $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was demonstrated surpassing the theoretical limit at $\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [50]. Charge carriers in graphene was found to be massless Dirac fermion, in other words, its behaviour is described by Dirac equation rather than the usual Schrodinger equation. Graphene possesses half integer Quantum Hall effect at room temperature and its ballistic transport is long range [51]. The resistivity of graphene around $10^{-6} \Omega\text{cm}$ is lower than that of silver [52]. Mechanically the single layer graphene is one of the toughest materials ever tested [53], with a tensile strength of 130 GPa and a Young’s modulus of 1 TPa [54].

1.2.2 Production

The staggering properties of graphene can only be realised for the individual graphene sheets. The main obstacle relating to large-scale production of graphene is its irreversible agglomeration due to Van der Waals interaction between each layer. Although the

micromechanical cleavage can provide single sheet of graphene with high quality, the prospect of bulk-quantity production is rather low. A number of processes have been developed over the past decade and are reviewed here as follows.

1.2.2.1 Exfoliation

Solution based exfoliation can be done with graphite or graphite oxide as starting materials. Thermal exfoliation of graphite or graphite oxide requires large energy consumption since high temperature over 500 °C is generally needed [55]. Direct exfoliation of graphite by means of harsh ultrasonication in either aqueous or organic-based solvents has also been demonstrated. For instance, defect-free monolayer graphene was produced by exfoliation of graphite in N-methylene-pyrrolidone (NMP) solvent [56]. An industrial important method utilises thermal-shock procedure to achieve exfoliation and reduction of graphene oxide simultaneously [57]. Another approach is to oxidise graphite to graphene oxide via Hummers method or its variations utilising a combination of oxidants, potassium permanganate and sulphuric acid, followed by chemical reduction [58]. The reduction of graphene oxide yields bulk amount of graphene-like sheets that despite having some defects are highly processable [59] and is thus the strategy employed in this study. This chemically based technique and the properties of the output graphene materials will be extensively discussed later in section 1.2.3 below.

1.2.2.2 CVD and Epitaxial Growth

Bottom-up approaches have also been developed such that the main methods including chemical vapour deposition (CVD) and epitaxial growth. CVD is a promising technique to produce large area single or few layers graphene in a highly controllable fashion. The method relies on the carbon-saturation of a transition metal upon exposure to a hydrocarbon gas at high temperature [60]. Thin film of carbon then precipitates on the metal surface upon

cooling and the metal substrate is etched away at the end. Epitaxial growth technique on the other hand grows graphitic layers on silicon for carbon faces of SiC wafer by sublimating Si atoms [61] with a fine control over the number of graphene layers grown. These two techniques although enable high quality of graphene to be produced, the main drawbacks are the expensive cost, high energy demand, the complication of such sophisticated techniques involved and most importantly the issue with the prospect of large-scale process.

1.2.2.3 Other Possible Routes

Other techniques albeit less common have also been demonstrated such as unzipping of CNTs to produce graphene nanoribbons which provides better control over functionalisation and the quality of the edges [62]. High-quality graphene nanoribbons can also be synthesised from coupling of monomer precursor into linear polyphenylenes followed by cyclodehydrogenation, which resulted in graphene with even more complex structures [63]. Laser ablation could provide deposition of graphene nanoplatelets on arbitrary substrates [64]. These processes are however still in its infancy and require further development to rival the more common, aforementioned methods.

1.2.3 Chemically Derived Graphene from Graphene Oxide

The oxidation of graphite is a chemical approach for exfoliation as the interaction between each layer was weakened. The interlayer spacing between adjacent sheets increases from 3.35 Å in graphite to around 6.8 Å in graphene oxide powder [65]. The hydrophilic nature of GO is owing to it being highly oxidised with many oxygenated functional groups and as a result can be well dispersed in aqueous and polar organic solvents [66]. After a decade-long debate over the structure of graphene oxide, recent study based on solid state NMR of ^{13}C labelled GO shows that the basal plane is decorated with epoxy and hydroxyl groups, whereas carbonyl and carboxylic acid groups are present along the sheet edges [67]. This structure of

GO agrees well with the model proposed earlier by Lerf–Klinowski [68, 69]. GO paper or free-standing film shows a high tensile strength up to 42 GPa [70].

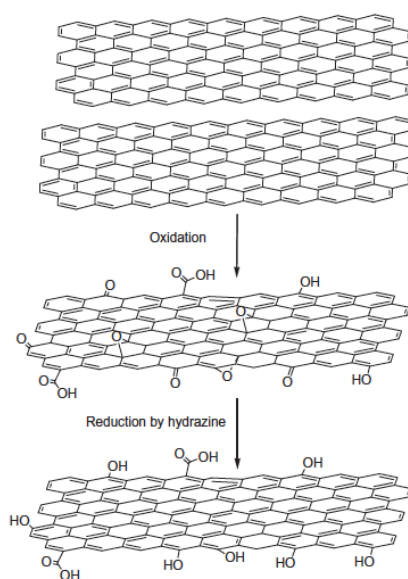


Figure 1.6 shows chemical structures of graphene (top), graphene oxide (middle) and hydrazine reduced graphene oxide (bottom) [43]

The advantage of graphene oxide over pristine graphene is its availability for various chemical functionalisations with the oxygenated groups acting as the active sites and hence many surface modifications and graphene based composites can be developed. Graphene oxide can partially regain its conductivity and sp^2 -hybridised system via undergoing reduction methods, the most common routes being chemical and thermal. Chemical reduction of graphene oxide has been performed with a variety of reductants, the most prominent ones however are hydrazine and sodium borohydride. Reduction by hydrazine mainly removes epoxides and leaves carboxylic acids intact [71] hence provides graphene with lower conductivity than those reduced by sodium borohydride, which is a more effective reductant [43]. For a more environmentally friendly approach, L-ascorbic acid or vitamin C [72] and bovin serum albumin (BSA) [73] were shown to be able to reduce graphene oxide as well.

The most beneficial advantages of the production of reduced graphene oxide method are probably its low-cost and the ease to be scaled-up. The late arrival of large-scale defect-free graphene sheets has also put forward the work on solution-based reduced graphene oxide (rGO). As rGO comes with residual chemical moieties, it can be readily functionalised, which renders its versatile compatibility. As a consequence, a large number of graphene based composite materials has been reported along with their proposed and usually demonstrated applications. The majority of the work on graphene based composite is arguably related to polymer and metal nanoparticles.

1.2.4 Graphene Based Composites

1.2.4.1 Graphene-Polymer Composites

Graphene and its derivatives are found to be important filler materials for polymer composites. To obtain the best quality of such composites, it is down to the control over fabrication processes. The properties of the composites generally depend on the dispersity of graphene inside the polymer matrix, the interaction between them and the optimal ratio of the two main components [74]. The fabrication method of graphene and polymer composites lends itself from the conventional polymer processing, which are solution mixing [75], melt blending [76] and in-situ polymerisation [77]. The major objective for composition with graphene is to enhance the properties of polymer to suit the requirement of the corresponding applications. Examples have been well documented over the past years. For instance, polyaniline, which is main host for graphene was shown to exhibit better electrochemical performances especially for supercapacitor and sensor applications. Graphene reinforced polymer matrices such as epoxy and PVC were demonstrated to be more thermally conductive [78, 79]. Effective load transfer between graphene and polymer in a composite can also enhance its mechanical property such that seen in the increase in tensile strength of graphene-polystyrene composite [80].

1.2.4.2 Graphene-Nanoparticles Composites

Graphene has also been decorated with nanoparticles of different types to introduce new functionality and make it even more useful in many applications. In general, nanoparticles (NPs) can be directly deposited on graphene sheets without the need for any linker. Graphene has been demonstrated as an ideal template for metal nanoparticles such as Au [81], Ag [82], Pt [83] and Pd [84]. One of the most common methods for the preparation of NPs-graphene composites is *in-situ* reduction of graphene in presence of metal precursors. This method provides good contact between graphene and the deposited metal NPs. The surface functional groups on graphene along with its defects can also act as nucleation sites for the growth of metal NPs. As a result, surface chemistry of graphene can affect the nucleation process of the growing NPs as well as the control over the particle size and distribution.

1.2.5 Applications Overview

The attractive properties of graphene and its composites as discussed have brought about a broad range of applications, which at present are highly promising to supersede the current available technologies. Highlighted here are the state-of-the-art developments along with their prospects and practicalities in the real commercial markets.

1.2.5.1 Electronics

The most promising application for graphene in electronic department is flexible electronics such as touch panels, rollable e-paper and foldable OLED, attributed to its flexibility and high mechanical strength, which exceeds other available materials. Graphene has already been featured in OLED test cells [85] and should become commercialised in the next few years once some device integration issues are resolved [62].

1.2.5.2 Photonics

The fact that electrons in graphene behave as massless Dirac fermions leading to its high optical transmittance in the visible range has allowed its usage for many photonic devices. One example is graphene photodetectors, which is currently a highly active field of study and can be central to imaging, sensing, communication and spectroscopy technologies. Recently, a highly responsive graphene photodetector was developed which can operate at room temperature and believed to be promising for optoelectronic applications [86].

1.2.5.3 Energy Generation and Storage

Enhanced performances of energy devices have been achieved by the use of graphene. Apart from fuel cells, batteries and supercapacitors applications, graphene based material also finds itself in the centre stage for solar cells development. Graphene is highly advantageous as a transparent conductive electrode in both quantum dots [87] and dye-sensitised solar cells [88].

1.2.5.4 Biological Applications

Another impressive property of graphene, which is not yet mentioned, is its biocompatibility. This extra benefit allows graphene to be employed for a number of interesting biological related applications. Graphene on its own or in a composite form can be used as a biological sensor *in vivo* or *in vitro* to detect a wide range of biological molecules such as glucose [89], neurotransmitters [90] or even DNA [91]. Graphene derivatives can solubilise and bind with drug molecules and have been shown recently to potentially kill tumour cells in mouse xenograft models for photothermal cancer treatment [92]. Tissue engineering based on graphene is also investigated. However before graphene can be clinically implemented, further studies on biodistribution and toxicity in manufacture conditions must be well understood.

1.3 Diamond

Diamond is another crystalline allotropic form of carbon. In diamond, each carbon atom is tetrahedrally surrounded by 4 equidistant neighbours at 154.45 pm. The tetrahedra are arranged to form a cubic unit cell with a lattice parameter, $a_0 = 356.68$ pm. Although diamond is not close-packed, it is built up with two interpenetrating fcc lattices, which are off-set along the body diagonal by a quarter of its length [93]. Diamond is well known for its unusual material properties such as the high hardness (1×10^4 kg mm⁻²), high thermal conductivity (2600 W m⁻¹ K⁻¹) and high charge carrier mobilities [94]. Naturally occurring diamond usually found with 0.05-0.25% of nitrogen atoms and is essentially insulating with a large bandgap of 5.47 eV at 300 K [95]. Doping is therefore required to make it conductive.

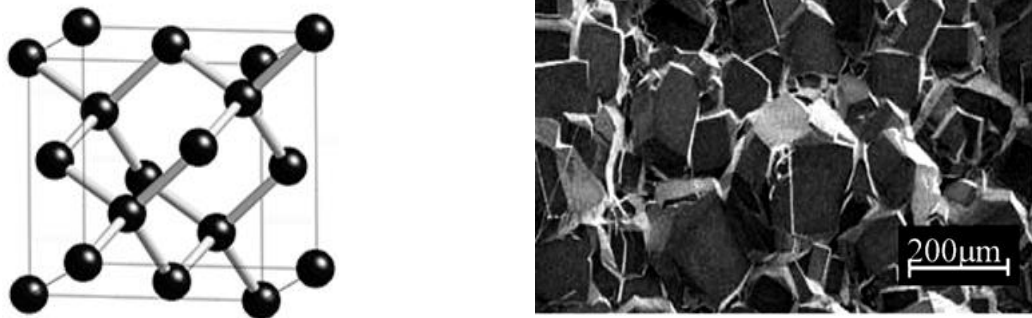


Figure 1.7 surface morphology with a surface roughness of several tens of microns [96]

Boron-doped diamond or BDD is the most common because boron has a low charge carrier activation energy of 0.37 eV [97]. A low-temperature metal to insulator transition occurs at a boron-doping level of 3.92×10^{21} cm⁻³ [98]; a p-type semiconductor of boron-doped diamond can be obtained at a lower doping level of 10^{17} - 10^{18} cm⁻³. However, BDD with higher doping level of around 10^{20} to 10^{21} cm⁻³ exhibits semi-metal behaviour due to overlapping of p-type

holes on diamond with boron-acceptor state; this allows current to flow without thermal activation.

1.3.1 Growth of Diamond

Chemical Vapour Deposition (CVD) is the most common technique to grow thin-film of diamond on a conductive substrate such as silicon. It is imperative to deposit sp^3 -bonded carbon and simultaneously suppress the formation of graphitic sp^2 -bonds therefore hydrogen is used to terminate the dangling bonds on carbon [99]. CVD is a plasma-assisted procedure using hot filaments [100-102] or microwave radiation [103] to activate a gas phase held constant at 10-50 mbar at 2200–2800 °C. In both cases, the gas phase mixture consists of a carbon source and hydrogen as the carrier gas with boron as the dopant [103]. The undoped CVD diamond has become an important industrial material for radiation windows in high power laser and microwave systems and in cutting tool applications [104-106]. Many future applications are also being investigated such as radiation detectors and dosimeters, high power electronics, quantum computing and biosensors [107-111].

1.3.2 Electrochemical Properties of BDD

Diamond films can be doped to display semi-metallic properties and the electrochemical properties make it a useful and versatile electrode material. In particular, the material displays

- a high overpotential for both oxygen and hydrogen evolution in aqueous media which leads to a wide potential window of ~3.5 V [112-116]. This opens up several important applications which cannot be accomplished with conventional electrode materials [99]
- a very low capacitance and pseudo-capacitance signal leading to enhanced signal-to-background ratios for chemical sensing [117]
- Low adsorption of contaminants leading to low fouling and high electrochemical

stability under severe conditions [115, 118-122]

- Biocompatibility [123-125], therefore, available for *in-vivo* analysis

1.3.3 Modification of BDD Surface by Metal Deposition

Metallic nanoparticles can be electrodeposited on a doped diamond substrate from their corresponding salts. This is aimed to utilise the much higher catalytic activity of ultra-fine particles (nanoparticles) compared to the conventional bulk material [126]. For some applications, the metal nanoparticles have to be immobilised on a substrate, which must be electrochemically inactive at the corresponding potentials. The unique properties of BDD make it well-suited for this purpose [94]. The high tolerance to corrosion of diamond compared to sp^2 carbon supports make it suitable as a support of metal nanoparticles. The modification of BDD with nanoparticles can broaden the application of a BDD substrate itself into other useful branches such as in fuel cell catalysis and enhanced performance in electroanalysis.

1.3.4 Nanodiamond

Apart from the diamond electrode discussed above, diamond can also exist as nanoparticles thus given a name 'nanodiamond'. This nanoscale diamond was first produced accidentally in a detonation in the 1960s but only become known in the end of 1980s [127, 128]. In the late 1990s, many groundbreaking studies had led nanodiamond to become widely interested [129]. Nanodiamond or ND can be synthesised by detonation of explosive chemicals in low oxygen condition under high temperature and pressure. Therefore nanodiamond can essentially be produced as a useful by-product of explosive waste disposals. It is suggested that in such condition nanodiamond is formed from homogeneous nucleation of the supersaturated carbon vapour by condensation and crystallisation of liquid carbon [129].

The detonation soot with sp^3 diamond core however also carries with it graphitic carbon and

incombustible impurities. Liquid phase purification involving harsh oxidation condition was employed on industrial level but this method is costly and hazardous. Recently more environmentally benign approaches have been demonstrated; the most prominent one is to oxidise the ND soot in ozone-enriched air at elevated temperature. This method also disaggregates the ND clusters into smaller particles with average size of 3-5 nm and leaves the surface carbon atoms functionalised with oxygen-containing groups at the same time [130].

ND can undergo a broad range of surface modification without losing its diamond core properties and hence has been developed to be suited for a large number of applications. This availability of the tunable surface chemistry along with its superior diamond properties, high mechanical and thermal stability, make ND ideal for composite materials. Significant improvements in terms of mechanical strength, [131] adhesion [132] and thermal conductivity [133] have been reported for polymers in composite with ND. In addition, the presence of Nitrogen-Vacancy in ND enables its fluorescent properties, which see a promising opportunity in bio-imaging applications [134]. ND is also highly biocompatible and as a consequence can be employed in biosensing [135], drug-delivery [136], tissue engineering and regenerative medicine [137].

1.4 Aims

This thesis consists of eight chapters in total. The aims and objectives of the following chapters are introduced here.

Chapter 2 - explains theories governing electrochemistry, the main subject of nanoparticle deposition and characterisation alike. Structural and chemical characterisation techniques are also described covering background and detailed instrumentation employed in the actual measurements.

Chapter 1

Chapter 3 - exploits the performance of platinum nanoparticles and graphene nanoplatelets composite as a glutamate biosensor in comparison with electrochemically deposited Pt nanoparticles on BDD and glassy carbon electrodes.

Chapter 4 - develops on from Chapter 3 where Prussian blue was electrochemically fabricated on graphene nanoplatelets covered glassy carbon electrode aiming to further minimise interfering signals observed in the preceding chapter and to enhance the overall performance of the biosensor.

Chapter 5 - focuses on energy storage application of graphene based materials. In Chapter 5 polyaniline, graphene and nanodiamond composite was fabricated as a 2-electrode cell for supercapacitor application with great attention paid on the enhancement of cycling stability, which is generally the main drawback for the otherwise excellent pseudocapacitor like polyaniline.

Chapter 6 - investigates the use of thermally reduced graphene oxide as an electrochemical double layer capacitor (EDLC) on its own and as a composite substrate for electrochemically produced nickel and cobalt hydroxides in order to maximise the specific capacitance.

Chapter 7 - compares and contrasts a certain range of carbon materials as a substrate for electrodeposited Pt nanoparticles and their performances as electrodes for direct methanol fuel cells.

Chapter 8 - utilises oppositely charged functionalised Pt-graphene nanoplatelets composites in the fabrication of uniform self-assembled thin films, which were subsequently developed as a modification method for glassy carbon and boron-doped diamond electrodes in hydrogen peroxide oxidation purposes.

References

- [1] <http://www.worldometers.info/world-population/>.
- [2] P. B. Weisz, Vol. 57, Physics Today, 2004, p. 47.
- [3] BP Statistical Review of World Energy, 2014.
- [4] R.-S. Liu, Electrochemical technologies for energy storage and conversion, Weinheim : Wiley-VCH, Weinheim, 2012.
- [5] R. Western, Radiation Protection Dosimetry 68:143 (1996).
- [6] X. Zhou, J. Qiao, L. Yang, and J. Zhang, Advanced Energy Materials 4:1301523 (2014).
- [7] M. Winter and R. J. Brodd, Chemical Reviews 104:4245 (2004).
- [8] D. V. S. o. A. E. Ragone, Review of battery systems for electrically powered vehicles, Society of Automotive Engineers, New York, 1968.
- [9] W. R. Grove, London and Edinburgh Philosophical Magazine 13:430 (1838).
- [10] Space applications of hydrogen and fuel cells., National Aeronautics and Space Administration, 2009.
- [11] A. Kirubakaran, S. Jain, and R. K. Nema, Renewable and Sustainable Energy Reviews 13:2430 (2009).
- [12] I. Breakthrough Technologies Institute, in Washington, and D.C., U.S. Department of Energy, 2013.
- [13] M. Liu, R. Zhang, and W. Chen, Chemical Reviews 114:5117 (2014).
- [14] D.S. Falcão , V. B. Oliveira, C. M. Rangel, and A. M. F. R. Pinto, Renewable and Sustainable Energy Reviews 34:58 (2014).
- [15] K. Kleiner, Nature 441:1046 (2006).
- [16] R. Dillon, S. Srinivasan, A. S. Arico, and V. Antonucci, Journal of Power Sources 127:112 (2004).
- [17] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, and J. M. Leger, Journal of Power Sources 105:283 (2002).
- [18] C. Lamy, E. M. Belgsir, and J. M. Leger, Journal of Applied Electrochemistry 31:799 (2001).
- [19] E. Antolini and E. R. Gonzalez, Journal of Power Sources 195:3431 (2010).
- [20] M. Cifrain and K. V. Kordesch, Journal of Power Sources 127:234 (2004).

- [21] E. Gulzow and M. Schulze, *Journal of Power Sources* 127:243 (2004).
- [22] G. F. McLean, T. Niet, S. Prince-Richard, and N. Djilali, *International Journal of Hydrogen Energy* 27:507 (2002).
- [23] J. S. a. J. Marcinkoski, DOE Fuel Cell Technologies Program Record 12020, 2012.
- [24] J. R. Miller and P. Simon, *Science* 321:651 (2008).
- [25] A. G. Pandolfo and A. F. Hollenkamp, *Journal of Power Sources* 157:11 (2006).
- [26] A. F. Burke and T. C. Murphy, in Materials Research Society Symposium - Proceedings, Vol. 393, 1995, p. 375.
- [27] X.-L. Wu and A.-W. Xu, *Journal of Materials Chemistry A* 2:4852 (2014).
- [28] L. L. Zhang and X. S. Zhao, *Chemical Society Reviews* 38:2520 (2009).
- [29] A. K. Shukla, S. Sampath, and K. Vijayamohanan, *Current Science* 79:1656 (2000).
- [30] S. Toth, M. Fule, M. Veres, I. Pocsik, and M. Koos, in Materials Science, Testing and Informatics III, Vol. 537-538 (J. Gyulai and P. J. Szabo, eds.), Trans Tech Publications Ltd, Stafa-Zurich, 2007, p. 263.
- [31] C. Kim, Y. O. Choi, W. J. Lee, and K. S. Yang, *Electrochimica Acta* 50:883 (2004).
- [32] J. Li, X. Y. Wang, Q. H. Huang, S. Gamboa, and P. J. Sebastian, *Journal of Power Sources* 158:784 (2006).
- [33] K. H. An, K. K. Jeon, J. K. Heo, S. C. Lim, D. J. Bae, and Y. H. Lee, *Journal of the Electrochemical Society* 149:A1058 (2002).
- [34] E. Frackowiak, K. Metenier, V. Bertagna, and F. Beguin, *Applied Physics Letters* 77:2421 (2000).
- [35] C. G. Liu, Z. N. Yu, D. Neff, A. Zhamu, and B. Z. Jang, *Nano Letters* 10:4863 (2010).
- [36] F. B. Max Lu, Elzbieta Frackowiak, (M. Lu, ed.), Wiley, 2013.
- [37] T. T. M. Endo, Y. J. Kim, K. Koshiba and K. Ishii, *Carbon Science* 1:117 (2001).
- [38] Y. Huang, J. Liang, and Y. Chen, *Small* 8:1805 (2012).
- [39] Z. S. Wu, D. W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li, and H. M. Cheng, *Advanced Functional Materials* 20:3595 (2010).
- [40] V. Subramanian, H. W. Zhu, R. Vajtai, P. M. Ajayan, and B. Q. Wei, *Journal of Physical Chemistry B* 109:20207 (2005).
- [41] C. Z. Yuan, X. G. Zhang, L. H. Su, B. Gao, and L. F. Shen, *Journal of Materials Chemistry* 19:5772 (2009).

- [42] Q. Wu, Y. X. Xu, Z. Y. Yao, A. R. Liu, and G. Q. Shi, *Acs Nano* 4:1963 (2010).
- [43] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, and S. Seal, *Progress in Materials Science* 56:1178 (2011).
- [44] Graphene:The worldwide patent landscape in 2013, Patent Informatics Team, The intellectual property office, 2013.
- [45] P. R. Wallace, *Physical Review* 71:622 (1947).
- [46] S.-H. Lee, H.-J. Chung, J. Heo, H. Yang, J. Shin, U. I. Chung, and S. Seo, *Acs Nano* 5:2964 (2011).
- [47] E. Stolyarova, K. T. Rim, S. Ryu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hybertsen, and G. W. Flynn, *Proceedings of the National Academy of Sciences* 104:9209 (2007).
- [48] A. Fasolino, J. H. Los, and M. I. Katsnelson, *Nat Mater* 6:858 (2007).
- [49] A. Ghosh, K. S. Subrahmanyam, K. S. Krishna, S. Datta, A. Govindaraj, S. K. Pati, and C. N. R. Rao, *The Journal of Physical Chemistry C* 112:15704 (2008).
- [50] A. S. Mayorov, R. V. Gorbachev, S. V. Morozov, L. Britnell, R. Jalil, L. A. Ponomarenko, P. Blake, K. S. Novoselov, K. Watanabe, T. Taniguchi, and A. K. Geim, *Nano Letters* 11:2396 (2011).
- [51] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim, *Science* 315:1379 (2007).
- [52] J. H. Chen, C. Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, *Nature Nanotechnology* 3:206 (2008).
- [53] M. Yang, Y. Hou, and N. A. Kotov, *Nano Today* 7:430 (2012).
- [54] C. Lee, X. Wei, J. W. Kysar, and J. Hone, *Science* 321:385 (2008).
- [55] C. Zhang, W. Lv, X. Xie, D. Tang, C. Liu, and Q.-H. Yang, *Carbon* 62:11 (2013).
- [56] P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim, and K. S. Novoselov, *Nano Letters* 8:1704 (2008).
- [57] H. C. Schniepp, J.-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, and I. A. Aksay, *The Journal of Physical Chemistry B* 110:8535 (2006).
- [58] W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society* 80:1339 (1958).
- [59] O. C. Compton and S. T. Nguyen, *Small* 6:711 (2010).
- [60] M. J. Allen, V. C. Tung, and R. B. Kaner, *Chemical Reviews* 110:132 (2009).

- [61] I. Forbeaux, J. M. Themlin, and J. M. Debever, *Physical Review B* 58:16396 (1998).
- [62] K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, *Nature* 490:192 (2012).
- [63] J. Hackley, D. Ali, J. DiPasquale, J. D. Demaree, and C. J. K. Richardson, *Applied Physics Letters* 95 (2009).
- [64] S. Dhar, A. R. Barman, G. X. Ni, X. Wang, X. F. Xu, Y. Zheng, S. Tripathy, Ariando, A. Rusydi, K. P. Loh, M. Rubhausen, A. H. C. Neto, B. Ozyilmaz, and T. Venkatesan, *Aip Advances* 1 (2011).
- [65] A. B. Bourlinos, D. Gournis, D. Petridis, T. s. Szabó, A. Szeri, and I. Dékány, *Langmuir* 19:6050 (2003).
- [66] J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso, and J. M. D. Tascon, *Langmuir* 24:10560 (2008).
- [67] W. Cai, R. D. Piner, F. J. Stadermann, S. Park, M. A. Shaibat, Y. Ishii, D. Yang, A. Velamakanni, S. J. An, M. Stoller, J. An, D. Chen, and R. S. Ruoff, *Science* 321:1815 (2008).
- [68] H. He, J. Klinowski, M. Forster, and A. Lerf, *Chemical Physics Letters* 287:53 (1998).
- [69] A. Lerf, H. He, M. Forster, and J. Klinowski, *Journal of Physical Chemistry B* 102:4477 (1998).
- [70] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, and R. S. Ruoff, *Nature* 448:457 (2007).
- [71] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon* 45:1558 (2007).
- [72] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, and S. Guo, *Chemical Communications* 46:1112 (2010).
- [73] J. Liu, S. Fu, B. Yuan, Y. Li, and Z. Deng, *Journal of the American Chemical Society* 132:7279 (2010).
- [74] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, and H. Zhang, *Small* 7:1876 (2011).
- [75] Y. Xu, W. Hong, H. Bai, C. Li, and G. Shi, *Carbon* 47:3538 (2009).
- [76] A. Dasari, Z.-Z. Yu, and Y.-W. Mai, *Polymer* 50:4112 (2009).
- [77] A. Yu, P. Ramesh, M. E. Itkis, E. Bekyarova, and R. C. Haddon, *The Journal of Physical Chemistry C* 111:7565 (2007).

- [78] S. Xiaobo, R. Palanisamy, E. I. Mikhail, B. Elena, and C. H. Robert, *Journal of Physics: Condensed Matter* 22:334216 (2010).
- [79] S. Vadukumpully, J. Paul, N. Mahanta, and S. Valiyaveetil, *Carbon* 49:198 (2011).
- [80] M. Fang, K. Wang, H. Lu, Y. Yang, and S. Nutt, *Journal of Materials Chemistry* 19:7098 (2009).
- [81] X. Zhou, X. Huang, X. Qi, S. Wu, C. Xue, F. Y. C. Boey, Q. Yan, P. Chen, and H. Zhang, *The Journal of Physical Chemistry C* 113:10842 (2009).
- [82] J. Shen, M. Shi, N. Li, B. Yan, H. Ma, Y. Hu, and M. Ye, *Nano Research* 3:339 (2010).
- [83] Y. Si and E. T. Samulski, *Chemistry of Materials* 20:6792 (2008).
- [84] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, and R. . Muelhaupt, *Journal of the American Chemical Society* 131:8262 (2009).
- [85] T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B. H. Hong, J.-H. Ahn, and T.-W. Lee, *Nat Photon* 6:105 (2012).
- [86] C.-H. Liu, Y.-C. Chang, T. B. Norris, and Z. Zhong, *Nat Nano* 9:273 (2014).
- [87] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, and C. M. Li, *Angewandte Chemie-International Edition* 49:3014 (2010).
- [88] N. L. Yang, J. Zhai, D. Wang, Y. S. Chen, and L. Jiang, *Acs Nano* 4:887 (2010).
- [89] X. C. Dong, H. Xu, X. W. Wang, Y. X. Huang, M. B. Chan-Park, H. Zhang, L. H. Wang, W. Huang, and P. Chen, *Acs Nano* 6:3206 (2012).
- [90] Y. R. Kim, S. Bong, Y. J. Kang, Y. Yang, R. K. Mahajan, J. S. Kim, and H. Kim, *Biosensors & Bioelectronics* 25:2366 (2010).
- [91] C. A. Merchant, K. Healy, M. Wanunu, V. Ray, N. Peterman, J. Bartel, M. D. Fischbein, K. Venta, Z. T. Luo, A. T. C. Johnson, and M. Drndic, *Nano Letters* 10:2915 (2010).
- [92] K. Yang, S. A. Zhang, G. X. Zhang, X. M. Sun, S. T. Lee, and Z. A. Liu, *Nano Letters* 10:3318 (2010).
- [93] N. N. G. a. A. Earnshaw, Chemistry of the Elements, Reed Educational and Professional Publishing Ltd, Oxford, 1998.
- [94] A. Kraft, *International Journal of Electrochemical Science* 2:355 (2007).
- [95] A. T. Collins, P. J. Dean, Lightowl.Ec, and W. F. Sherman, *Physical Review* 140:1272 (1965).
- [96] C. E. Nebel, D. C. Shin, B. Rezek, N. Tokuda, H. Uetsuka, and H. Watanabe, *Journal of the Royal Society Interface* 4:439 (2007).

- [97] P. R. W. Haenni, M. Fryda and C. Comninellis, Thin film diamond Part B, Elsevier, 2004.
- [98] T. Tshepe, J. F. Prins, and M. J. R. Hoch, *Diamond and Related Materials* 8:1508 (1999).
- [99] J. H. T. Luong, K. B. Male, and J. D. Glennon, *Analyst* 134:1965 (2009).
- [100] F. Beck, W. Kaiser, and H. Krohn, *Electrochimica Acta* 45:4691 (2000).
- [101] M. Fryda, T. Matthee, S. Mulcahy, A. Hampel, L. Schafer, and I. Troster, *Diamond and Related Materials* 12:1950 (2003).
- [102] L. Schafer, M. Hofer, and R. Kroger, *Thin Solid Films* 515:1017 (2006).
- [103] T. Yano, D. A. Tryk, K. Hashimoto, and A. Fujishima, *Journal of the Electrochemical Society* 145:1870 (1998).
- [104] A. M. Khounsary and T. M. Kuzay, *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment* 319:233 (1992).
- [105] H. P. Godfried, S. E. Coe, C. E. Hall, C. S. J. Pickles, R. S. Sussmann, X. Tang, and W. K. L. van der Voorden, *Advanced High-Power Lasers* 3889:553 (2000).
- [106] H. Sein, W. Ahmed, M. Jackson, R. Woodward, and R. Polini, *Thin Solid Films* 447:455 (2004).
- [107] J. J. L. Morton, *Nature Physics* 2:365 (2006).
- [108] S. Praver and A. D. Greentree, *Science* 320:1601 (2008).
- [109] E. Kohn, J. Kusterer, and A. Denisenko, 2005 IEEE MTT-S International Microwave Symposium, Vols 1-4:901 (2005).
- [110] P. D. Taylor, D. J. Chamund, and A. Garraway, *Industrial Diamond Review*:19 (2006).
- [111] Y. L. Zhou and J. F. Zhi, *Talanta* 79:1189 (2009).
- [112] B. Marselli, J. Garcia-Gomez, P. A. Michaud, M. A. Rodrigo, and C. Comninellis, *Journal of the Electrochemical Society* 150:D79 (2003).
- [113] H. B. Martin, A. Argoitia, U. Landau, A. B. Anderson, and J. C. Angus, *Journal of the Electrochemical Society* 143:L133 (1996).
- [114] C. E. Nebel, in Thin-Film Diamond I, Vol. 76, Academic Press Inc, San Diego, 2003, p. 261.
- [115] Y. V. Pleskov, A. Y. Sakharova, M. D. Krotova, L. L. Bouilov, and B. V. Spitsyn, *Journal of Electroanalytical Chemistry* 228:19 (1987).

- [116] V. Chakrapani, S. C. Eaton, A. B. Anderson, M. Tabib-Azar, and J. C. Angus, *Electrochemical and Solid State Letters* 8:E4 (2005).
- [117] J. W. Strojek, M. C. Granger, G. M. Swain, T. Dallas, and M. W. Holtz, *Analytical Chemistry* 68:2031 (1996).
- [118] F. Beck, H. Krohn, W. Kaiser, M. Fryda, C. P. Klages, and L. Schafer, *Electrochimica Acta* 44:525 (1998).
- [119] N. Vinokur, B. Miller, Y. Avyigal, and R. Kalish, *Journal of the Electrochemical Society* 143:L238 (1996).
- [120] M. I. Landstrass and K. V. Ravi, *Applied Physics Letters* 55:975 (1989).
- [121] F. J. Shang, J. D. Glennon, and J. H. T. Luong, *Journal of Physical Chemistry C* 112:20258 (2008).
- [122] T. A. Ivandini, R. Sato, Y. Makide, A. Fujishima, and Y. Einaga, *Diamond and Related Materials* 13:2003 (2004).
- [123] L. Tang, C. Tsai, W. W. Gerberich, L. Kruckeberg, and D. R. Kania, *Biomaterials* 16:483 (1995).
- [124] H. J. Mathieu, *Surface and Interface Analysis* 32:3 (2001).
- [125] F. Z. Cui and D. J. Li, *Surface & Coatings Technology* 131:481 (2000).
- [126] G. Sine, I. Duo, B. El Roustom, G. Foti, and C. Comninellis, *Journal of Applied Electrochemistry* 36:847 (2006).
- [127] V. V. Danilenko, *Physics of the Solid State* 46:595 (2004).
- [128] N. R. Greiner, D. S. Phillips, J. D. Johnson, and F. Volk, *Nature* 333:440 (1988).
- [129] V. N. Mochalin, O. Shenderova, D. Ho, and Y. Gogotsi, *Nat Nano* 7:11 (2012).
- [130] O. Shenderova, A. Koscheev, N. Zaripov, I. Petrov, Y. Skryabin, P. Detkov, S. Turner, and G. Van Tendeloo, *Journal of Physical Chemistry C* 115:9827 (2011).
- [131] Q. Zhang, K. Naito, Y. Tanaka, and Y. Kagawa, *Macromolecules* 41:536 (2008).
- [132] A. Stravato, R. Knight, V. Mochalin, and S. C. Picardi, *Journal of Thermal Spray Technology* 17:812 (2008).
- [133] I. Neitzel, V. Mochalin, I. Knoke, G. R. Palmese, and Y. Gogotsi, *Composites Science and Technology* 71:710 (2011).
- [134] Y. R. Chang, H. Y. Lee, K. Chen, C. C. Chang, D. S. Tsai, C. C. Fu, T. S. Lim, Y. K. Tzeng, C. Y. Fang, C. C. Han, H. C. Chang, and W. Fann, *Nature Nanotechnology* 3:284 (2008).

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- [135] T. S. Huang, Y. Tzeng, Y. K. Liu, Y. K. Chen, K. R. Walker, R. Guntupalli, and C. Liu, *Diamond and Related Materials* 13:1098 (2004).
- [136] X. Q. Zhang, R. Lam, X. Y. Xu, E. K. Chow, H. J. Kim, and D. Ho, *Advanced Materials* 23:4770 (2011).
- [137] Q. W. Zhang, V. N. Mochalin, I. Neitzel, I. Y. Knoke, J. J. Han, C. A. Klug, J. G. Zhou, P. I. Lelkes, and Y. Gogotsi, *Biomaterials* 32:87 (2011).
- [138] <http://www.seas.ucla.edu/~pilon/EES.html>

Chapter 2 Experimental Theories and Techniques

2.1 Introduction

Electrochemistry is the main technique employed for characterisation and fabrication of nanomaterials featured in this thesis. Particular interest will be on cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The morphological characterisations were conducted using scanning electron microscope (SEM) and atomic force microscopy (AFM). Chemical, structural and elemental analysis was elucidated via a number of spectroscopic techniques including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), UV-Vis and Raman spectroscopy. This chapter will also discuss other important characterisation techniques; dynamic light scattering (DLS) for measurement of particle size and zeta potential and Brunauer–Emmett–Teller analysis (BET) for surface area measurement.

2.2 Electrochemistry

Electrochemistry is the study of chemical reactions at interfaces via transferring of electrons. The most common interface investigated in the subject is between a solid electrode and an electrolytic solution thus it is a ‘heterogeneous’ process, which results in chemical changes of the species involved by oxidation and reduction processes.

2.2.1 Electrochemical Cells

Electrochemical systems are concerned with the phenomena of charge transfer between interfaces of chemical phases and factors controlling it. Herein, the transition between electronic conduction from electrodes and the connecting wires to ionic conduction from

electrolyte is considered. When an electrode is in contact with electrolyte solution, the electron transfer occurs as driven by the energy difference between the two phases [1]. This fundamental process gives rise to the potential difference predicted by Nernst equation, which will be discussed later. This potential drop between the single electrode and the electrolyte solution is however not possible to be measured experimentally, hence at least one other electrode is required. This collection of interfaces comprises to 'electrochemical cell'. If one of these two electrodes possesses a constant potential difference with the electrolyte, it can act as a reference electrode against which the potential difference of all other electrodes connected to it can be determined. The two-electrode setup is therefore containing an electrode of interest, working electrode and a reference electrode, which Ag/AgCl in 3 M KCl was used throughout the work in this thesis unless stated otherwise. The two-electrode system is also beneficial for battery or capacitor testing cell type, which would give values that are closer to the practical values. However, in the system where current passes through the reference electrode, the potential read-off on the working electrode largely relies on the stability of the reference electrode. A third electrode is therefore introduced as 'an auxiliary electrode' or 'a counter electrode'. This gives rise to a three-electrode cell with zero current passing through the reference electrode and the potential on the counter electrode, which is usually not measured, is adjusted so as to balance the electrochemical reaction taking place at the working electrode.

2.2.2 Faradaic and Nonfaradaic Processes

There are two different types of electrode processes depending on the transfer of electrons. Oxidation and reduction are caused by electron transfer, which is governed by Faraday's law. That is the relation between the total amount of charge transferred across the interface and the equivalence of the chemical reaction taken place [2].

Faraday's law can be expressed in a mathematical form as

$$m = \left(\frac{Q}{F}\right) \left(\frac{M}{n}\right) \quad (2.1)$$

where Q is the total charge passed in the circuit, n is the number of electrons involved in the reaction, F is Faraday constant which takes the value of 96485 C/mol, m and M is the mass and molar mass of product respectively.

The redox current which is the rate of flow of coulombs can then be expressed as equation 2.2 below where N is the number of moles of product or m/M from equation 2.1.

$$I = \frac{dQ}{dt} = nF \frac{dN}{dt} \quad (2.2)$$

The deviation from Faraday's law can occur as a result of transient currents produced from the second type of electrode process. This is concerned with transfer of charge from other processes other than redox reactions such as movement of electrolyte ions, reorientation of solvent dipoles, adsorption/desorption [3] hence called 'nonfaradaic' processes. This gives rise to the background current in voltammetric measurements.

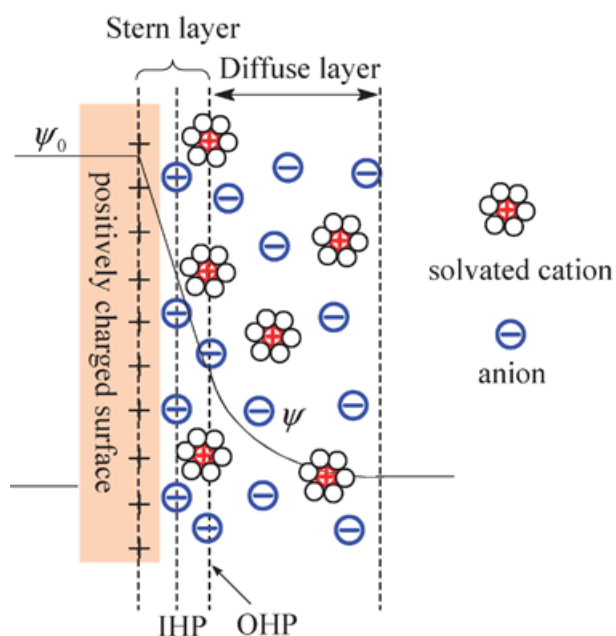


Figure 2.1 A schematic presentation of electrical double layer by Stern model [4]

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Some electrode-electrolyte systems can behave almost as ‘ideal polarised electrode’ over a certain potential range. That is no charge transferred across the interface even when there is a potential change. This behaviour of the electrode electrolyte interface is analogous to the main principle governing the charge storing mechanism of dielectric capacitor and electric double-layer capacitor (EDLC). Charges gradually accumulate at the metallic plates separated by an insulating dielectric layer. This then causes the excess and deficiency of electrons on the two plates, leading to the flow of charging current. The amount of electrical charge stored per unit voltage between the plates is capacitance and can be calculated by equation 2.3

$$C = \frac{q}{E} \quad (2.3)$$

where C is the capacitance in Farad (F), q is the charge stored in Coulombs (C) and E is the potential across it in Volts (V). The model of the interfacial region resembles that of the double layer capacitance as depicted in **Figure 2.1**. The Stern model shows multiple layers of solution phase [5]. The nearest zone to the electrode is called the inner Helmholtz layer, which contains solvent molecules and other specifically adsorbed species. Through the centres of these adsorbed species lies the inner Helmholtz plane. Next to this region is the outer Helmholtz layer where solvated ions and non-specifically adsorbed species reside. This is the closest distance that ions in solution can approach the electrode via long-range electrostatic interaction only. Further away from the outer Helmholtz plane to the bulk solution region is called diffuse layer. Each of these layers contributes to Helmholtz C_H and diffuse layer capacitance C_{diff} . These are conjugate elements of the overall capacitance of the double layer and can be described by the equation 2.4 [6, 7].

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (2.4)$$

The charging current must also be taken into account especially for very low concentration of electroactive species.

2.2.3 Equilibrium Electrochemistry

Consider a redox couple in solution (aq) with a metallic electrode (m):



At equilibrium, the rate of reduction of species O is equal to the rate of oxidation of species R. A charge transfer process could occur at the interface between electrode and solution. As this involves the transfer of electrons from/to the solution, charge separation between the two phases develops. The potential difference between metallic electrode and solution interface is given by

$$\Delta\Phi_{M-S} = \Phi_M - \Phi_S \quad (2.6)$$

According to the aforementioned, this potential drop is not however easily measured experimentally. A reference electrode is required. By convention, the standard hydrogen electrode is defined to possess zero potential. This enables standard electrode potentials of redox couples to be established. Once the equilibrium is reached, there is no net current flow and almost negligible change of concentrations of the active redox species. Hence a relationship of equilibrium potential and activity of redox species could be described by Nernst's equation

$$E_e = E^\theta + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad (2.7)$$

where E_e and E^θ denote equilibrium potential and standard electrode potential respectively, R is the ideal gas constant (8.314 J K⁻¹ mol⁻¹), T is the temperature in Kelvin, n is the number of

electrons involved in the redox reaction, F is the Faraday constant and a_O and a_R represent the activity of electroactive species which can be replaced by its concentration if an ideal model is assumed.

2.2.4 Dynamic Electrochemistry and Electrode Kinetics

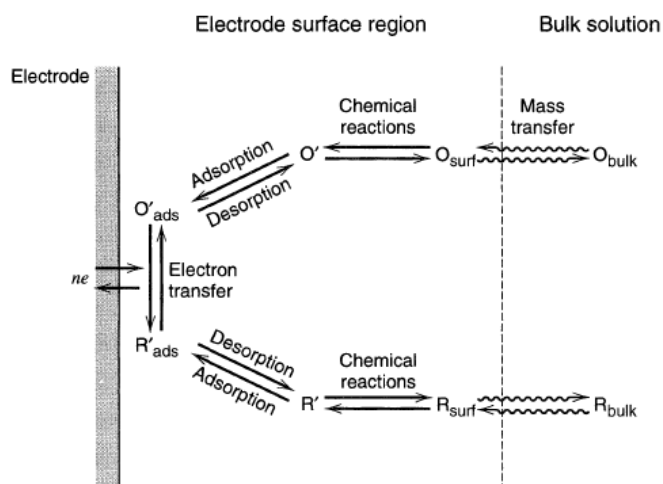


Figure 2.2 Diagram of a general pathway of an electrochemical reaction [2]

In general, there are two systems of electrochemical processes; galvanic and electrolytic processes depending on the change in Gibbs free energy. Galvanic process is associated with spontaneous reactions ($\Delta G < 0$) while electrolytic process ($\Delta G \geq 0$) requires external potential different to its open-circuit potential to be applied in order for a reaction to occur. In electrolysis, there are two main factors controlling the electrolytic current. First is the electrode kinetics concerning the rate at which electron is transferred between the electrode and solution [8]. Second is the dependence on mass transport of reactants and products to and from the electrode surface. The simple diagram explaining electrochemical processes can be depicted as in **Figure 2.2**.

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If current is applied to the system above so that reduction of O occurs, the concentration of O near the electrode surface and that in the bulk becomes different due to the faster rate of depletion compared to diffusion of O from bulk. For the reduction assuming a one-electron transfer process, the cathodic current can be expressed as

$$i_c = F A k_{red} [O]_0 \quad (2.8)$$

and in the same way as the anodic current, $i_c = F A k_{red} [R]_0$ for the oxidation process where $[]_0$ denotes concentration at the electrode surface.

The net current of the redox reaction is therefore

$$i_c = F A (k_{ox} [R]_0 - k_{red} [O]_0) \quad (2.9)$$

In transition state theory, a rate constant k is predicted to be:

$$k = A \exp\left(\frac{\Delta G^\ddagger}{RT}\right) \quad (2.10)$$

where $\Delta G^\ddagger$ is free energy of activation and A is frequency factor. The free energy of activation for a reduction process can be separated into two exponential terms according to its dependence on electrode potential as:

$$k_{red} = A \exp\left(\frac{\Delta G_{red}^\ddagger}{RT}\right) \exp\left(\frac{-\alpha F \eta}{RT}\right) \quad (2.11)$$

where $\eta = E - E_e$ or an overpotential, which is the extent to which the experimentally measured electrode potential differs from the equilibrium electrode potential i.e. when no current flows. α is a transfer coefficient having a value between 0 and 1. It is close to unity when the transition state resembles the product and close to zero when the transition state behaves more like reactants [8]. Often however α lies around 0.5 implying that the transition state is at the intermediate between reactants and products.

Oxidation process rate constant, k_{ox} can be given in a similar manner as

$$k_{ox} = A \exp\left(\frac{\Delta G_{ox}^\ddagger}{RT}\right) \exp\left(\frac{(1-\alpha)F\eta}{RT}\right) \quad (2.12)$$

The net current of the redox reaction can be expressed in the form;

$$i = i_0 \left(\frac{[R]_0}{[R]_{bulk}} \exp\left(\frac{(1-\alpha)F\eta}{RT}\right) - \frac{[O]_0}{[O]_{bulk}} \exp\left(\frac{-\alpha F\eta}{RT}\right) \right) \quad (2.13)$$

This is the Butler-Volmer equation, which is a fundamental equation for electrode kinetics. i_0 is the standard exchange current density which has two limiting cases. One is when i_0 is large, a small overpotential is required to drive a reaction, essentially a reversible process. By contrast a small value of i_0 results in the necessity of a high overpotential and hence such a process is described as irreversible. The Butler-Volmer equation although provides good qualitative prediction, this macroscopic model does not permit any other rationalisation of the molecular nature of the electrochemical reactions than a possible indication of the position of the transition state [9]. Therefore the alternative Marcus theory and Marcus-Hush-Chidsey formalism have been increasingly employed to acquire more physical insights of various electrochemical reactions particularly for surface-bound redox couples [10].

2.2.5 Mass Transport

The effect of electrode kinetics to the overall rate and electrolytic current has so far been discussed. We next consider the effect from mass transport which could become the rate-determining step as electron transfer often occurs at much faster timescale. The main forms of mass transport consist of diffusion, migration and convection. Their contribution to the overall mass transport can be written as equation 2.14 for one-dimensional mass transfer along the x-axis.

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (2.14)$$

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where $J_i(x)$ is the flux of species I at distance x from the surface, D_i is the diffusion coefficient, $\frac{\partial C_i(x)}{\partial x}$ is the concentration gradient at distance x , $\frac{\partial \phi(x)}{\partial x}$ is the potential gradient, z_i is the charge and C_i is concentration of species i, $v(x)$ is the velocity with a volume element moving along x-axis.

Migration is the movement of charged species to or from the electrode surface induced by an external electric field, which exists at the electrode/electrolyte interface as a result of the potential drop between the two phases. In other words, this is the movement of ions along a gradient of electrical potential. Hence the migratory flux (j_m) can be described by the equation

$$j_m \propto -u[A] \frac{\partial \phi}{\partial x} \quad (2.15)$$

where $\frac{\partial \phi}{\partial x}$ is the electric field strength, $[A]$ is the concentration of the ion, and u is the ionic mobility dependent on the ionic charge, size and the viscosity of the solution.

The combined effects of migration and electrolysis can cause difficulty in the interpretation of electrochemical reaction. When a charge transfer process occurs, the change in electric field local the electrode surface is altered leading to the change in the migratory flux. In order to overcome this problem, chemically and electrochemically inert background electrolyte is required. The electrolyte needs to be highly conductive but inert to the electrochemically active species of interest and is commonly in the concentration range around 0.1 M.

Convection as another means of mass transport is also known as hydrodynamic transport. It is associated with fluid flow influenced by density or temperature gradient. Stagnant solution is employed to diminish this type of transport. However, in the case that convection is

deliberately chosen as the dominating mode of transport i.e. forced convection then devices such as rotating disc electrode (RDE) or mechanical stirring of solution can be used.

We are now left with diffusion as the only mode of transport that is significantly involved in electrode dynamics measurements. Diffusion is the movement of species according to the concentration gradient created by electrochemical reaction at the electrode surface. Consider the simplest case of linear diffusion to a planar surface, the diffusional flux can be determined by *Fick's* first law as

$$j = -D_A \frac{\partial[A]}{\partial x} \quad (2.16)$$

where $[A]$ is the concentration of species A and D_A is a diffusion coefficient which is constant and characteristic to the species of interest. In a more interesting situation, diffusion is concerned with a change in concentration at a point as a function of time. This gives rise to *Fick's* second law of diffusion which can be described as the equation 2.17 below if considered for diffusion in three dimensional Cartesian directions

$$\frac{\partial[A]}{\partial t} = D_A \frac{\partial^2[A]}{\partial x^2} + D_A \frac{\partial^2[A]}{\partial y^2} + D_A \frac{\partial^2[A]}{\partial z^2} \quad (2.17)$$

This law enables the prediction of concentration changes near the electrode surface. In practical terms, when electrochemical reaction occurs at the electrode surface there is the depletion of reactants and the generation of products. This in turn means that the concentrations of the two species at the interfacial region are different from the bulk solution leading to the movement of them down the concentration gradient. A diffusion layer is consequently established and the thickness of the diffusion layer (δ_d) increases progressively to the bulk solution. Due to the natural convection of the solution this growth of diffusion

layer will reach a limit at the steady state conditions. To this limit, the diffusion layer is called ‘Nernst Diffusion Layer’ and outside this region the concentration of the active species is the same as in the bulk solution. As the transport of electroactive materials to the electrode is crucial for electrolysis to occur, there is a maximum to which electrical current can flow. This is called ‘limiting current’, i_L

$$i_L = \frac{D_A F A [A]_{bulk}}{\delta_d} \quad (2.18)$$

where D_A and $[A]_{bulk}$ is the diffusion coefficient and the bulk concentration of species A, F is the Faraday constant, A is the electrode area and δ_d is the diffusion layer thickness.

2.3 Electrochemical Methods

2.3.1 Cyclic Voltammetry

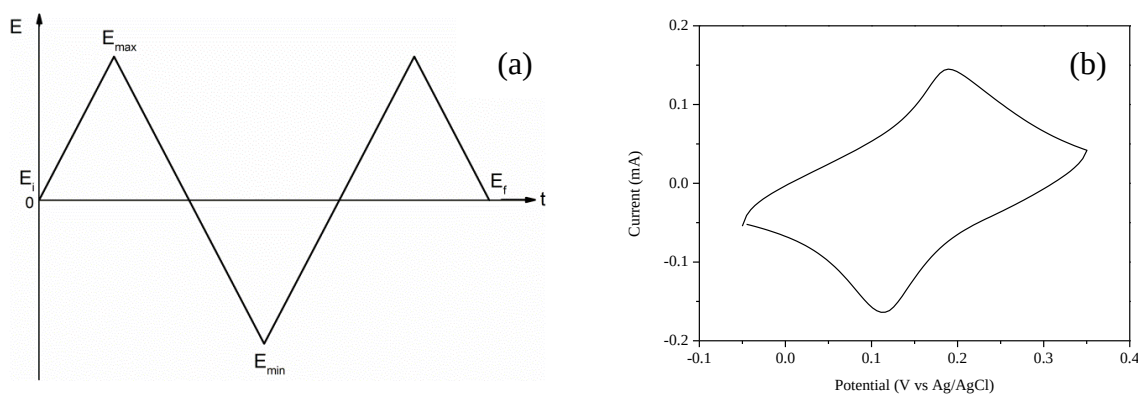


Figure 2.3 (a) Scheme of potential applied with time in cyclic voltammetry experiment, (b) example of a voltammogram, which is a typical plot recorded in a CV experiment

This potential sweep technique employs application of an electrode potential that is varied with time to a working electrode as shown in the diagram in **Figure 2.3** (a) and measurement of the current that flows through the working electrode as a function of applied potential. The

plot of current against potential recorded is thus obtained and known as a ‘voltammogram’ with an example presented in **Figure 2.3** (b).

When the potential applied reaches a limit ($E_{\max}$ in this case), the direction of sweep is reversed and the electrode potential is either scanned back to E_i or further to $E_{\min}$ as shown. Normally the potential is varied linearly with time. The current observed from the voltammogram is contributed from both electrochemical reaction and double layer capacitance referring back to the Faradaic (I_F) and non-Faradaic (I_C) currents mentioned in section 2.2.2 and shown in the equation below.

$$I = I_C + I_F = \nu C_d + I_F \quad (2.19)$$

where ν is the sweep rate and C_d is the double layer capacitance. As a consequence, the charging current I_C is proportional to its scan rate.

Factors affecting the observed voltammogram include the standard electrochemical rate constants, the formal potential of the couple, the diffusion coefficients of chemical species involved, and the voltage sweep rate between $E_{\max}$ and $E_{\min}$ [11]. This in turn implies that CV could provide a range of information on electrode kinetics and reaction mechanism. As for fast electron transfer giving rise to reversible electrochemical reaction, the peak current I_p can be given by Randles-Sevcik equation as

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} [A]_{\text{bulk}} \nu^{1/2} \quad (2.20)$$

As the number of electrons involved (n), electrode surface area (A), and diffusion coefficient (D) are all constant, the peak current is therefore varied linearly with bulk concentration and square root of scan rate. Another main characteristic in CV for reversible processes is the separation of peak potentials which is given by

$$\Delta E_{pp} = E_{pa} - E_{pc} \cong \frac{0.059}{n} \text{ (at 289K)} \quad (2.21)$$

The separation of peak potentials is hence a parameter of how reversible the reaction is. As obviously seen from the above equation, the peak separation should be a constant and independent on scan rate. As the reaction becomes less reversible the peak separation progressively increases away from the value of 0.059 V and begins to be varied as a function of scan rate.

2.3.2 Chronoamperometry

For this potential step technique, the applied potential of a working electrode is instantaneously stepped from a value E_1 where no reaction occurs to E_2 at which all species reaching the working electrode surface react as shown in **Figure 2.4** (a).

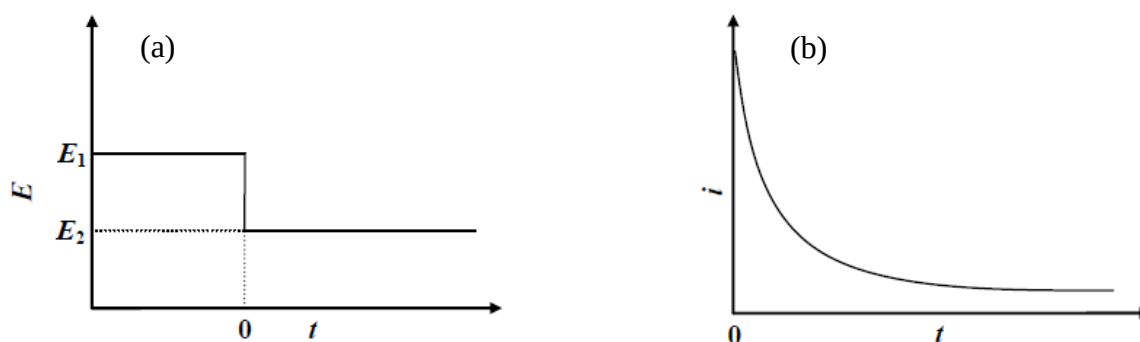


Figure 2.4 (a) Scheme of applied potential step and (b) Current response to applied potential as a function of time

The current variation with time for a planar electrode uniformly accessible to species from bulk solution can be given by the Cottrell equation.

$$I = nFAJ = \frac{nFAD^{1/2}c_{\infty}}{(\pi t)^{1/2}} \quad (2.22)$$

where I is the current flow, n is the number of electrons involved, F is Faraday constant, A is the electrode area, j is the flux of electroactive species which depends on D , its diffusion coefficient, C_∞ bulk concentration and time, t . The decay of current with time is controlled by the rate of diffusion to the electrode surface. From **Figure 2.4** (b) initially, the concentration gradient immediately after the potential step is very large due to short time for depletion and thus large current. As depletion occurs, this causes the diffusion layer thickness to increase and the current, on the other hand, to decrease.

In this thesis, chronoamperometry finds its use in both electrodeposition of metal nanoparticles and electroanalysis of hydrogen peroxide and glutamate, which will be discussed in later chapters.

2.3.3 Pulsed Electrodeposition

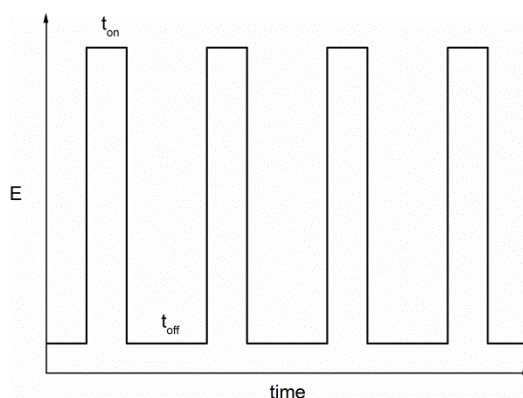


Figure 2.5 Scheme of pulsed electrodeposition

The potential step method discussed in the preceding section provides a simple method for electrodeposition at electrode surfaces. An alternative approach, pulsed electrodeposition is a more versatile method used for fabrication of nanostructured materials by electrodeposition. The deposition of nanoparticles depends on fundamental factors; nucleation rate and growth

of existing grains, and the diffusion of species to the electrode surface and these factors are better controlled in this method.

Figure 2.5 shows the scheme of potential applied as a function of time in pulsed electrodeposition experiment. Two distinct potentials are applied and the electrode alternates between them. A particular potential (as indicated by pulse time, t_{on}) applied is for the deposition process to take place whereas the other potential (as indicated by pulse time, t_{off}) is for redox active species to diffuse to vacant nucleation sites. The main advantage of the pulsed electrodeposition technique is that varying the applied potentials or the current pulse amplitude can control nucleation and growth of the redox active particles. In general, high overpotential and short deposition time favour formation of small particles [12].

2.3.4 Electrochemical Impedance Spectroscopy (EIS)

In real circuits, there are both resistive and capacitive elements hence it is not viable to just consider the resistance to acquire useful information about a circuit. Impedance measurement has nowadays replaced the measurement of resistance alone. Impedance is a measurement of the ability of a circuit to resist the flow of electrical current without limitations as in the case of resistance .

In electrochemical impedance spectroscopy (EIS), the frequency response of an electrochemical system to an external voltage perturbation at certain AC frequencies is measured. To this, we can generate an expression analogous to Ohm's law to describe impedance as

$$Z = \frac{E_t}{I_t} = Z_{Re} + jZ_{Im} \quad (2.23)$$

where it is presented as the sum of the real, Z_{Re} and imaginary components jZ_{Im} (real and

complex numbers). The ability of the circuit to resist the flow of electrical current contributes to the real part of the impedance while the imaginary part reflects the capacitive property of the circuit taking into account any phase difference between current and voltage.

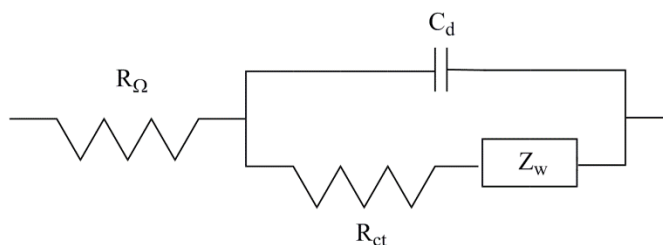


Figure 2.6 Randles circuit – equivalent circuit of an electrochemical cell

An equivalent circuit called ‘Randles circuit’ can be drawn as shown above in **Figure 2.6**. This is an equivalent circuit to an electrochemical cell consisting of a charge transfer resistance (R_{ct}) and Warburg impedance (Z_w) which are in parallel to a double layer capacitance (C_d). The Randles circuit consists of a series resistance (R_Ω), a capacitor (C_d) which models the electrical double layer capacitance that is in parallel with a charge transfer resistance (R_{ct}) and the Warburg impedance (Z_w) representing resistance to mass transfer in electrochemical systems. The R_{ct} and Z_w model the resistance to faradaic current while C_d is associated with double layer charging current.

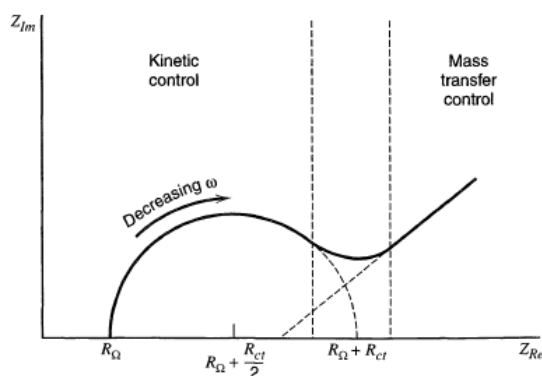


Figure 2.7 Nyquist plot for an electrochemical system [2]

The parallel element and the corresponding impedance are normally presented as ‘Nyquist plot’ which is the plot of the imaginary component (Z_{Im}) against the real component (Z_{Re}) of the circuit at a particular frequency as plotted in **Figure 2.7**. Information can be retrieved from the Nyquist plot as follows. At the high frequency region, the main contribution to the impedance is from the series resistance R_{Ω} . This can be determined from the Nyquist plot as an x-intercept. The value of R_{Ω} can also account for the equivalent series resistance in a supercapacitor system [13] which will be explained later in the thesis.

2.3.5 Instrumentation and Experimental setup

Electrochemical experiments were conducted with a μ Autolab Type II system (Eco Chemie, The Netherlands) connected to a PC running GPES (General Purpose Electrochemical System) software version 4.9. The electrochemical cell was a typical three-electrode system. A Pt wire was used as a counter electrode and a reference electrode was 3 M NaCl saturated Ag/AgCl. All the potentials reported in this work are referenced to this electrode. Solutions used were prepared by high-quality Millipore water with 18 M Ω cm resistivity. All experiments were carried out at room temperature unless stated otherwise.

2.4 Scanning Electron Microscope (SEM)

This technique is widely used to obtain information about surface topography of a sample. Due to its large depth of field, SEM images are 3D in appearance. The technique employs the use of electron beams to create images instead of light as in optical microscopes. This allows much higher magnification ($>100,000\times$) [14]. Incident electrons are produced from a heated metallic filament. The electron beam interacts with the sample at the surface or near surface region and two different types of image can be obtained according to the type of electron scattering. Secondary electrons are resulted from inelastic scattering of an incident beam. Backscattered electrons are due to elastic scattering and higher in energy than secondary electrons. The intensity of backscattered electrons increases with atomic number and thus this is useful for examining chemical compositions.

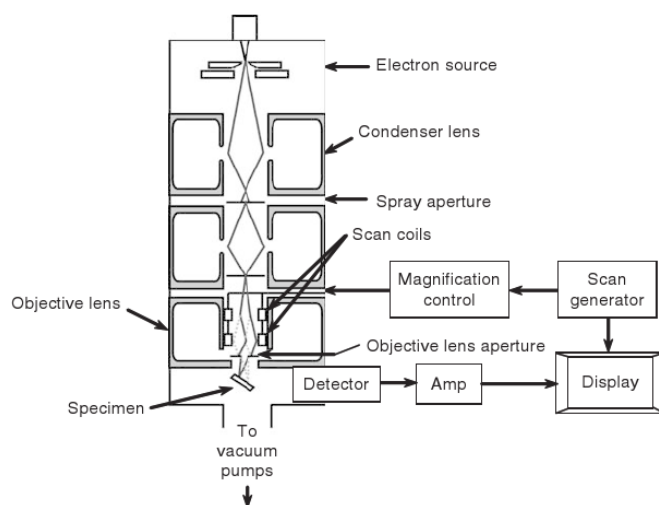


Figure 2.8 Simplified schematic diagram of the basic components of an SEM [15]

2.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a powerful tool for the study of films or adsorbed layers on electrode

surfaces [16]. In this work XPS was used to investigate chemical state and surface composition of metal nanoparticles and polyelectrolyte polymer used for surface modification of electrode materials. This method utilises emitted core and valence electrons of an atom by X-ray radiated to the sample. The radiated X-ray source can penetrate up to approximately 10 μm but only electrons from very near the surface will be emitted without energy loss. These elastic photoelectrons contribute to the distinguish peaks in XPS spectra while those experiencing inelastic scattering are responsible for the background signals. The sampling depth of the XPS technique is therefore depending on the elastic mean free path of the photoelectron. The maximum distance was discovered to be 20 $\text{\AA}$ for a conventional XPS spectrometer equipped with $\text{Al}K_\alpha$ or $\text{Mg}K_\alpha$ radiation source [17]. XPS is hence a surface sensitive technique as only electrons from the few top layers can be detected. The kinetic energy (E_K) of emitted core electrons is indicative of chemical species as they are least affected by the surroundings unlike valence electrons. The binding energy (E_B) of emitted electrons can be calculated from the following equation

$$E_B = h\nu - \phi - E_K \quad (2.24)$$

where $h\nu$ is energy of the radiated x-ray and ϕ is a work function or minimum energy required to remove an electron from its Fermi level to a vacuum level.

The binding energy, which is unique to each element, enables qualitative determination of elemental surface composition by XPS. The precise binding energy of core electrons is however slightly affected by the oxidation state of an atom as formation of chemical bonds may cause charge transfer leaving the atom partially charged. This leads to the shift of core energy levels. As a result, higher oxidation state of an atom causes binding energy to shift to higher values relative to that of the lower oxidation state. This phenomenon is the so-called

“*chemical shift*”. The post-photoemission processes such as relaxation of photoionisation, core hole screening, and polarisation of surrounding ions can also give rise to chemical shift [18]. For example, consider the binding energies of carbon 1s in different functional groups in **Table 2.1** below.

Table 2.1 Binding energy of C 1s in different functional groups [19]

Functional groups		Binding energy (eV)
Hydrocarbon	C-H, C-C	285.0
Alcohol, Ether	C-O-H, C-O-C	285.4
Cl bound to carbon	C-Cl	287
F bound to carbon	C-F	287.8
Carbonyl	C=O	287.8
Acid, Ester	O-C=O	288.9

Carbon that is bound to more electronegative atoms will have its binding energy shifted to a larger extent as expected since there is less electron density in the core level. Apart from this ‘initial state’ effect, chemical shift is also altered by ‘final state’ effect. That is electron configuration can be changed during photoemission leading to lower binding energy. Other final state effects also include multiplet splitting and shake-up satellites.

Apart from the chemical shift seen, another important phenomenon in XPS spectra is the spin-orbit coupling. When photoelectron is emitted from the other core levels than s orbital the effect of spin-orbit coupling can be observed in particular for 3p and 3d core levels. This is also a ‘final state’ effect where there becomes an unpaired electron after photoemission which if from p, d or f orbitals. Consequently this leads to the coupling between unpaired spin and its orbital angular momentum. For example if electron from 4f level of platinum is ionised, spin-orbit coupling gives rise to two distinct states as $4f_{5/2}$ and $4f_{7/2}$ with different binding energies. The intensity ratio of the two peaks is proportional to the degeneracy of

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each state as in equation 2.25 where I is the intensity, g is the degeneracy and J is the total angular momentum.

$$\frac{I}{I'} \propto \frac{g}{g'} = \frac{2J + 1}{2J' + 1} \quad (2.25)$$

If homogeneity is assumed over the sampling depth then XPS can be used to quantitatively determine elemental surface composition of the sample. The intensity of a characteristic peak can be described by the equation

$$I = j\rho\sigma K\lambda \quad (2.26)$$

where I is the intensity, j is the flux of photons, ρ is the concentration of atoms, σ is the photoionisation cross-section, K is instrumental dependent parameter and λ is the electron mean free path. The intensity is determined by the integrated area of the peak. To account for the number of atoms giving rise to any particular peak, a relative atomic sensitivity factor must be considered such that

$$\frac{[A]}{[B]} = \frac{I_A S_B}{I_B S_A} \quad (2.27)$$

where $[x]$ is surface concentration, I_x is peak intensity and S_x is surface sensitivity of species x . Assumption must be made however that the instrument used is in a similar setting as that used for obtaining the particular set of sensitivity factors.

2.5.1 Instrumentation

The XPS measurements were conducted using an X-ray photoelectron spectrometer with Al K_{α} . This is equipped with a 300 nm hemispherical electron analyser, an aluminium anode source ($h\nu = 1486.6$ eV) at 600 W, and a pulse counting detection system. The experiments

were run at room temperature and under ultrahigh vacuum conditions with pressure below 10^{-8} mbar. The spectra obtained were peak-fitted using the XPSPEAK 4.1 and CasaXPS software.

2.6 X-Ray Diffraction

X-ray diffraction is a non-destructive analytical technique used to characterise or to identify crystalline materials [20]. An X-ray diffraction pattern is produced as a result of constructive interference of scattered X-ray beams when the conditions satisfy Bragg's law. The position and the relative intensity of the scattered beams at each angle are indicative of the polycrystalline structure.

XRD patterns presented in this thesis were obtained from Philips X'Pert PRO diffractometer operating at 30 mA and 40 KV. This produces $K_{\alpha 1}$ $\lambda=1.540510$ Å and $K_{\alpha 2}$ $\lambda=1.544390$ Å respectively. A sample was scanned spanning the angular range from 10° to 85° with a step size of 0.020. The experiments ran over a long time, 350 s per step to ensure the appearance of peaks from Pd particles, as conventional XRD is not a surface sensitive technique [21].

2.7 Dynamic Light Scattering and Zeta Potential Measurement

The average size and size distribution of particles in aqueous suspension can be estimated by dynamic light scattering technique (DLS) and also known as Photon Correlation Spectroscopy (PCS). In a typical DLS measurement, a monochromatic laser beam is illuminated to a sample. Particles in the sample will scatter the laser light due to the Brownian motion, which is the random movement of particles in a liquid caused by the bombardment by the surrounding molecules [22]. The Brownian motion of a particle is dependent on its size. Small particles move quickly and larger particles move more slowly.

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The detector placed at 90 degrees to the laser source will detect the scattered light at this angle. Overtime the intensity will appear to fluctuate due to this Brownian movement of the sample. The DLS instrument will measure this fluctuation of intensity and relate it to the size of the particles in a particular sample by using Stokes-Einstein equation describing a relationship between particle size and its speed [23].

Zeta potential can be defined as the potential at the slipping plane of a particle in double layer model. When charged particles are dispersed in liquid medium, it will be surrounded by ions of opposite charge. The inner of these attached ions is called the Stern layer and the outer layer is called the diffuse layer. This model is similar to the interfacial double layer region described for the equilibrium electrochemistry in section 2.2.3. The difference is that it is applied here for a charged particle rather than electrode surface. Only ions that are inside this double layer region i.e. up to the slipping plane will travel with the charged particle. Zeta potential can be determined by considering the movement of the dispersed particles relative to the liquid medium under uniformly applied electric field or a so-called electrophoresis. When electric field is applied, charged particles will move towards the oppositely charged electrode and the viscosity of the liquid medium will oppose this movement. Once an equilibrium is reached, the velocity of this motion, which is termed electrophoretic mobility will be measured by laser Doppler velocimetry (LDV). The corresponding zeta potential can be calculated from Henry law [24] as follows

$$U_E = \frac{2\varepsilon z f(ka)}{3\eta} \quad (2.28)$$

where U_E is the electrophoretic mobility, ε is the dielectric constant, z is the zeta potential, η is the viscosity and $f(ka)$ is called Henry's function which takes an approximate value of

either 1.5 or 1.0 depending on the size of the particles and the dielectric constant of the media being measured.

The more highly charged particles in the colloidal system will give rise to higher value of zeta potential either with positive or negative signs. As expected, the higher charged the system, the stronger each particle will repel one another. Hence it is less likely for the colloidal system with higher zeta potential to flocculate. The value of ± 30 mV is used as a boundary to classify the stability of the colloidal system that is if the value is higher than ± 30 mV the system can be described as '*stable*'.

2.8 BET Theory and Analysis

Porosity can be divided systematically according to their dimension into three types as micropores (less than 2 nm), mesopores (between 2-50 nm) and macropores (greater than 50 nm).

Adsorption is defined as concentration of gas molecules near surface of solid materials and takes place due to the intrinsic surface energy. The attractive Van der Waals forces between the exposed solid surface and the gas molecules results in physisorption. The surface area of a porous material includes both the external surface and the internal pore walls. Specific surface area and mesopore distribution of porous materials can be estimated via the physisorption with inert gas such as nitrogen or argon. The uptake of adsorbed gas depends on the gas, the mass of the solid m , the vapour pressure p and the temperature T as

$$n = f(p, T, \text{gas}, \text{solid}) \quad (2.29)$$

At constant temperature, an adsorption isotherm can be simplified to

$$n = f(p)_{T,gas,solid} \quad (2.30)$$

Or pressure can be expressed as the relative vapour pressure p/p° where p° is the saturation vapour pressure of the adsorptive as

$$n = f(p/p^\circ)_{T,gas,solid} \quad (2.31)$$

Due to weak interactions between adsorbed gas molecules and solid surfaces, adsorption is reversible. The analysis of adsorption/desorption at constant temperature is called adsorption isotherm and can be classified into six standard types by the B.D.D.T. system as outlined below. Type I is associated with microporous system, while type II is related to physical adsorption on non-porous solids. Type III is characteristic of weak interactions between adsorbate and adsorbent [25] and is most commonly associated with both non-porous and microporous adsorbents. Type IV has a unique shape of a hysteresis loop and mainly characteristic for mesoporous system. Adsorption isotherm for most of activated carbon materials in supercapacitor application lies in this category. Type V is also a hysteresis loop associated with weak adsorbate-adsorbent interactions and indicative of either microporous or mesoporous system. Type VI is the stepped isotherm, relatively rare amongst all the other types. The unique shape of type VI is due to adsorption on homogeneous, non-porous surfaces where the monolayer capacity corresponds to the step height [26].

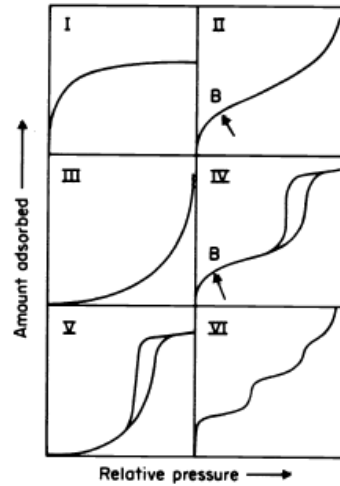


Figure 2.9 Classification of physisorption isotherm [27]

Surface area of a sample can be estimated based on information obtained from the adsorption isotherm by BET equation which takes the form of

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_o} \quad (2.32)$$

where p is the partial pressure of the adsorbed gas in equilibrium at 77 K and p_o is the saturated pressure of the gas, v is the volume of gas adsorbed at standard temperature and pressure, v_m is the monolayer volume of adsorbed gas, and c is a constant associated with the enthalpy of adsorption.

The measurement was carried out on CE Instrument Sorptomatic 1990 Series which is a completely computerized based on a static volumetric principle to characterise solid samples by the technique of gas adsorption.

2.9 Raman Spectroscopy

When monochromatic light is scattered by matter, two types of interactions occur. Elastic scattering gives rise to scattered photon having the same energy as the incident photo and is

referred to as Rayleigh scattering. On the other hand if the scattering is inelastic, this is known as Raman scattering.

Raman Effect is the molecular deformation in electric field E determined by polarisability α . Electric dipole, P is induced such that $P = \alpha E$ and molecules start to vibrate with frequency ν . The selection rule for the Raman phenomenon to occur is when there is a change in polarisability of molecule $\frac{d\alpha}{dQ} \neq 0$ where Q is the normal coordinates.

Raman can be employed for chemical characterisation of graphite and graphene particularly by considering two main bands, D and G, at 1370 and 1583 wavenumbers corresponding to the breathing mode of A_{1g} and the in-plane bond-stretching motion of pairs of $C sp^2$ atoms, E_{2g} mode respectively [28]. The shift of the G band and the ratio of I_D to I_G can be inferred to the extent to which graphene oxide is reduced. This will be explained in more details in the following chapter.

Raman spectroscopy was acquired using Horiba Jobin Yvon Laser Raman Microscope, LabRam Series, equipped with red light laser.

2.10 Atomic Force Microscopy (AFM)

AFM is employed for elucidating the surface morphology of graphene oxide, graphene nanoplatelets and its composites. AFM is a technique to obtain images or information of topography of various samples with high resolution at nanometre level. A probe is made of a sharp tip integrated with a cantilever, which is usually made of silicon or silicon nitride [29]. The vertical deflection of the tip is detected by laser. The probe is moved precisely along the sample by a scanner made of piezoelectric element. AFM was developed from scanning tunnelling microscopes for insulating samples. AFM can operate in three main modes

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according to the motion of the tip; contact, tapping and non-contact mode. Contact mode or also known as static mode utilised low stiffness of cantilever to enlarge the deflection amplitude. Attractive forces can be very strong at the near surface region hence this mode operates at overall repulsive force. For tapping mode, the movement of the cantilever in z-direction to maintain the tip-surface interaction at a set level can be taken to obtain the topographical information of the sample.

In this thesis, AFM was operated at the tapping-mode and conducted with Digital Instruments Multimode Nanoscope Scanning Probe Microscope (Veeco Metrology Group).

References

- [1] R. G. Compton, G. H. W. Sanders, and G. Sanders, Electrode potentials, Oxford : Oxford University Press, Oxford, 1996.
- [2] A. J. Bard, L. R. Faulkner, C. G. Zoski, J. Leddy, and J. Leddy, Electrochemical methods : fundamentals and applications, New York Chichester : Wiley, New York Chichester, 2001.
- [3] E. Gileadi, Physical electrochemistry : fundamentals, techniques and applications, Weinheim : Wiley-VCH, Weinheim, 2011.
- [4] L. L. Zhang and X. S. Zhao, Chemical Society Reviews 38:2520 (2009).
- [5] J. Araki, Soft Matter 9:4125 (2013).
- [6] A. G. Pandolfo and A. F. Hollenkamp, Journal of Power Sources 157:11 (2006).
- [7] S. Levine and C. W. Outhwaite, Journal of the Chemical Society-Faraday Transactions II 74:1670 (1978).
- [8] A. C. Fisher, Electrode Dynamics, Oxford University Press New York, 1996.
- [9] M. C. Henstridge, E. Laborda, N. V. Rees, and R. G. Compton, Electrochimica Acta 84:12 (2012).
- [10] D. Suwatchara, N. V. Rees, M. C. Henstridge, E. Laborda, and R. G. Compton, Journal of Electroanalytical Chemistry 665:38 (2012).
- [11] C. E. B. Richard G Compton, in Understanding Voltammetry, World Scientific Publishing Co. Pte. Ltd., 2007, p. 108.
- [12] H. Natter and R. Hempelmann, Journal of Physical Chemistry 100:19525 (1996).
- [13] L. L. Zhang, X. Zhao, M. D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, and R. S. Ruoff, Nano Letters 12:1806 (2012).
- [14] Materials Evaluation and Engineering Inc., Handbook of analytical methods for materials, 2009.
- [15] D. Stokes, Principles and Practice of Variable Pressure : Environmental Scanning Electron Microscopy (VP-ESEM), Wiley, Chichester, GBR, 2009.
- [16] P. M. A. Sherwood, Surface Science 101:619 (1980).
- [17] S. Hüfner, Photoelectron spectroscopy : principles and applications, Berlin : Springer, Berlin, 1996.
- [18] E. Pehlke and M. Scheffler, Physical Review Letters 71:2338 (1993).

- [19] B. V. Crist, Handbook of monochromatic XPS spectra, Chichester : Wiley, Chichester, 2000.
- [20] B. E. Warren, X-ray Diffraction, Addison-Wesley, London, 1990.
- [21] P. Dutta, Current Science 78:887 (2000).
- [22] R. Brown, The Philosophical Magazine, or Annals of Chemistry, Mathematics, Astronomy, Natural History and General Science 4:161 (1828).
- [23] M. I. Ltd., Zetasizer Nano User Manual, Malvern Instruments Ltd., Worcestershire, 2007.
- [24] R. J. Hunter, Zeta potential in colloid science : principles and applications, London New York : Academic Press, London New York, 1981.
- [25] A. V. Kiselev, Journal of Colloid and Interface Science 28:430 (1968).
- [26] G. Halsey, Journal of Chemical Physics 16:931 (1948).
- [27] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, Pure and Applied Chemistry 57:603 (1985).
- [28] S. Reich and C. Thomsen, Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences 362:2271 (2004).
- [29] P. Eaton and P. West, Atomic force microscopy [electronic resource], Oxford : Oxford University Press, Oxford, 2010.

Chapter 3 Amperometric Glutamate Sensing based on Platinum Graphene Nanoplatelets Composite Platform

3.1 Introduction

Glutamate is one of the principal and the most prevalent excitatory neurotransmitters secreted by the vertebrate central nervous system. It is implicated in axonal development, cognitive functions and neurological disorders such as stroke, epilepsy, Alzheimer's and Parkinson's diseases [1-5]. Over the past two decades, there have been considerable attempts into developing effective systems to monitor the dynamic level of glutamate in the living brain extracellular fluid (ECF) [6]. L-glutamate is most widely monitored *in vivo* by microdialysis methods, which are limited by poor spatial, slow time resolution [7] and depletion of ECF [8]. An alternative approach, using electrochemical sensing methods, has been developed recently, using platinum [9, 10], glassy carbon [10, 11], and carbon nanotube electrodes [12], which provide an approach to an implantable amperometric sensor for continuous long term sensing, with a high spatial and temporal resolution.

Carbon stands out as one of the major electrode materials in amperometric sensors due to its low cost, wide potential window and electrocatalytic activity for a number of redox reactions [13]. Apart from the conventional carbon electrodes consisting of graphite, glassy carbon and diamond, over the past decade however research has focused more on the dispersed form of carbon; of which the most important is carbon nanotubes because its nanoscale size makes it suitable for functionalisation with metallic nanocatalysts, enzyme immobilisation, and enhanced electrochemical activity through edge-plane like defects [14]. The main drawback associated with the development of carbon nanotube-based electrode lies however in the

difficulty in the purification process, potentially leading to undesired properties [15]. Graphene as another form of dispersed carbon materials since its recent discovery [16], has evoked high interest from both experimental and theoretical fields as a better alternative to carbon nanotube. The obvious advantages of graphene over its close relative are enhanced surface area ($2630\text{m}^2/\text{g}$, twice that of SWCNTs) [17], low cost, ease of processing [18], unique thermal and mechanical properties and high electrical conductivity. Graphene has therefore become an attractive and promising novel nanomaterial in various applications. For example, in fuel cell development, a graphene-based electrode was shown to outperform CNT-based ones in terms of electrocatalytic activity [19] and provided better macroscopic scale conductivity in biosensing application [20]. Benefitting also from its biocompatibility and flat surface accessible for effective and uniform enzyme functionalisation, graphene has been widely employed for bioanalytical applications such as in detection of glucose [21, 22], dopamine [23], NADH [24, 25], H_2O_2 [26] and glutamate based on field effect transistor from CVD grown graphene [27].

The glutamate biosensor is based on the oxidation of glutamate in the presence of glutamate oxidase.



The H_2O_2 produced in this reaction is electroactive at electrodes such as Pt so providing a route to infer the concentration of glutamate, although it is inactive at many typical carbon-based electrodes which are often used, necessitating addition of various electrocatalytic material such as Pt nanoparticles [9], hydrous iridium oxide [28], Prussian blue [29] or peroxidase enzymes including horseradish peroxidase [30], cytochrome c peroxidase [31], or catalase enzyme [32], or heme peptide such as haemoglobin [33]. Platinum is known for its electrocatalytic activity towards H_2O_2 and was reported to be superior to gold and palladium

in the type I glutamate sensor [10]. Aiming to combine the benefits of both platinum and graphene into the development of glutamate sensor, a facile method for the simultaneous reduction of Pt precursor complex and PDDA functionalised graphene oxide was introduced for the production of Pt nanoparticles assembled on graphene nanosheets.

In this thesis the extent to which electrochemical detection of glutamate can be achieved using graphene as the electrode material was thus investigated, and activated with Pt electrocatalytic species that can catalyse the oxidation of hydrogen peroxide [9, 10]. However, even in the presence of a platinum electrocatalyst, a high positive potential (>0.5 V vs Ag/AgCl) is expected for the oxidation of H_2O_2 . At this potential, some endogenous electroactive species, such as ascorbate, urate, acetaminophen, and catecholamines are also oxidized. This undermines the selectivity of the biosensor [29] and requires screening strategies to eliminate the problem. The polymer poly-phenylenediamine is used in this regard in the present work. The performance of graphene based glutamate sensors formed in this way is explored in this chapter. In particular, the sensitivity, selectivity and stability of the biosensors are characterised and compared with those based on the more established conventional glassy carbon and boron-doped diamond based electrodes which were fabricated using similar methods.

3.2 Experimental

3.2.1 Reagents and Solutions

The enzyme glutamate oxidase (GluOx, EC 1.4.3.11) from *Streptomyces* sp. was supplied from Sigma Aldrich, as was L-glutamic acid (Glu, $>99.5\%$), m-phenylenediamine (PPD, $>99\%$), glutaraldehyde (GA, 50% in water), hydrogen peroxide (50 wt% in water), L-ascorbic acid (AA), uric acid (UA, Sigma) and 4-acetamidophenol (AP, Aldrich).

Dihydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%) was obtained from Alfa Aesar. NaBH_4 (Fluka), poly(diallyldimethylammonium chloride) solution 20 wt% in water (Aldrich), sodium chloride (Fluka) were in analytical grade and used as supplied. Graphene oxide (GO) 0.5 wt% in water with a thickness of around 3 nm and 550 nm in size was purchased from Angstrom Materials.

The supporting electrolyte used was phosphate buffered saline solution (PBS) consisting of 0.137 M NaCl (Aldrich, >99%), 0.0027 M KCl (Fluka, >99.5%), 0.01 M Na_2HPO_4 (Sigma-Aldrich, >99%) and 0.002 M KH_2PO_4 (Sigma, >99%), and adjusted to pH 7.4 with sodium hydroxide (Fisher, 98.7%). All solutions were prepared with distilled Milli-Q water (>18 M Ω cm).

3.2.2 Instrumentation

Experiments were conducted at 20 ± 2 °C using a CHI900B electrochemical workstation in a standard three-electrode setup with a Ag/AgCl reference electrode against which all potentials quoted in this paper are measured with respect to, and a platinum counter electrode. The electrode was stored in PBS in a fridge (4 °C) after GluOx functionalization.

TEM images were taken using JEOL JEM-2000FX equipment with an accelerating voltage of 200 kV. Tapping-mode AFM was conducted with Digital Instruments Multimode Nanoscope Scanning Probe Microscope (Veeco Metrology Group). The XPS measurements were conducted using an in-house built spectrometer with Al K_α radiation ($h\nu=1486.6\text{eV}$). Raman spectroscopy was acquired using Horiba Jobin Yvon Laser Raman Microscope. Zeta potential was measured using a Zetasizer NanoZS (Malvern Instruments) at 25 °C and all the samples were diluted to 0.1 mg/mL.

For comparison boron-doped diamond (BDD) and glassy carbon (GC) were used as electrode materials. Polished smooth (average roughness $R_a < 30$ nm) BDD and glassy carbon discs of 3 mm diameter and 0.5 mm thickness obtained from Element Six Ltd (Ascot, UK) were used as rotating disk electrodes (RDE). Prior to use, the BDD electrode was cleaned by potential cycling between -1.6 and 2.5 V in 0.5 M sulphuric acid for 20 cycles to remove contaminants from the surface. The glassy carbon electrode was cleaned by polishing with alumina powder to a mirror finish and ultrasonication in ethanol and water respectively.

3.3 Results and Discussions

3.3.1 Preparation and Characterisation of Graphene Oxide

Graphene oxide (GO) materials were first examined by means of AFM to characterise the thickness. From **Figure 3.1** (a) it can be seen that the dimension of the graphene oxide sheets is of a few hundreds nanometers and the thickness lies in the range of 4 – 5 nm. In order to obtain higher surface area, graphene oxide was treated by ultrasonication in water. As a result, after four hours of sonication the sheets become thinner at 0.9- 1.0 nm as shown in **Figure 3.1** (b) and this thickness corresponds to a monolayer of graphene oxide with thickness in the range of 0.7 – 1.0 nm [34-36].

The wrinkle structure of the graphene oxide sheet is also noticeable in **Figure 3.1(b)**. Further ultrasonication for another two hours did not seem to affect the thickness of the GO sheet anymore but indeed decreases the lateral dimension of the sheets. Therefore intensive ultrasonication of graphene oxide suspension was carried out prior to its reduction to obtain graphene nanoplatelets.

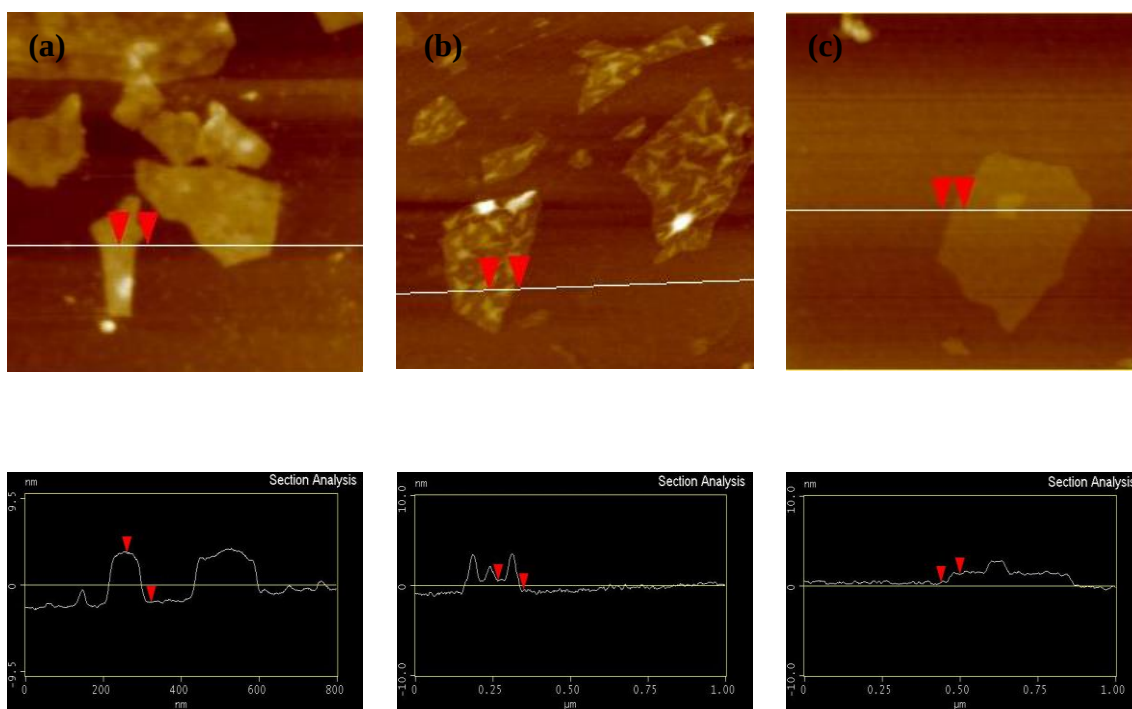


Figure 3.1 AFM images of as-received graphene oxide (a) and after 4 hours (b) and 6 hours (c) of sonication

The sonicated form of graphene oxide was further characterised by means of X-ray diffraction (XRD) and Raman spectroscopy as presented in Figure 3.2(a) and (b) respectively. The diffraction pattern shows a peak at 10.8 degrees which belongs to the (002) peak. Using Bragg's diffraction equation, the interlayer spacing was found to be 0.82 nm. This d-spacing corresponds to that commonly found for graphene oxide [37] and is due to the intercalated water molecules [38] in the structure which could be adsorbed on the graphene oxide surface because of its hydrophilic nature via oxygenated functional groups. In comparison to the as-received graphene oxide, the d spacing is similar at 0.95 nm. From FWHM and Scherrer equation, the stacking height was found to be 7 and 8 layers for GO before and after 1 hour sonication respectively. The most striking difference however lies in the disappearance of a small peak at 26.4° visible in the as-received sample, which is characteristic for graphite.

This finding indicates that 1 hour sonication followed by centrifugation could remove larger graphite residual from the graphene oxide in use.

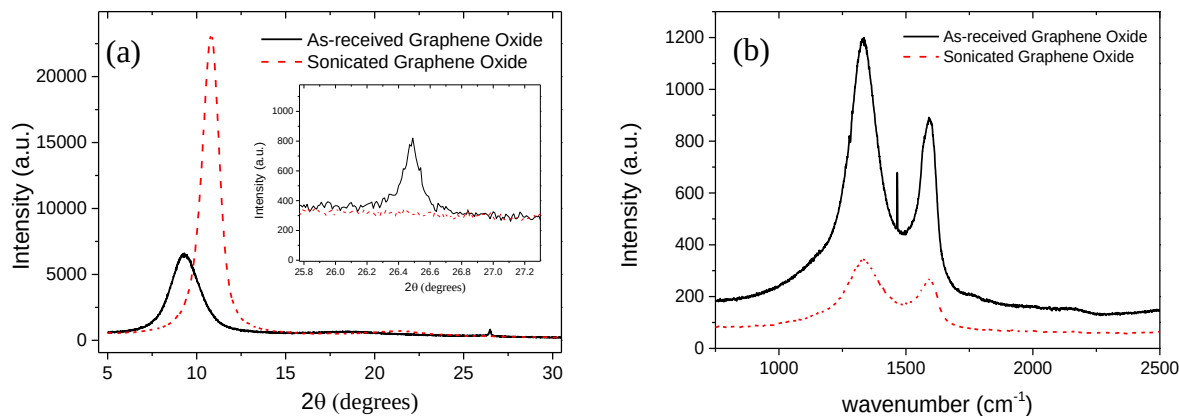


Figure 3.2 (a) XRD patterns and (b) Raman spectrum of graphene oxide before and after sonication treatment

The Raman spectrum of both samples show similar characteristics; two main peaks at around 1330 cm^{-1} and 1591 cm^{-1} are owing to D and G bands of respectively. The G-band at 1591 cm^{-1} is associated with sp^2 carbon and is due to the E_{2g} phonon at the centre of the Brillouin zone [39]. The D-band at 1330 cm^{-1} on the other hand is related to sp^3 carbon and arises from the out-of-plane breathing mode of the sp^2 carbon, which is due to the presence of defects that were introduced in the oxidation process [40].

3.3.2 Preparation and Characterisation of Platinum Nanoparticle Decorated Graphene Nanoplatelets

The first step in sensor fabrication was the preparation of electrode materials decorated with Pt nanoparticles. A wet chemical approach was chosen to prepare Pt functionalised graphene, which has the ability to form dispersed materials. To achieve this, 5 mg graphene oxide was dispersed in 10 mL of water by ultrasonication followed by adding 2.34 mg of H_2PtCl_6 and 50 mM HCl and was ultrasonicated for 15 minutes. This sample is referred to as 15%

loading, which corresponds to the percentage weight in the Pt-graphene composite if complete reaction between the added graphene and Pt occurred. 0.5 mL of 200 mM NaBH₄ (in large excess) in 200 mM NaOH was added dropwise to this mixture under vigorous stirring for 1 hour. The resulting solution was filtered using a 0.2 µm cyclopore filter membrane and washed several times with distilled water. The obtained powder was then left to dry overnight at ambient conditions.

The morphology of platinum and graphene nanoplatelets (Pt-GNPs) composites produced from the simultaneous reduction described above was elucidated by transmission electron microscopy and TEM images are shown in **Figure 3.3** (a) and (b). The wrinkled structure of graphene nanosheet was apparent in **Figure 3.3** (a). The wrinkle feature observed here, unlike the rippled structure in pristine graphene, was suggested to be resulting from the reduction process [41, 42] and is useful for preventing graphene sheets from collapsing to graphite hence the high surface area is maintained [43]. In some area of the sample dark spots are observed and likely to be platinum particles with an average size of 50 nm as depicted in **Figure 3.3** (b). The distribution of these particles is however not uniform and the particle size obtained is very large for chemically synthesised Pt-graphene composites appearing to be around 50 nm in diameter.

It was therefore suspected that the synthesis of Pt/graphene hybrid by simultaneous reduction poses a problem as both components; graphene oxide and Pt precursor [PtCl₆]²⁻ are partially negatively charged and hence electrostatic repulsion between them could prevent high Pt loading and uniform distribution to be obtained. To overcome this problem, poly(diallyldimethylammonium chloride) (PDDA), a positively charged polymer was chosen for functionalisation of graphene oxide. This changed the graphene oxide surface to possess a positive charge, thus attracting the [PtCl₆]²⁻ to its surface.

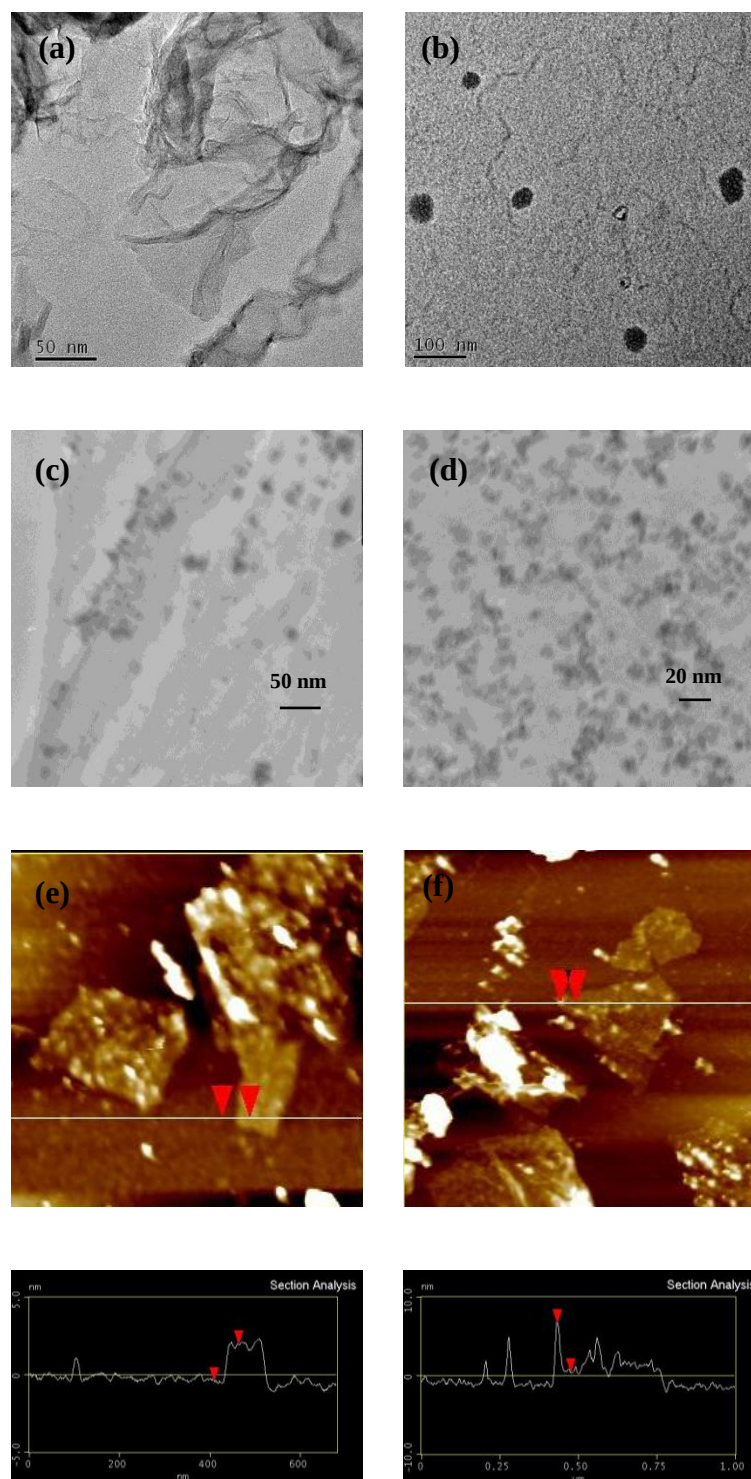


Figure 3.3 TEM images of platinum deposited on graphene nanoplatelets prepared from graphene oxide (a), (b). TEM (c), (d) and AFM images (e), (f) of platinum-graphene nanoplatelets composite synthesised from PDDA functionalised graphene oxide

To achieve this, graphene oxide was first functionalised with poly(diallyldimethyl - ammonium chloride) (PDDA) by mixing 50 mg of graphene oxide with 0.5 wt% of PDDA

and 1 wt% of NaCl in aqueous solution. The mixture was filtered and washed several times to remove excess PDDA, and dried in air for 24 hours. It was then ultrasonicated to obtain a stable suspension. Then 5 mg of this 1 mg/mL suspension was used in the simultaneous reduction step as described above instead of graphene oxide to synthesise the Pt-graphene nanoplatelets composite (Pt-GNPs). In this way, graphene oxide becomes more susceptible to reaction with the $[\text{PtCl}_6]^{2-}$ complex and the amount of Pt on the graphene can be easily tuned by simply adjusting the quantity of the added platinum precursor. For example, 50% loading or 50 wt% Pt-GNPs can be obtained by adding 10.5 mg of H_2PtCl_6 to the reaction mixture above. Pt-GNPs with 30% and 70% Pt loading were also prepared in the same way.

The morphology of the 50 wt% Pt-GNPs prepared with PDDA-GO was also investigated by TEM as shown in **Figure 3.3** (c) and (d). The average Pt particle size was estimated to be around 8 nm with a narrow range of size distribution. **Figure 3.3** (e) and (f) show the typical AFM images of Pt-GNPs on Si substrate. The Pt particle size was also about 8 nm which is consistent with that estimated from the TEM images. It is also obvious from the TEM analysis that Pt particles are much smaller and more uniformly distributed than that prepared without the PDDA functionalisation. The wrinkled structure of graphene sheets is still visible in Figure 3.3 (c). The thickness of reduced graphene oxide sheet was found to be 2.4 nm on average corresponding to a few monolayers of graphene and is comparable to the thickness of PDDA functionalised graphene nanoplatelets reported elsewhere [44].

Table 3.1 Zeta potentials of graphene oxide and different Pt-GNPs samples

<i>Sample</i>	<i>Zeta Potential (mV)</i>
Graphene Oxide	-26.7
PDDA-Graphene Oxide	63.7
15 wt% Pt- graphene (without PDDA)	-34.9

15 wt% Pt- graphene	36.0
50 wt% Pt- graphene	41.0
70 wt% Pt- graphene	42.7

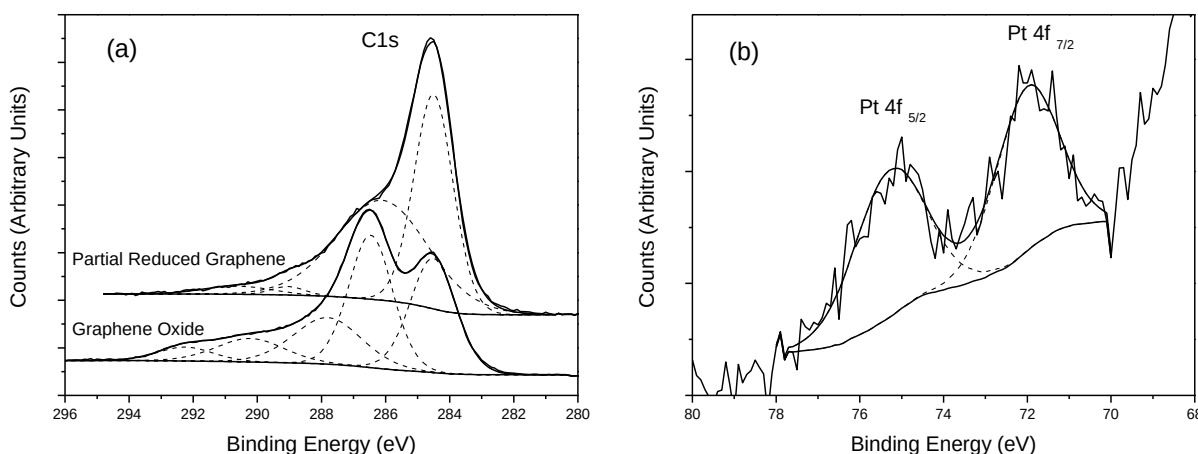
The successful adsorption of PDDA on graphene oxide was also confirmed by zeta potential measurements; graphene oxide possesses negative zeta potential of -26.7 mV and this switched to positive zeta potential of 63.7 mV after functionalisation with PDDA as tabulated in **Table 3.1**. This non-covalent adsorption is facilitated by the electrostatic interaction of the two oppositely charged substances as well as by a minor effect of π - π interaction from the contaminant PDDA as previously reported for PDDA functionalised carbon nanotubes [45]. After modification with Pt, zeta potentials are still positive for all platinum loadings. Although the values are lower than 63.7 mV for the PDDA-GO but are higher than 30 mV which is a typical value to be classified as a stable suspension. The zeta potentials also appear to be insignificantly affected by the difference in Pt loading.

To further characterise the surface chemical composition of the Pt-GNPs hybrid, XPS analysis was carried out. In the survey scan (data not shown), there are three main peaks observed at around 72 eV, 285 eV, and 531 eV in all Pt-graphene nanosheets samples, which correspond to Pt 4f, C 1s and O 1s respectively. A small peak at 402 eV due to N 1s due to PDDA can also be observed in the Pt-GNPs samples prepared from graphene oxide functionalised with the polymer.

XPS peak fitting was performed using CasaXPS or XPSPEAK software. The procedure started with baseline fitting, the background type was specifically chosen to suit the type of recorded data. In general, Shirley type background was adopted for C 1s, O 1s and N 1s peaks. On the other hand, peaks from heavier elements such as Pt 4f or Ni 2p and Co 2p were fitted with linear background.

The binding energy of aliphatic (C-C) C 1s peak was assigned to 284.5 eV. All the other spectra in the same data set were charge corrected by referencing to this peak. Peak shape was fitted based on Gaussian-Lorentzian function; the typical fitting would employ GL(30) which refers to a combination of 70% Gaussian and 30% Lorentzian. Fine tuning of other parameters such as FWHM, peak position and peak area was made such that the lowest RMS (root mean square) of the fitted and the recorded spectra was obtained.

The higher resolution spectra provide closer investigation of the chemical states on the surface of C 1s and Pt 4f as illustrated in **Figure 3.4** (a) shows two obvious humps according to contributions from C-C bonds at 284.5 eV and carbon oxygen bonds in various forms at higher binding energies. The carbon-oxygen region becomes smaller and appears as a shoulder to the main peak at 284.5 eV after the reduction. The percentage of C-C to the total C 1s region can be quantified from the fitted peak area to be 31.5% for graphene oxide and increased to 45.4% for reduced graphene oxide (without PDDA). This finding is indicative for the reduction of graphene oxide, which is essential in order to obtain the high conductivity of graphene.



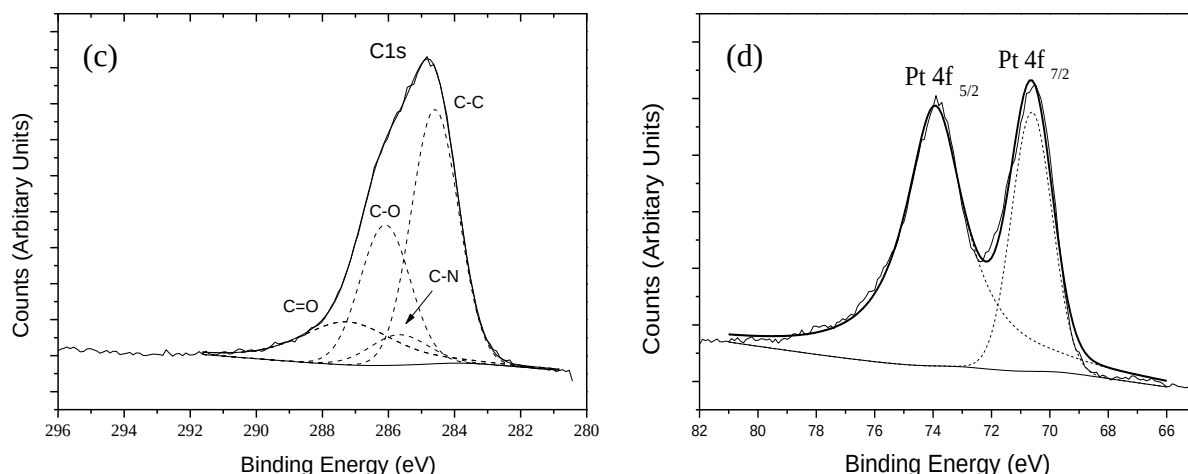


Figure 3.4 (a) C1s XPS spectra of graphene oxide and partially reduced graphene oxide, (b) Pt 4f XPS spectrum of platinum deposit on partially reduced graphene oxide, (c) C1s and (d) Pt 4f XPS spectra of Pt-graphene nanoplaletelets composite prepared with PDDA functionalised graphene oxide

The peak fitting and assignment can be done in the same manner for Pt-GNPs prepared with PDDA. The C 1s spectrum shows 4 prominent peaks as with the graphitic C-C bond at 284.5 eV also, while those at higher binding energies correspond to C-OH (286.2 eV) and C=O (287.2 eV) bonds [46]. Additionally, a small peak observed at 285.7 eV is suggested which is consistent with the presence of C-N bonds from PDDA. In this case, the C-C bonds contribution is accounted for 50.2% of the total C 1s region which is only slightly higher than that prepared without PDDA. The amount of PDDA loading on graphene oxide was estimated from the intensity ratio of nitrogen to carbon peak (subtracting contribution of carbon from PDDA itself) observed by XPS analysis taking into account the atomic surface sensitivity of 0.25 and 0.42 for carbon and nitrogen respectively. This resulted in PDDA loading of 53.3% by weight.

On the other hand, the Pt 4f spectra are also obtained for both samples as presented in **Figure 3.4** (b) and (d). Both exhibited the same characteristic features for Pt 4f peak; the peak splitting is due to the effect of spin-orbit coupling as previously discussed in Chapter 2. In the Pt-GNPs (without PDDA) sample, the two peaks occur at 72.0 eV and 75.3 eV corresponding

to Pt 4f 7/2 and Pt 4f 5/2 respectively. Similarly, for Pt-GNPs (with PDDA), these peaks also appear at 70.6 eV and 73.9 eV which are close to the sample without PDDA.

Table 3.2 Surface composition of platinum to carbon in Pt-GNPs samples with different loadings of platinum precursor in the synthesis step

<i>Pt loading (Amount of Pt precursor)</i>	<i>Percentage of surface composition Pt:C (at%)</i>
15 wt% Pt- graphene (without PDDA)	0.92%
15 wt% Pt- graphene	2.8%
50 wt% Pt- graphene	5.5%
70 wt% Pt- graphene	5.2%

The relative surface composition of platinum to carbon shown in **Table 3.2** is estimated from XPS data using atomic sensitivity factor of Pt 4f and C 1s which are 4.4 and 0.25 respectively [47] and this is presented for all the different platinum loadings. Consider the same Pt loading of 15wt% Pt loading, an approximately three-fold increase in Pt surface concentration is achieved with PDDA functionalisation. The Pt percentage also increases with Pt loading up to 50wt% and reached a maximum at 5.5%. This gives rise to 2.4 μg loading of Pt for 5 μg Pt-GNPs used for the sensor fabrication which is in good agreement with the 50% weight loading of Pt precursor to the reaction mixture in the synthesis step. The electrochemical active surface area of the Pt was estimated by the charge associated with the oxidation of adsorbed hydrogen [48] and found to be 2.6 cm^2 .

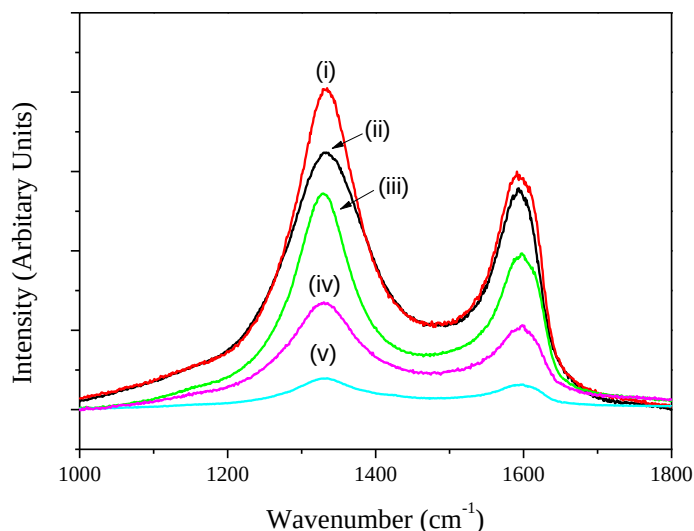
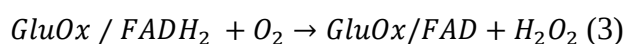
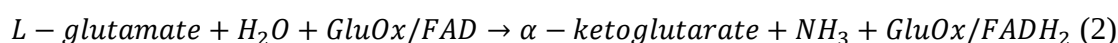


Figure 3.5 Raman spectra of Pt-GNPs prepared without PDDA (i), graphene oxide (ii), Pt-GNPs prepared with PDDA at different Pt loading of 15wt% (iii), 70wt% (iv) and 50wt% (v).

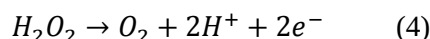
Raman spectra in **Figure 3.5** show 2 peaks at 1602cm^{-1} (G band) and 1350cm^{-1} (D band). The intensity ratios of D to G band of all Pt-graphene nanosheets hybrids are higher than that of graphene oxide. This suggests a decrease in size of the in-plane sp^2 domains and a partially ordered crystal structure of graphene nanosheets [34]. According to these results the simultaneous chemical reduction of Pt and graphene oxide to the formation of the Pt-graphene nanosheets hybrid is verified.

3.3.3 Hydrogen Peroxide Detection

As briefly explained in the introduction, the mechanism of the oxidation of L-glutamate catalysed by L-glutamate oxidase enzyme can be represented by the following a two-step process.



The first step is the deamination process catalysed by glutamate oxidase enzyme with the cofactor flavin adenine dinucleotide (FAD) acting as a redox centre. Upon the uptake of the oxygen co-substrate in the second step, hydrogen peroxide is produced as a by-product. The production of H_2O_2 can then be directly detected at the electrode by the electrocatalytic oxidation as shown below.



Measurement of H_2O_2 oxidation activity was therefore investigated on the Pt-graphene nanoplatelets electrode (Pt-GNPs), which was prepared as follows. A glassy carbon electrode was carefully polished to a mirror finish with alumina polishing powder and ultrasonicated in distilled water. The GCE was dried by compressed air before being drop-casted by $4\mu\text{L}$ of 1 mg/mL Pt-GNPs hybrid dispersed in water.

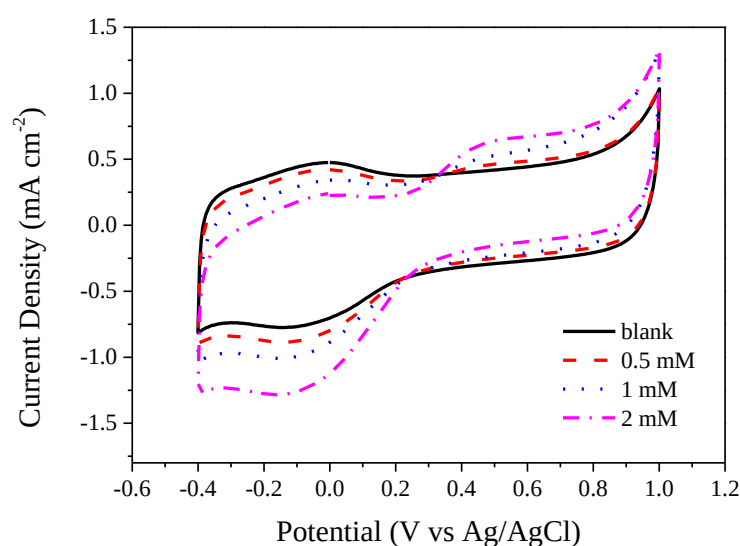


Figure 3.6 Cyclic voltammograms of Pt-GNPs in blank PBS solution (solid line) and with different concentrations of hydrogen peroxide

Cyclic voltammograms were recorded for the Pt-GNPs electrode in blank PBS solution at 50 mV/s and presented as a solid line in **Figure 3.6**. When hydrogen peroxide was added to the solution, the as-prepared electrode shows a reproducible oxidation peak at about 0.5 V in

the anodic scans of cyclic voltammograms and the peak current increases with the concentration of H_2O_2 . As a consequence, the chronoamperometric response of the electrode was thus measured at 0.5 V in PBS for varying hydrogen peroxide concentrations by addition of small amounts of 10 mM H_2O_2 solution using a RDE electrode rotated at 1500 rpm to accelerate the mixing.

The linear plots of current density against concentration of H_2O_2 was observed at least up to 100 μM and presented in **Figure 3.7** (a). The benefit of using PDDA to functionalise graphene oxide is clearly evident at 15wt% Pt loading of which H_2O_2 sensitivity is almost doubled that produced without PDDA as a result of increased Pt surface concentration suggested from XPS analysis. For the control experiment, platinum nanoparticles (PtNPs) and graphene nanoplatelets (GNPs) synthesised separately in the presence of PDDA were also tested however the H_2O_2 sensitivity of both falls below Pt-GNPs at all different loadings.

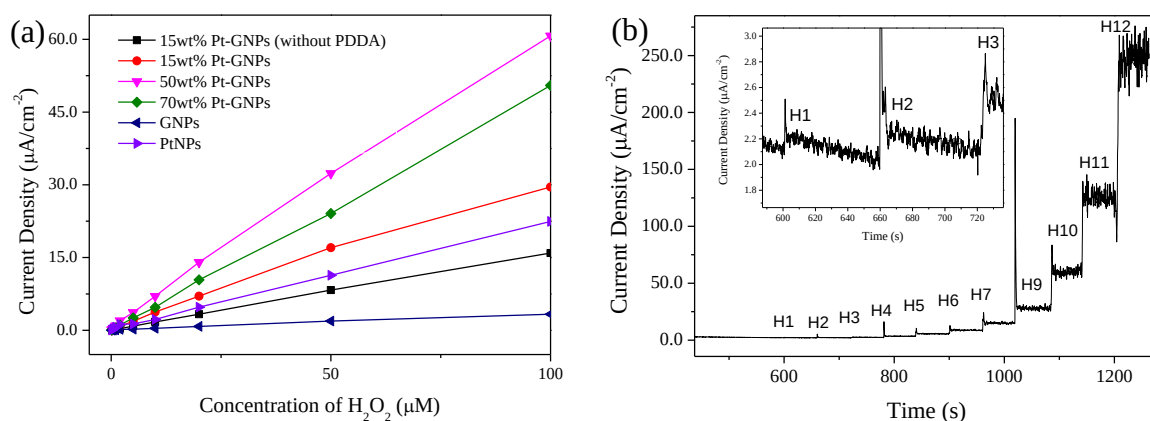


Figure 3.7 (a) Linear plot of responses to hydrogen peroxide of Pt-GNPs samples prepared with different Pt loading. (b) a typical current time transient of the 50wt% Pt-GNPs electrode after each addition of increasing concentration of H_2O_2 to stirred PBS solution (H1 to H12 represents 0.1 μM to 200 μM respectively) with the inset showing the response at low H_2O_2 concentration range

It can therefore be concluded that the synergistic effect between Pt nanoparticles and graphene nanoplatelets enhances the electrocatalytic oxidation of hydrogen peroxide as

suggested in other Pt-graphene systems [22, 49, 50]. The sensitivity more or less follows the trend of the surface composition of Pt to C in different Pt loadings investigated by XPS in **Table 3.2** such that the sensitivity is lower at 15 wt% but does not increase at higher loading of 70 wt%. As a result, the optimal Pt loading is 50 wt% of which the highest H₂O₂ sensitivity of 0.69 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ was established. This could possibly be driven by two main factors: the highest Pt surface composition and the maximised synergistic effect between graphene and Pt.

Another parameter to assess the performance of a sensor is the limit of detection (LoD). LoD is defined as the lowest concentration of an analyte that an analytical process can reliably detect [51]. This parameter can be quantified by using the signal-to-noise ratio method with the ratio of three being generally accepted for LoD [52]. The LoD can be calculated from the equation below

$$LoD = 3x \left(\frac{S}{N} \right) \quad (5)$$

where S is the slope from the linear regression of the calibration plot and N is the noise level determined manually from the chronoamperometric experiment.

The limit of detection (S/N=3) for the best performing electrode, the 50wt% Pt-GNPs, was found to be 0.16 μM with a linear range up to 200 μM ($R^2=0.998$). **Figure 3.7** (b) features the typical amperometric response of 50wt% Pt-GNPs to the addition of hydrogen peroxide at increasing concentration with the inset showing the response to low concentration of H₂O₂ at 0.1 μM , 0.2 μM and 0.5 μM . It can be seen that even at 0.1 μM concentration which is lower than the quoted limit of detection of 0.16 μM , the increase in current density is however clearly evident.

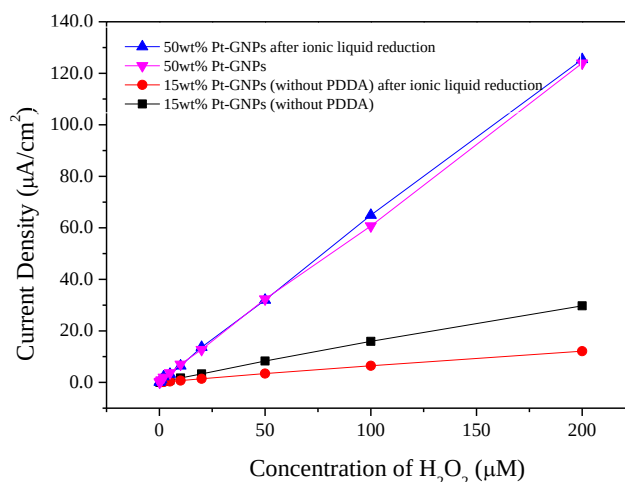


Figure 3.8 Effect of post-treatment by reduction in ionic liquid to H₂O₂ response by Pt-GNPs prepare with an without PDDA

Since the XPS study showed that some traces of oxygenated carbon species are still present further reduction by cathodic polarisation at -2.0 V against an Ag electrode for 10 minutes in an ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆), was carried out in order to enhance the conductivity and hence electrocatalytic activity of the electrode. In contrast to what is expected, the sensitivity shown in **Figure 3.8** decreases dramatically by nearly three times while remaining almost constant for Pt-GNPs produced from graphene oxide without and with PDDA functionalisation respectively. This result might suggest that further reduction in the ionic liquid caused restacking of graphene sheets thus reducing its surface area and thus lowering the H₂O₂ sensitivity. When PDDA is present however, this process could be prevented and hence the sensitivity remains unchanged.

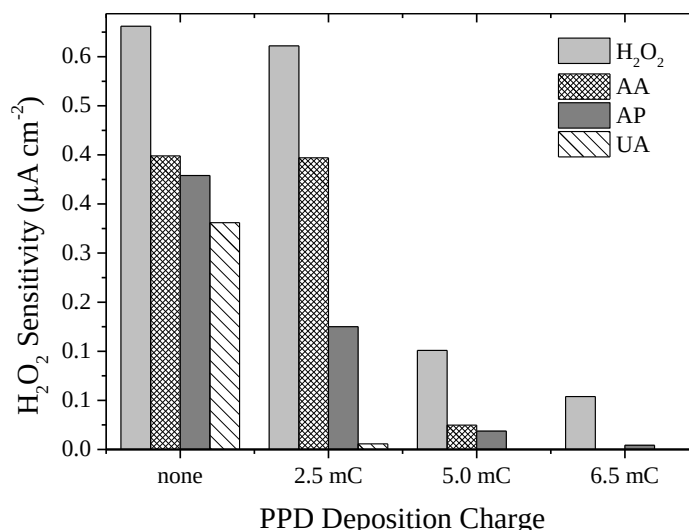


Figure 3.9 shows the response to hydrogen peroxide and other interfering species including ascorbic acid (AA), Acetamidophenol (AP) and Uric Acid (UA) of the 50 wt% Pt-GNPs prepared with differing amount of deposited polyphenylenediamine

In practical use of a biosensor, several ubiquitous electrochemically active species in physiological system may interfere with the sensor affecting the detection of hydrogen peroxide and glutamate. This nonetheless can be minimised by the use of an electropolymerised membrane to prevent the interfering species interacting with the electrode. The use of m-phenylenediamine polymer (PPD) as an outer layer membrane to minimise interfering effect by charge exclusion was demonstrated. This permselective membrane provides cation-selective permeability [53] and hence successfully eliminates the interference from uric acid, ascorbic acid and the 4-acetaminophenol at pH 7.4. Electrodeposition of the PPD layer was carried out by applying a constant potential of 0.7 V to the Pt-GNPs electrode. The optimisation of the deposited charge of PPD to minimise the response from the interfering species is presented as a bar chart in **Figure 3.9**. It is obvious that without the PPD layer, the sensor is active towards all three common interferences with the response from ascorbic acid (AA) at almost 70% of the H₂O₂ response. Once the initial amount of 2.5 mC PPD was deposited the responses acetamidophenol (AP) and uric acid (UA) are substantially reduced while that from AA is only slightly decreased. Increasing the

amount/thickness of PPD layer at 5 mC deposition charge, the response from UA is negligible and the signals from AA and AP were lowered to 25% and 20% of H₂O₂ response respectively. It must be mentioned however that the response from hydrogen peroxide at this particular charge is also dramatically suppressed. In order to completely diminish the interfering signals at this stage, a further increase in the amount of PPD was inevitable. At 6.5 mC of deposition charge, both signals from AA and UA become completely eliminated and only 8% of AP response was observed. As a result, this deposition charge was chosen as a compromise of maintaining the hydrogen peroxide response as well as minimising the interfering effect.

3.3.4 Glutamate Detection

To fabricate a glutamate biosensor, the glutamate oxidase (GluOx) enzyme immobilisation step was carried out. It is crucial that the immobilisation method is suitable for maintaining the enzyme activity. From the recent biosensor developments, glutaraldehyde, which has been shown to efficiently immobilise glutamate oxidase on surfaces through cross-linking of amino groups [54] and chitosan are the two main compounds that were extensively used as an enzyme cross-linker. The glutamate biosensors were therefore prepared using either one of these two as a linker with the detailed method as follows. Drop evaporation of glutamate oxidase using 1 mg glutamate oxidase in 5 μ L of PBS solution [10] was first done on the 50wt%Pt-GNPs electrode. It was then stabilised on the surface by exposure to glutaraldehyde (GA) vapour for 10 minutes. Or if chitosan was in use, the GluOx enzyme was mixed in chitosan suspension before drop-casting onto the Pt-GNPs electrode surface and left to dry before immersing in PBS solution. The response of the electrodes to glutamate was then tested at a potential of 0.5 V for well-stirred PBS solutions containing differing concentrations of glutamate. The concentration of glutamate is around 10 μ M in the brain

extracellular fluid [8] and around 20 μM in serum and cerebrospinal fluids [55], so concentrations in this range are of primary interest for practical applications.

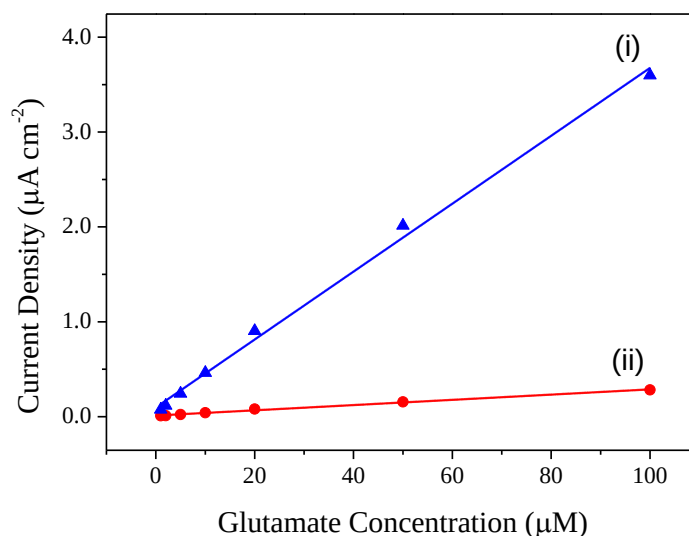


Figure 3.10 Linear responses of glutamate sensors (i) prepared with glutaraldehyde and (ii) with chitosan as an enzyme cross-linker for the immobilisation of glutamate oxidase enzyme

The linear responses of glutamate biosensors based on low loading of Pt on Pt-GNPs electrode fabricated by two different enzyme cross-linkers; glutaraldehyde and chitosan, are compared in **Figure 3.10**. The response from the sensor prepared with glutaraldehyde is well above that from the sensor prepared with chitosan. It was also observed that the cast film on the electrode surface was flaky which might be due to the instability or aggregation of the enzyme. As a result it can be concluded from this experiment that glutaraldehyde serves as a better enzyme cross-linker and provides a more efficient immobilisation of glutamate oxidase enzyme on Pt-GNPs electrode prepared in this manner.

Glutamate biosensors prepared from all different Pt loading samples of Pt-GNPs composite were also tested and compared in terms of their activity towards glutamate. The result from a comparative study is shown below as a bar chart in **Figure 3.11**.

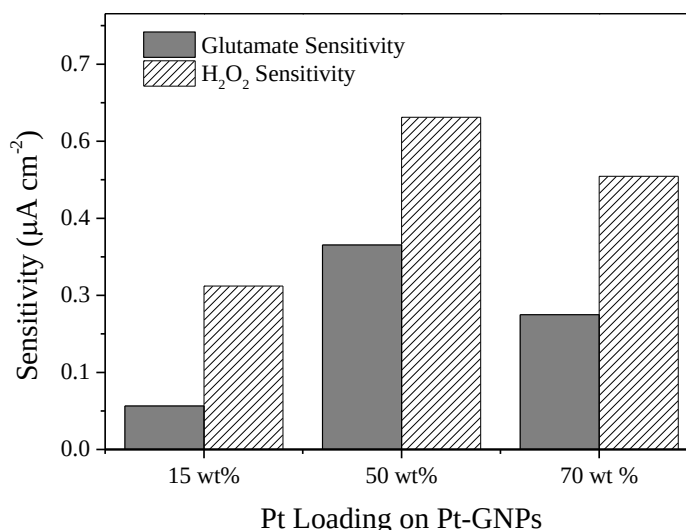


Figure 3.11 A bar chart shows the comparison of glutamate and hydrogen peroxide sensing at different Pt loadings of Pt-GNPs

The bar chart shows that the sensitivity towards glutamate is all lower than the hydrogen peroxide sensitivity for the three different platinum loadings. The same trend is observed for the detection of glutamate by different Pt-loading on Pt-GNPs, that is the sensitivity reached a maximum at 50wt%. For this sample, the glutamate sensitivity is about 60% of the hydrogen peroxide sensitivity. The lower sensitivity observed could arise from the low activity of the immobilised enzyme. In addition, this could also be due to the fact that some of the produced hydrogen peroxide could diffuse away from the electrode surface and did not get oxidised thus lowering the glutamate response compared to hydrogen peroxide.

As previously discussed above in section 3.3.3 for the hydrogen peroxide detection, it is important for a biosensor to be able to operate in physiological conditions with ubiquitous interference. Consequently, PPD layer was deposited with the charge of 6.5 mC on top of this GluOx immobilised on 50wt% Pt-GNPs and then it was kept in PBS solution at 4°C until used. The performance of the electrode in glutamate sensing was investigated also by amperometric sensing at 0.5 V with successive injections of increasing glutamate

concentration into thoroughly stirred PBS solution. The typical i-t transient was shown in **Figure 3.12 (a)**.

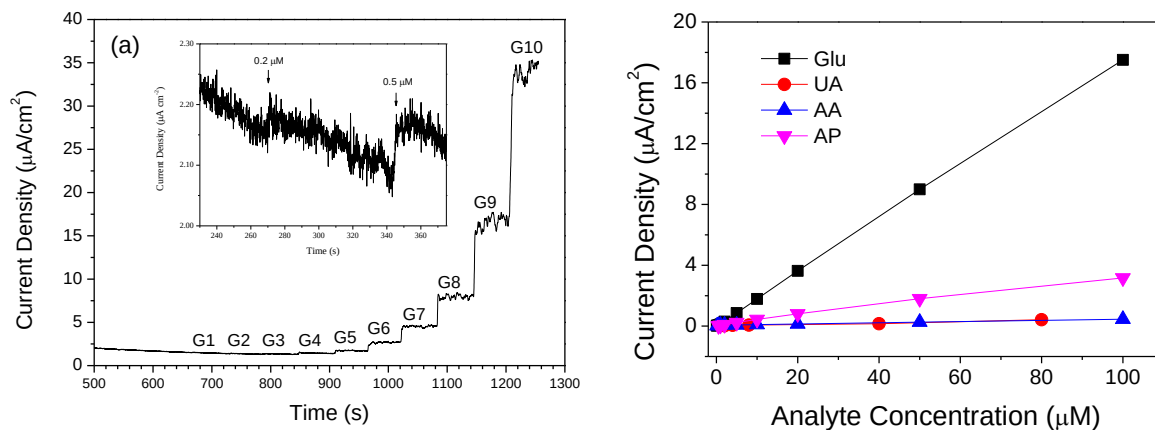


Figure 3.12 (a) Amperometric response i-t transient of the glutamate sensor after each addition of increasing concentration of glutamate to stirred PBS solution (G1 to G10 represents 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100 μM respectively) with the inset showing the response at low concentration level. (b) Linear response of the glutamate sensor to glutamate compared with other analytes found to be interfering species in physiological conditions.

The electrode exhibited a linear response range up to 100 μM with the correlation coefficient of 0.999 sufficient for monitoring of glutamate in extracellular fluid (ECF) as the basal level which usually lies below 10 μM . This leads to the high sensitivity of $174 \text{ nA}\mu\text{M}^{-1}\text{cm}^{-2}$. The reproducibility of the sensor was also tested. Among five independently prepared sensors ($n=5$), the sensitivity was found to deviate within $\pm 16.6 \text{ nA}\mu\text{M}^{-1}\text{cm}^{-2}$. This small deviation of less than 10% from the mean sensitivity value reflects the good reproducibility of the fabrication method employed. The detection limit, LOD ($S/N=3$) was found to be 0.75 μM however a linear response is established at concentration as low as 0.2 μM as shown by the inset of **Figure 3.12 (a)**. As the ultimate aim of the construction of glutamate sensor is to measure the real-time change of synaptic glutamate level *in vivo*, this in turn requires fast glutamate response of the sensor. In our system, 95% of the signal recovered after each

glutamate injection within 4 seconds. This confirms the suitability of the sensor for real-time measurement and strengthens its temporal resolution over the conventional method like dialysis which requires much longer time [56].

As for the interfering effect, the linear response of the biosensor towards glutamate is plotted in **Figure 3.12** (b) in comparison with the response to uric acid, ascorbic acid and acetamidophenol. It is clear that the response from UA and AA are excluded and become negligible compared to the response from glutamate. The signal from AP on the other hand is only approximately 15% of that from glutamate. This proves the efficiency of interference exclusion of the PPD layer and increases the potential of the sensor to be used '*in vivo*'.

3.3.5 Kinetics and Stability

With regard to Michaelis-Menten kinetics, the activity of the L-glutamate oxidase enzyme immobilised on the electrode was investigated. According to the aforementioned mechanism of glutamate oxidation by the GluOx enzyme, a two-substrate model is required. However, when the concentration of the co-substrate oxygen is constant the model can be simplified based on only one substrate. At high glutamate concentrations, the sensor current becomes non-linear as expected and shows characteristics of the Michaelis-Menten kinetics mechanism, as depicted in **Figure 3.13**. The enzyme catalysed reaction can be described by the Michaelis-Menten equation,

$$I_{ss} = V_m[S]/(K_m + [S])$$

where I_{ss} is the steady state current at a given reagent concentration $[S]$, representing the overall rate of the enzyme reaction, V_m is the value of I_{ss} at the enzyme saturation hence corresponding to the amount of active enzyme being present, and K_m is the Michaelis-Menten constant, corresponding to the reagent concentration when I_{ss} is equal to half of maximum

current (V_m) and is effectively the inverse of enzyme affinity. As a result, a higher V_m value and a lower K_m value are desired for the best sensitivity.

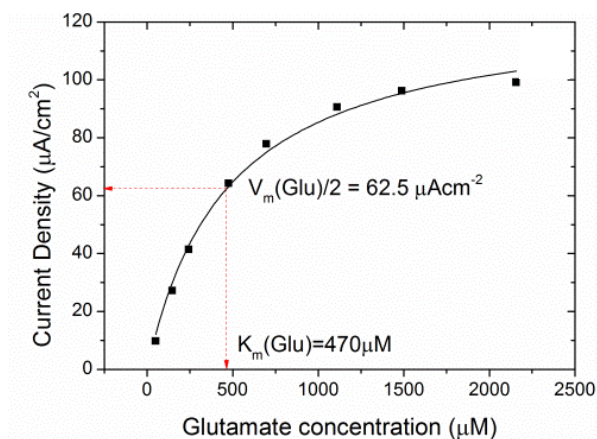


Figure 3.13 Michaelis-Menten plot of current density against concentration of glutamate at 0.5 V by 50% Pt-GNPs

The fitted Michaelis-Menten curve of the electrode plotted in **Figure 3.13** reveals that K_M equals to 470 μM . The K_m value here despite being greater than the value of 0.2 mM for the isolated glutamate oxidase enzyme, encouragingly lies to the lower end of the reported range of K_m values for surface bound glutamate oxidase (250 – 2800 μM) [8, 57]. The variation of K_m value is influenced by several aspects, such as steric and electrostatic hindrance by neighbouring GluOx enzymes [57]. The lower K_m value found in this work indicates the relatively high activity of glutamate oxidase enzyme immobilised onto the electrode by this manner. The V_m value depends especially on the loading of GluOx enzyme, and the sensor fabricated here shows a V_m value of 125 $\mu\text{A cm}^{-2}$. As observed elsewhere, the PPD layer has little influence on K_m but reduces V_m [57]. The relatively high V_m indicates faster kinetics.

3.4 Comparison with Glutamate Biosensor Based on Boron-Doped

Diamond and Glassy Carbon

Table 3.3 Comparison of glutamate sensing performance by sensors developed on different substrates, which emphasizes the largely enhanced sensitivity and linearity range by Pt-graphene hybrid electrode

	<i>GC/Pt-GNPs/GluOx/PPD</i>	<i>GC/Pt/PPD/GluOx</i>	<i>BDD/Pt/PPD/GluOx</i>
Pt loading/μg	2.4	5.1	5.1
LoD/μM	0.75 $\pm$ 0.04	2.4 $\pm$ 0.02	0.35 $\pm$ 0.01
Linearity/μM	0.2-100	0.5-50	0.5-50
Sensitivity/$\text{nA}\mu\text{M}^{-1}\text{cm}^{-2}$	174 $\pm$ 16	91 $\pm$ 8	24 $\pm$ 2
Time response/s	4 $\pm$ 1	5 $\pm$ 1	4 $\pm$ 1
$V_m/\mu\text{Mcm}^{-2}$	125	-	2.8
$K_m/\mu\text{M}$	470	-	400

A comparative study was carried out on other glutamate sensors developed in the same manner as described above based on electrodeposited Pt nanoparticles on glassy carbon or diamond electrode. Since similar sensor fabrication approaches were used to produce devices on three different substrates, the suitability of the characteristics of these substrates with regard to the fabrication procedures used can be judged. Relevant parameters and overall sensor performance, for the devices fabricated, are summarised in **Table 3.3**.

The mass of Pt was calculated for the diamond and glassy carbon electrodes from the electrolysis charge, whereas for the graphene electrodes from mass added during drop coating using the Pt content as deduced from XPS. The GC/Pt-GNPs/GluOx/PPD electrode structure exhibited superior overall performance particularly in terms of enhanced sensitivity and wide linear range, with the diamond platform showing poor sensitivity, largely because more activity seemed to be lost here when PPD was deposited in comparison to the other electrode materials. However the BDD/Pt/PPD/GluOx sensor on the other hand shows a more desirable

detection limit due to very low background and electrical noise. The GC/Pt/PPD/GluOx although exhibited medium sensitivity, the limit of detection is relatively high which could be due to the high noise level of the background of the glassy carbon electrode. All the sensors exhibited fast time response making them suitable for real-time measurement. Similar K_m values are observed but a much lower V_m for the case of Pt-BDD electrode due also to the loss of activity after PPD deposition.

The stability of the fabricated graphene glutamate sensors was examined, and compared with that of diamond and glassy carbon based sensors, as shown in **Figure 3.14**. All three sensors show an increasing sensitivity in the initial days after fabrication, which may be attributed to opening of membrane channels in the PPD layer [58], the swelling of PPD membrane [59, 60] and conformational relaxation of the glutamate oxidase enzyme [61] when the electrode was stored in buffer solutions. After the relaxation period, the glassy carbon based sensor shows faster decay to less than 50% of its best performance in a week, as seen for similar devices such as SWCNT and Os-gel-HRP modified glassy carbon sensor for glutamate or NADH [54, 62].

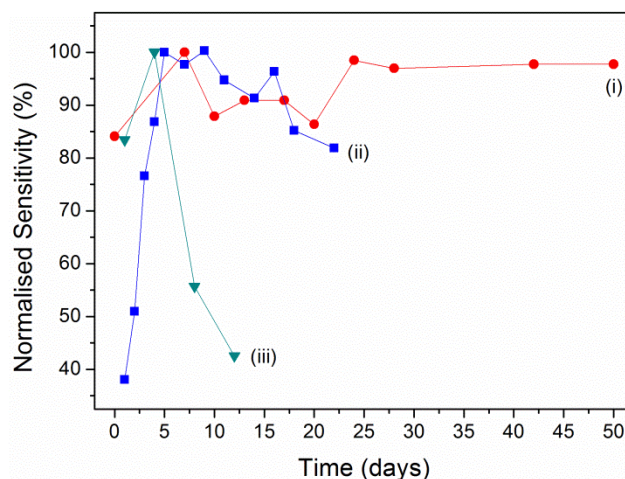


Figure 3.14 Normalised sensitivity of glutamate sensors based on (i) Pt-GNPs (ii) Pt-BDD and (iii) Pt-glassy carbon as a function of storage time from fabrication

Frequent measurements and high cumulative concentration of glutamate also have shown adverse effect on the stability of glutamate biosensors, probably due to denaturation of enzyme by local decrease of pH value as a result of hydrogen peroxide oxidation [59]. Despite the high glutamate concentrations used in the stability test, the diamond based glutamate sensors still demonstrated rather stable performance with less than 20% decay in the next three weeks. The graphene based sensor on the other hand maintained around 90% of its highest sensitivity over a long period of 7 weeks. The good long term stability of diamond and graphene based glutamate sensor is attributed to good biocompatibility and the excellent electrochemical stability of the two substrates [63].

3.5 Comparison with Established Results and Concluding Remarks

Electrochemical glutamate biosensors for bioelectronic applications have been demonstrated using platinum and graphene nanoplatelets composite platforms. In terms of limit of detection, stability and sensitivity, the devices exhibit comparable or in many cases significantly improved levels of performance compared to similar electrochemical devices produced on other platforms in the past [12, 64-67] as further clarified in **Table 3.4**.

Table 3.4 A comparison of the performance of some sensor platform for glutamate detection

No.	Sensor	Linear Range(μM)	LoD (μM)	Sensitivity ($\text{nA}/\mu\text{Mcm}^{-2}$)	Response time (s)	Ref.
Microelectrode						
1	Pt/PPy/MWCNT/GluOx	140	0.3	384	7	[68]
2	Pt/PPy/MWCNT/GluOx/PU	500	0.3	250	15	[68]
3	Pt/PEI/GluOx/PPD			62 ± 8		[26]
4	OPP GLuOx Pt MEAs			97 ± 9	1	[69]
5	GluOx+Chitosan film on Pt	0.5-200	0.1	85 ± 8	3	[66]
6	PPD/Ru-Rh		5	620	45-50	[70]
8	MEAs on Pt, chitosan, PPY and Nafion	2.5 - 217	2.5 ± 1.2	38.1 ± 5.4	1	[65]
Nanoparticles						
9	GluOx Nanoporous Pt/Pt-Ir			155		[9]
10	OPP GluOx Pt black on Pt wire	up to 250	2	80 ± 10		[64]
11	GC/MWCNT/Pt NPs/GluOx	up to 100	0.250	423 ± 11.3		[12]
12	(GLDH/Pt-PAMAM)n/CNTs	0.2–250	0.010	433	3	[71]
Others						
13	HRP/CSCNTs/GC electrode with FIA, enzyme PTFE reactor	0.003 to 10	0.0012	120		[72]
14	Pt/STA/PPD/BSA/GLOx		0.15	0.129 ± 0.34		[8]
15	GC/CHIT-FCNT/GDH		25	1.29 ± 0.18	4	[67]
16	Enzymeless Pt-Ni nanowire array	500-8000	135	96		[73]

In comparison to glutamate sensor based on glutamate oxidase enzyme immobilised on Pt microelectrode, the sensitivity is, in terms of current density, higher than most sensors (No. 3-5, 8) but still lower than No. 1, 2 and 6 noting however that the sensor in No. 6 exhibited very slow time response of 45-50 s which might not be sufficiently rapid for a real-time *in vivo* measurement. With regard to nanoparticles based sensors, the sensitivity of GC/Pt-GNPs/GLOx/PPD is also superior to nanoporous Pt and Pt black modified Pt microelectrodes reported in No. 9 and 10 respectively suggesting the role of graphene nanosheets in enhancing the detection performance. When compared to either functionalised CNTs (No. 13, 15) or Platinum (No.14) as an electrocatalytic material alone, the Pt-GNPs sensor in this work also shows much higher sensitivity suggesting the synergistic effect of the concurrent platinum and graphene for the materials of the sensor. However, it should also be noted here

that the sensitivity is still lower than sensors developed on Pt-CNTs system. This could be arising from the difference in fabrication of the composite materials and the method of immobilisation of glutamate oxidase enzyme as well.

The limit of detections are found to be 0.75 μM for Pt-GNPs and 0.35 μM for Pt-BDD based sensors and seem to be competent and comparable to many other established sensors as indicated in the table and are inferior to some of the-state-of-the-art sensors that claim to exhibit limit of detection as low as 10 and 1.2 nM (No. 12, 13 respectively). The linear range of detection and the response time of sensors developed in this work are shown to be comparable to the established results.

The long-term stability of the sensor is also of interest where most of the sensors established also reported stability of up to a few weeks of storage only. By marked contrast, the sensor based on Pt-GNPs is stable up to 50 days (90% of initial response was maintained) of storage and successive testing. To emphasise its enhanced stability, a comparison can be made to the enzymeless sensor based on Ni nanowire array where 90% of the sensitivity was retained after 60 days of storage. Overall, the present work illustrates how platinum and graphene materials can be used successfully for glutamate sensing.

References

- [1] B. S. Meldrum, *Neurology* 44:14 (1994).
- [2] J. T. Coyle and P. Puttfarcken, *Science* 262:689 (1993).
- [3] B. T. Hyman, G. W. Vanhoesen, and A. R. Damasio, *Annals of Neurology* 22:37 (1987).
- [4] F. Blandini, R. H. P. Porter, and J. T. Greenamyre, *Molecular Neurobiology* 12:73 (1996).
- [5] F. Fonnum, *Journal of Neurochemistry* 42:1 (1984).
- [6] S. Qin, M. van der Zeyden, W. H. Oldenzien, T. Cremers, and B. H. C. Westerink, *Sensors* 8:6860 (2008).
- [7] J. J. Burmeister, F. Pomerleau, M. Palmer, B. K. Day, P. Huettl, and G. A. Gerhardt, *Journal of Neuroscience Methods* 119:163 (2002).
- [8] M. R. Ryan, J. P. Lowry, and R. D. O'Neill, *Analyst* 122:1419 (1997).
- [9] J. H. Han, H. Boo, S. Park, and T. D. Chung, *Electrochimica Acta* 52:1788 (2006).
- [10] R. D. O'Neill, S. C. Chang, J. P. Lowry, and C. J. McNeil, *Biosensors & Bioelectronics* 19:1521 (2004).
- [11] R. Maalouf, H. Chebib, Y. Saikali, O. Vittori, M. Sigaud, and N. Jaffrezic-Renault, *Biosensors & Bioelectronics* 22:2682 (2007).
- [12] K. B. Male, S. Hrapovic, and J. H. T. Luong, *Analyst* 132:1254 (2007).
- [13] R. L. McCreery, *Chemical Reviews* 108:2646 (2008).
- [14] C. E. Banks, T. J. Davies, G. G. Wildgoose, and R. G. Compton, *Chemical Communications*:829 (2005).
- [15] I. Dumitrescu, P. R. Unwin, and J. V. Macpherson, *Chemical Communications*:6886 (2009).
- [16] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* 306:666 (2004).
- [17] A. K. Geim and K. S. Novoselov, *Nature Materials* 6:183 (2007).
- [18] M. Segal, *Nature Nanotechnology* 4:611 (2009).
- [19] R. I. Jafri, T. Arockiadoss, N. Rajalakshmi, and S. Ramaprabhu, *Journal of the Electrochemical Society* 157:B874 (2010).

- [20] S. Alwarappan, A. Erdem, C. Liu, and C. Z. Li, *Journal of Physical Chemistry C* 113:8853 (2009).
- [21] C. S. Shan, H. F. Yang, J. F. Song, D. X. Han, A. Ivaska, and L. Niu, *Analytical Chemistry* 81:2378 (2009).
- [22] X. H. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu, and Y. H. Lin, *Biosensors & Bioelectronics* 25:901 (2009).
- [23] N. G. Shang, P. Papakonstantinou, M. McMullan, M. Chu, A. Stamboulis, A. Potenza, S. S. Dhesi, and H. Marchetto, *Advanced Functional Materials* 18:3506 (2008).
- [24] L. H. Tang, Y. Wang, Y. M. Li, H. B. Feng, J. Lu, and J. H. Li, *Advanced Functional Materials* 19:2782 (2009).
- [25] H. Liu, J. Gao, M. Q. Xue, N. Zhu, M. N. Zhang, and T. B. Cao, *Langmuir* 25:12006 (2009).
- [26] M. Zhou, Y. M. Zhai, and S. J. Dong, *Analytical Chemistry* 81:5603 (2009).
- [27] Y. X. Huang, X. C. Dong, Y. M. Shi, C. M. Li, L. J. Li, and P. Chen, *Nanoscale* 2:1485 (2010).
- [28] C. Terashima, T. N. Rao, B. V. Sarada, N. Spataru, and A. Fujishima, *Journal of Electroanalytical Chemistry* 544:65 (2003).
- [29] F. Ricci and G. Palleschi, *Biosensors & Bioelectronics* 21:389 (2005).
- [30] Y. J. Teng, S. H. Zuo, and M. B. Lan, *Biosensors & Bioelectronics* 24:1353 (2009).
- [31] L. Zhang, *Biosensors & Bioelectronics* 23:1610 (2008).
- [32] K. B. O'Brien, S. J. Killoran, R. D. O'Neill, and J. P. Lowry, *Biosensors & Bioelectronics* 22:2994 (2007).
- [33] N. Q. Jia, Q. Lian, Z. Y. Wang, and H. B. Shen, *Sensors and Actuators B-Chemical* 137:230 (2009).
- [34] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon* 45:1558 (2007).
- [35] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, *Acs Nano* 4:4806 (2010).
- [37] L. Pu, Y. Ma, W. Zhang, H. Hu, Y. Zhou, Q. Wang, and C. Pei, *RSC Advances* 3:3881 (2013).
- [38] Z. Hu, Y. Chen, Q. Hou, R. Yin, F. Liu, and H. Chen, *New Journal of Chemistry* 36:1373 (2012).
- [39] C. Soldano, A. Mahmood, and E. Dujardin, *Carbon* 48:2127 (2010).

- [40] K. Zhang, Y. Zhang, and S. Wang, *Scientific Reports* 3:1327 (2013).
- [41] H. C. Schniepp, J. L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, and I. A. Aksay, *Journal of Physical Chemistry B* 110:8535 (2006).
- [42] Y. Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y. H. Lin, *Electroanalysis* 22:1027 (2010).
- [43] L. J. Cote, F. Kim, and J. X. Huang, *Journal of the American Chemical Society* 131:1043 (2009).
- [44] K. Liu, J. Zhang, G. Yang, C. Wang, and J.-J. Zhu, *Electrochemistry Communications* 12:402 (2010).
- [45] D. Q. Yang, J. F. Rochette, and E. Sacher, *Journal of Physical Chemistry B* 109:4481 (2005).
- [46] S. Stankovich, R. D. Piner, X. Q. Chen, N. Q. Wu, S. T. Nguyen, and R. S. Ruoff, *Journal of Materials Chemistry* 16:155 (2006).
- [47] M. P. Seah, C. D. Wagner, *Practical Surface Analysis*, J. Wiley and Sons, 1990.
- [48] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, and L. Giorgi, *Journal of Power Sources* 105:13 (2002).
- [49] Y. Y. Shao, S. Zhang, C. M. Wang, Z. M. Nie, J. Liu, Y. Wang, and Y. H. Lin, *Journal of Power Sources* 195:4600 (2010).
- [50] W. Qin and X. Li, *Journal of Physical Chemistry C* 114:19009 (2010).
- [51] ACS Committee on Environmental Improvement, *Analytical Chemistry* 52:2242 (1980).
- [52] A. Shrivastava, V. Gupta, *Chronicles of Young Scientists* 2:21 (2011).
- [53] J. M. Elliott, L. M. Cabuche, and P. N. Bartlett, *Analytical Chemistry* 73:2855 (2001).
- [54] Z. M. Liu, O. Niwa, T. Horiuchi, R. Kurita, and K. Torimitsu, *Biosensors & Bioelectronics* 14:631 (1999).
- [55] R. L. Villarta, G. Palleschi, A. Suleiman, and G. G. Guilbault, *Electroanalysis* 4:27 (1992).
- [56] C. J. Watson, B. J. Venton, and R. T. Kennedy, *Analytical Chemistry* 78:1391 (2006).
- [57] C. P. McMahon, G. Rocchitta, P. A. Serra, S. M. Kirwan, J. P. Lowry, and R. D. O'Neill, *Analyst* 131:68 (2006).
- [58] E. Ekinici, S. T. Ogunc, and A. E. Karagozler, *Journal of Applied Polymer Science* 68:145 (1998).

- [59] K. S. Chang, W. L. Hsu, H. Y. Chen, C. K. Chang, and C. Y. Chen, *Analytica Chimica Acta* 481:199 (2003).
- [60] X. N. Zhang and G. A. Rechnitz, *Electroanalysis* 6:361 (1994).
- [61] S. A. M. Marzouk, S. S. Ashraf, and K. A. Al Tayyari, *Analytical Chemistry* 79:1668 (2006).
- [62] L. Meng, P. Wu, G. X. Chen, C. X. Cai, Y. M. Sun, and Z. H. Yuan, *Biosensors & Bioelectronics* 24:1751 (2009).
- [63] H. L. Fan, L. L. Wang, K. K. Zhao, N. Li, Z. J. Shi, Z. G. Ge, and Z. X. Jin, *Biomacromolecules* 11:2345 (2010).
- [64] N. Hamdi, J. J. Wang, E. Walker, N. T. Maidment, and H. G. Monbouquette, *Journal of Electroanalytical Chemistry* 591:33 (2006).
- [65] T. T. C. Tseng, J. Yao, and W.-C. Chan, *Biochemical Engineering Journal* 78:146 (2013).
- [66] M. Zhang, C. Mullens, and W. Gorski, *Electrochimica Acta* 51:4528 (2006).
- [67] S. Chakraborty and C. R. Raj, *Journal of Electroanalytical Chemistry* 609:155 (2007).
- [68] M. Ammam and J. Fransaer, *Biosensors & Bioelectronics* 25:1597 (2010).
- [69] E. Walker, J. Wang, N. Hamdi, H. G. Monbouquette, and N. T. Maidment, *Analyst* 132:1107 (2007).
- [70] O. M. Schuvailo, S. Gaspar, A. P. Soldatkin, and E. Csoregi, *Electroanalysis* 19:71 (2007).
- [71] L. H. Tang, Y. H. Zhu, L. H. Xu, X. L. Yang, and C. Z. Li, *Talanta* 73:438 (2007).
- [72] T. U. Tatsuo Noda, Toshio Yao, *Analytical Sciences* 26:675 (2010).
- [73] M. Jamal, M. Hasan, A. Mathewson, and K. M. Razeeb, *Biosensors and Bioelectronics* 40:213 (2013).

Chapter 4 Glutamate Detection by Prussian blue Electrodeposited on Graphene Nanoplatelets

4.1 Introduction

In the previous chapter the glutamate detection based on oxidation of the by-product, hydrogen peroxide was investigated. Although good overall performance was observed, problems with interference were seen with other electroactive species at the positive potentials needed to oxidise peroxide; although it could be alleviated by the use of a polymer coating, this resulted in loss of sensitivity. In this section therefore the focus lies on the detection of glutamate at lower potential, aiming to completely remove the signals from all the common interfering species tested. The detection of glutamate in this case is based on reduction of hydrogen peroxide via electrodeposited Prussian blue and reduced graphene oxide composite.

Prussian blue or ferric hexacyanoferrate $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ is one of the most ancient coordination materials known [1, 2]. The study of the thin films of this mixed valence compound was initiated in 1978 by Neff and co-workers [3]. Six years later in 1984 Itaya *et al.* demonstrated that Prussian blue exhibited catalytic activity towards oxygen [4]. Since then much research attention has been focused on the high electrocatalytic activity toward important molecules such as O_2 , hydrazine and especially H_2O_2 . Prussian blue can catalyse the reduction of H_2O_2 at low overpotentials in the presence of oxygen with the high rate constant very close to that of the peroxidase enzyme [5]. This in turn leads to avoidance of the interfering effect caused by coexisting biological reductants such as ascorbic acid, uric acid, and 4-acetamidophenol [6]. This is the main benefit of applying Prussian blue in

biosensing compared to common noble metals like Pt and Au. The peculiar “zeolite” structure of Prussian blue, which selectively allows low molecular weight molecules to penetrate through its crystal is believed to be responsible for this advantageous effect [7].

However, to achieve such advantages of Prussian blue, high-performance support material is required. Graphene, which possesses numerous attractive properties including a large surface area, high conductivity, and excellent thermal and chemical stability, is chosen here. In addition, it also offers an ease of production and purification, which makes it a promising candidate for a high-quality support for Prussian blue.

So far there are a limited number of publications associated with graphene or graphene oxide and Prussian blue nanocomposites, most of which employed chemical methods for the deposition of Prussian blue and only focused on the detection of hydrogen peroxide [8-10]. Electrochemical methods on the other hand offer a straightforward and convenient approach for the deposition of Prussian blue on various substrates such as Au [11], glassy carbon paste [12], graphite [13] and graphene [14]. Herein we demonstrated the use of electrodeposition to produce Prussian blue-graphene nanoplatelets composite. This is the first time that a glutamate biosensor has been developed based on this composite material. The study also compared and contrasted the glutamate sensing performance with a sensor based on Pt-graphene nanoplatelets utilising the hydrogen peroxide oxidation process as a probe reaction accounted for earlier in the thesis.

4.2 Materials and Methods

4.2.1 Materials

Reagents required for electrodeposition of Prussian blue are Iron(III) chloride (Sigma) and Potassium hexacyanoferrate(III) (Fluka). Both are of analytical grade and were used as-received.

4.2.2 Apparatus

All the apparatus used are the same as described in Chapter 3 on glutamate detection by Pt-GNPs.

4.2.3 Preparation of Prussian blue-graphene electrode

Graphene nanoplatelets (GNPs) were prepared by the same method via the reduction of PDDA-functionalised graphene oxide by NaBH_4 without the addition of platinum precursor as explained in details in the preceding chapter. The reaction mixture was then filtered and dried overnight. The suspension of GNPs was prepared by ultrasonication with H_2O for an hour to obtain a stable and uniform suspension.

A glassy carbon electrode was carefully polished to a mirror finish and subsequently was drop-casted with 5 μL of 1 mg/mL GNPs suspension in water. Electrochemical deposition of Prussian blue was carried out by exploring a potentiostatic method or by cyclic voltammetric (CV) method. For a potentiostatic method, a constant potential of 0.4 V was applied at the GNPs electrode for 40 s in 10 mM solution of Iron(III) chloride and Potassium hexacyanoferrate(III) with 0.1 M KCl and HCl as background electrolyte. For a CV method the same growing solution was used but the electrode was cycled from -0.2 V to 0.56 V for 20 cycles at 20 mV/s instead. After electrodeposition step, the as-prepared electrode was activated in the background solution of 0.1 M KCl and HCl by cyclic scan from -0.05 V to 0.35 V for 20 cycles at 40 mV/s.

The preparation of glutamate sensor by immobilisation of L-glutamate oxidase enzyme was also as described in the preceding chapter.

4.3 Results and Discussion

4.3.1 Electrodeposition of Prussian blue

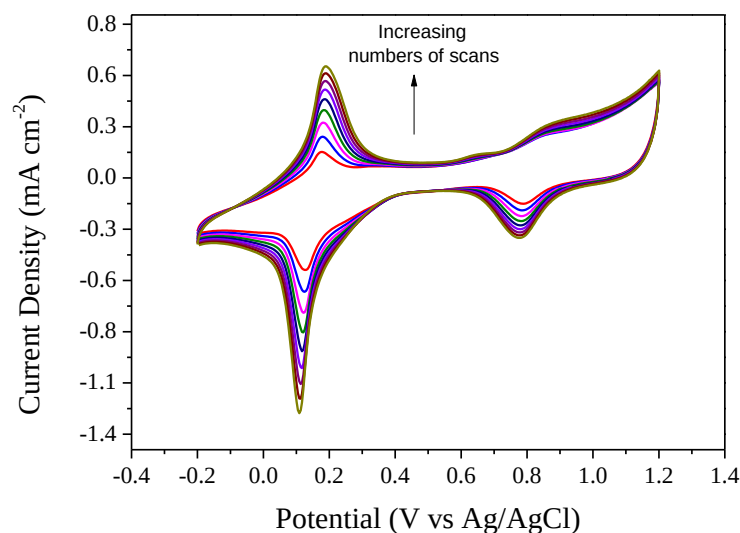
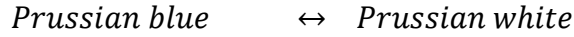
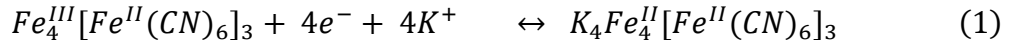


Figure 4.1 Cyclic voltammograms of graphene nanoplatelets modified glassy carbon electrode in 10 mM FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution at a scan rate of 50 mV/s

The cyclic voltammogram of reduced graphene oxide in an equimolar mixture of ferric and ferricyanide ions in **Figure 4.1** shows two main features owing to the characteristic redox processes of Prussian blue. The sharp reduction peak at 0.11 V and the corresponding oxidation peak at 0.19 V are attributed to the reduction of Prussian blue to Prussian white as shown in equation 1. This gives the peak separation of 0.08 V. The sharpness of the peaks indicates regular structure and homogeneous distribution of charge and ion transfer [15].

At the more positive potential a much broader peak can be observed at around 0.87 V and this is attributed to the oxidation from Prussian blue to Prussian yellow or also called Berlin green as indicated in equation 2. These features are characteristic of Prussian blue as also observed on glassy carbon paste [12] and mirrored glassy carbon electrode [15]. The fact that peak current increases with successive cycles means that Prussian blue has been successfully electrochemically deposited on the electrode.



It is obvious that Prussian blue is thus formed in the region of 0.4 V to 0.6 V, between these reduction and oxidation transformations. This is consistent with the suggested mechanism for electrodeposition of Prussian blue, which at the more negative potentials of 0.4 V involves reduction of Fe^{3+} to Fe^{2+} which can then react with hexacyanoferrate (III) to form Prussian blue; at more positive potentials reduction of the $Fe^{III}[Fe^{III}(CN)_6]$ complex which forms in solution is implicated [15]. The pH of the initial growing solution is also essential for the regularity of the deposit due to the strong interaction between ferric ions and hydroxyl ions which forms $Fe(OH)_3$ [16] and pH 1 is suggested to be the optimum [17, 18]. Chronopotentiometry was thus carried out at 0.4 V for 40 s in the electrolyte solution of pH 1. The corresponding current-time transient was recorded and presented in **Figure 4.2** below.

The charge of Prussian blue deposition was controlled to be around 0.5 mC. After the deposition, Prussian blue on reduced graphene oxide was activated in an electrolyte solution of 0.1 M KCl and HCl (pH 1) at a relatively slow scan rate of 40 mV/s from -0.05 V to 0.35 V. The deposition is followed by successive voltammetric cycling in 0.1 M KCl and HCl solution at a scan rate of 40 mV/s, which causes the transformation to the more stable form of Prussian blue on the electrode surface [19-21].

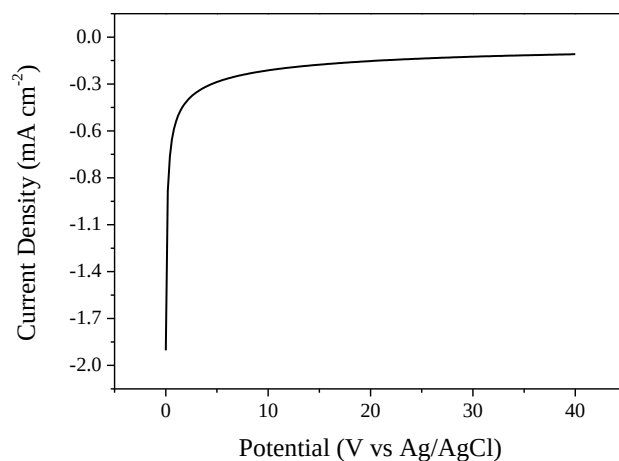


Figure 4.2 Typical current time transient of the electrodeposition of Prussian blue at 0.4 V in 10 mM FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution

Figure 4.3 shows the cyclic voltammogram of the activation of the Prussian blue on reduced graphene oxide. Coupled redox peaks are observed. The reduction peak occurs at 0.12 V and oxidation peak at 0.21 V. Integration of the area under the reduction peak (in this case equals to 0.288 mC) gives rise to the surface concentration (τ) of deposited Prussian blue by assuming 4 electrons ($n=4$) involved according to equation 1 above. This can be calculated from equation 3 below [21].

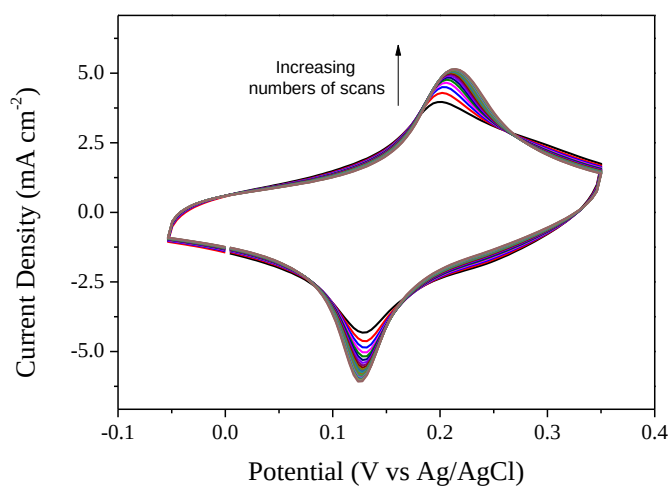


Figure 4.3 CV of Prussian blue modified GNPs on GC electrode in 0.1 M KCl and HCl at 40 mV/s

$$I_p = n^2 F^2 A \nu \tau / 4RT \quad (3)$$

This was found to be 10.5 nmol/cm², which is slightly higher than the value found for Prussian blue on nanoelectrode arrays [22] and on graphite electrode [21].

Electrodeposition by cyclic voltammetry was also carried out from -0.2 V to 0.56 V at 20 mV/s for 20 cycles. However, this results in delamination of the deposited layer of Prussian blue from the GNPs modified GC electrode surface. As a result, the potentiostatic method was employed throughout all further experiments.

4.3.2 Characterisation

4.3.2.1 Electrochemical Characterisation

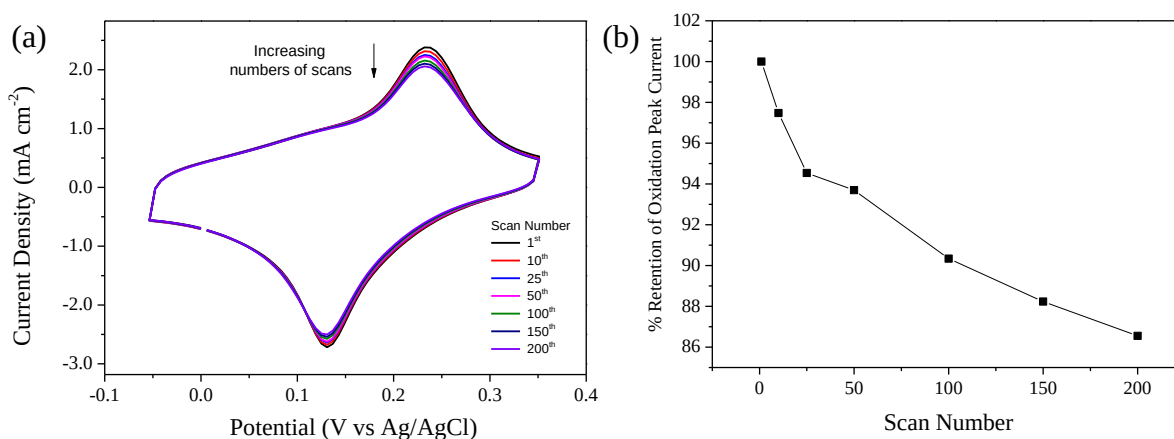


Figure 4.4 (a) CV of PB modified GNPs electrode in phosphate buffer solution pH 6.0 (b) plot of the retention of oxidation peak current against number of scan

The stability of electrodeposited PB reduced graphene oxide electrode was assessed by 200 voltammetric cycles in phosphate buffer solution pH 6.0 as this is the operational pH and condition. From **Figure 4.4** (a) in the initial cycle the redox couple is again observed at 0.13 V and 0.23 V for the reduction and oxidation respectively. It is obviously seen from the CV that the current density of the oxidation peak decreases gradually as the number of scans

increases. The decrease in current density of the oxidation peak is plotted against the number of scans as in **Figure 4.4** (b). After 200 cycles the retention of the peak current remains approximately 87%. This indicates a good cycling stability of the deposited Prussian blue by potentiostatic method.

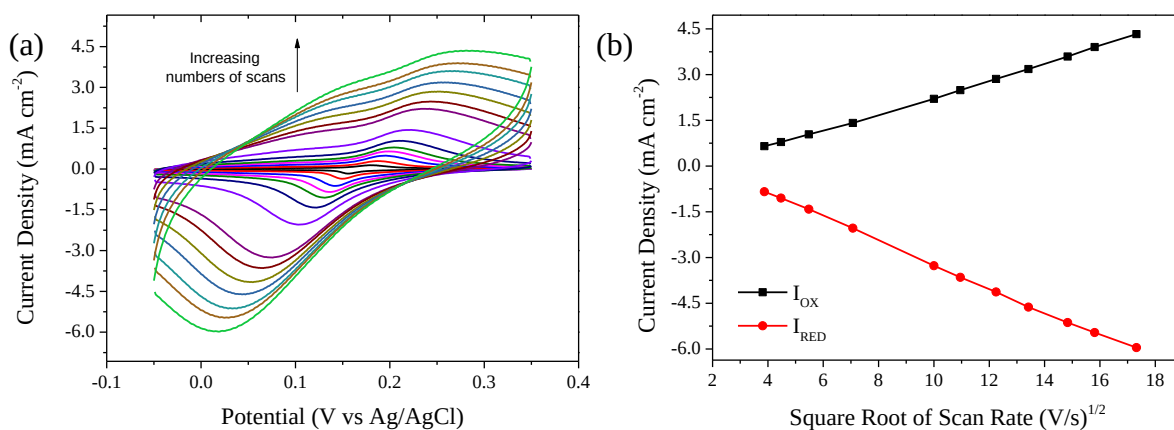


Figure 4.5 (a) CV of PB modified GNPs electrode in phosphate buffer solution pH 6.0 at different scan rates and (b) the corresponding linear plots of peak current density against square root of scan rate

Electrochemical behaviour of the composite was also investigated by the study on the effect of scan rate shown in **Figure 4.5**. Both the oxidation and reduction peak currents show a linear dependence on the square root of scan rate, which is indicative of a diffusion-controlled process. This might be related to the slow diffusion of potassium ions into a limited reaction layer or more precisely the lattice of Prussian blue nanoparticles [9, 21]. The formal potential $E^{\circ'} = 1/2(E_{pa} + E_{pc})$ was found to be 0.27 V and the redox peak separation at 10 mV/s is 0.053 V. This is not too far from the value of 0 mV, which is an ideal value for an adsorbed electroactive species on the electrode surface with a facile electron transfer [23, 24].

4.3.2.2 Raman Spectroscopy

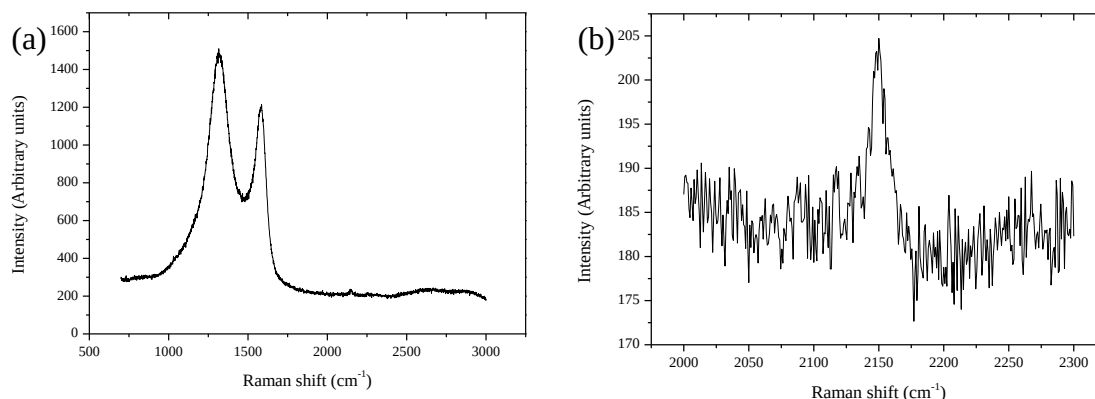


Figure 4.6 (a) Raman spectrum of PB modified GNPs on glassy carbon electrode (b) Magnification of Raman spectrum in the range of 2000-2300 cm^{-1} showing a small peak due to Prussian blue

The Raman spectrum of Prussian blue chronoamperometrically deposited on graphene nanoplatelets in **Figure 4.6** (a) shows two main peaks at 1314 and 1585 cm^{-1} . These correspond to the D and G bands of graphene respectively [25]. A weak band was also observed at 2150 cm^{-1} as shown in **Figure 4.6** (b). This band is most likely related to the stretching vibration of the CN group of Prussian blue [24], which in turn indicates the successful deposition of Prussian blue onto the graphene nanoplatelet substrate.

4.3.2.3 SEM

The morphology of the Prussian blue deposit was elucidated by SEM. The SEM image shows the film of as-grown Prussian blue on GNPs modified GC electrode. From the SEM micrograph, a uniform coverage of PB film across the electrode surface is observed. And the film appeared to completely cover the graphene nanoplatelets underneath such that it could not be seen in the SEM image shown in **Figure 4.7**.

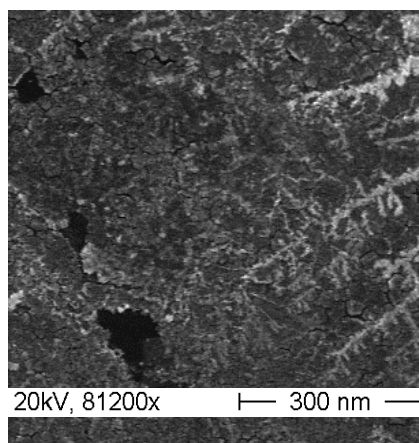


Figure 4.7 SEM image of Prussian blue modified graphene nanoplatelets on glassy carbon electrode

4.3.3 Detection of H_2O_2

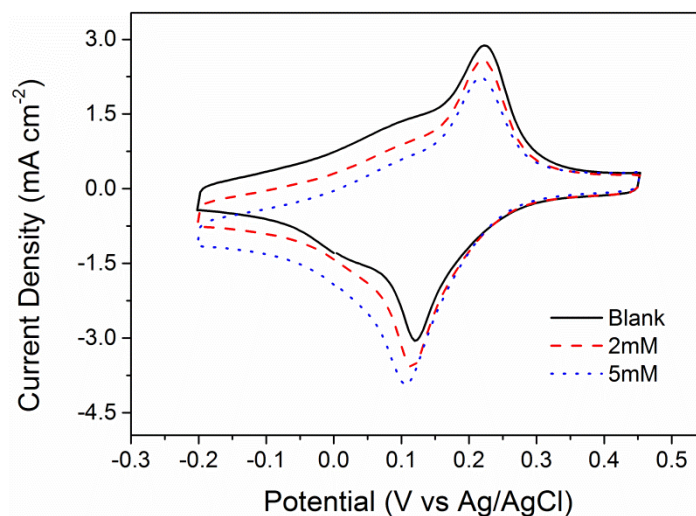


Figure 4.8 CV of Prussian blue modified graphene nanoplatelets electrode in Phosphate buffer solution pH 6.0 with different concentration of H_2O_2 as indicated in the plot

The stability of Prussian blue and the glutamate oxidase enzyme is pH dependent. Enzyme will be denatured at too high or low pH from its optimal condition. However, it is reported that Prussian blue becomes unstable and dissolves into the solution at higher pH than 7 [26,

27]. Consequently pH 6.0 was chosen as a compromise to maintain the stability of both Prussian blue and the enzyme.

Similarly it is known that Prussian blue is unstable at negative potentials. The instability of Prussian blue at potentials more negative than that of the Prussian blue/Prussian white redox couple could be due to the partial solubility of the reduced form, Prussian white [27]. The response of the PB modified electrode to H_2O_2 can be seen in **Figure 4.8**. The cathodic current at 0.1 to -0.15 V increases in magnitude with increasing hydrogen peroxide concentration. -0.05 V was thus chosen as the potential for reduction of hydrogen peroxide in chronoamperometric measurements.

4.3.3.1 Effect of Heat Treatment on Detection of H_2O_2

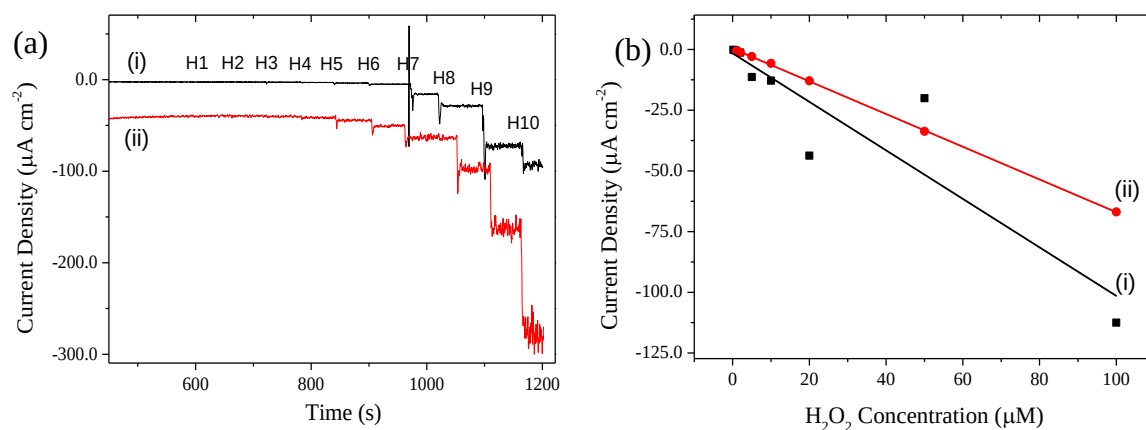


Figure 4.9 (a) Typical chronoamperometric response of as-prepared PB modified GNPs electrode (i) and after heat treatment (ii) to increasing concentration of H_2O_2 (H1 to H10 represents the concentration of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0 and 200.0 μM). (b) the corresponding linear calibration plot of the electrodes in (a)

Figure 4.9 above shows the amperometric responses of the sensors towards injection of increasing concentration of hydrogen peroxide before and after heat treatment. Each Prussian blue deposited sample was heated at 100°C for 1 hour. It is obvious from the linear plot in (b) that the current density in unheated electrode is largely scattered especially at higher

concentration of H_2O_2 giving rise to $R^2 = 0.825$. The heated PB-reduced graphene oxide is, on the other hand, linearly responsive to the increase in concentration of the analyte as reflected by the R^2 value of 0.999. This enhanced linearity of the electrode with heat treatment, despite exhibiting lower sensitivity towards H_2O_2 , hence suggests improved stability towards increasing peroxide concentration. This finding agrees well with the established results where it was suggested that water content could affect the stability of the Prussian blue deposit [27]. Heating the electrode at 100°C for an hour could effectively remove zeolitic water which is described as physically adsorbed water molecules in the inorganic solid of Prussian blue [28]. As a result, more active sites on Prussian blue are available for detection of hydrogen peroxide and more stable response was achieved even at higher concentration of the analyte.

4.3.3.2 Effect of Deposition Time

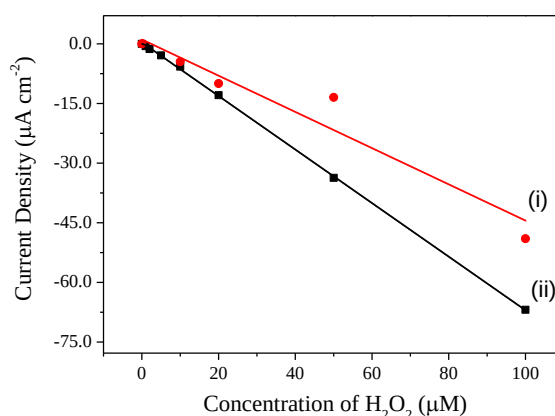


Figure 4.10 Linear calibration plot of Prussian blue modified GNPs electrodes prepared by electrodeposition at 0.4 V for 40 seconds (i) and 60 seconds (ii)

The variation of the deposition time for Prussian blue using the chronoamperometric method was examined. Increasing deposition time from 40 to 60 seconds seems to only slightly affect the sensitivity towards H_2O_2 as indicated by the linear plot of current against H_2O_2 concentration in **Figure 4.10**. This is in agreement with the i - t transient plotted in Figure 4.2 as the current was observed to decrease very rapidly within the first 10 seconds of the

deposition time. After that, the current seems to reach the limit and stays constant close to 0 A throughout. Hence, the deposition time of 40 seconds was chosen as the optimum.

4.3.3.3 H₂O₂ Detection Performance and Interference

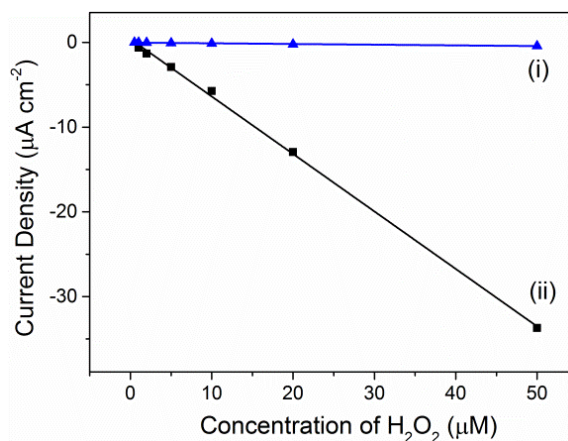


Figure 4.11 Linear response of Prussian blue deposited on glassy carbon electrode (i) and on GNPs (ii)

The response of the PB modified electrode, described as prepared above to H₂O₂ using the chronoamperometric method at a potential of -0.05 V and pH 6 was measured for differing peroxide concentrations and the results are shown in **Figure 4.11**. From the amperometric experiment, the hydrogen peroxide sensing of the Prussian blue modified graphene electrode can be summarised as follows. The linearity of the detection range is from 0.2 μM up to at least 5 mM. This is a very wide range in comparison to other reported Prussian blue-based sensors which will be compared and discussed later in more detail. It is also very suitable for the detection of glutamate in physiological systems as mentioned earlier in the work on Pt-GNPs. This wide range is also suitable for detection of hydrogen peroxide in various systems for example in food, pharmaceuticals and cosmetics. Additionally, in comparison to PB deposited on bare GC, it is clear from **Figure 4.11** that the sensitivity is considerably lower

than the PB-GNPs electrode. Hence, this result supports the statement that the larger surface area and more defect sites of GNPs lead to a better support for PB in this application.

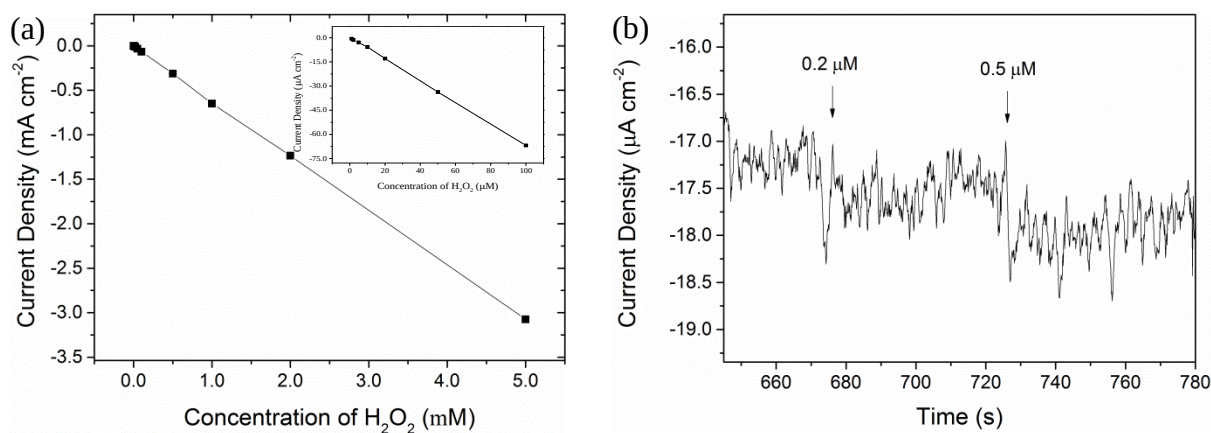


Figure 4.12 (a) the linear calibration plot over a long range up to 5 mM of H_2O_2 with the inset showing the magnification of the same plot at low concentration of H_2O_2 up to 100 μM . (b) the chronoamperometric response when adding small amount of H_2O_2 of 0.2 and 0.5 μM

In **Figure 4.12** (a) above, the linearity plot is shown at low concentration. The sensitivity was determined to be $0.62 \mu\text{A}/\mu\text{M cm}^{-2}$ with the limit of detection being 2.2 μM ($\text{S/N} = 3$). Again a similar phenomenon is observed as in the case of the limit of detection of the glutamate sensor where the apparent limit of detection is literally lower than the value calculated. This is clearly seen from **Figure 4.12** (b), where the current density decreases after the addition of 0.2 μM and 0.5 μM of H_2O_2 in a well-stirred solution at a potential of -0.05 V. This significant difference in the apparent and calculated LoD possibly results from the large noise level as can be seen in **Figure 4.12** (b). The reproducibility was also assessed by preparing three electrodes independently. The standard deviation of the hydrogen peroxide sensitivity was found to be $0.045 \mu\text{A}/\mu\text{M cm}^{-2}$, which is less than 10% of the sensitivity value. This indicates the good reproducibility of the electrode fabrication method. Time response is also another important parameter to assess the practicality of the sensor. This electrode also shows relatively similar time response as the Pt-GNPs electrode, that is the current response was stabilised within 4-5 seconds immediately after the injection of the analyte.

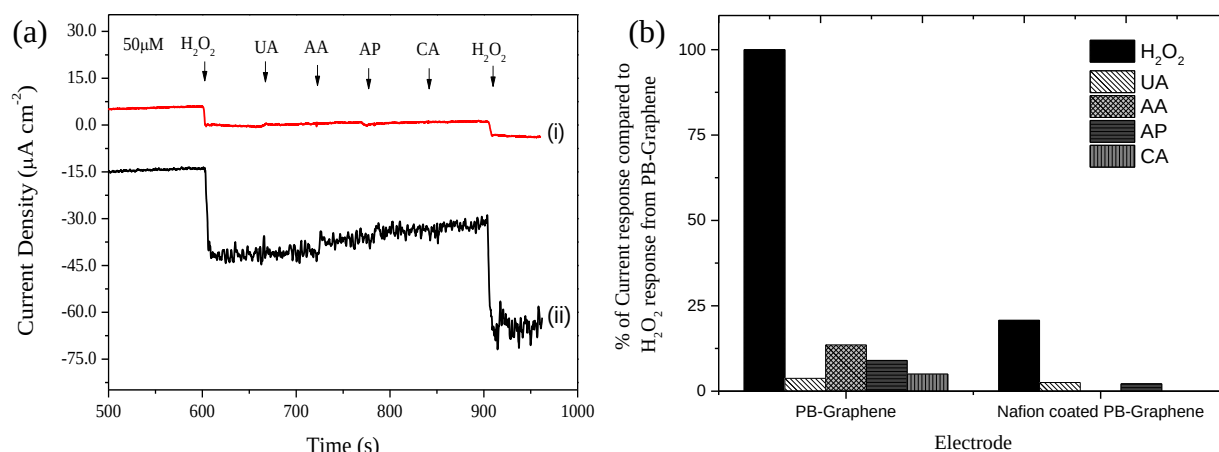


Figure 4.13 (a) Amperometric response of Prussian blue modified GNPs electrode to addition of H_2O_2 and commonly found interfering compounds (ii) and with the coated layer of Nafion (i) UA is uric acid, AA is ascorbic acid, AP is 4-aminophenol, CA is citric acid. (b) Bar charts summarise the amperometric data shown in (a) showing the response towards each analyte by the two electrodes (in percentage to H_2O_2 response from PB-Graphene electrode).

As mentioned in the beginning of this chapter, a purpose for using this artificial peroxidase material is to lower the detection potential and hence reduce the interference from the ubiquitous electroactive species that exist in the physiological system. The amperometric sensing at pH 6 was conducted by injection of the analytes of interest at equal concentration of 50 μM in the order as indicated in **Figure 4.13** above. It is clear that the electrode only responds to the addition of hydrogen peroxide. A comparative experiment was also carried out with Nafion drop-casted on the Prussian blue modified graphene electrode. The amperometric response of this Nafion coated electrode is shown in plot (i). The response is the same as in the case of electrode without the layer of Nafion. The only main difference lies in the nearly 5 times lower current response after coating with Nafion as it is harder for the analyte to permeate through the polymer layer to reach the electrode surface underneath. This finding confirms the successful elimination of interference effect using Prussian blue for the detection of hydrogen peroxide in comparison to the Pt-GNPs electrode.

4.3.4 Glutamate Detection Performance

A glutamate biosensor based on Prussian blue modified graphene electrode was fabricated using the same method as described in the previous chapter for the Pt-GNPs work. The biosensor was first tested in terms of the response to the interfering species at equal concentration of 50 μM and the corresponding response is shown in **Figure 4.14** below.

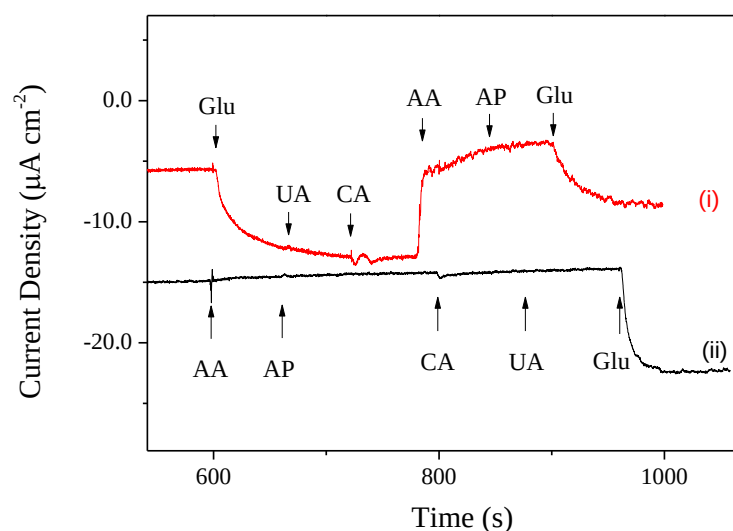


Figure 4.14 Amperometric response of the glutamate sensor based on PB-GNPs electrode (i) and that modified with PPD as an outer layer (ii) at -0.05 V in Phosphate buffer pH 6.0 to glutamate (Glu) and other concomitant electroactive species all at equal concentration of 50 μM

The as-prepared glutamate sensor in **Figure 4.14** (i) shows a current which becomes more negative due to the addition of glutamate, however this is accompanied with a change, in current when ascorbic acid (AA) is added to the buffer solution as well. On the other hand, the response from UA, CA and AP was not observed. This finding is different from that previously found for the non-enzymatic Prussian blue modified graphene electrode explained in section 4.3.3.3 above. In order to obtain improved performance against interference, again polyphenylenediamine (PPD) was electrodeposited on top of the enzyme layer. And this gives rise to the response as recorded in **Figure 4.14** (ii). The selectivity of the sensor is

enhanced as an amperometric response is in this case only observed for glutamate. This confirms the successful application of the polymer to inference elimination.

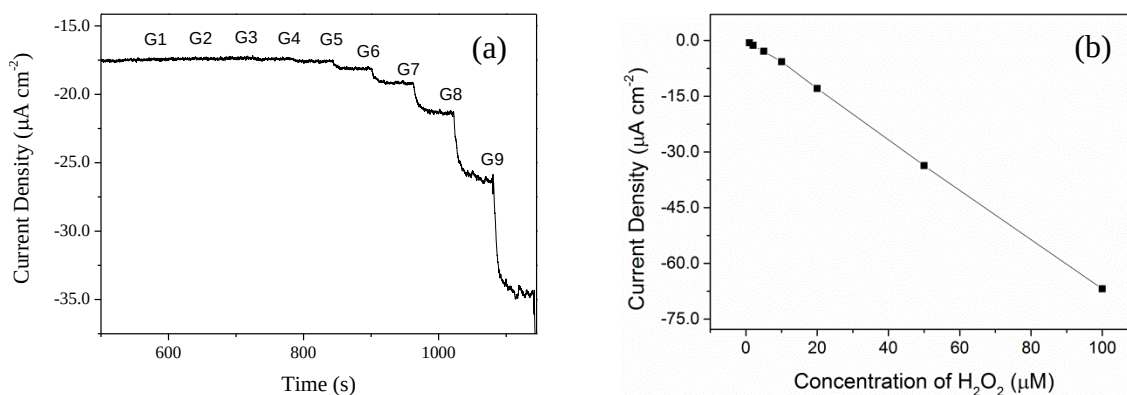


Figure 4.15 (a) Amperometric response of PPD modified glutamate sensor based on Prussian blue-GNPs electrode to addition of increasing concentration of glutamate in Phosphate buffer pH 6.0 at -0.05 V and (b) is the corresponding calibration plot where G1-G9 represents the concentrations of added glutamate; 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0 μM respectively

The performance of the glutamate sensor with the PPD layer was examined via the amperometric response at -0.05 V at increasing concentration of glutamate. The current plot against time and the corresponding linear plot of current against the concentration of the added glutamate are presented in **Figure 4.15**. The linear range for glutamate detection is from 1.0 to 100 μM . At 200 μM the response starts to become non-linear. This range is narrower than that found for hydrogen peroxide detection. This is as expected due to the effect of the polymer PPD and also the activity of the glutamate oxidase enzyme. The sensitivity was found to be $0.083 \mu\text{A}/\mu\text{M cm}^{-2}$, which is approximately 6 times lower than the hydrogen peroxide sensitivity. The limit of detection comes out to be 1.0 μM , which is the same for both the apparent value and that determined by S/N ratio = 3. The time response is slightly slower and 95% of the response was recovered about 10 seconds after the addition of glutamate despite the same fabrication method for the enzyme immobilisation employed.

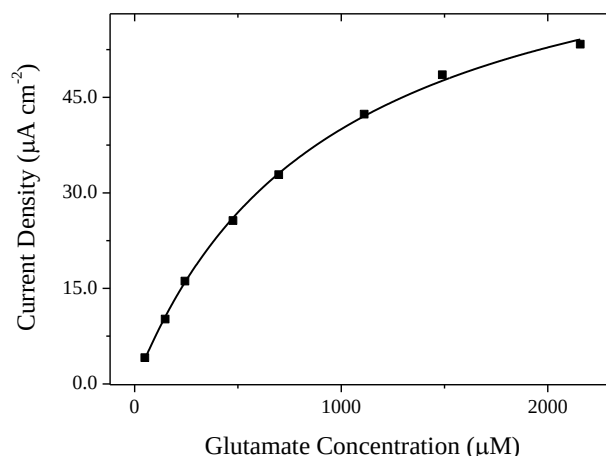


Figure 4.16 Michaelis-Menten plot of the glutamate sensor

The kinetics study on the enzymatic electrode was carried out and the Michaelis-Menten plot was shown in **Figure 4.16**. The Michaelis-Menten constant (K_m) value is equal to 944 μM , which is much higher than 470 μM found for the glutamate sensor based on Pt-GNPs. The V_m was found to be 77.8 $\mu\text{A}/\text{cm}^2$, which is again lower than that found for glutamate sensor from Pt-GNPs. The result suggests the more sluggish kinetics in this system compared to the Pt-GNPs system.

The long-term stability of the sensor was recorded over a period of ten days and the resulting responses are tabulated in **Table 4.1** below.

Table 4.1 The sensitivity of the glutamate sensor during the period of 10 days storage

<i>Number of days</i>	<i>Sensitivity/ $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$</i>	<i>%</i>
1	0.083	100.0
3	0.072	87.2
7	0.066	79.7
10	0.050	59.9

The decay in the sensitivity was gradual in the first 7 days of the storage. However, after ten days only about 60% of the initial response was maintained.

4.3.5 Concluding Remarks and Comparison

To evaluate the performance of the sensor, it was compared with the sensor based on Pt-GNPs prepared for the oxidation of hydrogen peroxide. The summary of their overall performances is presented in **Table 4.2** where the Pt-GNPs and PB/GNPs are in No.16 and 17 respectively. The detection conditions of the two sensors are different in terms of detection potential and pH of the background electrolyte. The potential of 0.5 V was applied for the Pt-GNPs electrode as this is the potential at which the oxidation of H_2O_2 occurs while -0.05 V was applied for the PB-GNPs electrode where the reduction of H_2O_2 could be observed. PBS solution of pH 7.4 was used for Pt-GNPs whereas this pH is too basic for Prussian blue to be stable and hence pH 6.0 was selected instead.

Despite opposite redox reaction being employed, both sensors exhibit similar response to H_2O_2 with the sensitivity of 0.62 and 0.69 $\text{A M}^{-1} \text{cm}^{-2}$ for Prussian blue and platinum modified graphene electrodes respectively. The detection limit is however more than an order of magnitude lower for Pt-GNPs at 0.16 μM compared to 2.2 μM for PB-GNPs. This difference reflects the background noise level being much lower at the more positive potential employed for the oxidation of H_2O_2 . The linear range is however much wider for the Prussian blue based electrode reaching as high a concentration as 5 mM. By contrast the platinum based electrode only goes up to 0.2 mM. The wider linear range of the sensor enables the PB-GNPs sensor to be more applicable in other areas apart from biosensing. Interference effect, on the other, hand poses a major advantage towards Prussian blue modified electrode for H_2O_2 sensing as this could produce a sensor which is interference free, making it even more desirable for the detection in physiological conditions. As discussed earlier, to obtain the H_2O_2 sensor based on Pt-GNPs with minimal interference,

polyphenylenediamine polymer is required and this has been shown to dramatically lower the H_2O_2 sensitivity as well.

With regard to other established results of the H_2O_2 sensors previously reported, the PB-GNPs developed in this work exhibits very competitive performance with a notably high sensitivity and a relatively good linear range. It should be noted that most of the work reported for the reduction of H_2O_2 by Prussian blue modified electrodes were recorded at pH 5-7 with the majority lies at pH 6.0. The detection potential also varies slightly from 0.2 V to -0.2 V with potentials closer to 0 V such as 0.05 V or -0.05 V being more frequently employed.

As can be seen in **Table 4.2** that the sensitivity of PB-GNPs in this work lies at the higher end of the table where most of the work previously reported show the sensitivity in the range of $0.1 - 0.3 \text{ A M}^{-1} \text{ cm}^{-2}$. The highest reported data at $15.3 \text{ A M}^{-1} \text{ cm}^{-2}$ is from No. 6 which is based on PB-CNT paste electrode but this only measured at the much lower range of concentration of 5.0×10^{-7} to $3.0 \times 10^{-5} \text{ M}$. In comparison to Prussian blue modified graphene based sensors, our sensor also exhibits the highest sensitivity reflecting the efficiency of electrodeposition method employed for the fabrication of the PB-GNPs electrodes.

The linear range of detection is also comparable to many published results but is still inferior to the sensors in No. 1-4 with detection system based on Flow-injection-analysis (FIA) technique. The different detection system also affects the limit of detection as the sensors in No. 1-4 exhibit detection limit lower than 10^{-7} M . Although the PB-GNPs in this work has a higher detection limit of $2.2 \text{ }\mu\text{M}$, the value is still comparable to many reported sensors especially in No.12 and 13, which are also based on graphene.

Table 4.2 Comparison to other H₂O₂ and glutamate sensors based on Prussian blue modified electrodes and their figures of merit

No.	H ₂ O ₂ Sensors	Sensitivity/A M ⁻¹ cm ⁻²	linear range/M	LOD/M	Ref.
1	Nanoelectrode arrays of PB	0.06	10 ⁻⁸ -10 ⁻²	10 ⁻⁸	[22]
2	NanoPB via sol-gel templat	0.7	10 ⁻⁹ - 10 ⁻²	10 ⁻⁹	[29]
3	NanoPB on crystalline graphite	0.2	10 ⁻⁸ -10 ⁻²	10 ⁻⁸	[30]
4	oPD/PB	0.3	10 ⁻⁷ - 10 ⁻²	10 ⁻⁷	[31]
5	PB/GC	0.188	2.5x 10 ⁻⁷ – 5x10 ⁻⁴	2.5x10 ⁻⁶	[12]
6	PB/CNT paste electrodes	15.3	5.0×10 ⁻⁷ - 3.0x10 ⁻⁵	1.94x10 ⁻⁸	[32]
7	PB/Graphite	0.139	2.1×10 ⁻⁶ -1.4x×10 ⁻⁴	1.0x10 ⁻⁶	[21]
8	PB/PtNPs/CNT	0.150	1.0×10 ⁻⁴ -5.0×10 ⁻³	1.0x×10 ⁻⁴	[33]
9	Nafion/PB/screen printed Au	2.0	-	-	[34]
<i>PB-Graphene Composite</i>					
10	PB/rGO/ITO microelectrode array	0.25	10 ⁻⁸ -5×10 ⁻⁶	10 ⁻⁸	[35]
11	PB/Graphene oxide	0.41	5.0×10 ⁻⁶ -1.2×10 ⁻³	1.22x10 ⁻⁷	[36]
12	PB/Graphene/GCE	0.53	10 ⁻⁵ –1.44×10 ⁻³	3.0x10 ⁻⁶	[14]

13	Nafion/Graphene/PB nanosheets chemical method	0.197	2×10^{-5} - 2×10^{-4}	1.9×10^{-6}	[9]
14*	PB nanocube/reduced GO chemical method	0.13	5×10^{-5} - 1.2×10^{-4}	4.5×10^{-8}	[37]
15*	PB/GO sheet chemical method	0.0184	5×10^{-5} - 1.4×10^{-1}		[38]
16	<i>Pt</i> -GNPs	0.69	1.0×10^{-7} - 2×10^{-4}	1.6×10^{-7}	<i>This work</i>
17	<i>PB</i> /GNPs	0.62	2.0×10^{-6} - 5×10^{-3}	2.2×10^{-6}	<i>This work</i>
Glutamate Sensors					
18	GluOx/Nafion-PB (pH 6.0)	0.21	10^{-7} - 10^{-4}	10^{-7}	[39]
19	GluOx/Carbon film (pH 6.0)	0.035	10^{-5} - 7×10^{-4}	10^{-5}	[40]
20	Glox/PB/GC (pH 7.0)	0.086	5×10^{-6} - 5×10^{-4}	5×10^{-6}	[41]
21	<i>mPD</i> /GluOx/ <i>Pt</i> -GNPs (pH 7.4)	0.174	10^{-7} - 10^{-4}	7.5×10^{-7}	<i>This work</i>
22	GluOx/ <i>PB</i> /GNPs (pH 6.0)	0.083	10^{-6} - 10^{-4}	1.0×10^{-6}	<i>This work</i>

Additionally, in **Table 4.2** the data for glutamate sensors developed in this work are compared with those based also on Prussian blue modified electrodes. Despite the PB-GNPs electrode exhibiting higher sensitivity towards H_2O_2 , the activity seems to be lost after enzyme immobilisation and applying the PPD layer. However, the sensitivity of $0.083 \text{ A M}^{-1} \text{ cm}^{-2}$ is comparable to the other three glutamate sensors in No. 18-20. It is worth pointing out that the work on glutamate sensors based on Prussian blue is very limited. Our work is the first to report the use of Prussian blue and graphene materials for detection of glutamate. The LoD is also comparable to the Pt-GNPs system and lower than those reported in No. 19 and 20. Again FIA is used for the detection system in No. 18; hence good detection limit is as expected. One other very important issue regarding biosensing is concerned with long-term stability. This seems to be the main drawback of the PB-GNPs sensor when compared to Pt-GNPs as the PB-GNPs only stayed active over a week while it is quite common for most of the Prussian blue based sensors to remain stable only for 1-2 weeks of operation.

To conclude, overall the most advantageous feature of using Prussian Blue-GNPs electrode over Pt-GNPs lies in the complete elimination of interfering effect especially from 4-Acetamenophen but the PB-GNPs sensor is much less stable in the long run.

References

- [1] L. J. M. Coleby, *Annals of Science* 4:206 (1939).
- [2] G. G. Alexander Kraft, *Bull. Hist. Chem.* 33:61 (2008).
- [3] V. D. Neff, *Journal of the Electrochemical Society* 125:886 (1978).
- [4] K. Itaya, N. Shoji, and I. Uchida, *Journal of the American Chemical Society* 106:3423 (1984).
- [5] B. B. Hasinoff and H. B. Dunford, *Biochemistry* 9:4930 (1970).
- [6] S. Wu, Y. Liu, H. Wu, and H. Ju, *Electrochemistry Communications* 10:397 (2008).
- [7] F. Ricci and G. Palleschi, *Biosensors & Bioelectronics* 21:389 (2005).
- [8] L. Y. Cao, Y. L. Liu, B. H. Zhang, and L. H. Lu, *Acs Applied Materials & Interfaces* 2:2339 (2010).
- [9] E. Jin, X. F. Lu, L. L. Cui, D. M. Chao, and C. Wang, *Electrochimica Acta* 55:7230 (2010).
- [10] X.-W. Liu, Z.-J. Yao, Y.-F. Wang, and X.-W. Wei, *Colloids Surf B Biointerfaces* 81:508 (2010).
- [11] C. Wang, S. Chen, Y. Xiang, W. Li, X. Zhong, X. Che, and J. Li, *Journal of Molecular Catalysis B-Enzymatic* 69:1 (2011).
- [12] F. Ricci, C. Goncalves, A. Amine, L. Gorton, G. Palleschi, and D. Moscone, *Electroanalysis* 15:1204 (2003).
- [13] N. F. Zakharchuk, B. Meyer, H. Hennig, F. Scholz, A. Jaworksi, and Z. Stojek, *Journal of Electroanalytical Chemistry* 398:23 (1995).
- [14] Y. Jiang, X. Zhang, C. Shan, S. Hua, Q. Zhang, X. Bai, L. Dan, and L. Niu, *Talanta* 85:76 (2011).
- [15] A. A. Karyakin, *Electroanalysis* 13:813 (2001).
- [16] B. J. Feldman and R. W. Murray, *Inorganic Chemistry* 26:1702 (1987).
- [17] A. A. Karyakin, E. E. Karyakina, and L. Gorton, *Talanta* 43:1597 (1996).
- [18] A. A. Karyakin, E. E. Karyakina, and L. Gorton, *Journal of Electroanalytical Chemistry* 456:97 (1998).
- [19] J. J. GarciaJareno, J. NavarroLaboulais, and F. Vicente, *Electrochimica Acta* 41:835 (1996).
- [20] A. Roig, J. Navarro, J. J. Garcia, and F. Vicente, *Electrochimica Acta* 39:437 (1994).

- [21] B. Haghighi, H. Hamidi, and L. Gorton, *Sensors and Actuators B-Chemical* 147:270 (2010).
- [22] A. A. Karyakin, E. A. Puganova, I. A. Budashov, I. N. Kurochkin, E. E. Karyakina, V. A. Levchenko, V. N. Matveyenko, and S. D. Varfolomeyev, *Analytical Chemistry* 76:474 (2004).
- [23] E. Laviron, *Electroanalytical Chemistry* 12:53 (1982).
- [24] L. Xia and R. L. McCreery, *Journal of the Electrochemical Society* 146:3696 (1999).
- [25] C. Soldano, A. Mahmood, and E. Dujardin, *Carbon* 48:2127 (2010).
- [26] T. Li, Z. H. Yao, and L. Ding, *Sensors and Actuators B-Chemical* 101:155 (2004).
- [27] A. A. Karyakin, E. E. Karyakina, and L. Gorton, *Electrochemistry Communications* 1:78 (1999).
- [28] I. L. de Mattos, L. Gorton, T. Ruzgas, and A. A. Karyakin, *Analytical Sciences* 16:795 (2000).
- [29] A. A. Karyakin, E. A. Puganova, I. A. Bolshakov, and E. E. Karyakina, *Angewandte Chemie-International Edition* 46:7678 (2007).
- [30] E. A. Puganova and A. A. Karyakin, *Sensors and Actuators B-Chemical* 109:167 (2005).
- [31] L. V. Lukachova, E. A. Kotel'nikova, D. D'Ottavi, E. A. Shkerin, E. E. Karyakina, D. Moscone, G. Palleschi, A. Curulli, and A. A. Karyakin, *Sensors Journal, IEEE* 3:326 (2003).
- [32] E. Nossol and A. J. G. Zarbin, *Advanced Functional Materials* 19:3980 (2009).
- [33] J. Zhang, J. Li, F. Yang, B. Zhang, and X. Yang, *Journal of Electroanalytical Chemistry* 638:173 (2010).
- [34] I. L. de Mattos, L. Gorton, and T. Ruzgas, *Biosensors & Bioelectronics* 18:193 (2003).
- [35] F. Li, M. Xue, X. Ma, M. Zhang, and T. Cao, *Analytical Chemistry* 83:6426 (2011).
- [36] Y. Zhang, X. Sun, L. Zhu, H. Shen, and N. Jia, *Electrochimica Acta* 56:1239 (2011).
- [37] L. Cao, Y. Liu, B. Zhang, and L. Lu, *Acs Applied Materials & Interfaces* 2:2339 (2010).
- [38] X.-W. Liu, Z.-J. Yao, Y.-F. Wang, and X.-W. Wei, *Colloids and Surfaces B-Biointerfaces* 81:508 (2010).
- [39] A. A. Karyakin, E. E. Karyakina, and L. Gorton, *Analytical Chemistry* 72:1720 (2000).

Chapter 4

- [40] S. De Luca, A. Florescu, M. E. Ghica, A. Lupu, G. Palleschi, C. M. A. Brett, and D. Compagnone, *Talanta* 68:1406 (2006).
- [41] S. Varma, Y. Yigzaw, and L. Gorton, *Analytica Chimica Acta* 556:319 (2006).

Chapter 5 Detonation Nanodiamond, Graphene and Polyaniline Composites for Supercapacitor Applications

5.1 Introduction

As mentioned in the introduction chapter of the thesis, a supercapacitor is a type of energy storage device, which has been in a focal point of energy research and development as a promising candidate to complement battery technology and improve electrical energy technology in a number of applications. This growing trend has arrived as a consequence of higher demand for portable systems and hybrid electric vehicles requiring high power pulses in a short time [1]. Supercapacitors based on electrical double layer capacitance can deliver energy with high rate due to simple charge separation mechanism similar to the conventional capacitors and the charge storage mechanism is reversible, it therefore features better cycling life compared to fuel cells and batteries in general making it more sustainable and environmentally friendly as well.

The very high capacitance featured by supercapacitors which makes them superior to the conventional capacitors are attributable to many factors including small distances that separate the opposite charges and the porous structure of electrode materials giving rise to high surface area [2]. To realise its full potential in today's competitive commercial market, all these requirements should be met at a reasonable price. As a consequence, carbon is the most common material for EDLC electrodes. Various forms of carbon have recently been reported; these include carbon black [3], CNTs [4], carbon aerogels [5], activated carbon [6] and graphene [7].

On the other hand, another different charge transfer mechanism can also operate via Faradaic reaction. The materials being investigated for this type of supercapacitor especially include metal oxides and conducting polymers. In this chapter, the emphasis is placed on the use of conducting polymer as it provides fast electron transfer via reversible redox reaction.

Graphene and polyaniline composite has attracted much interest in supercapacitor applications due to its high capacitance, good conductivity, low cost and ease of preparation [8]. Polyaniline or PANI is known to be one of the most studied materials due to its unique chemical and physical properties [9]. The polymer also shows good environmental stability in both doped and undoped states [10] and has probably been the most promising candidate among other conductive polymers to be used as a pseudocapacitor [8]. The main drawback associated with it though is the swelling of the polymer causing volume changes during charge/discharge cycle. To circumvent this problem, anchoring sites were introduced into the polymer matrix [11, 12].

Nanodiamond (ND) particles have received attention owing to their large-scale production with narrow size range, biocompatibility and facile surface modification [13]. Recently, there have been a large number of nanocomposite materials based on nanodiamond in a wide range of applications including sensors, biosensors, imaging and IR fluorescence, electrocatalysis, thermal applications and energy storage. The composite of polyaniline and nanodiamond has been reported as a corrosion inhibitor due to interactions at the molecular level of the two components. Electrochemical and chemical methods were employed for the synthesis of the composite in supercapacitor application [14, 15]. Particularly promising performance was exhibited for the chemically synthesized composite having detonation nanodiamond as an additional material to polyaniline producing ND-PANI composite with impressive stability after 10,000 charge/discharge cycles [14].

However so far, there is no report regarding the composite of these three materials – PANI, graphene and ND as a supercapacitor. Therefore, it is interesting to investigate the effect of addition of ND to the composite of graphene and PANI in terms of both the specific capacitance as well as the cycling stability, which is the topic of interest in this chapter.

5.2 Experimental

5.2.1 Materials

Detonation nanodiamond (4-6 nm) with more than 99% purity was purchased from Shandong Gold Group Jcoic Nanoscience & Technology Co., Ltd. Graphene oxide used was from Angstrom materials, the same specification as previously used in other chapters. Aniline, L-ascorbic acid, and potassium hydroxide were obtained from Sigma Aldrich in analytical grade. Hydrochloric acid was obtained from Fischer Chemical.

5.2.2 Reduction of graphene oxide

A greener approach was adopted for the synthesis of graphene in this chapter. Instead of using sodium borohydride, a more environmentally friendly reducing agent, L-ascorbic acid was used instead. The method was modified from that developed by Fernandez-Merino *et al.* [16]. For a typical synthesis, 2 mL of 5 mg/mL suspension of graphene oxide was sonicated in 100 mL of water for an hour then 0.04 g of L-ascorbic acid was added and briefly sonicated to dissolve the acid. The pH of the solution mixture was adjusted to 11 by dropwise addition of 1 M KOH. In a round bottom flask, the mixture was heated in an oil bath at 90 °C for an hour under vigorous stirring. Reduced graphene oxide was retained by vacuum filtration of the reaction mixture as previously described for the reduction of graphene oxide by NaBH₄.

5.2.3 Synthesis of Polyaniline, Graphene and Nanodiamond Composites

Aniline was first dried on CaH_2 for 4 days prior to the double vacuum distillation on Ar line to give colourless liquid. NMR was recorded for the distillate and showed that uncontaminated Aniline was obtained. The distillate was kept in a schlenk wrapped around with aluminium foil at 4 °C when not in use as the compound is sensitive to air and light. Synthesis of the PANI composite was done by in-situ polymerisation of aniline monomers in presence of graphene and/or detonation nanodiamond powder in 1 M HCl. Ammonium persulfate (with 1.5:1 molar ratio to aniline monomer in 1 M HCl) was added dropwise to the solution mixture under moderate stirring in an ice bath. The reaction was left to continue at an ice bath temperature for another 5 hours. Polyaniline and its composite were retrieved by vacuum filtration and several washings with ethanol and distilled water until the filtrate was colourless. The precipitate was dried in vacuum overnight at 50 – 60 °C to assure the complete water removal.

5.2.4 General Characterisation

SEM was carried out on a Hitachi S-520 based in the Chemistry Department which is equipped with Tungsten filament, accelerating voltage of 1 ~ 30 kV (1 kV step) and a 3-stage reduction Lens system. FTIR experiment was conducted with FTS6000 equipped with DuraSamplIR Diamond ATR. Purging of the system is required to remove all moisture from the equipment. Measurement was performed by placing the sample in direct contact with the diamond surface of the accessory. A background spectrum was recorded of the clean diamond surface and was subsequently used to subtract from the sample spectra.

UV-Vis spectroscopy was performed with Perkin Elmer Lambda 750S spectrometer. The details on the instrumentation for the Raman, XRD, and DLS measurements were as described in Chapter 2.

5.2.5 Electrochemical Measurements

A three-electrode system set up was initially used and the detailed arrangement is the same as that used throughout the thesis. The electrolyte employed for this work is 0.5 M H_2SO_4 and 6 M KOH. A two-electrode system was also set up for the electrochemical measurements in basic electrolyte. Polyaniline or its composite (active material) was ground to fine powder then mixed with carbon black as a conductive agent and a small amount of PTFE binder in a ratio of 85:10:5 by mass. The mixture was then dispersed in ethanol to form slurry, which was subsequently pressed at 1 N pressure onto Ni foam. The cell assembly is illustrated in **Figure 5.1** below.

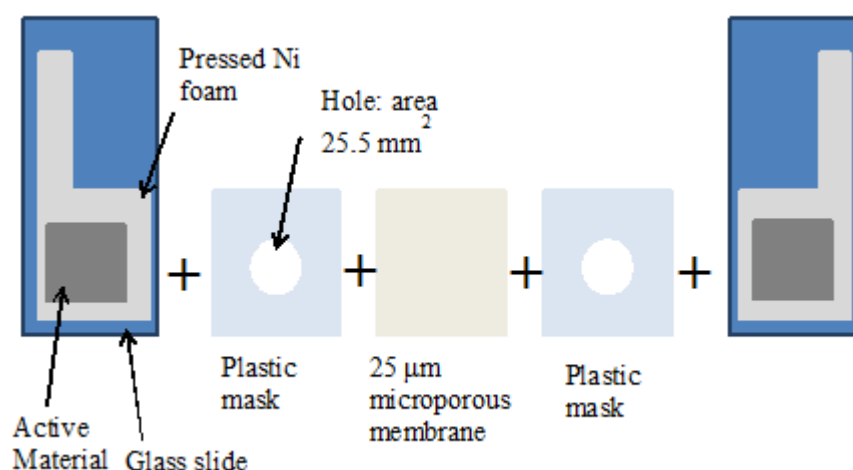


Figure 5.1 A 2-electrode cell set up for capacitance measurement of polyaniline and its composite

5.3 Results and Discussion

5.3.1 Preparation and characterisation of nanodiamond

Dispersion of nanodiamond powder (ND) to obtain individual particles is a challenge due to the attractive interaction between each nanoparticle via Van der Waals forces. To incorporate nanodiamond powder to polyaniline and composites, disaggregation must be carried out to obtain finer diamond particles. Annealing in air was found to be an effective and relatively straightforward method [17]. As the sp^2 carbon of ND can be oxidised to form oxygenated functional groups and thus the Van der Waals interaction caused by sp^3 carbon can be eliminated giving rise to finely divided ND particles. Thermogravimetric analysis (TGA) was first performed on a sample of detonation nanodiamond and the result is shown in **Figure 5.2** (a). The weight loss of ND sample started at around 400 °C to almost 560 °C. The temperature range between 425 °C to 450 °C was chosen as this is at the initial stage of the weight loss and before the sharp decrease. The experiment to heat ND powder at different temperatures and time periods was carried out. To compromise between the heating time and the corresponding weight loss, an optimal heat treatment was found to be at 437 °C for 5 hours, which resulted in about 30% weight loss.

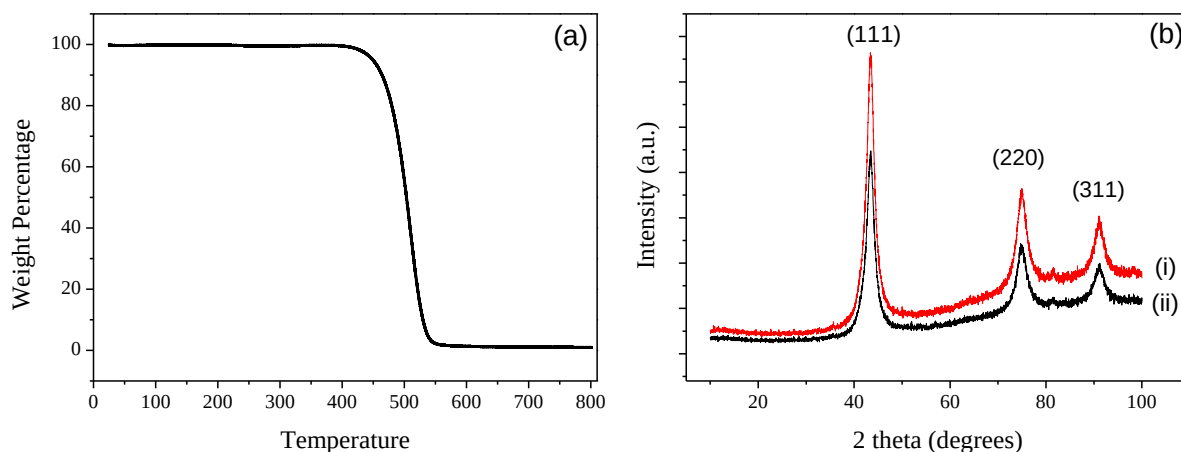


Figure 5.2 (a) TGA curves of nanodiamond powder (heating rate 1 °C per minute in air) and (b) XRD patterns of as-received nanodiamond (i) and after heat treatment (ii)

An X-ray diffraction pattern was then recorded for the heated ND in comparison to the as-received powder as shown in **Figure 5.2** (b). The reflection profiles of both non-heated and heated ND powders are similar in features and correspond to diamond-type cubic lattice. Three main peaks observed at 43.4°, 74.9° and 91.1° angles correspond to (111), (220) and (311) orientations respectively [18]. The small peak at 81.7° could be arisen from unknown impurity in ND powder during its synthesis. As no significant difference between the two samples was observed, this implies that heating in air does not affect the lattice structure of nanodiamond and no bulk graphitisation process occurred. From determining FWHM and Scherrer equation with a shape factor of 0.94 [19], an estimated particle size is found for the polycrystalline nanodiamond powder to be approximately 5.0 nm.

To further investigate the heat-treated ND powder, dynamic light scattering experiment was performed on the suspension of ND in water (neutral conditions). The intensity based average size of the heated ND is 4.6 (± 0.1) nm (27.5%) along with larger particles of around 640 nm and 1 μm . As for the as-received ND, average size by intensity is 6.3 (± 0.23) nm (24%) and larger particles of around 180 nm were also found. The contribution to the size distribution by intensity is affected also by the fact that larger particles carry more weight to the total

intensity than smaller particles. It is worth noting that the water suspension of the non-heated sample is considered unstable as a significant amount of aggregates was found at the bottom of the vial even only a few minutes after prolonged sonication. As a consequence, the size estimated from the DLS experiment is only accounted for those smaller particles that are stable in the suspension. This was not observed however for the case of the heated ND sample.

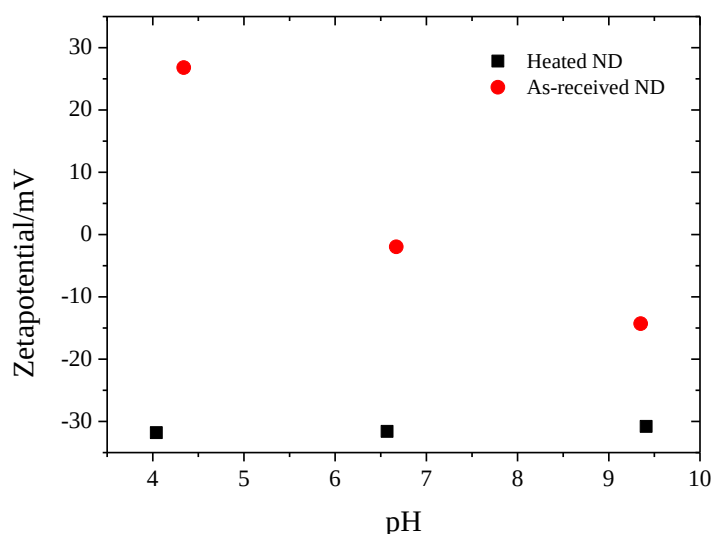


Figure 5.3 Zetapotentials of ND powder in water suspension with different pH values

Figure 5.3 shows the plot of measured zetapotential with respect to pH of the ND suspension for both as-received and heated ND samples. The stability of the suspension is reflected by its zetapotential. As for the treated nanodiamond, the zetapotential is around -31.0 to -32.0 mV regardless of pH. On the other hand, the zetapotential of the untreated ND decreases with the increase of pH. By convention, the heated ND can be classified as ‘stable’ over the whole pH range tested while the as-received ND remains unstable throughout. The increase to more positive zetapotential with increasing acidity of the untreated particles were explained [20, 21] as caused by the acid cleaning leaving oxygen groups on the surface; as pH is increased it becomes progressively more negative due to the OH groups of the solution.

Heat treatment is believed to result in the formation of oxygenated groups on the nanodiamond surface giving it a negative zeta potential and it is the repulsion between these oxygenated groups that stabilises the suspension. According to S. Osswald *et al.* [17], heating in air causes oxidation and hence removal of sp^2 carbon bridging the nanodiamond particles to clusters. The suspension is therefore more stable after heat treatment and also left with oxygenated groups on the nanodiamond surface. The almost constant zeta potential of the treated sample compared with the untreated one could therefore be attributed to the extent to which the surface groups were oxidised.

5.3.2 Reduction of Graphene Oxide by L-Ascorbic Acid

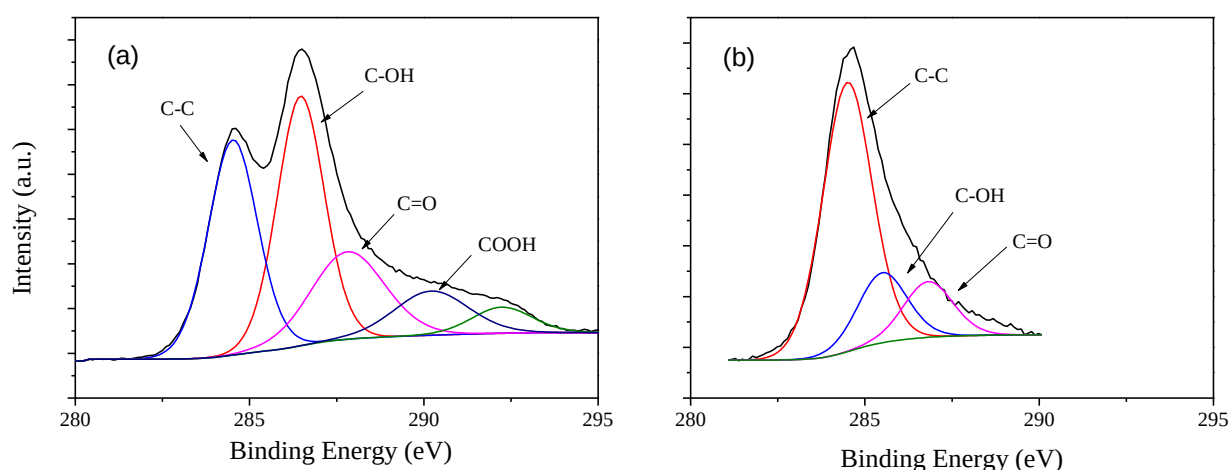


Figure 5.4 XPS spectra of graphene oxide (a) and reduced graphene oxide (b)

Graphene nanoplatelets (GNPs) were prepared by L-ascorbic acid reduction of graphene oxide. The surface composition of the GNPs was investigated by XPS. The spectra for graphene oxide and its reduced form are given in **Figure 5.4**. It is clear that the XPS spectrum of GO spans over a longer range of binding energy as a result of more oxygenated functional groups found in the sample compared to its reduced form. The C 1s graphitic band is observed at 284.5 eV for both samples. The peaks owing to C-OH and C=O are found at 285.5 eV and 286.8 eV respectively in **Figure 5.4** (b) for the reduced graphene oxide

spectrum. The surface composition of the graphitic C 1s peak also increases from 31.5% in GO to 68.2% after the reduction. From the elemental analysis, the oxygen content in the sample is also lowered from 35.8% in GO to 24.9% indicating that deoxygenation had occurred during the reaction. The XPS analysis hence suggests the successful reduction of graphene oxide by ascorbic acid.

To confirm the reduction of graphene oxide by this method, FTIR spectroscopy was carried out and the spectra obtained for graphene and its reduced form are presented in **Figure 5.5**.

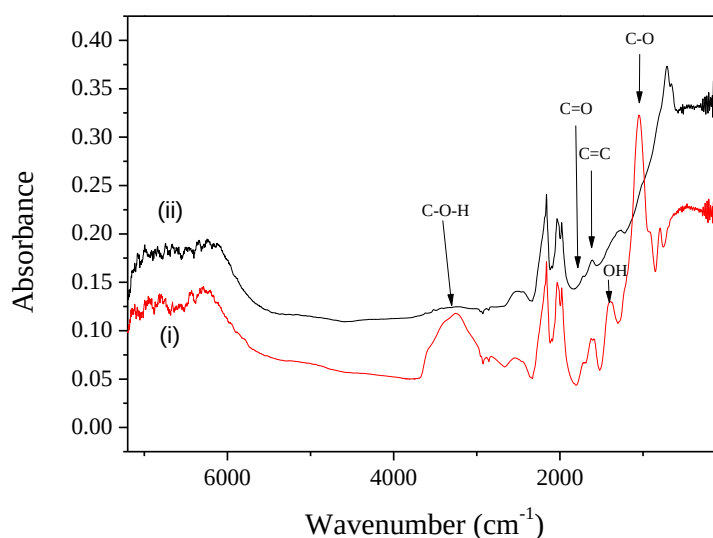


Figure 5.5 FTIR spectra recorded for graphene oxide (i) and its reduced form, graphene nanoplatelets (ii)

Graphene oxide spectrum (i) shows characteristic features owing to several oxygenated functional groups on carbon [22]. The intense broad band observed at $3000 - 3400 \text{ cm}^{-1}$ arises from an O-H stretching mode. A relatively weak and narrower peak at around 1720 cm^{-1} is associated with stretching vibrations of C=O from carbonyl and carboxyl groups. In the similar region to this peak but slightly more intense, at approximately 1630 cm^{-1} is a peak reflected stretching vibrations of C=C at sp^2 carbon centre. Another band at around 1400 cm^{-1}

corresponds to a C-O stretch mode; the sharp and very intense peak at 1060 cm^{-1} comes from absorptions of C-O-C bond present in epoxy and ether groups.

After reduction by ascorbic acid, the FTIR spectrum in (ii) shows marked contrast to the spectrum of graphene oxide in (i) [16]. Only very weak band observed for the O-H stretching mode at around 3200 cm^{-1} . The intensity of the two bands at 1720 and 1630 cm^{-1} is also significantly reduced. The disappearance of the sharp peaks at 1400 cm^{-1} and 1060 cm^{-1} is obvious. The FTIR results hence conform to the XPS analysis and suggest the removal of the majority hydroxyl groups during reaction of graphene oxide with ascorbic acid. Functional groups with C-O single bond such as epoxides, alcohols, ethers, and peroxides were also reduced. The suppressed intensity of the C=O band in graphene platelets signifies the removal of this group possibly related to those present as carbonyls.

5.3.3 Synthesis of Polyaniline Composites and Characterisation

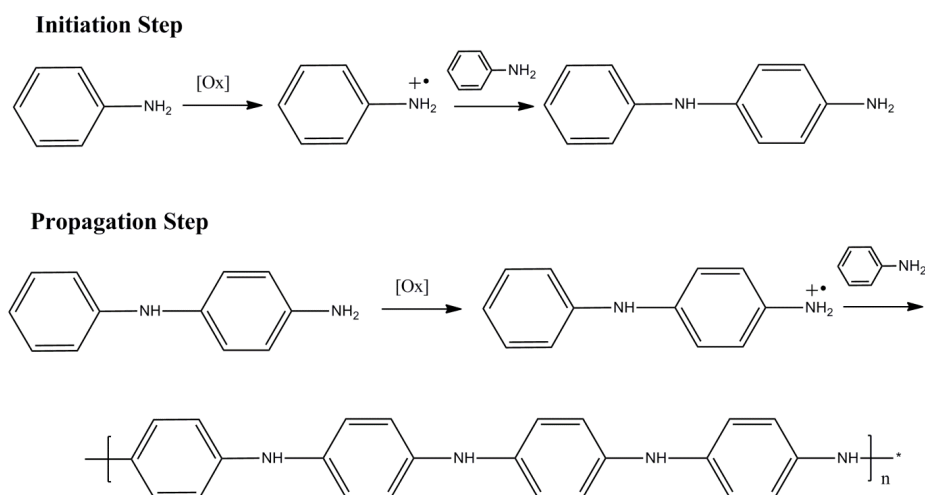


Figure 5.6 illustrates the oxidation polymerisation mechanism of polyaniline from aniline monomers [23]

Polyaniline (PANI) and its composites were synthesised by in-situ polymerisation in presence of graphene and/or nanodiamond as detailed in section 5.2.3 where ammonium persulfate

acting as an oxidative initiator was added slowly to the solution mixture of the starting materials at low temperature. During the course of the reaction, the mixture appeared to be dark blue in colour at the beginning and slowly turned into dark green. The dark green colour of the reaction mixture indicates the formation of polyaniline. The dark blue colour arose at the initial state due to the formation of pernigraniline, which then turned into a more stable state as emeraldine, which leads to the dark green colour of the solution during the progress of the reaction and also the colour of the product collected. During filtration and washing with ethanol and water, the filtrate was light blue and rusty pink in colour. These colours observed are associated with oxidised aniline dimers called 'semidines' [24] which later form trimer nucleates and other aniline oligomers. As a result, it is essential to wash the precipitate many times until colourless filtrate was achieved in order to maximise the conductivity of PANI.

5.3.3.1 XRD

A range of structural and chemical characterisation techniques was carried out for the synthesised PANI and its composites with 3%ND and/or 6%GNP by weight. It should be pointed out however that this value of weight percentage refers to the mass loading of the materials in the synthesis and not its actual composition. Powder diffraction patterns of PANI and its composite with GNPs and ND show characteristic peaks owing to emeraldine salt [25]. The reflections at the following 2θ angles; 15.7° , 21.0° , 25.4° and 27.4° can be indexed to (011), (020), (200) and (121) respectively as indicated in **Figure 5.7**. XRD results therefore verify the successful polymerisation of aniline.

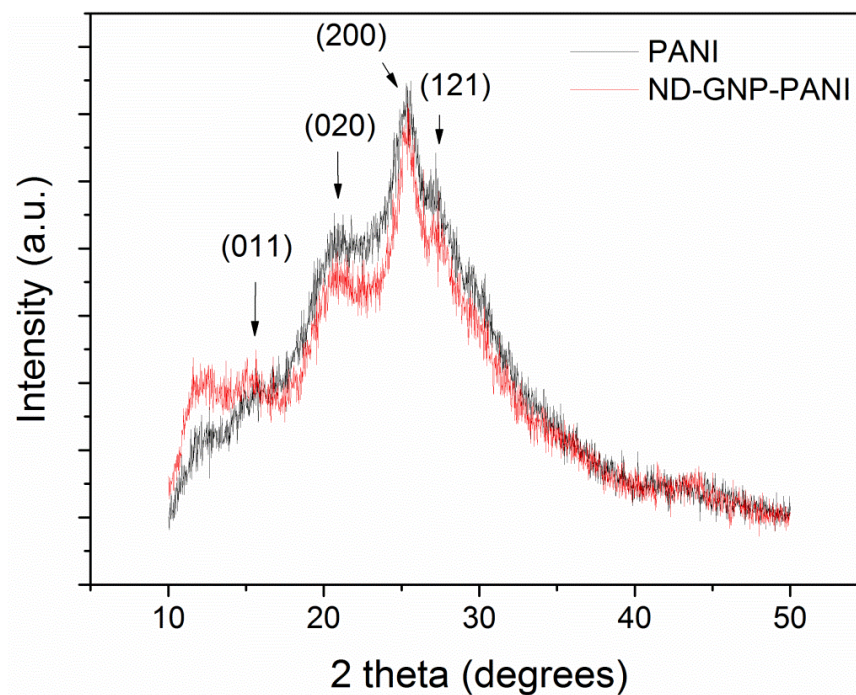


Figure 5.7 XRD patterns of PANI and nanodiamond-graphene-PANI composite

5.3.3.2 Raman Spectroscopy

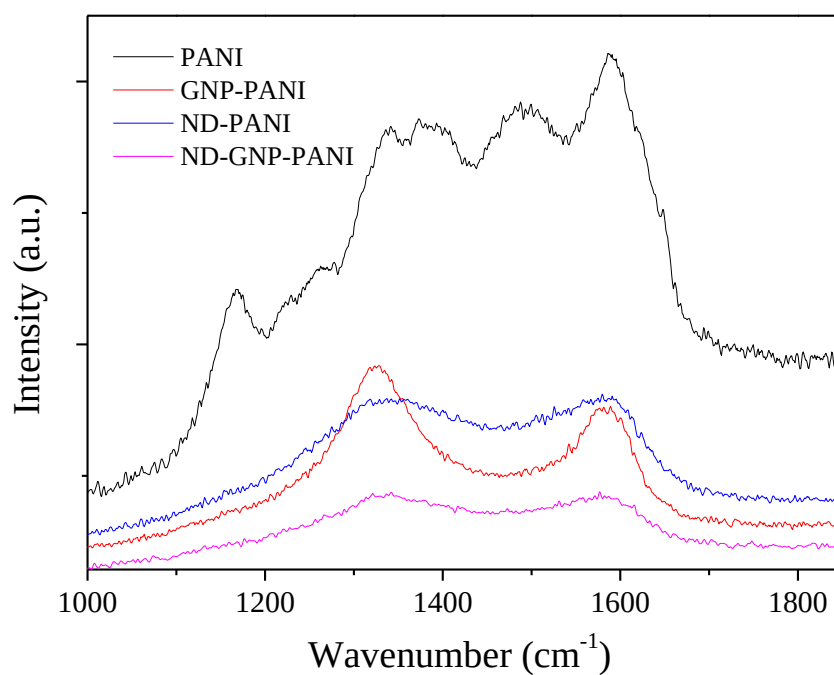


Figure 5.8 Raman spectra recorded for polyaniline (PANI), its composites; with graphene (GNP-PANI), with nanodiamond (ND-PANI) and with both graphene and nanodiamond (ND-GNP-PANI)

Raman spectroscopy, as a tool to probe microstructure of carbon based materials [26], was also performed on PANI and ND-GNP-PANI with additional composite samples; ND-PANI and GNP-PANI for comparison purposes. The recorded spectra are shown in **Figure 5.8**.

Raman spectra were recorded by drop-casting the water suspension of each sample on Si substrate. PANI sample shows the characteristics of polyaniline as suggested in the literature [27]. Assignments of the multiple Raman peak features of PANI are based on a comparison with established results from literature [28-30]. The peak at 1583 cm^{-1} is due to C=C bond stretching vibration of quinonoid ring, Raman shift at 1488 cm^{-1} is arisen from C=N stretching vibration also of the imine group of quinoids. This C=N bond is characteristic of the polaron unit of PANI. A shift at 1396 cm^{-1} can be ascribed to C-C bond stretch also of the quinonoid ring. Two peaks at 1342 and 1227 cm^{-1} are both attributed to C~N⁺ bond stretching modes of the semiquinone or benzenoid. The vibration of this polaronic group is therefore indicative of the conducting state of polyaniline. The peak at 1165 cm^{-1} is due to the in-plane bending of C-H bond in quinonoid ring. This result suggests the success in preparation of the conducting state of polyaniline.

The PANI composite with ND only sample (ND-PANI) shows two broad peaks at around 1300 and 1600 cm^{-1} regions, which are characteristic of nanocrystalline diamond. By contrast, PANI composite with GNPs only show peaks, which correspond to graphitic carbons; D and G bands at 1350 and 1620 cm^{-1} respectively. The higher intensity of the D band than the G band is ascribed to the defects and more disordered structures of GNP. Hence this notable difference of the I_D to I_G is prominent in GNP-PANI composite. It has to be borne in mind however that Raman is a spectroscopic technique that has approximately 50 times greater sensitivity towards sp^2 than sp^3 carbon [13]. In the three-component composite, ND-GNP-PANI, only two bands are observed in similar regions as seen for ND-PANI and

GNP-PANI but with the more equal I_D and I_G . The fact that the laser excitation wavelength is at 633 nm (red light region), which is much less sensitive than for example an equipment with a blue/green laser as Raman scattering efficiency is proportional to λ^{-4} (λ is laser wavelength) [31], could also contribute to the result seen. Another possible reason could be that polyaniline was actually covered with graphene platelets as observed in a report on nanocomposite of graphene and polyaniline where the Raman spectrum of the composite only exhibited the D and G bands of graphene in contrast to the more complex multiple bands observed in pure polyaniline [32].

5.3.3.3 UV-Vis Spectroscopy

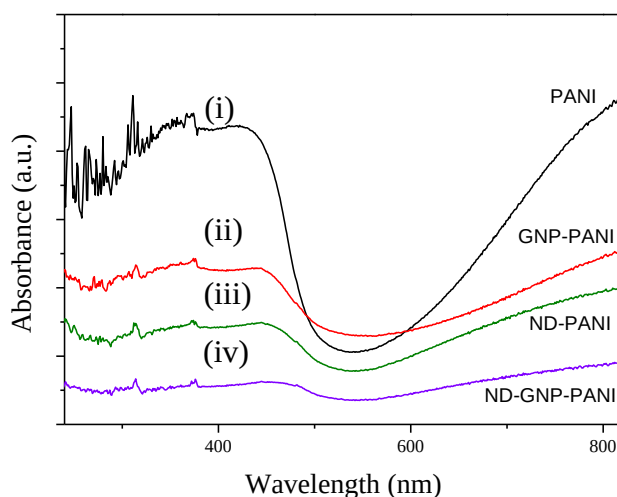


Figure 5.9 UV-Vis spectra of PANI (i) and its composites; GNP-PANI (ii), ND-PANI (iii) and the three component composite ND-GNP-PANI (iv)

UV-Vis was conducted to confirm the presence of the conducting state of PANI and the composites. The absorption maxima of the polymer composites are compared in **Figure 5.9**. Seen across all four samples are broad absorption bands at around 430 nm and 800 nm. The peak at 430 nm can be assigned to protonation of PANI chain and related to the broad band at 800 nm which is caused by transitions of polarons [33]. The intensity of the two bands is differed amongst the samples. This difference could distinguish pure polyaniline sample

(PANI) from the rest, which are in composite forms. It is also interesting to note that the 800 nm absorption is lowest for the three-component composite (ND-GNP-PANI) reflecting the lowest amount of polyaniline present confirming that the composite formation had taken place. Small absorption peak at around 370 nm is ascribed to transitions from polaron to π^* benzenoid to quinoid excitonic transition [34]. All these transitions are characteristic of emeraldine form of polyaniline and thus verify that the conducting state of PANI was successfully synthesised in all samples tested.

5.3.3.4 FTIR

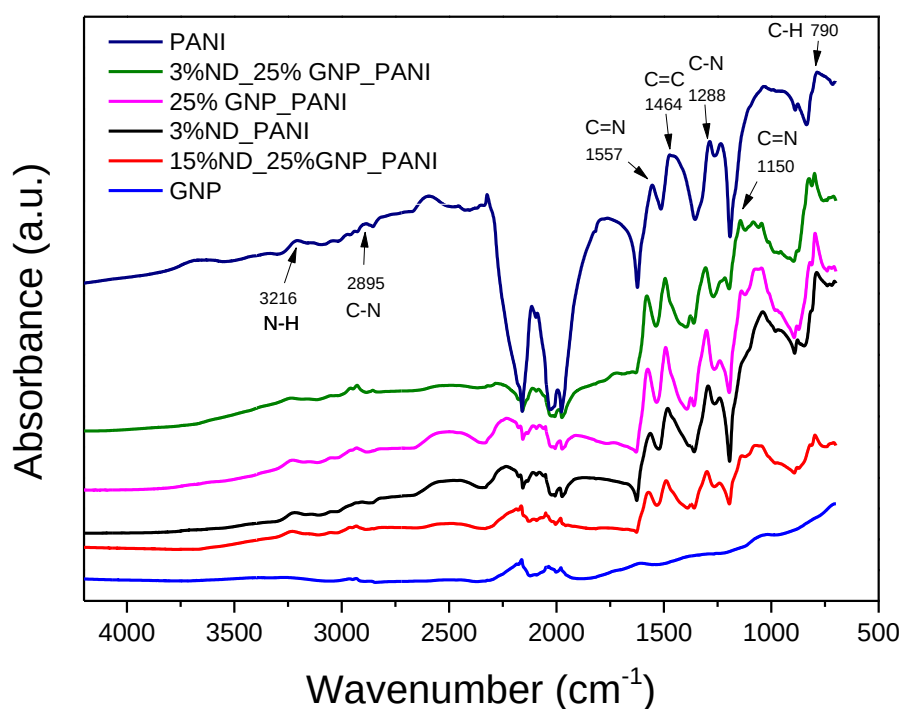


Figure 5.10 FTIR spectra of polyaniline composites in comparison with polyaniline alone (PANI) and GNPs. The different loadings of GNP and ND were also added to PANI as indicated in the plot

The presence of particular groups on polyaniline and its composites can be investigated further by means of FTIR. The absorption spectra of polyaniline and its composite with graphene and nanodiamond are shown together in **Figure 5.10**. Characteristic peaks owing to fundamental structural units in polyaniline chain can be observed across PANI and composite

samples, and can be assigned as follows [28]. A weak band at 3216 cm^{-1} is assigned to N-H stretching vibrational mode, while another weak band at 2895 cm^{-1} can be ascribed to C-N stretch of secondary aromatic amine in the form of N-benzenoid-N. C=N double bond shows a band at 1557 cm^{-1} . Very close to this band, a peak at 1464 cm^{-1} is owing to C=C bond stretch. Both of these bands are arisen from the stretching mode in quinoid and benzenoid structures. C-N bond stretching of N-Benzenoid-N contributes to absorption maximum at 1288 cm^{-1} . Another C=N bond stretch, which comes from N=quinoid=N part exhibits a peak at around 1150 cm^{-1} . In the red region, a peak at 790 cm^{-1} is attributed to aromatic C-H bending out of plane of aromatic ring.

5.3.3.5 SEM

For SEM analysis, PANI and 25% GNP-PANI samples prepared with different composition of ND were investigated. The powder samples were simply spread on carbon sticky tape prior to being examined under the electron microscope. In general, globular structure can be observed in most of the samples at lower magnification. Comparison of the morphology of polyaniline and 25wt% graphene-polyaniline with different amount of nanodiamond loading can be elucidated upon higher resolution. Fibrous morphology can be seen as depicted in **Figure 5.11** (d) for 25%GNP-PANI sample, which is the main difference from the pure PANI sample in **Figure 5.11** (a). The average diameter of the nanofibers is estimated to be in the range between 100 to 200 nm. The nanofiber nature is expected as PANI has the intrinsic property to grow in 1-D nanowires differentiating it from other conducting polymers [35].

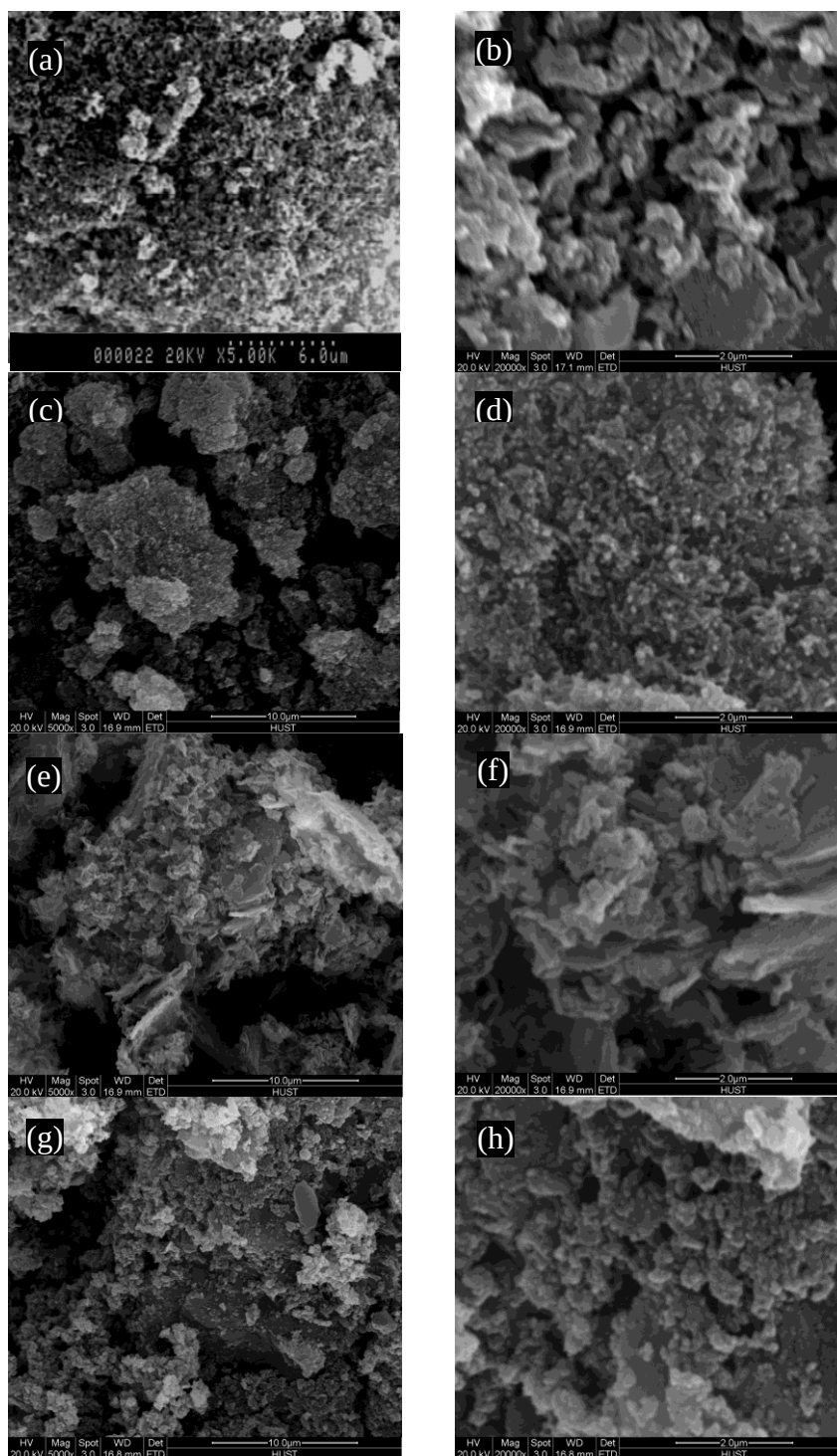


Figure 5.11 SEM micrographs of (a-b) pure PANI (c-d) 25%GNP-PANI (e-f) 3%ND-25%GNP-PANI and (g-h) 15%ND-25%GNP-PANI

It can therefore be concluded from the SEM analysis that nanofibrous structure was formed for the 25% GNP-PANI composite. Electrochemical characterisation was also carried out to investigate also the effect from different morphology observed among each composite.

5.3.4 Electrochemistry in 3-Electrode Cell System

Polyaniline and its composites were electrochemically characterised by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). Samples were dispersed in 7:3 water to ethanol mixture (2 mg/mL). This is a compromise between good dispersion and droplet's stability when coated on glassy carbon electrode. 5 μ L of the dispersion was drop-casted on the GCE and left to dry. The estimated sample weight is therefore 10 μ g for each electrode assuming good dispersion of the sample.

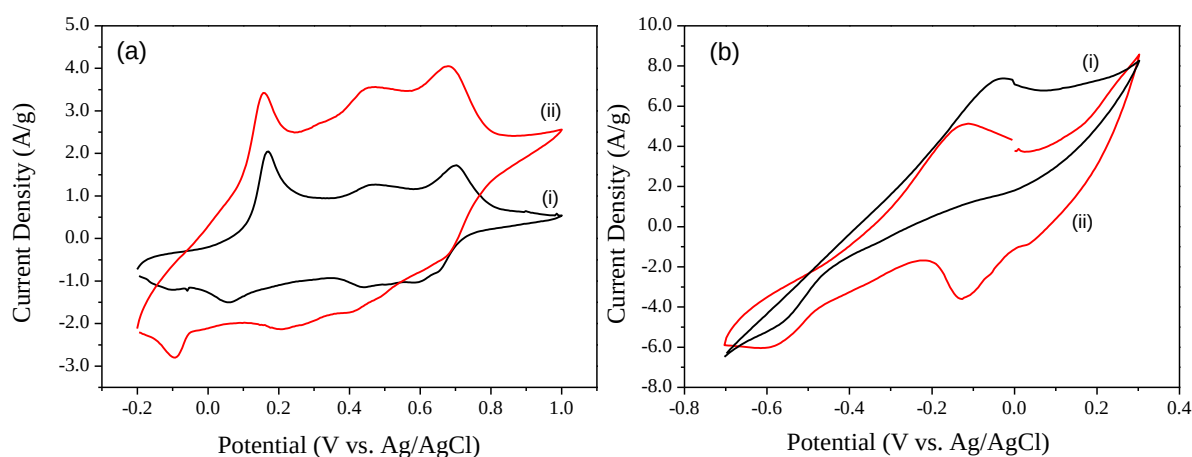
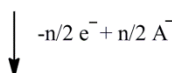
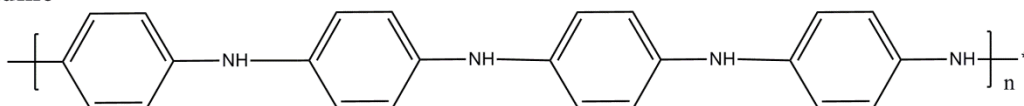


Figure 5.12 Cyclic voltammograms of PANI (i) and ND-GNP-PANI (ii) in different electrolyte; (a) in 0.5 M H₂SO₄ and (b) in 6 M KOH utilising 3-electrode cell set up

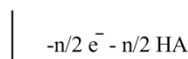
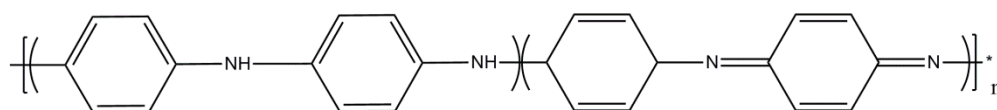
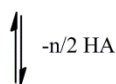
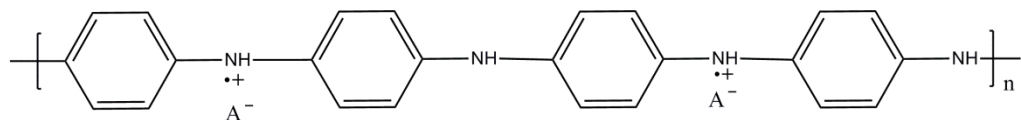
The composite used for this experiment was 3 wt% ND and 6 wt% graphene with PANI and will be shortened as ND-GNP-PANI. The three main oxidation peaks on CV in **Figure 5.12** are well recognised to be for the transitions between three distinct oxidation states of polyaniline, leucoemeraldine, emeraldine and pernigraniline [15]. The structures of the three oxidation states of PANI are illustrated below in **Figure 5.13**. Consider the CV of PANI (i) in **Figure 5.12**, the anodic peak at 0.17 V and the corresponding cathodic peak at 0.05 V are attributable to the redox reaction between leucoemeraldine and the polaronic emeraldine forms. The second redox couple at 0.47 V and 0.44 V is arisen from the transition between benzoquinone and hydroquinone forms of emeraldine. The forward peak at 0.7 V is due to

the oxidation reaction of the emeraldine form to the bipolaronic pernigraniline form. By contrast to the CV in acid, the voltammograms recorded in 6 M KOH only show one redox couple at around -0.12 V. This is consistent with that found for graphene-PANI composite describing the peaks to be due to the electron transfer between leucoemeraldine which is semiconducting and the conducting polaronic emeraldine states [8].

Leucoemeraldine



Emeraldine



Pernigraniline

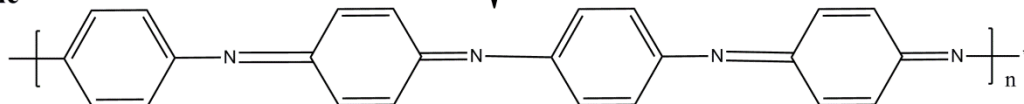


Figure 5.13 Chemical structures of the electrochemically active forms of PANI [36]

The charge storage capacity of PANI and its composites or more precisely the specific capacitance can be evaluated following the simple expression

$$C = q/V$$

where q is the voltammetric charge and V is the potential window applied. As the anodic and cathodic charges in the CV above are not ideally symmetric, the average charge from the

integrated area under the CV curve was hence considered for the determination of specific capacitance.

$$C = \int_{E_1}^{E_2} i(E) dE / 2(E_2 - E_1)mv$$

The specific capacitance, C was calculated according to this equation where E_1 and E_2 are the cutoff potentials in the CV, m is the mass loading of the sample and v is the scan rate [37]. From the voltammograms shown in **Figure 5.12**, the specific capacitance of PANI and ND-GNP-PANI composite were found to be 178 F/g, 377 F/g in 0.5 M H_2SO_4 and 256 F/g, 367 F/g in 6 M KOH respectively. This shows the increase in capacitance when PANI was composited with graphene and nanodiamond powder. The higher specific capacitance found in the case of PANI in 6 M KOH compared to that in 0.5 M H_2SO_4 could be because of the higher electrolyte concentration of KOH than H_2SO_4 .

Electrochemical test in 3-electrode system is useful for providing preliminary information on the characteristics of the redox peaks of polyaniline and its composite in different electrolytes. However, due to infinitesimal active mass of the material used and the dependence on the degree of dispersion of the sample, the capacitance calculated from this test is therefore not entirely reliable. Two-electrode test cell also resembles the packaged cell capacitor in terms of physical configuration and internal voltage hence provides better indication of a material performance than a three-electrode set up [38]. A 2-electrode cell system was then developed as a test system in 6 M KOH electrolyte as illustrated in **Figure 5.1**.

5.3.5 Electrochemistry at 2-Electrode Cell System

5.3.5.1 Low Loading of Graphene and Effect of Nanodiamond

In this 2-electrode system, the features observed on CV are differed from the 3-electrode system previously described. Specific capacitance, C_{sp} can be calculated from the CVs in **Figure 5.14** (a). Polyaniline shows a low C_{sp} of 88 F/g, but this increases to 175 when 3% ND was added. However, a large increase in C_{sp} is observed when PANI was composited with 6 wt% of graphene giving rise to a C_{sp} of 314 F/g. This higher C_{sp} dropped slightly to 263 F/g when 3 wt% ND was added to the GNP-PANI composite. Apart from CV, galvanostatic charge-discharge can also evaluate the specific capacitance of a sample. The specific capacitance of pure PANI albeit relatively low is comparable to the value reported earlier [8] for two-electrode system. In addition, measurement technique can affect the specific capacitance significantly, especially for the two-electrode and three-electrode system among which the difference can be by a factor of 3 or 4 [14, 38].

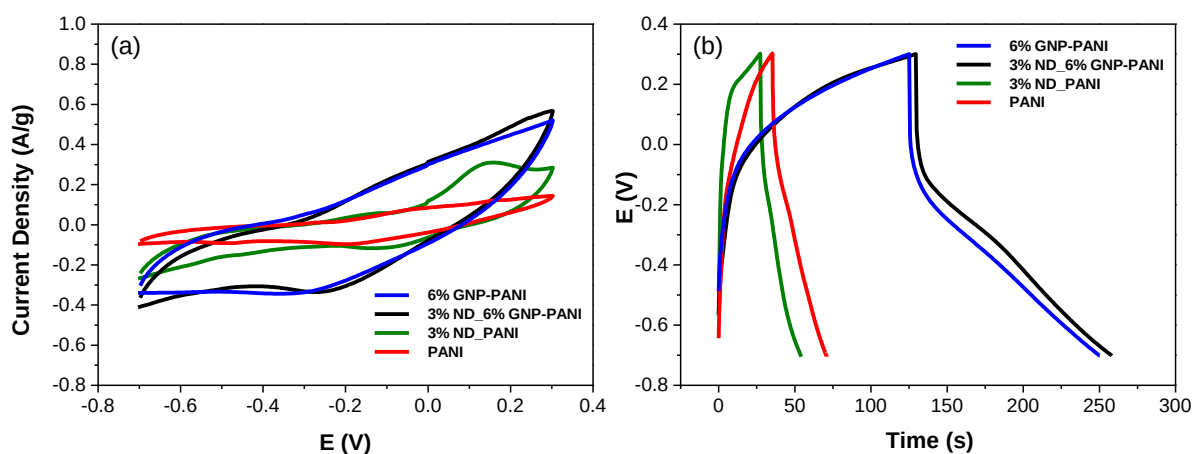


Figure 5.14 (a) shows CV of PANI and its composites electrodes in 6 M KOH at 2 mV/s and (b) shows the galvanostatic charge-discharge curve of the same samples in 6 M KOH

Galvanostatic charge discharge technique involves applying a constant current to a working electrode and its change in voltage is measured and plotted against the time period of the

change within the cutoff limits [39]. The information obtained from the plot provides insight into how a supercapacitor works under applied positive and negative current of the same magnitude or in other words under charging and discharging conditions. Therefore, GCD is a technique resembling the performance of a supercapacitor in more practical situation. Numerous successive cyclings over the applied current density also allows the assessment of the cycling stability to be measured.

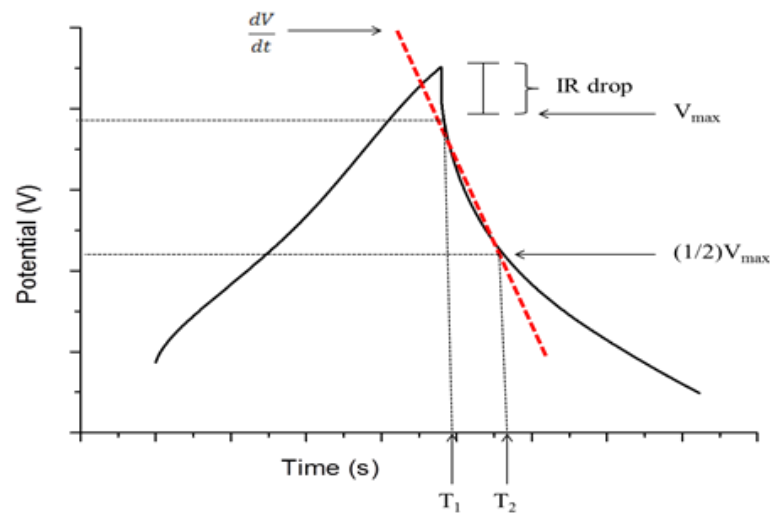


Figure 5.15 A diagram shows the method for calculation of specific capacitance from galvanostatic charge discharge curve

Specific capacitance can also be calculated from the GCD curve as outlined in **Figure 5.15**. It is a good practice to omit the instant vertical drop of voltage at the initial discharging period as this drop accounts for the IR drop, which is the internal resistance of the system. The gradient of the discharging curve is determined by

$$\frac{dV}{dt} = \frac{(V_{max} - \frac{1}{2}V_{max})}{(T_2 - T_1)}$$

The reason to use only the upper half of the curve is due to the non-ideal behaviour at the lower part, which could potentially leads to the overestimation of the capacitance [38]. This gives rise to the specific capacitance according to the equation below.

$$C = \frac{\int_{V_1}^{V_2} I dV}{2vm\Delta V}$$

GCD measurement was carried out in 6 M KOH with potential range from 0.3 V to -0.7 V and the results are plotted in **Figure 5.14** (b). The non-linear GCD profiles observed differ from the typical linear characters revealed by EDLCs, indicative of a redox reaction and pseudocapacitive nature of polyaniline [40]. At 0.5 A/g of applied current density, initial C_{sp} value estimated from the charge-discharge curve for 6% GNP-PANI is around 280 and 250 F/g for the samples with and without ND respectively. On the other hand, ND-PANI exhibited capacitance of 96 F/g. For this experiment PANI was measured at 0.1 A/g and showed a capacitance of 110 F/g. Again the increase in C_{sp} is obvious when PANI is in composite with graphene regardless of ND addition. The slightly higher C_{sp} of PANI than ND-PANI in contrast to what observed for CV is owing to the lower applied current density. In general, at higher charging rates the redox process is surface-confined and only limited area of electrode material becomes involved thus lower capacitance [40]. However, overall a similar trait can be deduced from the CV and GCD experiments. At this low loading (6wt%), graphene showed to largely enhance the specific capacitance of polyaniline while nanodiamond did not show such significant contribution to the capacitance of either PANI or GNP-PANI. It is worth pointing out that the lower value observed with the 2-electrode cell compared to the 3-electrode cell is also seen in the literature for low applied current density [38].

Cycling stability of the four samples was assessed by 300 successive GCD cycles between 0.3 V to -0.7 V with the initial and final specific capacitances presented in a bar chart below (**Figure 5.16**). From the chart, two obvious phenomena can be observed; without ND capacitance declines to about 80% but increases by roughly 30% when ND was added with either PANI or GNP-PANI. The relatively poor stability of PANI could result from swelling, shrinkage or breaking of the polymer chains undergoing redox reactions at high voltages leading to deterioration of conductivity and volumetric changes [41]. From this preliminary outcome, it is worth investigating further on the effect from variation of the loading of graphene and nanodiamond. The slight increase in capacitance after 300 cycles of the ND composites could be explained by the more available electrochemically active sites for the charge transfer to take place [8, 42, 43].

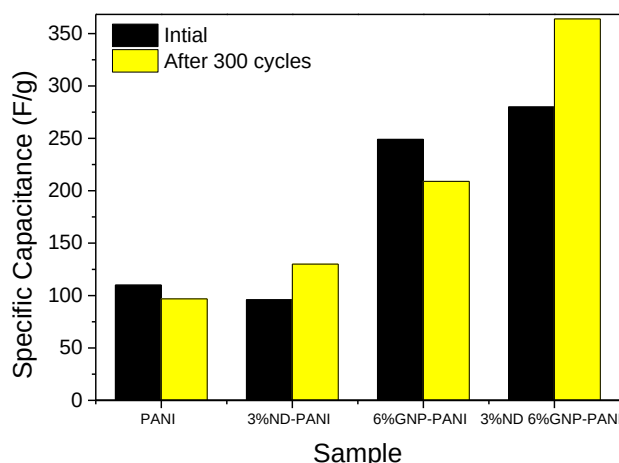


Figure 5.16 Bar chart shows retention of specific capacitance of PANI and its composites electrode after 300 charge-discharge cycles in 6 M KOH at 0.5 A/g

As a comparison, unheated ND powder was also embedded in the polymer to test the stability upon 300 GCD cycles at 0.5 A/g. The specific capacitance was 88.4 F/g and increased to 97.2 F/g after the stability test, which is about 110% of the initial capacitance. The good retention of capacitance is not surprising since at low pH the zeta potential of the as-received ND in

Figure 5.3 is almost +30 mV indicating the better dispersion of its suspension than at neutral

or higher pH. The good dispersion of the untreated ND particles among PANI matrix could therefore be responsible for the retention observed in both cases. The lower specific capacitance compared to heated ND-PANI, on the other hand, is possibly due to the stronger interaction between the positively charged aniline monomers and the oxygen functional groups on the heated ND particles at the low pH of the synthesis conditions in 1 M HCl.

5.3.5.2 Different Loadings of GNPs at Fixed ND Loading

First, the loading of nanodiamond powder was fixed at 3wt%. Again the C_{sp} was evaluated from the voltammetric charge from CV at 2 mV/s scan rate and plotted in **Figure 5.16** within the same range of potential from -0.7 V to 0.3 V. It must be noted that the specific capacitance of the 2-electrode cell can be calculated from CV in a similar manner as outlined in the equation above but with a factor of 4 such that;

$$C_{electrode} = 4xC_{cell}/m$$

where $C_{electrode}$ is the C_{sp} of interest and C_{cell} is the capacitance value obtained from the integral charge of the CV. The factor of 4 is arisen from two reasons. First is that when capacitors are connected in series, $C_{cell} = 2xC_{electrode}$ and the mass of an electrode is only half that of the total cell.

The different GNPs loadings studied are 6 wt%, 15 wt%, 25 wt% and 50 wt%. As observed from the CVs in **Figure 5.17**, a general trend of increase in specific capacitance with the increasing loading of GNPs can be deduced. From the value of 263 F/g for the 6 wt% graphene, this rose to 390 and 659 F/g when the amount of added graphene was raised to 15 wt% and 25 wt% respectively. However, the C_{sp} reduces slightly to 566 F/g with 50 wt% graphene loading. The boost in C_{sp} by the addition of graphene is because graphene itself can also provide electrochemical double layer capacitance along with pseudocapacitance from

PANI. The large surface area of graphene can act as the site for growing of polyaniline fibers as suggested by the SEM images and hence provide higher active surface area of the electrode for supercapacitor. The main CV features observed in the 3-electrode set up are not present in the case of 2-electrode cell. This is typical for 2-electrode test cell, where rectangular shape of CV curve is observed for an ideal symmetrical ultracapacitor. The irregularity of the CV curve is owing to one electrode being exposed more to the higher voltage, which leads to stronger degradation [14, 44].

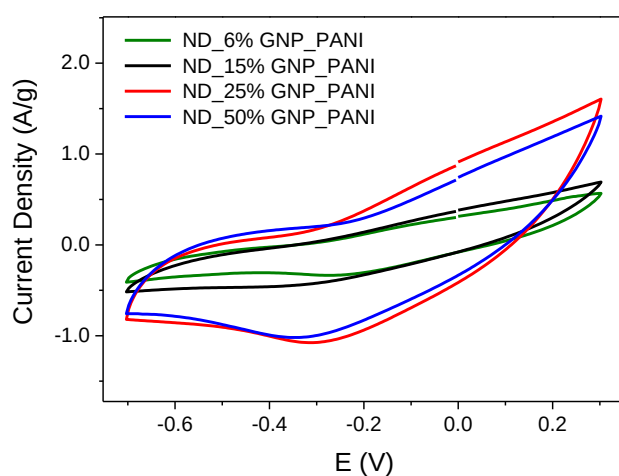


Figure 5.17 CV of ND-GNP-PANI composite with 3wt% ND and varied loading of graphene in 6 M KOH at 2 mV/s employing two-electrode cell set up

GCD was also investigated on these samples based on the same set up at 0.5 A/g for the lower capacitance samples and at 2.0 A/g for the higher capacitance samples. The resultant GCD curves are plotted in **Figure 5.18** below. At 0.5 A/g, 6 wt% and 15 wt% graphene in ND-PANI composites exhibited specific capacitance of 280 F/g and 319 F/g respectively. On the contrary, at 2 A/g applied current density, 25 wt% and 50 wt% graphene composites showed nearly twofold higher specific capacitance of 551 F/g and 609 F/g. This finding iterates the trend of increasing capacitance towards higher loading of GNPs.

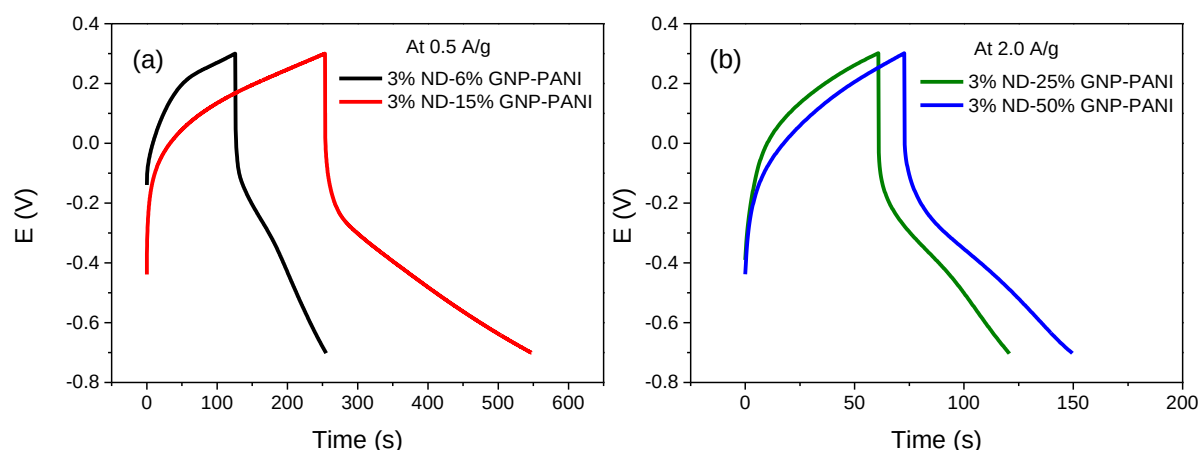


Figure 5.18 GCD (a) at 0.5 A/g and (b) 2.0 A/g for ND-GNP-PANI composites with different ND compositions as indicated in the diagrams

However, as the aim of the project is to overcome the shortfall in the cycling stability of the conducting polymer as a supercapacitor, successive GCD cycling of the samples with different GNP loading was investigated. **Figure 5.19** shows explicitly the initial and final specific capacitance after 300 GCD cycles at 0.5 A/g for 6 wt% and 15 wt% and 2 A/g for 25 wt% and 50 wt% respectively. The sample with low loading of GNP is the only sample with increasing of capacitance after the stability whereas the highest loading of graphene shows the largest drop in capacitance with only 80% retention after 300 cycles. The moderate loading in the middle exhibits only a small drop of capacitance retaining about 90% and 97% in the case of 15wt% and 25wt% graphene loading respectively. It should be reminded that all of these samples are composited with 3 wt% of ND powder thus the high retention of capacitance is expected. At this point, it was demonstrated that although increasing amount of graphene could enhance the capacitance of the sample but too high loading could have a negative effect on the cycling stability of the supercapacitor.

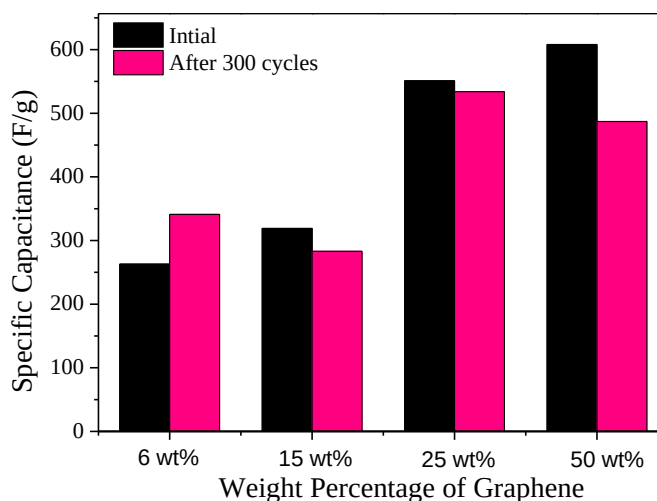


Figure 5.19 A bar chart presents the capacitance retention after 300 GCD cycles in 6 M KOH of 3 wt% ND-PANI composite with different loadings of GNPs

5.3.5.3 Different Loadings of ND at Fixed GNP Loading

More electrochemical testing was carried out on 25 wt% GNP-PANI as it showed to possess relatively high capacitance with good stability over 300 GCD cycles. It is therefore interesting to see how the variation on the amount of added ND powder will affect this. The loading of ND was varied from 3 wt% to 15 wt% denoted as 3%ND-25%GNP-PANI and 15%ND-25%GNP-PANI respectively. For a comparison 25 wt% GNP-PANI composite was also prepared without ND (25%GNP-PANI). Cyclic voltammetry was conducted at 2 mV/s. Similar features were observed in all three samples. The resultant specific capacitance from the CV is very similar among the three samples in the value of around 650 F/g as plotted in **Figure 5.20 (a)**.

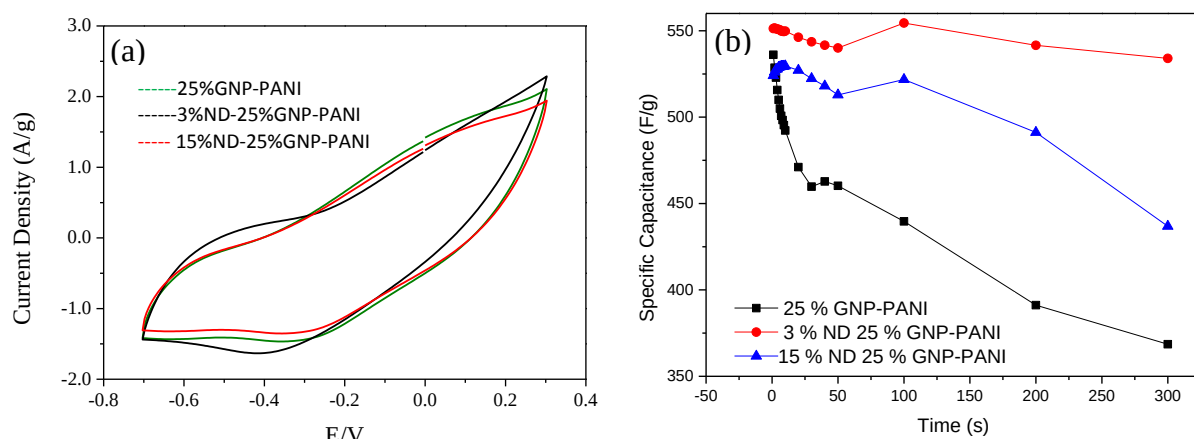


Figure 5.20 (a) CV in 6 M KOH and (b) plots of C_{sp} against number of GCD cycles for 25wt% GNP-PANI with different loading of ND

The galvanostatic charge discharge experiment was also carried out at 2 A/g. The specific capacitance from GCD is plotted against the cycle number in **Figure 5.20** (b). The initial capacitance at the first few cycles is approximately 550 F/g with the 15%ND-25%GNP-PANI showing the slightly suppressed capacitance of 525 F/g. The better retention of capacitance is clearly exhibited by 3%ND-25%GNP-PANI sample reaching about 97% of the initial capacitance. The stability of the composite material however did not directly increase with the increase in ND loading as exemplified by the 15%ND-25%GNP-PANI sample where only about 85% of the initial capacitance was indeed maintained. Despite this fact, the even poorer stability was observed with the 25%GNP-PANI composite without ND of which only 69% retention was achieved. It was suggested that the improved stability when ND is embedded in PANI was arisen from the hydrogen bonding between the amine groups of aniline and the carboxylic acid group of the heated and hence oxidised ND [14]. The reason for the suppressed stability after higher amount of ND (15wt%) was added is still open for discussion. One possible explanation could be the non-conductivity of the ND powder [45], which could disrupt the conductive pathways during charging and discharging process of the supercapacitor.

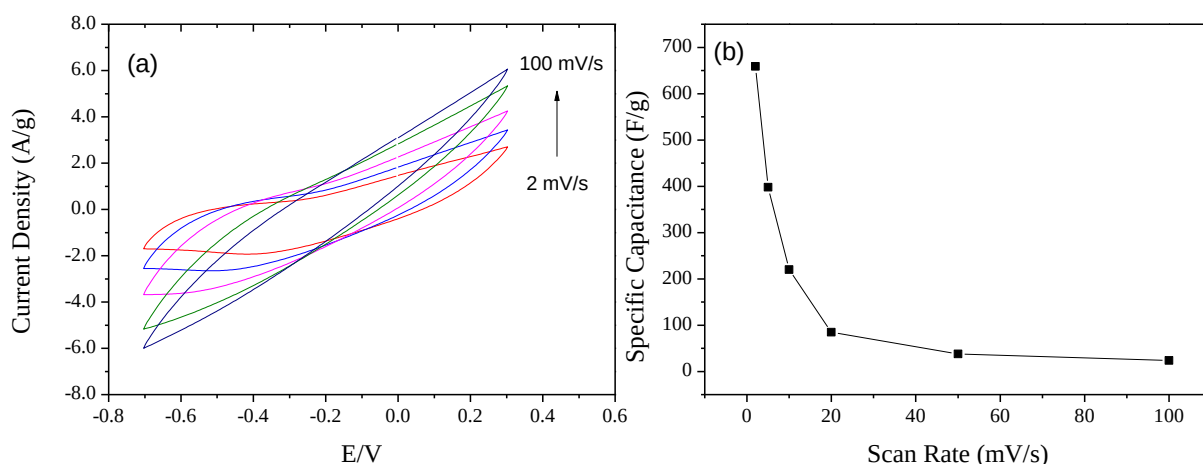


Figure 5.21 (a) CVs at different scan rates of 3%ND-25%GNP-PANI composite in 6 M KOH and (b) the corresponding C_{sp} plotted against scan rate

As the 3%ND-25%GNP-PANI sample exhibited the best performance in terms of high specific capacitance and enhanced cycling stability, CV was recorded at different scan rates. The resulting capacitance with respect to the scan rate is shown in **Figure 5.21** (b). The decay in capacitance with increasing scan rate is seen. At faster scan rate, there is limited time for the transfer of electrons and charged species to penetrate through or adsorb on the electrode surface causing the decline in capacitance. It can be concluded here that nanodiamond only enhanced the stability of the GNP-PANI composite possibly by a physical means but did not improve the rate capability of the sample.

Electrochemical Impedance Spectroscopy (EIS) was carried out for 3%ND-25%GNP-PANI sample, the recorded Nyquist plots in **Figure 5.22** are very similar between the two measurements, before and after 300 GCD cycles, confirming the good stability of the sample.

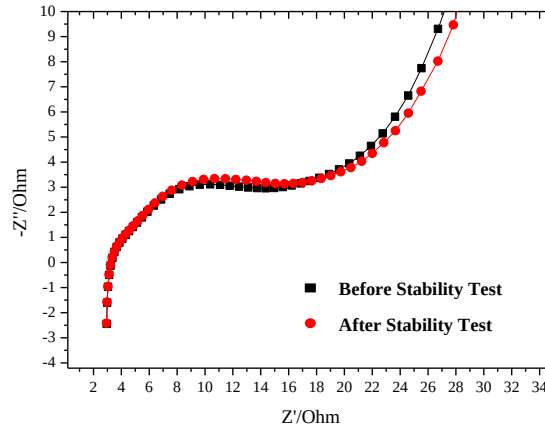


Figure 5.22 Nyquist plot from EIS experiment on 3%ND-25%GNP-PANI sample in 6 M KOH at open circuit voltage before and after 300 GCD cycles in 6 M KOH

Equivalent series resistance or ESR, a characteristic parameter of a cell can be measured at high frequency region in EIS where the imaginary component is zero. ESR is important in the evaluation of the power density of the sample via the equation

$$P = V^2/4R$$

where V is the potential range against which the capacitor was tested and R can be calculated from the x-intercept on the Nyquist plot from electrochemical impedance experiment. The ESR can be read off from the Nyquist plot in **Figure 5.22** to be 3Ω . Power density is found to be 27.8 kW/kg . Energy density on the other hand can be determined from the equation

$$E = CV^2/2$$

This gives the value of 76.4 Wh/kg . The high power density is as expected as one of the main characteristics of a supercapacitor. Energy density on the other is also relatively high which rivals the previously reported high power and energy density supercapacitor based on polyaniline, CNTs and graphene composite [46]. The market-leading commercial Li-ion batteries exhibited energy density in the range of $100\text{-}200 \text{ Wh/kg}$ [47]. Regarding this value,

the energy density provided by this ND-GNS-PANI supercapacitor device of 76.4 Wh/kg is not far off the mark and could well be developed further to rival such commercial devices.

5.4 Conclusion

- The three-component composites of nanodiamond, graphene nanoplatelets and polyaniline were successfully synthesised via *in-situ* polymerisation at low temperature as judged by a range of chemical and structural characterisation techniques.
- The electrochemical study on the composite performance as a supercapacitor suggests that a small amount of nanodiamond added to graphene-polyaniline composite can greatly enhance the cycling stability of the electrode. However when too much nanodiamond was added, a negative effect could occur to the cycling stability possibly due to the low conductivity of the diamond. Similarly, specific capacitance is also largely increased when graphene up to 25 wt% of loading is added to polyaniline samples. By contrast, the effect of graphene on the cycling stability and the effect of ND on specific capacitance are not as significant and cannot be readily concluded.

References

- [1] J. R. Miller and P. Simon, *Science* **321**:651 (2008).
- [2] A. G. Pandolfo and A. F. Hollenkamp, *Journal of Power Sources* **157**:11 (2006).
- [3] P. Kossyrev, *Journal of Power Sources* **201**:347 (2012).
- [4] K. Byungwoo, C. Haegeun, and K. Woong, *Nanotechnology* **23**:155401 (2012).
- [5] R. Saliger, U. Fischer, C. Herta, and J. Fricke, *Journal of Non-Crystalline Solids* **225**:81 (1998).
- [6] G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong, and Y. Li, *Advanced Materials* **26**:2676 (2014).
- [7] K. Wang, L. W. Li, T. Z. Zhang, and Z. F. Liu, *Energy* **70**:612 (2014).
- [8] J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang, and F. Wei, *Carbon* **48**:487 (2010).
- [9] Z. M. Tahir, E. C. Alocilja, and D. L. Grooms, *Biosensors and Bioelectronics* **20**:1690 (2005).
- [10] G. A. Rimbu, M. Iordoc, R. Vasilescu-Mirea, I. Stamatina, I. Iordache, and T. Zaharescu, *Optoelectronics and Advanced Materials-Rapid Communications* **2**:876 (2008).
- [11] X.-X. Liu, Y.-Q. Dou, J. Wu, and X.-Y. Peng, *Electrochimica Acta* **53**:4693 (2008).
- [12] J. Yan, C. Wang, Y. Gao, Z. Zheng, S. Zhong, X. Miao, X. Cui, and H. Wang, *Chemical Engineering Journal* **172**:564 (2011).
- [13] H. Gomez, M. K. Ram, F. Alvi, E. Stefanakos, and A. Kumar, *Journal of Physical Chemistry C* **114**:18797 (2010).
- [14] I. Kovalenko, D. G. Bucknall, and G. Yushin, *Advanced Functional Materials* **20**:3979 (2010).
- [15] X. Y. Zhao, J. B. Zang, Y. H. Wang, L. Y. Bian, and J. K. Yu, *Electrochemistry Communications* **11**:1297 (2009).
- [16] M. J. Fernández-Merino, L. Guardia, J. I. Paredes, S. Villar-Rodil, P. Solís-Fernández, A. Martín-Alonso, and J. M. D. Tasco, *The Journal of Physical Chemistry C* **114**:6426 (2010).
- [17] S. Osswald, G. Yushin, V. Mochalin, S. O. Kucheyev, and Y. Gogotsi, *Journal of the American Chemical Society* **128**:11635 (2006).
- [18] K. Fabisiak and F. Rozploch, *Applied Magnetic Resonance* **12**:53 (1997).

- [19] E. Olson, *Journal of GXP Compliance* 15:85 (2011).
- [20] O. A. Williams, J. Hees, C. Dieker, W. Jaeger, L. Kirste, and C. E. Nebel, *Acs Nano* 4:4824 (2010).
- [21] H. P. Boehm, *Carbon* 40:145 (2002).
- [22] Sudesh, N. Kumar, S. Das, C. Bernhard, and G. D. Varma, *Superconductor Science and Technology* 26:095008 (2013).
- [23] I.Yu. Sapurina and M.A. Shishov, New Polymers for Special Applications, In Tech, 2012.
- [24] I. Sapurina and J. Stejskal, *Polymer International* 57:1295 (2008).
- [25] R. Liu, H. Qiu, H. Zong, and C. Fang, *Journal of Nanomaterials* 2012:1 (2012).
- [26] X. Yan, J. Chen, J. Yang, Q. Xue, and P. Miele, *Acs Applied Materials & Interfaces* 2:2521 (2010).
- [27] T. Lindfors and A. Ivaska, *Journal of Electroanalytical Chemistry* 580:320 (2005).
- [28] M. Grzeszczuk, A. Granska, and R. Szostak, *International Journal of Electrochemical Science* 8:8951 (2013).
- [29] J. Zhang, C. Liu, and G. Shi, *Journal of Applied Polymer Science* 96:732 (2005).
- [30] L. Wang, Y. Ye, X. Lu, Z. Wen, Z. Li, H. Hou, and Y. Song, *Scientific Reports* 3:1919 (2013).
- [31] R. L. McCreery, Raman spectroscopy for chemical analysis, New York : Chichester : John Wiley & Sons, New York : Chichester, 2000.
- [32] Y. Luo, D. Kong, Y. Jia, J. Luo, Y. Lu, D. Zhang, K. Qiu, C. M. Li, and T. Yu, *RSC Advances* 3:5851 (2013).
- [33] J. Stejskal, P. Kratochvíl, and N. Radhakrishnan, *Synthetic Metals* 61:225 (1993).
- [34] M. Alam, A. A. Ansari, M. R. Shaik, and N. M. Alandis, *Arabian Journal of Chemistry* 6:341 (2013).
- [35] H. D. Tran, Y. Wang, J. M. D'Arcy, and R. B. Kaner, *Acs Nano* 2:1841 (2008).
- [36] E. Song and J.-W. Choi, *Nanomaterials* 3:498 (2013).
- [37] W. Chen, Z. Fan, L. Gu, X. Bao, and C. Wang, *Chemical Communications* 46:3905 (2010).
- [38] M. D. Stoller and R. S. Ruoff, *Energy & Environmental Science* 3:1294 (2010).

- [39] A. J. Bard, L. R. Faulkner, C. G. Zoski, J. Leddy, and J. Leddy, Electrochemical methods : fundamentals and applications, New York Chichester : Wiley, New York Chichester, 2001.
- [40] S. B. Kulkarni, U. M. Patil, I. Shackery, J. S. Sohn, S. Lee, B. Park, and S. Jun, *Journal of Materials Chemistry A* 2:4989 (2014).
- [41] K. Zhang, L. L. Zhang, X. S. Zhao, and J. Wu, *Chemistry of Materials* 22:1392 (2010).
- [42] A. V. Murugan, T. Muraliganth, and A. Manthiram, *Chemistry of Materials* 21:5004 (2009).
- [43] D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G. Q. Lu, and H.-M. Cheng, *Acs Nano* 3:1745 (2009).
- [44] Y. R. Nian and H. S. Teng, *Journal of the Electrochemical Society* 149:A1008 (2002).
- [45] V. N. Mochalin, O. Shenderova, D. Ho, and Y. Gogotsi, *Nat Nano* 7:11 (2012).
- [46] Q. Cheng, J. Tang, N. Shinya, and L.-C. Qin, *Journal of Power Sources* 241:423 (2013).
- [47] http://na.industrial.panasonic.com/products/batteries/rechargeable-batteries/lithium-ion/series/prismatic-series/CS531?reset=1&sort=asc&order=2&order_type=N

Chapter 6 Metal Hydroxides and Thermally Reduced Graphene Oxide Composites for Supercapacitor Applications

6.1 Introduction

From the preceding chapter supercapacitors were synthesised by polymerisation following a number of steps for preparation of materials and post-synthesis fabrication to prepare a cell ready for electrochemical testing. In this chapter, a much more facile method was employed to produce supercapacitor based on composite of reduced graphene oxide (rGO) with metal hydroxides/oxides. In the recent years, graphene as an electrode for supercapacitors has been extensively studied either on its own or in composite with a wide range of materials [1-4]. This chapter focuses more on porous architecture of graphene as an electrical double layer capacitor (EDLC) as well as a support for metal oxide particles with pseudocapacitance to produce a hybrid supercapacitor with high specific capacitance.

Porosity in graphene related materials have been introduced by many different methods including freeze-drying [5], incorporation of polystyrene spheres [6] and leavening process of graphene layers by reduction with hydrazine [7]. This chapter introduces a more environmentally friendly approach for the simultaneous reduction of graphene oxide and pore formation to produce a freestanding reduced graphene oxide film via incorporation of bicarbonate salt.

Transition metal oxides were predicted to provide very high specific capacitance theoretically. For example, the initially studied oxides for supercapacitor applications, RuO₂ and MnO₂ were reported to produce as high capacitance as 1358 F/g [8] and 1370 F/g [9]

respectively. The theoretical specific capacitance of NiO [10] and Ni(OH)₂ [11] on the other hand could be over 2500 F/g. Since the cost for nickel compounds is more economical [12] than ruthenium oxides for instance, nickel compounds were therefore chosen as an inorganic material to boost the specific capacitance when deposited on the porous graphene film synthesised.

Oxides and hydroxides of nickel have often been incorporated with carbon supports such as CNTs or graphene via chemical precipitation method [13] or via hydrothermal method [14]. In this work however, a facile method based on electrochemistry was carried out in the deposition of the nickel hydroxide/oxide particles on reduced graphene oxide film. Following up the fabrication of the materials, a range of characterisation techniques including SEM, XPS, BET and FTIR were performed for elucidation of its chemical and structural properties. In order to boost the specific capacitance further, cobalt hydroxide was also deposited with nickel oxide on reduced graphene oxide support.

6.2 Experimental

6.2.1 Materials

Graphene oxide suspension of 0.05 wt% (5 mg/mL) with 500 nm in lateral dimension and 3 nm thickness was purchased from Angstrom materials. Sodium hydrogen carbonate, NaHCO₃, potassium hydroxide (KOH), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6(H₂O)) and cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6(H₂O)), Triton X-100 were in analytical grade and obtained from Sigma Aldrich.

6.2.2 Methods

6.2.2.1 Fabrication of Graphene Oxide Film

The suspension of graphene oxide with known amount of NaHCO₃ was first ultrasonicated for an hour to ensure a good dispersion of graphene oxide and uniform distribution of

bicarbonate salt within the suspension. A freestanding graphene oxide film was achieved via a flow-directed self-assembly technique utilising a vacuum filtration with polyacetate filter membrane with a pore size of 200 nm. The film was left to dry under filtration prior to further modifications.

6.2.2.2 Deposition of Metal Hydroxides

Nickel oxide and cobalt oxide were electrodeposited on graphene oxide film by chronopotentiometry using optimal electrolyte concentration of nickel nitrate and cobalt nitrate for 600 seconds. After electrodeposition, the metal oxide decorated graphene oxide film was heated prior to electrochemical testing.

6.2.2.3 Electrochemical Characterisation

Three-electrode system was set up as before but with a different electrode holder. The holder is composed of a PTFE part and a metal part. Reduced graphene oxide film was mounted on top of a gold-coated glass slide between an O-ring underneath the PTFE part and a metal part as depicted in the diagram below. The mass of the film was measured using a balance accurate to 0.01 mg and an estimated area was measured using a Vernier calliper with 0.01 mm accuracy.

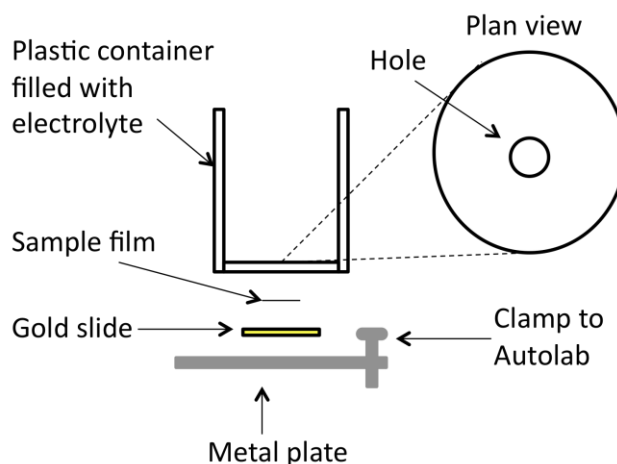


Figure 6.1 A diagram of electrochemical cell holder [15]

6.2.2.4 Structural and Chemical Characterisation

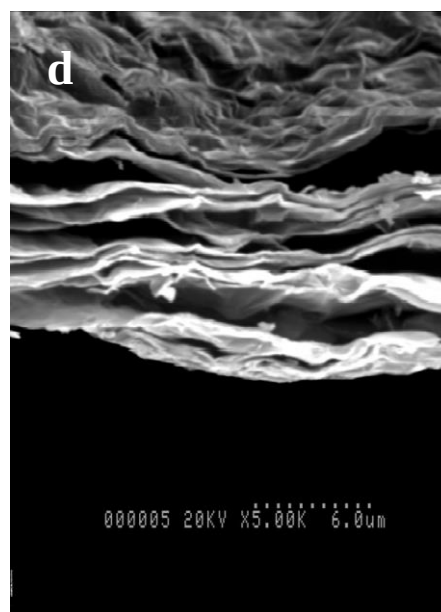
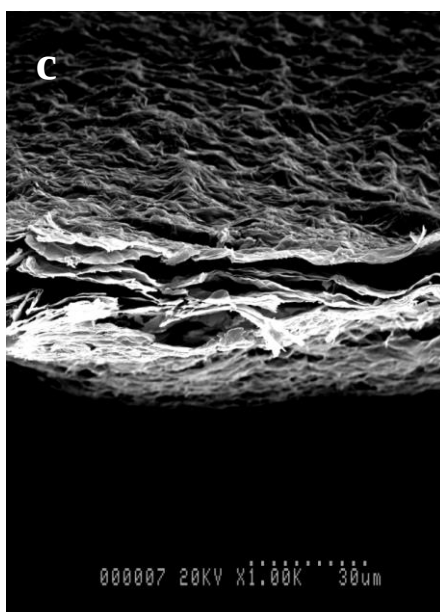
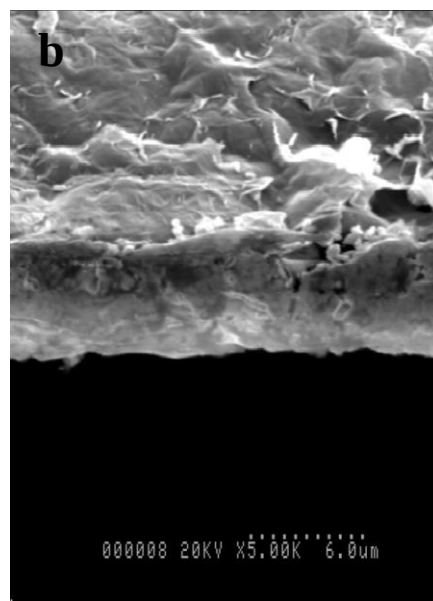
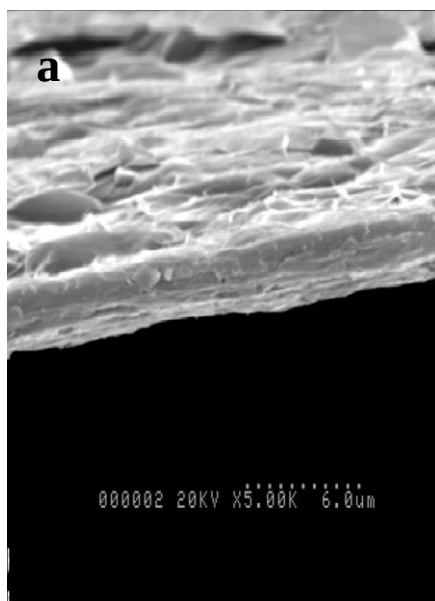
SEM, FTIR and XPS equipments used were the same as detailed in previous chapters. BET analysis was performed on CE Instrument Sorptomatic 1990 Series using N₂ gas adsorption. An additional SEM, SEM 3000, is equipped with a tungsten filament and operates at 5 or 15 kV. The SEM also comes with Energy Dispersive X-ray Spectroscopy unit (EDX) for elemental mapping.

6.3 Results

6.3.1 Characterisation of Reduced Graphene Oxide Film

Freestanding graphene oxide film prepared with known amount (0.630 or 0.945 g) of NaHCO₃ could be peeled off from a filter membrane quite easily. Afterwards, the film was heated at 300 °C in a conventional oven for 1 hour. For comparison purposes, graphene oxide film without any bicarbonate salt was also prepared. The films produced in such conditions were subject to a collection of chemical and structural characterisation techniques as follows.

6.3.1.1 SEM



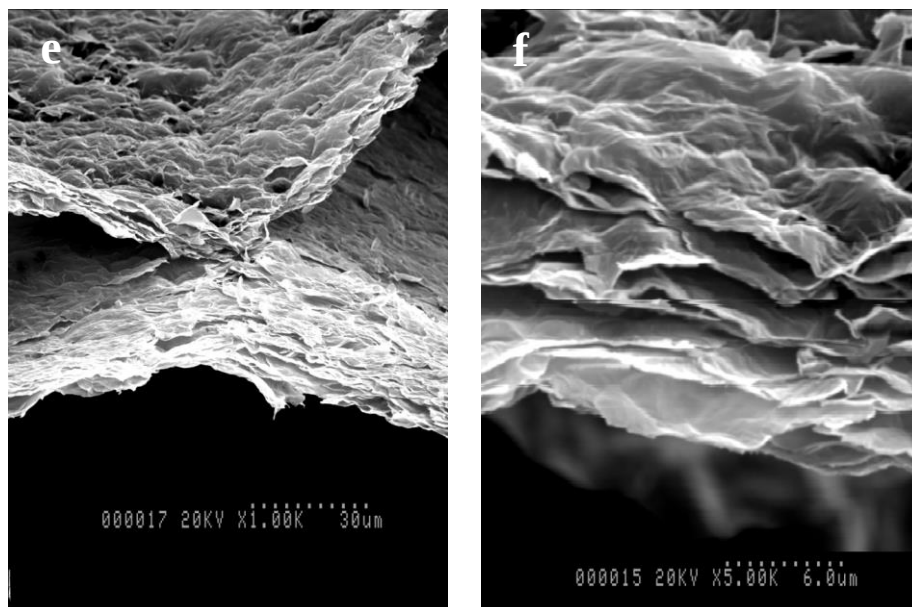


Figure 6.2 Graphene oxide (a) and graphene oxide with incorporated NaHCO_3 (b). Heated graphene oxide (c, d) and heated graphene oxide with NaHCO_3 (e, f).

The morphology of the heated graphene oxide film was elucidated using SEM. The micrographs in **Figure 6.2** show the surface structure of the film before and after heating. The roughness seen in the sample after heating suggests the more crumpled structure leaving more exposed surface and increase in surface area [16]. The cross-sectional images provide the information on the physical changes during the heat treatment to the film. The expansion of the graphene layers is clearly observed which signifies the successful leavening process taken place upon heating. It is therefore expected that the surface area of the heated film should increase significantly compared to the unheated graphene oxide. BET analysis was utilised for the estimation of the surface of the heated graphene oxide film.

6.3.1.2 BET Analysis

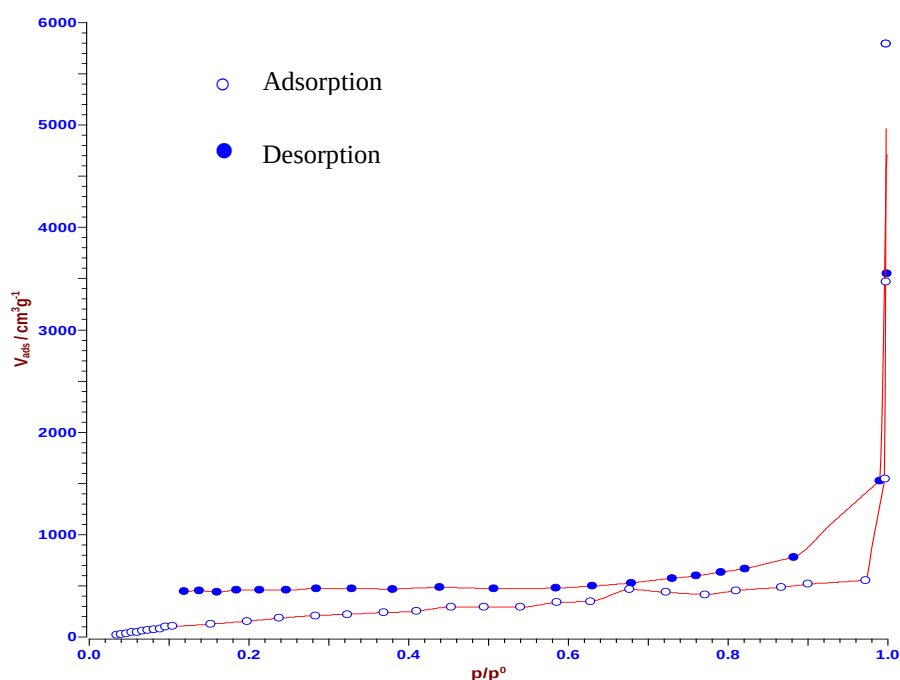


Figure 6.3 BET adsorption isotherm of heated graphene oxide in presence of N₂ gas

Nitrogen sorption measurement on heated graphene oxide film was carried out at 77 K. The technique can determine the adsorption/desorption behaviour of N₂ molecule on the surface of the sample and thus its textural characteristics. The adsorption isotherm is plotted in **Figure 6.3**. Hysteresis loop is featured suggesting Type IV of adsorption isotherm was taken place, which is commonly seen for mesoporous materials [17]. At the beginning of the adsorption, simple mechanism occurs where adsorption was onto the limited area of the monolayer structure. At higher pressure of N₂, adsorption can also occur in small pores and reached a saturation point. On the reverse of the loop is the desorption process. The unclosed gap between the two curves suggests the adsorption/desorption to a curvature surface or in other words inside the pores. The BET analysis result suggests mesoporous structure of the film. This can be confirmed by considering the pore size distribution calculated based on

Barrett-Joyner-Halenda (BJH) model as seen in **Figure 6.4** (a). The majority of the pores are in the within less than 50 nm range conforming to the mesoporous structure predicted from the sorption isotherm.

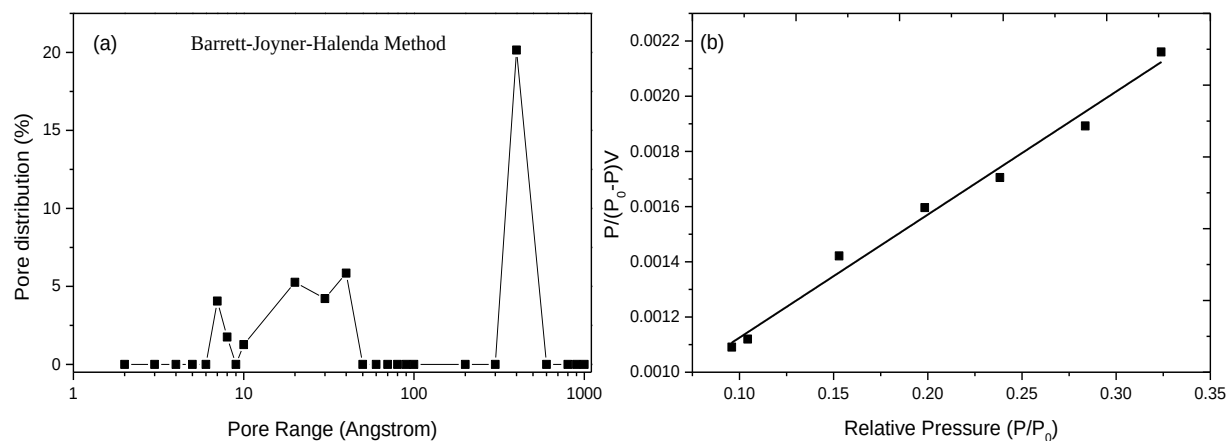


Figure 6.4 (a) pore distribution based on BJH model and (b) linear plot of BET analysis for surface area determination

SSA can be calculated from the equation derived in Chapter 2. The plot of P/P_0 against $P/V(P_0-P)$ in **Figure 6.4** (b) should be a straight line with a gradient being $(C-1)/V_m C$ and $1/V_m C$ is the intercept. The resulting surface area is $854 \text{ m}^2/\text{g}$, which is still lower than the theoretical surface area for completely isolated graphene sheets of $2620 \text{ m}^2/\text{g}$ [18]. The lower value may result from the aggregation of the sheets upon filtration, which could not be fully delaminated after heating with bicarbonate salt. However, $854 \text{ m}^2/\text{g}$ is in the higher range of thermally reduced graphene oxide reported elsewhere ($600\text{--}900 \text{ m}^2/\text{g}$) [19, 20]. The surface area for this sample is competitive in this respect verifying the effectiveness of the preparation method employed.

6.3.1.3 FTIR Spectroscopy

The chemical changes of the graphene oxide film upon heating at 300°C can be monitored by FTIR spectroscopy. The resulting spectra are as shown in **Figure 6.5**. The functional groups observed for the graphene oxide film in spectrum (i) is the same as previously

described in Chapter 5. The assignment of the absorbance is as follows; a broad band at 3250 cm^{-1} is due to O-H stretching mode from alcohols, the peak at 1730 cm^{-1} is from C=O stretching vibrations, at 1613 cm^{-1} a peak is due to the aromatic and sp^2 C=C bond vibrations. The band at 1400 cm^{-1} and a sharp intense peak at 1060 cm^{-1} correspond to C-O stretching modes in alcohols, ether and epoxy groups. Heated graphene oxide film with and without NaHCO_3 , spectra (iii) and (ii), show similar characteristics in the FTIR spectra where most of the oxygenated functional groups have almost vanished. Among all heated samples, the small bands at 2932 and 2963 cm^{-1} can be ascribed to aromatic C-H stretches. The appearance of aromatic C-H band suggests that reduction of oxygen moieties did occur and thus resulted in restoring of aromaticity. Similarly, the C-H stretch from aldehyde groups appearing at 2864 cm^{-1} also implies the reduction of carboxylic groups.

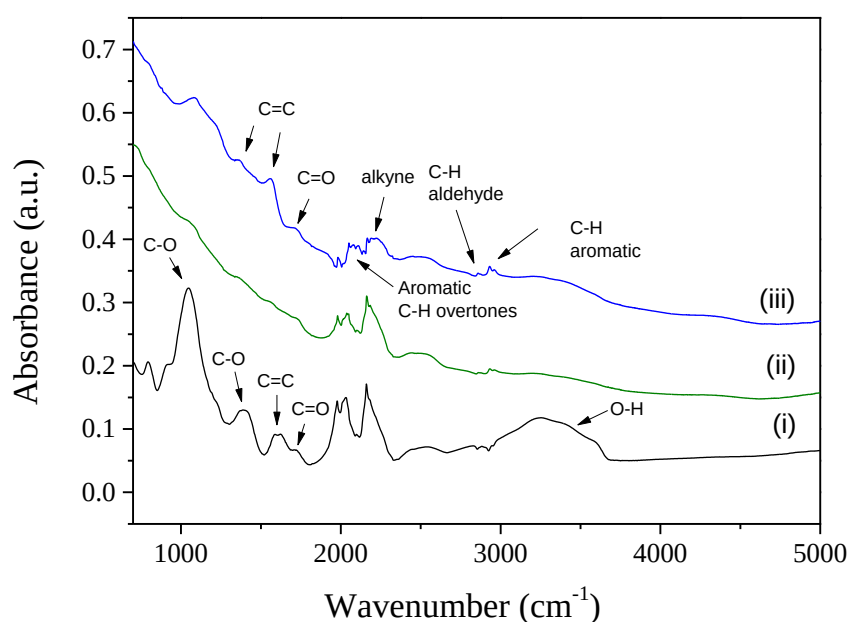


Figure 6.5 FTIR of (i) graphene oxide film, (ii) graphene oxide heated at $300\text{ }^{\circ}\text{C}$ and (iii) graphene oxide heated with NaHCO_3

Overall, the much less intense absorbance or disappearance of bands owing to the oxygenated functional groups in the GO samples heated with and without NaHCO_3 suggests that reduction of graphene oxide was taking place. The extent to which graphene oxide with

incorporated NaHCO_3 was reduced after heating in air at $300\text{ }^\circ\text{C}$ for an hour can be investigated by XPS, which is later described. It is worth mentioning that the minor difference between the heated samples with and without embedded NaHCO_3 is in the slightly more intense bands owing to $\text{C}=\text{C}$ and $\text{C}-\text{H}$. This difference could possibly suggest the involvement of NaHCO_3 in the thermal reduction, however the conclusion cannot be explicitly drawn herein. Thus, Hall Effect measurement was performed in order to assess the resistivity of the individual sample.

6.3.1.4 Hall Effect

Hall Effect measurement was carried out at 300 K with applied current of 0.550 mA and applied magnetic field strength of 0.550 T . The average sample thickness was taken to be approximately $2\text{ }\mu\text{m}$ as judged by SEM cross-sectional images. For comparative purposes, the chemically reduced graphene oxide by ascorbic acid sample synthesised as detailed in Chapter 5 was also included in the experiment. The obtained data show that the smallest Hall resistivity or in other words the most conductive sample is indeed the chemically reduced graphene oxide with a resistance of $0.031\text{ }\Omega\text{m}$, which is although higher than that for pristine single sheet graphene, still considerably lower than what reported for graphene oxide and hydrazine treated graphene oxide [21, 22]. By contrast, both thermally reduced samples exhibit very similar resistance of $0.17\text{ }\Omega\text{m}$ and $0.16\text{ }\Omega\text{m}$ for GO film heated with and without NaHCO_3 respectively. As a result, it can be inferred here that there is either none or only insignificant involvement of bicarbonate salt in the thermal reduction in air of graphene oxide at $300\text{ }^\circ\text{C}$.

6.3.1.5 XPS Analysis

The XPS spectra in **Figure 6.6** show the surface functionality of carbon $1s$ for graphene oxide film embedded with NaHCO_3 before (GO) and after heating (rGO). As for graphene

oxide, four distinct peaks are observed at 285.0 eV for C 1s graphitic (C-C), 286.9 eV for C-O from epoxides or alcohols, 288.2 eV for C=O group from carbonyls, and 289.3 eV for O-C=O from carboxylic groups. The carbonate group of NaHCO_3 could also contribute to the peak at 289.3 eV. On the other hand, after heating, the GO film with the embedded salt only exhibited three XPS peaks at 285.0, 287.5, and 289.4 eV binding energies, which correspond to C-C, C=O and O-C=O functional groups respectively. The relative surface composition of sodium 1s was found to be 3.62% for the unheated GO.

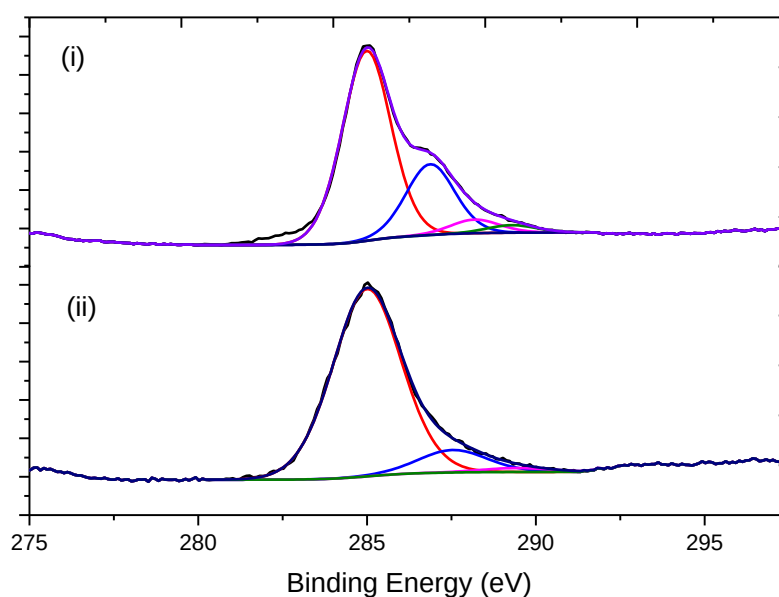


Figure 6.6 XPS of (i) graphene oxide and (ii) heated graphene oxide with NaHCO_3 at 300 °C. The ratio of graphitic C 1s to oxygenated carbon can be compared before and after heating GO film with implanted NaHCO_3 . The calculation gives the ratio of 2:1 and 7:1 for unheated and heated samples respectively. The dramatic decrease in the ratio indicates that the reduction of graphene oxide is achieved. It might be counter-intuitive to some extent that heating graphene oxide in air could lead to a more reduced product instead of an oxidised product. It is well documented however that thermal reduction of graphene oxide could occur at a temperature as low as 450 K [23]. This phenomenon can be explained by considering the

possible mechanism during heating graphene oxide. At high temperature, decomposition of oxygenated functional groups could occur which resulted in loss of small gaseous species such as CO, H₂O and CO₂ leaving also defects and porous texture. Simultaneously, the formation of these gases causes high pressure reaching 40 MPa at 300 °C between graphene oxide layers resulting in exfoliation of the stacked layers [24]. Mechanistic study by R. Larciprete *et al.* also shows that the basal plane oxygen atoms and high epoxide coverage of graphene oxide are the key catalysing factor for its thermal reduction [23].

6.3.2 Heating Methods and Electrochemical Characterisation

Graphene oxide and its thermally reduced form were electrochemically characterised by means of cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) as previously used for testing of supercapacitors based on nanodiamond, graphene and polyaniline composite in Chapter 5. Cyclic voltammetry was again carried out to justify the specific capacitance of a sample in 6 M KOH with three-electrode cell set up. A comparison between different amounts of bicarbonate salt added was exploited in terms of features in CV and the corresponding specific capacitance as summarised in the following section.

6.3.2.1 Effect of the Amount of NaHCO₃

Cyclic voltammograms of graphene oxide and heated graphene oxide with varied amounts of NaHCO₃ added were recorded from -0.1 V to 0.35 V at 5 mV/s in 6 M KOH and presented in **Figure 6.7**. It is clear from the voltammograms that graphene oxide shows almost negligible capacitance in comparison to its heated forms; 4.3 F/g as compared to 37.3 F/g. By adding the bicarbonate salt to the suspension of graphene oxide prior to the formation of the freestanding film, there is an immense increase in specific capacitance to almost triple the value exhibited by heated GO without any added salt as summarised in **Table 6.1** below.

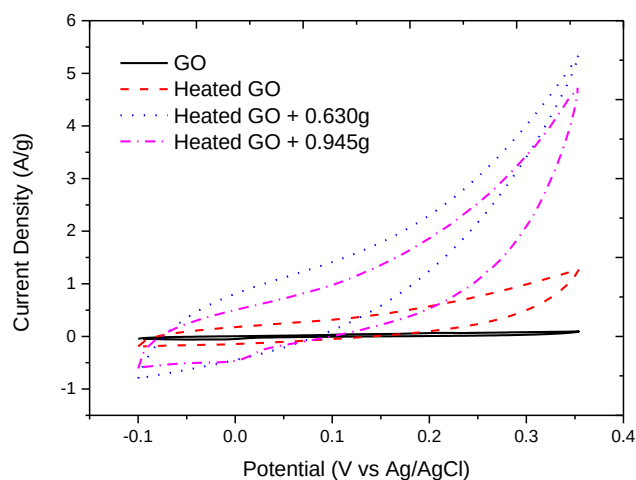


Figure 6.7 CV of graphene oxide and heated graphene oxide with varying amounts of NaHCO_3

The amount of incorporated salt is obviously affected the specific capacitance. Increasing the amount of NaHCO_3 to 0.945 g slightly increases the specific capacitance to 103.3 F/g and thus chosen as the optimal amount for NaHCO_3 to be added. It is worth reminding here that this value is the amount of added salt, which is meant to be lost during filtration. The quantity of the remaining salt in the film is indeed significantly lower than the added amount as resulted in the XPS analysis featured in section 6.3.1.5 where the surface concentration of sodium is only 3.62% in contrast to approximately over 30% if all the added 0.945 g of the salt is to be maintained.

Table 6.1 Summary of Specific capacitance as a result of heating graphene oxide with different amount of added salt

Sample	Added NaHCO_3/g	Capacitance/ Fg^{-1}
GO	-	4.3
Heated GO	-	37.3
Heated GO	0.630	98.0
Heated GO	0.945	103.3

According to this preliminary result, it is worth investigating further on the variation of the heating method in order to maximise the specific capacitance of the heated graphene oxide samples.

6.3.2.2 Effect of Heating Rate and TGA Analysis

So far the heating was performed in a preheated conventional oven at 300 °C. It is interesting however to observe how changing of the heating rate would affect the capacitance of the salt incorporated graphene sample. TGA analysis was thus carried out to investigate the mass loss during heating as well as to provide accurate variation on the rate of heating by Pyris software programme.

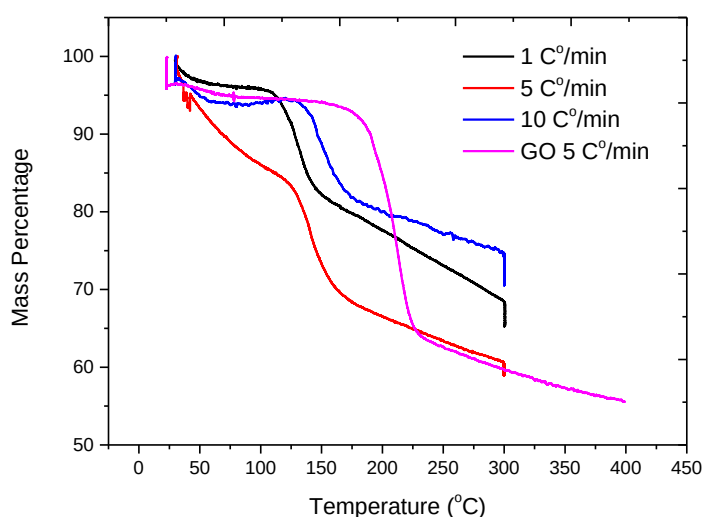


Figure 6.8 TGA profiles of GO and GO with NaHCO₃ films at different heating rates

The plot in **Figure 6.8** shows the percentage of mass loss over the period of the applied temperature under airflow. The TGA curve in pink represents the heating profile of graphene oxide without any added salt, which was heated at a rate of 5 degrees per minute. The profile shows the loss of about 5% up to 100 °C due to the loss of absorbed water molecules. A sharp decrease in mass is seen from 175 °C to 225 °C temperature range resulting in a further 30% loss in mass. This TGA profile is in concurrence with the literature where the loss of

mass was described to be from the decomposition of labile oxygen functional groups [25]. From 225 °C onwards, there is a progressive decline in mass but at a much slower rate reaching to about 55% mass retained at 400 °C.

On the other hand for the salt incorporated GO samples, the TGA program was slightly altered such that the temperature was held at 300 °C for an hour. The heating profile of graphene oxide with embedded salt heated at 1, 5 and 10 °C/min, denoted as black, red and blue curves respectively, show a marked difference to the pure GO sample where the sharp loss in mass is in the lower range of temperature from just over 100 °C to around 175 °C. And this accounts for about 10-15% of mass loss for the 1 and 10 °C/min and 20% for 5 °C/min heating rate. After holding at 300 °C, around 5% of mass loss is further seen. The decrease in temperature where the pronounced mass loss occurred and smaller mass loss observed within the particular temperature range could be due to the incorporation of the added bicarbonate salt that helps facilitate the decomposition process of the labile oxygen functionalities at lower temperature than the pure GO sample.

The heated graphene oxide with incorporated salt at different heating rates in the TGA chamber was further electrochemically characterised. The resulting CVs are plotted above in **Figure 6.9** (a) where the significant increase in capacitance is seen throughout in comparison to the conventional oven method. It must be noted however that the potential range tested is different from that reported in section 6.3.2.1 above such that the range is wider and spanning from -0.8 V to 0.4 V.

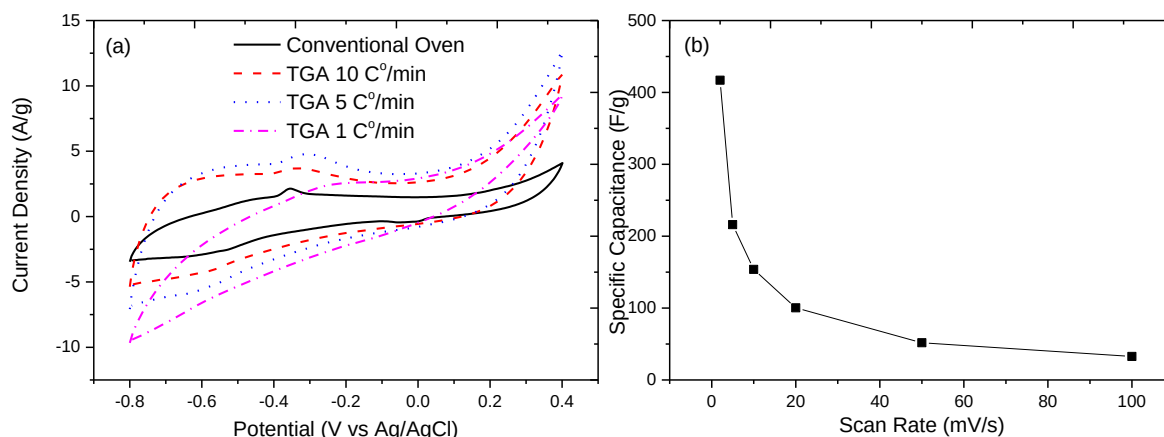


Figure 6.9 (a) CV of heated salt incorporated GO film at different conditions and (b) the effect of the scan rate to specific capacitance of conventionally heated graphene oxide

Table 6.2 below summarises the specific capacitance of each heated graphene oxide sample. The highest specific capacitance is exhibited from the 5 °C/min heating rate reaching as high as 561.5 F/g which is more than double that of the conventional oven method. The reason for the increase in the specific capacitance seen is still inconclusive as it is equally likely to be from the effect of heating rate itself or the prolonged time during which the sample was exposed to heating.

Table 6.2 Comparison of different heating methods and its resulting specific capacitance

Heating Method	Specific Capacitance/Fg ⁻¹
Conventional Oven	216.3
TGA: 10°Cmin ⁻¹	455.8
TGA: 5°Cmin ⁻¹	561.5
TGA: 1°Cmin ⁻¹	353.6

The optimised sample produced by heating at 5 °C/min with 0.945 g of NaHCO₃ was cycled at different scan rates and the resulting specific capacitance is plotted against the scan rate in **Figure 6.9** (b). The low rate capability can be implied from the large decrease in specific capacitance upon the increase of scan rate. It can be explained in terms of charge transfer mechanism such that at higher scan rate there is less time for charge carriers or ions which in

this case are most likely to be OH^- and K^+ from KOH to be adsorbed on the graphene surface giving rise to lower specific capacitance.

6.3.2.3 Galvanostatic Charge Discharge and Stability

Apart from CV, another important technique for the assessment of a supercapacitor is galvanostatic charge discharge or GCD. The stability is also another crucial parameter to judge the performance of supercapacitors in terms of its practicality for real usage. The optimised sample of heated graphene oxide that is the 0.945 g NaHCO_3 implanted in graphene oxide heated at 5 °C/min was therefore subjected to the stability test via prolonged successive GCD cycles in 6 M KOH at the applied current density of 2 A/g between -0.4 V to 0.1 V potential range. The calculated specific capacitance regarding the number of cycles is shown in **Table 6.3**. The lower capacitance observed in GCD compared to that from CV was seen earlier with the nanodiamond, polyaniline and graphene composite studied in the preceding chapter. This could be a result of a relatively high current density applied, which renders the kinetics faster leaving electrolyte ions less time to migrate and thus lowers the capacitance. After 1000 GCD cycles, the decreasing trend in specific capacitance is observed with the remaining capacitance of 42.0% of its initial value. This capacitance retention shows only a moderate stability of the freestanding film as a supercapacitor.

Table 6.3 Summary of stability testing of rGO by GCD cycling at 2 A/g in 6 M KOH

Number of Cycles	Specific Capacitance (F/g)	Capacitance Retention (%)
1	122.4	100
200	78.6	64.2
400	59.5	48.6
600	54.7	44.6
800	53.6	43.7
1000	51.4	42.0

It is speculated that the progressive decrease in specific capacitance observed during the stability test could be owing to the physical rupture of the more brittle film after heating. An

attempt was therefore made in order to enhance its stability. This was done by soaking the heated film in a surfactant for 20 minutes and rinsing well with distilled water prior to the electrochemical testing. The surfactant of choice was Triton X-100 at 2 wt% concentration. Triton X-100 was chosen as it is neutral and no effect of charge interaction with the electrolyte needs to be concerned with. The outcome shows the specific capacitance rise to 836.4 F/g based on calculation from CV in 6 M KOH in the same potential range from -0.8 V to 0.4 V. The resulting GCD curves at applied current density of 1, 2 and 5 A/g are depicted in **Figure 6.10**. The calculated specific capacitance is 534.3, 513.0 and 436.4 F/g for the current density of 1, 2 and 5 A/g respectively. The small decrease observed with the higher current density applied could be resulting from the low rate capability as discussed in the effect of scan rate above.

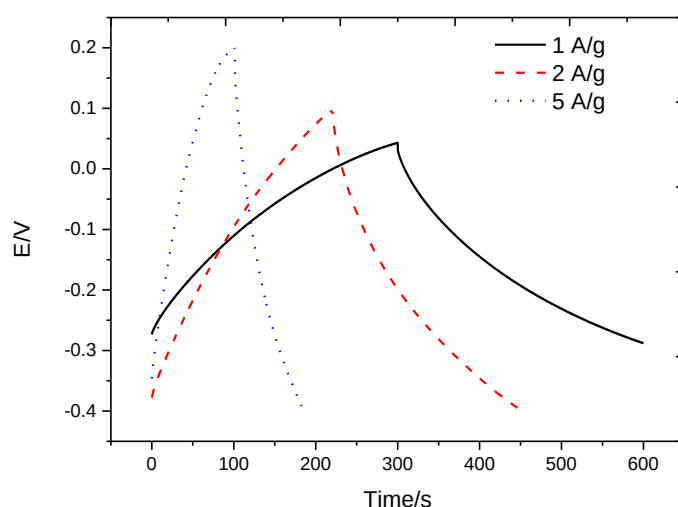


Figure 6.10 Galvanostatic Charge Discharge curve of rGO at different applied current densities

Upon the stability testing, however, the capacitance retention dropped to only 30.3% of the initial value. The increase in capacitance observed can be understood in terms of the enhanced hydrophilicity of the heated film upon soaking in the surfactant. However, the effect seems to be short-lived as the capacitance plummets even further than the non-soaking

film. The reason behind this artefact effect is possibly because the surfactant molecules diffused away from the film to the solution during the testing. A further effort to add the surfactant to the electrolyte solution actually caused precipitation and the solution turned cloudy due to the reaction with hydroxide ions in the highly basic conditions employed.

Another approach was also carried out in the attempt to enhance the stability where nitrogen gas was bubbled to the solution and the whole electrochemical cell was kept under nitrogen atmosphere in a glove bag. This experiment was set up as to clarify whether oxygen would involve in the decrease in capacitance seen. The outcome however sees no distinguished capacitance retention from the stability testing in normal conditions.

6.3.3 Electrodeposition of Nickel Hydroxides

The main aim of the project is to develop a hybrid supercapacitor by combining the electric double layer capacitance and the pseudocapacitance together; this was achieved by a formation of composite material of reduced graphene oxide and transition metal hydroxides. To approach this, nickel hydroxide was introduced to the graphene oxide film by a facile and convenient method of electrochemical deposition. The basic chronoamperometric technique of electrodeposition via applying a constant potential to the carbon support/electrode, in other words, a potentiostatic deposition method was carried out. The electrodeposition was performed in two slightly different approaches regarding the form of the graphene support. First is to directly electrodeposit nickel hydroxides onto graphene oxide film and then simultaneously heat the composite at 300 °C for an hour in a pre-heated conventional oven. Or as an alternative, the graphene oxide film was heated in advance at 300 °C for an hour then followed by electrodeposition of nickel hydroxide. The metal decorated graphene film was subsequently subject to an additional heat treatment again at the same condition of 300 °C in a preheated oven under ambient atmosphere. Note that both types of the films were

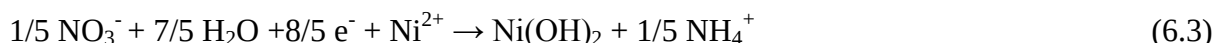
incorporated with the bicarbonate salt at 0.945 g added with the graphene oxide suspension as this was the optimal amount as previously mentioned.

The potentiostatic electrodeposition method was adopted and modified from [26]. As the heated graphene oxide film can be hydrophobic, to ensure the homogeneous absorption of nickel nitrate electrolyte throughout the film, both forms of unheated and heated graphene oxide film were soaked thoroughly in nickel nitrate electrolyte for an hour prior to the electrodeposition step. The mechanism of electrodeposition of nickel hydroxide can be explained in terms of the redox reaction, which takes place as follows.

At adequately negative potential, in this case -1.0 V was initially chosen, the reduction of nitrate ions can occur as shown in equation 6.1. This reduction process produces hydroxide ions giving rise to the highly basic environment at the near electrode-electrolyte interface. This high concentration gradient of hydroxides in turn leads to the reaction with already adsorbed Ni(II) ions or those near the electrode surface and thus the precipitation of nickel hydroxide was achieved as exemplified in equation 6.2.



As the calculation of specific capacitance requires known mass of the sample, Faraday's law is implemented for the estimation of the mass of nickel hydroxide deposit. The overall redox reaction takes into account both the processes in equation 6.1 and 6.2, which hence becomes



The value for n or the number of electrons involved in the process for one mole of nickel hydroxide formed is therefore $8/5$. This evaluation of mass is however approximate and relies on these following assumptions. Firstly, it assumes uniform current throughout the circuit [27] and the total current passing through the electrode is solely for the formation process of nickel hydroxide. Secondly, the assumption of 100% efficiency in hydroxide ions production must be made. As a result, this approximation is only valid when dilute concentration (< 0.1 M) of electrolyte is concerned [28] which is applicable in this work as the typical electrolyte concentration is 10 mM.

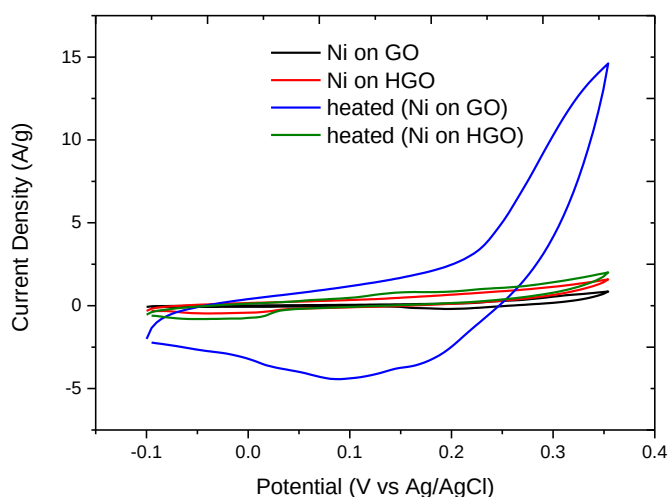


Figure 6.11 CV of nickel hydroxide deposited on GO or rGO in 6 M KOH at 5 mV/s

The resulting specific capacitance based on the CVs plotted in **Figure 6.11** is summarised in **Table 6.4**. rGO denotes the heated graphene oxide film with 0.945 g incorporated bicarbonate salt and Ni refers herein as a short term for nickel hydroxide species. It is interesting to see that the capacitance after electrodeposition of nickel hydroxide (before heating) is lower in the case of GO than rGO. However, the reverse trend is observed after heating the nickel hydroxide decorated GO and rGO electrodes. It can be explained such that rGO is more conductive and possesses considerably higher surface area than GO, as a result, nickel hydroxide can be deposited with better distribution giving rise to higher specific

capacitance. It should be noted however that the specific capacitance of rGO decreases upon nickel hydroxide deposition. This adverse effect on capacitance could stem from pore-blockage of rGO substrate by the deposited nickel hydroxide particles. Even after the second heating of Ni(OH)₂-rGO, only a small increase in capacitance is seen but this is still significantly lower than that exhibited by rGO itself. By contrast, after heating Ni(OH)₂-GO is converted into Ni(OH)₂-rGO and exhibits very high capacitance at 442.2 F/g which is more than four times higher than that of rGO. It is therefore conclusive that simultaneous heating of GO decorated with nickel hydroxide is more beneficial than the stepwise heating procedure which sees the detrimental effect on its specific capacitance.

Table 6.4 Comparison of Specific Capacitance of Ni deposition at -1.0 V

Sample	Capacitance/Fg ⁻¹
GO	4.33
rGO	103.3
Ni deposited GO	17.9
Ni deposited rGO	47.0
Ni deposited GO then heated	442.2
Ni deposited rGO then heated	63.28

The insight into the features of the CV can be made by considering the comparison between the voltammograms of bare GO and Ni(OH)₂-GO before and after being annealed at 300 °C. The CV in 6 M KOH at 5 mV/s of unheated nickel hydroxide deposited on GO in **Figure 6.12** (a) below shows the main redox couples at 0.20 and 0.24 V for the reduction and oxidation peaks respectively of the overall reaction in equation 6.4.



After the annealing process, the massive increase in capacitance is seen. The shoot up of the capacitance could be owing to two main factors. First is the higher double layer capacitance

of rGO than GO and second is the higher pseudocapacitance of the nickel hydroxide. The CV of heated nickel species on rGO also differs from the unheated form such that the redox peaks become featureless. The suggested redox reaction for nickel oxide species is outlined in equation 6.5.

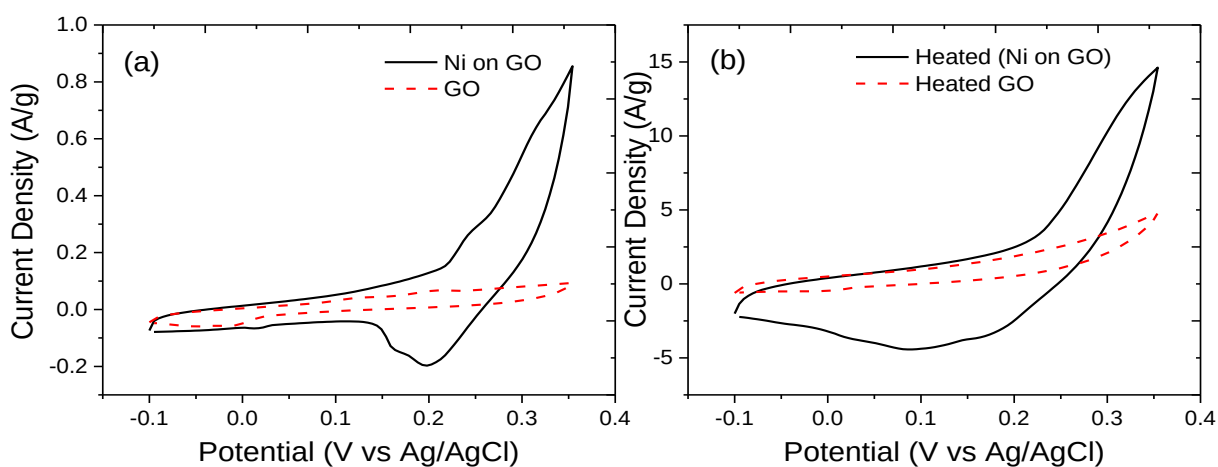


Figure 6.12 CV in 6 M KOH at 5 mV/s of GO and nickel hydroxide decorated GO before (a) and after heating (b)

The optimisation of the electrodeposition parameters was made such that the highest capacitance possible is obtained with good time efficiency. These parameters include the concentration of the electrolyte (10 mM), the deposition time (600 s), the applied potential (-1.2 V), the soaking time (1 hour), the heating temperature (300 °C) and duration (1 hour). The resultant specific capacitance is 936.5 F/g.

6.3.3.1 Characterisation of Nickel Hydroxide Deposited on rGO

6.3.3.1.1 SEM

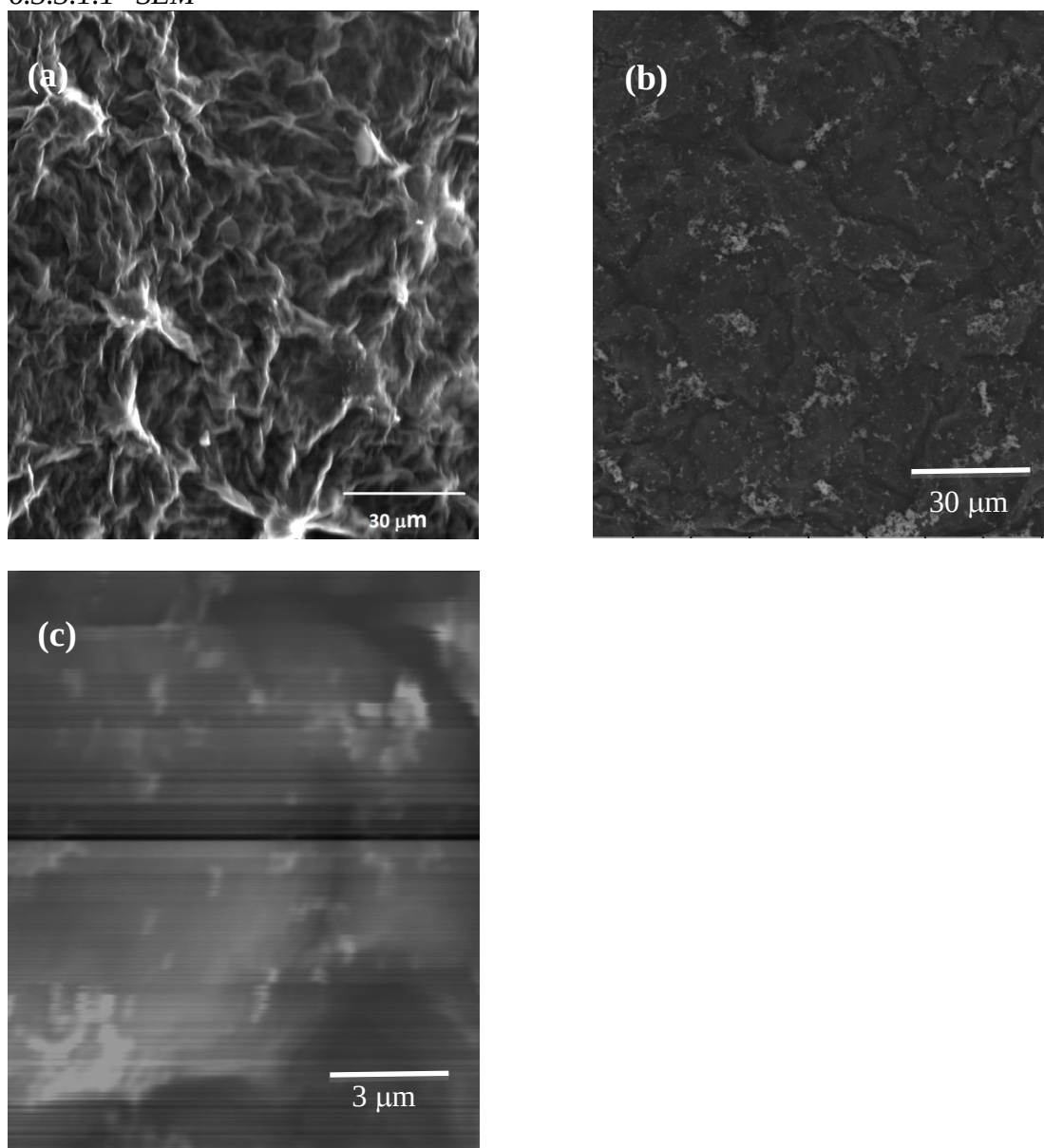


Figure 6.13 SEM images of bare heated graphene oxide film (a), Heated nickel hydroxide deposited on graphene oxide film (b) and (c) at different magnification

The morphology of GO and the nickel hydroxides/oxides deposit on rGO was shown in **Figure 6.13** (a) and (b) respectively. The SEM micrographs feature the wrinkled structure of heated graphene oxide. After the electrodeposition of nickel hydroxides, the surface of graphene is covered with small particles and clusters. At a higher magnification, due to the poor resolution of the electron microscope, the blurry image was obtained. However, it could

still be observed at the least that small particles in size of around 100 nm were produced alongside aggregates forming clusters in a few microns of dimension.

6.3.3.1.2 XPS

XPS analysis was taken as to gain insightful information regarding the surface composition of the nickel hydroxide decorated GO film before and after annealing at 300 °C in air for one hour. The spectrum in **Figure 6.14** below shows explicitly XPS multiplets owing to Ni2p. The doublets appearing at the lower binding energy of 854.8 and 872.5 eV can be ascribed to Ni2p_{3/2} while the higher BE doublets corresponding to Ni2p_{1/2}. The shoulders to the main peaks are the shake-up peaks [29]. The binding energy where these two doublets occur can infer the oxidation and the closest species of nickel. The Ni2p_{3/2} peak at 854.8 eV is very close to 854.9 eV for Ni²⁺ and further away from 857.1 eV for Ni³⁺ or 852.3 eV for metallic nickel, thus this suggests the divalent species of nickel is present [30, 31]. The gap between the two doublet peaks is 17.69 eV. This also indicates that the chemical species of nickel deposit is Ni(OH)₂ and is in good agreement with previous reports on nickel hydroxide and graphene composites [30-32]. This result is as expected as described by the formation and the proposed mechanism that could occur during the electrodeposition step.

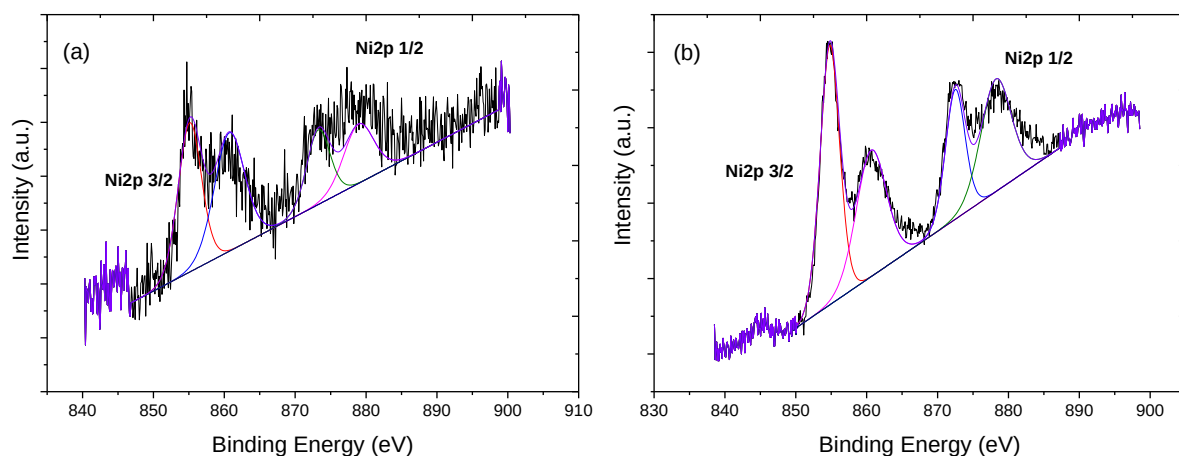


Figure 6.14 XPS spectra of Ni2p before (a) and after heating (b) of nickel hydroxide deposited on GO

After heating, again the characteristic doublet peaks of Ni2p are still visible. This time the doublets appear at 854.8 eV for Ni2p_{3/2} and at 872.6 eV for Ni2p_{1/2}. The gap between the two doublets increases slightly to 17.85 eV. From the literature, it is suggested that the characteristic energy gap between Ni2p_{3/2} and Ni2p_{1/2} for NiO is 18.40 eV [33]. Consequently, this indicates that some of the deposited Ni(OH)₂ has transformed to NiO phase after heating at 300 °C but mostly the sample still contains Ni(OH)₂. And for all nickel deposited samples, the O1s peak has shifted from 532.0 eV to around 531.6 (±0.3) eV, which is indicative of bound hydroxide groups of nickel [34]. It is also worth mentioning that the ratio of graphitic C1s to oxygenated carbon is enhanced from 7:1 to 9:1 after heating, confirming the reduction of graphene oxide also took place with the nickel decorated sample. The higher ratio of the unheated sample of 7:1 compared to 2:1 of bare NaHCO₃ implanted graphene oxide could be due to the exposure of the sample to negative potential applied during the electrodeposition of nickel hydroxides.

Table 6.5 below summarises the features from XPS data of the electrodeposited nickel hydroxides sample on graphene oxide before and after heating. By taking the relative atomic

surface sensitivity factors to be 1 for carbon, 2.93 for oxygen and 22.2 for nickel, the surface composition of the sample can be calculated. The results are similar for unheated and heated samples exhibiting the surface nickel at 3.48% and 3.08% respectively. Overall it can be implied that heating does not significantly alter the deposited nickel species either in physical or chemical terms.

Table 6.5 Summary of XPS Analysis

<i>Sample</i>	<i>C-C to C-O ratio</i>	<i>% Surface Composition of Ni</i>	<i>Energy Gap (eV)</i>
Unheated Ni-GO	7:1	3.48	17.69
Heated Ni-rGO	9:1	3.08	17.85

Further structural investigation by XRD only resulted in reflections from the graphene support which could be due to the fact that XRD is not surface sensitive and thus the small amount of nickel deposited (only around 3% as suggested by XPS) did not show peaks in XRD. Or another reason could be that the nickel deposit is amorphous.

6.3.3.1.3 Effect of scan rate and stability

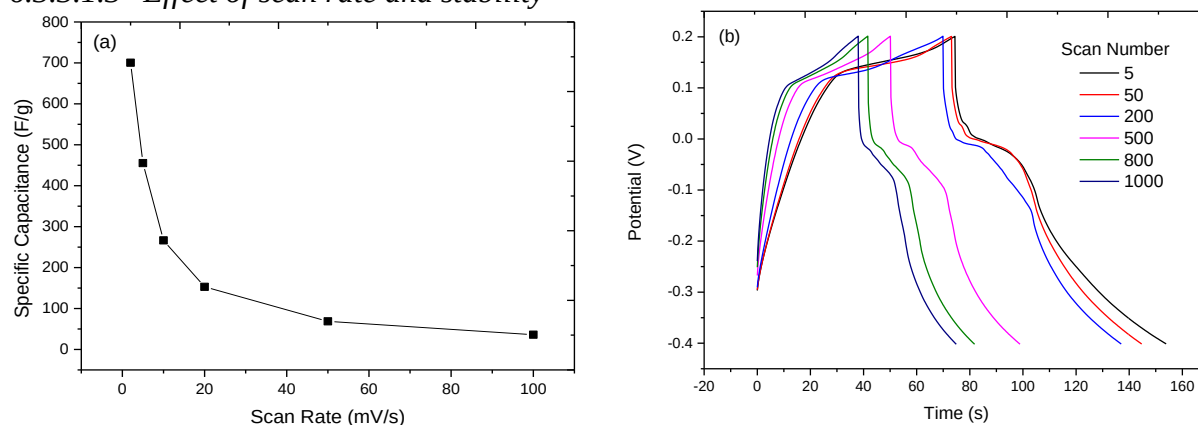


Figure 6.15 (a) Effect of scan rate on specific capacitance and (b) GCD curves of nickel hydroxide deposited rGO

To complete the performance test of a supercapacitor, stability over GCD cycles and changing of scan rate was carried out. The effect of scan rate is similar to bare rGO. The

specific capacitance calculated from the obtained CVs decreases with increasing scan rate. This finding is again a result of relatively low rate capability. At slow scan rate ions are more able to migrate around active surface area, whereas at faster rate diffusion limit prohibits the migration and the available active area becomes less accessible.

Table 6.6 Summary of stability testing of nickel hydroxide decorated rGO by GCD cycling at 2 A/g in 6 M KOH

Number of Cycles	Specific Capacitance (F/g)	Capacitance Retention (%)
1	261.1	100
200	268.2	102.7
400	213.6	81.8
600	168.9	64.7
800	153.1	58.6
1000	142.6	54.6

GCD experiment was implemented for the stability test at the applied current density of 2 A/g for 1000 successive cycles between the potential range of -0.4 V and 0.2 V in 6 M KOH. The non-linear feature on the GCD curves presented in **Figure 6.15** (b) is indicative of pseudocapacitance from the metal oxide. The specific capacitance obtained from GCD alone gives a lower value compared to that calculated from CV at only 261.1 F/g for the first cycle, which can be understood in much the same way as the similar phenomenon observed for bare rGO. The interesting aspect however is the increase in the capacitance retention from 40.2% in bare rGO to 54.6% after nickel hydroxide deposition. The remarkable capacitance retention is observed especially for the first 400 cycles where over 80% of specific capacitance was maintained compared to less than 50% recovered in bare rGO. This could be due to the fact that pseudocapacitance of nickel hydroxide contributes more to the overall specific capacitance than the capacitance from rGO. Also, nickel hydroxide particles could probably tolerate the successive cycling condition better than rGO. The significant drop in the latter part of the stability testing could be arisen from the dissolution of the nickel hydroxide particles from the rGO as evident in the SEM image taken after the test. The rGO surface

became more prone to deterioration during the testing process and therefore led to the further drop in capacitance seen.

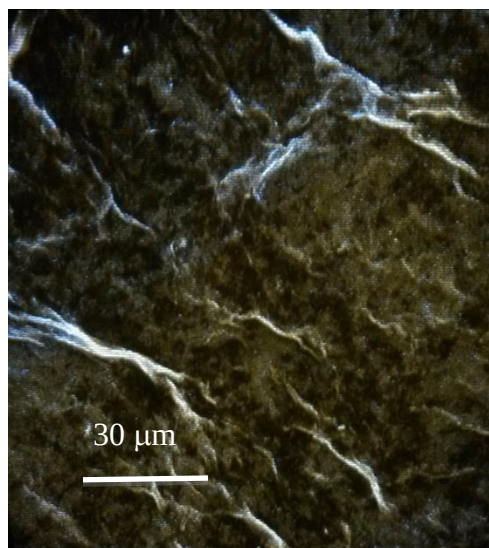


Figure 6.16 SEM image of heated Ni-rGO after stability test

SEM micrograph taken for the Ni(OH)_2 decorated rGO after the stability test was investigated and the image is shown in **Figure 6.16**. It is clear from the SEM image that the surface structure has been ruptured and occurs with much less well-defined wrinkled structure seen for the initial rGO before the stability test. Additionally, there is no clear sight of nickel deposits either in particulate or cluster forms. Therefore it is reasonable to imply that the nickel deposit might dissolve to the electrolyte solution during the long exposure to 1000 potential cycles, which in turn leads to the lower capacitance at higher number of scans.

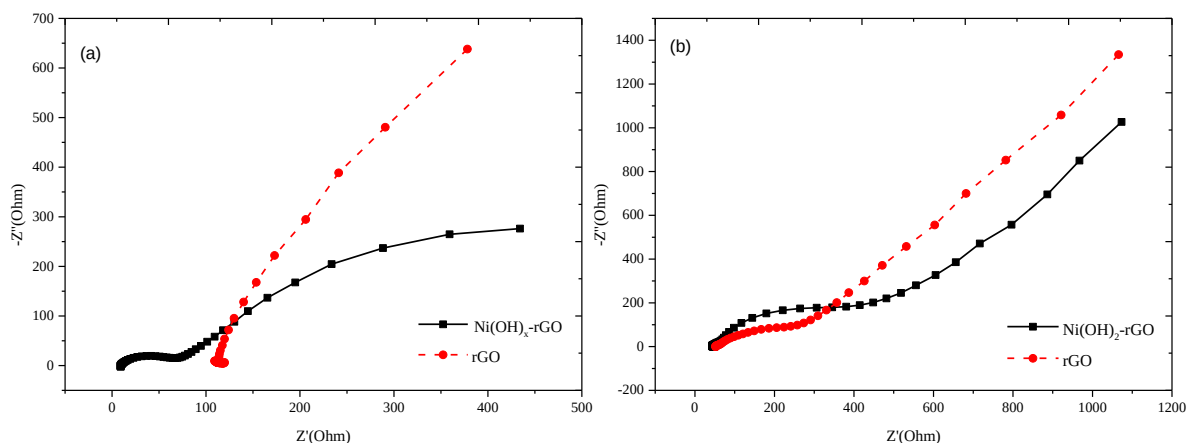


Figure 6.17 Nyquist plots from EIS of Nickel hydroxide deposited rGO compared to bare rGO before (a) and after (b) heating

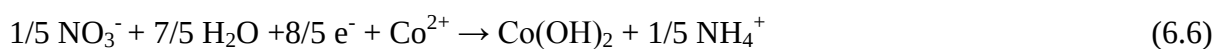
To further understand the loss in capacitance during the stability test, electrochemical impedance or EIS was employed. The technique allows equivalent series resistance or ESR of each sample to be evaluated from the x-intercept of the recorded Nyquist plots, which are presented in **Figure 6.17** above. The ESR values are found to be 114.5 Ω and 9.2 Ω for bare rGO and nickel hydroxide decorated rGO respectively. The semicircle in the high frequency region of the Nyquist plot indicates the charge transfer resistance and the gradient of the line in the low frequency region demonstrates the rate of ion-diffusion. Consider the pre-stability test of rGO and Ni-rGO samples, the nickel decorated graphene film exhibits smaller semicircle. This in turn leads to the implication that the deposited nickel hydroxide lowers the charge transfer which is due to the lower electrical conductivity of bare rGO compared to nickel hydroxide deposited rGO.

The steeper slope of $\text{Ni(OH)}_2\text{-rGO}$ compared to its bare graphene counterpart signifies the higher rate of ion-diffusion [35], which can be explained by the small size of the nickel deposits providing larger electroactive area and thus minimises the ion transport path between the electrode and electrolyte [36]. Although after heating the nickel deposited rGO still shows smaller charge transfer resistance and faster ion diffusion rate, the ESR increases from 9.2 Ω

to 47.1 Ω . By contrast a marked decrease in ESR of rGO is seen. This drop in ESR of rGO is considered to be because of the long exposure to the negative potential used in the GCD cycle, which could potentially reduce rGO further giving rise to higher conductivity. On the other hand, the significant increase in resistance of Ni(OH)₂ decorated rGO to the similar value of the post-stability rGO is in agreement with the SEM analysis above such that it relates to the loss of nickel particles over 1000 GCD cycles in the stability test performed.

6.3.4 Cobalt Hydroxide Electrodeposition

The same potentiostatic method was employed for the electrodeposition of cobalt hydroxide as with that for nickel hydroxide. CV was recorded for the deposited cobalt hydroxide on GO before and after heating at 300 °C for an hour in air. The same mechanism is expected to proceed during the electrodeposition step as in the case of nickel.



The specific capacitance calculated was tabulated in **Table 6.7** and compared with the value obtained for Ni(OH)₂-rGO. The as-prepared cobalt hydroxide decorated GO shows higher capacitance than its nickel counterpart, however after annealing the capacitance of nickel hydroxide-rGO largely outweighs that of cobalt. This shows the efficiency of electrodeposition on GO of cobalt hydroxide over nickel hydroxide but heating seems to affect the nickel hydroxide to a greater extent. It is therefore interesting to see how this result will affect the capacitance of the composite of nickel and cobalt hydroxide with rGO.

Table 6.7 Comparison of specific capacitance of GO and rGO decorated with cobalt or nickel hydroxides

Substrate	Capacitance (F/g)	
	Co(OH) ₂ deposit	Ni(OH) ₂ deposit
GO	110.8	36.9
rGO	300.4	936.5

6.3.5 Electrodeposition of nickel and cobalt hydroxides

Electrodeposition of nickel and cobalt hydroxides was performed also by chronoamperometric method with similar conditions used for electrodeposition of nickel hydroxide alone. The difference in the deposition method was made to distinguish between the simultaneous and sequential depositions, which are referred to as co-deposition and step deposition respectively. The stepwise deposition employs the deposition of nickel hydroxide on GO first, followed by the deposition of cobalt hydroxide. Afterwards, the composite will be heated as usual. The co-deposition features the use of cobalt nitrate solution mixed with nickel nitrate solution as the electrolyte for the electrodeposition, which was carried out at -1.2 V for 600 s in the total electrolyte concentration of 10 mM. The ratio between the concentration of nickel (II) and cobalt (II) ions was kept at 1:1 at first, this value was then varied to obtain the optimal ratio that gives the highest specific capacitance possible. As a control, the total deposition charge was kept at 50 mC for all samples.

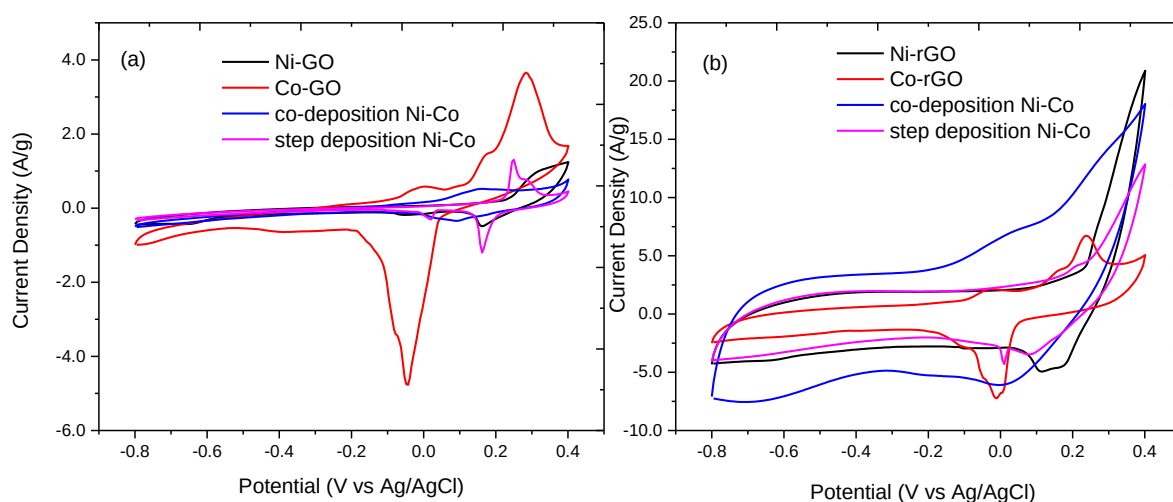


Figure 6.18 CV of (a) unheated and (b) heated nickel/cobalt hydroxide deposited on GO in 6 M KOH at 5 mV/s

The recorded CVs for the heated nickel-cobalt hydroxide on rGO prepared by the two approaches were presented in **Figure 6.18** (b). The specific capacitance of the co-deposited

nickel and cobalt hydroxide on rGO exhibits the highest capacitance among the samples tested at 1030.5 F/g, which is higher than nickel hydroxide on rGO alone. In marked contrast, the stepwise deposition results in the specific capacitance of 535.5 F/g, which is higher than cobalt hydroxide-rGO but still lower than nickel hydroxide-rGO. The main feature of the CV is also different between the two with the co-deposition produces CV similar to that found for Ni(OH)₂-rGO whereas the stepwise deposition gives rise to two distinct reduction peaks at 0.10 V and -0.02 V. The peak at more negative potential is ascribed to be due to cobalt possibly in a form of CoOOH [37]. Consequently, the results suggest the advantage of co-deposition over stepwise method.

Table 6.8 Summary of specific capacitance of co-deposition of cobalt and nickel hydroxides onto rGO substrate at different Co:Ni ratio

Co(NO ₃) ₂ .6H ₂ O	Ni(NO ₃) ₂ .6H ₂ O	Capacitance/Fg ⁻¹
1	1	1030.5
2	1	1551.9
1	2	1384.4
3	1	971.2
1	3	314.9

The optimisation of the cobalt to nickel ratio was subsequently carried out for the co-deposition method. It has to be noted here however that the ratio is associated with Co²⁺ and Ni²⁺ ions in the depositing electrolyte and cannot be directly referred to the actual composition of the composites produced. According to **Table 6.8**, the highest value, 1551.9 F/g, was exhibited by 2:1 cobalt to nickel ratio. A higher percentage of cobalt than nickel in the composite seems to favour the rise in capacitance however at even higher ratio of 3:1 Co to Ni the decline in capacitance value is seen dropping to 971.2 F/g. The impressively high capacitance when the percentage of cobalt is higher than nickel is also previously reported by Wang *et al.* [38]. The structural and electrochemical characterisations were studied and the results are as follows.

6.3.5.1 SEM

SEM analysis of the nickel and cobalt hydroxide composite on rGO was performed for the 1:1 ratio of Co:Ni produced by the two different methods as well as the 2:1 Co:Ni co-deposited sample possessing the highest capacitance as reported above and presented in **Figure 6.19**.

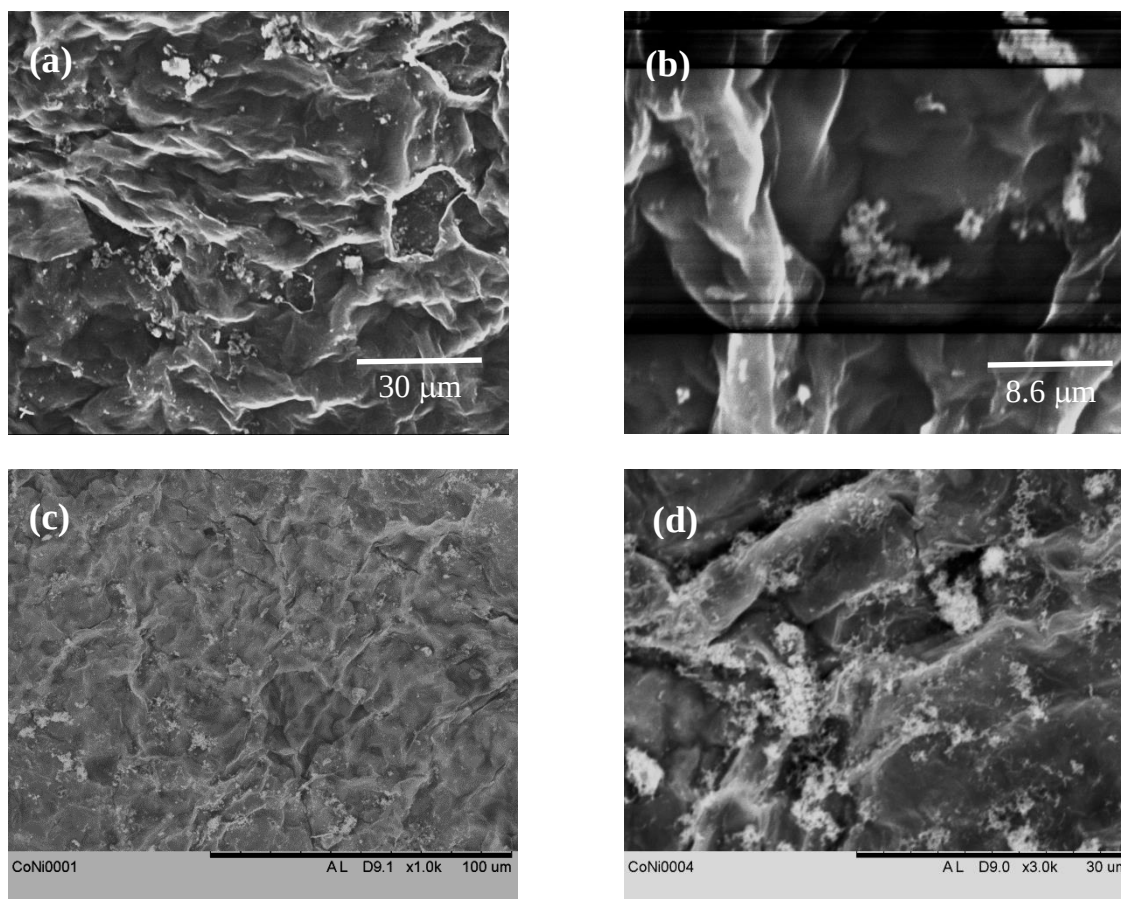


Figure 6.19 SEM images of heated nickel and cobalt hydroxides deposited on GO by (a) co-deposition and (b) stepwise deposition. (c) and (d) show the surface morphology of heated 2Co:1Ni hydroxide deposited on GO at 1000x and 3000x magnification respectively

The main difference between the codeposition in **Figure 6.19** (a) and the stepwise deposition (b) is that in the step deposition, more clusters are observed compared to better distributed particles produced in the co-deposition method. This observation could suggest the different pathway in which metal ions migrate along the active surface area of GO to form the hydroxide precipitate. In the step deposition, cobalt hydroxide seems to be more

preferentially deposited onto the more electroactive site of the deposited nickel hydroxide than directly onto vacant GO surface. **Figure 6.19** (c) and (d) show the surface coverage of the 2:1 Co:Ni hydroxide on rGO at two different magnifications. The SEM results possibly can explain the difference in specific capacitance, C_{sp} seen between the two methods. The lower C_{sp} for the stepwise method could stem from the larger clusters formed and hence less active surface area available for the electrochemical processes.

6.3.5.2 XPS

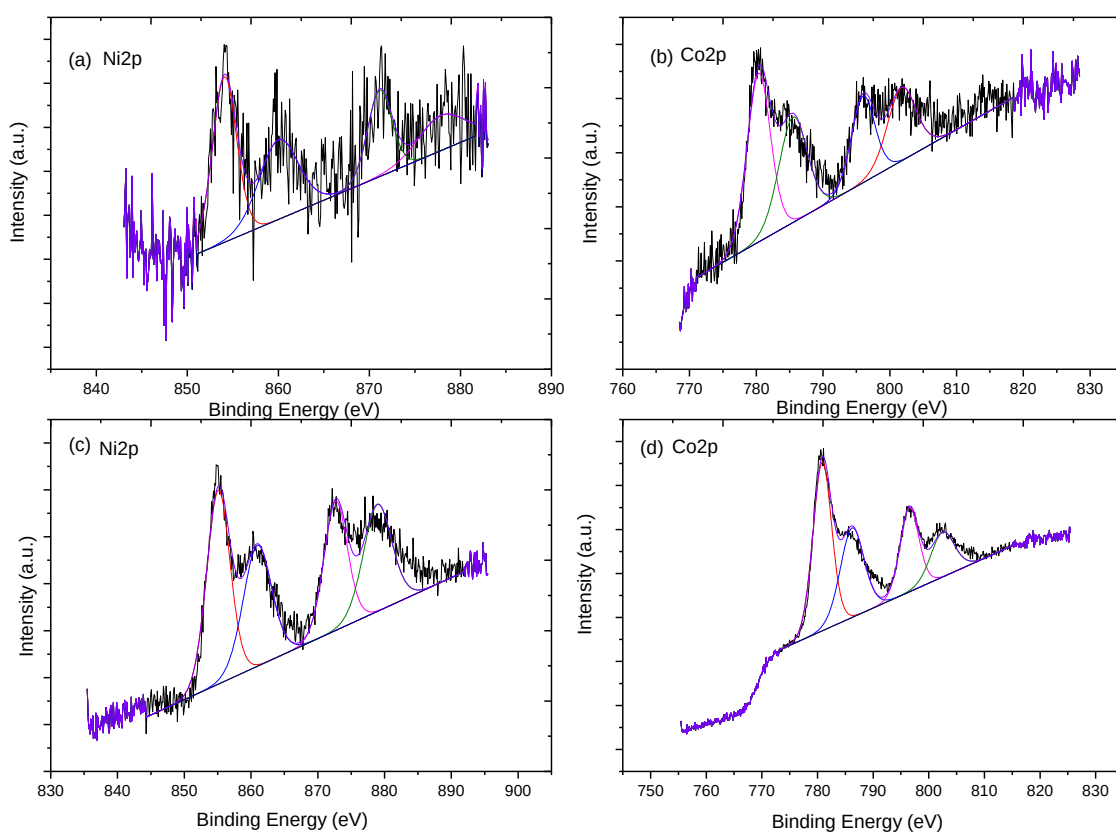


Figure 6.20 XPS spectra of Ni2p in (a) and (c), and Co2p in (b) and (d) from unheated nickel and cobalt hydroxides decorated on GO from co-deposition (a), (b) and stepwise deposition (c) and (d)

For both unheated samples (stepwise and co-deposited Ni-Co hydroxide on GO), C1s is found to be similar as before featuring peaks at 285.0, 287.0 and 289.0 eV for graphitic carbon, carbonyl and carboxyl groups respectively. The O1s peak lies at 531.4 for stepwise

and 531.6 eV for co-deposition indicating bound hydroxide ions and thus suggesting the presence of Ni(OH)_2 and Co(OH)_2 as expected.

Figure 6.20 (a) shows Ni2p peak from co-deposition with $\text{Ni2p}_{3/2}$ and $\text{Ni2p}_{1/2}$ present at 855.2 and 872.8 eV respectively with the energy gap of 17.61 eV. For the Ni2p peak from stepwise deposition presented in (c), the data resembles that of Ni(OH)_2 -GO and co-deposition as well where the doublet $\text{Ni2p}_{3/2}$ lies at 855.1 eV and $\text{Ni2p}_{1/2}$ is at 872.7 eV with the separation of 17.57 eV in binding energy. This range of the Ni2p peak separation justifies the presence of Ni(OH)_2 for these unheated samples [30, 31].

On the other hand, the Co2p peak also appears as doublet peaks as seen in (b) and (d). In **Figure 6.20** (b) $\text{Co2p}_{3/2}$ and $\text{Co2p}_{1/2}$ lie at 780.4 and 796.0 eV respectively for the co-deposited sample. Similarly, as for the stepwise sample Co2p doublet peaks are present at 780.3 and 796.5 eV. The binding energy at which the Co2p peaks occur is characteristic of Co(OH)_2 [39]. The energy gap between the $\text{Co2p}_{3/2}$ and $\text{Co2p}_{1/2}$ peaks is also similar at 15.6 eV. Although there seems to be no significant difference in terms of chemical functionality of the Ni-Co deposits, the more striking distinction comes from the relative surface composition of Ni and Co. The co-deposition results in rather similar amount of surface Ni and Co found and gives rise to the ratio of 1:1 as used for the electrolyte deposition. By contrast the stepwise deposition leads to the Ni to Co ratio of 1:2 which suggests the preferential deposition of cobalt onto the nickel decorated GO surface, presumably due to nickel deposit being more electrochemically active than GO and hence results in higher cobalt deposits. This finding again confirms the interpretation of the SEM images such that stepwise deposition results in more directional deposition and less uniformly dispersed particles and deposition of cobalt could be on top of the deposited nickel hydroxide surface lowering its ability to fully involve in the redox reactions.

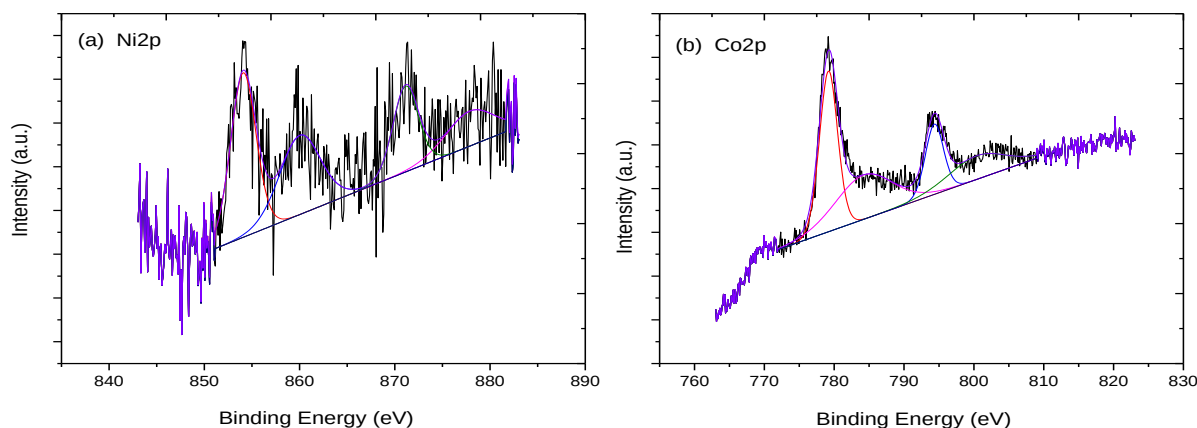


Figure 6.21 XPS spectra of (a) Ni2p and (b) Co2p from the optimal 2Co:1Ni sample after heating

The optimal sample, heated 2:1 Co-Ni hydroxide on rGO, produced from co-deposition gives rise to the Ni2p and Co2p spectra as shown in **Figure 6.21** (a) and (b). The doublet peak of Co2p appears at 779.2 and 794.3 eV while the Ni2p doublet occurs at 854.1 and 871.1 eV. Interestingly, the estimation of the surface composition shows that the percentage of cobalt is about four times higher than that of nickel, 6.6% compared to 1.5%. This evaluation gives the actual composition ratio of Co:Ni as 4:1 despite the use of 2:1 ratio in the depositing electrolyte. This sample will therefore be referred to as $\text{Co}_{4x}\text{Ni}_x\text{-rGO}$.

6.3.5.3 Scan Rate, Stability and Reproducibility

Figure 6.22 shows the CVs at different scan rate of $\text{Co}_{4x}\text{Ni}_x\text{-rGO}$ sample; again the specific capacitance drops dramatically at higher scan rates. The stability test was set up with the same potential range and conditions used as previously mentioned. After 1000 cycles, the capacitance retention is 50.2%, which is unsurprisingly similar to that found for Ni-rGO. The Nyquist plot from the EIS measurement also resembles the Ni-rGO with a small increase in the charge transfer resistance after the stability test. The same explanation is thus valid here where long-term exposure of the $\text{Co}_{4x}\text{Ni}_x\text{-rGO}$ film to the highly concentrated and basic electrolyte can cause damage to the rGO surface as well as the numerous GCD cycle renders

the dissolution or disintegration of the deposited metal hydroxide particles from the rGO surface. An attempt has been made to double the thickness of the rGO film however no improvement is seen for the retention of capacitance.

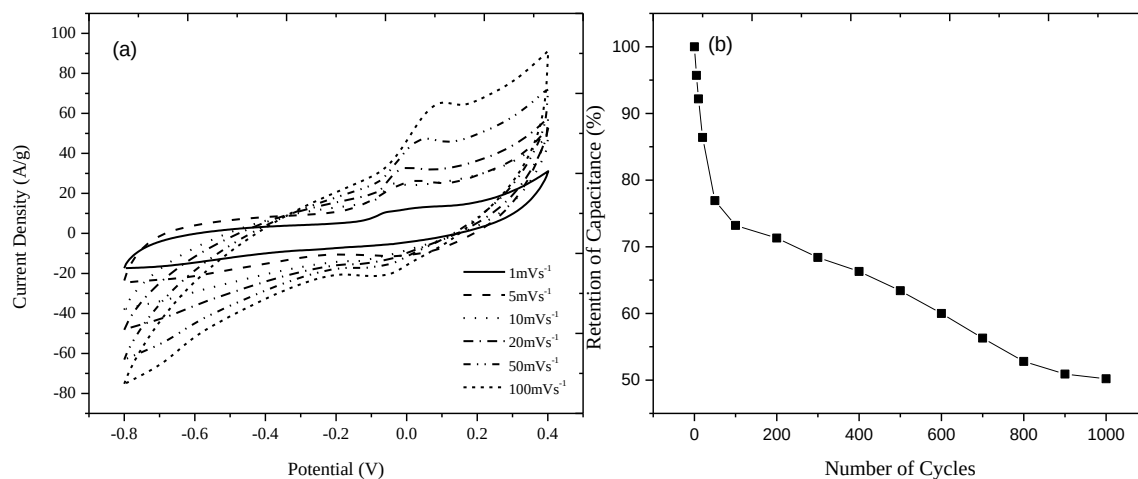


Figure 6.22 (a) CV at different scan rate of the $\text{Co}_{4x}\text{Ni}_x\text{-rGO}$ sample and (b) Specific capacitance retention after 1000 GCD cycles in 6 M KOH

6.3.5.4 Power and energy densities

To provide a full specification of a supercapacitor, energy density as well as power density is considered. The evaluation of the two parameters is by the same equations described in the previous chapter. As for the $\text{Co}_{4x}\text{Ni}_x\text{-rGO}$ sample, which is the sample with the highest specific capacitance of 1551.9 F/g the energy and the power densities are determined to be 18.6 Wh/kg and 38.7 kW/kg respectively. The specific capacitance itself of 1551.9 F/g has shown to compare favourably with the literature where the specific capacitance based on nickel and cobalt hydroxide composite is in a broad range from 882 F/g to 2680 F/g [38, 39, 41-47] for the mixed Co and Ni hydroxide/oxide composites as a supercapacitor.

6.4 Concluding Remarks

- It has been shown that a thermal reduction of graphene oxide incorporated with NaHCO_3 can effectively produce highly porous free-standing reduced graphene oxide

(rGO) film with good supercapacitor characteristics possessing a high specific capacitance of 561.5 F/g as judged by CV in 6 M KOH at a scan rate of 5 mV/s. The reduction of graphene oxide was confirmed by XPS and FTIR due to the reduced amount of oxygen presence via the loss of C-O bond upon heating. Although NaHCO_3 might not significantly involve in the reduction of GO, its decomposition gave rise to the high porosity of the rGO film as verified by BET analysis.

- The specific capacitance of this graphene-based material can be enhanced further to 936.5 F/g with improved galvanostatic cycling stability by the electrodeposition of a pseudocapacitive material, nickel hydroxide, onto the graphene surface.
- The co-deposition of nickel and cobalt hydroxide gave rise to more uniform distribution of particles than the stepwise method and thus provided the state-of-the-art supercapacitor with a specific capacitance exceeding 1500 F/g. The only moderate stability of ~50% after 1000 GCD cycles however remains an issue to be developed upon.

References

- [1] S. Biswas and L. T. Drzal, *Acs Applied Materials & Interfaces* 2:2293 (2010).
- [2] X. Zhao, H. Tian, M. Zhu, K. Tian, J. J. Wang, F. Kang, and R. A. Outlaw, *Journal of Power Sources* 194:1208 (2009).
- [3] S. Biswas and L. T. Drzal, *Chemistry of Materials* 22:5667 (2010).
- [4] Z. Gao, J. Wang, Z. S. Li, W. L. Yang, B. Wang, M. J. Hou, Y. He, Q. Liu, T. Mann, P. P. Yang, M. L. Zhang, and L. H. Liu, *Chemistry of Materials* 23:3509 (2011).
- [5] S. Ye, J. Feng, and P. Wu, *Acs Applied Materials & Interfaces* 5:7122 (2013).
- [6] Q. Shao, J. Tang, Y. Lin, F. Zhang, J. Yuan, H. Zhang, N. Shinya, and L.-C. Qin, *Journal of Materials Chemistry A* 1:15423 (2013).
- [7] Z. Niu, J. Chen, H. H. Hng, J. Ma, and X. Chen, *Advanced Materials* 24:4144 (2012).
- [8] C. D. Lokhande, D. P. Dubal, and O.-S. Joo, *Current Applied Physics* 11:255 (2011).
- [9] M. Toupin, T. Brousse, and D. Bélanger, *Chemistry of Materials* 16:3184 (2004).
- [10] Z. Lu, Z. Chang, J. Liu, and X. Sun, *Nano Research* 4:658 (2011).
- [11] S. Chen, J. Duan, Y. Tang, and S. Zhang Qiao, *Chemistry – A European Journal* 19:7118 (2013).
- [12] S. Ding, T. Zhu, J. S. Chen, Z. Wang, C. Yuan, and X. W. Lou, *Journal of Materials Chemistry* 21:6602 (2011).
- [13] A. Bello, K. Makgopa, M. Fabiane, D. Dodoo-Ahrin, K. I. Ozoemena, and N. Manyala, *Journal of Materials Science* 48:6707 (2013).
- [14] C.-h. Zheng, X. Liu, Z.-d. Chen, Z.-f. Wu, and D.-l. Fang, *Journal of Central South University* 21:2596 (2014).
- [15] M. J. Hegarty, in *Chemistry*, Master of Chemistry, University of Oxford, Oxford, 2013, p. 60.
- [16] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon* 45:1558 (2007).
- [17] W. Si, X. Wu, J. Zhou, F. Guo, S. Zhuo, H. Cui, and W. Xing, *Nanoscale Research Letters* 8:247 (2013).
- [18] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, *Nature* 442:282 (2006).

- [19] M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, and I. A. Aksay, *Chemistry of Materials* **19**:4396 (2007).
- [20] H. C. Schniepp, J. L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, and I. A. Aksay, *Journal of Physical Chemistry B* **110**:8535 (2006).
- [21] H. c. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, and Y. Chen, *Acs Nano* **2**:463 (2008).
- [22] S. Eigler, *Carbon* **47**:2936 (2009).
- [23] R. Larciprete, S. Fabris, T. Sun, P. Lacovig, A. Baraldi, and S. Lizzit, *Journal of the American Chemical Society* **133**:17315 (2011).
- [24] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, *Chemical Society Reviews* **39**:228 (2010).
- [25] M. J. Fernandez-Merino, L. Guardia, J. I. Paredes, S. Villar-Rodil, P. Solis-Fernandez, A. Martinez-Alonso, and J. M. D. Tascon, *Journal of Physical Chemistry C* **114**:6426 (2010).
- [26] L. A. Hutton, M. Vidotti, A. N. Patel, M. E. Newton, P. R. Unwin, and J. V. Macpherson, *The Journal of Physical Chemistry C* **115**:1649 (2010).
- [27] M. Paunovic, M. Schlesinger, S. Electrochemical, and Ecs, Fundamentals of electrochemical deposition, New York Chichester : John Wiley, New York Chichester, 1998.
- [28] C. C. Streinz, S. Motupally, and J. W. Weidner, *Journal of the Electrochemical Society* **142**:4051 (1995).
- [29] J. Xiao and S. Yang, *Journal of Materials Chemistry* **22**:12253 (2012).
- [30] H. B. Li, M. H. Yu, F. X. Wang, P. Liu, Y. Liang, J. Xiao, C. X. Wang, Y. X. Tong, and G. W. Yang, *Nature Communications* **4**:1894 (2013).
- [31] J. W. Lee, T. Ahn, D. Soundararajan, J. M. Ko, and J.-D. Kim, *Chemical Communications* **47**:6305 (2011).
- [32] J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, and F. Wei, *Advanced Functional Materials* **22**:2632 (2012).
- [33] A. Agrawal, H. R. Habibi, R. K. Agrawal, J. P. Cronin, D. M. Roberts, R. S. Caron-Popowich, and C. M. Lampert, *Thin Solid Films* **221**:239 (1992).
- [34] M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson, and R. S. C. Smart, *Surface and Interface Analysis* **41**:324 (2009).

- [35] X. Xia, J. Tu, Y. Mai, R. Chen, X. Wang, C. Gu, and X. Zhao, *Chemistry – A European Journal* 17:10898 (2011).
- [36] H. Zhang, X. Zhang, D. Zhang, X. Sun, H. Lin, C. Wang, and Y. Ma, *The Journal of Physical Chemistry B* 117:1616 (2012).
- [37] Y. Cheng, H. Zhang, C. V. Varanasi, and J. Liu, *Energy & Environmental Science* 6:3314 (2013).
- [38] G. Wang, L. Zhang, J. Kim, and J. Zhang, *Journal of Power Sources* 217:554 (2012).
- [39] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, *Applied Surface Science* 257:2717 (2011).

Chapter 7 Electrodeposition of Textured Pt Nanoparticles on Graphene Nanoplatelets for Electrocatalytic Oxidation of Methanol

7.1 Introduction

The direct methanol fuel cell (DMFC) has attracted widespread interest as one of the leading candidates for an alternative power source due to its low carbon footprint, pollutant-free compared to combustion of fossil fuels, a high energy density, a low operating temperature, and ease of liquid fuels transportation. However, the application of DMFC is limited by the electrocatalytic activity of anodes for methanol oxidation and high cost of noble metal catalysts such as platinum [1]. Platinum has shown to be the most efficient catalyst for methanol oxidation since it possesses the highest catalytic activity towards dissociative adsorption of methanol [2]. However, in order to reduce the loading of this costly noble metal and enhance the catalysts activity, different deposition strategy and supporting materials have been explored to improve the dispersion of catalysts.

Carbon materials stand out as the most common support for fuel cell applications due to its properties matching the requirement of low cost, high surface area and good electrical conductivity. Carbon support with a high degree of graphitisation is more corrosion-resistant as the more delocalised π bonds (sp^2) strengthen interaction with noble metal catalysts [3]. Among the highly graphitised carbon support materials, graphene, a single layer of sp^2 -bonded carbon atoms in a 2D close packed honeycomb crystal lattice, has attracted enormous attention recently [4]. Besides its excellent physical properties, such as electrical conductivity, robust mechanical properties, optical properties and thermal properties, it also

demonstrates promising electrochemical properties as an ideal support material for electrocatalysts due to extremely high specific surface area and excellent electrical conductivity [5].

Examples of studies on the synthesis of platinum nanoparticles on graphene include chemical reduction by sodium borohydride or ascorbic acid [6-10], microwave assisted reduction [11], impregnation [12, 13], colloidal method [14] or vacuum sputter deposition in [5], but little work was done on electrodeposition of platinum on graphene sheet. Electrodeposition is a promising method as catalytic particles are selectively deposited only onto the electrode regions where both ions and electrons are accessible for an efficient utilisation of the noble metal catalyst. In this study, we have systematically studied the electrodeposition of platinum on graphene nanoplatelets (GNPs). This work compared chronoamperometric deposition and potential step deposition methods on graphene, and compared graphene with other carbon supports including carbon nanotube (CNT), graphite, and glassy carbon (GC). The morphology and Pt crystalline structure were characterised by SEM and XRD and the electrocatalytic activity was evaluated by cyclic voltammetry.

7.2 Experimental

Graphene nano-platelet of 3 μm diameter and less than 10 nm thickness was obtained from Angstrom materials. Synthetic graphite micropowder (1-2 μm) and multi-walled carbon nanotube (diameter 110-170 nm, length 5-9 μm , >90%) were purchased from Aldrich. Sulfuric acid 95-97% (Fisher Scientific) and methanol of HPLC grade (Rathburn Chemicals Ltd) were used. Dihydrogen hexachloroplatinate(IV) hexahydrate (99.9%, Alfa Aesar) was used for deposition of Pt. All aqueous solutions were prepared by milli-Q water with a resistivity greater than 18 $\text{M}\Omega\cdot\text{cm}$ at 25 $^{\circ}\text{C}$.

X-ray diffraction pattern was acquired using Philips X'Pert PRO diffractometer operating at 30 mA and 40 KV with Cu K α radiation at a step size of 0.017°. The morphology was measured using a Hitachi 530 SEM with a 20 kV acceleration voltage.

Glassy carbon electrodes were mechanically polished to a mirror finish and cleaned with distilled water and ethanol in an ultrasonic bath. The dried glassy carbon electrode was subsequently drop-casted with 4 μ l aqueous suspension of graphene, graphite, or MWCNT (1 mg/ml) and left to dry overnight prior to use. Platinum was deposited via either potentiostatic or potential step deposition method using 2 mM H₂PtCl₆ in 0.5 M H₂SO₄. Potentiostatic deposition was conducted by applying a constant potential of -0.2 V for 600 seconds, and potential step deposition was carried out by applying a stepped potential from 0.3 V to -0.2 V with a step of 0.1 V and 30 seconds per step for 5 cycles.

7.3 Results and discussion

7.3.1 Electrodeposition

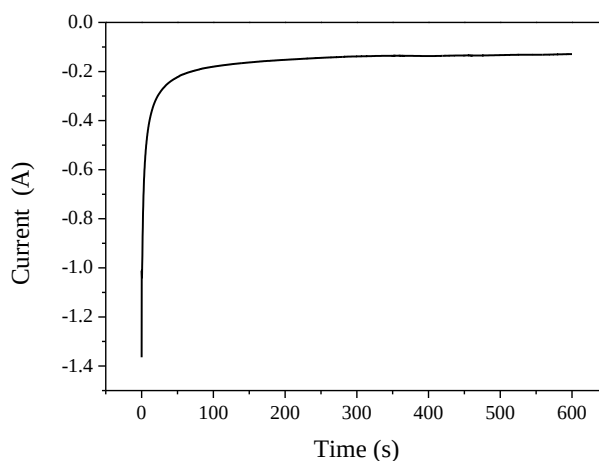


Figure 7.1 Typical current-time transient for electrodeposition of platinum on graphene nanosheets by applying constant potential of -0.2 V

Platinum nanoparticles were introduced on to graphene substrates by means of electrochemical deposition. Two distinguished methods were carried out and the corresponding plots of current as a function of time during the deposition period are

displayed in **Figure 7.1**. When the applied potential is constant or a so-called potentiostatic method, the instantaneous negative current at the initial time is viably observed. This is followed by the current becoming less negative at longer time and shows to reach a limit after 100 s as seen in **Figure 7.1**. The overall charge of deposition (Q_{Pt}) was found from graphical integration of current over time and is equal to 9.3 mC.

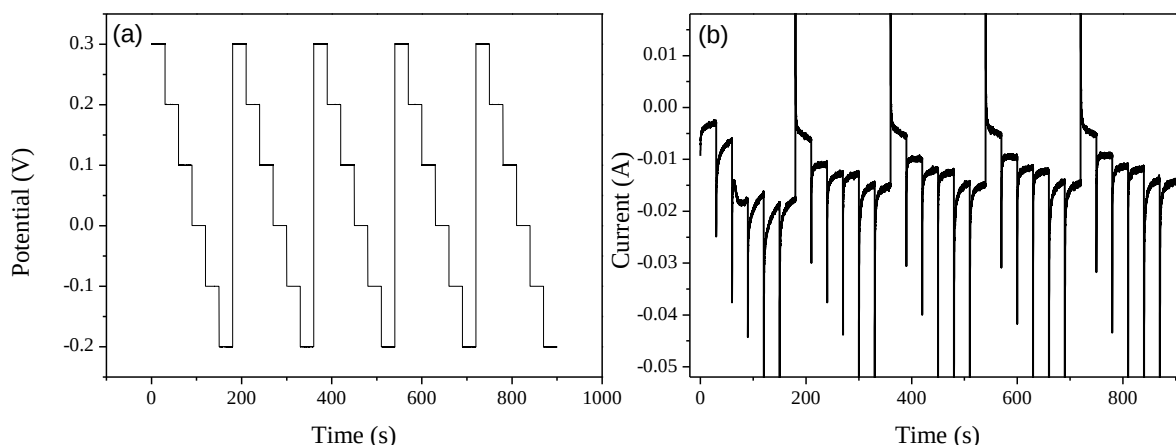


Figure 7.2 (a) Schematic representation of the stepwise applied potential and (b) the resulting current-time transient for the electrodeposition of platinum on graphene substrate

On the other hand, the current time transient resulted from the stepped potential deposition of platinum is not continuous and changes with the potential that was stepped. It is clear that the current also decreases with the decrease in applied potential throughout the five cycles. Similarly, the deposition charge was estimated by integration and is equal to 11.60 mC. This charge value is in close proximity to that found for the potentiostatic method, hence the mass loading of Pt deposit should also be comparable.

The mass loading of Pt (m_{Pt}) can be calculated by assuming 100% current efficiency and that the charge value from the integration is solely from the Faradaic process in the formation of Pt as outlined in equation 7.1 below.



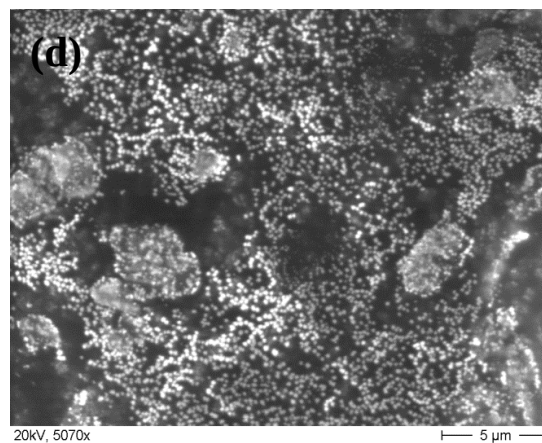
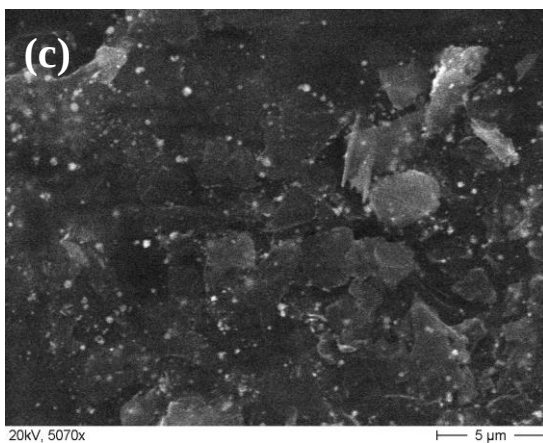
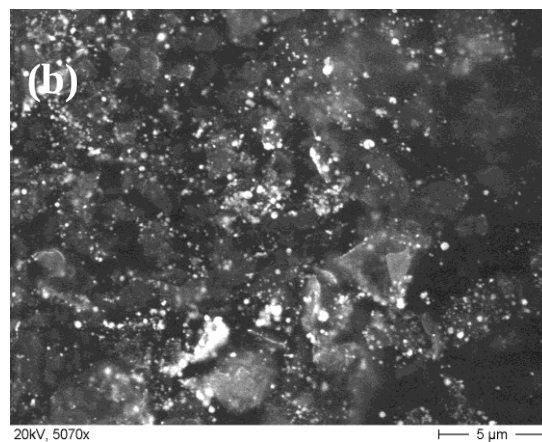
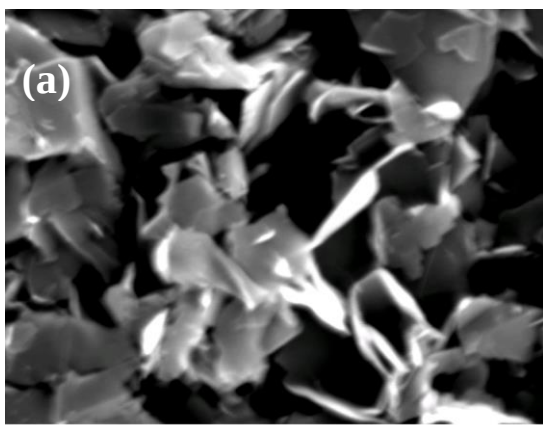
The m_{Pt} can hence be determined by a relationship according to Faraday's law as

$$m_{Pt} = \frac{Q_{Pt}M}{4F} \quad (7.2)$$

where M is the atomic mass of Pt (195.09 g/mol) and F is the Faraday constant (96485 C/mol). As a result, the mass loadings of Pt are 4.70 μg and 5.88 μg for the potentiostatic and potential step electrodeposition respectively.

7.3.2 Characterisation of Pt deposits

7.3.2.1 SEM



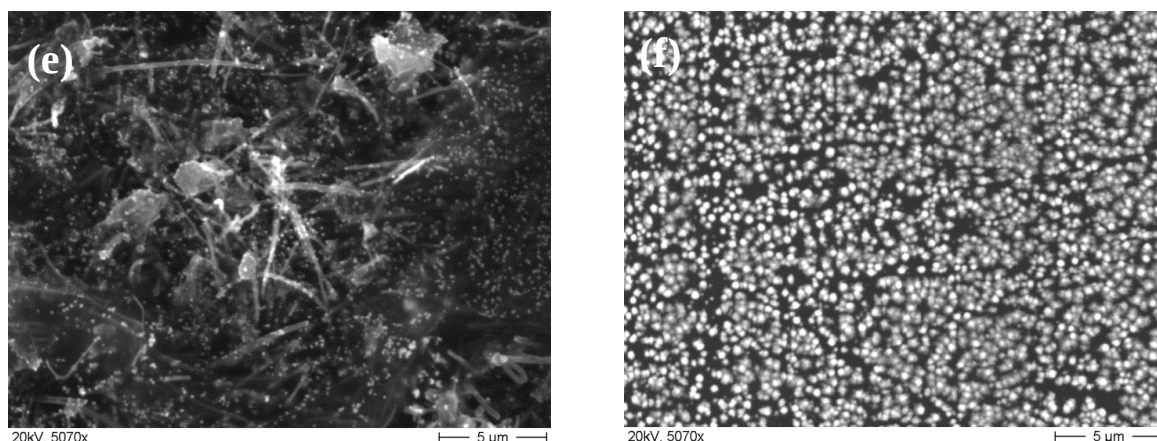


Figure 7.3 SEM micrographs of graphene nanoplatelets (a) and Pt deposit on carbon support: (b) Pt potential step deposition on graphene, and Pt potentiostatic technique on (c) graphene, (d) graphite micropowder, (e) MWCNT and (f) bare glassy carbon plate.

The morphology of graphene nanoplatelets (GNPs) and platinum nanoparticles deposited on different carbon substrates was investigated using SEM, as shown in **Figure 7.3**. The GNPs were used as received. The dimension of the GNPs is of a few micrometres as seen from the SEM micrograph. The thickness of GNPs was reported to be around 10 nm, which is higher than the thickness of pristine monolayer graphene as expected due to the stacking of the single layers.

After decoration with platinum nanoparticles by electrodeposition, small particles with an average diameter of 170 nm were observed after potentiostatic deposition in **Figure 7.3** (c). By contrast, larger particle size with an average diameter of 250 nm and less uniformly distributed particles were seen from the potential step deposition method in **Figure 7.3** (b). In order to compare graphene with other carbon materials as an electrode support in this work, potentiostatic deposition method was adopted as this method led to more uniform distribution and smaller particles.

The morphology of Pt decorated GNPs, MWCNT, graphite micro-powder, and glassy carbon are compared in **Figure 7.3** (c)-(f). The average Pt particle size is different in each material,

with the smallest particle of around 160 nm on MWCNT, followed closely by 170 nm on graphene, whereas considerably larger particles of 270 nm and 350 nm on graphite micro-powder and glassy carbon support respectively. The smaller size of Pt particles obtained on MWCNT and graphene nanoplatelets could be attributable to the large surface area and dense surface defects which provide a relatively large number of nucleation sites available on these two materials [15].

Nucleation process during electrodeposition can be predicted from the particle size distribution. There are two modes of nucleation process according to Scharifker and Hills models [16], which are termed ‘instantaneous’ and ‘progressive’ processes. With regards to instantaneous nucleation, all vacant sites on the surface are instantaneously converted into nucleation sites at the similar time. On the other hand, as for the progressive nucleation, new nuclei are being formed continuously throughout the deposition period.

From the morphological information above, such uniform size distribution is observed in all four supports from potentiostatic deposition; therefore this could indicate an instantaneous nucleation process [17, 18]. By contrast, a rather broad distribution of particle size is observed from potential step deposition, and this might suggest that a progressive nucleation took place which is consistent with the previous finding of step potential electrodeposition of Pt nanoparticles on various carbon substrates [19].

7.3.2.2 Electrochemical Active Surface (EAS)

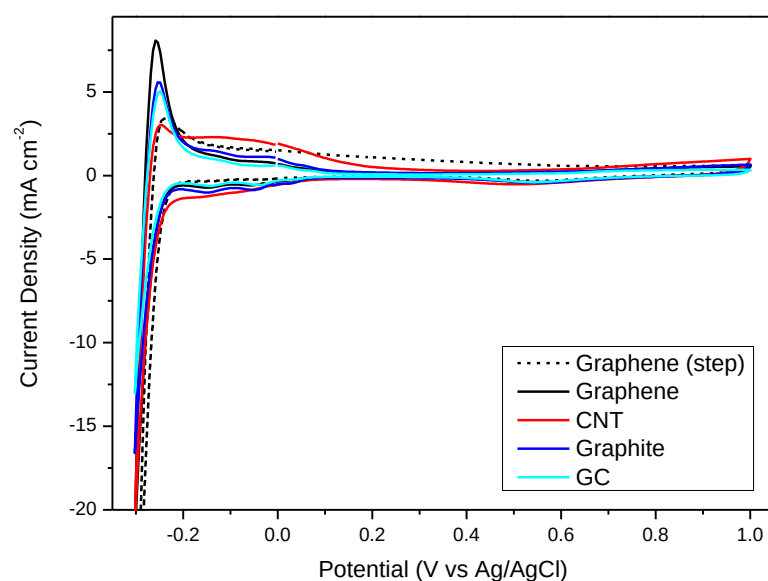


Figure 7.4 CV of Pt nanoparticles decorated graphene produced by potential step method (dashed line) and potentiostatic method (solid line), and compared to difference carbon supports in 0.5 M H_2SO_4

The electrochemical activity of Pt nanoparticles deposited by the two methods on graphene nanoplatelets is characterised by cyclic voltammetry in 0.5 M H_2SO_4 at a scan rate of 0.05 V/s, and compared to the activity on other carbon supports, as shown in **Figure 7.4**. The voltammograms display a prominent anodic peak at around -0.25 V, which corresponds to the oxidation of hydrogen, and faradaic currents at more positive potentials due to oxidation of adsorbed hydrogen on the surface of Pt nanoparticles. The associated coulombic charge during hydrogen desorption was calculated by integrating the anodic current after background subtraction. From the hydrogen desorption charge, the electrochemical active surface area (EAS) can be calculated based on the assumption that 0.21 mQ/cm^2 charge is required to oxidise a monolayer of platinum on Pt (111) surface [20], and summarised in **Table 7.1**.

Table 7.1 Comparison of electrocatalytic activity of platinum nanoparticles on various carbon supports

Carbon support	Pt loading (μg)	Hydrogen desorption (mC)	EAS (cm^2)	Specific EAS ($\text{cm}^2/\mu\text{g}$)	Calculated Pt particle size (nm)
Graphene (stepped potential)	5.88	0.71	3.38	0.57	4.9
Graphene	4.70	0.85	4.05	0.86	3.3
MWCNT	4.80	0.98	4.67	0.97	2.9
Graphite	4.95	0.78	3.71	0.75	3.7
Glassy Carbon	4.47	0.61	2.90	0.65	4.3

From EAS, the specific Pt active area (S) can be calculated by normalizing with platinum loading which is estimated from integration of platinum reduction current, and the particle diameter can be estimated from equation $d=6\times 10^3/\rho\times S$ where ρ is the density of platinum (21.45 g/cm^3) assuming a spherical geometry [21].

Platinum nanoparticles prepared by potentiostatic method on graphene nanoplatelets support exhibit much larger hydrogen desorption current, larger EAS value and smaller calculated particles diameter than by potential step deposition method, which is consistent with the smaller Pt particle size and better dispersion shown in SEM observations and agrees with the calculated particle diameter. The particle size from theoretical calculation is much smaller than visual SEM observations because the Pt particles observed in SEM are due to agglomerates of finer particles giving rise to significant porosity and enhanced surface area [22]. The trends of both calculated and observed particle sizes however are consistent with each other despite the large difference in the actual values reported.

The EAS values and the specific active area vary significantly on differing carbon supports, with the highest arising from MWCNT followed closely by graphene, and graphite and glassy carbon are the lowest. Pt decorated MWCNT shows a distinguishably different shape of hydrogen oxidation peak compared to Pt functionalised graphene nanoplatelets, micro

graphite powder and glassy carbon electrode, as shown in **Figure 7.4**. Voltammogram on MWCNT exhibits a broad anodic peak from -0.25 V to 0.1 V with a wide shoulder, which is characteristic of hydrogen desorption on Pt(111) surface occurring at relatively more positive potential [23]. The differing specific area more or less reflects the variation of average particle size. The large specific active area on graphene and MWCNT originates from the superior property of these two materials especially in terms of higher surface area of the substrates, which could potentially increase the number of nucleation sites.

7.3.2.3 X-Ray Diffraction

Further investigation into the crystallinity of the deposited Pt nanoparticles was carried out by X-ray diffraction method and the recorded patterns are presented in **Figure 7.5**. As the XRD samples are prepared on the glassy carbon substrates modified with graphene, graphite or MWCNTs and then decorated with Pt particle, the XRD patterns of all samples hence show the predominating signals from the glassy carbon base. These broad and highly intense peaks at approximately 25°, 44° and 80° angles are possibly due to the amorphous and disordered nature of glassy carbon. Graphite and graphene substrates show two additional peaks at 26.8° and around 55° angles which can be attributed to (002) and (004) phases. The (002) is very sharp compared to the broad peak appear around 25° of glassy carbon, indicating significantly more crystalline structure of graphene and graphite over glassy carbon. However these two distinguishable peaks are obscured in the case of MWCNTs.

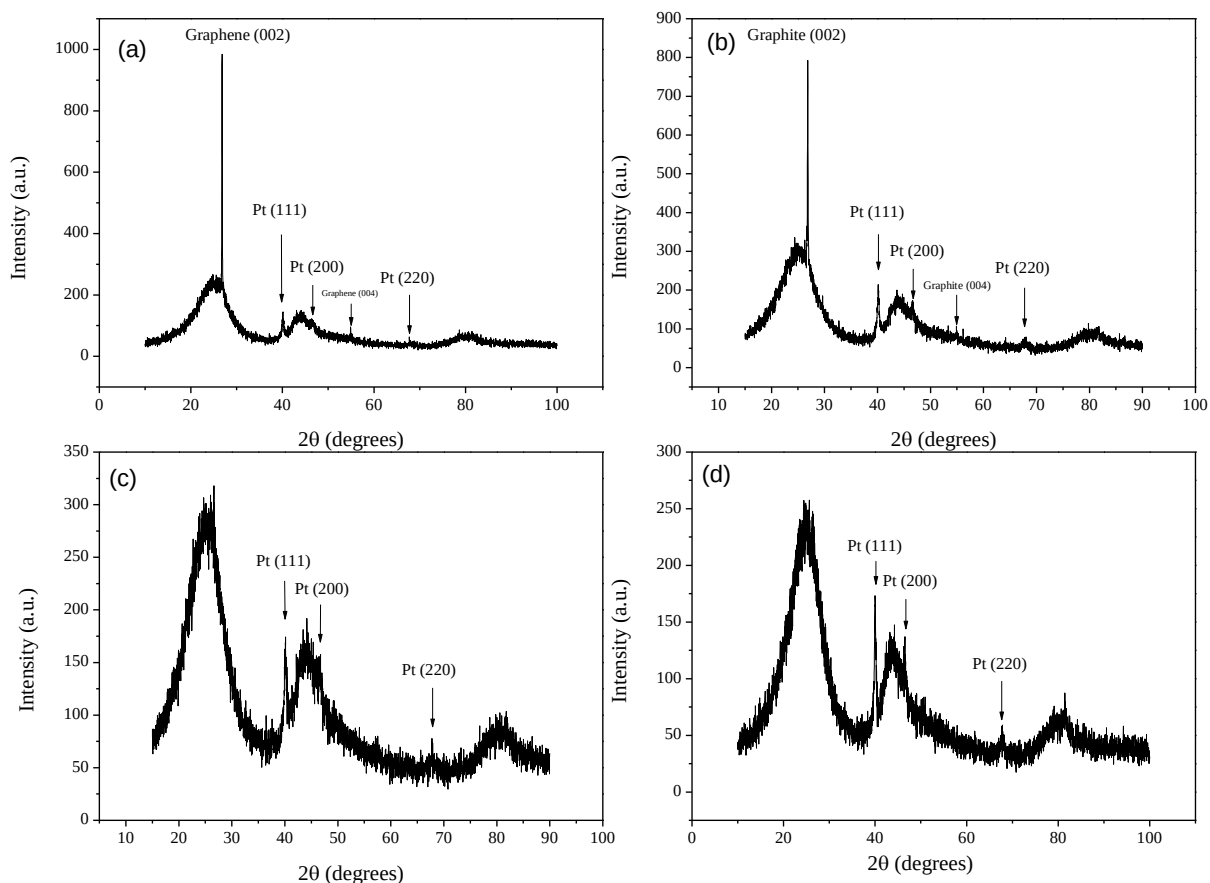


Figure 7.5 XRD patterns of Pt deposits on (a) graphene (b) graphite (c) MWCNT and (d) glassy carbon

The recorded XRD patterns for all the different four samples also show the same reflections at 40° , 46° and 66.8° which correspond to Pt(111), Pt(200) and Pt (220) respectively (JCPDS, No. 04-0802). This indicates that the deposited Pt crystallised in face-centred cubic. The estimated peak area of the three peaks owing to Pt is determined for each sample and the relative ratio is tabulated in **Table 7.2** below.

Table 7.2 Relative ratio of peak area of Pt(111), Pt(200) and Pt(220) of Pt deposited on different carbon supports

Carbon support	Pt (111)	Pt(200)	Pt(220)
bare GC	1.00	0.43	0.30
MWCNT	1.00	0.22	0.16
Graphite	1.00	0.29	0.20
Graphene	1.00	0.43	0.18

XRD analysis shows that amongst the different carbon supports, MWCNT exhibits a predominate (111) peak, as shown in **Table 7.2**. In comparison, a dominant (200) peak structure is found on graphene and a dominated Pt(220) structure is found on glassy carbon from XRD characterisation. These changes in XRD peak ratios must reflect either changes in texture or structure of the deposited nanoparticles. The XRD peak ratio can be considered in the interpretation of the hydrogen desorption peak discussed in the section above. In the case of MWCNTs, these two experimental data agree well as both strongly suggest (111) as the predominating phase. In the case of graphene, XRD data indicates that the dominating phase reflection is (100) compared to other supports. Although Pt(100) exhibits a hydrogen desorption peak at more anodic potential on clean single crystalline Pt surface, the hydrogen desorption peak in the CV appears at more cathodic potential. The peak shifts cathodically to present potential possibly due to a reduced surface energy and an increase of the fraction of open facets on the surface as a result of oxygen absorption [24, 25].

The impact of the dominant crystalline phase structure is not only observed in the hydrogen desorption characteristics but also in the catalytic oxidation of methanol. This will be discussed in the next section.

7.3.3 Methanol Oxidation

The electrocatalytic activity of the Pt decorated graphene electrodes towards methanol oxidation was investigated in 1.0 M methanol in 0.5 M H₂SO₄ for electrode prepared by potentiostatic deposition and potential step deposition, as shown in **Figure 7.6**. The former electrode shows a peak in forward (anodic) scan at 0.65 V attributable to the oxidation of freshly adsorbed methanol and a peak in the backward scan at 0.51 V ascribed to the removal of incompletely oxidised carbonaceous intermediates, mostly in the linearly bonded Pt-CO form [26].

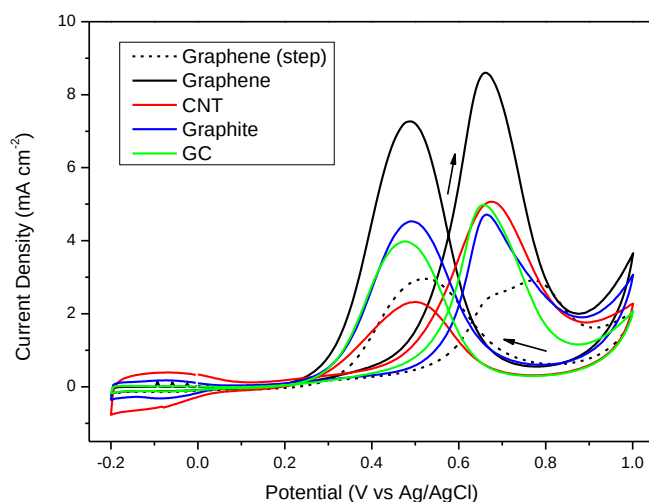


Figure 7.6 CV of Pt nanoparticles decorated graphene produced by potential step method (dashed line) and potentiostatic method (solid line), and compared to difference carbon supports in 1.0 M Methanol at a scan rate of 0.05 V s^{-1} .

By comparison, a secondary and stronger peak at a more anodic potential (0.76 V) is observed besides a peak at 0.65 V in the forward scan for the latter electrode. The forward peak at 0.65 V corresponds to facile direct oxidation of absorbed carbonaceous intermediates to CO_2 on both types of electrodes, while the second forward peak at 0.76 V might be owing to a parallel non-CO route with formate intermediates at higher potentials for Pt decorated graphene electrode prepared by potential step method [27, 28]. The significantly lower current density in the latter electrode arises as a result of a much lower electroactive surface area and a more sluggish methanol oxidation process.

Table 7.3 Comparison of methanol oxidation catalytic activity of platinum nanoparticles on various carbon supports.

Carbon support	Onset Potential (V)	I_f/I_b ratio
Graphene (stepped potential)	0.083	0.98
Graphene	0.096	1.18
MWCNT	0.16	2.18
Graphite	0.13	1.04
Glassy Carbon	0.11	1.25

The methanol oxidation performance of Pt decorated graphene electrode is compared with platinum functionalised MWCNT, graphite powder and glassy carbon electrodes prepared by potentiostatic deposition, as depicted in **Figure 7.6**. All electrodes exhibit a peak in forward and backward scan at similar potentials as the Pt-graphene electrode. Despite possessing the highest EAS, Pt-MWCNT only shows a moderate peak current density (around 5.0 mAcm^{-2}) towards methanol oxidation, similar to graphite and glassy carbon electrode but much less to Pt-GNPs, which displays the highest current density of 8.6 mAcm^{-2} . The difference in current density may originate from the texture of Pt nanoparticle surface on differing carbon support. As discussed above, the predominant surface structure is Pt(111) on MWCNT, and Pt(200) on Pt-graphene. Study on structural effects in electrocatalysis reveals that the catalytic activity for methanol oxidation on Pt is in an order of $\text{Pt}(110) > \text{Pt}(100) > \text{Pt}(111)$ [24], so Pt on graphene exhibits a higher methanol oxidation current than on MWCNT. Among the four electrodes, Pt-Graphene exhibits the lowest onset potential and Pt-MWCNT exhibits the highest onset potential, as shown in **Table 7.3**, which is consistent with a lower onset potential observed on Pt(100) facets of Pt nanocubes attributable to the easy breakage of C-C bond on the edge of stepped (100) facets [29]. The ratio of current density in forward scan (i_f) to reverse scan (i_b) reveals the tolerance to CO like carbonaceous species accumulation on catalyst surface. Despite a lower methanol oxidation current, the i_f/i_b ratio observed on MWCNT supported electrode is much larger than other supports including graphene, which is consistent with the fact that the Pt(111) plane is the most tolerant to CO poisoning [15, 30].

In order to obtain information on reaction kinetics and mechanism, the Tafel slope analysis was carried out. By fitting the data points in the linear range, Tafel slopes for ethanol oxidation at Pt deposited on different carbon substrates can be estimated.

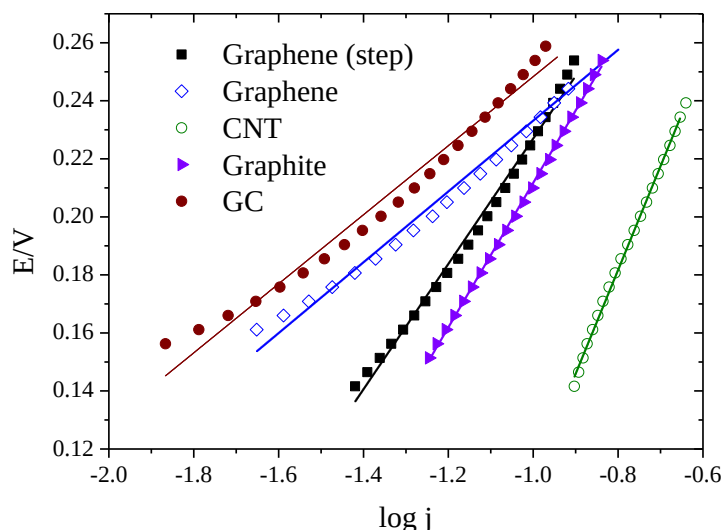
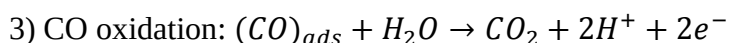
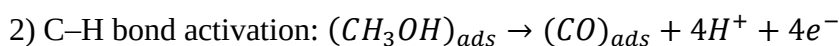
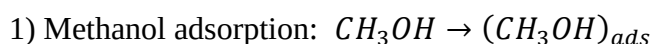


Figure 7.7 Tafel plots of 1.0 M methanol oxidation in 0.5 M H₂SO₄ at Pt deposited on differing carbon substrates

The mechanism of methanol oxidation by Pt surface can be presented as a three-step process as outlined below [2]



From the Tafel plots presented in **Figure 7.7** the Tafel slopes, as obviously observed from the plots, are divided roughly into two different sets of values. Pt deposits on graphene and GC show the slope of 122 and 119 mV/dec whereas Pt on CNT, graphite and graphene prepared by potential step method exhibit the slope of 357, 249 and 216 mV/dec respectively. These two differing sets of values can refer back to the mechanistic pathway of the methanol oxidation catalysed by Pt deposits. In the low potential region, the similar Tafel slopes of Pt on GC and graphene suggest the same mechanistic pathway for methanol oxidation. The lower value of the slope (~ 120 mV/dec) from Tafel analysis was previously reported to imply

that the rate determining step of the reaction is the dehydrogenation of methanol or, in other words, slow scission of C-H bond [31]. The higher value of Tafel slope however might suggest the difference in mechanistic pathway or a different predominant process such as formation of oxygenated species [32]. The Tafel slope value of 300 – 700 mV/dec is commonly described as the rate determining step being the oxidation of adsorbed CO by hydroxyl group [33].

7.3.4 Stability

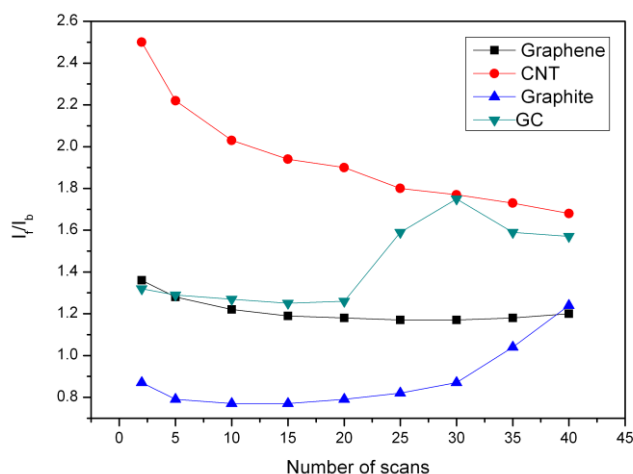


Figure 7.8 Plots of I_f/I_b ratio for 40 CV scans in 1 M methanol and 0.5 M H_2SO_4

To assess the durability of the electrodes in methanol oxidation, the I_f/I_b ratio was determined for 40 CV scans in 1 M methanol and 0.5 M H_2SO_4 electrolyte solution. The resulting plots are presented in **Figure 7.8**. Two trends can be observed here. First is the decreasing I_f/I_b after 40 scans, which is exhibited by Pt on both graphene and CNT. By contrast, an increasing trend is observed for graphite and glassy carbon supports. On the other hand, the forward peak current densities of the 40th and 5th scans were also compared. For Pt-graphene, the peak current remained 98.6% of the initial value and for Pt-graphite the peak current for the 40th scan is actually slightly higher than its initial value giving the overall 114%.

However, such peak current retention is not observed for CNT and GC supports as both give significantly lower value of 87.7% and 83% respectively. Apart from poisoning effect, the significant loss in activity of Pt on GC support implies the better property of dispersed form of carbon supports; graphene, graphite and CNT, which could provide better anchoring sites for the deposited Pt nanoparticles. Also, the 2D nature of graphene and graphite supports could act as a barrier to prevent Pt leaching by dissolution or agglomeration of the nanoparticles [3].

7.4 Conclusion

Electrodeposition of platinum nanoparticles on graphene nanoplatelet was explored using two deposition methods, potentiostatic deposition and potential step deposition, and compared with Pt decorated MWCNT, graphite micro-powder and glassy carbon electrodes. The Pt-graphene electrode prepared by potentiostatic deposition exhibits smaller particle size, larger EAS and specific active area, and facile methanol oxidation compared to electrode from potential step deposition.

Both Pt decorated graphene and MWCNT show higher electrochemical activity than on other carbon electrodes, and the latter exhibits a slightly higher activity than the former together with a rather different shape of hydrogen desorption peak. The hydrogen desorption behaviour on the former is a characteristic of predominated Pt(111) surface structure, and the latter is a predominated Pt(200) surface, differences which are also suggested by the XRD analysis. Pt decorated graphene demonstrates a larger methanol oxidation current than MWCNT, and Pt functionalised MWCNT shows a stronger resistance to CO_{abs} poisoning. The predominated Pt(200) texture from electrostatic deposition and the large surface area makes graphene nanoplatelet an ideal platform for DMFC applications. Overall the work

Chapter 7

shows that if a Pt electrodeposition approach is used, significant differences arise between the behaviour of the differing carbon supports.

References

- [1] A. Esmaeilifar, S. Rowshanzamir, M. H. Eikani, and E. Ghazanfari, *Energy* **35**:3941 (2010).
- [2] Y. Xu and B. Zhang, *Chemical Society Reviews* **43**:2439 (2014).
- [3] M. Cao, D. Wu, and R. Cao, *Chemcatchem* **6**:26 (2014).
- [4] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj, *Angewandte Chemie-International Edition* **48**:7752 (2009).
- [5] N. G. Shang, P. Papakonstantinou, P. Wang, S. Ravi, and P. Silva, *Journal of Physical Chemistry C* **114**:15837 (2010).
- [6] R. S. Dey and C. R. Raj, *Journal of Physical Chemistry C* **114**:21427 (2010).
- [7] B. Seger and P. V. Kamat, *Journal of Physical Chemistry C* **113**:7990 (2009).
- [8] R. I. Jafri, T. Arockiadoss, N. Rajalakshmi, and S. Ramaprabhu, *Journal of the Electrochemical Society* **157**:B874 (2010).
- [9] Y. M. Li, L. H. Tang, and J. H. Li, *Electrochemistry Communications* **11**:846 (2009).
- [10] S. J. Guo, S. J. Dong, and E. W. Wang, *Acs Nano* **4**:547 (2010).
- [11] S. J. Guo, D. Wen, Y. M. Zhai, S. J. Dong, and E. K. Wang, *Acs Nano* **4**:3959 (2010).
- [12] L. F. Dong, R. R. S. Gari, Z. Li, M. M. Craig, and S. F. Hou, *Carbon* **48**:781 (2010).
- [13] E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura, and I. Honma, *Nano Letters* **9**:2255 (2009).
- [14] S. Bong, Y. R. Kim, I. Kim, S. Woo, S. Uhm, J. Lee, and H. Kim, *Electrochemistry Communications* **12**:129 (2010).
- [15] J. Zhang, *PEM Fuel Cell Electrocatalysts and Catalyst Layers Fundamentals and Applications*, Springer, 2008.
- [16] B. Scharifker and G. Hills, *Electrochimica Acta* **28**:879 (1983).
- [17] G. J. Lu and G. Zangari, *Electrochimica Acta* **51**:2531 (2006).
- [18] M. Paunovic and M. Schlesinger, *Fundamentals of electrochemical deposition*, John Wiley and Sons, New Jersey, 2006.
- [19] S. Domínguez-Domínguez, J. n. Arias-Pardilla, Å. Berenguer-Murcia, E. Morallón, and D. Cazorla-Amorós, *Journal of Applied Electrochemistry* **38**:259 (2008).
- [20] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, and L. Giorgi, *Journal of Power Sources* **105**:13 (2002).

- [21] Y. H. Xu and X. Q. Lin, *Journal of Power Sources* 170:13 (2007).
- [22] J. Hu, X. Lu, and J. S. Foord, *Electrochemistry Communications* 12:676 (2010).
- [23] A. Więckowski, *Interfacial Electrochemistry : Theory, Experiment, and Applications*, New York, 1999.
- [24] N. Tian, Z. Y. Zhou, and S. G. Sun, *Journal of Physical Chemistry C* 112:19801 (2008).
- [25] N. Seriani and F. Mittendorfer, *Journal of Physics-Condensed Matter* 20 (2008).
- [26] R. Manoharan and J. B. Goodenough, *Journal of Materials Chemistry* 2:875 (1992).
- [27] K. Kunitatsu, H. Hanawa, H. Uchida, and M. Watanabe, *Journal of Electroanalytical Chemistry* 632:109 (2009).
- [28] S. Jones, K. Tedsree, M. Sawangphruk, J. S. Foord, J. Fisher, D. Thompson, and S. C. E. Tsang, *Chemcatchem* 2:1089 (2010).
- [29] S. B. Han, Y. J. Song, J. M. Lee, J. Y. Kim, and K. W. Park, *Electrochemistry Communications* 10:1044 (2008).
- [30] C. Lamy, J. M. Leger, J. Clavilier, and R. Parsons, *Journal of Electroanalytical Chemistry* 150:71 (1983).
- [31] J. S. Spendelow, J. D. Goodpaster, P. J. Kenis, and A. Wieckowski, *Langmuir* 22:10457 (2006).
- [32] A. Oliveira Neto, J. Perez, W. T. Napporn, E. A. Ticianelli, and E. R. Gonzalez, *Journal of the Brazilian Chemical Society* 11:39 (2000).
- [33] G. Wu, L. Li, and B.-Q. Xu, *Electrochimica Acta* 50:1 (2004).

Chapter 8 Hydrogen Peroxide Oxidation by Self-Assembled Pt-Graphene Composites

8.1 Introduction

In chapter 3 and 4 the modification of electrodes of interest by graphene nanoplatelets (GNPs) is solely by drop-casting method. In this chapter however the focus is to explore a different fabrication technique, which is layer-by-layer (LbL) self-assembly of the functionalised Pt-GNPs composites to produce the ultrathin film in a more controllable manner. In general, LbL self-assembly features the alternate adsorption of different components possessing attractive forces between them on a solid substrate [1]. These attractive interactions are mainly non-covalent and can be varied ranging from van der Waals forces, hydrogen bonding, electron exchange and many others but arguably the most common one is electrostatic interaction between opposite ionic charges located on the molecular structures. The origin of LbL technique can be dated back to 1966 with work by Iler on the fabrication of multilayer by alternating deposition of positively and negatively charged colloid particles [2]. Nevertheless it was a few decades later that LbL self-assembly raised considerable attention as a promising new tool for fabrication of nanostructured multilayer film with high organisation at nanoscopic level [3, 4]. The immense research interest on LbL technique in fabrication of thin films has come about as a result of a large number of its advantages over other solution-based methods available. These benefits are arisen from the LbL technique being low cost [5], simple and straightforward to implement, versatile for any size and shape of a substrate [6] and especially useful for flexible substrates [7]. The technique also allows incorporation of multiple components to be deposited on a substrate [8]

in a predesigned fashion and enables the nanoscopic control to fine tune the corresponding properties resulting in homogeneous and uniform structure [9].

Graphene nanoplatelet with its planar structure therefore stands out as an ideal candidate to mostly benefit from the LbL technique. During the assembling process, energy minimisation allows graphene sheets to self-organise parallel to each other in a manner resembling biological system [1]. Non-covalent surface modification on graphene can provide an important driving force for the self-assembly approach without disrupting its π -conjugation system and thus preserving its featured intrinsic properties. In particular, the functionalisation of graphene by polyelectrolytes to enhance electrostatic interactions between assembled layers has been well developed from the likes of CNTs functionalisations [10-12]. These functionalised CNTs or graphene can be composited with platinum nanoparticles and found useful in many aspects including chemical reaction catalysis [10], sensors and fuel cells [12]. On the other hand, the applications of self-assembled multilayer films based on graphene and its composites are not only dominant in the production of transparent conductive electrodes [13, 14] but also widespread in a larger range such as sensors [15-17], solar cells [18], supercapacitors [6], fuel cells [19, 20] and biological devices [21] to name a few.

This chapter features the study on the self-assembly of Pt-graphene composites in a modified approach from what has been published so far in the literature such that the Pt-GNPs composites were pre-functionalised to exhibit opposite charges facilitating the self-assembly rather than employing the LbL technique to produce Pt-GNPs composite [19].

8.2 Experimental

8.2.1 Materials and Equipment

Graphene oxide 0.5 wt% in water with a thickness of around 3 nm and 550 nm in size was purchased from Angstrom Materials. Dihydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%) was obtained from Alfa Aesar. Hydrogen peroxide (50 wt% in water), Poly(diallyldimethylammonium chloride) solution (PDDA) 20 wt% in water, Poly(styrene sulfonate) sodium salt (NaPSS), Potassium hexacyanoferrate (III), hexamineruthenium (III) chloride and ferrocenemethanol were purchased from Sigma Aldrich in analytical grade and used as-received.

8.2.2 Functionalisation of Oppositely Charged Pt-GNPs

The positively charged platinum-graphene composite (Pt-PDDA-GNPs) was similarly prepared by the protocol used for the functionalisation of GNPs stated in Chapter 3 for 50wt% Pt-GNPs. The process involves the simultaneous reduction of platinum precursor and the PDDA functionalised graphene oxide by sodium borohydride, NaBH_4 . PDDA is positively charged polyelectrolyte polymer and thus gives rise to the positively charged Pt functionalised GNPs.

The negatively charged Pt-GNPs on the other hand were synthesised by the use of negatively charged polyelectrolyte polymer, polystyrene sulfonate or PSS. The synthesis was also based on the method of in-situ reduction by NaBH_4 . The detailed method is as follows. 2 mL of 5 mg/mL GO suspension was sonicated in dimethylformamide (DMF) with 0.07 g NaPSS and 0.025 g of H_2PtCl_6 for 30 minutes. Then excess amount of NaBH_4 were added to a round-bottom flask. The reaction mixture was heated at 80 °C for 4 hours. The product was

collected via filtration through 200 nm pore filter membrane. The product is referred to as Pt-PSS-GNPs.

8.2.3 Self-Assembly of the Oppositely Charged Pt-GNPs

Self-assembly of Pt-graphene composites was performed on glass substrates. Therefore, it is essential to clean a glass slide thoroughly and this was achieved by using Piranha solution. As the Piranha solution is composed of concentrated sulfuric acid and nitric acid in 3:1 ratio by volume, the process was conducted with extreme care and cautions. The glass slide was heated using a water bath at 80 °C in Piranha solution for 30 minutes. Afterwards, the glass slide was rinsed with large amount of distilled water and dried with compressed N₂ gas.

The typical self-assembly procedure started with immersion of the cleaned glass slide to the solution of PDDA in 0.5 M NaCl and then following this step; 1 mg/mL aqueous suspension of PSS-Pt-GNPs, PDDA-Pt-GNPs, and finally PSS in 0.5 M NaCl solution. The step was repeated until a desired number of bilayers of Pt-GNPs was achieved. Each step requires immersion of the slide for 20 minutes in the case of PDDA and PSS solutions and 0.5 to 1 hour for Pt-GNPs suspension. In between each immersion, the coated glass slide must be rinsed by doubly distilled water for 3 times to remove the excess assembling materials and drying with N₂ gas before being immersed in the next solution/suspension.

8.2.4 Electrode Preparation and Characterisation

Self-assembly of Pt-GNPs composites was also carried out on glassy carbon and boron-doped diamond electrodes. The preparation process of each electrode prior to the self-assembly is as follows. Glassy carbon electrodes (GCE) were polished with alumina powder to a mirror finish followed by ultrasonication in ethanol and doubly distilled water to remove any

residual powder. BDD electrodes were cleaned by heating in Aqua Regia at 80 °C to remove any heavy metal residuals from previous usage. This was followed by voltammetric cycling in 0.1 M nitric acid for 20 scans from -1.2 V to 2.4 V. Subsequently, the self-assembly of oppositely charged Pt-GNPs on GCE and BDD was performed in the same manner as the aforementioned for glass slides. Electrochemical measurement was conducted as mentioned in the preceding chapters.

Characterisation techniques involved zeta-potential measurement, XPS analysis, AFM, UV-Vis spectroscopy and were performed with the same equipments stated earlier in the thesis.

8.3 Results and Discussion

8.3.1 Characterisation

The characterisation of Pt-PDDA-GNPs is as reported in Chapter 3 since the composite was produced using the same protocol as the materials used for glutamate sensor in the chapter. The characterisation in this chapter therefore focuses more on the negatively charged platinum graphene composite (Pt-PSS-GNPs) instead. The excess amount of NaPSS was used in the synthesis to ensure that rGO was thoroughly functionalised. The high concentration of PSS is also required to prevent graphene platelets from self-agglomeration, which was proved to be more favourable than the interaction between the polymer and the rGO surface [22, 23].

8.3.1.1 Zeta Potential Measurement

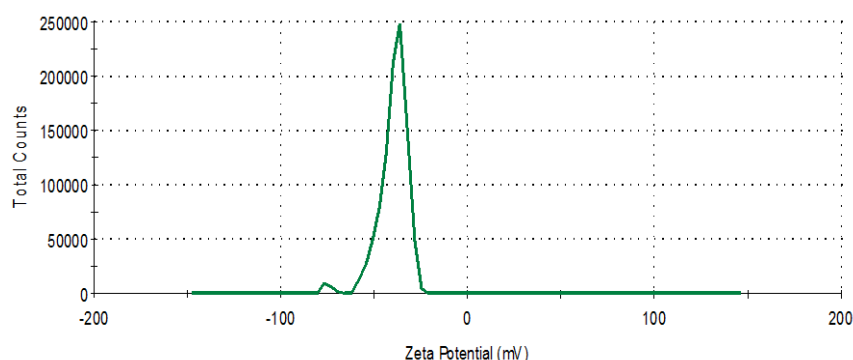


Figure 8.1 Zeta potential measure in 0.5 mg/mL aqueous suspension of Pt-PSS-graphene

Zeta potential measurement was performed on Pt-PSS-graphene in a form of 0.5 mg/mL aqueous suspension. The recorded zeta potential with respect to number of counts was plotted in **Figure 8.1**. The average zeta potential was found to be -39.0 ± 5.7 mV in the typical suspension that would later be used for self-assembly. This value of zeta potential indicates stable suspension and proves that the negative zeta potential was achieved by this non-covalent functionalisation of Pt-GNPs with PSS polymer. The recorded zeta potential, more negative than -30 mV, is considered to be ‘stable’ and suggests that the repulsive interaction between the nanosheets is adequately strong to prevent the sheets from agglomeration in the solution [24, 25].

8.3.1.2 XPS Analysis

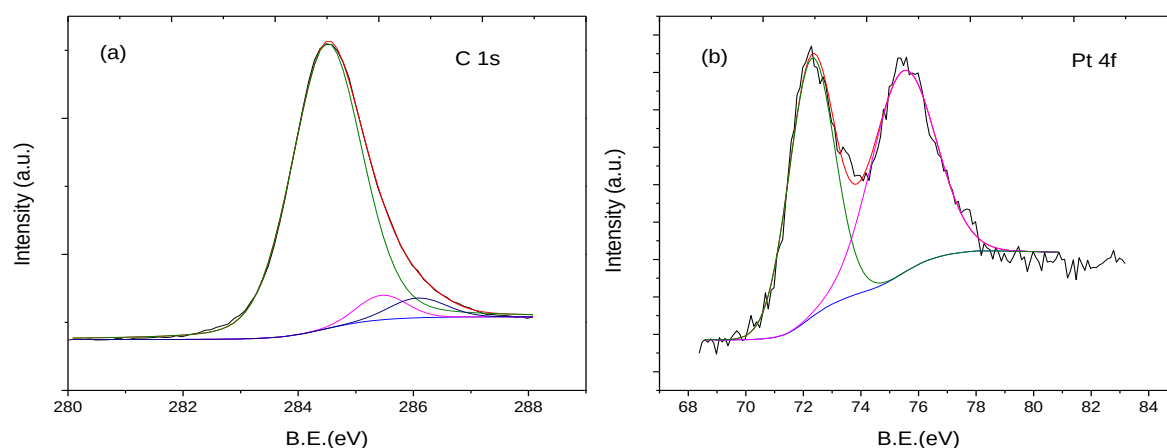


Figure 8.2 (a) C1s and (b) Pt4f XPS spectra of Pt-PSS-GNPs composite

The surface composition of the composited PSS-Pt-GNPs was elucidated by XPS. There are four main components namely carbon, oxygen, platinum and sulphur, discovered from a survey scan spanning from 0 to 1050 eV of binding energy. The more insightful investigation was performed by scanning narrowly for each specific element. The spectra for Pt 4f and C 1s are presented in **Figure 8.2**. The Pt4f spectrum shows two peaks of Pt 4f_{5/2} and Pt 4f_{7/2} owing to the spin-orbit coupling, which lie at 72.4 and 75.6 eV respectively. The binding energy at which the Pt 4f peak lies indicates metallic platinum and thus verifies the deposition method adopted. On the other hand, C 1s spectrum can be fitted to three components at 284.5, 285.5 and 286.1 eV, which correspond to graphitic carbon, C-OH and C-O-C respectively. The relative ratio between the graphitic carbon to the oxygenated carbon is 9.5:1 which is higher than 0.45:1 found in graphene oxide. This is as expected since the complete removal of oxygen functional groups is generally difficult [26] and by using the relatively mild conditions in this synthesis this ratio of C:O is acceptable. Besides, the residual oxygen-containing group can be beneficial for anchoring Pt particles, the reduction of GO is thus confirmed. Additionally, the other two elements, O1s and S2p peaks appear at 530.5 and 168.4 eV respectively. The appearance of S2p, corresponding to sulfonate [22, 27]

suggests that the Pt-GNPs produced in this manner was successfully functionalised by polystyrene sulfonate.

Table 8.1 Details of surface composition of each element found from XPS spectrum of Pt-PSS-GNPs

Peak	Intensity (a.u.)	Sensitivity factor	Surface composition (%)
C 1s	38828.6	0.25	73.6
O 1s	29857.6	0.66	21.4
S 2p	4986.7	0.54	4.4
Pt 4f	5787.2	4.4	0.62

By considering the relative surface sensitivity factor for each element as presented in **Table 8.1**, the relative surface composition can be determined from the XPS data recorded. From this set of data, sulphur was found to be 4.4% of the overall elements. As one sulphur atom is associated with 8 carbon atoms in one monomer unit of PSS, this in turn suggests that the carbon distribution from graphene alone is about 38.6%. The ratio of Pt:C from graphene is therefore 1.6%. This composition ratio is around three times lower than the Pt:C in PDDA-Pt-GNPs, which is 5.5%. The lower surface percentage of Pt:C in PSS-Pt-GNPs compared to PDDA-Pt-GNPs is probably due to the unfavoured repulsive interaction of Pt precursor, $[\text{PtCl}_6]^{2-}$, and the negatively charged PSS coated rGO in the reaction mixture whereas the PDDA is positively charged and can significantly enhance the Pt deposition as exemplified in Chapter 3.

8.3.1.3 AFM

The morphology and the thickness of the Pt-PSS-GNPs were investigated by AFM. The AFM images and thickness profile were presented in **Figure 8.3** below. The average roughness or the cross-sectional height of the functionalised graphene sheets is around 2 to 2.3 nm as shown in the surface plot. This thickness is consistent with the previously published result on PSS functionalised rGO by Bose *et al.* [23], which explained the cause of the increase in

thickness from pristine graphene monolayer or exfoliated graphene oxide sheets to be due to the adsorption of PSS on rGO surface as well as the possible formation of a few layers of graphene. The thickness found in this work is still lower than the reported thickness, 4 nm, of PSS functionalised rGO by S. Stankovich *et al.* [22] noting however that the author used graphite oxide as a starting material.

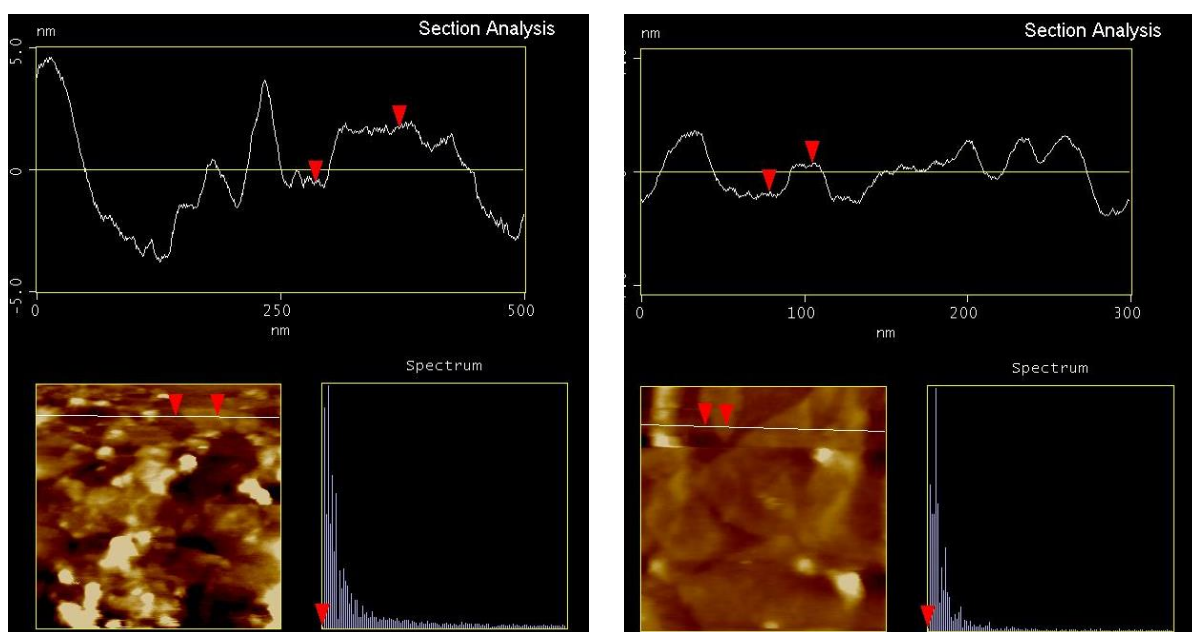


Figure 8.3 AFM images of Pt-PSS-GNPs showing the thickness of graphene nanoplatelets decorated with Pt particles

The other area of interest from the image on the left of **Figure 8.3** is the bright spots appeared on the surface of graphene nanosheets. These bright spots are expected to be platinum particles; the estimated height of the spots is around 10-11 nm, which refers to the size of the deposited Pt particles. The dimension of the graphene sheets are of a few hundreds nanometres. The appearance of the Pt particles seems to be in clusters of smaller particles covering the surface of graphene nanosheets.

8.3.2 Self-Assembly of Functionalised Pt-GNPs

The protocol for self-assembly of the oppositely charged functionalised Pt-GNPs was briefly mentioned in the experimental section above. Notably, the intermittent rinsing steps are crucial in determining the materials performance because both the excess and disorderly adsorbed components can be removed leading to the components strongly adhering to the previously adsorbed layer or the substrate itself [1]. UV-Vis spectroscopy was performed as a characterisation technique to probe the on-going process and the success of the self-assembly. Two alterations were made to assess the self-assembly. First is to alter the immersion time between 30 minutes and 1 hour. And second is to study the effect of immersing the glass slide in PDDA solution prior to immersing the slide in functionalised Pt-GNPs suspensions.

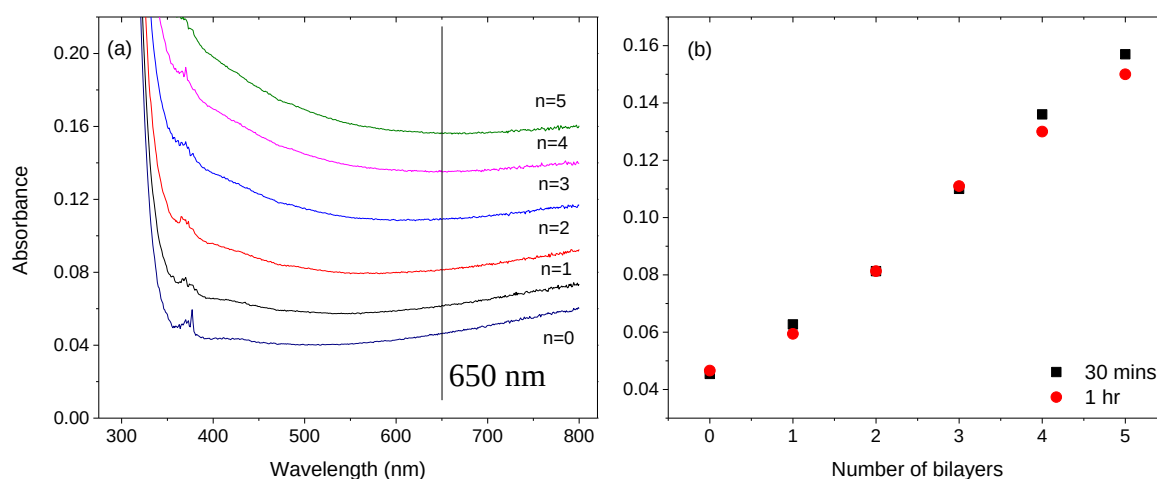


Figure 8.4 (a) UV-Vis spectra of self-assembled thin films of Pt-GNPs on a glass slide with 30-minute immersion time where n is the number of bilayers and (b) the corresponding plot of the absorption at 650 nm against the number of bilayers

The UV-Vis spectra recorded for the 30-minute immersion are presented in **Figure 8.4** (a). The spectra were recorded after each completion of one bilayer of [PDDA-(Pt-PSS-graphene)-(Pt-PDDA-Graphene)-PSS] $_n$. It is clear from the UV-Vis spectra that absorbance increases linearly with the number of bilayers completed in the self-assembly process. Plotting the absorbance at 650 nm against the number of bilayers deposited on the glass slide

results in a straight line with $R^2=0.992$ for the 30 minute-immersion time. Doubling the immersion time to 1 hour sees similar phenomenon as illustrated by the linear plot with $R^2=0.989$. The similarity of the absorbance and the linear plot between the two immersion times allows the shorter time of 30 minutes to be chosen as an optimal duration for each immersion step. The linear increment of the absorbance with the number of bilayers deposited indicates the uniform film growth, which yields the homogeneous composite film with the thickness directly proportional to the number of bilayers [28].

The film thickness can be calculated using the simple relation based on Beer-Lambert law:

$$I = I_0 e^{-\lambda l}$$

where λ is an absorption coefficient of graphene and l is the path length which in this case is the film thickness, I_0 is the intensity of absorbance by the blank glass slide. Assuming homogeneity of the assembled film, and taking the value of λ to be $301,655 \text{ cm}^{-1}$ [29], the film thickness is estimated to be 16 nm. This estimation is in the expected range if consider the simple addition of the thickness found from AFM of PSS-Pt-GNPs and PDDA-Pt-GNPs for 5 bilayers.

8.3.2.1 Mechanical Stability Testing

Table 8.2 Details of stability testing of self-assembly vs drop-casting techniques

Sample	Absorbance at 650nm		% change
	Before testing	After testing	
Drop-casted Pt-PDDA-Graphene	0.071	0.04	43.7
Drop-casted Pt-PSS-Graphene	0.068	0.042	38.2

Drop-casted Mixed Pt-GNPs	0.067	0.058	13.4
Self-assembly LbL	0.075	0.074	1.33

Prior to the application of the self-assembled functionalised Pt-GNPs, the glass slide coated with the bilayers of the self-assembled Pt-GNPs was tested in terms of its mechanical stability in comparison with the glass slide substrate coated with the functionalised Pt-GNPs by drop-casting technique. The amount of the solution for drop casting was controlled such that the initial absorbance of the coated glass slide is similar to the LbL counterpart. **Table 8.2** shows the change in absorbance at 650 nm before and after the coated glass slide was subjected to ultrasonication in distilled water for 60 seconds. The percentage decrease of absorbance is immense, around 40%, when only positively charged or negatively charged Pt-GNPs was drop-casted on a glass slide. With the mixed solution of both PSS-Pt-GNPs and PDDA-Pt-GNPs however, the loss in absorbance drops to around 13%. These are in marked contrast to the LbL self-assembled system however as only 1.3% loss of absorbance is observed. This result strongly suggests the enhanced mechanical stability of the LbL film over its drop-casted analogue.

Assembled graphene films will be practically useful for electrical applications if a good electrical conductivity is provided. However the assembled films still contain large amount of charged functional groups from PDDA and PSS polymers. Electrons are prone to be trapped by these charged groups resulting in high sheet resistance of the film [19]. The LbL coated glass substrate was thus subjected to annealing at 475 °C in hydrogen atmosphere for one hour. After annealing, UV-Vis spectroscopy was performed which resulted in a threefold increase in absorbance at 650 nm as depicted in **Figure 8.5** below. This large increase in

absorbance is expected to be due to the proliferated sp^2 binding between graphene sheets upon thermal annealing [13] as well as further thermal reduction of the existing oxygenated functional groups of graphene. The post reduction of the film after the assembly could see the restoration of the conjugate system as well as strengthening the multilayers via the greater Van der Waals forces and π - π stacking interactions between graphene sheets.

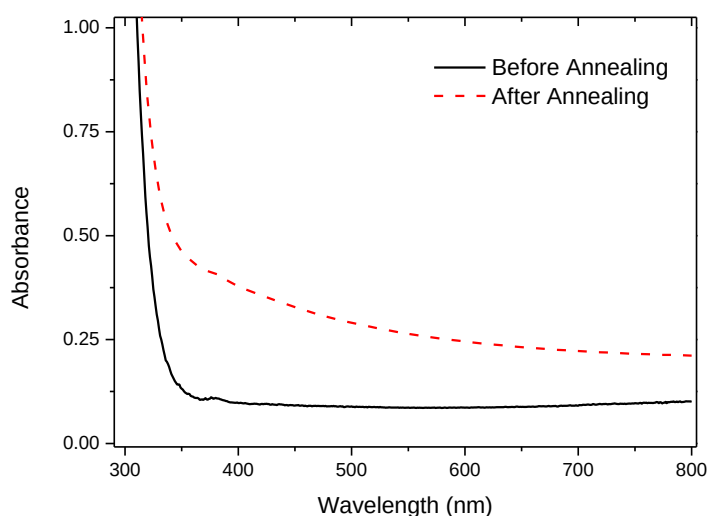


Figure 8.5 UV-Vis spectra of Pt-GNPs films on a glass substrate before and after annealing at 475 °C

The resistance of annealed LbL film on a glass substrate was measured by a simple multimeter, which gave rise to approximately 0.72×10^6 Ohm per 1 cm. This large resistance even after the annealing in H_2 atmosphere prohibits it from being directly used in electrochemistry. However as the LbL technique is proved to be useful and gives rise to more mechanically stable functionalised substrate, it was therefore adopted for the modification of the more established carbon electrodes such as glassy carbon (GC) and boron-doped diamond (BDD).

8.3.3 Electrochemistry of LbL Modified GCE

First glassy carbon electrode (GCE) was decorated with the functionalised Pt-GNPs by LbL self-assembly method as described earlier. The CVs of the modified electrode in three different electrolytes were compared with the bare GCE and the GCE coated with only PDDA. The redox probes utilised consisted of hexacyanoferrate (II/III) $[\text{Fe}(\text{CN})_6]^{4-/3-}$, hexaammineruthenium (II/III) chloride $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ and ferrocene/ferrocenium Fc/Fc^+ .

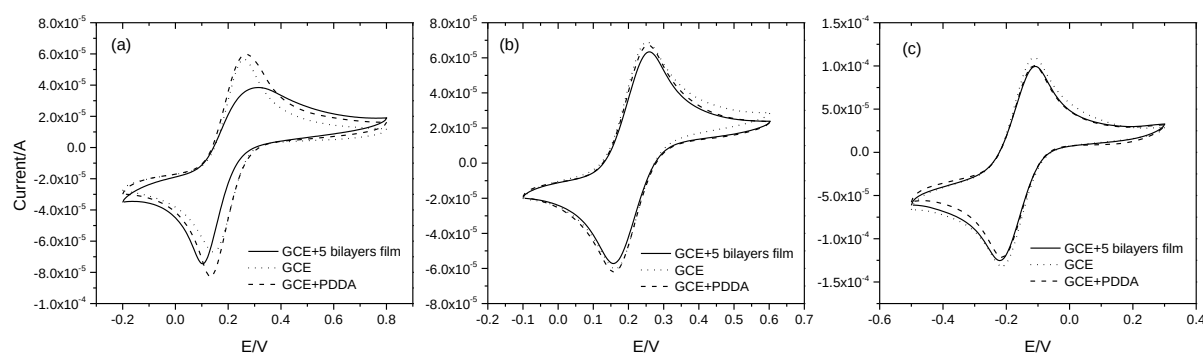


Figure 8.6 CV of GCE and LbL modified GCE at 0.1 V/s in 5mM of (a) Ferricyanide, (b) Ruhex and (c) Ferrocenemethanol electrolytes; the background electrolyte is 0.1 M KCl

According to the CVs in **Figure 8.6**, the electrochemical features including peak shape and peak potential are very similar between the bare and modified GCEs in the ruthenium complex, or the so-called Ruhex and ferrocene methanol electrolytes. The small difference lies in the slightly lower peak currents observed with the LbL film. The most distinguished feature was however observed in CV of 5 bilayers of Pt-graphene films modified GCE in ferricyanide, $[\text{Fe}(\text{CN})_6]^{4-/3-}$ solution where the oxidation peak exhibited by the LbL modified GCE becomes broader with lower peak current and the reduction peak shifts to a more negative potential. These differences in the CV features suggest that even though the resistance of Layer-by-Layer assembled films is too high for a transparent electrode, it might be useful for modifying conventional electrodes such as GCE in this case.

CVs in 0.5 M H_2SO_4 was conducted on the 10 bilayers modified GCE as shown in **Figure 8.7**

(a). The recorded voltammogram feature is characteristic of platinum modified electrodes.

The reduction peak of platinum is prominent at 0.28 V. The hydrogen desorption peak is also obvious at 0.0 to -0.2 V.

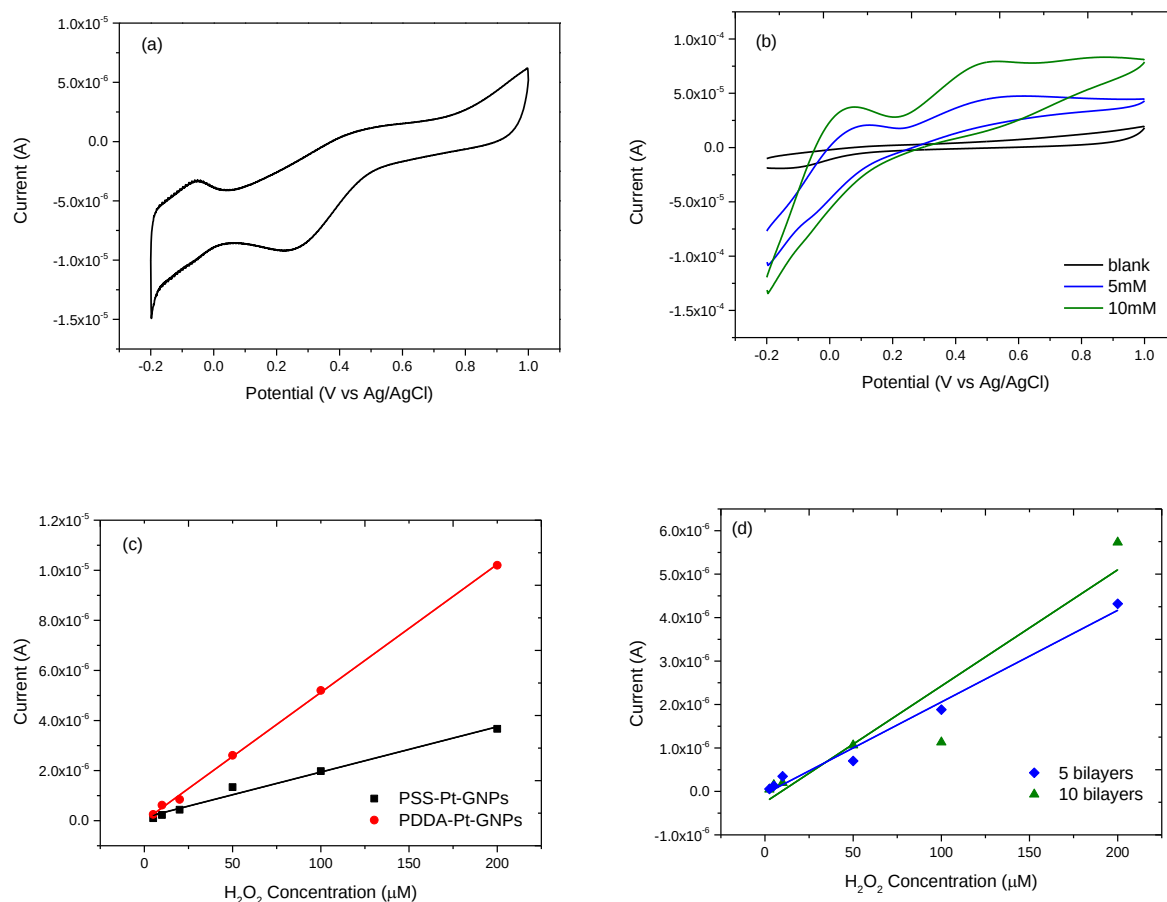


Figure 8.7 (a) CV of 10 bilayers Pt-GNPs in 0.5 M H_2SO_4 (b) in different concentrations of H_2O_2 (c) H_2O_2 Calibration plots of Pt-PDDA-GNPs and Pt-PSS-GNPs and (d) H_2O_2 calibration plots of 5 and 10 bilayers of Pt-GNPs

The electroactivity of the modified GCE towards H_2O_2 oxidation was also investigated by means of CV at a scan rate of 0.05 V/s and chronoamperometry. The CVs of 10 bilayers modified GCE against 5 and 10 mM H_2O_2 in PBS solution were plotted in **Figure 8.7** (b).

The increasing in oxidation current is clearly observed at around 0.5 V. Chronoamperometric

measurements at 0.5 V were therefore carried out by adding increasing concentration of H_2O_2 to 0.1 M PBS at pH 7.4. For a comparison between the modified electrodes, the drop-casted GCE with either Pt-PDDA-GNPs or Pt-PSS-GNPs alone were also included. As summarised in **Table 8.3**, the sensitivity was determined to be the highest for the drop-casted PDDA-Pt-GNPs alone, followed by the 10 bilayers LbL-GCEs, the 5 bilayers LbL-GCEs and the lowest sensitivity was observed from the PSS-Pt-GNPs. According to this result, the H_2O_2 oxidation activity is higher for PDDA-Pt-GNPs than PSS-Pt-GNPs thus when the two composites were combined in the LbL modified GCE the sensitivity lies in somewhat the average between the two values.

Table 8.3 Summary of hydrogen peroxide sensitivity at 0.5 V in PBS at pH 7.4

Electrode	H_2O_2 sensitivity ($\text{A}/\mu\text{M cm}^2$)
Pt-PDDA-GNPs	7.24×10^{-7}
Pt-PSS-GNPs	2.56×10^{-7}
5 bilayers Pt-GNPs	2.98×10^{-7}
10 bilayers Pt-GNPs	3.78×10^{-7}

8.3.4 Electrochemistry of Modified BDD

BDD electrodes were modified by LbL functionalised Pt-GNPs in the same manner as for GCE. The high thermal stability of BDD electrodes enables the study of the annealing effect on the LbL modified electrodes. Additionally, BDD electrodes were subject to different surface terminations and the effect of which on the LbL modified electrode performance was also investigated.

8.3.4.1 Effect of Number of Bilayers

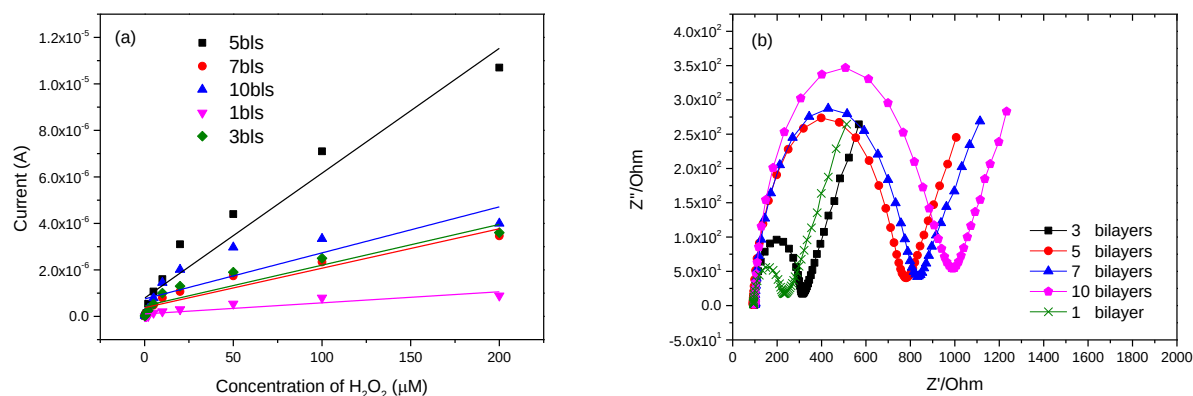


Figure 8.8 (a) H_2O_2 calibration plots of different numbers of bilayers of self-assembled Pt-GNPs on BDD and (b) Nyquist plots of the same samples measured in 10 mM of equimolar solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ and 0.1 M KCl

The effect of number of bilayers of the deposited Pt-GNPs film was assessed in terms of the electrocatalytic activity towards hydrogen peroxide oxidation at 0.5 V via chronoamperometric measurement. The number of self-assembled bilayers was varied from 1, 3, 5, 7 and 10 bilayers in total. Among which, 5 bilayers self-assembled film on BDD established the highest sensitivity of $1.40 \times 10^{-7} \text{ A}/\mu\text{Mcm}^2$ for hydrogen peroxide oxidation at 0.5 V showing the dramatic increase in sensitivity from 1 and 3 bilayers as seen in the calibration plots in **Figure 8.8** (a). The increment in H_2O_2 sensitivity however stopped and the hydrogen peroxide activity suffered the adverse effect once the number of bilayers increased to 7 and 10. This result might suggest that after 5 bilayers, it is more difficult for the newly adsorbed graphene sheets to be in good contact with the electrode [30] as being hindered by number of polymer layers at the same time. This reasoning can be confirmed by the electrochemical impedance spectra (EIS) where the diameter of the semicircle in the high frequency region reflecting the charge transfer resistance [31] increases with the number of bilayers of the film deposited as shown in **Figure 8.8** (b).

The observation of 5-bilayer film exhibiting the highest H_2O_2 sensitivity is in contrast to the 10-bilayer in the case of GCE. The 5-bilayer film on BDD also shows higher sensitivity than the 10-bilayer film on GCE. The difference between the surface roughness of the two electrodes might be an important determining factor for the LbL film performance such that the smoother surface of GCE can facilitate the assembling of the graphene nanosheets to a greater extent than the rougher BDD.

8.3.4.2 Effect of Pre-treatment on BDD

Pre-treatment of the BDD consists of anodic oxidation (AO), cathodic reduction (CR) and hydrogen termination (HT). Each pre-treatment method can be specifically described in more details as follows. As for anodic oxidation, BDD electrodes were anodically oxidised by applying a constant potential of 3.0 V for 30 minutes in 0.5 M H_2SO_4 . During the treatment, oxygen bubbles appeared on the BDD surface in the sulphuric acid solution. Cathodic pre-treatment was carried out in a similar manner to the anodic oxidation except for the holding potential to be -3.0 V instead. Hydrogen surface termination of BDD was performed by exposure of the BDD electrodes to hydrogen plasma at 600 °C for 1 hour. Self-assembly of the functionalised Pt-graphene bilayers was conducted immediately after the pre-treatment had finished. Additionally, the LbL modified BDD electrodes with different pre-treatment were subject to annealing in hydrogen atmosphere at 475 °C for 1 hour.

Table 8.4 Hydrogen desorption charge from CV in 0.5 M H_2SO_4 of 5-bilayer film on differently treated BDD electrodes

Electrodes	Hydrogen Desorption Charge (C cm^{-2})	
	As-prepared	Annealed
5-bilayer-BDD	1.20	1.76
5-bilayer-AO-BDD	0.61	3.66

5-bilayer-CR-BDD	1.79	2.36
5-bilayer-HT-BDD	3.19	3.19

The area under the hydrogen desorption peak in the CV of Pt-graphene film modified BDD electrodes in 0.5 M H₂SO₄ could provide information on the activity of Pt nanoparticles ensembled on graphene platelets and are tabulated in Table 8.4. Without annealing, Pt-graphene films assembled on H-terminated BDD exhibits the largest EAS. However, after annealing amongst all the self-assembled films modified electrodes, the annealed 5-bilayer AO-BDD possesses the largest EAS. Annealing shows an effect to increase the EAS of all electrodes except for the H-terminated sample.

Table 8.5 H₂O₂ sensitivity from amperometric sensing at 0.5 V in PBS pH 7.4 solution and charge transfer resistance from EIS experiment of 5-bilayer film on differently treated BDD electrodes

Electrodes	H ₂ O ₂ Sensitivity ($\times 10^{-7}$ A/uMcm ⁻²)		Charge Transfer Resistance from Nyquist plot (Ω)	
	As-prepared	Annealed	As-prepared	Annealed
5-bilayer-BDD	1.40	0.87	781	311
5-bilayer-AO-BDD	0.23	1.37	439	337
5-bilayer-CR-BDD	0.79	1.41	399	280
5-bilayer-HT-BDD	0.92	0.86	179	331

The highest sensitivity towards hydrogen peroxide oxidation at 0.5 V by means of amperometric sensing is still from Pt-PDDA graphene alone without being assembled with Pt-PSS graphene as reported earlier. Within all the self-assembled films on BDD electrodes, the sensitivity does not vary largely. Annealing effect is also less pronounced in terms of the sensitivity as compared to the hydrogen desorption charge. 5-bilayer-AO-BDD however still exhibits much better performance after annealing. Charge transfer resistance recorded from

the Nyquist plot of each LbL modified BDD electrode exhibited a general trend of significant decrease after annealing as shown in **Table 8.5** above except for 5-bilayer-HT-BDD. The generally better conductivity of the sample after annealing could be due to the evaporation of the polymer when annealed at high temperatures.

Although annealing shows to increase the conductivity of most of the sample as well as to activate the surface of Pt nanoparticles, it does not seem to benefit the oxidation of hydrogen peroxide in any obvious aspect. This probably means that annealing results in the destruction of graphene leaving more Pt nanoparticles prone at the surface and hence higher EAS. Since graphene also shows the electrocatalytic activity towards hydrogen peroxide oxidation, if annealing really destroys some of graphene from the sample then the lower sensitivity to hydrogen peroxide oxidation is therefore as expected. The loss of the synergistic effect between graphene and Pt could also contribute to the results observed.

8.4 Concluding Remarks

- Oppositely charged functionalised Pt-GNPs were successfully prepared by means of non-covalent functionalisation with polyelectrolyte polymers. The layer-by-layer self-assembly of the Pt-GNPs film was demonstrated on three different substrates including glass slide, glassy carbon and BDD electrodes. The film was uniformly assembled in a controllable fashion with enhanced mechanical stability compared to drop-casting method.
- The self-assembled film however shows lower H_2O_2 sensitivity than the Pt-PDDA-GNPs alone which could be a compounded result of lower Pt amount present in Pt-PSS-GNPs and the lower conductivity posed by the large amount of polymer used for functionalisation.

- The roughness of the substrate surface also shows significant effect towards the performance of Pt-GNPs self-assembled films where better electrochemical activity was observed with smoother surface of GCE rather than the rougher surface of BDD. On the other hand, the effect of the surface treatment of BDD is still inconclusive.
- Annealing lowers the charge transfer resistance of the self-assembled Pt-GNPs film on BDD possibly via the loss of the polymer but at the same time graphene nanoplatelets were also deteriorated and thus the H_2O_2 sensitivity was reduced.

Overall it can be concluded that the LBL technique produces a highly controllable route for the growth of graphene films. However the high polymer content of the films is problematic as regards electrical applications, and a route to increase the Pt loading would also be desirable from an electrochemical standpoint.

References

- [1] M. Yang, Y. Hou, and N. A. Kotov, *Nano Today* 7:430 (2012).
- [2] X. Zhang, H. Chen, and H. Zhang, *Chemical Communications* 14:1395 (2007).
- [3] Y. Lvov, F. Essler, and G. Decher, *Journal of Physical Chemistry* 97:13773 (1993).
- [4] Y. Lvov, H. Haas, G. Decher, H. Mohwald, and A. Kalachev, *Journal of Physical Chemistry* 97:12835 (1993).
- [5] Y. Zhu and J. M. Tour, *Nano Letters* 10:4356 (2010).
- [6] W. Liu, X. Yan, J. Lang, J. Chen, and Q. Xue, *Electrochimica Acta* 60:41 (2012).
- [7] Z. Wang, S. Eigler, and M. Halik, *Applied Physics Letters* 104 (2014).
- [8] S.-C. Wang, J. Yang, X.-Y. Zhou, J. Xie, L.-L. Ma, and B. Huang, *Journal of Electroanalytical Chemistry* 722:141 (2014).
- [9] J. S. Park, S. M. Cho, W.-J. Kim, J. Park, and P. J. Yoo, *ACS Applied Materials & Interfaces* 3:360 (2011).
- [10] J. Shen, Y. Hu, C. Qin, and M. Ye, *Langmuir* 24:3993 (2008).
- [11] G. Guo, F. Qin, D. Yang, C. Wang, H. Xu, and S. Yang, *Chemistry of Materials* 20:2291 (2008).
- [12] S. Wang, F. Yang, S. P. Jiang, S. Chen, and X. Wang, *Electrochemistry Communications* 12:1646 (2010).
- [13] C. Mattevi, G. Eda, S. Agnoli, S. Miller, K. A. Mkhoyan, O. Celik, D. Mastrogiovanni, G. Granozzi, E. Garfunkel, and M. Chhowalla, *Advanced Functional Materials* 19:2577 (2009).
- [14] Y. Wang, L. Zhang, N. Hu, Y. Wang, Y. Zhang, Z. Zhou, Y. Liu, S. Shen, and C. Peng, *Nanoscale Research Letters* 9:1 (2014).
- [15] H. Gu, Y. Yu, X. Liu, B. Ni, T. Zhou, and G. Shi, *Biosensors and Bioelectronics* 32:118 (2012).
- [16] D. Zhang, J. Tong, and B. Xia, *Sensors and Actuators B: Chemical* 197:66 (2014).
- [17] O. Parlak, A. Tiwari, A. P. F. Turner, and A. Tiwari, *Biosensors and Bioelectronics* 49:53 (2013).
- [18] F. Gong, H. Wang, and Z.-S. Wang, *Physical Chemistry Chemical Physics* 13:17676 (2011).
- [19] C. Zhu, S. Guo, Y. Zhai, and S. Dong, *Langmuir* 26:7614 (2010).

- [20] A. Sartorel, M. Truccolo, S. Berardi, M. Gardan, M. Carraro, F. M. Toma, G. Scorrano, M. Prato, and M. Bonchio, *Chemical Communications* 47:1716 (2011).
- [21] D. G. Reuven, K. Suggs, M. D. Williams, and X.-Q. Wang, *ACS Nano* 6:1011 (2012).
- [22] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, and R. S. Ruoff, *Journal of Materials Chemistry* 16:155 (2006).
- [23] S. Bose, N. H. Kim, T. Kuila, K.-t. Lau, and J. H. Lee, *Nanotechnology* 22: 295202 (2011).
- [24] B.-Y. Hua, J. Wang, K. Wang, X. Li, X.-J. Zhu, and X.-H. Xia, *Chemical Communications* 48:2316 (2012).
- [25] D. H. Everett, C. Royal Society of, Rsc, and RsoC, Basic principles of colloid science, London : Royal Society of Chemistry, London, 1988.
- [26] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, and G. G. Wallace, *Nat Nano* 3:101 (2008).
- [27] T.-Y. Wu, Z.-Y. Kuo, J.-J. Jow, C.-W. Kuo, C.-J. Tsai, P.-R. Chen, and H.-R. Chen, *International Journal of Electrochemical Science* 7:8076 (2012).
- [28] J. Shen, Y. Hu, C. Li, C. Qin, M. Shi, and M. Ye, *Langmuir* 25:6122 (2009).
- [29] S. Eigler, *Carbon* 47:2936 (2009).
- [30] G. Zeng, Y. Xing, J. Gao, Z. Wang, and X. Zhang, *Langmuir* 26:15022 (2010).
- [31] H.-L. Guo, X.-F. Wang, Q.-Y. Qian, F.-B. Wang, and X.-H. Xia, *ACS Nano* 3:2653 (2009).
- [32] Z. Tai, H. Ma, B. Liu, X. Yan, and Q. Xue, *Colloids and Surfaces B-Biointerfaces* 89:147 (2012).