Graphene, chemically modified graphenes, and two-dimensional layered materials : electrochemical fundamentals and applications

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**GRAPHENE, CHEMICALLY MODIFIED GRAPHENES,
AND TWO-DIMENSIONAL LAYERED MATERIALS –
ELECTROCHEMICAL FUNDAMENTALS AND
APPLICATIONS**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY

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**Graphene, Chemically Modified Graphenes,
and Two-Dimensional Layered Materials –
Electrochemical Fundamentals and
Applications**

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Abstract

Graphene, chemically modified graphenes (CMGs), and two-dimensional layered nanomaterials have attracted a huge interest within the electrochemistry community for a wide variety of interesting properties. This thesis first focuses on graphene oxides (GOs) for their characteristic inherent electrochemistry, where differences were observed based on the production route. Secondly, factors that influence the observed heterogeneous electron transfer (HET) on CMG-modified electrodes were studied. Primarily, chemical composition and morphology were found to affect the observed HET rates at reduced graphene and hydrogenated graphene surfaces. Practical applications were also explored, in the enhancement of supercapacitor charge storage capability and fluorescence properties of functionalised GO. Finally, exfoliated transition metal dichalcogenides were also studied as an emerging class of 2D-layered materials which exhibited improved catalysis of the hydrogen evolution reaction, as an important part of the hydrogen economy. As more 2D nanomaterials are made or discovered, the knowledge garnered is invaluable in the search for solutions that these materials may provide.

List of Publications

First author articles

1. Facile labelling of graphene oxide for superior capacitive energy storage and fluorescence applications.
A.Y.S. Eng, C.K. Chua, M. Pumera. *Phys. Chem. Chem. Phys.* **2016**, *18*, 9673.
2. Refinements to The Structure of Graphite Oxide: Absolute Quantification of Functional Groups *via* Selective Labelling.
A.Y.S. Eng, C.K. Chua, M. Pumera. *Nanoscale* **2015**, *7*, 20256.
3. Hydrogenated Graphenes by Birch Reduction: Influence of Electron and Proton Sources on Hydrogenation Efficiency, Magnetism, and Electrochemistry.
A.Y.S. Eng, Z. Sofer, S. Huber, D. Bousa, M. Marysko, M. Pumera. *Chem. Eur. J.* **2015**, *21*, 16828.
4. Intrinsic Electrochemical Performance and Precise Control of Surface Porosity of Graphene-Modified Electrodes Using the Drop-Casting Technique.
A.Y.S. Eng, C.K. Chua, M. Pumera. *Electrochem. Commun.* **2015**, *59*, 86.
5. Electrochemistry of Transition Metal Dichalcogenides: Strong Dependence on the Metal-to-Chalcogen Composition and Exfoliation Method.
A.Y.S. Eng, A. Ambrosi, Z. Sofer, P. Simek, M. Pumera. *ACS Nano* **2014**, *8*, 12185.
6. Direct Voltammetry of Colloidal Graphene Oxides.
A.Y.S. Eng, M. Pumera. *Electrochem. Commun.* **2014**, *43*, 87.
7. Highly Hydrogenated Graphene through Microwave Exfoliation of Graphite Oxide in Hydrogen Plasma: Towards Electrochemical Applications.
A.Y.S. Eng, Z. Sofer, P. Simek, J. Kosina, M. Pumera. *Chem. Eur. J.* **2013**, *19*, 15583.
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A.Y.S. Eng, A. Ambrosi, C.K. Chua, F. Šaněk, Z. Sofer, M. Pumera. *Chem. Eur. J.* **2013**, *19*, 12673.
9. Searching for Magnetism in Hydrogenated Graphene: Using Highly Hydrogenated Graphene Prepared via Birch Reduction of Graphite Oxides.
A.Y.S. Eng, H.L. Poh, F. Sanek, M. Marysko, S. Matejkova, Z. Sofer, M. Pumera. *ACS Nano* **2013**, *7*, 5930.
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Co-authored articles

11. Bipolar Electrochemical Synthesis of WS₂ Nanoparticles and Their Application in Magneto-Immunosandwich Assay.

C.C. Mayorga, B. Khezri, **A.Y.S. Eng**, Z. Sofer, P. Ulbrich, M. Pumera. *Adv. Funct. Mater.* **2016**, 26, 4094.

12. Electrochemistry of Layered Graphitic Carbon Nitride Synthesised from Various Precursors: Searching for Catalytic Effects.

Y.T. Yew, C.S. Lim, **A.Y.S. Eng**, J. Oh, S. Park, M. Pumera. *ChemPhysChem.* **2016**, 17, 481.

13. Metallic 1T-WS₂ for Selective Impedimetric Sensing.

C.C. Mayorga, A. Ambrosi, **A.Y.S. Eng**, Z. Sofer, M. Pumera. *Adv. Funct. Mater.* **2015**, 25, 5611.

14. Assessments of Surface Coverage after Nanomaterials are Drop Cast onto Electrodes for Electroanalytical Applications.

Y.Y. Chan, **A.Y.S. Eng**, M. Pumera, R.D. Webster. *ChemElectroChem* **2015**, 2, 1003.

15. Ternary Transition Metal Oxide Nanoparticles with Spinel Structure for the Oxygen Reduction Reaction.

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16. Iridium- and Osmium-decorated Reduced Graphenes as Promising Catalysts for Hydrogen Evolution.

C.S. Lim, Z. Sofer, R.J. Toh, **A.Y.S. Eng**, J. Luxa, M. Pumera. *ChemPhysChem* **2015**, 16, 1898.

17. Transition Metal Dichalcogenides (MoS₂, MoSe₂, WS₂ and WSe₂) Exfoliation Technique has Strong Influence Upon Their Capacitance

C.C. Mayorga, A. Ambrosi, **A.Y.S. Eng**, Z. Sofer, M. Pumera. *Electrochem. Commun.* **2015**, 56, 24.

18. Iridium-Catalyst-Based Autonomous Bubble-Propelled Graphene Micromotors with Ultralow Catalyst Loading.

H. Wang, Z. Sofer, **A.Y.S. Eng**, M. Pumera. *Chem. Eur. J.* **2014**, 20, 14946.

Review articles

19. Graphene and Its Electrochemistry – An Update.

A. Ambrosi, C.K. Chua, N.M. Latiff, A.H. Loo, C.H.A. Wong, **A.Y.S. Eng**, A. Bonanni, M. Pumera. *Chem. Soc. Rev.* **2016**, 45, 2458.

20. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides.

X. Chia, **A.Y.S. Eng**, A. Ambrosi, S. M. Tan, M. Pumera. *Chem. Rev.* **2015**, 115, 11941.

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Chapter 1 –

Introduction and Literature Review

Short selected excerpts of the literature review presented in this chapter have also been published in the following review and journal articles. All discussions herein are written by the author of the thesis, and reproduced here with permission.

1. Graphene and Its Electrochemistry – An Update.

A. Ambrosi, C.K. Chua, N.M. Latiff, A.H. Loo, C.H.A. Wong, **A.Y.S. Eng**, A. Bonanni, M. Pumera. *Chem. Soc. Rev.* **2016**, *45*, 2458.

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2. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides.

X. Chia, **A.Y.S. Eng**, A. Ambrosi, S. M. Tan, M. Pumera. *Chem. Rev.* **2015**, *115*, 11941.

Article may be retrieved at <http://dx.doi.org/10.1021/acs.chemrev.5b00287>

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3. Facile Labelling Of Graphene Oxide for Superior Capacitive Energy Storage and Fluorescence Applications.

A.Y.S. Eng, C.K. Chua, M. Pumera. *Phys. Chem. Chem. Phys.* **2016**, *18*, 9673.

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4. Electrochemistry of Transition Metal Dichalcogenides: Strong Dependence on the Metal-to-Chalcogen Composition and Exfoliation Method.

A.Y.S. Eng, A. Ambrosi, Z. Sofer, P. Simek, M. Pumera. *ACS Nano* **2014**, *8*, 12185.

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1.1. Graphene – A Brief History and Types of Chemical Modification

Pristine *graphene* may be simply defined as “a single atomic layer of graphite”, consisting of sp^2 hybridised carbon atoms in a honeycomb-like structure. It can also be described as being analogous to a “polycyclic aromatic hydrocarbon of quasi infinite size”.¹ Despite graphite being used by mankind for millennia, graphene was only isolated and properly characterised in 2004 via the exfoliation of graphite with common adhesive tape,² and since then, graphene research has proliferated. Although corporations have been developing various graphene applications over the past decade or so, the vast majority of these have yet to make it into the market. Currently, most commercial graphene products are limited to basic consumer products such as sports equipment, where the advantage of graphene over conventional materials can be somewhat uncertain. Some products which actually exploit its inherent properties include conductive inks, adhesives, or graphene elastomers. In contrast, there remains uncertainty over the more anticipated applications, in energy storage such as batteries and supercapacitors, and also in biosensing and therapeutics. While graphene undoubtedly possesses various exciting properties, it still remains to be seen if they can eventually outweigh the economic costs of developing such applications to market.

In contrast, the term “*chemically-modified graphene*” (CMG) was first coined as a realisation that current techniques produce graphenes that are substantially different in their structure and compositions from pristine graphene, and would therefore necessitate a more precise term.³ CMGs may be defined as any graphene-related material that has functional groups covalently bound to the carbon backbone of its individual graphitic layers.^{4,5} In particular, graphite oxides and graphene oxides (GO) form the foundation of CMGs. These materials are first obtained from the oxidation of graphite and subsequently act as the parent material from which reduced graphene

oxides (rGOs) and other functionalised graphenes are produced. Additionally, CMGs include other forms of graphenes like those manufactured with intentional doping/functionalization with heteroatoms, or decorated with metal nanoparticles. This thesis, however, will specifically focus only on two forms of CMGs: (1) graphene oxide and graphite oxide materials produced from the chemical oxidation of graphite, and also (2) the hydrogenation of graphenes to hydrogenated graphenes (*i.e. graphane*).

1.1.1. The Top-down Approach in The Production of Graphenes

Numerous approaches exist for the production of graphene, where “pure” graphene (or at least the ones of the highest purity) may be obtained by mechanical exfoliation, such as that first achieved by Geim and Novoselov in 2004,² and also includes those employing “bottom-up” approaches (*i.e.* from the assembly of small molecules) like the use of epitaxial growth^{6,7} and direct chemical synthesis.^{8,9} These two approaches, however, have a major shortcoming in that only small quantities of graphene are attainable from each preparative procedure.

The “top-down” approach (*i.e.* decomposition of higher ordered graphitic structures), however, is of much greater interest, especially with regards to industrial applications due to its potential for large-scale bulk production processes. Bulk graphite is first oxidised to graphite oxide and then subsequently reduced to graphene (rGO) *via* thermal, chemical and/or electrochemical means (Figure 1.1).^{10,11,12,13} Of the reduction routes, thermal reduction and exfoliation at high temperatures is usually favoured for its typically low content of inherent oxygen-containing groups.^{10,14} Chemical reduction employing reducing agents such as sodium borohydride and hydrazine are used in the selective removal of certain functional groups, providing selectivity for control over desired groups for subsequent functionalization towards requirements in specific

applications.^{11,12} Lastly, electrochemical reduction provides the fastest option of GO reduction (typically ranging from hundreds of seconds to no longer than a few minutes), but is ineffective in removing certain groups such as hydroxyls and it is also the least scalable of the three reduction techniques.¹³

Figure 1.1. Schematic illustration of the top-down approach of graphene production, first involving the oxidation of graphite via various methods followed by thermal, chemical or electrochemical reduction to give thermally-reduced graphene oxide (TRGO), chemically-reduced graphene oxide (CRGO), and electrochemically-reduced graphene oxide (ERGO). Reproduced from reference 15.

Thus, the “*top-down*” approach presents various advantages, such as the ability to produce sizable quantities of graphenes, and it also allows for the tailoring of the final CMG products for specific needs by varying the conditions and chemicals used.

1.1.2. Graphite Oxide and its Inherent Oxygen Functionalities

The initial objective of fundamental scientific research into the *top-down* approach was to produce rGOs with the highest purity and likeness in structure to pristine graphene. There is now however a steadily increasing interest in graphite oxide (GO), which was once thought of as a mere reaction intermediate. Despite its earliest synthesis in 1859 by Brodie,¹⁶ the current interest in GO was reignited after the celebrated discovery of graphene in 2004.² GO, like many amorphous carbon materials, contains a large variety of covalently bound oxygen functionalities, and common groups may include hydroxyls, peroxy, aldehyde, epoxy, carbonyl and carboxylic acid moieties on the carbon backbone.^{10,11,12,17} Its numerous types and amounts of inherent oxygen functionalities can serve important purposes such as anchoring points on graphene for covalent functionalization and biological sensing applications.^{17,18,19}

Many attempts have also been made to propose structural models of GOs (including the Hofmann,²⁰ Ruess,²¹ Scholtz-Boehm,²² Nakajima-Matsuo,²³ Lerf-Klinowski,²⁴ Dékány,⁵ and Ajayan²⁵ models) but as succinctly surmised by Ruoff and co-workers, GO is essentially an “amorphous and non-stoichiometric” material,¹⁰ and one should thus not treat any specific model as an accurate description of GO. Nonetheless, the Lerf-Klinowski model (Figure 1.2) is arguably the most widely accepted in the graphene research community. It acknowledges structural ambiguity but emphasises two important characteristics. Firstly, it highlights an abundance of hydroxyl and epoxy groups on the basal plane of graphene, and these tend to be congregated in small oxidised regions, leaving the sp^2 conjugation in some aromatic graphitic regions untouched. Also, it is believed that carboxylic acid groups exist on the edges of the graphene plane.^{24, 26, 27}

Figure 1.2. Two variations of the Lerf-Klinowski graphene oxide model, demonstrating the prevalence of carboxylic groups at the edges and both hydroxyl and epoxy groups on the basal plane. Reproduced with permission from references 24 and 26. Copyright 1998 American Chemical Society.

A more recent report also described GO using a “dynamic structural model”, where it undergoes gradual changes upon interaction with water and slowly forms acidic functionalities,²⁸ thus further highlighting the highly reactive and variable nature of GO. In addition, various oxidation methods are available for the oxidation of graphite (Scheme 1.1). All these methods require a combination of strong concentrated acids for the intercalation and expansion of graphite, and are followed by the oxidation of the graphitic layers based either on *chlorate* (of the Brodie,¹⁶ Staudenmaier²⁹ and Hofmann³⁰ methods) or *permanganate* (Hummers³¹ and Tour³² methods) oxidants. Hence, considering the variation in oxidants and specific procedural differences between the methods, it is not unreasonable to expect significant differences between GOs

produced by different methods, which results in differences in the observed structural, chemical, and electrochemical properties.

Scheme 1.1. Schematic illustration of common graphite oxidation procedures to graphite oxide.

However, there was little appreciation and knowledge of this causal link within the research community at the time. Few studies had existed which investigated possible differences in GOs based on their production methods. Chua *et al.* reported some variation in GO chemical compositions using techniques such as X-ray photoelectron spectroscopy (XPS) and NMR spectroscopy, particularly the lack of carboxylic groups in chlorate-GO that were erstwhile thought to be chiefly responsible for the acidity of GO.³³ Electrochemical studies also showed varying peak reduction

potentials for the GOs.³⁴ Physical effects include different solvation properties and extent of exfoliation depending on the choice of oxidation route.³⁵ In this regard, it is conceivable that some disagreement in GO structural models over the past decades might have stemmed from the different oxidation methods used by the various authors. A close inspection shows that only the models by Lerf-Klinowski²⁴ and Tour²⁸ found a presence of carboxylic groups, while the Ajayan model²⁵ included lactols as a carboxyl derivative; it is noted that these models exclusively studied permanganate-oxidized GOs. This is in contrast to earlier proposed models²⁰⁻²³ and the Dékány model,⁵ which mainly employed chlorate-GOs. No obvious evidence for carboxylic moieties was reported in these studies. Hence, the nature of inherent oxygen functionalities in GO continues to be an important aspect of graphene research and further insight is necessary to form a more unified understanding of their chemical structures.

1.1.3. Hydrogenation of Graphene-Towards Graphane

Graphane refers to the fully hydrogenated derivative of graphene with the theoretical composition $(C_1H_1)_n$, and was first hypothesized by several authors.^{36,37} Its hexagonal lattice is buckled, unlike that of planar graphene (Figure 1.3), and all carbon atoms are sp^3 -hybridised, giving it the *-ane* suffix in accordance with organic chemistry nomenclature.³⁸ Nevertheless, in all examples represented in the current literature, only partially hydrogenated graphene has been achieved, while the fully hydrogenated derivative remains an elusive theoretical goal. Hydrogenated graphenes are a group of materials that present a variety of potential uses in devices and applications, exhibiting interesting properties such as a tuneable band gap,³⁹ variable fluorescence emissions,⁴⁰ ferromagnetism⁴¹ and also as a material to reversibly store hydrogen.⁴⁰

Figure 1.3. Side view of graphene in the chair (top) and boat (bottom) conformations, and the corresponding bond lengths. Reproduced from reference 38.

Reported approaches that have been used to prepare hydrogenated graphenes are centred on two strategies: (1) the gas phase hydrogenation of graphene⁴²⁻⁴⁶ and (2) the liquid phase hydrogenation of graphite.^{40,47,48} The gaseous hydrogenation approach using H₂ gas or hydrogen plasma typically leads to a lower level of hydrogenation (<10 atomic percent).^{43,46} A recent report in 2016 by Smith *et al.* however, proposed that their method utilising high temperature and pressure may be used to produce fully hydrogenated graphane for the first time, although no quantification of the hydrogen content was given.⁴⁹ Also, a major drawback is the high pressure required of between 2.6 and 5.0 GPa. In comparison, liquid phase hydrogenation employs the Birch reduction reaction, which traditionally involves reduction in a solution of elemental lithium or sodium in liquid ammonia, and a subsequent supply of protons from water or short-chain alcohols. This approach has consistently been shown to produce higher extents of hydrogenation achievable in graphene at present, at up to 5.8% hydrogen by weight.⁴⁸ As a point of comparison, the maximum limit is at 7.7 wt% hydrogen in graphane with a stoichiometric composition of C₁H₁.^{50,51}

Additionally, an interesting point exists in the use of GO as the parent material in the Birch hydrogenation process in place of graphite or graphene, where its reducing nature (sodium dissolved in liquid ammonia) may serve to remove some inherent oxygen-containing functionalities,⁵² thereby possibly avoiding the need for an additional reduction step as shown in a recent article by Feng *et al.*⁵³ While the wet chemistry technique has been reported to aid the elimination of oxygen-containing groups to only a small degree, the gaseous approach is arguably the more conventional and superior method in this respect. Particularly, the involvement of high temperatures is analogous to the thermal reduction process from the top-down approach, and an inclusion of a plasma would allow the generation of high local temperatures on graphene leading to superior deoxygenation.^{54,55} Hence, both approaches present diverse benefits: the liquid phase procedure giving higher hydrogenation rates, while a gaseous plasma would result in a more effective removal of oxygen functionalities from GO. Consequently, a key focus of this thesis is the investigation of differences in properties of hydrogenated products obtained from both approaches and the implications towards their electrochemistry, as presented in **Chapters 9-11**.

1.2. Electrochemistry of Graphenes and Chemically-Modified Graphenes

The electrochemical research of graphenes and other carbon nanomaterials encompass numerous directions and are typically related to properties like their conductivity, capacitance, and the heterogeneous electron transfers (HET) between these materials and molecules. Graphene has been shown to possess useful electrochemical properties,^{2,12,15} such as a high electronic conductivity. Additionally, processed graphenes contain various *defect* types which include point defects (*e.g.* Stone-Wales defects and single vacancies), multiple defects, and edge defects.^{56,57} Some

of these in particular, such as edge defects, can lead to fast observed HET rates as a result of a higher electronic density of states (DOS), or higher electron densities in the conduction band. Disorder to the pristine sp^2 structure results in defect states with energies between the conduction and valence bands, effectively filling in the DOS near the Fermi level.⁵⁸ Pristine graphene, in comparison, only has a small overlap of valence and conduction bands which leads to a low DOS at the Fermi level.⁵⁸ These factors have led to the study of many other modified-graphene materials in a plethora of electrochemical applications. While much of graphene electrochemical literature in the past decade has been dedicated towards applied work, fundamental research is also of interest and is, furthermore, crucial to better our understanding of the chemical nature of graphene and its many chemically-modified variants. An excellent example is the behaviour of reactive species such as the oxygen-containing functional groups in graphite oxide.

Other less-explored areas include experimental and procedural considerations, since graphene-type materials can have large disparities in terms of their lateral sizes and structures varying from nanoscale sheets to stacked graphene platelets. They are commonly found in their bulk form as fine powders and prior electrode preparation is therefore necessary, where the materials are first deposited on solid electrodes for study. The electrochemistry fundamentals, applications, and experimental considerations of graphene and CMGs are explored throughout **Chapters 4-12**.

1.2.1. Inherent Electrochemistry of Oxygen Functionalities in Graphenes

The electrochemical reductions of graphene materials and fullerenes as deposited on electrodes have previously been reported,^{59,60,61} based on the cycling of the applied potential from cyclic voltammetry. In particular, the technique is useful in

determining the presence of electrochemically reducible oxygen-containing groups.⁵⁹ While graphenes contain numerous forms of oxygen functionalities, not all groups may be electrochemically reduced, such as hydroxyl groups.⁵⁹ In addition, certain groups such as carboxylic acids are only reducible under specific conditions such as a highly reductive potential of -2.0 V vs. Ag/AgCl and only in strongly acidic media.⁶² Only the peroxy,^{63,64} aldehyde,⁶⁵ epoxy^{60,66} and carbonyl⁶² moieties may be electrochemically reduced at comparatively milder conditions of approximately -0.7 V, -1.0 V, -1.5 V, and -2.0 V, respectively.

These electroactive oxygen-containing groups inherent in graphene and carbon nanomaterials may be electrochemically reduced either by the application of a reductive potential sweep (*e.g.* from cyclic voltammetry)^{59,61,67,68} or a fixed step potential (*i.e.* chronoamperometry) as demonstrated in Figure 1.4.^{15,69} Voltammograms corresponding to the reduction of oxygen groups are known to exhibit a large chemically irreversible wave starting from approximately -0.7 V with a peak potential range from about -0.9 V to -1.5 V.^{68,69} The reduction peaks are only observed during the initial scan, indicating that all reducible groups are reduced within the first sweep. These electroreductions require the participation of protons from the solution, and produce water molecules with the loss of oxygen atoms from the graphene framework (Scheme 1.2). Most occur *via* a two-electron/two-proton reduction process, and includes the peroxy, aldehyde, epoxy, and carbonyl functionalities.⁶²⁻⁶⁶ On the other hand, the reduction of a carboxylic acid requires a total of four electrons and protons, first involving a two-electron/two-proton process to the aldehyde, followed by a second two-electron/two-proton process to the corresponding hydroxyl.⁶²

Figure 1.4. Cyclic voltammograms (left) and chronoamperometric curves (right) illustrating the electrochemical reduction of oxygen-containing groups in graphene oxide. Reproduced with permission from reference 68, and reference 69. Copyright 2009 John Wiley & Sons.

Scheme 1.2. Proposed scheme for the electrochemical reduction of graphene oxide. Reproduced from reference 69.

However, a key hurdle in the electrochemical study of inherent oxygen groups is the inability to differentiate between the electrochemical redox reactions of the various oxygen species. While both voltammetry and X-ray photoelectron spectroscopy have been employed to ascertain the types and amounts of oxygen groups, there remains some limitations with these techniques. In the case of cyclic voltammetry, although the peak reduction potentials of the different groups are well documented and may be used for their identification, the presence of the various groups complicates the precise quantification of *each specific* moiety due to the close proximities of their reduction potentials, resulting in their reduction occurring as a single overlapped wave as shown in

Figure 1.4.^{60,70-74} This situation is somewhat similar in XPS from the proximity of binding energies between some carbon-oxygen bonds.⁷⁵ More importantly however, quantitative analysis in XPS is only with respect to the *bonding modes* between carbon and oxygen and not for the exact *type of oxygen functionalities* on carbon; an example is where the total amount of C-O bonds may arise from functionalities like hydroxyls but also phenols or epoxylys.⁷⁶ Other techniques like infrared spectroscopy pose similar problems to XPS as discussed, and the opacity of carbon samples also causes a significant decrease in the quality of the spectral data.⁷⁶ Consequently to address the limitations discussed, a new approach of selective functionalization of specific groups is taken for the purposes of their identification and quantification, as detailed in **Chapter 5** of this thesis.

Another interesting aspect is the different chemical structures of GO which depend on their oxidation methods as discussed in Section 1.1.2. Differences in the electrochemical behaviour are studied in **Chapter 4**, where despite well-documented chemically irreversible nature of the electrochemical reduction of inherent oxygen groups, it is found that some functionalities exhibiting chemically reversible behaviour are found only in permanganate-oxidised GOs.⁷⁷ A comprehensive discussion and summary of the different GO compositions may then be found in **Chapter 5.2.2**.

1.2.2. Graphenes as Electrochemical Transducers and Capacitors

In contemporary literature for electrochemical sensing and biosensing applications, there is a great interest in graphene materials, undoubtedly stemming from its exceptional properties, such as a high electronic conductivity, large surface area and its fast heterogeneous electron transfer (HET) kinetics, particularly at the edge plane sites.^{13,19,78} The study of the electrochemical kinetics of graphenes and CMGs is one of

fundamental importance, since electrode materials with fast HET rates provide benefits such as potential savings in energy costs in the development of sensing devices. Consequently, a direction pursued in this thesis is to investigate a variety of factors that influence the observed HET rates at graphene and CMG surfaces, which are herein focused on (1) the density of edges or edge defects,^{79,80} (2) type and amounts of oxygen-containing groups,^{81,82} and also (3) the effects of hydrogenation, which are currently contentious and not well-understood in the literature.^{83,84} The experimentally observed HET rate constants (k_{obs}^o) may be conveniently measured for a suitable redox probe using the electrochemical technique of cyclic voltammetry, which is a very popular method used to measure quasi-reversible kinetics due to its ease of use.⁸⁵ In essence, the classical Nicholson method⁸⁶ relates the observed peak separation (ΔE_p) of a cyclic voltammogram to a dimensionless kinetic parameter (Ψ), from which k_{obs}^o is then calculated (e.g. Figures 1.5a, 7.1a-b). It is important to note, however, that the method is only reliable for a planar electrode surface under semi-infinite diffusion control. This limitation is examined in detail in **Section 1.2.3**, and a full investigation in **Chapter 7**.

The first effect of defect density on HET rates is arguably the most established and straightforward. Computational and empirical data by the groups of McCreery,⁷⁹ Papakonstantinou,⁸⁷ and Pumera⁸⁸ all agree that a larger defect density increases the observed HET rate as disorder and edge terminations can fill the electronic DOS at the Fermi level.⁷⁹ In contrast, the effect from oxygen-containing groups on the resultant HET is dependent on the redox probe employed.⁸⁹ These groups only affect inner-sphere redox probes, which are so-termed due to their surface sensitivity and can either be catalysed or inhibited by specific interactions with certain functionalities.⁹⁰ In a systematic assessment of graphene oxide, it is seen that for ferrocyanide [$\text{Fe}(\text{CN})_6^{3-/4-}$] and iron (II/III) [$\text{Fe}^{2+/3+}$] as inner-sphere probes,⁹⁰ a strong negative interaction between

the redox probe and surface oxygen exists for ferrocyanide (Figure 1.5ai) compared to a weak positive correlation in iron (II/III) (Figure 1.5aii).⁹¹ Ferrocyanide experiences charge repulsion with negatively charged surface species and its peak separation decreases after their removal through electrochemical reduction (Figure 1.5ai), while $\text{Fe}^{2+/3+}$ has positive interactions with surface carbonyls in its hydrated state akin to a chelate, thus showing slightly faster HET after oxidation. Reduction instead removes carbonyls which slows the HET, observed as a wider peak separation in Figure 1.5aii. Subsequently, ruthenium hexaamine $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ is an outer-sphere redox probe affected only by factors like surface area and the DOS, and is thus largely uninfluenced by the amount of surface oxygen (Figure 1.5aiii). Finally for ascorbic acid (AA), electrochemical reduction of GO was seen to reduce the overpotential for AA oxidation by removing oxygen moieties that would otherwise experience electrostatic repulsion with the negatively charged AA molecule (Figure 1.5aiv). The choice of redox probe is thus important as different system-specific behaviour may exist for different analytes, and the precise description of the obtained k_{obs}^0 value corresponds only to that of the electrochemical reaction between the graphene electrode material and a chosen redox couple.

Figure 1.5. Effects of electrochemical modification of graphene oxide on the observed heterogeneous electron transfer. **a)** Cyclic voltammograms of (i) $\text{Fe}(\text{CN})_6^{3-/4-}$, (ii) $\text{Fe}^{2+/3+}$, (iii) $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, and (iv) ascorbic acid redox probes on GO after electrochemical oxidation or reduction activation treatments. Scan rate: 100 mV s^{-1} ; supporting electrolyte: 50 mM PBS at pH 7.2. Reprinted from Ref 91. **b)** High-resolution carbon-1s XPS spectra of GO-modified screen printed electrodes after application of different potentials for 5 min. Cyclic voltammograms of 5 mM ferro/ferricyanide obtained on GO-modified electrodes after the electrochemical treatments at different potentials. Conditions: 0.1 M KCl; scan rate, 0.1 V s^{-1} ; potentials are with reference to Ag/AgCl. HET rate constants (k_{obs}^0) calculated from the peak-to-peak separation of ferro/ferricyanide.

Inset: enlarged graph for untreated GO film and after application of –0.25 and –0.50 V.

Reprinted from reference 92.

It is also relatively easy to control the oxygen content through electrochemistry. Application of increasingly reductive potentials results in the loss of greater amounts of oxygen species in GO as tracked by XPS (Figure 1.5b), which as a surface sensitive technique is especially suited for this purpose.⁹² Low reductive potentials first induce the removal of C-O and C=O groups, and O-C=O moieties are then lost with more cathodic potentials approximately past –1.5 V. Correspondingly, due to the above-discussed effects, peak separations for the ferro/ferricyanide redox couple decreased, with HET rates increasing three orders of magnitude from $k_{obs}^o = 1.6 \times 10^{-6} \text{ cm s}^{-1}$ for the untreated GO film to $4.0 \times 10^{-3} \text{ cm s}^{-1}$ with an applied potential of –1.50 V. Thus throughout this thesis examining graphene and CMG materials, the redox couple of choice is the commonly used ferro/ferricyanide $[\text{Fe}(\text{CN})_6]^{3-/4-}$ couple, which is sensitive to both inherent oxygen groups in GO and CMGs in addition to surface structures such as edge defects.^{79,82} XPS is also employed in **Chapter 4** to study the electrochemical redox reactions that the various GOs undergo depending on their preparation method.

Comparatively, the third factor of hydrogenation on the HET at carbon surfaces has not been extensively studied and any correlation at present is ambiguous with conflicting data. Chandrachud *et al.* showed based on density functional theory calculations that the DOS at the Fermi level increases significantly as the hydrogen content increases,⁹³ which suggests a faster HET. Poh *et al.* experimentally showed instead a decrease in HET rates with gaseous hydrogenation of graphene.⁸³ Drawing parallels from glassy carbon electrodes, Swain and co-workers⁹⁴ reported that hydrogen plasma treatments improved HET towards ferrocyanide, while Kuo and McCreery⁸⁴

observed differing effects based on the choice of redox probe. It was also noted that concomitant removal of oxygen groups might have been a contributing factor to the observations.⁹⁴ Overall, **Part II** of this thesis (**Chapters 8-11**) cover the investigations of various chemically-modified graphenes (particularly graphene obtained from the thermal reduction of GO, and hydrogenated-graphenes produced from various methods) as electrochemical transducers.

Another major field of study using graphene and CMGs is their application in electrochemical energy storage. It is well-known that graphene possesses capacitive charge storage properties important for energy storage.⁹⁵⁻¹⁰⁰ In its pristine state, graphene possesses high electrical conductivity, tensile strength, and optical transparency. In practice, however, such properties vary with preparation technique and these advantageous qualities are not always realized. Graphene-based supercapacitors are one such example. With an intrinsic capacitance of *ca.* $21 \mu\text{F cm}^{-2}$,¹⁰¹ a specific capacitance of 550 F g^{-1} is theoretically achievable for single-layer graphene due to its large surface area.¹⁰² Many groups have employed a variety of means to achieve a large capacitance through enhancement of the *electrochemical double layer capacitor* (EDLC) character of graphite/reduced graphenes using treatments to increase the active surface area (*e.g.* hydrogels,¹⁰³ sheet crumpling^{104,105} or ball milling^{106,107}) for charge storage.

However, preparation methods inadvertently introduce defects and oxygen groups, rendering any comparison to pristine graphene erroneous. Groups such as those of Hwang and Aksay are increasingly providing computational^{108,109,110} and experimental^{111,112,113} evidence that defects and functionalities are instead the main contributors to the resultant capacitance. This leads to a promising second *pseudo-capacitive* approach towards developing graphene-based supercapacitors, but which requires the introduction of a Faradaic process, like the reversible redox reactions of

oxygen groups within GO. Xu *et al.* first posed the question in 2011 if GO might be a better supercapacitor candidate material compared to graphene.¹¹⁴ Graphene had a larger surface area of $617 \text{ m}^2 \text{ g}^{-1}$ than GO at $332 \text{ m}^2 \text{ g}^{-1}$ (Figure 1.6c), but a smaller mesopore distribution limited to within 2-5 nm (Figure 1.6d) compared to GO which extends its pore size to more than 20 nm. On a side note, although the theoretical surface area of graphene stands at $2630 \text{ m}^2 \text{ g}^{-1}$, typical surface areas of most graphene powders vary between $600\text{--}800 \text{ m}^2 \text{ g}^{-1}$ due to re-stacking of the sheets after preparation. The cyclic voltammogram of GO then exhibited a broad peak at 0–0.8 V (Figure 1.6e), and deviation of the charge-discharge curve from linearity (Figure 1.6f) also indicated the presence of pseudocapacitance. As a consequence, the specific capacitance of GO at 189 F g^{-1} was found to be higher than graphene at 165 F g^{-1} . Considering its higher capacitance, lower cost, and shorter processing time, GO was thus cited as a superior alternative to graphene. Furthermore with its wide variety of highly reactive functional groups,¹⁷ one can envision a wide assortment of available molecules to functionalize GO with to further enhance its capacitance.

Figure 1.6. Comparison of structures of graphene oxide and graphene. SEM images of **a)** graphene oxide and **b)** graphene. **c)** Adsorption-desorption isotherms of nitrogen gas on graphite, GO, and graphene at 77 K. **d)** Pore size distributions of graphite, GO, and graphene. Comparison of capacitive behaviour of GO and graphene in a 6 M KOH electrolyte, based on **e)** voltammetric cycling at a scan rate of 2 $\text{mV} \cdot \text{s}^{-1}$, **f)** Charge-discharge curves at a current density of 50 $\text{mA} \cdot \text{g}^{-1}$. Reproduced with permission from reference 114. Copyright 2011 Royal Society of Chemistry.

One major problem with this pseudo-capacitance enhancement approach however, is the need to maintain electrical conductivity which is greatly reduced due to loss of sp^2 -hybridized conjugation in GO. In the literature to date this has been largely addressed just by the physical mixing or functionalization of GO with a secondary conductive and/or electroactive material such as polyaniline (PANI),¹¹⁵⁻¹¹⁷ carbon black,¹¹⁸ or carbon nanotubes.¹¹⁹ It is also interesting to note that in comparison to the EDLC approach for reduced-graphenes, there is an overall lack of attempts in the literature to enhance the inherent pseudo-capacitance of GO. In light of this, the effects of chemical-functionalization on the supercapacitor properties of GO are studied in **Chapter 12**.

1.2.3. Experimental Measurements of Electrode Kinetics on Porous Nanomaterial-Modified Electrode Surfaces

Commonly, there are three methods for the preparation of modified electrodes, involving either drop-casting,^{14,15} spin coating,¹²⁰ or the more tedious method of carbon-paste electrodes.¹²¹ A disadvantage in the preparation of carbon paste electrodes is that they require the mixing of the material-of-interest with mineral and/or paraffin oil and would therefore need optimisation of the graphene and oil compositions.¹²¹ This also leads to difficulty in obtaining precise quantification of the material of interest. In comparing drop-casting and spin coating, the only significant benefit in using a spin-coat is in its controllable thickness as required in special applications such as thin films.¹²⁰ Hence, the drop-casting technique is usually employed in studies for its ease in quantifying the amount of material studied and is also used throughout this thesis.

Despite its simplicity and prevalence in the electrochemical literature, the drop-casting technique is not without problems. One such issue arises due to the porous, non-

planar surfaces of nanomaterial-modified electrodes. While many reports have attributed the fast kinetics of graphene materials to their intrinsic properties, other factors may have also inadvertently contributed to the observed HET but are often neglected and not taken in consideration. Kinetic information may be reliably extracted from experimental data *only* under diffusion control of the analyte from the bulk solution, and any negative influence from thin-layer effects or adsorption should first be excluded. These issues are particularly prevalent for porous electrode materials since analyte molecules may become trapped within pores giving rise to a “thin-layer” across the surface of the electrode, or otherwise experience significant adsorption of molecules onto the drop-casted material, which is further exacerbated by the typically large specific surface areas of various nanomaterials. This topic is currently under study by several groups,^{90,122,123} and is clearly important as an understanding of the factors involved would prevent any erroneous interpretation of electron transfer data within the graphene community.

Compton and co-workers first confirmed a thin-layer effect in carbon nanotubes.¹²⁴ Although it is clear for carbon nanotubes that the thin-layer effect dominates the electrochemical response, the case with graphenes is less certain. As planar sheets, graphene sheets may undergo self-assembly by re-stacking when drop cast, giving surfaces that do not exhibit the effect. Hallam and Banks showed that the thin-layer effect does not exist for commercially-obtained pristine graphene nanosheets.¹²² With ruthenium hexamine, they observed a gradient of approximately 0.5 from a double logarithmic plot of peak current against scan rate expected for semi-infinite diffusion (Figure 1.7a; Inset). The plot would yield instead a gradient ~ 1 if the analyte was surface-bound from thin-layer effects or adsorption. Experimental preparation procedures were also noted to influence the mass-transfer profile. Aksay

and co-workers showed for ferrocyanide that peak currents remained constant as expected when normalised to the square root of the scan rate, if the graphene dispersion was prepared from deionized water (Figure 1.7bi).¹²³ A dispersion in ethanol instead results in increased porosity effects at higher scan rates as thinner diffusion layers result in pores being filled with analyte. Such disparity arises from different solvent drying behaviours, with graphene aggregation occurring in the ethanol droplet during drying and resulting in rough morphology seen by SEM. The authors also introduced a simple but useful porosity factor empirically measured from peak currents at different scan rates, allowing correlation of high porosity with small peak separations particularly for ethanolic suspensions that in some cases were lower than the reversible limit of ~ 59 mV (Figure 1.7bii), and is therefore an obvious indication of other effects occurring in addition to diffusion.¹²³ Alternatively, Bond and co-workers suggested that rotating disk electrode voltammetry provides a better view of electrochemical performances.¹²⁵ This is because of convection being the primary mode of mass transport in opposition to just semi-infinite diffusion, thus diminishing the impact from thin-layer and other surface-confined effects. Hence, different experimental procedures may give varying observations, which in turn influences the interpretation of electrochemical performance, and it is important to not only consider characteristics of graphene materials studied but also the manner in which electrodes are prepared. A thorough study of porosity effects in graphene-modified electrodes is given in **Chapter 7** of the thesis.

Figure 1.7. a) Cyclic voltammogram of a graphene-modified GC electrode in 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}^+ / 1 \text{ M KCl}$. Scan rates: $0.005\text{--}0.2 \text{ V s}^{-1}$ (vs. SCE); inset figure shows double logarithmic plot of current versus scan rate. Reprinted with permission from Ref 122. Copyright 2011 Elsevier. **b) (i)** Peak current I_{max} as a function of scan rate ν for bare GC electrode and functionalised-graphene electrodes using an ammoniated deionised water-based (DI) and an ethanol-based (eth) suspension; (ii) Ferrocyanide peak separation E_{pp} as a function of an experimentally-determined porosity factor; SEM images of graphene-coated electrode surfaces using (iii) ammoniated DI water and (iv) ethanol. Reprinted with permission from Ref 123. Copyright 2010 John Wiley and Sons.

1.3. Inorganic Two-Dimensional Layered Materials as Graphene Analogues

1.3.1. Layered Transition Metal Dichalcogenides – An Introduction

Many layered transition metal dichalcogenides (TMDs) occur naturally in the Earth's crust as mineral ores. At present, the most widely studied TMD material (molybdenum disulphide) is most abundant as the mineral molybdenite.¹²⁶ In spite of the large number of other TMDs available in nature, a sizable percentage of contemporary literature is devoted almost exclusively to MoS_2 with others progressively emerging. Most interestingly though, the properties of these TMD materials in their bulk

crystal states vastly differ from their exfoliated counterparts in the nanoscale regime, and efforts at obtaining two-dimensional (2D) layered TMDs are ongoing since initial reports in the 1970s.¹²⁷⁻¹²⁹ More recently, the current scientific fervour in 2D layered nanomaterials first brought about by graphene has led to the fortuitous resurgence of interest in TMDs,^{130,131,132} and which extends to further include analogues such as boron nitride, silicene and germanene.^{133,134}

Most Group VI TMDs have a chemical composition of MX_2 , where M is a transition metal (like molybdenum or tungsten) and X is a chalcogen (sulphur, selenium, or tellurium). Structurally, they are highly anisotropic akin to the layers of graphite, existing as indefinitely large two-dimensional atomic sheets that are weakly held together by van der Waals forces.¹³⁵⁻¹³⁷ However, unlike a graphene sheet that has the thickness of a single carbon atom, TMDs have a sandwich-like structure where a central metal atom is covalently bound to chalcogen atoms (Figure 1.8). The *d*-electron count of the metal atom is crucial in determining the coordination, layer stacking, and electronic properties of the material. In their native state, Group VI TMDs like MoS_2 have fully occupied orbitals, and exist as semiconductors in the 2H phase.¹³⁶ Polymorphs are denoted based on their symmetry: 2H indicating two layers with hexagonal symmetry and 1T for a single layer with tetragonal symmetry. Most commonly in the literature, phase transition of bulk native 2H-TMDs is effected by chemical or electrochemical lithium-intercalation to the meta-stable 1T phase.^{127,129,135} Strong organolithium reductants such as butyl-lithium are reacted with the bulk TMD powder under protection from atmospheric exposure, and an electron from the C–Li bond is transferred to the central metal atom inducing a phase change.¹²⁷ This changes the TMD to exhibit metallic character and additionally increases the inter-layer distance (analogous to the oxidation of graphite to graphite oxide) as a result of Li-intercalation,

giving a Li-intercalated compound with the formula Li_nMX_2 , where n is the number of Li atoms. It is then typically sonicated in water, and the ensuing reaction between lithium and water generates hydrogen gas while pushing the individual layers apart.¹³⁵ Overall, this intercalation/exfoliation method is highly popular as a “top-down” approach to obtaining exfoliated TMD sheets.

Figure 1.8. Structure variation of Group VI transition metal dichalcogenides, illustrating differences in metal coordination and stacking sequence for layers with tetragonal (1T) or hexagonal (2H) symmetries. Reproduced with permission from Reference 137. Copyright 2015 American Chemical Society.

To date, numerous reports have demonstrated the effective use of layered TMDs from advanced energy storage and conversion, to electrochemical catalysis and sensing,¹³⁸ including Li-ion batteries¹³⁹ to supercapacitors¹⁴⁰ and solar cells.¹⁴¹ Of note, however, is their efficiency towards the electrochemical hydrogen evolution reaction (HER), or the generation of hydrogen from water.¹⁴²⁻¹⁴⁵ Conceivably, such applications

would require the synthesis of substantial amounts of material to achieve mass production potential for future commercialization. Liquid-phase exfoliation approaches^{129,144,146} and colloidal solution syntheses^{147,148} present an advantage in this regard, although other methods like mechanical exfoliation^{149,150} and chemical vapour deposition^{151,152} techniques also offer other benefits that include higher purities, more pristine conditions and control of size and layer thickness. Some of these factors represent real problems faced by the liquid-phase exfoliation approach in spite of its popularity, and greater understanding of exfoliation processes and TMD properties is required to address such challenges.

Despite extensive research with varied directions in the field ranging from synthesis methods to device development, a general literature search reveals a comparative lack of basic knowledge on the inherent electrochemical properties of TMDs, especially after the exfoliation of their layers. In light of current interest to exploit TMDs for a myriad of applications, a fundamental study of TMD exfoliation and its consequences on their material and electrochemical properties is prudent.

1.3.2. Inherent Electrochemistry of Transition Metal Dichalcogenides

The proliferation of TMD research is largely due to the promise that they hold for various scientific applications. Nevertheless, the current knowledge of fundamental TMD properties is not keeping in pace with the fast development of TMD-based applications. This is a crucial aspect of study since changes that TMD materials can undergo during operational use will inadvertently alter the efficacy of devices. Herein, the term “*inherent electrochemistry*” is used to describe the characteristic behaviour of different TMDs when used as electrode materials in electrochemical sensing or catalysis. These properties arise due to redox reactions which the TMD electrode surface itself

undergoes as a result of applied oxidation or reductive potentials, independent of the analyte in solution. Observations can, however, be influenced by various conditions, such as pH, the potentials applied, and nature of electrolyte.

A foremost report by Chorkendorff and co-workers¹⁵³ demonstrated the inherent electrochemical oxidation of MoS₂ particles supported on carbon paper under conditions usually employed in HER electrocatalysis. The voltammogram in Figure 1.9a illustrates the inherent oxidation of MoS₂ beginning at 0.6 V vs. NHE, which reaches a maximum at 0.98 V. This oxidation was reported to be irreversible and consequently resulted in a decrease in HER activity. Interestingly, the authors were also able to correlate the peak oxidation potentials at 0.7 V and 0.98 V to oxidation of the MoS₂ edge and basal planes, respectively. The larger oxidation potential required for the basal planes is a consequence of their greater resistance towards corrosion.¹⁵⁴ Additionally, it was determined from XPS that the observed electrochemical oxidation process was due to changes in the surface chemical composition, primarily the conversion of MoS₂ to MoO₃, SO₄²⁻ and S₂²⁻. Nonetheless, there remains some difficulty in obtaining a conclusive reaction mechanism as the sulphur in MoS₂ is found to only undergo partial oxidation during anodic scans.

More recently, electrochemical reductions of MoS₂ have also been observed.^{155,156} Zhang and co-workers report an irreversible reduction occurring at -0.71 V vs. Ag/AgCl in aqueous electrolyte (Figure 1.9b), but this reduced state can be re-oxidised at approximately 1.87 V if conducted in an organic electrolyte of acetonitrile and tetrabutylammonium tetrafluoroborate.¹⁵⁵ The authors proposed from XPS data that the reduction process arises from a phase change to the material. Subsequently, Ambrosi *et al.* investigated the effects of chemical exfoliation on MoS₂ using organolithium reagents, where both *n*-BuLi and *t*-BuLi were found to be most

effective.¹⁵⁶ Both oxidation and reduction processes were noted in all MoS₂ materials with differing degrees of exfoliation. An oxidation wave at 1.3 V vs Ag/AgCl and a broad reduction peak at *ca.* -1.0 V were seen for bulk MoS₂ (Figure 1.9c). In comparison, peak current intensities were largest after BuLi exfoliations, attributed to the efficient exfoliation giving rise to larger specific surface areas (Figures 1.9d and f). In all cases, both oxidation and reduction waves diminished in current intensities with each potential sweep; the most rapid decrease occurred with the *n*-BuLi and *t*-BuLi exfoliated materials. More importantly, a clue to the origins of the processes involved may lie in the fact that the reduction peak only occurs after an initial anodic sweep, thus suggesting that the -1.0 V wave corresponds to the reduction of the oxidised state formed at 1.3 V.

Figure 1.9. Cyclic voltammograms demonstrating inherent electrochemical activity of MoS₂ under conditions of **a)** N₂ purged 0.5 M H₂SO₄, scan rate 2 mV s⁻¹. Inset shows a decrease in the oxidation peak during the second sweep. Reproduced from reference 153. Copyright 2009 Royal Society of Chemistry. **b)** APTES-MoS₂ modified electrode in aqueous 0.5 M NaCl saturated with N₂. Scan rate: 50 mV s⁻¹, potentials given with respect to the Ag/AgCl reference electrode. Reproduced from reference 155. Copyright

2012 John Wiley & Sons. **c)** as-received bulk MoS₂ and **d-f)** after chemical exfoliation with methyllithium, *n*-butyllithium and *t*-butyllithium. Conditions: Starting potential 0 V vs Ag/AgCl scanned in the anodic direction; 0.1 M KCl; scan rate, 100 mV s⁻¹. Reproduced from reference 156. Copyright 2014 John Wiley & Sons.

Compared with MoS₂, less is known in the literature of the inherent electrochemistries of other TMDs. In the same work on inherent MoS₂ electrochemistry, Bonde *et al.* also explored the activity of WS₂, cobalt sulphide (CoS_x), cobalt-promoted MoS₂ (Co-Mo-S) and WS₂ (Co-W-S) (Figure 1.10 d-f).¹⁵³ These materials exhibit irreversible oxidations which reduce their HER catalytic activities. Cobalt incorporated MoS₂ and WS₂ also experienced shifts in the inherent oxidation peaks toward higher potentials, and are further postulated to also have improved HER activity. Despite several similarities, it can be expected for electrochemical differences to exist between TMDs because of the species involved, their reactivities, and also the diversity of products formed after oxidation. Considering that these redox reactions occur as surface processes, X-ray photoelectron spectroscopy is therefore highly suitable for studying chemical changes in the materials.^{153,157,158}

Figure 1.10. Cyclic voltammograms of **a)** cobalt sulphide (CoS_x), **b)** Co-promoted MoS₂, and **c)** Co-promoted WS₂ deposited on carbon paper. Conditions: N₂ purged 0.5 M H₂SO₄, scan rate 2 mV s⁻¹. Reproduced from ref. 153. Copyright 2009 Royal Society of Chemistry.

Other than XPS, one might gain preliminary insights into elemental composition by considering the thermodynamic stability of the investigated TMD. Potential-pH diagrams, otherwise known as Pourbaix diagrams, may provide an idea of the products generated from inherent oxidations/reductions occurring at specific potentials. Under acidic HER conditions ($\text{pH} \sim 0.5$), it is suggested that TMDs like MoS_2 and WS_2 (Figure 1.11a-b) are thermodynamically stable only within a small potential window just positive of potentials where hydrogen evolution occurs.¹⁵⁹ In practice, however, variations in the “operating window” (*i.e.* potential range where the electrode material is inert) exist as seen from Figures 1.9 and 1.10. The various species predicted to exist at the more extreme anodic or cathodic potentials then represent likely identities of actual products formed. Based on XPS data, significant dissolution of material was discovered after oxidation and a number of solid state and aqueous products were proposed including molybdenum and tungsten oxides, sulphates and selenates. Dissolution of sulphur or selenium can also occur under cathodic potentials giving H_2S and H_2Se , or HS^- and HSe^- ions depending on the solution pH (Figure 1.11c-d).

Another important consideration is the reactivity of the native TMDs on exposure to the environment. Jaegermann and Schmeisser correlated TMD reactivity towards atmospheric oxygen based on their electronic structures, with sulphides being the most resistant to oxidation followed by selenides, while MoTe_2 fully corrodes.¹⁵⁸ Most chalcogenides exhibit some thermodynamic instability in the presence of O_2 and oxidation can occur during processing steps such as crushing or grinding.¹⁶⁰ This results in some passivation from surface oxides, which themselves possess electrochemical activity. One difference between molybdenum and tungsten dichalcogenides is the far poorer solubility of passivating WO_3 compared to MoO_3 ,¹⁵⁴ and is therefore likely to

account for the observation that WS_2 requires numerous potential sweeps for its inherent oxidation peak to disappear and its HER current to be negatively affected.¹⁵³

Figure 1.11. Potential-pH diagrams illustrating thermodynamic stabilities of a **a)** molybdenum-sulphur-oxygen-hydrogen system, **b)** tungsten-sulphur-oxygen-hydrogen system, **c)** sulphur-oxygen-hydrogen system, and **d)** selenium-oxygen-hydrogen system.

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In summary, the redox activity of TMDs and their surface passivation layers have been shown to be responsible for observed inherent electrochemistry. Such properties are however often overlooked even in contemporary literature, despite that they may pose limitations to certain electrochemistry applications. Additional factors that influence inherent electrochemistry vary from experimental conditions such as pH, applied potential, and the choice of electrolyte. It should, nevertheless, be emphasized that much difficulty remains in conclusively determining reaction mechanisms corresponding to observed behaviour. Key reasons for this are that a TMD and its surface oxide can undergo reaction simultaneously, and even then both reactions will proceed on variable fractions of the total electrode surface. Nevertheless, a general awareness of TMD character is essential for applications utilising TMDs as electrode materials. A new comprehensive study on the inherent electrochemistry of up-and-coming Group VI TMDs (MoSe_2 , WS_2 , WSe_2) is presented in **Chapter 13**.

1.3.3. Application in Electrocatalytic Hydrogen Evolution

Hydrogen is a clean and renewable fuel which may be generated sustainably through electrochemical or photoelectrochemical (*i.e.* solar-powered) water splitting, and may therefore serve as part of our future energy storage needs. Water splitting produces hydrogen gas at the cathode through the hydrogen evolution reaction (HER), while water is oxidised at the anode to give oxygen gas.¹⁶¹ When required, both gases may then be consumed by fuel cells to generate electricity. Focusing our attention on the HER, the mechanism of the hydrogen evolution on different surfaces can be described from the elementary steps under acidic conditions as follows:^{137,143}

1. Volmer adsorption step: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ $b \approx 120 \text{ mV/dec}$

2a. Heyrovsky desorption step: $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2(\text{g}) + \text{H}_2\text{O}$ $b \approx 40 \text{ mV/dec}$

2b. Tafel desorption step: $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2(\text{g})$ $b \approx 30 \text{ mV/dec}$

Protons in the form of hydronium ions are first reduced on the surface to give adsorbed hydrogen atoms through the Volmer step. A second electron transfer may subsequently occur near the first adsorbed hydrogen, which together desorb from the catalyst surface as a hydrogen molecule in what is known as the Heyrovsky step, or two neighbouring adsorbed hydrogen atoms may undergo recombination through the Tafel step. Each step is roughly associated with an experimentally determined Tafel slope, and as an inherent property of the catalyst is therefore indicative of the step involved.¹⁴³

It is widely acknowledged that current state-of-the-art platinum catalysts are simply not commercially viable,¹⁶² and it is this lack of a cost-effective HER catalyst that drives the abundant interest within the scientific community to search for an alternative. Nørskov *et al.* first computed the activity of various metals,¹⁶³ and showed that exchange current densities for hydrogen evolution are related to the Gibbs energy of absorbed atomic hydrogen ΔG_{H} (Figure 1.12a); the greatest HER activity is associated with the energy of the absorbed hydrogen being thermoneutral with the catalyst surface (*i.e.* $\Delta G_{\text{H}} \approx 0$). Conversely, should the bond between hydrogen and metal be too strong, the second step of the reaction (either the Heyrovsky or Tafel step) is rate-limiting; if the bond is too weak, the initial Volmer step becomes rate-limiting.¹³⁷ Jaramillo *et al.* further showed experimentally in 2007 that in MoS_2 the sheet edges are the active sites, where the edge length correlates linearly with HER activity.¹⁴²

Figure 1.12. **a)** Volcano plot of the exchange current density as a function of the DFT-calculated Gibbs energy of adsorbed atomic hydrogen for nanoparticulate MoS₂ and the pure metals. Reproduced with permission from reference 142. Copyright 2007 AAAS. **b)** Schematic illustration of hydrogen evolution on MoS₂ nanoparticles; **c)** linear sweep voltammogram of exfoliated MoS₂ nanosheets obtained from different treatments; **d)** corresponding Tafel plots of various exfoliated MoS₂ nanosheets. Reproduced with permission from reference 144. Copyright 2013 American Chemical Society.

Subsequently in 2013, Chorkendorff and co-workers reported that a phase change could be used to improve the HER. Metallic MoS₂ nanosheets in the 1T phase obtained from chemical exfoliation (Figure 1.12b) had substantially enhanced HER performance, with a lowered overpotential of approximately 100 mV compared to >250 mV for sheets in the native semiconducting 2H phase (Figure 1.12c).¹⁴⁴ The reaction kinetics was also seen to improve (Figure 1.12d) based on the observed Tafel slope (*i.e.*

overpotential required for every 10 fold increase in HER current); 1T-MoS₂ had low Tafel slopes of ~40 mV/decade compared to 2H-MoS₂ at 75-85 mV/dec. It was however not known if the superior charge transfer kinetics was simply due to increased conductivity conferred by the metallic nature of the sheets, or if the 1T phase was inherently more active. Only recently, Tang and Jiang confirmed intrinsic HER activity on the basal-plane of the 1T phase in addition to its edges, unlike the unreactive 2H basal-plane.¹⁶⁴ Yu *et al.* also observed that the HER overpotential can be reduced by decreasing the number of stacked atomic layers.¹⁶⁵

Thus, various approaches are accessible for improving the HER efficiency: by (1) exploiting active edge sites,^{142,166} (2) phase transition to the more catalytic 1T phase through reductive chemical treatments^{127,144} and (3) reducing the potential barrier for electron hopping through exfoliation and decreasing the number of layers.¹⁶⁵ While much effort is seen within the electrochemical literature to further improve the performance of MoS₂ HER electrocatalysts, it is instinctive to pursue similar investigations on the effectiveness of affiliated TMD materials. For instance, an insightful computational study by Tsai *et al.* suggested the feasibility of MoS₂ analogues.¹⁶⁷ The Gibbs energy for hydrogen adsorption is close to neutral at the various edge sites of Mo and W chalcogenides with the exception of the S-edge in MoS₂ and the W-edge in WSe₂ as illustrated in Table 1.1. In this respect, both MoSe₂ and WS₂ may be purported to be better HER catalysts compared to MoS₂. Nevertheless at the point of writing, there were only a limited number of HER studies on other TMDs, such as the few on WS₂,¹⁴⁷ MoSe₂,¹⁴⁸ and WSe₂.¹⁴⁹ A detailed investigation of these MoS₂ analogues was thus carried out, with the materials exfoliated under different conditions and the resulting effects studied. This is discussed and presented in **Chapter 13**.

Table 1.1. The structures and Gibbs energies for hydrogen adsorption (ΔG_H) for TMDs in vacuum. Only the most stable edge configurations are shown. All ΔG_H are shown for the final adsorbed hydrogen at the corresponding coverage of hydrogen (θ_H). Reproduced with permission from reference 167. Copyright 2014 Royal Society of Chemistry.

System	Surface	Stable structure	θ_S (ML)	θ_H (ML)	H adsorption ΔG_H (eV)	System	Surface	Stable structure	θ_{Se} (ML)	θ_H (ML)	H adsorption ΔG_H (eV)
MoS ₂	Basal plane (0001)			0.0625	1.92	MoSe ₂	Basal plane (0001)			0.0625	2.13
	Mo-edge (10 $\bar{1}$ 0)		0.5	0.25	0.06		Mo-edge (10 $\bar{1}$ 0)		0.5	0.25	0.02
	S-edge ($\bar{1}$ 010)		1.0	1.0	-0.45		Mo-edge (10 $\bar{1}$ 0)		0.75	0.25	-0.04
WS ₂	Basal plane (0001)			0.0625	2.23	WSe ₂	Se-edge ($\bar{1}$ 010)		1.0	1.0	-0.05
	W-edge (10 $\bar{1}$ 0)		0.5	0.25	-0.04		Basal plane (0001)			0.0625	2.31
	S-edge ($\bar{1}$ 010)		1.0	1.0	-0.06		W-edge (10 $\bar{1}$ 0)		0.5	0.25	0.17
(Mo = , W = , S = , Se = , H =)						WSe ₂	Se-edge ($\bar{1}$ 010)		1.0	0.50	-0.05

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Chapter 2 –

Objectives of the Thesis

This thesis titled *“Graphene, Chemically Modified Graphenes, and Two-Dimensional Layered Materials – Electrochemical Fundamentals and Applications”* focuses on the modification and functionalization of graphenes and layered nanomaterials, explores the fundamental aspects of their electrochemistry and changes in physicochemical properties, and consequently their use in various scientifically-relevant applications. An overview of contemporary literature on graphene and its related materials may be found in **Chapter 1**, with particular focus on graphene oxide, its various inherent groups, and their functionalization. Chemically modified graphenes such as reduced and hydrogenated graphenes are also discussed. This ends with a review on transition metal dichalcogenides as 2D layered analogues of graphene. The general experimental methods and procedures used are then summarized in **Chapter 3**. Following this, works performed herein are arranged into three Parts.

Part I covers the fundamental aspects of graphenes and CMGs, including the structure of graphene oxide, and experimental considerations in graphene electrochemistry. As discussed in the literature review, different physical and chemical properties had been previously observed between GOs from different production methods. In addition, we made a serendipitous observation of unusual reversible electrochemistry of certain functional groups in permanganate-oxidised GOs unlike previous data which showed that GOs may only be irreversibly reduced. This process of discovery is documented in **Chapter 4**, and the first objective is thus to investigate and explain the electrochemical behaviour of different GOs. Consequently, the next logical aim is to attempt the identification and quantification of the various types of oxygen groups in the GOs, as shown in **Chapter 5**. **Chapter 6** then moves to investigate if the observed inherent GO redox character may be exploited for their detection as colloidal

particles in aqueous media, analogous to Faradaic detection in particle coulometry. Relevant factors such as the particle size, pH, and concentration of colloidal solutions are studied. **Chapter 7** investigates possible caveats of the commonly employed drop-casting method for electrode preparation. This is an important consideration for the studies in Part II where the HET is studied at a variety of CMG surfaces, as the kinetics is studied in the presence of possible influences from porosity effects that may be inadvertently introduced during electrode preparation.

This leads to **Part II** where the primary objective is to study the effects of novel reduction and hydrogenation treatments on the electrochemical and material properties of CMGs. It starts with the thermal reduction of graphene assisted by potassium in **Chapter 8**. Subsequent research moves to hydrogenated graphenes prepared by the two different approaches discussed in Section 1.1.3: **Chapter 9** employs the gaseous microwave hydrogenation approach in contrast with wet chemistry hydrogenation in **Chapter 10** *via* the Birch reduction. **Chapter 11** then further examines the experimental conditions (*e.g.* electron and proton sources) for improving the extent of hydrogenation.

Finally, **Part III** summarizes the development of layered materials for use in applications. As detailed in Section 1.2.2, the majority of capacitive charge storage studies on graphene-type materials have taken the approach to increase their electrochemical double-layer capacitance. Studies pursuing pseudocapacitive enhancements are comparatively lacking, such as the introduction of Faradaic processes using redox-active surface groups. Hence, the main objective in **Chapter 12** is to attempt the latter approach based on covalent functionalization of graphene oxide, not only to improve its charge storage capability but also to recover electrical conductivity that is necessary to utilise non-conductive GO as a candidate supercapacitor material.

Interestingly, fluorescence enhancement of the functionalized GO was also observed, and probable origins were proposed. Finally in **Chapter 13**, 2D layered transition metal dichalcogenides are examined as a fascinating analogue to graphene. The bulk of TMD electrochemistry literature at the time of investigation was limited mostly to MoS₂ and its HER performance, with new computational data suggesting that other TMDs like MoSe₂ and WS₂ may have greater HER activity. Hence, this forms the main motivation for this work on MoSe₂, WS₂, and WSe₂, with special emphasis placed on their electrochemical hydrogen evolution. Also in consideration of factors such as edge sites and the metastable 1T-phase reported to improve performance, the second objective was to study the influence of different chemical exfoliation methods. In addition, fundamental studies on their inherent electrochemical redox activities and heterogeneous electron transfer at the TMD surfaces were performed.

Chapter 3 –

Experimental Methods

This chapter summarises the various experimental preparation procedures, material characterisation techniques, and electrochemistry studies performed throughout the ensuing Chapters of this thesis. All characterisation and procedures described herein are of the author's work. Where applicable, additional synthetic procedures and/or characterisation methods (collaborators' contributions unless otherwise stated) are detailed at the end of each respective Chapter.

3.1. Characterisation Procedures and Apparatus

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique allowing the study of elemental and chemical composition data,¹ based on the principle of the photoelectric effect. Graphene materials were studied with a Phoibos 100 spectrometer and a monochromatic magnesium X-ray radiation source (SPECS, Germany) for the measurement of wide-scan survey spectra for all elements present, and also the high resolution spectra of specific elements such as the carbon 1s peak. Relative sensitivity factors were used in the quantification of elemental compositions and for the evaluation of C/O ratios from the survey XPS spectra. Preparation of solid samples was achieved by compaction of a layer of the materials on a conductive carbon tape. In the analysis of materials that involved prior electrochemical treatments, screen-printed electrodes were first drop-casted with GO, and were mounted directly onto sample holders with conductive carbon tapes after their pre-treatments.

Raman spectroscopy is a standard technique in graphene chemistry that allows the elucidation of structural information of carbon materials,^{2,3} with the primary objective of studying the defect densities of the graphene materials. Information on the relative amounts of pristine graphene in comparison to disordered and defective regions may be directly obtained from characteristic peaks, therefore providing a better understanding of the inherent structure. Measurements were done using a confocal

micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector, with excitation from a 514.5 nm Argon laser from a 100× objective lens mounted on an Olympus optical microscope. Calibration of the instrument was achieved with a silicon reference wafer which gives a peak position at 520 cm^{-1} and a resolution of less than 1 cm^{-1} . All Raman spectra were measured between 1000 and 3000 cm^{-1} . For the measurements, materials were compressed onto a glass slip and placed on top of a glass slide on the sample stage.

Scanning electron microscopy (SEM) was performed using a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) in gentle-beam mode at 2 kV. All graphene samples studied were first attached onto a conductive carbon tape and then mounted on an aluminium sample stub for imaging. In particular for the characterisation of dispersed graphene oxide samples, $3\text{ }\mu\text{L}$ of a 0.5 mg mL^{-1} ultra-sonicated dispersion in dimethylformamide (DMF) was deposited on silicon wafers and dried in a desiccator prior to imaging. Additionally for non-conductive samples, a thin platinum layer was sputtered on over samples with a JEOL JFC-1600 auto fine coater. Energy dispersive X-ray spectroscopy (EDS) data was collected with an electron beam accelerating voltage of 15 kV.

Scanning transmission electron microscopy was also performed using a JEOL 7600F field-emission scanning electron microscope but operated at an accelerating voltage of 30 kV. Samples were directly deposited onto lacey carbon copper grids (Ted Pella, USA) using a 0.1 mg mL^{-1} dispersion in DMF and dried overnight in air.

Fourier-transform infrared (FTIR) spectroscopy was performed for materials to obtain qualitative information on their chemical bonding, and are especially important for oxygen moieties such as hydroxyls (O-H stretches), carbonyls and carboxylic acids (C=O stretch), and also chemisorbed hydrogen in form of C-H stretches in hydrogenated

graphenes. FTIR spectra are obtained with a PerkinElmer Spectrum 100 system with a universal attenuated total reflectance (ATR) accessory using a Diamond/ZnSe crystal. Where higher resolution spectra of C-H bonds were required, measurements were also performed in transmittance mode on a Shimadzu IR spectrophotometer (Shimadzu, Japan). A small amount of graphene materials were ground together with anhydrous potassium bromide and subsequently compressed into translucent pellets for analysis.

UV-visible spectroscopy was performed on a Cary 100 Bio spectrophotometer in transmittance mode with 0.1 mg mL^{-1} suspensions of the material in DMF contained in quartz cuvettes.

Fluorescence was investigated using a Cary Eclipse fluorescence spectrophotometer (Varian, USA) in quartz cuvettes with a 0.1 mg mL^{-1} suspension of the material in DMF. A high photomultiplier tube voltage was employed for the detector.

N_2 adsorption/desorption analysis was performed with a Quantachrome Instruments Nova 2200e BET surface area and pore size analyzer at 77.4 K. For heat sensitive samples such as graphene oxide, de-gassing was performed at 110°C for 20 h to prevent loss of inherent functionalities. Pore analyses were performed with the NovaWin software (Quantachrome Instruments, USA), with non-local density functional theory (NLDFT) calculations using an equilibrium slit-pore model on carbon. The method is an accepted standard for pore characterisation that allows for both micro- and mesopore analysis, and the carbon slit pore model was chosen as it approximates the planar graphitic sheets in graphene-type materials. The reference isotherm and model parameters are described by Ravikovitch *et al.*⁴

3.2. Electrochemistry Studies

Electrochemical studies were performed in a 5 mL electrochemical cell at room temperature (approximately 23 °C) with a standard three-electrode configuration using an Autolab PGSTAT 101 electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) and controlled by the NOVA Version 1.8 software (Eco Chemie). All electrochemical potentials reported are with reference to the Ag/AgCl reference electrode. Glassy carbon (GC) electrodes and a platinum electrode (Pt) purchased from CH Instruments, Texas, USA with a diameter of 3 mm were used as the working and auxiliary electrodes, respectively. Deionised water with a resistivity of 18.2 MΩ cm was used throughout all experiments in the preparation of solutions. All experiments were performed using a 50 mM phosphate buffered saline solution (PBS, pH 7.2) as supporting electrolyte unless stated otherwise. Using the NOVA 1.8 software, potentials were applied using a staircase (with step potential of 0.00244 V), and the current sampled at 0.0244 s intervals (at a scan rate of 100 mV s⁻¹). It should be noted here that smaller peak currents and larger peak-to-peak separations for diffusional redox processes could inadvertently result if large step sizes were used, as compared to a true analogue waveform.⁵

In the study of electrode kinetics in Part II of this thesis (Chapters 8 to 11), cyclic voltammetry experiments on GC electrodes were performed at a fixed scan rate of 100 mV s⁻¹ for the 10 mM ferro/ferricyanide redox probe. The classical Nicholson method⁶ is employed, which essentially relates the observed peak separation (ΔE_p) of a cyclic voltammogram first to a dimensionless kinetic parameter (Ψ), from which the k_{obs}^o is calculated using the equation: $k_{obs}^o = \Psi \left(\pi D_o \frac{nFv}{RT} \right)^{\frac{1}{2}}$

The roughness factor was not taken into account in our studies, and the diffusion coefficient of $D_o = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used in our calculations.⁷ The parameters of n , F , ν , R and T refer to their standard physical quantities of the number of transferred electrons, Faraday's constant, scan rate, the gas constant, and temperature, respectively. Where given, calculation of the quasi-reversible limits for k_{obs}^0 is based on the definition by Matsuda and Ayabe.⁸

The drop-casting procedure for the purpose of electrode modification first involves renewal of the GC electrode surfaces by polishing with 0.05 μm alumina particles on a polishing pad, followed by thorough washing with deionized water prior to measurements. Unless otherwise stated, immobilization of the graphene materials onto the working electrode was then performed by first preparing a suspension of specific materials with a concentration of 0.5 mg mL^{-1} in DMF. Consequently, ultrasonication of materials was done to achieve a good dispersion of the materials. In particular, thermally reduced graphenes were ultrasonicated for 5 minutes while graphite oxides were initially ultrasonicated for 1 hour to obtain the graphene oxides. Lastly, a 1 μL aliquot of the suspension was deposited onto the electrode surface and the coating was allowed to dry at room temperature before a new aliquot was deposited. This process was repeated to obtain 3 layers of coatings on the electrode surface, with the aim of this repeated drop-casting procedure being to achieve a random but uniformly distributed film on the GC electrode surface. With the final evaporation of the solvent, graphene-modified electrodes were then used, and results are calculated from triplicate measurements.

Specifically for our study on the inherent electrochemistry of oxygen functionalities in GO (Chapter 4), GO suspensions with a concentration of 1.0 mg mL^{-1} in DMF were used in place and the drop-casting process was repeated twice to obtain two

layers of the coating on the GC electrode surface giving a fixed sample mass of 2.0 μg of GO immobilised per electrode. For the purpose of XPS studies performed before and after electrochemical pre-treatment, disposable screen-printed carbon electrodes were used. Immobilization of the GOs was similarly performed, but 8.0 μL aliquots from a 1.0 mg mL^{-1} ultrasonicated suspension in deionised water were used instead. Subsequently, GO-modified screen-printed electrodes were electrochemically treated either by potential cycling at a scan rate of 20 mV s^{-1} , or with chronoamperometry by the application of a fixed potential for a period of 100 s. This allowed a controlled electrochemical reduction or oxidation of the GO films prior to XPS analysis.

In calculating the density of oxygen-containing groups in graphene oxides, the total *theoretical surface area* of graphene at 2630 $\text{m}^2 \text{g}^{-1}$ is used, but this is divided by two to obtain the *effective surface area* (1315 $\text{m}^2 \text{g}^{-1}$). This is in consideration that oxygen groups are accessible on both sides on a single plane of graphene. Hence, the effective surface area of a typical sample of mass 2.0 μg as immobilised on a GC electrode is $2.63 \times 10^{15} \text{ nm}^2$. Thus, the surface coverage or number of oxygen groups per square nanometre = (number of moles of oxygen groups calculated electrochemically $\times$ Avogadro's constant) / $2.63 \times 10^{15} \text{ nm}^2$.

Electrical conductivity measurements were performed on a gold interdigitated array electrode (ALS Corporation, Japan) by deposition of a 2.0 μL suspension of the relevant material (at 1 mg mL^{-1} concentration in deionised water) onto the interdigitated region 2 mm wide (individual gold contacts are spaced 10 μm apart) and left to dry in air. Linear sweep voltammetric scans were then performed at a scan rate of 20 mV s^{-1} . The gradient of the resulting current-voltage curves affords a relative comparison of the conductivities between materials.

For studies on capacitor performance in Chapter 12, cyclic voltammetry and galvanostatic charge/discharge measurements were performed in 6 M KOH. Capacitance values are calculated from discharge cycles after they have stabilized past the initial charge/discharge cycles. 1.0 μL aliquots of each GO at a 5.0 mg mL^{-1} concentration in DMF were used, giving a loading capacity of 70.7 $\mu\text{g cm}^{-2}$ per electrode.

In Chapter 13, voltammetric measurements of the oxygen reduction reaction (ORR) on TMDs were also obtained in an oxygen-saturated solution of 0.1 M KOH achieved by bubbling with an air pump. A scan rate of 50 mV s^{-1} was used. The hydrogen evolution reaction (HER) was investigated by linear sweep voltammetry in 0.5 M H_2SO_4 at a scan rate of 2 mV s^{-1} .

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Part I

Chapter 4 –

Inherent Electrochemistry of Oxygen Functionalities in Graphene Oxides

Part of the results and discussion presented in this chapter were published in the following journal article:

1. Unusual Inherent Electrochemistry of Graphene Oxides Prepared Using Permanganate Oxidants.

A.Y.S. Eng, A. Ambrosi, C.K. Chua, F. Šaněk, Z. Sofer, M. Pumera. *Chem. Eur. J.* **2013**, *19*, 12673.

Article may be retrieved at <http://dx.doi.org/10.1002/chem.201301889>

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4.1. Introduction

The primary difference between the electrochemistry of graphene and graphene oxide is that graphene oxide (GO) is intrinsically electroactive; where its abundant oxygen functionalities can be oxidized or reduced. In contrary, pure graphene does not exhibit any inherent electrochemical reductions due to the total absence of oxygen-containing groups. This has been demonstrated for GO, prepared in particular by the Staudenmaier oxidation method.¹ However, only a few studies exist on investigating differences in the *types* of GOs produced from different methods, and recent studies are beginning to show that the use of each oxidation method leads to materials with very different structures and thus different *chemical properties*.²

Thus, it is not unreasonable to extend this hypothesis to include possible differences in their *electrochemical properties* as well. In all previously reported cases, it is observed that GO exhibits strong *chemically irreversible* cathodic waves originating from the irreversible reduction/removal of its electroactive oxygen-containing groups. However, a major difference in their intrinsic electrochemistry is observed in this study; graphene oxides prepared using chlorate oxidants (of the Staudenmaier and Hofmann methods) exhibit the usual *chemically irreversible* reductions, while GOs prepared by the permanganate methods of Hummers and Tour show unusual inherent *chemically reversible* electrochemistry of oxygen-containing groups.³ The Staudenmaier, Hofmann, Hummers and Tour graphene oxides are abbreviated as GO-ST, GO-HO, GO-HU and GO-TO respectively.

4.2. Results and Discussion

Cyclic voltammetry of the various GOs was first performed in an aqueous pH 7.2 buffer, and the voltammograms are shown in Figure 4.1. As seen from Figure 4.1a, the reduction of GO-ST starts at -0.7 V with a peak potential at about -1.1 V, while the reduction of GO-HO (Figure 4.1b) occurs at more negative potentials and peaks around -1.3 V. It should also be emphasised that these reductions are only observed during the initial reductive sweep and no peaks are recorded for all subsequent scans, thus indicating that all the surface-bound electro-reducible groups are reduced in the first scan. Similarly for the permanganate-oxidised Hummers and Tour GOs, the initial reductive sweeps give rise to large voltammetric peaks around -1.6 V and -1.7 V respectively in Figures 4.1c and 4.1d. The occurrence of these reduction peak potentials at more negative values probably suggest a higher carbonyl content in permanganate-oxidised GOs, which concur with our XPS observations. It is also seen in Figure 4.1c that the main reduction of GO-HU shows two small shoulder peaks at approximately -1.2 and -1.9 V, and may be taken as an indication of the numerous types of oxygen functionalities present as various groups are reduced at their respective potentials.

Figure 4.1. Cyclic voltammograms of graphene oxides prepared via the methods of a) Staudenmaier, b) Hofmann, c) Hummers, d) Tour scanned towards reducing potentials; and the graphene oxides of e) Hummers, f) Tour scanned towards oxidising potentials. Conditions: supporting electrolyte: 50 mM phosphate buffered saline (PBS) at pH 7.2; scan rate: 100 mV s^{-1} . Arrows indicate the direction of the first scans (in black). All starting potentials are at 0.0 V and are with reference to the Ag/AgCl reference electrode.

These observed reductions of electroreducible oxygen-containing groups in GOs during the initial reductive scans are expected, due to a wealth of documented evidence.^{1,4,5,6} However, to the best of our knowledge, no observation has been made with respect to significant amounts of these groups undergoing electrochemical *re*-oxidation after their reduction. Thus, it is very interesting that when the applied potential was reversed towards the anodic direction after the initial reduction of GO-HU (Figure 4.1c), a sharp oxidation peak first appeared at about 0.3 V followed by a second broader peak at 1.3 V. On reversal of the potential scan, another reduction peak appeared at *ca.* -0.7 V which was not observed during the first scan. An illuminating observation was made when an initial anodic sweep was used instead in Figure 4.1e. In this case, neither of the two oxidation peaks nor the reduction peak at -0.7 V was observed in the first scan. Only after the main reduction of the inherent oxygen moieties at approximately -1.6 V did the peaks at 0.3, 1.3 and -0.7 V consequently appear. We also report that these same voltammetric waves were obtained from a separate batch of GO-HU synthesised. In addition, no differences were found when the electrolyte was purged with nitrogen gas for two hours, indicating that dissolved oxygen cannot have contributed to the unusual observations. It is also important to note that no voltammetric peaks were detected for bare glassy carbon electrodes within their operational potential range.

Likewise, we note similar electrochemical behaviour in GO-TO as shown in Figure 4.1d and f. A major difference is that although the main reduction peak at -1.6 V in GO-HU is significantly diminished during its second sweep, the peak current is either maintained or increased during the second sweep for GO-TO. Therefore from these data, we can unambiguously draw two important conclusions. Firstly, the types of oxygen functionalities in GOs prepared from the permanganate routes must be intrinsically

different from those in chlorate-oxidised GOs, or contain groups that are entirely absent from chlorate-oxidised GOs. Secondly, the *chemically reversible* nature of these group(s) responsible is such that it first requires a preceding electroreduction at considerably harsh potentials of up to -1.7 V vs Ag/AgCl to activate its subsequent unusual electrochemistry.

Thus, we proceed to investigate both the chemically reversible redox nature and *activation* aspects of the oxygen groups in GO-HU. From Figure 4.2a, it is clear that following the initial reduction at -1.6 V, all subsequent scans at this applied potential no longer show discernible peaks, indicating that all electroreducible groups have already been reduced during the first voltammetric sweep. For the first oxidation at 0.3 V, the peak in the first scan appears sharp while successive scans show broader peaks that not only decrease in height but also shift towards higher peak potentials. In comparison, the oxidation peaks at 1.3 V shift towards lower potentials while the sharp reduction peaks at -0.7 V move towards more negative potentials with consecutive scans. With regard to the reversible nature of these moieties, we note that all voltammetric peaks progressively decrease in height until they are no longer noticeable beyond the tenth or eleventh sweeps, and a possible explanation could be the passivation of these groups on the electrode surface. As the appearance of some peaks seemingly require the prior application of specific potentials, their inter-dependence was then studied by limiting the range of the applied potential. As in Figure 4.2b, we first limit the maximum applied potential to 0.7 V. After its initial reduction and its first oxidation at 0.3 V, the potential was immediately reversed. Interestingly, no reduction peak at -0.7 V was seen, implying that the voltammetric wave at this potential must correspond to the reduction of the oxidised species first generated at 1.3 V. Subsequently, the oxidation wave at 0.3 V became greatly diminished in height, and its absence from the second scan onwards

therefore implies that for the continued oxidation of the involved functionality at this potential, a preceding reduction at -0.7 V must first occur. Next, considering that a shoulder in the main reduction wave was earlier observed at about -1.9 V, we now restrict the lower potential to -1.5 V as in Figure 4.2c and not allowing the reduction at -1.9 V to occur. Here, we note a further relation between the 0.3 V oxidation wave and the reduction at -1.9 V, such that the reduction of the moiety at -1.9 V must occur prior to its subsequent oxidation at 0.3 V. On a separate note, the presence of the voltammetric waves at -0.7 V and 1.3 V further highlights a similar observation from Figure 4.2b, that these two peaks likely correspond to the reduced and oxidised forms of a specific oxygen group. The absence of this pair in Figure 4.2d again supports this proposition. We then move our attention back to the electrochemical oxidation process(es) occurring at 0.3 V, which has a far more complex nature. To begin with, an initial reduction beyond -1.9 V is required for this particular moiety to become *activated*, only after which a sharp peak at 0.3 V may be observed in the first oxidative sweep (Figure 4.2b). Accordingly, the lack of a reductive sweep beyond -1.9 V results in its absence (Figure 4.2c and d). However, for the occurrence of voltammetric waves at 0.3 V in all subsequent sweeps, a preceding reduction at -0.7 V is first required, as exemplified in Figure 4.2b. Furthermore, the difference in the peak shapes of the first scan at 0.3 V in comparison to those of successive scans suggest different processes involved; the broader peak from later scans may be attributed to possible reasons such as a slower electron transfer and/or the involvement of diffusion-limited species such as protons in solution. Hence, there exists complex relationships between the redox cycling of these groups and investigations into their exact mechanisms are beyond the scope of the present study. In all cases nonetheless, we establish that an initial reduction pass -1.6 V

is first required for the activation and consequent appearance of all other voltammetric waves, as clearly exemplified in Figure 4.2c and Figure 4.2e.

Figure 4.2. Multiple-cycle voltammograms of the Hummers graphene oxide scanned over different potential ranges; a) Full range of -2.0V to 1.8 V, and limited ranges from b) -2.0 V to 0.7 V, c) -1.5 V to 1.8 V, d) -1.5 V to 0.7 V. Conditions: supporting electrolyte: 50 mM PBS at pH 7.2; scan rate: 100 mV s^{-1} . Arrows indicate the voltammetric peaks absent. All starting potentials are at 0.0 V with initial cathodic sweep and are with reference to the Ag/AgCl reference electrode.

Considering that this unusual voltammetry was only seen in permanganate-oxidised GOs, one might propose that they may originate from manganate esters formed between the oxidant and the inherent oxygen functionalities.⁷ However, there are several pieces of evidence that would refute this possibility. As no manganese had

initially been detected by XPS, we then proceeded to use ICP-MS as a sensitive technique suitable for the trace detection of metallic impurities.⁸ In GO-HU, a significant amount of Mn was found at 2058 ppm by weight, while GO-TO had a significantly lower Mn concentration of 344 ppm. These data were then used to evaluate the possibility if manganese esters could have resulted in the observations, achieved by the absolute quantification of the reduced species per amount of GO deposited on an electrode and compared against the actual concentration as obtained by ICP-MS. In the electroreduction of GO-HU, the total charge passed during the main reduction at -1.6 V is obtained from the integrated peak area in the initial scan of Figure 4.2c, which on average has a value of 2.04 mC. Assuming the extreme case of a 7-electron reduction process of Mn, it is possible to calculate the total amount of manganese that would have to be present using Faraday's Law of electrolysis:⁵

$$n = \frac{Q}{z \times F}$$

where n is the number of moles of the reduced species, Q is the total charge passed, z is the number of electrons exchanged per electroreducible group, and F is Faraday's constant. Thus, based on the measured charge passed, we calculate that the concentration of Mn would have to be 83000 ppm (8.3 wt%), many times more than the actual concentration of 2058 ppm, while a single-electron Mn reduction would need an unreasonable manganese concentration of 580000 ppm (58 wt%). Conversely, we can also calculate the total charge that would be measured if all the manganese present had been reduced; the reduction of 2058 ppm of manganese in GO-HU would correspond to a total charge of only 5.06×10^{-5} C even with the extreme assumption of a 7-electron reduction. Hence, the actual reduction charge passed is at least two orders of magnitude larger than if manganese esters or impurities were responsible for the observed

voltammetric peaks, essentially removing the likelihood that the observed electrochemical responses could have been a result of the residual permanganates.

For the case of oxygen functionalities as the electroactive species, Faraday's Law may also be used to quantify the electrochemically reducible oxygen-containing groups.^{5,9} Peroxyl, aldehyde, epoxyl and carbonyl groups all involve a two-electron reduction process. Thus it is possible to calculate for GO-HU the average number of reducible oxygen groups per unit surface area of graphene. From the integrated area of the reduction peak and the theoretical surface area of graphene, the surface coverage of groups is 2.42 groups per square nanometre. This is very close to the value of 3.0 groups per square nanometre previously obtained for GO synthesized from the Staudenmaier method,⁵ providing further credibility to the view that inherent oxygen groups in GO-HU are responsible for its unique electrochemistry. Thus, it is verified using cyclic voltammetry that surface oxygen groups in GOs produced via the permanganate oxidants may be reversibly reduced and re-oxidised by cycling of the applied potential.

To achieve a substantial level of reduction and oxidation of surface oxygen groups on GO, various potentials were applied to the Hummers GO deposited on screen-printed electrodes before XPS analysis. This pre-treatment of the GO is analogous to chronoamperometry, and is shown to allow precise tuning of the oxygen content in GO.¹⁰ The exact potentials applied were selected from preceding cyclic voltammetry runs, and the resulting survey XPS spectra are shown in Figure 4.3. The relative peak intensities of carbon to oxygen (abbreviated as C/O ratios) are tabulated in Table 4.1, with a higher C/O ratio indicating less surface oxygen. Investigation of the high resolution C 1s peak then allows for identification of changes in the bonding modes between carbon and oxygen. The increase in the C/O ratio is substantial after the initial reduction; with a value of 7.30 after an applied potential of -1.60 V. This ratio then

decreases to 5.69 and 4.20 after both oxidations, representing an increase in oxygen content, and the C/O ratio eventually increases again to 5.94 after the second reduction. In the C 1s spectra, there is a visible increase in the shoulder peak near 286.4 eV upon the first oxidation at 0.16 V, corresponding to an higher amount of C-O bonds on GO (from 14.2 at.% to 18.3 at.%). With the subsequent application of a higher potential of 1.29 V, this shoulder further increases in intensity together with a shift towards higher binding energies. Deconvolution of this spectrum reveals a significant increase in the presence of the carbonyl (C=O) and carboxyl (O-C=O) functionalities to 11.8 at.% and 6.2 at.% respectively, effectively doubling both the carbonyl and carboxyl contents after this oxidation step. A final reduction with a -0.84 V applied potential is then observed to cause the disappearance of these groups. From an overlay of the C 1s spectra in Figure 4.4, the first oxidation process results in a decrease in the sp^2 aromatic regions (284.5 eV) together with a slight increase at approximately 286.4 eV from hydroxyl groups. The main 284.5 eV peak further decreases upon the second oxidation, while an obvious and simultaneous increase of the carbonyl/carboxyl peaks occur at higher energies. Most importantly, the sp^2 carbon peak reverts to its original intensity upon reduction. These observations could suggest that the electrochemical oxidation of GO-HU converts a portion of aromatic sp^2 carbons towards carbonyl groups, but the process is seemingly reversible and the aromatic regions are regenerated upon reduction. Normalisation of the spectra to the main 284.5 eV peak in Figure 4.4 also clearly demonstrates the increased presence of C=O and O-C=O groups after the oxidation at 1.29 V.

Figure 4.3. Survey (left) and high resolution C 1s (right) X-ray photoelectron spectra of the Hummers graphene oxide after fixed potential pre-treatments. The potentials applied are based on peak potentials obtained by cyclic voltammetry, and are as such- *1st reduction*: -1.60 V; *1st oxidation*: -1.60 V followed by 0.16 V; *2nd oxidation*: -1.60 V followed by 1.29 V; *2nd reduction*: -1.60 V followed by 1.29 V and then -0.84 V. Each

potential is applied for a period of 100 s. Conditions: supporting electrolyte: 50 mM PBS at pH 7.2. Potentials are with reference to the Ag/AgCl reference electrode.

Table 4.1. Tabulated carbon/oxygen ratios from the X-ray photoelectron spectra of Hummers graphene oxide after electrochemical pre-treatment with fixed applied potentials, and quantitative distributions of deconvoluted peaks from their high resolution C 1s spectra.

Material (GO-HU)	C/O Ratio	C 1s Peak Distributions (atomic %)				
		C=C	C-C	C-O	C=O	O-C=O
Control (without electrochemical treatment)	2.26	38.9	7.6	38.2	9.5	5.9
After initial reduction	7.30	57.0	20.2	14.2	5.5	3.1
After 1 st oxidation	5.69	56.4	16.6	18.3	5.5	3.3
After 2 nd oxidation	4.20	49.4	16.1	16.4	11.8	6.2
After 2 nd reduction	5.94	55.7	15.5	14.5	8.4	5.8

Figure 4.4. Unnormalised (left) and normalised (right) high resolution C 1s X-ray photoelectron spectra of the Hummers graphene oxide after electrochemical reduction/oxidation at the various potentials.

As a control experiment, we performed similar electrochemical treatments on a non-permanganate oxidised graphene oxide sample obtained from the chlorate-based

Staudenmaier oxidation. The spectra of GO-ST are shown in Figure 4.5 and the amounts of specific groups are in Table 4.2. In this instance, no significant trend was noted in the C/O ratio as a result of the potentials applied other than the expected increase from its initial reduction. There were also no specific changes in the content of any oxygen-containing group from the C 1s spectra. Particularly, the presence of hydroxyl/epoxyl groups (C-O) remained consistently high at approximately 21 at% regardless of the applied potentials, and no noteworthy changes were specifically observed for any oxygen group. Hence, while the reduction of oxygen groups in GO-ST at -1.6 V is complete,¹⁰ it is also chemically irreversible; as compared to GO-HU where electroreduction at this potential activates groups for further redox cycling.

Figure 4.5. Survey (left) and high resolution C 1s (right) X-ray photoelectron spectra of the Staudenmaier graphene oxide after fixed potential pre-treatments. As a control experiment, the potentials applied are the same as for the Hummers graphene oxide. Each potential is applied for a period of 100 s. Conditions: supporting electrolyte: 50 mM PBS at pH 7.2.

Table 4.2. Tabulated carbon/oxygen ratios from the X-ray photoelectron spectra of the non-permanganate-oxidised Staudenmaier graphene oxide after electrochemical pre-treatment with same applied potentials as for Hummers graphene oxide, and quantitative distributions of deconvoluted peaks from their high resolution C 1s spectra. Potentials are with reference to the Ag/AgCl reference electrode.

Material (GO-ST)	C/O	C 1s Peak Distributions (atomic %)				
	Ratio	C=C	C-C	C-O	C=O	O-C=O
Control (without electrochemical treatment)	4.66	46.0	14.5	28.2	8.4	2.9
$E_{\text{applied}} = -1.60 \text{ V}$	6.80	49.7	19.5	22.4	6.6	1.8
$E_{\text{applied}} = 0.16 \text{ V}$	7.81	53.6	19.5	20.6	4.4	1.9
$E_{\text{applied}} = 1.29 \text{ V}$	6.96	52.9	18.8	21.6	4.3	2.4
$E_{\text{applied}} = -0.84 \text{ V}$	6.67	56.0	16.4	22.1	4.4	1.1

Collectively, these observations provide clear evidence that the application of electrochemical potentials directly controls the conversion of oxygen functionalities between its numerous redox states, and this is unique only to the permanganate-oxidised GOs such as GO-HU. It is important to emphasise that the observed increase in oxygen-content in GO-HU at oxidative potentials is the result of the formation of groups such as carbonyls and/or carboxyls on graphene itself, and not as a consequence of other physical processes such as an increase in interlamellar water. This is supported by the core level carbon XPS spectra, which shows changes in the oxygen-bonded carbon moieties.

Finally, we employ a pH study in an attempt to assign possible oxygen groups that are responsible for its redox activity. Figure 4.6a illustrates changes in the

voltammograms across a large pH range. All peaks are seen to progress towards cathodic potentials with an increase in pH, which agrees with the theoretical relationship derived from the Nernst equation.¹¹ In addition, splitting of the main reduction peak is seen in acidic conditions. At pH 2, the first reduction peak occurs roughly at -1.0 V with a second drawn out wave centred at -1.55 V (Figure 4.6b). Between the pH values of 4 to 6, up to three separate peaks are seen. These gradually merge again as the pH increases. Interestingly, the cumulative peak currents from individual peaks at acidic conditions approximate those for a single reduction peak seen at neutral to basic pH.

Figure 4.6. Cathodic cyclic voltammograms of the Hummers graphene oxide in 50 mM PBS. a) at varying pH. b) Inset showing splitting of main reduction peaks at acidic pH from 2.0 to 6.0. c) Plot of peak potential of the first reduction peaks against pH. Scan rate: 100 mV s^{-1} . Arrows indicate the initial direction of the scans. All starting potentials are at 0.0 V and are with reference to the Ag/AgCl reference electrode.

Peak potentials corresponding to the first reduction wave are plotted against pH, as shown in Figure 4.6c. It may be seen that there are roughly two pH independent regions between pH 2-6, and above pH 9. Of significance is a pH-dependent region between pH 6-8, with an inflection at approximately pH 8-9. While this confirms a pH dependence for the reduction of the oxygen groups in GO-HU, the system certainly does not adopt a simple Nernstian behaviour. Indeed, this may be the case when we consider the different types of oxygen groups in GO and their non-stoichiometric amounts.

Nonetheless, qualitative evidence may be used to propose possible candidate functionalities for the unusual electrochemistry of GO-HU. Of the known electroreducible groups in GO, the reduction of epoxyls⁴ and peroxy¹² are irreversible, while some carbonyl and aldehyde reductions can occur reversibly. Aliphatic carbonyls require both harsh reducing potentials of around -2.1 V and strongly acidic solutions for their reduction and are thus unlikely candidates.¹³ Aldehydes¹⁴ and conjugated carbonyls such as quinones on the other hand, may be reduced at milder potentials.¹⁵ Estimated potentials for quinones and catechols vary over a large range between -0.2 V and +0.7 V vs. SCE.¹⁵ Quinone-hydroquinone electrochemistry is also known to exhibit cycling between its oxidised and reduced forms, and a reported oxidation peak at 0.3 V for benzoquinone may be related to the first oxidation peak in Figures 4.1c-f.¹⁶ It is also possible that the inflection in the E-pH plot around pH 8 to 9 may relate to the presence of quinone-hydroquinones and/or conjugated aldehydes which mostly have similar pKa values.^{14,16} Considering the ubiquity of quinones in many carbon materials including carbon black¹⁷ and glassy carbon,¹⁸ it is not unreasonable to suggest that they may also be found in graphene oxides. Indeed, a recent study of Hummers GO reductions also noted redox couples likely to arise from “aromatic quinone-hydroquinone type transformations” in their electrochemistry.¹⁹

4.3. Conclusions

Major differences in the electrochemistry of graphene oxides were observed when they are prepared from the permanganate oxidant routes (Hummers and Tour) compared to those prepared using chlorate oxidants (Staudenmaier and Hofmann). Combining electrochemical pre-treatments with XPS analysis, it was established that the use of permanganate oxidants generate distinctive oxygen functionalities which do not arise from other sources such as manganese impurities introduced during the oxidation procedure. Specifically, the increased presence of carbonyl and/or carboxyl groups is a unique phenomenon of graphene oxides prepared by the Hummers and Tour methods. Data from a pH study suggested that *quinone-hydroquinone* electrochemistry is a likely source of this unique reversible character of permanganate-oxidised graphene oxides. Therefore, these functionalities potentially present themselves as target groups with controllable redox states in electrochemical and bio-sensing applications using graphene oxides.

4.4. Detailed Synthetic Methods

Graphite oxide preparation with Staudenmaier method

The synthesis of GO-ST was performed according to the procedure previously reported.²⁰ Briefly, 87.5 ml of sulfuric acid (98 %) and 27 ml of nitric acid (98 %) were first cooled to 0 °C, before addition of 5 g of graphite to the acid mixture. The mixture was stirred vigorously while 55 g of potassium chlorate was added over 30 minutes. The reaction flask was loosely capped to allow the escape of chlorine dioxide gas. The mixture was continuously stirred for 96 hours at room temperature and then poured into 3 L of deionized water. After decantation, the graphite oxide was re-dispersed in 5 % hydrochloric acid, before a second decantation from hydrochloric acid. The GO was

repeatedly centrifuged and re-dispersed until a negative reaction for chloride and sulfate ions (with $\text{Ba}(\text{NO}_3)_2$ and AgNO_3) was observed. Graphite oxide slurry was finally dried in a vacuum oven at 60 °C for 48 hours before further use.

Graphite oxide preparation with Hofmann method

GO-HO was synthesised according to the standard method reported in literature.²¹ 87.5 ml of sulfuric acid (98%) and 27 ml of nitric acid (68%) were first cooled to 0 °C before 5 g of graphite were dispersed into the reaction mixture by intensive stirring. KClO_3 (55 g) was then added over a period of 30 minutes. The reaction mixture was loosely capped to allow the escape of the gaseous product (ClO_2) with continued stirring at room temperature for 96 hours. Upon completion of reaction, the mixture was poured into 3 L of deionized water and decanted. The product was then re-dispersed in 2 L of 5 % HCl and again decanted. Graphite oxide was repeatedly centrifuged and re-dispersed in deionized water until a negative reaction on sulfate and chloride ions (with $\text{Ba}(\text{NO}_3)_2$ and AgNO_3 respectively) was achieved. The final graphite oxide slurry was lastly dried in a vacuum oven at 60 °C for 48 hours before further use.

Graphite oxide preparation with modified Hummers method

The synthesis of HU-GO was based on the method reported previously.²² 115 ml of sulfuric acid (98%) was initially cooled to 0 °C with subsequent addition of 5 g graphite and 2.5 g of NaNO_3 . With vigorous stirring, 15 g of KMnO_4 were added over a period of two hours. The reaction mixture was then removed from the ice bath and stirred at room temperature for 4 hours. The reaction mixture was then heated to 35 °C for 30 minutes, and poured into 250 ml of deionized water with heating to 70 °C. After 15 minutes the mixture was poured into 1 L of deionized water. Unreacted KMnO_4 was decomposed with 10 % hydrogen peroxide. The reaction mixture was then decanted and repeatedly centrifuged and re-dispersed until a negative reaction for sulfate ions (with

Ba(NO₃)₂) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 hours before further use.

Graphite oxide preparation with Tour method²³

Graphite (0.3 g) was added into a mixture of concentrated H₂SO₄/H₃PO₄ (9:1), followed by the addition of KMnO₄ (1.8 g). The reaction mixture was then heated to 50 °C and stirred for 12 hours. The reaction was then cooled to room temperature and poured in ice water with the addition of H₂O₂ (30%, 0.5 mL). The mixture was then filtered and washed with water, HCl (30%), ethanol, and diethyl ether. The obtained solid materials were kept in the oven at 50 °C for five days before further use.

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Part I

Chapter 5 –

Refining the Structure of Graphite Oxides *via* Selective Labelling of Functional Groups

The results and discussion presented in this chapter were published in the following journal article:

1. Refinements to the Structure of Graphite Oxide: Absolute Quantification of Functional Groups *via* Selective Labelling.

A.Y.S. Eng, C.K. Chua, M. Pumera. *Nanoscale* **2015**, 7, 20256.

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Note: Associated content, which includes X-ray photoelectron spectra and FTIR spectra, may be retrieved online at the following link:

<http://www.rsc.org/suppdata/c5/nr/c5nr05891k/c5nr05891k1.pdf>

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5.1. Introduction

Graphite oxide (GO) is a highly oxidized form of graphite produced through its reaction with various combinations of strong acids and oxidants. Although it was first produced more than 150 years ago,¹ current interest in GO can be much accredited to the initial isolation of graphene² and the ensuing fervor to produce large quantities of the material; GO is the key intermediate in the “top-down” approach to producing reduced-graphenes. The enthusiasm in GO research stems from its uniqueness as a carbon-based material with an assortment of reactive functional groups. Its inherently high specific surface area further enhances its appeal to both materials scientists and synthetic chemists alike as an excellent material on which to perform functionalization or conversion of specific moieties.^{3,4,5} Thus, a plethora of applications exploit these surface groups,⁶ including bio-functionalization,⁷ advanced structural assembly,^{8,9} filtration devices,¹⁰ environmental remediation,¹¹ and electrochemical and biological sensing.^{3,12,13} Furthermore, the physical properties of graphenes and GO are tunable through functionalization,^{14,15} and its oxygen groups directly influence its biological toxicity.^{16,17}

Despite such widespread utilization of GO, there still remains much debate regarding its complex chemical structure and GO can only be best described as an amorphous material with non-stoichiometric surface functionalities.¹⁸ No less than eight GO structural models have been proposed to date. Chronologically, the earliest model by Hofmann and Holst in 1939 proposed the dominance of epoxides on the basal plane,¹⁹ while Ruess subsequently included hydroxyl groups.²⁰ Scholz and Boehm²¹ then showed the presence of ketones and hydroxyls but excluded epoxides. Much later in 1994, the Nakajima-Matsuo model²² suggested a lattice structure interspersed with hydroxyl groups. In what is arguably now the most well-known and accepted Lerf-

Klinowski model, solid-state nuclear magnetic resonance (NMR) spectroscopy was employed to identify two distinct basal plane regions consisting of pristine aromatic regions separated by aliphatic 6-membered rings containing hydroxyls, epoxyls, and C=C double bonds.^{23,24} An additional refinement to the model included carboxylic groups in low quantities at the edge sites.²⁵ Following this, the Dékány model proposed the presence of quinone groups in addition to tertiary alcohols, 1,3-ethers, ketones, and phenols.²⁶ A later NMR study by Ajayan next included lactols shown to exist at peripheral edges.²⁷ The latest “Dynamic Structural Model” put forth by Tour in 2013 is then a significant milestone in defining GO as a variable system undergoing structural changes as it interacts with water, but agrees with earlier models describing the existence of epoxyls, hydroxyls, carbonyls, and carboxyl groups.²⁸ Figure 5.1a depicts a general model of GO summarizing typical oxygen functionalities most commonly proposed.

Figure 5.1. a) General model of graphite oxide demonstrating various oxygen functional group types distributed across aromatic regions. **b)** Schematic illustration of graphite oxidation methods based either on chlorate or permanganate oxidation routes.

The variance in structural models is similarly mirrored in the choice of available methods from which GO are produced. All oxidation procedures involve the use of strong concentrated acids with either potassium chlorate or permanganate as oxidizing

agent (Figure 5.1b). Those commonly found in the literature include the pioneering method by Brodie,¹ the Staudenmaier method,²⁹ and the Hofmann method³⁰ all utilizing chlorate as oxidant. In comparison, the subsequent methods introduced by Hummers³¹ and Tour³² employ the permanganate route, where the Hummers method is traditionally the most popular due to its short reaction time. Interestingly, close examination of the numerous proposed models reveals that different oxidation methods were used within each study. Thus, it is reasonable that different oxidation routes inevitably lead to disparate findings between models. Such a view is not without basis since some variation in chemical composition has been determined by techniques including X-ray photoelectron spectroscopy (XPS) and NMR spectroscopy.³³ Electrochemical measurements further demonstrated unusual reversible behavior of specific surface functionalities only in permanganate GOs, but not within chlorate GOs.³⁴⁻³⁷ Other physical effects also include their dissimilar solvation properties and exfoliation extents depending on oxidation route.³⁸ Despite this, investigations into the different structures of permanganate and chlorate-oxidized GOs are few and far between, thus with little recognition of this notion within the graphene community.

Towards our objective of identifying the differences in permanganate *versus* chlorate GOs, we employ an established technique previously applied to studying surface functionalities in all manner of carbon materials ranging from pristine graphite, carbon nanotubes and electrodes to their oxidized counterparts, as extensively developed by the groups of Compton and McCreery.³⁹⁻⁴⁷ The two-step approach first involves specific functionalization of different oxygen group types in GO (namely hydroxyls, carboxyls, quinones, carbonyls and epoxylys) with electrochemically active labels, followed by their sensitive voltammetric detection. The nature of voltammetry allows for *absolute* quantification of each labelled group type, and based on the

combination of labels chosen the relative content of each functional group is used to quantitatively elucidate the structure of GO. As our current understanding is largely based upon spectroscopic data obtained from XPS, NMR and infrared spectroscopy methods, the application of this electrochemical technique allows for new insights to be obtained. One such advancement is the ability to distinguish between different carbonyl functionalities, such as aromatic *ortho*- and *para*-quinones from aliphatic ketones. In this study, we focus our investigation specifically on the Staudenmaier and Hummers GOs due to their prevalence in the literature today,⁴⁸ each representing the chlorate and permanganate oxidation routes, respectively.

5.2. Results and Discussion

5.2.1. *Selective Labelling and Electrochemical Quantification Approach in Studying Graphite Oxide Structures*

In this study, we characterize the inherent differences in oxygen functionalities present within permanganate-oxidized Hummers GO and the chlorate-oxidized Staudenmaier GO, abbreviated as GO-HU and GO-ST, respectively. In the functionalization step, each oxygen group type is reacted with a specific label containing either an inherently electroactive moiety, or which forms a new electroactive species after reaction. Absolute quantification of each species is then achieved through voltammetry based on the amount of charge passed during their characteristic electrochemical redox processes. Four reactive labels are chosen that encompass the numerous oxygen group types existing in GO. These reactions are summarized in Scheme 5.1, with the first reaction between carbonyl groups and 2,4-dinitrophenylhydrazine (2,4-DNPH) to form a new azo-bond with an electroactive nitro moiety. Quinones are further differentiated by selective labelling with 1,2-

phenylenediamine (1,2-PD) to give a benzophenazine ring in the case of *ortho*-quinones and a diimine-like adduct when reacted with surface *para*-quinones.⁴⁵ Subtraction of quinones from the total carbonyl content thus gives the amount of aliphatic ketones present.⁴⁶ Carboxylic groups are first activated with thionyl chloride before the attachment of 4-nitrophenol (4-NP) through esterification. Finally, hydroxyls are labelled using 3,5-dinitrobenzoyl chloride (3,5-DNBC) through condensation with its highly reactive acyl chloride moiety.

Scheme 5.1. Selective labelling reactions between functional groups on graphite oxide with electrochemically active labels. Electrochemically active moieties in the final functionalized products are shaded. Labelling of: **a)** carbonyl moieties with 2,4-DNPH to form a new azo-linkage; **b)** *ortho*-quinones with 1,2-PD forming a phenazine adduct; **c)** *para*-quinones with 1,2-PD to give a diimine; **d)** carboxylic acids *via* activation with thionyl chloride and their subsequent esterification with 4-NP; **e)** hydroxyl groups with 3,5-DNBC *via* esterification reaction.

Cyclic voltammetry is subsequently performed on both GOs after their individual reaction with one of the four labels. Figure 5.2 displays the voltammograms observed for GO-HU after functionalization of its carbonyl, quinonyl, carboxyl and hydroxyl groups, respectively. Firstly, after functionalization with 2,4-DNPH, the voltammetry of GO-HU shows a characteristically large reduction peak centered near -1.0 V that is not observed in the control GO material. Previous investigations into the reduction mechanism of labelled carbonyls have determined this peak to be from an irreversible $6e^-/6H^+$ process corresponding to the simultaneous reduction of both the azo linkage and the nitro group in the 4-position, followed by cleavage of the entire 2,4-DNPH group leaving behind a nitroso/hydroxylamine moiety.⁴³ This new surface-bound group is reported to exhibit quasi-reversible electrochemistry between its oxidized and reduced (nitroso/hydroxylamine) states *via* a $2e^-/2H^+$ process centered at approximately -0.1 V vs the standard calomel electrode (SCE).⁴³ An identical redox couple is observed in our case after functionalization with 2,4-DNPH, with its oxidation peak at -0.1 V vs Ag/AgCl as illustrated in the Inset of Figure 5.2a. In addition, the absence of all voltammetric waves within the control GO confirms that the oxidation peak at -0.1 V occurs only due to labelled carbonyl groups and we therefore use the coulombic charge passed for quantification. The second functional group type studied are quinones, which we label with 1,2-PD. As seen in Figure 5.2b, two distinct oxidation peaks are observed at -0.5 V and 0.0 V. These peak potentials correspond well to the $2e^-/2H^+$ oxidations of benzophenazine and diimine adducts obtained from the reaction of 1,2-PD with *ortho*-quinones and *para*-quinones, respectively (illustrated in Scheme 5.1b-c).⁴⁵ It is most interesting to also note a significant increase in the capacitive current of the 1,2-PD functionalized GO compared to the control GO material, and this was also similarly observed in the earlier case with carbonyl functionalization. Such phenomena are largely

expected as a result of extensive functionalization with the labelling molecules,^{15,49} likely causing intrinsic changes in the electrical double layer at the GO surface. We subsequently investigate the functionalization of carboxyls with 4-NP but with their prior conversion to highly reactive acyl chlorides. Figure 5.2c shows the voltammetry of GO-HU after 4-NP labelling, with a familiar oxidation peak at -0.1 V arising from the reversible $2e^-/2H^+$ oxidation of hydroxylamines to nitroso groups.⁴⁷ This electrochemistry characteristic of the nitroso/hydroxylamine pair is the same electroactive species that was generated from 2,4-DNPH-labelled GO after cleavage of the azo-linkage. In the present instance with 4-NP-labelled carboxyl groups, hydroxylamines are instead formed from the nitro moiety in the 4-position during the initial cathodic scan past -0.8 V.⁴⁷ Although this conversion of nitro groups to hydroxylamines is not seen as an obvious voltammetric wave, the initial reductive sweep is still important in activating the hydroxylamines which later undergo oxidation to nitroso groups at -0.1 V during the reverse anodic sweep. Additionally, there is a slightly positive shoulder peak at $+0.1$ V that is also present in the control GO material. Comprehensive controls performed by Compton and co-workers established inherent quinone/hydroquinone systems to be responsible for this peak.⁴⁷ Hence, quantification of carboxyl functionalities are based solely on the nitroso/hydroxylamine system at -0.1 V. Finally, hydroxyls were studied through labelling with 3,5-DNBC and their voltammograms displayed in Figure 5.2d. A pair of small voltammetric peaks were observed at approximately $+0.1$ V at the same potentials reported by Jannakoudakis *et al.*³⁹ This electrochemistry is again based on the nitroso/hydroxylamine system formed from the reduction of nitro groups during the initial cathodic sweep.³⁹ The slight positive shift in peak potentials is due to the use of an acidic electrolyte at pH 4.0 instead of the neutral pH used for the other materials, and was done to avoid large capacitive

background currents that prevented accurate quantification at neutral pH. At this point, the generally small voltammetric peaks and insignificant changes to the capacitances of GO-HU after its carboxyls and hydroxyls are labelled further support their low contents observed.

Figure 5.2. Cyclic voltammograms of permanganate-oxidized Hummers GO after selective labelling of **a)** inherent carbonyl groups with 2,4-DNPH, **b)** *ortho*- and *para*-quinones with 1,2-PD, **c)** carboxyl groups with 4-NP, and **d)** hydroxyl groups with 3,5-DNBC. Voltammograms of labelled-GOs are shown with solid lines and dotted lines correspond to the control materials. Black open arrows indicate peak oxidations of specific labelled groups as magnified in the Inset figures. Grey arrows indicate the initial starting potentials scanned towards the cathodic direction. Potentials are with respect to the Ag/AgCl reference electrode.

The same experimental labelling and quantification conditions were consequently applied to GO-ST to study its inherent oxygen functionalities. Figure 5.3a-d illustrates the voltammograms of GO-ST after functionalization of its carbonyl, quinonyl,

carboxyl and hydroxyl groups. First examining 2,4-DNPH functionalized GO-ST in Figure 5.3a, we observe a contrasting feature in the initial cathodic reduction sweep. Unlike the large reduction peak in functionalized GO-HU that was absent in its control material, the reduction peak of functionalized GO-ST overlapped significantly with the reduction of inherent surface oxygen groups such as epoxides^{50,52} (as seen in the GO-ST control). This overlap happens because the electro-reduction of GO-ST starts at comparatively lower reductive potentials at *ca.* -0.8 V vs. Ag/AgCl, as compared to GO-HU requiring greater cathodic potentials past *ca.* -1.1 V.^{33,34} Such a difference in reduction potentials between GO-ST and GO-HU is typically construed as evidence of their different inherent functional group types. Other features in 2,4-DNPH-labelled GO-ST absent in GO-HU are the small oxidative waves observed between -0.6 V to -0.35 V. Since these are not observed in the control GO-ST, we postulate that they must arise from interactions of the 2,4-DNPH label and specific groups in GO-ST not found in GO-HU. In spite of these, quantification of labelled carbonyl groups in GO-ST is nevertheless possible based on the same nitroso/hydroxylamine system at -0.1 V. Next, the voltammetry of 1,2-PD-labelled GO-ST (Figure 5.3b) is largely analogous to the GO-HU case, albeit with discernibly smaller oxidation peak currents from *ortho*- and *para*-quinones at -0.4 V and 0.0 V along with a greatly reduced capacitive background current. This result signifies the relatively lower quinonyl composition in GO-ST. The most interesting observation however is for 4-NP-reacted GO-ST in Figure 5.3c, where the voltammograms of both the reacted material and its control were virtually indistinguishable, thus indicating a total absence of carboxyls in GO-ST. We similarly noted this finding based on solid-state ^{13}C NMR spectroscopy previously.³³ Lastly, the oxidation peak of the nitroso/hydroxylamine system is seen at 0.0 V (Figure 5.3d) for 3,5-DNBC-labelled GO-ST with similar current intensities as GO-HU.

Figure 5.3. Cyclic voltammograms of chlorate-oxidized Staudenmaier GO after selective labelling of **a)** inherent carbonyl groups with 2,4-DNPH, **b)** *ortho*- and *para*-quinones with 1,2-PD, **c)** carboxyl groups with 4-NP, and **d)** hydroxyl groups with 3,5-DNBC. Voltammograms of labelled-GOs are shown with solid lines and dotted lines correspond to the control materials. Black open arrows indicate peak oxidations of specific labelled groups as magnified in the Inset figures. Grey arrows indicate the initial starting potentials scanned towards the cathodic direction. Potentials are with respect to the Ag/AgCl reference electrode.

As this is the first instance that the above labelling and voltammetric quantification approach has been applied to the study of GO functional groups and their structures, we deem it prudent to emphasize the fundamental requirements for quantifying the functionalities in GO. These include (1) attaining complete functionalization of all groups in GO with the labelling molecules used, and also (2) the absence of non-covalent attachment (*e.g.* physical adsorption) of electroactive labels that would otherwise result in an overestimate of the amount of functional groups.

Nevertheless, steps can be taken to effectively mitigate these. The first requirement is easily addressed by utilizing reactions involving highly reactive moieties that typically attain near 100% reaction yields. One such example is the activation of carboxylic groups to the acyl chloride before covalent attachment with 4-NP, in consideration of the weakened nucleophilicity of 4-NP conferred by the nitro group. Thus, the final amounts measured provide for a realistic elucidation of actual GO structures. It was also confirmed that there are no contributing effects from non-specific adsorption of the nitroaromatic labels used, by performing additional control reactions with GO and nitrobenzene. Specifically, the characteristic voltammetric waves of the nitro moiety were absent and no changes were observed in the inherent electrochemistry of GO-HU. This was further corroborated with XPS showing neither a new nitrogen peak nor any change in the high resolution C 1s spectra. Hence, it is shown that selective functionalization of oxygen-containing groups in GO allows for their reliable detection through absolute quantification of the covalently attached electroactive labels.

5.2.2. Comparison of Functional Groups in Graphite Oxides Produced From Permanganate *versus* Chlorate Oxidation Methods and Their Correlation to Proposed Models

Based on the observed voltammetry of the various electroactive labels, the amount of each surface functional group in GO was calculated by use of Faraday's Law of Electrolysis.^{34,45,47,50} Table 5.1 summarizes the quantification data of the various functionalities in GO-HU and GO-ST after their labelling. The amounts of some functionalities present are found to be strikingly different for the permanganate-oxidized GO-HU in comparison to GO-ST from the chlorate route. In terms of absolute mole quantities, the total average labelled-group content detected in GO-HU (8.5×10^{-10}

mol) is one order of magnitude larger than in GO-ST (6.6×10^{-11} mol). Within both GOs, carbonyls were also seen to represent the vast majority of surface groups at $\sim 95\%$. However, our use of 1,2-PD labelling further discerns quinones from isolated ketones, where the amount of ketones can be acquired by direct subtraction of quinones from the total carbonyl content (and that each quinone contains two C=O groups). We observed for the case of GO-HU that *ortho*-quinones constitute more than 60% of all labelled oxygen groups, followed by isolated ketones at 23% and *para*-quinones at just about 11%. This distribution is however very different with GO-ST where isolated ketone groups were deduced to be dominant at nearly 95%, compared to insignificant amounts of quinones at $\leq 1\%$ each. The small absolute quantity of *ortho*-quinones, particularly in GO-ST, is also likely to have resulted in its high percentage error. Nonetheless *ortho*-quinones were found to be more abundant than *para*-quinones in both GOs, and since carbonyls have been shown to mainly decorate sheet edges,⁵⁴ we reason that *para*-quinones simply cannot exist in sizable amounts because its 1,4-geometry would structurally limit the size of GO sheets. Such abundance of quinones in GO-HU, as opposed to its scarcity in GO-ST, is in line with our earlier proposition that quinone/hydroquinone couples are likely responsible for the unusual reversible electrochemistry observed only in permanganate-oxidized GOs.^{34,36} Subsequent computation of the carboxyl content shows that it contributes only a low 5.5% in GO-HU and is entirely absent in GO-ST. Finally, examination of hydroxyls reveals comparable amounts at between 2.4×10^{-12} mol and 2.9×10^{-12} mol for GO-HU and GO-ST. These values constitute surprisingly low quantities relative to the overall oxygen group content at only 3.7% for GO-ST and a mere 0.3% for GO-HU, in disagreement with many proposed models citing hydroxyls as amongst the most prevalent species.²⁰⁻²⁸ Since hydroxyls tend to cluster together in highly oxidized regions,^{53,54} it may be possible that

steric effects could hinder functionalization of the label onto some closely assembled hydroxyl groups and the amount detected might therefore represent a lower bound of the actual value. This is likely to have also resulted in the amount of hydroxyls having the largest percentage error of all functional groups in GO-HU.

Table 5.1. Mole quantities and relative percentages of various functional group types in Hummers graphite oxide (GO-HU) and Staudenmaier graphite oxide (GO-ST) after their functionalization with electroactive labels.

Type of Functional Group	No. of moles measured (mol)		Percentage of total labelled groups (%)	
	GO-HU	GO-ST	GO-HU	GO-ST
Carbonyl (total)	8.0×10^{-10} ($\pm 6\%$)	6.4×10^{-11} ($\pm 16\%$)	94.2%	96.3%
• <i>ortho</i> -quinone	• 2.6×10^{-10} ($\pm 12\%$)	• 3.4×10^{-13} ($\pm 58\%$)	• 60.4%	• 1.0%
• <i>para</i> -quinone	• 4.6×10^{-11} ($\pm 11\%$)	• 2.0×10^{-13} ($\pm 20\%$)	• 10.8%	• 0.6%
• Ketone	• 2.0×10^{-10} ($\pm 26\%$)	• 6.3×10^{-11} ($\pm 16\%$)	• 23.0%	• 94.7%
Carboxyl	4.7×10^{-11} ($\pm 2\%$)	N.D.	5.5%	0% (N.D.)
Hydroxyl	2.9×10^{-12} ($\pm 35\%$)	2.4×10^{-12} ($\pm 12\%$)	0.3%	3.7%
Total labelled groups	8.5×10^{-10} ($\pm 6\%$)	6.6×10^{-11} ($\pm 15\%$)	100%	100%

^{a)} Calculations of absolute functional group contents are based on the coulombic charges passed during electrochemical oxidation of each label. GO mass per electrode = 2.0 μg . $n = 3$, absolute mole quantities given to two significant figures. N.D. denotes “not detected”.

We then correlate these results with materials characterization data providing chemical compositions and bonding information to confirm the functionalization of labels. As XPS is a surface sensitive technique well suited to studying surface functionalization of carbon materials,⁵⁵ one measure of successful labelling is the carbon-to-oxygen ratio (C/O ratio) where a lower value corresponds to a greater distribution of surface oxygen groups. Wide-scan XPS spectra of all functionalized and control GO-HU materials were measured. Respective C/O ratios of the parent GO-HU

and GO-ST are typically low at 2.12 and 2.48 indicating high surface oxygen contents. Consequently, from the high extents of functionalization of inherent carbonyls and quinonyls, C/O ratios more than double due to the loss of oxygen as a result of the condensation reactions (Scheme 5.1a-c), thus corroborating with voltammetry results. Moreover, the C/O ratios of the control materials remained low with negligible change, proving that experimental conditions did not intrinsically alter the GO. These findings concur with high resolution carbon 1s spectra showing decreases in C–O and C=O groups after labelling; again no changes were observed between the controls and the parent GOs.³³ Most importantly, a benefit of employing nitrogenous labels is the introduction of new nitrogen 1s signals that permit assessment of the functionalization.^{45,46,47} Both 2,4-DNPH-labelled GO-HU and GO-ST were observed to have two peaks at 400 eV from the azo-linkage and at 406 eV from nitro groups, whereas the reaction of 1,2-PD with *ortho*- and *para*-quinones gives characteristic peaks at about 398.5 eV and 399.5 eV, respectively, from pyrazine and arylamine adducts.^{56,57} With 4-NP and 3,5-DNBC-labelled GO, however, only minor differences in XPS were observed in relation to their controls. The use of thionyl chloride in the activation of carboxyls inevitably led to its reaction with other moieties like hydroxyls and epoxy groups which resulted in their removal. Negligible changes in C/O ratios and the C 1s spectra of GOs were seen after hydroxyl labelling, in agreement with their small amounts as we detected. Despite this, minute peaks from the nitro moiety of the 3,5-DNBC label were nonetheless discernible in their N 1s spectra. In comparison, we find that FTIR spectroscopy holds minimal diagnostic ability due to its lack of surface sensitivity, but more so because the opaque nature of GO frequently results in poor quality spectra.⁴⁶ This is further complicated with the overlap of many important stretches arising from both surface groups themselves and the labelling molecules, such as inherent C=C stretches^{26,33} from the sp² carbon lattice

with azo ($-\text{N}=\text{N}-$) and imino ($-\text{C}=\text{N}-$) moieties⁵⁸ from GO adducts all occurring within the same $1690\text{--}1575\text{ cm}^{-1}$ region. Hence, chemical information from XPS but not FTIR can be effectively used to track the labelling process and thus validates the results from the electrochemical labelling and detection of functional groups in GO.

Thus far, we have yet to acquire inherent epoxyl concentrations despite its known prevalence in GO.^{23-28,33,53,54,59} However, the information garnered from the four labels chosen for this study allows us to deduce the epoxyl quantity present in GO-HU. Of the four labels, only 2,4-DNPH and 1,2-PD contain amine moieties, which as strong nucleophiles are commonly used to attack epoxide groups in GO.⁶⁰⁻⁶³ Our XPS data supports this conclusion due to the loss of C-O bonding modes in GO after both reactions. While the reaction between 1,2-PD and epoxyls does proceed to give secondary amines, these adducts are electrochemically inactive. 4-NP in comparison is a much weaker nucleophile, and more importantly the prior use of thionyl chloride deactivates hydroxyls and epoxyls (as observed from XPS), therefore preventing any complication should epoxyl functionalization occur. Hence, only the 2,4-DNPH label maintains electroactive nitro moieties from which to quantify labelled epoxides. As discussed in the previous section, the electrochemical redox mechanism of 2,4-DNPH labels involves an initial $6\text{e}^-/6\text{H}^+$ reduction at -1.0 V due to a $2\text{e}^-/2\text{H}^+$ reduction of the azo-linkage occurring simultaneously with a $4\text{e}^-/4\text{H}^+$ reduction of nitro groups at the 4-position.⁴³ Assuming this similar mechanism for labelled epoxyls, we can then deduce the epoxyl amount through subtraction of the labelled carbonyls with their oxidation occurring at -0.1 V . The average epoxyl content for GO-HU is therefore determined at $2.6 \times 10^{-9}\text{ mol}$. This is re-calculated with all functionalities to give the relative abundance of oxygen groups in GO-HU, as tabulated in Table 5.2. Regrettably, the above derivation

of epoxyl moieties is only possible for GO-HU and not for GO-ST due to a large overlap of its inherent reduction with that of the 2,4-DNPH label as illustrated in Figure 5.3a.^{33,34}

Table 5.2. Relative abundances of various functional groups in Hummers graphite oxide (GO-HU).

Type of Functional Group	Percentage of total labelled groups (%)
Epoxyl ^a	75.4%
Carbonyl (total)	23.2%
• ortho-quinone	• 14.9%
• para-quinone	• 2.6%
• Ketone	• 5.7%
Carboxyl	1.3%
Hydroxyl	0.1%

Percentages are calculated based on voltammetric quantification. ^aThe epoxyl content is deduced indirectly based on its reaction with 2,4-DNPH, with assumption of the $6e^-/6H^+$ reduction mechanism from Reference 43.

Therefore, a summary of the functionalities in GO-HU detected through the electrochemical labelling approach is as such: (1) epoxyls are most abundant in GO at approximately three-quarters of all functionalities; (2) carbonyls account for slightly less than a quarter of all groups, of which *ortho*-quinones represent the majority followed by aliphatic ketones and finally *para*-quinones; (3) carboxyls exist at only 1.3% despite the traditionally held view that they contribute to the inherent acidity of GO;⁶⁴ and also that (4) the amount of labelled hydroxyls is unexpectedly small. In assessing the significance of the quantification data with respect to current GO models, we first examine the dominance of epoxyl groups in GO, which is largely accepted based on NMR evidence.^{23-28,33,59} They are known to be dispersed throughout the basal plane,^{53,54} and exhibit high reactivities to nucleophiles such as amines.^{60,62} In contrast, hydroxyls can congregate in

densely oxidized regions⁵³ and we cannot exclude the possibility of a small contribution from steric effects which lead to the low proportion of hydroxyls detected from labelling. Two *in situ* processes would however pose a greater influence that likely resulted in the relatively small amount of hydroxyl groups measured: Klinowski and co-workers first acknowledged the instability of C–OH groups that condense to form C–O–C (ether or epoxide) linkages,²³ while Tour further expounded upon a possible disproportionation of C–OH bonds to give C=C and C=O bonds.²⁸ It is thus conceivable that some hydroxyls have disproportionated as such to give the significantly high amounts of both epoxyl and quinone groups detected. Additionally, an interesting association between carbonyls and hydroxyls was also found with most existing in the form of vinylogous acids,²⁸ accounting for the inherent acidity of GO which cannot arise from such small concentrations of carboxylic groups at *ca.* 1% measured for GO-HU. Predominant only at the sheet edges,⁶⁵ they are unlikely to even be present in considerable amounts. Moreover, this acidity is characteristic in all GOs, including chlorate-oxidized GO-ST where we found a total absence of carboxylic groups. Our results strongly suggest that only the permanganate oxidation methods produce carboxyl functionalities, however little may be present. In further support of our proposition, only the models by Lerf-Klinowski²⁵ and Tour²⁸ found any presence of carboxyls while the Ajayan model²⁷ included a minute contribution from lactols as a carboxyl derivative; it is interesting to note that these models studied permanganate-oxidized GOs exclusively. We contrast this to earlier models¹⁹⁻²² and also the Dékány model²⁶ primarily employing chlorate oxidations with the effect that no obvious evidence for carboxyls were found. Hence, while the relative percentages of groups generally agree well with current proposed models, we also note that GO is intrinsically variable due to functional group conversions. The use of this selective labelling approach

coupled with electrochemistry detection has thus given much insight into dissimilar GO structures obtained through different oxidation routes.

5.3. Conclusions

In this study, an electrochemical detection approach was applied towards investigating the structure of graphite oxide through functionalization of its various oxygen groups, providing a new perspective from current knowledge predominantly based upon spectroscopic techniques. This selective labelling method is established within the study of surface functionalities for a diverse selection of carbon materials, but is as yet unexploited for any graphene-type material. Four reactive labels containing electrochemically active moieties were chosen to individually target carbonyl, quinonyl, carboxyl, and hydroxyl groups in GO, allowing for their quantitative information to be obtained *via* voltammetric analysis. The results interestingly reveal major differences in functional group distributions within permanganate-oxidized (Hummers) GO *versus* chlorate-oxidized (Staudenmaier) GO. The selectivity also enables us for the first time to distinguish the different types of carbonyl species present in GO, namely *ortho*- and *para*-quinones from aliphatic ketones. Hummers GO was found to have a substantial amount of *ortho*-quinones as compared to Staudenmaier GO with aliphatic ketones forming the vast majority of its carbonyl content. More notably, only a small amount of carboxyls were found (in Hummers GO) consistent with latest reports, and are furthermore absent entirely from Staudenmaier GO. As is expected from proposed models, we similarly deduced that epoxides are the predominant species within Hummers GO. The hydroxyl contents observed after labelling are also generally low, suggesting the occurrence of proposed disproportionation reactions that result in the formation of other groups. In light of these observations, we wish to emphasize the

importance of the choice of oxidation routes in the manufacture and application of GO materials since variations in their structure can radically influence intended results. Although minor limitations currently exist (particularly in the analysis of epoxides present in chlorate GO), their absolute quantification may be achieved in future with the use of orthogonal labels specifically targeting epoxy groups. Nevertheless, this approach has provided new information towards a better overall understanding of GO as the key intermediate in top-down graphene production.

5.4. Detailed Experimental Section

All synthetic procedures and analyses described below were of the author's work.

2,4-Dinitrophenylhydrazine (2,4-DNPH) Functionalization of Carbonyl Groups^{43,44}

Each GO (20 mg) was ultrasonicated in EtOH (20 mL, 1 mg mL⁻¹) for 1 h. Excess 2,4-DNPH (5.4 mL, 0.2 M) in phosphoric acid was added to the GO suspension, and the same volume of phosphoric acid (85%) was added to the control mixture. The mixture was stirred for 20 h at 80 °C under reflux. The GO was obtained by vacuum filtration and sequentially washed with EtOH, water and ether until a more neutral pH (5-6) was obtained. The functionalized material was then dried in under vacuum at 30 °C for 48 hours before analysis.

1,2-Phenylenediamine (1,2-PD) Functionalization of Quinonyl Groups^{45,46}

GOs (20 mg) were first ultrasonicated for 1 h in glacial acetic acid at 1 mg mL⁻¹ concentration. 1,2-PD (77 mg) was separately dissolved in EtOH (2 mL) and then added to the GO suspension; only pure EtOH was added to the control mixture. The mixture was then stirred for 1 h at 95 °C. The reacted GO was obtained by vacuum filtration and washed with EtOH, water and ether. The pH of the filtrate increased with each wash

giving a final stable value *ca.* pH 6. The reacted GO was finally dried in vacuum oven at 30 °C for 48 hours before experimental usage.

4-Nitrophenol (4-NP) Functionalization of Carboxylic Groups^{46,47}

The first step involves conversion of carboxylic groups to the highly reactive acid chloride moiety as modified from previous procedures.^{66,67} Each GO (60 mg) was ultrasonicated for 1 h in pure DMF at 1 mg mL⁻¹ concentration. SOCl₂ (1 mL, 0.014 mol) was added dropwise and the mixture stirred at r.t. for 20 h. The reaction was carried out with a Schlenk line under N₂ atmosphere. Excess SOCl₂ was subsequently removed by heating to ~80 °C with the reaction flask fitted with a CaCl₂ guard tube. This acyl chloride-converted GO mixture was split into two 30 mL portions. Under N₂ atmosphere, 4-NP (960 mg) was dissolved in DMF (5 mL) and added to the reaction mixture, and only pure DMF added to the control. Triethylamine (2 mL) was added dropwise to each mixture (Note: small amounts of white triethylamine hydrochloride salt forms upon initial addition). Both mixtures were stirred for 20 h and the final functionalised GO obtained by vacuum filtration and washed with large amounts of DMF, followed by water and ether. The product was lastly dried in a vacuum oven at 30 °C for 48 hours before use.

3,5-Dinitrobenzoyl Chloride (3,5-DNBC) Functionalization of Hydroxyl Groups^{39,40,41,42}

Each GO (20 mg) was ultrasonicated for 1 h in THF at a concentration of 1 mg mL⁻¹. 3,5-DNBC (165 mg) was separately dissolved in THF (1.5 mL) and added to the GO suspension slowly under stirring, while only pure THF was added to the control mixture. 2 mL of triethylamine was added dropwise subsequently and the mixture was stirred for 20 h at room temperature. The functionalized GO was obtained by vacuum filtration and

washed with copious amounts of THF, followed by deionised water and ether. The final product was lastly dried in a vacuum oven at 30 °C for 48 hours before use.

Voltammetric Quantification of Labelled Functional Groups

Functionalized graphene oxides and their control materials were first dispersed in DMF at 1 mg mL⁻¹ concentrations by ultrasonication for 10 min to obtain stable graphene oxide suspensions, while a 5 min sonication was performed before each electrode modification step. GC working electrodes were cleaned and renewed just prior to every measurement by polishing with a 0.05 µm alumina particle slurry on a polishing pad and followed by copious washing with deionized water. 1.0 µL aliquots were deposited onto the GC electrode surface, and the solvent left to evaporate at room temperature. This process was performed twice to achieve a uniform coating, thus giving a fixed sample mass of 2.0 µg immobilized per electrode. Electrochemical measurements were performed in 50 mM phosphate-buffered saline (PBS) solution as supporting electrolyte. A neutral buffer of pH 7.2 was used in the detection of all functionalized oxygen groups with the exception of labelled hydroxyls which required an acidic pH of 4.0. A fixed scan rate of 100 mV s⁻¹ was used in all cyclic voltammetry experiments other than a slower 50 mV s⁻¹ employed specifically for labelled carbonyls to allow for full development of its broad reduction peak centered at -1.0 V. Absolute quantification of labelled surface groups is based on Faraday's Law of electrolysis:^[34,45,47,50]

$$n = \frac{Q}{z \times F} \quad (1)$$

where n is the number of moles of surface-bound species undergoing an electrochemical redox reaction, Q is the total charge passed, z is the number of electrons exchanged per surface group, and F is the Faraday constant (96485 C mol⁻¹). For consistency, calculations are based on the charges passed within the oxidation peak occurring during

the initial anodic scan. The geometric surface area of each electrode is 0.0707 cm². Functional group contents are calculated based on the average from triplicate measurements.

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Part I

Chapter 6 –

Direct Voltammetry of Colloidal Graphene Oxides

The results and discussion presented in this chapter were published in the following journal article:

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6.1. Introduction

Graphene-related materials such as graphene oxide (GO) have garnered much attention in the field of analytical electrochemistry.¹⁻⁵ This significant interest can be attributed to the use of GOs either as labels,¹⁻³ or for enhancement of analytical signals^{4,5} in electrochemical and biological sensing applications. Many such approaches rely on the characteristic electroactivity of GO itself, arising from inherent oxygen functionalities that are abundant in GO.^{6,7} The large majority of electrochemical research on graphene materials involves solid-state modification of electrodes, using common techniques such as drop-casting⁸ and carbon paste electrodes.^{9,10} To the best of our knowledge, however, there is a scarcity of reports on direct electrochemistry of free GOs in solution.

The first reported use of cyclic voltammetry (CV) in colloidal GO solutions was by Liu *et al.*, where a thin layer of reduced GO can be deposited onto glassy carbon as a result of the cycled potential.¹¹ The aim of employing the CV technique in their seminal work and also in other studies that followed was only to achieve electrodeposition of a reduced-graphene film on the electrode surface for a variety of sensing purposes.¹¹⁻¹³ The aim of this work, however, is to study the voltammetry of the colloidal GO itself, arising from the redox activity of inherent oxygen-containing groups including epoxy, carbonyl and quinonyl groups.^{6,7,14,15} Therefore, the foremost difference in purpose from earlier CV studies is not to achieve deposition of a graphene film but to exploit the electroactive nature of colloidal GOs for potential future use in analytical electrochemical sensing. Firstly, the functional groups present in GO allow covalent attachment to proteins.¹⁶ With its inherent electroactivity, one could envisage that colloidal GO sheets could then be used as a label for detection of non-electroactive biomolecules.

In addition to the inherent reduction of oxygen functionalities in all GOs, we have also recently reported on the *chemically reversible* electrochemistry of GOs¹⁵ specifically produced through the permanganate oxidation methods of Hummers¹⁷ and Tour.¹⁸ An important implication we identified for future research is that electrochemically-reduced GO can continue to exhibit distinctive electroactive behaviour,^{7,15} in contrast to the traditionally held notion that their reductions are irreversible.^{19,20} As such, a secondary goal is to ascertain if such unique electrochemistry may also be observed when GOs exist freely in solution, in comparison to our prior study utilising electrode surface modification. Towards these objectives, a systematic investigation was performed with regard to experimental conditions that support direct voltammetric measurement in colloidal solution.

6.2. Results and Discussion

A fundamental study into factors that could affect the voltammetric measurement of GO colloidal solutions was first performed, with particular focus on the concentration of the GO dispersions, pH of the electrolyte, and the GO particle sizes. Figure 6.1 summarises the voltammetric data obtained. Both high purity vein graphite and stacked graphite nanofibres were used for the production of graphite oxide. Vein graphite was obtained from Sri Lanka, while synthetic graphite nanofibres (50 x 50 nm dimensions) were purchased from Strem Chemicals (Newburyport, USA). The oxidation of graphite to graphite oxide was performed using the Hummers oxidation method, as previously reported in the literature.^{15,17} Firstly, for the concentration of the GO colloid, we observed in all cases that no characteristic voltammetric waves were noticeable with 0.1 mg mL⁻¹ colloidal GO solutions regardless of the pH or type of parent graphite material used. In comparison, distinctive peaks corresponding to the redox behaviour of

GO were observable with a concentration of 1.0 mg mL^{-1} under specific conditions, and is thus the minimum concentration required to perform voltammetry for both forms of GO investigated.

Figure 6.1. Cyclic voltammograms of colloidal GO solutions at various pH, at the concentrations of 0.1 and 1.0 mg mL^{-1} . Colloidal GOs are obtained based on the Hummers oxidation route from both natural vein graphite (left panel) and synthetic graphite nanofibre (right panel) sources. Inset diagrams of oxidation peaks are also

shown whenever observed. Conditions: quiescent 50 mM PBS solution, starting potential from 0.0 V scanned towards cathodic direction, $\nu=100 \text{ mV s}^{-1}$.

Subsequently, the effects of pH were examined. An initial investigation at pH 9.2 was done as this basic pH was employed throughout earlier works.¹¹⁻¹³ No discernible peaks were obtained either at this pH or at a neutral pH of 7.2. It is important to highlight here that similarly inconspicuous peaks were previously observed, concurring with our current observations. We postulate that for the sole purpose of exfoliating GO sheets a basic pH may be advantageous as a result of deprotonation of acidic oxygen groups with a $\text{pK}_a \sim 3$, resulting in negatively charged groups that aid dispersal in aqueous solution by increasing hydrophilicity of the sheets.²¹ However, these consequently charged sheets may inadvertently result in their electrostatic repulsion from the electrode surface when a negative potential is applied during the initial cathodic scan, preventing effective reduction of the oxygen groups. Indeed only under acidic conditions at pH 2.0 and 3.5 were characteristic reduction peaks observable in colloidal GOs prepared from vein and nanofibre graphite. Voltammograms obtained under these optimised conditions are shown in Figure 6.2. Thus for the purposes of performing voltammetry on colloidal GO, we suggest that a dispersion in an aqueous acidic buffer may be preferable.

Figure 6.2. Cyclic voltammograms of colloidal GO solutions under optimised conditions of: 1.0 mg mL^{-1} concentration in pH 2.0 buffer for GO obtained from vein graphite (left), and a 1.0 mg mL^{-1} concentration in pH 3.5 buffer for GO obtained from graphite nanofibres (right). Inset diagrams of oxidation peaks are shown on the right. Conditions: quiescent 50 mM PBS solution, $\nu=100 \text{ mV s}^{-1}$. Also shown are scanning electron images of vein GO and nanofibre GO particles, with a measurement of a single nanofibre GO particle as indicated by vertical lines.

The last factor of particle size is significant if we consider the likelihood that aggregation of graphene layers may occur to a greater extent over time. This stems from the possibility that hydrophobic π -stacking interactions can occur between pristine graphene regions, especially for the case of large sheets in an aqueous dispersion. This difference is studied using two highly dissimilar forms of parent graphite; namely natural graphite (with flake sizes that can vary up to hundreds of micrometres)²², as compared to synthetic nanofibres with distinct dimensions.²³ After oxidation, actual sizes of vein

GO from SEM analysis reveal a minimum 200-300 nm width, and a uniform 50 nm size for nanofibres (Figure 6.2). Comparing the voltammograms for vein and nanofibre GO colloids at their optimised pH values in Figure 6.2, we noted that the -1.6 V cathodic peak representative of the reduction of oxygen functionalities was most distinct for vein GO, and which also increased in peak current with successive scans typically up till about the fourth scan. The peak reduction current for colloidal nanofibre GO is approximately one order of magnitude smaller, with no observable increase in peak height. Also, both materials exhibited an oxidation peak at *ca.* 0.5 V, for which the shift towards less positive potentials with successive scans is larger for vein GO. More importantly, an additional reduction peak at -0.5 V was observed for nanofibre GO, forming part of a chemically reversible couple that we previously propose to arise from quinone/hydroquinones.¹⁵ Along with the presence of a second broader oxidation peak at 1.3 V, these voltammetric characteristics are most similar to those we observed from electrode-surface adsorbed GO. Additionally, based on triplicate measurements at a scan rate of 100 mV s^{-1} , the reduction and oxidation peak potentials are $-1.52 \text{ V} \pm 0.04 \text{ V}$ and $0.47 \text{ V} \pm 0.01 \text{ V}$ for vein graphene oxide, and $-1.51 \text{ V} \pm 0.01 \text{ V}$ and $0.34 \text{ V} \pm 0.03 \text{ V}$ for nanofibre GO. Despite minor differences in observations between the two GO forms, these results confirm that voltammetry of colloidal GOs is viable by exploiting their intrinsic electroactive nature.

6.3. Conclusions

We demonstrate the direct voltammetry of colloidal GOs in solution, in development from current techniques utilising solid-state modified electrodes. In the case of colloidal GOs, prior studies focussed on the deposition of reduced-graphene films on electrode surfaces, which were achieved under basic pH. For a pure

voltammetry study, however, we note that acidic conditions are instead necessary to observe the inherent electroactivity of GO. Voltammetric characteristics of colloidal GO nanofibres at pH 3.5 are most similar to those of GO drop-casted electrodes. Advancing the understanding of colloidal GO electrochemistry supports its future development for sensing applications.

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Part I

Chapter 7 –

Controlling Surface Porosities of Graphene-Modified Electrodes

The results and discussion presented in this chapter were published in the following journal article:

1. Intrinsic Electrochemical Performance and Precise Control of Surface Porosity of Graphene-Modified Electrodes Using the Drop-Casting Technique.

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7.1. Introduction

Graphenes and related materials continue to hold important positions in the fields of electrochemical sensing and catalysis.¹⁻⁶ Amongst its various interesting properties those most essential to applications in electrochemistry are its high electrical conductivity^{7,8} and high density of electronic states (DOS) at the edges,^{1,9} but also includes a perceived “electrocatalytic effect” that is at best loosely described by lowered overpotentials and increased faradaic currents.^{1,10,11} Studies on nanomaterial electrochemistry generally require some form of prior electrode preparation, commonly achieved by the drop-casting,^{5,6,11-14} abrasive immobilisation,¹⁵⁻¹⁷ or electrochemical deposition techniques.^{10,18,19} Of these, the drop-casting (or drop-coating) technique is highly favoured by many due to its simplicity and ease of preparation.

Despite its advantages, it is increasingly recognised within the electrochemistry community that porosity and roughness are fundamental concerns when performing electrode modification. Particularly in the case of nanomaterials, such as carbon nanotubes and graphenes, porosity can result in possible occurrences of thin-layer diffusion and/or adsorption effects^{1,10,11,14,20,21} due to internal pore structures and the concomitant surface area increase.²² Effects of electrode porosity have also been theoretically treated.²³⁻²⁷ There also remains uncertainty over the general extent to which porosity (as an extrinsic property) can influence experimental data, which may result in erroneous interpretations of apparent enhancements arising from intrinsic material properties. For example, while it is commonly accepted that carbon nanotube electrochemistry involves thin-layer diffusion due to their structure, the case with graphenes is less certain. Work by Aksay and co-workers showed that different porosities can result simply from the use of different solvents during preparation.²⁰ Hallam and Banks later reported that only semi-infinite diffusion was present despite a

rough and non-uniform graphene-modified surface.¹³ Such contrasting observations likely result from specific differences in experimental practice, and are further compounded by a great variation in graphene-type materials studied today.

In this light, it is important to achieve control of electrode porosity during preparation, and to ultimately maintain minimal porosity such that it does not contribute significantly or even dominate the electrochemical response. Our main objectives are to first identify the diffusion profile of graphene-modified electrodes prepared by the drop-casting method under typical conditions, and thus if any kinetic information extracted is justifiable. The apparent porosity is then varied by increasing the graphene mass loading, either through increasingly concentrated dispersions or by the application of multiple aliquots. This porosity is monitored using a simple experimental method.^{20,21} It is then shown that for a fixed mass loading, the apparent porosity can be precisely controlled by employing multiple aliquots of graphene dispersions at lower concentration. Scanning electron microscopy (SEM) is further used to study associated changes in surface morphology.

7.2. Results and Discussion

7.2.1. Investigating the Origin of Electrochemical Enhancement in Graphene-Modified Electrodes

The nature of mass-transfer in graphene-modified electrodes is first investigated by cyclic voltammetry. Figure 7.1a illustrates voltammograms for the ferro/ferricyanide redox couple at graphene-modified electrodes over a wide range of scan rates between 1000 mV s^{-1} and 4 mV s^{-1} , with voltammograms of unmodified bare GC electrodes shown in Figure 7.1b for comparison. Clearly, there is an enhancement in the electrochemical redox signal represented by smaller peak-to-peak separations (ΔE_p) and

larger peak currents (i_p) for the graphene electrode. We then investigate the dependence of i_p versus scan rate (ν) in Figure 7.1c. From the Randles-Ševčík equation based on the semi-infinite diffusion model, i_p is expected to vary with the square root of the scan rate:¹

$$i_p = 0.446 FAC (FD\nu/RT)^{1/2} \quad (1)$$

where F is Faraday's constant, A is the electrode surface area in cm^2 , C is the bulk analyte concentration in mol cm^{-3} , D is the analyte diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, ν is the scan rate in V s^{-1} , R is the gas constant, and T is the temperature in K.

Additionally, we predicted oxidative currents assuming the geometric surface area of bare GC electrodes. It is seen that experimental currents for bare electrodes are in fact smaller than predicted, indicating a lower electroactive area. This situation might inevitably occur for electrodes after some period of use. More importantly however, there is only a small enhancement in i_p after graphene modification but this remains less than values predicted for the bare electrode. Hence, this implies that even with increased porosity from graphene, the electroactive area of the modified electrode still does not exceed the geometric area of the bare surface. The electroactive area was obtained from the slope of the i_p versus $\nu^{1/2}$ plot (Figure 7.1d) at 0.0470 cm^2 after graphene modification compared to the 0.0707 cm^2 geometric electrode area, thus confirming no drastic surface area increase due to porosity which in turn promotes thin-layer diffusion.

Figure 7.1. Cyclic voltammograms of 10 mM ferro/ferricyanide on **(a)** graphene-modified electrodes at 1.0 μg mass loading and, **(b)** unmodified bare glassy carbon electrodes. Scan rates range between 0.004 V s⁻¹ and 1 V s⁻¹. **(c-d)** Plots of oxidative peak current versus scan rate and the square root of the scan rate, dotted curves represent predicted currents based on the Randles-Ševčík equation and geometric surface area of the bare electrode; error bars represent the standard deviation based on triplicate measurements. **(e)** Double logarithmic plot of oxidative peak current versus scan rate.

Plots of i_p against $\nu^{1/2}$ for both bare and graphene-modified electrodes were also observed to be linear with R^2 values >0.99 (Figure 7.1d), and a double logarithmic plot exhibiting slopes of 0.45 and 0.46 (Figure 7.1e) close to the expected 0.5 value for semi-infinite diffusion.¹³ In contrast if adsorption effects were present, a linear relation between i_p and $\nu^{1/2}$ would not exist and the slope of the double logarithmic plot would vary between 0.5 and 1 depending on extent of adsorption.¹ Hence, with confirmation of

semi-infinite diffusion control kinetic parameters may be reliably obtained.²⁸ Calculated HET rate constants are observed within the quasi-reversible regime, where the $k_{obs}^0 = 3.0 \times 10^{-3} \text{ cm s}^{-1}$ at the graphene surface is faster compared to $6.9 \times 10^{-4} \text{ cm s}^{-1}$ for bare GC at a moderate scan rate of 125 mV s^{-1} . Hence, the electrochemical enhancement seen for bulk-produced graphene most likely arises from an intrinsic property since no obvious porosity effects were observed, similar to the case of untreated pristine graphene sheets.¹³

7.2.2. Precise Control of Electrode Porosity and Factors Influencing Surface Morphology

Numerous factors are expected to result in increased porosity during drop-casting. It was also seen previously that different solvents had drastically different effects on the resultant electrode porosity; graphene-modified surfaces prepared from ethanol suspensions were vastly more porous compared to ammoniated water.²⁰ Here, we observe significant variation in electrode porosities from seemingly trivial differences in experimental practice: while porosity is expected to positively correlate with mass loading, the method from which material is deposited is another important determining factor. Graphene dispersions were prepared in DMF at concentrations ranging from 1.0 mg mL^{-1} to 7.0 mg mL^{-1} , by ultrasonication for an initial 10 mins followed by 5 mins before each subsequent drop-casting event.

Figure 7.2a-b demonstrates the voltammetry of the ferro/ferricyanide probe on graphene at a fast 500 mV s^{-1} , prepared either through drop-casting multiple aliquots of graphene at fixed 1.0 mg mL^{-1} concentration or from single aliquots of increasing concentrations up to 7.0 mg mL^{-1} . A decrease in ΔE_p is observed immediately after application of $1.0 \mu\text{g}$ graphene, with a corresponding increase in i_p . It is clear however

that at similar mass loadings, larger i_p values are obtained from electrodes prepared with a single graphene aliquot at high concentration, in addition to larger capacitive currents. Data is also obtained at a slow 10 mV s^{-1} , for which ΔE_p and i_p values are much more consistent over the range of mass loadings (Figure 7.2c-d). Based on a simple but useful relation,^{20,21} the experimental porosity factor can be determined:

$$P = \frac{\sqrt{10} \times i_p(\text{at } v=500 \text{ mV s}^{-1})}{\sqrt{500} \times i_p(\text{at } v=10 \text{ mV s}^{-1})} \quad (2)$$

Since i_p varies with $v^{1/2}$ for semi-infinite diffusion in the case of planar electrodes, $i_p/v^{1/2}$ is ideally a constant and $P=1$. Thus, positive deviations from unity indicate greater porosity due to increased electroactive area. Figure 7.2e illustrates the porosities of graphene-modified electrodes with increasing mass loads. As in Section 7.2.1, the apparent porosity of the bare electrode starts at a low 0.66 due to attrition of the GC surface from common use, and increases to 0.81 after $1.0 \mu\text{g}$ graphene-modification. It increases further to 0.89 with a second $1.0 \mu\text{g}$ coat, but more importantly the porosity is notably higher at 1.06 if the same $2.0 \mu\text{g}$ was instead applied as a single coat. Further from this, the porosity factor continues to increase up to a maximum of 1.44 when a single coat of the highest 7.0 mg mL^{-1} concentration is applied. In contrast, when the same $7.0 \mu\text{g}$ of graphene was successively applied using seven 1.0 mg mL^{-1} aliquots, the apparent porosity maintains at a constant value <1.1 similar to the porosity measured at $3.0 \mu\text{g}$, and this is only slightly larger than the ideal planar case. Thus for applications where larger catalyst loadings are required, porosity can be controlled simply by employing multiple aliquots for drop-casting.

Figure 7.2. Cyclic voltammograms of 10 mM ferro/ferricyanide on graphene-modified electrodes measured at **(a-b)** fast scan rate of 500 mV s⁻¹ and **(c-d)** slow scan rate of 10 mV s⁻¹, as prepared by drop-casting multiple 1.0 μL aliquots of a graphene dispersion at fixed 1.0 mg mL⁻¹ concentration (left column) and single 1.0 μL aliquots of increasingly concentrated graphene (middle column). **(e)** Experimental porosity factors of graphene-modified electrodes at different mass loadings. Error bars represent the standard deviation based on triplicate measurements.

We then explore possible reasons behind the variation in apparent porosity by performing the same drop-casting on silicon oxide wafer to investigate the surface morphology. Graphene was drop-casted onto silicon wafers (Graphene supermarket, USA) for imaging. Figure 7.3 shows SEM images under various drop-casting conditions, and *three* distinct regions are typically seen: zones with well-dispersed flakes, but also bare areas and regions with thick graphene aggregates. A marginal “coffee-ring effect” can occur especially if a single graphene coat at the lowest 1.0 mg mL⁻¹ concentration is used. This effect arises due to the outward motion of colloidal particles during solvent evaporation.²⁹ Other effects such as the agglomeration of graphene typically occur at random when fewer (one/two) drop-casts are performed. It is also important to note

that bare unmodified regions exist when only 1-2 coats are used, such as in all instances when a single aliquot of graphene is deposited regardless of concentration (right panel of Figure 7.3). Particularly, a single thick aggregate forms when concentrated dispersions greater than 5.0 mg mL^{-1} are employed, resulting in bare regions surrounding the aggregate. This may be explained by strong inward capillary forces during the drying process, and can be both particle shape and size-dependent.^{30,31} No uniformly dispersed graphene regions were noted from either 5.0 or 7.0 mg mL^{-1} deposits. For our objective of achieving a well-dispersed coverage, the most uniform and fully covered surfaces are observed when multiple coats are employed, as seen from SEM images using 3-7 successive coats of a 1 mg mL^{-1} suspension and confirmed experimentally with a porosity factor maintained below 1.1. In summary, multiple coats from graphene dispersions at lower concentrations are preferable in achieving uniform drop-casts such that electrode porosity may be adequately controlled at a minimum.

Figure 7.3. Scanning electron micrographs illustrating morphologies of deposited graphene layers, as prepared by drop-casting of multiple aliquots of a graphene dispersion at fixed 1.0 mg mL^{-1} concentration (left panel), and single aliquots of increasing graphene concentration (right panel) on silicon wafers. Black open arrows

indicate presence of a “coffee ring effect” and white arrows indicate thick aggregates. All scale bars represent 100 μm unless stated otherwise.

7.3. Conclusions

The electrochemistry of graphene-modified electrodes was investigated, and it was found that electrode porosity does not noticeably contribute to any electrochemical enhancement under typical preparation conditions. Using the drop-casting technique, we also observed that resultant electrode porosities can in fact be controlled. For larger mass loadings, the optimal route should involve multiple aliquots from a graphene dispersion of lower concentration instead of a single coat from a concentrated dispersion. Thus, notwithstanding specific characteristics of other porous nanomaterials, drop-casting modification continues to be practical and reliable with a caveat that certain experimental protocols should be observed.

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Part II

Chapter 8 –

Electrochemistry of Potassium- Assisted Thermally-Reduced Graphenes

The results and discussion presented in this chapter were published in the following journal article:

1. Potassium Assisted Reduction and Doping of Graphene Oxides: Towards Faster Electron Transfer Kinetics.

A.Y.S. Eng, H.L. Poh, J. Luxa, Z. Sofer, M. Pumera. *RSC Adv.* **2013**, 3, 10900.

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8.1. Introduction

The top-down approach to graphene production is centred on the oxidation of graphite to graphite oxide, and its subsequent reduction typically *via* thermal exfoliation, or through chemical and electrochemical means. As a reducing agent, elemental potassium is amongst the strongest known with a chemical potential of about $E = -2.93$ V vs. the standard hydrogen electrode.¹ Therefore, in this Chapter we explore the effects of elemental potassium as a strong reductant in the thermal exfoliation of graphite oxides.² The Hofmann and Hummers graphite oxides are used as parent GOs which undergo thermal reduction at 500 °C both in the presence and absence of elemental potassium as illustrated in Scheme 8.1. Graphenes reduced in the presence of potassium are abbreviated as (K)G-HO and (K)G-HU, and graphenes reduced in the absence of potassium are G-HO and G-HU.

Scheme 8.1. Schematic illustration for the production of thermally reduced graphenes. Oxidation of graphite was performed *via* the Hofmann (68% nitric acid and sulfuric acid in the presence of KClO_3) or the Hummers (sulfuric acid in the presence of NaNO_3 and

KMnO₄) methods to give their graphite oxide products. The graphite oxides were subsequently thermally exfoliated at 500 °C both in the presence and absence of metallic potassium to yield our thermally reduced graphenes.

8.2. Results and Discussion

We first carried out scanning electron microscopy (SEM) on the two graphene oxides and four thermally reduced graphenes, and their images are shown in Figure 8.1. All thermally reduced graphenes showed structures typical of exfoliated products, where the flakes are held together as macrostructures.^{3,4} In comparing the thermally reduced graphenes and their parent GOs, there is a characteristic wrinkling and relatively uniform flake size of the graphene sheets/platelets in contrast to the large GO particles of variable sizes, and this may be seen as an indication of a successful exfoliation procedure.⁴ Graphenes reduced from GO-HO also showed a platelet-like appearance, while the graphenes exfoliated from GO-HU exhibited a more sheet-like appearance. However, no major differences in morphology were observed when comparing between graphenes exfoliated with elemental potassium to those without.

Figure 8.1. Scanning electron micrographs of thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and their unreduced graphene oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods. Scale bars are 1 μm .

Also, Raman spectroscopy was used to gain insight into the graphene structures and their defect densities. Figure 8.2 demonstrates the two characteristic signals typical of graphenes and all carbon materials in general, with the G (graphitic) band at approximately 1560 cm^{-1} characteristic of pristine sp^2 graphene lattices.^{5,6,7} A second D (disorder) band at roughly 1350 cm^{-1} only occurs in the presence of sp^3 defects.^{5,7,8} Consequently, the ratio of the intensities of the D to G bands (abbreviated as the I_D/I_G ratio) is a common measure of the defect densities in graphenes, and a higher I_D/I_G ratio is associated with increased disorder in the graphene lattice. I_D/I_G ratios for all materials are calculated and are as tabulated in Table 8.1. It is observed that the defect density of

the graphenes generally increased after thermal exfoliation, except G-HU which showed a slight decrease. The increase is in agreement with previous reports, since the rapid deoxygenation during the exfoliation process leads to the generation of defects in the graphene as a result of the harsh treatment.⁹

Figure 8.2. Raman spectra of thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods.

Table 8.1. Comparison of I_D/I_G peak intensity ratios and crystallite sizes from the Raman spectra for thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods. $N=8$

Material	I_D/I_G Ratio	Crystallite size (nm)
(K)G-HO	0.87 ($\pm$ 0.02)	19.3 ($\pm$ 0.4)
(K)G-HU	1.0 ($\pm$ 0.1)	17 ($\pm$ 2)
G-HO	0.9 ($\pm$ 0.1)	18 ($\pm$ 2)
G-HU	0.92 ($\pm$ 0.02)	18.2 ($\pm$ 0.4)
GO-HO	0.83 ($\pm$ 0.03)	20.3 ($\pm$ 0.9)
GO-HU	0.937 ($\pm$ 0.007)	17.9 ($\pm$ 0.1)

The average sp^2 crystallite sizes (L_a) of the graphenes may also be calculated from the relative intensities of G to D bands with the use of the following equation:¹⁰

$$L_a = 2.4 \times 10^{-10} \times \lambda_{laser}^4 \times I_G/I_D$$

where λ_{laser} is the wavelength of the excitation laser in nanometers, and I_G and I_D are the intensities of the Raman G and D bands, respectively. The equation allows for the calculation of the average sp^2 crystallite size as the intensity of the G band is proportional to the extent of aromatic graphitic regions, while its inverse relation to the D band intensity arises from the incidence of sp^3 defects that limit the size of these aromatic islands.⁵ The average sp^2 crystallite sizes of the GOs generally decreased after thermal exfoliation to their reduced graphenes, as a result of the generation of defects during the procedure.

X-ray photoelectron spectroscopy (XPS) is then used to understand the extents to which oxygen groups are removed during the thermal exfoliation process. The wide-scan XPS spectra of the Hofmann and Hummers graphite oxides and thermally reduced graphenes are as presented in Figure 8.3. Peaks corresponding to electrons from the

core carbon 1s and oxygen 1s atomic orbitals are clearly seen at the binding energies of 285 eV and 534 eV, respectively. The C/O ratios for GO-HO and GO-HU are 2.58 and 2.05, and these increase to 11.65 and 8.93 for G-HO and G-HU, demonstrating an effective de-oxygenation. In contrast, the C/O ratios for (K)G-HO and (K)G-HU are lower at 6.76 and 6.83. This therefore suggests that in the thermal reduction process at 500 °C, the presence of elemental potassium does not improve the de-oxygenation process but instead results in less oxygen groups being removed.

Figure 8.3. Wide-scan X-ray photoelectron spectra of thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods.

Considering that different types of oxygen-containing groups are present in graphite oxide and their thermally reduced graphenes,¹¹ we also perform high resolution XPS of the carbon peak to elucidate the oxygen functionalities as in Figure 8.4. The usual spectra of the reduced graphenes include an asymmetric tailing towards higher binding energies while graphite oxides have a second higher intensity peak at approximately 286 eV. Deconvolution of the core C 1s peaks was performed to identify specific bonds. Six bond types were used in the fitting of the obtained spectra and their specific energies are as follows:¹² 284.5 eV for sp^2 hybridized carbons ($-C=C-$), 285.1 eV for the sp^3 hybridized carbon ($-C-C-$), 286.2 eV for alcohol and ether groups ($C-O$), 287.4 eV for carbonyl groups ($C=O$), 288.7 eV for carboxylic acid/ester groups ($O-C=O$) and *ca.* 291.0 eV for the $\pi-\pi^*$ shake-up signal typical of sp^2 hybridized carbons. The relative percentages of these oxygen-containing groups are quantified and tabulated in Table 8.2. There are no *major* differences in the *types* of groups present when comparing between (K)G-HO and G-HO, and also between (K)G-HU and G-HU. Nevertheless, there still exist minor differences between the GOs when reduced in the presence or absence of potassium. The contribution from sp^3 hybridized carbons ($-C-C-$) is higher when reduced in the presence of potassium [(K)G-HO and (K)G-HU: 20.7% and 22.6%] as compared to those in its absence [G-HO and G-HU: 15.4% and 16.4%]. In addition, the contribution of alcohol and ether groups ($C-O$) is lower for graphenes reduced in the presence of potassium [(K)G-HO and (K)G-HU: 10.9% and 7.5%] as compared to when it is absent [G-HO and G-HU: 11.9% and 13.0%]. Interestingly, in potassium reduced GOs slightly higher concentrations of $O-C=O$ groups were observed, compared to those without potassium. These carboxyl groups were probably stabilized by the formation of ionic compounds with potassium, in a manner analogous to carboxyl acid salts and chelate compounds.

Figure 8.4. High resolution X-ray photoelectron spectra of the C 1s peak for thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods.

Table 8.2. Comparison of carbon/oxygen ratios from core C 1s and O 1s peaks of the wide-scan X-ray photoelectron spectra, and quantitative distributions of deconvoluted high resolution C 1s core level X-ray photoelectron spectra for thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods.

	C/O Ratio	C 1s Distributions (%)					
		C=C	C-C	C-O	C=O	O-C=O	π - π^*
(K) G-HO	6.76	56.5	20.7	10.9	5.2	2.4	4.2
(K) G-HU	6.83	58.7	22.6	7.5	5.8	5.0	0.4
G-HO	11.65	61.7	15.4	11.9	8.6	1.8	0.5
G-HU	8.93	62.7	16.9	13.0	4.6	2.2	0.6
GO-HO	2.58	30.7	9.2	57.2	3.0	-	-
GO-HU	2.05	23.8	8.9	40.5	12.3	9.8	4.8

Since significant amounts of elemental potassium were used during the thermal exfoliation, the high resolution XPS spectra of potassium was also obtained for all materials as given in Figure 8.5. Electrons from the K 2p orbitals are centred at around 296 eV and may also be seen in the C 1s spectra due to their proximity in binding energies. Only in (K)G-HU were these peaks discernible. As the XPS technique specifically limits analysis to the sample surface,¹³ energy-dispersive X-ray spectroscopy (EDS) was also employed to provide information from deeper within the sample. We found that the addition of potassium in our thermal exfoliation process introduced about 0.5% K into the reduced graphenes. However, smaller amounts of potassium of about 0.1% were also detected in all the other normally exfoliated graphenes and graphite oxides. These are likely to be impurities that have been introduced during the synthesis of graphite oxides. Specifically in the Hofmann and Hummers methods, potassium chlorate

and potassium permanganate are used as oxidants, respectively. Therefore, it is reasonable to expect small amounts of impurities despite best efforts to remove them in the synthetic procedure.

Figure 8.5. High resolution X-ray photoelectron spectra of the K 2p peak for thermally reduced graphenes prepared in the *presence* of potassium (top), in the *absence* of potassium (middle), and the unreduced parent graphite oxides (bottom) prepared *via* the Hofmann (HO) and Hummers (HU) methods.

Cyclic voltammetry was finally used to quantify the HET kinetics of both graphenes and their corresponding graphene oxides. Figure 8.6 shows the cyclic voltammograms for materials prepared *via* the Hofmann and Hummers oxidation methods towards the ferro/ferricyanide redox couple. Peak separations at the graphene oxides [GO-HO and GO-HU: 469 mV and 453 mV] are much larger than the 270 mV for bare glassy carbon electrode. In contrast, ΔE_p values for thermally reduced graphenes

are significantly lower. In particular, graphenes exfoliated in the *presence* of potassium have smaller peak separations [(K)G-HO and (K)G-HU: 137 mV and 123 mV] than those without potassium [G-HO and G-HU: 178 mV and 190 mV].

Figure 8.6. Cyclic voltammograms of 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for thermally reduced graphenes prepared in the *presence* of potassium (blue), in the *absence* of potassium (red), and their corresponding graphene oxides (green) prepared *via* the Hofmann (left) and Hummers (right) methods. For comparison, bare glassy carbon electrode is also shown (black). *Conditions:* scan rate 100 mV s^{-1} , background electrolyte 50 mM PBS, pH 7.2.

These results correspond to the slowest HET rates of the redox probe on GOs [GO-HO and GO-HU: $2.86 \times 10^{-5} \text{ cm s}^{-1}$ and $3.56 \times 10^{-5} \text{ cm s}^{-1}$] as compared to glassy carbon [$4.24 \times 10^{-4} \text{ cm s}^{-1}$]. In addition, we note the larger k_{obs}^0 values of graphenes reduced with potassium [(K)G-HO and (K)G-HU: $2.59 \times 10^{-3} \text{ cm s}^{-1}$ and $3.13 \times 10^{-3} \text{ cm s}^{-1}$] as compared to standard thermally reduced graphenes [G-HO and G-HU: $1.48 \times 10^{-3} \text{ cm s}^{-1}$ and $1.25 \times 10^{-3} \text{ cm s}^{-1}$]. Hence, it may be concluded from our voltammetric study that the addition of elemental potassium during the thermal exfoliation process yields a graphene product with improved electrocatalytic effects, in particular an enhanced electron transfer towards the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox probe. It is seen from Raman

spectroscopy that there are no major differences in the defect densities of the various materials. However, a clear trend exists from XPS, where the oxygen content is seen to significantly decrease after thermal reduction. This lends itself as credible evidence that the lower oxygen content is the primary reason for the improved electron-transfer kinetics of thermally reduced graphenes over their parent graphene oxides, in agreement with previous reports.^{14,15} Interestingly, the opposite was observed in assessing the effect of the presence of potassium during thermal reduction, where graphenes exfoliated with potassium showed enhanced electron-transfer rates over normal ones, despite having a higher oxygen content. A likely reason that may account for this is the existence of potassium-complexed oxygen groups. These groups may contribute to the improved electrochemistry by reducing the electrostatic repulsion between negatively charged oxygen groups and the similarly charged ferro/ferricyanide, thereby increasing the heterogeneous electron transfer rates in TRGOs reduced with potassium. Indeed, a recent investigation of K-doped graphenes also showed improved electrochemistry, specifically a significant increase in sensitivity in the voltammetric detection of nitrites and sulfites.¹⁶ As such, small amounts of potassium complexes with oxygen groups in thermally reduced graphenes could be responsible for the increase in the rates of heterogeneous electron transfers of these materials in solution.

8.3. Conclusions

In this Chapter, we investigated the effects of the addition of elemental potassium during the thermal reduction of graphite oxides prepared from two methods, the Hofmann method with chlorate as oxidant and the Hummers method utilising permanganate. The density of sp^3 defects in the various graphene materials was not found to show significant differences. However, thermally reduced graphenes exfoliated

in the *presence* of potassium had a higher oxygen content in contrast to those reduced in the *absence* of potassium. Unlike previous reports where a greater presence of oxygen-containing groups corresponded to poorer electrochemistry, we observed an increase in the heterogeneous electron transfer rates towards the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox probe. Possibly, this observation may be attributed to the presence potassium complexes with oxygen groups on the graphene surface and a potential direction in future work may then be to elucidate the bonding modes between potassium and specific oxygen groups in doped graphene materials.

8.4. Detailed Experimental Procedures

Combustible elemental analysis (CHNS-O) was performed with a PE 2400 Series II CHNS/O Analyzer (Perkin Elmer, USA). In CHN operating mode (the most robust and interference free mode), the instrument employs a classical combustion principle to convert the sample elements to simple gases (CO_2 , H_2O and N_2). The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases, separation and detection. A microbalance MX5 (Mettler Toledo) is used for precise weighing of samples (1.5 – 2.5 mg per single sample analysis). The accuracy of CHN determination is better than 0.30% abs. Internal calibration is performed using N-phenyl urea.

Thermally reduced graphenes (with and without potassium)

For the thermal reduction of graphene, 0.2 g of GO was placed inside a 20 mL stainless steel autoclave. The filling was performed inside a glovebox with Argon atmosphere. For reduction with potassium, 3 g of 99.5 % potassium was added to the 0.2 g of GO inside the autoclave. The autoclave was closed under argon atmosphere and heated at 500 °C for 24 hours. After cooling to room temperature, the autoclave was

opened and any remaining potassium was decomposed by a methanol–water mixture (1:1 vol). The reduced GO was repeatedly washed with water, filtered through 0.45 µm nylon membrane and dried under vacuum at 50 °C for 48 h.

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Part II

Chapter 9 –

Microwave Reduction and

Hydrogenation of Graphite Oxides to

Hydrogenated Graphenes

The results and discussion presented in this chapter were published in the following journal article:

1. Highly Hydrogenated Graphene through Microwave Exfoliation of Graphite Oxide in Hydrogen Plasma: Towards Electrochemical Applications.

A.Y.S. Eng, Z. Sofer, P. Simek, J. Kosina, M. Pumera. *Chem. Eur. J.* **2013**, *19*, 15583.

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9.1. Introduction

In this Chapter, we explore the reduction and hydrogenation of graphite oxides towards hydrogenated graphenes in a one-step procedure.¹ The role of the microwave serves two intended purposes; the microwave absorption enables a fast yet efficient reduction of graphite oxide to graphene, while the introduction of hydrogen gas at low pressure generates a hydrogen plasma which achieves our second objective of hydrogenating the graphenes. The effectiveness of the simultaneous reduction and hydrogenation procedure is similarly investigated for three graphite oxides. We abbreviate the Staudenmaier, Hofmann and Hummers hydrogenated graphenes as G-ST, G-HO and G-HU, respectively, here.

9.2. Results and Discussion

The surface morphologies of the exfoliated hydrogenated graphenes are examined by scanning electron microscopy (SEM). Figure 9.1 illustrates their surface characteristics at various magnifications. Despite their different oxidation routes, all three graphenes exhibit similar characteristics as those from previous reports prepared by the microwave exfoliation and reduction of GO. We note their distinctive layered structures,² while the characteristic transparent wrinkled effect most obvious at high magnifications³ further suggest that the layers are exfoliated to a large extent. When viewed as a whole, the surface characteristics of our graphene materials hydrogenated under microwave H-plasma are not unlike those of thermally-reduced graphenes exfoliated at high temperatures; the flakes are observed to be agglomerated,^{4,5} and exist as macrostructures.⁶ Despite the fact that the microwave-induced plasma arises from ionized hydrogen, it is also important to highlight other mechanisms that can similarly contribute to the plasma as a result of microwave absorption. Firstly, polar molecules

that include water and carbon monoxide absorb microwaves due to the mechanism of dipolar polarization, but the process does not result in electronic excitation.⁷ In contrast, aromatic graphitic regions in GO absorb microwaves *via* the conductive mechanism, a direct effect of the extended π -conjugation networks. In this case, π -electrons in graphitic regions are known to ionize upon microwave irradiation.^{3,8} Collectively, these processes contribute to the microwave reduction of GO.

Figure 9.1. Scanning electron micrographs of hydrogenated graphenes as prepared by the hydrogenation of the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) graphite oxides in microwave H-plasma. Scale bars are 100 nm (left), 1 μ m (middle), and 10 μ m (right), respectively.

Figure 9.2a demonstrates the Raman signals typical of graphene materials, and a comparison of the I_D/I_G ratios is given in Figure 9.2b. It is seen that G-HO has a notably

high defect density with a value of 1.013, while the ratios of G-ST and G-HU are comparable at 0.814 and 0.822, respectively. A second-order (2D) band is also observed in G-ST and G-HO at around 2700 cm^{-1} .⁹ As shown in Figure 9.2c, G-HO also has the lowest average sp^2 crystallite size of the three hydrogenated graphenes at 16.6 nm, while G-ST and G-HU have larger sizes of 20.7 nm and 20.5 nm. Considering the synthetic procedure where a microwave H-plasma was employed both for the reduction of GO and its subsequent hydrogenation, one might infer that both the inherent oxygen groups that remain and chemisorbed hydrogen (existing as C-H bonds) can act to increase the amount of sp^3 defects. As such, these two factors together contribute to G-HO having the most defects observed in the hydrogenated graphenes.

Figure 9.2. (a) Raman spectra of hydrogenated graphenes as prepared by the hydrogenation of the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU)

graphite oxides in microwave H-plasma; (b) ratios of I_D/I_G band intensities and (c) comparison of sp^2 crystallite sizes of hydrogenated graphenes.

In the case of FTIR spectroscopy, two peaks are observed at *ca.* 2850-2950 cm^{-1} in all three samples of hydrogenated graphenes (Figure 9.3). These double bands correspond to alkyl C-H stretches,^{10,11,12} and therefore confirm that the microwave H-plasma had resulted in the formation of C-H bonds within the carbon backbone. Other bands include a weak and broad absorption from 3300 cm^{-1} to 3500 cm^{-1} arising from the O-H vibrations of hydroxyls and carboxyls, and a small peak approximately at 1100 cm^{-1} due to C-O stretches of alcohols and aromatic acids.^{13,14} These observations provide conclusive evidence of hydrogenation by the H-plasma, while there also remains a continued presence of oxygen groups in the hydrogenated materials.

Figure 9.3. FTIR spectra of hydrogenated graphenes as prepared by the hydrogenation of the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) graphite oxides in microwave H-plasma (left); Inset of the FTIR spectra of hydrogenated graphenes showing the double peaks corresponding to C-H stretches (right).

Subsequently, wide scan and high resolution XPS of the core level C 1s spectra is performed and as presented in Figure 9.4. Two distinctive peaks are observed in the

wide-scan spectra, corresponding to photoelectrons from the core C 1s and O 1s atomic orbitals at binding energies of *ca.* 285 eV and 534 eV, respectively, and C/O ratios are tabulated in Table 9.1. The respective C/O ratios of the hydrogenated graphenes are 12.8, 12.3 and 12.1 for G-ST, G-HO and G-HU; in comparison to their parent graphite oxides containing much greater amounts of oxygen with the ratios: 2.47 for GO-ST, 2.71 for GO-HO, and 2.05 for GO-HU.¹³ This firstly shows that the reduction process under microwave plasma was successful. It is also interesting to see a remarkable similarity in the C/O ratios of all microwave hydrogenated graphenes, despite significant differences in the oxygen functionalities of their parent GO forms. Additionally, in contrast to the thermal reduction/exfoliation process performed on the same GOs in a previous study, our current procedure yields hydrogenated graphenes with much improved consistency in their C/O ratios, despite a lower reduction extent.¹⁵ (C/O ratios for G-ST, G-HO, G-HU by thermal exfoliation at 1000 °C were much more variable with the values of 24.1, 18.2, and 19.3.) Deconvolution of the C 1s spectra was also performed and the relative abundances of each bond type are tabulated in Table 9.1. An asymmetric Gaussian-Lorentzian product line-shape (30% Lorentzian) was used in the deconvolution with a Shirley background, giving the best fit to the raw spectra. In line with the trend observed for the C/O ratios, no significant differences in the C 1s spectra were observed between the graphenes after their reduction in microwave plasma. In this aspect, we may conclude that microwave exfoliation produces reduced graphenes with residual oxygen groups that are similar in both their type and abundance regardless of the oxidation method employed. It should also be mentioned that C-H bonds have a similar chemical shift to C-C bonds in XPS, and it is therefore difficult to distinguish the two from XPS measurements alone.

Figure 9.4. Wide-scan (left) and high resolution core level carbon 1s (right) X-ray photoelectron spectra of hydrogenated graphenes as prepared from the hydrogenation of the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) graphite oxides in microwave H-plasma.

Table 9.1. Carbon/oxygen ratios from core-level C 1s and O 1s peaks of the wide-scan X-ray photoelectron spectra, and quantitative distributions of specific carbon bond types from the deconvoluted peaks of the high resolution C 1s spectra of hydrogenated graphenes.

Material	C/O	C 1s Distribution (atomic %)					
	Ratio	C=C	C-C	C-O	C=O	O-C=O	π - π^*
G-ST	12.8	57.4	20.2	11.9	5.0	3.3	2.2
G-HO	12.3	59.2	18.1	13.8	4.0	2.6	2.3
G-HU	12.1	57.8	19.4	11.8	5.1	3.7	2.2

Elemental analysis is able to provide quantitative data on the compositions of our hydrogenated graphenes. The general trend of the hydrogenation extent is seen to roughly follow that of the oxygen content, and increases in the following order of G-ST < G-HO < G-HU. The materials are by general formula; G-ST: $C_{9.60} H_{1.00} O_{0.78}$, G-HO: $C_{6.42} H_{1.00} O_{0.43}$, and G-HU: $C_{3.71} H_{1.00} O_{0.55}$. Thus, G-HU has the largest extent of hydrogenation amongst the graphenes. However, it is important to emphasize that while the hydrogenation occurs on graphene itself (in the formation of C-H bonds towards graphane), a certain amount of the hydrogen detected can be from oxygen groups such as hydroxyls and carboxyls. If we assume a 1:1 stoichiometry of oxygen to hydrogen in the form of hydroxyl groups, the remaining hydrogen must originate from C-H bonds themselves. Hence, subtracting the oxygen compositions from hydrogen, we obtain 1.29 at.% of chemisorbed hydrogen directly on the carbon backbone for G-ST, 7.23 at.% for G-HO, while G-HU has the highest amount of C-H bonds at 8.50 at.%. Additionally, the extreme assumption of a 1:1 stoichiometry of oxygen to hydrogen is highly unlikely as the materials contain other functional groups such as carboxyls (2:1 stoichiometry of O:H) and carbonyls (1:0 stoichiometry of O:H). Therefore, the 8.50 at.% of C-H bonds directly on the graphene lattice calculated in G-HU only represents the minimum amount possible, and the true value is expected to be significantly higher.

We subsequently perform cyclic voltammetry to quantify their heterogeneous electron transfer (HET) rates towards the ferro/ferricyanide $[Fe(CN)_6]^{4-/3-}$ redox probe. Figure 9.5 shows the cyclic voltammograms of $[Fe(CN)_6]^{4-/3-}$ on the hydrogenated graphenes as deposited on glassy carbon electrodes, and bare glassy carbon is also shown as a comparison. The peak separation for G-ST at 273 mV was only marginally lower than that for bare GC at 280 mV. In comparison, both G-HO and G-HU displayed much smaller peak separations of 135 mV and 155 mV, respectively. In terms of the

calculated HET rates, these results correspond to the slowest for bare GC with a k_{obs}^0 value of $3.7 \times 10^{-4} \text{ cm s}^{-1}$, and in increasing order: G-ST ($4.1 \times 10^{-4} \text{ cm s}^{-1}$), G-HU ($2.0 \times 10^{-3} \text{ cm s}^{-1}$) and G-HO ($2.7 \times 10^{-3} \text{ cm s}^{-1}$). The HET rates of the hydrogenated graphenes are notably faster compared to their parent graphite oxides¹³ and thus serve as a clear indication of the successful reduction and removal of oxygen groups.

Figure 9.5. Cyclic voltammograms of 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on hydrogenated graphenes as prepared from the hydrogenation of the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) graphite oxides in microwave H-plasma. Voltammogram for bare glassy carbon (GC) is also shown for comparison. Conditions: 50 mM phosphate buffered saline, pH 7.2, scan rate: 100 mV s^{-1} , potentials are *versus* the Ag/AgCl reference electrode.

The effects of hydrogenation on the observed electrochemical properties, however, are a more complex and challenging issue, especially with the limited reports on the electrochemistry of hydrogenated graphene materials. In its simplest terms, hydrogenation produces hydrogenated graphenes through the formation of C-H bonds directly on the graphene lattice. However, the chosen method of hydrogenation may

inadvertently cause additional changes in material properties that can also influence the observed HET rates. In a previous study, high-pressure hydrogenation at moderately high temperatures ranging from 200 °C to 500 °C were seen to result in a variable amount of defects, while the high gas pressures have a negative influence on the removal of oxygen-containing groups.¹⁶ As such, despite similar levels of hydrogenation between the materials, the observed HET rates were noticeably poorer than in our current H-plasma hydrogenated graphenes.

A better overall understanding of the electrochemistry of hydrogenated graphenes may then be gained from our current study when we closely examine the various properties of the three hydrogenated graphenes. Firstly, the HET rate of G-ST is only slightly better than that for glassy carbon. Its especially slow HET is probably a consequence of the significantly low level of hydrogenation, and the lack of edge-like defects would have otherwise catalysed the electrochemical redox of the ferro/ferricyanide couple.^{17,18} This effect is demonstrated with the lowest I_D/I_G ratio in the Raman spectra. On the other hand, G-HO shows the fastest HET rates together with the highest Raman I_D/I_G peak ratio, thus giving further credence to the fact that electrocatalysis does occur preferentially on graphene defects. Lastly, G-HU displays relatively fast HET and the largest hydrogenation extent. In combination with its low amount of oxygen, the HET is observed to be relatively fast. An interesting point in the case of G-HU is its fast HET despite a rather low Raman I_D/I_G peak ratio, which likely suggests that the large amount of hydrogenated carbons may have contributed to the fast electron transfers. Therefore, it is essential to highlight the competing factors of *edge defects* which increase the HET rate;^{17,18} *oxygen-containing groups* which slightly decrease the HET rate;^{19,20} and *C-H bonds* (whose effects are currently less well-understood).^{16,21} Nevertheless, our observations in G-HU seem to suggest that its

reasonably fast HET rates may arise from its high hydrogen content of more than 8.50 at.% in the form of C-H bonds. If we attempt to establish a trend here, G-HO too has a fast HET with at least 7.23 at.% chemisorbed hydrogen. These are in comparison to the slow HET of G-ST with its correspondingly low C-H content at 1.29 at.%. Hence, the quantity of C-H bonds in hydrogenated graphenes might play a significant role in determining its electrochemistry. Consequently, in furthering our understanding of electrochemical HET rates, a previously held notion that the HET rates of hydrogenated graphenes decrease with increasing hydrogenation¹⁶ may be a simplistic one, especially considering the competing influences involved. Additionally, one should also take heed that these influences are applicable only to the ferro/ferricyanide redox couple, and additional system-specific behaviour may apply for other redox probes. All the same, from our observations in the current study, fast heterogeneous electron transfers at highly hydrogenated graphenes may potentially open up a new field of applications of these materials.

9.3. Conclusions

The exfoliation of GO in microwave H-plasma towards reduction and hydrogenation of graphenes was investigated. The method is seen to produce reduced graphenes that exhibit similarities in morphology, defect density and oxygen contents in comparison to thermally reduced graphenes. Despite differences in the types and amounts of their parent GOs, microwave exfoliation in H-plasma yields graphenes with remarkably similar oxygen content. In addition to the removal of oxygen groups, the process also hydrogenates the graphene backbone towards graphane. Graphite oxide produced from the Hummers method is used to provide the most effective hydrogenation at 19 at.%. In addition, we demonstrate that highly hydrogenated

graphenes exhibit fast heterogeneous electron transfer, which has potential implications for application of these materials in electrochemical sensors.

9.4. Detailed Experimental Procedure

Synthesis of hydrogenated graphenes in microwave hydrogen plasma

The synthesis of hydrogenated graphenes was performed in low pressure hydrogen microwave plasma. The graphite oxides (GO-ST, GO-HO and GO-HU) prepared according to the various methods were individually placed inside a quartz glass reactor which was evacuated and flushed with hydrogen. At the base pressure of 1 mbar, the hydrogen flow was stopped and the graphite oxide was exfoliated by applying microwave radiation for 30 s (1 kW, 2.45 GHz). The exfoliation procedure was accompanied by the increase of the pressure to about 20 mbar. The reactor was again evacuated and flushed with hydrogen gas (50 ml min⁻¹) to remove the exfoliation byproducts and at the pressure of 8 mbar with continuous hydrogen flow, the microwave radiation was applied for 3 minutes, leading to the formation of a hydrogen plasma.

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Part II

Chapter 10 –

Wet Chemistry Hydrogenation of Graphite Oxides to Hydrogenated Graphenes

Part of the results and discussion presented in this chapter were published in the following journal article:

1. Searching for Magnetism in Hydrogenated Graphene: Using Highly Hydrogenated Graphene Prepared via Birch Reduction of Graphite Oxides.

A.Y.S. Eng, H.L. Poh, F. Sanek, M. Marysko, S. Matejkova, Z. Sofer, M. Pumera. *ACS Nano* **2013**, 7, 5930.

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10.1. Introduction

Hydrogenated graphenes are proposed to have a variety of properties that are fundamentally different from graphene. In this section, we study the properties of highly hydrogenated graphenes prepared from the Birch reduction.¹ Traditionally, the Birch reduction is used for 1,4-hydrogen addition to aromatic compounds. The first step involves transfer of the solvated electrons in ammonia (originally from sodium) to the compound, and the second step where the alcohol supplies a proton to the anion radical. The process occurs twice giving 1,4-cyclohexadiene as product from benzene.² In our case, the reaction first involves the reduction of GO in a solution of sodium in liquid ammonia, followed by the provision of hydrogen using methanol. We also investigate the potential differences in the use of different GOs on the hydrogenation rate. An additional control sample was also prepared from the Hofmann method but was instead exposed to sodium amide in liquid ammonia and used as a control for comparison. We abbreviate our reduced-GOs in this paper as G-ST, G-HO, G-HU and G-HO-Control.

10.2. Results and Discussion

To determine if the hydrogenation of GOs is successful, we use FTIR spectroscopy (Figure 10.1) to identify chemically bonded hydrogen. The inset spectra of the C-H vibration bands are also given in Figure 10.2. The two distinctive bands at 2850 cm^{-1} and 2950 cm^{-1} corresponding to C-H stretching confirm the hydrogenation on graphene.^{3,4,5} Other absorptions arising from oxygen-containing groups in GO are present, including a broad peak from 3300 cm^{-1} to 3500 cm^{-1} due to O-H vibrations from hydroxyl and carboxyl groups, a 1650 cm^{-1} peak due to conjugated C=O stretches, a peak at 1580 cm^{-1} due to aromatic C=C stretches and also a set of complex peaks from 1000 cm^{-1} to 1300

cm^{-1} from multiple C-C and C-O vibrations.^{6,7} Although these observations show a continued presence of oxygen groups within the reduced-GOs, it is nonetheless expected since no reduction can completely remove all oxygen groups.⁸

Figure 10.1. FTIR spectra of hydrogenated graphenes prepared from graphite oxides synthesized by the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods with subsequent Birch reduction in Na/NH_3 and methanol. Also shown is the FT-IR spectra of the control experiment, where Hofmann graphite oxide was treated by $\text{NaNH}_2/\text{NH}_3$ (G-HO Control).

Figure 10.2. Inset of the FTIR spectra of hydrogenated graphenes showing the double peaks corresponding to C-H stretches.

XPS was then used to study the surface compositions. Figure 10.3 shows the survey spectra of the hydrogenated graphenes and their surface atomic compositions are tabulated in Table 10.1. Three peaks corresponding to electrons from the core-level carbon-1s, oxygen-1s and sodium-1s orbitals are observed at binding energies of 285 eV, 534 eV and 1070 eV, respectively. The largest C/O ratio was calculated to be 8.79 for G-HO, in comparison to 2.78 for the control material using sodium amide in liquid ammonia. Interestingly, the procedure exhibits varying extents of reduction with different GOs, with a lower ratio of 5.53 for G-ST and a significantly low value of 2.25 for G-HU. For comparison, C/O ratios of unreduced GOs are 2.47, 2.71, and 2.05 for GO-ST, GO-HO, and GO-HU, respectively.⁹ A similar trend is noted with energy-dispersive X-ray spectroscopy (EDS). Hence, the Birch procedure is most effective for G-HO but has a practically negligible effect on the removal of oxygen groups in G-HU. It is also seen from XPS that a variable amount of sodium is introduced into the reduced graphenes, from 0.55% in G-HO up to 5.7% in G-HU. This observation is in agreement with previous reports utilizing a similar Birch hydrogenation process with lithium metal, suggesting a similar event of sodium-intercalation into graphene for our current study.^{3,5,10} In addition, a set of peaks due to Auger electrons arising from KLL transitions in sodium are observed at binding energies of 264 eV, 301 eV and 331 eV. These observations corroborate with additional evidence from EDS mappings, where we find the presence of Na specifically at carbon-rich sites and that it is less abundant at oxygen-rich areas.

Figure 10.3. Wide-scan XPS spectra of hydrogenated graphenes prepared from graphite oxides synthesized by the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods with subsequent Birch reduction in Na/NH₃ and methanol. Also shown is the XPS spectrum of the control experiment, where Hofmann graphite oxide was treated by NaNH₂/NH₃ (G-HO Control).

Table 10.1. Wide scan XPS quantitative comparison of the compositions of various hydrogenated graphenes prepared from graphite oxides.

		Atomic percentages			
Material	C/O Ratio	Carbon-1s (285 eV)	Oxygen-1s (534 eV)	Sodium-1s (1070 eV)	Sulfur-2p (165 eV)
G-HO-Control	2.78	71.96	25.84	1.56	0.64
G-ST	5.53	83.49	15.10	1.41	Not detected
G-HO	8.79	88.62	10.08	0.55	0.75
G-HU	2.25	64.17	28.55	5.71	1.56

Thus far, infrared spectroscopy and X-ray photoelectron spectroscopy have respectively shown proof of a successful hydrogenation and also of the removal of oxygen groups. However, neither technique is able to provide quantification of the absolute extent of hydrogenation nor the amount of oxygen, and combustible elemental

analysis (CHNS-O) is used to achieve both these objectives. The amount of hydrogen introduced was 37.42 at.% in G-HO (4.54 wt.%), comparable to the highest reported hydrogenation extent of 5 wt.% obtained by Rao.⁴ The level of hydrogenation then decreased to 2.55% for G-ST, 2.43% for G-HO-Control and only 0.95% for G-HU. The trend observed for the oxygen content is roughly the opposite, decreasing in the order: G-HO-Control > G-HU > G-ST > G-HO. If we express the composition of hydrogenated graphenes by general formula, we find that G-ST consists of $C_{2.31}H_1O_{0.66}$, G-HO: $C_{1.38}H_1O_{0.28}$, G-HU: $C_{4.75}H_1O_{2.98}$, while the control sample G-HO-Control consists of $C_{1.41}H_1O_{1.47}$. It is clear that for G-HO-Control as well as for G-HU, there is a larger content of O in comparison to H and it therefore cannot be ruled out that most H atoms are bonded to O atoms as hydroxyl or carboxyl groups. However, G-ST and G-HO exhibit larger amounts of H than O, where G-HO particularly shows a very high C:H ratio of 1.38:1. Thus, these demonstrate that hydrogenation of the carbon backbone itself was highly successful, such that the majority of hydrogen atoms are carbon-bonded (*i.e.* chemisorbed onto the graphene lattice) and not oxygen-bonded in the case of G-HU and G-HO-Control.

In order to investigate the intrinsic structure, Raman spectroscopy was employed. The samples with lower hydrogen contents exhibit spectra typical of graphene materials, which show the D band (1350 cm^{-1}) and G band (1560 cm^{-1}) representing defects in the sp^2 lattice and vibrations in pristine graphene layers, respectively. The density of defects can be compared between the various materials by calculation of the relative I_D/I_G band intensities. In the spectra, as shown in Figure 10.4, we also find broad peaks related to the 2D phonon mode located around 2650 cm^{-1} . The I_D/I_G ratio was 1.237 for the G-HU sample and 0.993 for G-ST. In comparison, the G-HO-Control sample has a lower I_D/I_G ratio 0.980.

Figure 10.4. Raman spectra of hydrogenated graphenes prepared from graphite oxides synthesized by the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods with subsequent Birch reduction in Na/NH₃ and methanol. Also shown is the Raman spectra of the control experiment, where Hofmann graphite oxide was treated by NaNH₂/NH₃ (G-HO Control).

In contrast to the other samples, the high degree of hydrogenation in the case of G-HO led to some photoluminescence of the sample, appearing as a broad emission over the entire range measured. The absolute intensities of the peaks are also about one to two orders of magnitude larger, and the I_D/I_G ratio was calculated to be 0.934. The presence of photoluminescence is typically attributed to band-gap splitting by the covalently bonded hydrogen in hydrogenated graphenes and strong photoluminescence has also been previously reported for graphene with considerably high hydrogen contents.³

Cyclic voltammetry of the reduced graphenes was also performed to understand the inherent electrocatalytic properties of our materials. Carbon materials typically exhibit electrochemically *quasi*-reversible behaviour, with k_{obs}^0 that vary over a large range of values roughly from 10^{-5} to 10^{-2} cm s⁻¹.¹¹ Cyclic voltammograms of the four graphenes towards the ferro/ferricyanide probe are shown in Figure 10.5. All hydrogenated graphenes were seen to display slow HET kinetics, with k_{obs}^0 in the order of 10^{-4} to 10^{-5} cm s⁻¹. On initial inspection, this may derive from the hydrogenation converting sp² to sp³-hybridised carbons which disrupt the intrinsic sp²-conjugation network, causing a decrease in in-plane conductivity. When a further comparison is made between the various materials, the peak separation ΔE_p is seen to increase from G-HU < G-ST < G-HO < G-HO-Control with the values of 340 mV, 391 mV, 442 mV and 469 mV, respectively. Hence, G-HU exhibited the fastest heterogeneous electron transfer ($k_{obs}^0 = 1.6 \times 10^{-4}$ cm s⁻¹) amongst the reduced graphenes, followed by G-ST ($k_{obs}^0 = 8.2 \times 10^{-5}$ cm s⁻¹), G-HO ($k_{obs}^0 = 4.1 \times 10^{-5}$ cm s⁻¹) and G-HO-Control ($k_{obs}^0 = 2.9 \times 10^{-5}$ cm s⁻¹). As a comparison, bare GC had the smallest peak separation of 234 mV, corresponding to the fastest k_{obs}^0 value in this study at 6.9×10^{-4} cm s⁻¹.

With the highest surface oxygen content as measured by XPS, G-HU may be expected to show the slowest HET; an increase in the presence of oxygen-containing groups is associated with a decrease in the speed of the electron transfer.^{12,13} Contrary to expectations, it demonstrates the fastest HET rate of the hydrogenated graphenes. Clearly, this would not be observed if oxygen-containing groups were solely responsible for influencing the HET rate. This is easily explained when the observed trend in HET rates is compared alongside the I_D/I_G ratios as calculated from Raman spectra. It is established that edge-like defects in graphene materials have an inherently higher HET rate as compared to its basal plane.^{14,15} As higher I_D/I_G ratios imply a higher defect

density, G-HU would therefore have the fastest HET rate with its correspondingly high I_D/I_G ratio of 1.237. Accordingly, the HET rate decreases with the decreasing defect densities of G-ST and G-HO. For G-HO-Control, its high content of oxygen groups also likely contributed to the lowering of its HET rate. One might also consider the possibility that the extent of hydrogenation might also affect the observed HET rates. However, there is no obvious relation seen between hydrogenation extents and the HET rates, especially in presence of the previous two more influential factors. The overall HET rates of Birch-reduced graphenes towards the ferro/ferricyanide redox probe are considerably slower than typical electron transfer rates at thermally reduced graphenes or even in comparison to glassy carbon electrodes that were used as a reference. The typical k_{obs}^0 values obtained were in fact very similar to their parent graphite oxides. Therefore, we may conclude that this technique is much less suitable for producing hydrogenated graphenes for electrochemical sensing compared to the microwave reduction and hydrogenation method, as its poor efficiency in the removal of oxygen groups does not produce materials displaying the fast HET required of good electrochemical transducers.

Figure 10.5. Cyclic voltammograms of 10 mM $[Fe(CN)_6]^{3-/4-}$ on hydrogenated graphenes prepared from graphite oxides synthesized by the Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods with subsequent Birch reduction in Na/NH₃ and methanol. Also shown is the control material, where Hofmann graphite oxide was

treated by $\text{NaNH}_2/\text{NH}_3$ (G-HO Control). The voltammogram for bare glassy carbon (GC) is shown as a comparison. Conditions: 50 mM phosphate buffered saline, pH 7.2, scan rate: 100 mV s^{-1} , potentials are *versus* the Ag/AgCl reference electrode.

10.3. Conclusions

An investigation of the Birch reduction procedure was performed on graphite oxides prepared by several methods, and a simultaneous reduction and hydrogenation was observed on these substrates. Extensive characterization was performed on the highly hydrogenated graphenes, and it was found that they were less suited for electrochemical sensing compared with hydrogenated graphenes prepared by the microwave hydrogenation technique detailed in Chapter 9. However, the high hydrogenation extents characteristic of the Birch reduction on graphene materials make it a much more promising option compared with gaseous hydrogenation methods for applications such as the storage of hydrogen as a fuel source.

10.4. Detailed Experimental Procedures

Reduction of graphite oxide with sodium in liquid ammonia (Birch reduction)

The reduction of GO with sodium in liquid ammonia was performed under argon atmosphere. For the cooling of the reflux condenser a dry ice-acetone mixture was used. 60 mL of ammonia was condensed into a 250 mL flask equipped with magnetic stirrer. 60 mg of each GO was added to the liquid ammonia and stirred for 10 minutes. The flask with liquid ammonia was held at -30°C . Subsequently, 1 g of sodium was added to the reaction mixture and the temperature was increased to -15°C to start reflux of ammonia. After 2 hours, 30 ml of methanol was added. After addition of methanol, the reaction mixture was allowed to warm to room temperature overnight. The reduced

graphene was filtered off using a nylon membrane (0.45 mm), washed several times with water and dried under vacuum for 48 hours at 60 °C. The reduced G-HU-Control sample included for comparison was similarly prepared, with the exception of 2 g sodium amide being used in place of elemental sodium.

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Part II

Chapter 11 –

Influence of Electron and Proton Sources on the Birch Reduction Method to Hydrogenated Graphenes

The results and discussion presented in this chapter were published in the following journal article:

1. Hydrogenated Graphenes by Birch Reduction: Influence of Electron and Proton Sources on Hydrogenation Efficiency, Magnetism, and Electrochemistry.

A.Y.S. Eng, Z. Sofer, S. Huber, D. Bousa, M. Marysko, M. Pumera. *Chem. Eur. J.* **2015**, *21*, 16828.

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11.1. Introduction

A wide range of covalent functionalizations have been performed on graphene including its functionalization with hydrogen.^{1,2,3} Hydrogenated graphenes demonstrate a myriad of interesting properties, such as fluorescence⁴ and ferromagnetism,^{5,6} and have valuable applications in devices including lithium batteries⁷ and the reversible storage of hydrogen.⁸ Of the two approaches to graphene hydrogenation,⁹ liquid phase (wet chemistry) hydrogenation proves more effective than gaseous procedures that employ hydrogen plasma^{10,11} or high temperatures and pressures.^{12,13} Numerous groups have applied the Birch reduction¹⁴ on carbon materials, first using graphite and carbon nanotubes, and in later attempts with graphite oxides towards the production of reduced graphenes and hydrogenated graphenes.^{4-8,15-17} More importantly, however, a closer look reveals that much variation exists between the choice of alkali metals and also the use of alcohols or water as the proton source, and different outcomes could result from these choices.

Thus, the effectiveness of (1) various alkali metals (as electron sources) and, (2) quenching agents (as the proton sources) in the Birch reduction method were studied. This is a continuation of the study in Chapter 10 employing sodium in liquid ammonia and quenching with methanol.⁶ It was then observed that utilizing parent Hofmann graphite oxide¹⁸ produces the most hydrogenated graphene, but the extensive hydrogenation led to strong photoluminescence within its Raman spectra preventing accurate elucidation of structural information.⁶ The Hummers graphite oxide¹⁹ was thus employed instead in this investigation. The alkali metals, namely, lithium, sodium, potassium, and caesium were dissolved in liquid ammonia and used as the reducing agent, while *t*-BuOH, *i*-PrOH, MeOH, and water were employed as quenching agents supplying protons for the consequent hydrogenation. The procurement of reactive

Group I metals is typically challenging due to their high instabilities and explosive natures as they are exposed to water.²⁰ The high reactivity of caesium is documented by its violent reaction in contact with graphite oxide due to remaining traces of water and oxygen functional groups. With safety considerations in mind, *t*-BuOH was employed as the quenching agent when investigating the effects of the different alkali metals on the efficiency of the hydrogenation of GO. Sodium is then used with liquid ammonia, based on the traditional reduction procedure reported by Birch,¹⁴ while the quenching agent is varied using different alcohols and water. The extent of hydrogenation is strongly dependent on the activity of the proton source in liquid ammonia, and slow reactions may be expected to lead to a higher degree of hydrogenation. This is clearly demonstrated on water which has low solubility in liquid ammonia at the reaction temperature and most of it freezes out. The hydrogenation efficiencies are then evaluated by infrared spectroscopy and elemental combustion analysis, and their material properties further characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Raman spectroscopy. Finally, we employ cyclic voltammetry to assess hydrogenated graphenes for potential use as electrode materials and discuss the hydrogenation extent in line with the observed heterogeneous electron transfer (HET) rates.

11.2. Results and Discussion

Of the numerous materials characterization techniques available, few are suited for the quantification of hydrogen contents or even qualitative identification of the extent of hydrogenation.^{9,21} Typically, the two accessible methods that yield such insight are infrared spectroscopy, which provides qualitative confirmation of C-H bond formation, and elemental combustible analysis giving the actual amount of hydrogen

within a material. Hence, we first attempted to observe the presence of the hydrogenated carbon backbone after Birch reduction treatment with the various electron and proton sources. Figure 11.1 shows the Fourier-transform infrared (FTIR) spectra of hydrogenated graphenes with commonly seen peaks from 1000 cm^{-1} to 1300 cm^{-1} due to a combination of C-C and C-O stretches from sp^3 hybridised carbons and small amounts of residual hydroxyl and epoxyl functionalities.^{11,22,23} Other peaks include the characteristic carbonyl C=O peak at 1720 cm^{-1} and those at 1570 cm^{-1} and approximately 1600 cm^{-1} arising from aromatic C=C stretches and H_2O bending modes, respectively.²⁴ The notably smaller C=O peak compared to the more intense C=C stretch is supportive of an effective removal of oxygen groups as these peaks usually appear with comparable intensities in their parent graphite oxides.^{23,24} Also, a broad but indistinct O-H peak around 3300 cm^{-1} occurs due to the presence of hydroxyls.²⁵ Nonetheless, our primary interest is in the C-H stretches at 2850 cm^{-1} and 2950 cm^{-1} whose presence effectively confirms a successful hydrogenation of the sp^2 carbon backbone.^{4,6,8,15} The strong intensities of C-H stretching modes indicate high concentrations of hydrogenated carbon atoms where CH_2 or even some CH_3 functional groups can be formed. This is observed only in samples with the highest degrees of hydrogenation and may further indicate a higher density of defects. It is in good agreement with results obtained by Raman spectroscopy where higher I_D/I_G ratios are observed. In the case of samples with highest degree of hydrogenation we can also observe C-H bending vibrations at $1400\text{-}1500\text{ cm}^{-1}$. In Figure 11.1a for hydrogenated graphenes produced with *t*-BuOH and varying alkali metals, both the lithium and sodium hydrogenated graphenes showed small peaks while the potassium produced material demonstrated the most intense adsorption from its C-H bonds in contrast to all other stretches. Only the material produced with caesium did not exhibit any discernible C-H

bands. Next, when a comparison is made between hydrogenated graphenes from various proton sources but with sodium fixed as the electron source, small absorptions from C-H stretches are seen with all three alcohols used. In contrast, a strong symmetric C-H absorption at 2850 cm^{-1} was observed with the Na, H_2O hydrogenated graphene and a much less intense asymmetric stretch at 2950 cm^{-1} .²⁶ Upon changing the metal to potassium with H_2O , however, the resultant hydrogenated graphene again exhibited both C-H stretches with high intensities. Hence, preliminary data based solely on FTIR suggests that the highest hydrogenation efficiency was obtained using potassium and water as electron and proton sources, respectively.

Figure 11.1. ATR-FTIR spectra of hydrogenated graphenes; **(a)** group I metal (electron source) series, **(b)** quenching agent (proton source) series.

Combustion analysis was subsequently performed to obtain the exact hydrogen contents within each material. Table 11.1 summarises the elemental compositions of all of the hydrogenated graphenes. Scrutinizing the hydrogenation efficiencies from different alkali metals, we note that the residual oxygen contents are very low in comparison to the parent Hummers GO with oxygen typically at about 50 at.%,²³ in support of an effective de-oxygenation of inherent oxygen groups. Interestingly, the de-

oxygenation is best with lithium and the residual oxygen increases in the order $\text{Li} < \text{Na} < \text{K} < \text{Cs}$. The hydrogenation extent roughly follows the opposite trend with the least hydrogen at 21.17 at.% in the (Li, *t*-BuOH) material and a high of 33.60 at.% for the (K, *t*-BuOH) H-rGO. The caesium reduced graphene showed the poorest hydrogenation with only 16.12 at.% H. As both its amounts of oxygen and hydrogen are comparable, we cannot exclude the possibility that they exist together with some groups in the form of hydroxyls. The other H-rGOs within the electron source series have considerably more hydrogen than oxygen signifying chemisorption directly onto the original sp^2 graphitic structure. The overall trend further agrees with FTIR data, and the (K, *t*-BuOH) hydrogenated material has the lowest carbon to hydrogen ratio with a formula of $\text{C}_{1.7}\text{H}_1\text{O}_{0.3}$.

Table 11.1. Elemental compositions of hydrogenated graphenes based on combustion analysis.

Treatment	General	Atomic Percentage %				
	Formula	C	H	O	N	S
Li, <i>t</i> -BuOH	$\text{C}_{3.4}\text{H}_1\text{O}_{0.3}$	72.00	21.17	6.39	0.44	0.00
Na, <i>t</i> -BuOH	$\text{C}_{3.0}\text{H}_1\text{O}_{0.3}$	69.78	23.00	6.77	0.45	0.00
K, <i>t</i> -BuOH	$\text{C}_{1.7}\text{H}_1\text{O}_{0.3}$	56.11	33.60	9.90	0.39	0.00
Cs, <i>t</i> -BuOH	$\text{C}_{4.1}\text{H}_1\text{O}_{1.0}$	66.65	16.12	16.39	0.83	0.00
Na, <i>i</i> -PrOH	$\text{C}_{4.2}\text{H}_1\text{O}_{0.6}$	72.10	17.20	10.37	0.32	0.00
Na, MeOH*	$\text{C}_{4.8}\text{H}_1\text{O}_{3.0}$	54.30	11.42	34.07	0.21	0.00
Na, H_2O	$\text{C}_{1.4}\text{H}_1\text{O}_{0.3}$	52.94	37.26	9.62	0.18	0.00
K, H_2O	$\text{C}_{1.6}\text{H}_1\text{O}_{0.1}$	58.78	35.87	5.13	0.22	0.00

*Data reproduced from Ref. 6.

Unlike the electron source series, the hydrogenation trend is less obvious with the proton sources. H-rGOs produced from sodium but with different alcohols show comparatively low amounts of hydrogen with the carbon to hydrogen ratios above 3. However, when water was used as the proton source instead, the efficacy dramatically improves to give the highest hydrogenation extent obtained of the studied materials with a ratio of 1.4 carbon atoms to every hydrogen atom. This is comparable to the most extensively hydrogenated graphene known currently with a formula of $C_{1.3}H_1$ reported by Billups.¹⁵ The small variation in the carbon-to-hydrogen ratio with our H-rGO is believed to be due to the minute presence of some residual oxygen groups considering our use of GO as starting material compared to graphite. Since potassium was found to be the most effective electron source, an additional investigation was performed using potassium and water, which attained an even lower oxygen content but with a marginally higher carbon-to-hydrogen ratio. Despite this, it must again be emphasized that some hydrogen could be bonded to oxygen groups instead of direct attachment on the graphene backbone, as is often overlooked in many reports. To obtain the true amount of chemisorbed hydrogen (existing as C-H bonds), the total oxygen quantity may be subtracted from the total hydrogen content to eliminate possible contribution from residual hydroxyls known to exist in GO,^{11,23,27-30} thus giving the *minimum* percentage of chemisorbed hydrogen. In this respect, there are two obvious conclusions; potassium gave the highest amount of C-H bonds between all *t*-BuOH quenched materials produced with the four electron sources at 23.70 at.%, secondly with sodium fixed as the electron source and varying the quenching agents, the (Na, H₂O) H-rGO gave the most chemisorbed hydrogen at 27.64 at.%. Combining the positive results of potassium and water then further increased the minimum C-H bond amount to 30.74 at.%. This high amount of direct C-H bonds is larger than in our previous report at 27.01 at.% for the

Hofmann GO reduced with Na/NH₃ and MeOH.⁶ Also, the nitrogen contents are insignificant at between 0.2-0.8 at.% despite the use of liquid ammonia, and sulphur is absent entirely although concentrated sulphuric acid played a major role as intercalant during the oxidation of graphite to GO.

With the above evidence proving effective hydrogenation of reduced graphenes, other material properties of the H-rGO materials are evaluated. XPS is a surface-sensitive technique suited to probing the surface elemental compositions of carbon-based materials.³¹ From Figure 11.2, all hydrogenated graphenes demonstrated substantial deoxygenation of surface oxygen functionalities with the exception of (Cs, *t*-BuOH) H-rGO. This is seen from the high carbon to oxygen ratios (C/O ratio) calculated from the relative peak intensities of the carbon 1s to oxygen 1s peaks. With the parent Hummers GO exhibiting a low surface C/O ratio at typically 2.0 to 2.1,^{23,29} this value increases to above 9.3 for (Na, MeOH) H-rGO, and up to the highest of about 12 for reductions employing potassium metal as the electron source. The disappearance of carbon-to-oxygen bonding modes near 286.4 eV within the high resolution C 1s spectra again confirms the deoxygenation process,¹⁶ and EDS mappings show only a limited and dispersed distribution of oxygen groups. We may also note from XPS that the H-rGOs produced are generally clean and largely free of the alkali metals or residual nitrogen employed during the Birch procedure; only indistinct peaks from nitrogen, lithium and caesium are observed in their respective materials in Figure 11.2.

Figure 11.2. Wide-scan X-ray photoelectron spectra of hydrogenated graphenes prepared from the Birch reduction/hydrogenation of graphite oxide with (a) different alkali metals (electron sources) and (b) quenching agents (proton sources).

The surface morphologies of H-rGOs were also investigated by SEM as in Figure 11.3. All materials display characteristic wrinkled surfaces due to expansion of the hydrogenated graphene sheets, therefore indicating their exfoliation.^{32,33} In some cases, such as in the (Na, *i*-PrOH) and (K, H₂O) H-rGOs, it is possible to observe separation of actual graphene layers indicated by white arrows. Additional structural information may

also be elucidated from their Raman spectra. As illustrated in Figures 11.4a and b, main features of the Raman spectra of H-rGOs are the D (disorder) band at 1350 cm^{-1} from an A_{1g} breathing mode due to sp^3 defects, and the E_{2g} mode from pristine sp^2 regions at *ca.* 1560 cm^{-1} denoted as the G (graphitic) band.³⁴ Also observed are the 2D peak close to 2650 cm^{-1} , and the D+D' phonon mode at 2890 cm^{-1} . The relative intensities of the D to G bands (I_D/I_G ratio) are also calculated which represent the density of defects (Figures 11.4c and d), and a higher ratio signifies a larger extent of sp^3 carbons as a result of hydrogenation or edge-like defects originating from graphite oxidation. The trend for I_D/I_G ratios of the alkali metals is seen to decrease only slightly down the group from a high of 1.17 for (Li, *t*-BuOH) H-rGO to 1.13 for (K, *t*-BuOH) H-rGO. (Cs, *t*-BuOH) H-rGO however has a distinctly low ratio of 0.90 in agreement with its poorest hydrogenation. I_D/I_G ratios in comparison are largely invariant for Na/NH₃ H-rGOs reduced with different proton sources. Only the (K, H₂O) H-rGO showed an unusually high ratio of 1.26, due to its high hydrogenation extent but also possibly from the reactivity of K/NH₃ and water during quenching. This is in good agreement with FTIR spectroscopy where the intensity of C-H stretching bands in highly hydrogenated samples suggests presence of CH₂ functional groups both at the edges and on the basal plane. The I_D/I_G ratio is further useful in its employment to subsequently obtain crystallite sizes of the hydrogenated graphenes.³⁵ The average sp^2 crystallite size (L_a) may be estimated by applying the equation:

$$L_a = 2.4 \times 10^{-10} \times \lambda_{\text{laser}}^4 \times I_G/I_D$$

where λ_{laser} is the wavelength of the excitation laser at 514.5 nm and I_G/I_D is the inverse of the I_D/I_G ratio. As such, the trend runs opposite from the I_D/I_G ratio with (Cs, *t*-BuOH) H-rGO exhibiting the largest sp^2 crystallites of $\sim 18.8\text{ nm}$ and the smallest with (K, H₂O) H-rGO at 13.3 nm .

Figure 11.3. Scanning electron images of hydrogenated graphenes as prepared from the Birch reduction/hydrogenation of graphite oxide with different alkali metals (electron sources) and quenching agents (proton sources). Scale bars represent 100 nm (left panels) and 1 μm (right panels). Arrows indicate the direction parallel to exfoliated graphene layers wherever they are observed.

Figure 11.4. (a-b) Raman spectra of hydrogenated graphenes as prepared from the Birch reduction/hydrogenation of graphite oxide with different alkali metals and quenching agents; relative intensity ratios of the D band to G band and corresponding crystallite sizes of hydrogenated graphenes produced with (c) different alkali metals and (d) different quenching agents. $\lambda_{\text{laser}} = 514.5$ nm. Error bars denote the standard deviation based on five measurements.

In contrast to the low defect density of pristine graphite, GO is considerably expanded from intercalation and also contains large amounts of surface oxygen functionalities.^{30,36} Although the subsequent reduction removes most of its oxygen groups, edges and edge-like defects remain present afterwards. Thus an advantage of

employing GO as opposed to graphite as the parent material for the Birch hydrogenation procedure is its high density of defects present in the hydrogenated graphene product, since such defects are known to be catalytic³⁷⁻⁴⁰ due to higher electronic density of states (DOS).^{41,42} In addition to the edges, hydrogenated carbon materials including hydrogenated graphenes are also shown to exhibit improved electrocatalysis towards certain redox species,^{11,43,44} due at least in part to the replacement of oxygen-terminated edges with comparatively stable C-H bonds. Consequently, the heterogeneous electron transfer rate at H-rGOs are investigated with ferrocyanide as an inner-sphere probe.^{45,46,47} Cyclic voltammograms are presented in Figures 11.5a and b for the various electron and proton sources, respectively. Of these, the lithium hydrogenated graphene demonstrated the fastest observed HET rate constant (k_{obs}^0) of $3.8 \times 10^{-3} \text{ cm s}^{-1}$. It is noted however that no obvious dependence exists between the alkali metals employed for the Birch reduction and the observed peak-to-peak separations (ΔE_p) for the ferro/ferricyanide redox couple (Figure 11.5c). Instead, a decreasing trend for ΔE_p was seen for the proton sources from $t\text{-BuOH} > i\text{-PrOH} > \text{MeOH} > \text{H}_2\text{O}$, corresponding to a quasi-reversible k_{obs}^0 of $2.6 \times 10^{-3} \text{ cm s}^{-1}$ for the (Na, H_2O) H-rGO (Figure 11.5d). This is significantly faster than the observed value for bare glassy carbon electrodes at $4.4 \times 10^{-4} \text{ cm s}^{-1}$.

Figure 11.5. Cyclic voltammograms of 10 mM $\text{Fe(CN)}_6^{3-/4-}$ on hydrogenated graphenes prepared from the Birch reduction/hydrogenation of graphite oxide with **(a)** different alkali metals and **(b)** quenching agents. Voltammogram for bare glassy carbon electrode is also shown for comparison. Peak separations (ΔE_p) of the ferro/ferricyanide redox couple observed on hydrogenated graphenes prepared using **(c)** different alkali metals and **(d)** quenching agents. Error bars represent the standard deviation based on triplicate measurements. Conditions: 50 mM PBS, pH 7.2, $\nu = 100 \text{ mV s}^{-1}$, potentials are with respect to the Ag/AgCl reference electrode.

The residual oxygen content, defect density and hydrogenation extent all impact the observed HET at hydrogenated graphenes.¹¹ Hence, not one factor can singularly influence the resulting HET rate. Within the convoluting effects, some insights may nevertheless be gained from inspection of the trend for the various proton sources. HET rates improve for the sodium reduced graphenes from *t*-BuOH to H_2O , which approximates the slight decrease in the I_D/I_G ratio. This may be explained since a

material with a low I_D/I_G ratio has less defects that damage the conjugated sp^2 carbon network that in turn confers graphene its intrinsically high electronic conductivity. It is thus probable that (Na, H_2O) H-rGO has a faster HET rate than the (K, H_2O) material as a result of its lower I_D/I_G ratio, which is also in agreement with our calculations showing a greater extent of C-H bonds directly on (K, H_2O) H-rGO. While partially hydrogenated graphene is a tunable bandgap semiconductor,⁴⁸⁻⁵¹ fully hydrogenated graphene (*ie.* graphane) is an insulator with a large bandgap of up to 5.4 eV close to that of diamond due to complete loss of its conductive sp^2 graphitic network.^{10,50,52} Hence in this regard, partially hydrogenated graphene would in fact be preferable to perfect graphane especially for electrochemical applications since electrical conductivity and other properties⁵³ may be lost should complete hydrogenation be achieved.

11.3. Conclusions

A systematic investigation of the Birch reduction/hydrogenation of graphite oxide is accomplished in this study with variation of electron sources (*ie.* alkali metals) and proton sources (*ie.* alcohols or water as quenching agent). Water performed best as the quenching agent with the highest extent of direct hydrogenation obtained with potassium and water. Although the GO reduced with Na and quenched with water gave the lowest carbon-to-hydrogen ratio with a composition of $C_{1.4}H_1O_{0.3}$, (K, H_2O) hydrogenated graphene demonstrated the highest extent of direct hydrogen chemisorption on the carbon lattice with a minimum of ~ 31 at.% C-H bonds. It is further noted that this calculation to eliminate the contribution of oxygen-bonded hydrogen is often overlooked in previous reports. It is also postulated that extensive hydrogenation might inadvertently disrupt the sp^2 conjugation resulting in lower electrical conductivity. This is in spite of hydrogenated carbons exhibiting potentially improved heterogeneous

electron transfer rates towards some analytes. Therefore, there exists a delicate balance between the hydrogenation extent and the observed HET rate at their surfaces. For the purposes of application as electrode materials, hydrogenated graphenes should generally have a low oxygen content and high defect density, but only a moderately high hydrogenation extent. This intricate relationship between the amount of hydrogenation and the HET rate may possibly extend to other interesting properties of hydrogenated graphenes such as ferromagnetism and/or fluorescence, and should therefore warrant further studies towards such intended applications.

11.4. Detailed Experimental Procedures

Reduction of graphite oxide with alkali metals in liquid ammonia (Birch reduction)

The hydrogenation/reduction procedure was performed based on a previously reported protocol.⁶ The reduction of GO with alkali metals in liquid ammonia was performed under argon atmosphere. For the cooling of reflux condenser a dry ice-acetone mixture was used. 180 mL of ammonia was condensed in 250 mL flask equipped with magnetic stirrer together with 250 mg of GO and 0.2 mol of alkali metal. The reaction mixture was vigorously stirred under ammonia reflux for 2 hours. Subsequently, 0.1 mol of a proton source (water, alcohol) was added throughout the course of 30 minutes. The reaction mixture was further stirred and refluxed for 2 hours. A second portion of proton source (0.1 mol) was then added over a period of 30 minutes. After 30 minutes of stirring the mixture under reflux the remaining alkali metal was decomposed using similar proton source (added till the blue color of solvated electron in ammonia disappears). Water was added to the reaction mixture (to fill 250 mL flask) and ammonia is left to evaporate overnight. The reduced/hydrogenated graphene is filtered out using a nylon membrane (0.45 μm) and washed several times with water and methanol and

dried under vacuum for 48 hours at 50 °C. In the case of synthesis using caesium for hydrogenation, a 10 times smaller mass of all compounds were used and synthesis was performed in 50 ml of liquid ammonia.

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Part III

Chapter 12 –

Facile Labelling of Graphene Oxide for Capacitive Energy Storage and Fluorescence Applications

The results and discussion presented in this chapter were published in the following journal article:

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12.1. Introduction

In light of the plentiful reactive oxygen functionalities available in GO, we exploit these moieties to enhance the electrical conductivity, capacitive charge storage, and fluorescence of GO together. The rational design of such a multifunctional GO material is performed by a facile one-step labelling reaction with 1,2-phenylenediamine (PD). PD labelling of GO to PD-GO creates new aromatic phenazine adducts^{1,2} at the sheet edges (Scheme 12.1) upon reaction with the *o*-quinone moieties present in GO.^{3,4} This firstly increases the overall electrical conductivity of the material. Furthermore, the specific capacitance increases by more than two orders of magnitude, from pseudo-capacitance of the phenazine adducts.^{1,2} Fluorescence is also observed from the labelled GO, as a result of changes brought about by the labelling of edge sites and also other reactive groups^{5,6} on the basal plane such as the epoxyls in large abundance.

Scheme 12.1. Synthetic labelling of the various graphene oxide inherent functional groups with 1,2-phenylenediamine (PD), both at the basal plane and edges.

12.2. Results and Discussion

We first investigated the process of graphene oxide labelling with PD in terms of its chemical nature using X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS), while structural morphology was probed using a combination of Raman spectroscopy and scanning transmission electron microscopy (STEM). As seen in Figure 12.1a, wide-scan XPS shows only carbon-1s and oxygen-1s peaks present in the

parent GO with a carbon-to-oxygen (C/O) ratio of 2.65 that is typical of most GOs.^{7,8} The C/O ratio increases to 5.61 after PD labelling, and now includes a new nitrogen-1s peak at 4.93 at.%. The concomitant decrease in oxygen content agrees well with the reaction scheme involving a hydrolysis reaction between PD and *o*-quinonyls, and also nucleophilic acyl substitution on carboxyl sites with the loss of water. It is also important to highlight that the labelling procedure does not constitute a reduction of GO as the C/O ratio of PD-GO remains low, in contrast to a much higher 10.3 for the case of reduced-GO.⁸ Examining changes to the carbon-1s XPS region in Figure 12.1b, we note a significant decrease in the C-O and C=O contributions at approximately 286.3 eV and 287.4 eV corresponding to the PD reaction with epoxide and carbonyl groups, respectively.^{7,9} High resolution scans of the nitrogen-1s region possesses two characteristic peaks at *ca.* 398.5 eV from pyrazine nitrogen confirming the labelling of *o*-quinones, and at 400 eV from arylamine produced upon epoxy and carboxylic functionalization.^{10,11} Additionally, we confirm that non-specific adsorption does not occur from further control experiments with nitrobenzene.¹² Hence, these data provide definitive proof for covalent labelling between PD and the individual functional groups in GO. From STEM imaging (Figure 12.1c), it is observed that the mild labelling procedure did not have considerable effect on the structure of large GO sheets. Subsequently, EDS mapping analysis corroborates the XPS results confirming only carbon and oxygen in the parent GO, and also the appearance of nitrogen throughout the basal plane of PD-GO indicating a successful labelling reaction.

Figure 12.1. Structural and chemical analysis of graphene oxide before and after chemical labelling with PD. **a)** Wide-scan X-ray photoelectron spectra of parent GO and PD-GO (Inset: high resolution scan of nitrogen 1s region); **b)** high resolution carbon 1s spectra of parent GO and PD-GO; **c)** scanning transmission electron micrographs with elemental mapping from energy-dispersive X-ray spectroscopy of parent GO and PD-GO.

Consequently, a comparison of electrical conductances between the parent and labelled PD-GO was performed. From the current-voltage curves of the materials performed on interdigitated gold electrodes (Figure 12.2a), both materials exhibited near-ideal Ohmic behavior with curves close to linearity. The I - V slope of GO is

expectedly low with an average conductance of just 8.24×10^{-4} mS. PD-GO in contrast demonstrated an improved conductance by almost three orders of magnitude to 0.185 mS. This change is corroborated with optical darkening of PD-GO as seen in Figure 12.2b. Also, the improved conductance of PD-GO is still lower than that of chemically-reduced GO (~ 75 mS) indicating that surface functionalities remain intact.¹³ Although the true conductivity was not measured in this instance, we can infer the improved electrical conductivity of PD-GO relative to its parent based on its significantly larger conductance.

Figure 12.2. **a)** Current-voltage curves of the parent GO and PD-GO as measured on interdigitated gold electrode. Inset: Comparison of electrical conductance. Error bars represent the standard deviation based on triplicate measurements. **b)** Dispersions of parent GO and PD-GO in *N,N*-dimethylformamide at 0.1 mg mL^{-1} , with optical darkening observed after PD-labelling.

With affirmation of the conductivity of PD-GO, we next investigate its capacitive storage ability by first employing the cyclic voltammetry technique in aqueous 6 M KOH electrolyte. Figure 12.3a illustrates the difference in capacitive voltammograms obtained for GO before and after labelling at 0.1 V s^{-1} . The parent GO only exhibits a very small

capacitance of approximately $1\text{--}2\text{ F g}^{-1}$ similar to a previous report (0.9 F g^{-1}),¹⁴ and remains relatively constant at varying scan rates (Figure 12.3b). In terms of wave shape, both the parent GO and PD-GO demonstrate typical wide rectangular-shaped voltammograms characteristic of electrochemical double layer capacitors (EDLCs) but with deviations which indicate additional pseudo-capacitive contributions^{15,16} from their inherent oxygen functionalities. Closer inspection of PD-GO voltammograms also reveals a set of Faradaic redox peaks at -0.4 V and -0.55 V vs. Ag/AgCl, and most likely arise from labelled phenazine adducts at the sheet edges as they correspond to previously reported potentials.^{1,2} No obvious effect was seen when the charging rate was varied as with the case of the GO parent (Figure 12.3c). Galvanostatic cycling was next employed to study the labelled GO, as seen in Figure 12.3d at increasing current densities. PD-GO displayed expected EDLC-type triangular-shaped charge/discharge cycles, with tapering of the charging potential occurring only at the lowest 0.2 A g^{-1} current density used, likely as more pores are accessed by the electrolyte. At this current density, PD-GO exhibits a far superior capacitor ability compared to the parent GO with a high specific capacitance of 191 F g^{-1} . This is two orders of magnitude greater than parent GO measured at 1.37 F g^{-1} , and is also considerably larger than other graphene-type materials,¹⁴ including graphite microparticles (0.88 F g^{-1}), chemically-reduced graphene (1.14 F g^{-1}), and even thermally-reduced graphene (26.1 F g^{-1}) with its characteristically large specific surface area. The capacitance of PD-GO was also observed to be larger than the 169 F g^{-1} value recently reported for a high surface area binder-free graphene supercapacitor in the same electrolyte.¹⁷ Hence, the idea of enhancing GO pseudo-capacitance may very well be a viable approach for supercapacitor design in addition to the more common approach of increasing the surface area of graphene, on condition that the electrical conductivity of GO is also improved.

Figure 12.3. Supercapacitor performances of parent GO and PD-GO in 6 M KOH. **a)** Cyclic voltammograms of parent GO and PD-GO at 100 mV s⁻¹ (boxed regions indicate pseudocapacitance of benzophenazine adduct after PD labelling); **b)** voltammograms of parent GO at varying scan rates; **c)** voltammograms of PD-GO at varying scan rates; **d)** galvanostatic charge-discharge curves of PD-GO at varying current densities; **e)** specific capacitance; and **f)** surface-normalized capacitance of parent GO and PD-GO at varying current densities.

We then further evaluated the *rate performance* of the capacitor for a consistent comparison with other previously studied materials.¹⁸ The specific capacitance of PD-GO follows the expected decrease as current density is increased (Figure 12.3e). However, the capacitance is maintained at a relatively high value of 162 F g⁻¹ when measured with a 10-fold higher current density at 2.0 A g⁻¹. This translates to an 85% capacity retention to the 191 F g⁻¹ at 0.2 A g⁻¹. The retention is similarly high at 83% comparing between the measured capacitances at 0.5 A g⁻¹ and 5.0 A g⁻¹, thus signifying the excellent rate capability of PD-GO.

Considering that surface areas can have a major influence on the gravimetric capacitance, normalization of capacitances was also done to the Brunauer-Emmett-Teller (BET) surface areas based on nitrogen adsorption isotherms (Figure 12.4a). The BET surface area of the parent GO was determined to be $96.9 \text{ m}^2 \text{ g}^{-1}$, and interestingly decreased to $30.4 \text{ m}^2 \text{ g}^{-1}$ for PD-GO. Nevertheless, the smaller surface area is a likely outcome of sheet re-stacking from stronger overall van der Waals forces resulting from PD-labelling. As such, the surface area-normalized capacitance of PD-GO was found to be a large $628 \text{ } \mu\text{F cm}^{-2}$ compared to just $1.42 \text{ } \mu\text{F cm}^{-2}$ for the parent GO. This is juxtaposed to a low theoretical intrinsic capacitance for single-layer graphene¹⁹ and empirically-determined for reduced graphene,¹⁷ both in agreement at approximately $21 \text{ } \mu\text{F cm}^{-2}$. We also considered the possibility that differences in pore-size may have resulted in the increased capacitance of PD-GO,^{20,21} and further investigated their pore-size distributions (Figure 12.4 c-d). Both the parent and PD-GO were found to consist primarily of narrow meso-pores (2-50 nm) with a maximum pore width close to 3 nm and increasing to 10 nm. However, only the parent GO contained micro-pores (< 2 nm) and these are absent in PD-GO, likely due to PD functionalization at oxygen groups which typically decorate the boundary of vacancies and edge-like defects. Thus in spite of the pore size effect of ion desolvation in carbon micro-pores known to result in larger specific capacitance,^{20,21} the capacitance of parent GO still remained lower than PD-GO. In summary, parent GO capacitance remained low notwithstanding a higher surface area, micro-pore structure and its numerous inherent oxygen functionalities. Hence, the superior PD-GO capacitance must therefore arise from a combination of pseudo-capacitance from newly labelled moieties (*e.g.* phenazine) and the restoration of electrical conductivity.

Figure 12.4. (a) N₂ adsorption/desorption isotherms of parent GO and PD-GO, (b) Brunauer-Emmett-Teller (BET) plots of parent GO and PD-GO; (c-d) cumulative surface area and differential pore areas of parent GO and PD-GO, respectively (N₂ at 77 K). Detailed procedures are described in Chapter 3, page 56.

GO is also unique in its ability to exhibit fluorescence over a range of wavelengths under different environments; factors influencing these properties include size of sp² domains, size confinement effects (e.g. quantum dots), defect sites, or functionalities.^{22,23,24} Figure 12.5a shows the excitation-emission map of the parent GO which displays no fluorescence except for a broad emission band from 420 nm to 540 nm that is also observed in PD-GO (Figure 12.5b). Control experiments using pure DMF and PD in solution confirm the origin to be from GO itself. More prominently, no emission near 500-600 nm was seen when excited in the near-UV or visible regions, as observed by some reports on GO.^{25,26} In the labelled PD-GO however, fluorescence was observed when excited at several wavelengths but only emitted over a single broad band from 460 nm to 640 nm (Figure 12.5b). A greenish glow was observable when the

PD-GO dispersion was irradiated with UV light at 365 nm (Figure 12.5c). The lack of such fluorescence in the control GO (prepared under similar reaction conditions without PD addition) confirm PD-labelling to be responsible. When excited at 290 nm and 430 nm in Figure 12.5d-e, PD-GO displays a broad peak with a same maximum at 540 nm for both excitation wavelengths.

Figure 12.5. Fluorescence of parent GO and PD-GO in *N,N*-dimethylformamide at 0.1 mg mL^{-1} . Dependence of fluorescence on wavelength of the excitation light for **a)** parent GO, and **b)** PD-GO. High intensity lines are due the scattering of excitation light and the second order diffracted beam. **c)** Dispersions of parent GO (left) and PD-GO (right) under illumination from a 365 nm UV light source. Emission spectra of parent GO and PD-GO at **(d)** 290 nm and **(e)** 430 nm excitation wavelengths.

We consequently investigated the origin for fluorescence in PD-GO, particularly the localisation of sp^2 domains which is a generally accepted mechanism for graphene fluorescence.^{22,25,27,28} Gradient centrifugation of the GO dispersions was first performed

(at increasing speeds of 1000, 3000, 6000, and 9000 rpm) to separate the sheets into their various sizes. Again, only PD-GO showed fluorescence and the smallest PD-GO sheets from the 9000 rpm supernatant exhibited strongest fluorescence intensities in the green visible region. Their morphology appeared as few-layered stacks of highly fragmented sheets, with the smallest disk-shaped fragments down to approximately 50 nm in diameter (Figure 12.6f). The smallest parent GO sheets which did not exhibit any fluorescence are instead considerably larger of up to a few hundred nanometres across (Figure 12.6d). Both parent GO and PD-GO precipitates from 1000 rpm centrifugation (Figure 12.6c and d) were large multi-layered sheets a few micrometres wide. Additional structural information was also gleaned from Raman spectroscopy in Figure 12.6a-b, with the D (disorder) band at *ca.* 1350 cm⁻¹ from an A_{1g} breathing mode arising from sp³ defect sites while the G (graphitic) band occurs near 1560 cm⁻¹ due to an E_{2g} mode from pristine sp² hybridised regions.²⁹ The ratio of the D to G bands (*I_D/I_G* ratio) in Figure 12.6g then provides an indication on the amount of sp³ defects, with larger ratios signalling less pristine sp² structures. Thus, the average sp² crystallite sizes (*L_a*) can be derived from the equation:³⁰

$$L_a = 2.4 \times 10^{-10} \times \lambda_{\text{laser}}^4 \times I_G / I_D$$

where λ_{laser} is the wavelength of the excitation laser at 514.5 nm, and *I_G* and *I_D* are the integrated intensities of the Raman G and D bands. As tabulated in Figure 12.6h, average *L_a* sizes were found to decrease after PD labelling: from 8.6 to 7.1 nm for large sheets in the precipitate, but more significantly from 9.7 to 6.0 nm in the smallest supernatant sheets. As such, both the smallest sp² crystallite and physical sheet sizes observed in PD-GO fragments strongly suggest that sp² domain localisation and size confinement of the sheets occurred due to functionalisation, thus resulting in the observed fluorescence. The observation is in line with the labelling process: while PD reacts at the edges with *o*-

quinones, it also reacts with epoxide and/or hydroxyl groups across the basal plane. Hydroxyl groups exist in clusters,³¹ while epoxyls are typically aligned and have been found to result in *unzipping* of the carbon basal plane.³² With its vicinal amines, PD can react with neighbouring hydroxyls on the same sheet or potentially between two different GO sheets. With such reactions occurring extensively across a sheet, one could envisage that warping of the sheet results,³² thus inducing strain on planar sp^2 domains scattered throughout. Moreover, both this induced strain and nucleophilic attack to epoxides could cause additional unzipping of the carbon sheet, as seen from the fragmentation that occurred (Figure 12.6f).

Figure 12.6. Raman spectra of the parent GO (a) and PD-GO (b); top spectrum corresponds to the precipitate after centrifugation at 1000 rpm for 20 mins and the bottom spectra is obtained from the supernatant after centrifugation at 9000 rpm ($\lambda_{exc}=514.5$ nm). Scanning transmission electron images of the parent GO precipitate (c) and supernatant (d), and PD-GO precipitate (e) and supernatant (f); Inset figures show

the particle dispersions under 365 nm UV light irradiation. Comparison of the D to G band intensity ratios from Raman spectra (**g**) and calculated sp^2 crystallite sizes (**h**). Error bars represent the standard deviation, $n = 5$.

The effect of size and fraction of sp^2 regions on the bandgap has been previously established, where the bandgap of the graphene material decreases with increasing size of an sp^2 cluster tending towards an approximate 2.1 eV for clusters of ~ 37 rings.^{24,27,28} For our case with PD-GO, the emission peak at ~ 540 nm corresponds to a bandgap of ~ 2.3 eV close to the calculation by Eda *et al.*²⁴ This is further supported by the similarity in fluorescence excitation and emission wavelengths from benzenediamine-functionalised graphene quantum dots at 410 nm and 502 nm respectively, and the red shift for PD-GO in the present case can be fittingly attributed to the larger π -conjugation system as we have seen.²⁷ The main difference however is that PD-GO undergoes excitation over both the UV and visible ranges, at the optimal wavelengths of 290 nm and 430 nm (Figure 12.5d-e). Nonetheless, if we consider that the phenazine moiety is itself a chromophore which also absorbs light at *ca.* 250 nm,^{33,34} we may postulate that these groups serve as additional sites for light absorption which are once again red shifted due to conjugation. Consequently, the energy is transferred to the emission sites²⁵ on PD-GO resulting in fluorescence at 540 nm. Hence, based on the similar 540 nm emission wavelength regardless of UV and visible excitations, we may conclude that it is from the same localised sp^2 regions that the fluorescence of PD-GO originates.

12.3. Conclusions

Chemical labelling of graphene oxide (GO) with 1,2-phenylenediamine (PD) produced a multifunctional GO material exhibiting supercapacitor ability in addition to

enhanced fluorescence. While many capacitor devices are based on EDLCs, an alternative approach was used in this study to enhance GO capacitance instead. The production of labelled PD-GO involves a fast and simple one-step GO functionalization that is cost-effective. A common problem of poor electrical conductivity in GO is also addressed. Effects such as surface area and pore-size were found to not have contributed to the large specific capacitance of PD-GO, but which arises from pseudo-capacitance of the phenazine groups after labelling. Interestingly, a yellow-green fluorescence was also observed, which we attribute to the effect of sp^2 domain localisation on the bandgap, and also UV absorbance of the phenazine adduct. The results suggest that future design of functionalized GO materials may similarly lead to their application in various diverse fields such as electronics and optical devices.

12.4. Detailed Synthetic Procedures

Labelling with 1,2-Phenylenediamine (PD)^{1,2}

GO (20 mg) was first dispersed in glacial acetic acid at 1 mg mL^{-1} concentration for 1 h with ultrasonication. In a second flask, 1,2-phenylenediamine (77 mg) was dissolved in EtOH (2 mL) and then added to the GO suspension. For the control experiment, only pure EtOH was added. The mixture was then stirred for 1 h at 95°C . The labelled GO was obtained by vacuum filtration and washed sequentially with EtOH, water, and ether, and the pH increasing to a final value of *ca.* 6. The labelled GO was lastly dried in a vacuum oven for 48 hours before usage. The above described synthetic procedure was the author's work.

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Part III

Chapter 13 –

Transition Metal Dichalcogenides as

Graphene Analogues –

Electrochemical Catalysis of the

Hydrogen Evolution Reaction

The results and discussion presented in this chapter were published in the following journal article:

1. Electrochemistry of Transition Metal Dichalcogenides: Strong Dependence on the Metal-to-Chalcogen Composition and Exfoliation Method.

A.Y.S. Eng, A. Ambrosi, Z. Sofer, P. Simek, M. Pumera. *ACS Nano* **2014**, 8, 12185.

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13.1. Introduction

In this fundamental study, we investigate the effects of chemical exfoliation on the consequent material and electrochemical properties of transition metal dichalcogenides (TMDs), namely MoSe_2 , WS_2 and WSe_2 . Additionally, their viability as electrocatalysts for the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) are examined. While butyl lithium (BuLi) is traditionally used in chemical exfoliation, little is understood regarding the effects of the accompanying alkyl moiety and its impact on the exfoliation. Thus, methyl lithium (MeLi) is alternatively employed and we evaluate its effectiveness. These treatments are illustrated in Scheme 13.1.

Scheme 13.1. Chemical exfoliation of bulk 2-dimensional layered MoSe_2 , WS_2 , and WSe_2 with organolithium reductants.

13.2. Results and Discussion

13.2.1. Chemical Exfoliation of Transition Metal Dichalcogenides

In line with the first objective of studying the exfoliation efficiency using different organolithium intercalants, we examine the surface morphologies of the products by SEM. Figure 13.1 shows the electron micrographs of the parent TMDs in comparison to their MeLi and BuLi exfoliated counterparts. In their bulk states, TMDs are observed as large polygonal stacks up to tens of microns across and with thicknesses in the range of a few hundred nanometers. With subsequent treatment using MeLi, the average flake

sizes of both tungsten dichalcogenides decreased, and WS_2 showed a noticeable representative expansion across its c-axis indicative of a successful intercalation. This was observed together with extensive wrinkling of the edges, likely formed as the result of the violent exfoliation process in water. MoSe_2 demonstrated a slight expansion of its layers but also some amount of exfoliation debris. As might be expected, BuLi exfoliation was observed to be most effective across all materials in contrast to MeLi, in line with its prior use in numerous chemical exfoliation procedures.^{1,2,3} Although MoSe_2 and WS_2 showed greater wrinkling and expansion across their layers, individual layers do not clearly delaminate and can remain as stacked macrostructures. In addition for MoSe_2 , the presence of surface oxides was found based on XPS data. A more obvious delamination of layers was achieved using BuLi in the case of WSe_2 , where straight-cut edges were observed with minimal longitudinal breakage of the sheets.

Figure 13.1. Scanning electron micrographs of MoSe_2 , WS_2 and WSe_2 in their bulk state (top), after treatment with methyl lithium (center) or butyl lithium (bottom), with

subsequent exfoliation in water. Scale bars represent 100 nm. White dotted arrows specify the direction parallel to sheets.

Raman spectroscopy was then exploited as a valuable tool in obtaining structural evidence of the layered TMDs after exfoliation treatment. Figure 13.2 displays the Raman spectra of both bulk and treated TMDs. Typical spectra for all materials consist primarily of two characteristic peaks; the Raman active in-plane E_{2g}^1 and out-of-plane A_{1g} modes which we denote based on the D_{6h} point group of the bulk material for consistency.^{4,5} Analysis of spectral characteristics for both vibrations consequently provides further information into their layered structures. While the in-plane E_{1g} mode is observed in all cases, its diagnostic value is comparatively limited.

Firstly for MoSe_2 , no significant changes in spectral features were seen after treatment with MeLi, but notable differences resulted with BuLi. Of note is the softening (4.6 cm^{-1}) and broadening (0.7 cm^{-1}) of the most intense A_{1g} line, which is correlated to the edges of individual layers.⁶ It is known that electron-doping results in our observed phenomena only for the A_{1g} phonon and not the E_{2g}^1 phonon which does not exhibit such a trend.^{7,8} Hence, this confirms that electron-donation from the C–Li bond to MoSe_2 had occurred with BuLi but not with MeLi.

Secondly for WS_2 , the broad trend observed is the lack of complete exfoliation of individual layers. An inspection of the E_{2g}^1 line reveals slight softening after treatment (2.3 cm^{-1}), with a clear increase in its full-width at half maximum (FWHM) from the bulk (9.0 cm^{-1}) to the MeLi (9.2 cm^{-1}) and BuLi-treated (13.5 cm^{-1}) materials, in agreement with earlier reports that the FWHM increases with a decreasing number of layers.^{9,10} However, the same trend was not paralleled for the A_{1g} line with no obvious changes in FWHM. More notable is the $I_{A_{1g}}/I_{E_{2g}^1}$ ratio which did not substantially decrease as is

expected if exfoliation had proceeded to give three layers or less.¹¹ Thus, both SEM and Raman spectroscopy suggest that while some intercalation may have indeed occurred with both organo-lithium treatments, there is as yet little evidence to confirm complete delamination of individual WS₂ layers.

Finally in the case of WSe₂, both E¹_{2g} and A_{1g} phonons are located in very close proximity at *ca.* 250 cm⁻¹ and 253 cm⁻¹.⁶ A principal phenomenon indicative of exfoliation is the splitting of the overlapping peak which occurs for flakes of three layers or less, with the maximum 11 cm⁻¹ splitting for a monolayer.¹² In the instance with BuLi exfoliation, the broad shoulder peak centered 11 cm⁻¹ higher than the main peak signifies that monolayer WSe₂ was indeed obtained. It is very likely that this splitting is obscured from the superimposed spectra of other few-layered structures, resulting in the observed shoulder. Additionally, the softening of the main peak (4.7 cm⁻¹) and its large increase in FWHM (3.3 cm⁻¹) compared to the bulk material further proves that exfoliation was achieved for WSe₂.

Figure 13.2. Raman spectra of MoSe₂, WS₂ and WSe₂ in their bulk state (top), after treatment with methyl lithium (center) or butyl lithium (bottom), with subsequent exfoliation in water. $\lambda_{\text{exc}} = 514.5 \text{ nm}$.

While insights were gained from microscopy and Raman spectroscopy, neither provides a truly quantifiable measure of exfoliation. Logically, the surface area is expected to increase after exfoliation, and it therefore serves as a good physical parameter to determine efficiency of exfoliation. Methylene blue adsorption has previously been employed for surface area determination of 2D layered materials, such as graphenes,¹³⁻¹⁵ and we now extend its application to include TMDs as a means to evaluate their exfoliation. As presented in Table 13.1, the measured surface area of each TMD is observed to increase considerably after MeLi treatment, but the highest values are only obtained with BuLi. Other key observations noted are: that the most significant increase in surface area is for MoSe₂ after BuLi exfoliation; and both MeLi and BuLi resulted in similar exfoliation extents for WSe₂. The overall conclusion is that the BuLi exfoliation route is most effective, and the different TMDs follow the order: MoSe₂>WS₂>WSe₂ from the highest to lowest surface area. Furthermore, the high surface area of BuLi-exfoliated MoSe₂ agrees well with colloidal MoSe₂ nanosheets determined using the BET method.¹⁶

Table 13.1. Surface area measurements based on methylene blue adsorption on MoSe₂, WS₂ and WSe₂ in solutions prepared from their bulk states and after treatment with methyl lithium or butyl lithium.

Treatment / Material	Surface Area (m ² /g)		
	MoSe ₂	WS ₂	WSe ₂
Bulk	1.6	7.0	2.0
MeLi-treated	23.1	9.5	16.8
BuLi-treated	50.7	30.6	16.7

To further understand the chemical changes associated with the structural transformations observed, we subsequently perform XPS to examine the surface elemental compositions and bonding information. We first study the bulk TMDs and Figure 13.3 illustrates the high resolution core-level Mo 3d and W 4f peaks. Deconvolution analysis of Mo bonding modes in bulk MoSe₂ shows a distinct pair of peaks (3d_{5/2} and 3d_{3/2}) originating primarily from the native semiconducting 2H phase in the (IV) oxidation state at *ca.* 229.5 eV and 232.5 eV.^{6,17,18} Although XPS is an indispensable technique for analysis of TMD elemental compositions, it is also important to emphasize that intricate factors exist, such as the close proximities in binding energies of different phases.¹⁹ Hence, the calculated atomic percentages reflect an overview of the relative changes in the materials as they undergo exfoliation, and individual values should not be interpreted as absolute quantities. In addition to the 2H phase, a small contribution of the 1T phase can also be found near 228.1 eV and 231.0 eV and a further pair from oxidized Mo(VI) species at approximately 232.7 eV and 235.8 eV. Similarly for the W 4f spectra of bulk WS₂ and WSe₂, three pairs of peaks indicate the major presence of the 2H phase (~33.2 eV and 35.3 eV), and also the 1T phase (~32.1 eV and 34.4 eV) and W(VI) oxidation state (~36.3 eV and 38.5 eV) in lesser concentrations.^{6,10,20} The 2H-polytype is dominant for all bulk TMDs at about 80 at.%, and is close to that for natural MoS₂ ore (molybdenite).²¹ At this point, it is enlightening to note that small amounts of the transition metals exist in the oxidized (VI) state even for native bulk TMDs. Particularly, the increasing oxidation of bulk TMDs from MoSe₂ < WS₂ < WSe₂ agrees with reported trends that selenides are more easily oxidized than sulfides²² and of tungsten over molybdenum dichalcogenides.²³

Moving to investigate the effects of organolithium chemical exfoliation, the most striking observation is in MoSe₂, showing a great increase in its Mo(VI) oxidation state

with exfoliation. The presence of the oxidized (VI) species increases significantly after treatment with MeLi, up to a maximum of 78 at.% with BuLi. As the concentration of the 1T phase remains fairly constant at about 12 at.%, it is possible that electron-doping of the original 2H phase *via* strong lithium-based reductants renders it unstable, leading to subsequent oxidation after atmospheric exposure. The surface Se/Mo atomic ratios were also seen to decrease considerably to only 0.7 after BuLi-treatment, indicating a chalcogen-deficient surface. This observation was not replicated in other TMDs which maintained their expected stoichiometric ratio at roughly 1:2. Moreover, both XPS and EDS also confirm a simultaneous increase in oxygen content. This trend is in direct opposition to the case of WS₂, where no significant oxidation of the material was discovered. Also, no substantial conversion of the 2H to 1T phase was measured after treatment with BuLi, though a marginally larger 1T content was obtained with MeLi.

The disparity in exfoliation effects of the TMDs is most obvious for WSe₂, as the only material showing a semblance of the 2H to 1T phase conversion known to occur in MoS₂ as a result of electron-doping.^{1,24} Peak deconvolution shows that the 1T percentage underwent a large increase from 2.6 at.% in the bulk to 66.7 at.% after exfoliation with BuLi. This conversion is seen from the experimental W 4f spectra, as denoted by the gradual shift of the main peaks towards lower binding energies: with respect to the W(VI) 4f_{5/2} peak with the highest energy at 38.5 eV, its separation to the main 4f_{5/2} peak increases in the measured spectra from ~3.3 eV for bulk WSe₂ to 3.7 eV with MeLi treatment, and 4.0 eV after BuLi treatment. Based on an earlier report,¹⁰ we identify that a measured separation of 4.0 eV exists between the 4f_{5/2} peaks of W(VI) and the 1T phase, while a smaller separation of ≤3.0 eV between the two 4f_{5/2} peaks denotes the presence of a 2H phase. Overall, the observed 0.7 eV shift of the main peaks concurs with a previous report attributing it to a change in the surface doping.²⁵

Figure 13.3. High resolution X-ray photoelectron spectra of Mo 3d and W 4f regions of metal dichalcogenides in their bulk state (top), after treatment with methyl lithium (center) or butyl lithium (bottom), with subsequent exfoliation in water. Deconvoluted peaks correspond to the metallic 1T phase (red), semiconducting 2H phase (blue), or the oxidized (VI) state (green).

Hence, all evidence firstly reveals that the effectiveness of methyl lithium is inferior to butyl lithium as the classical reagent employed for TMD exfoliation. Both tungsten dichalcogenides show no significant changes to their chemical composition after BuLi treatment and demonstrate a substantial expansion of its c-axis, but stops short of attaining actual detachment of layers in WS₂. MoSe₂ experienced the largest increase in surface area with BuLi-exfoliation but the treatment may have also resulted in its destabilization and consequent oxidation upon exposure to the environment.

13.2.2. Differences in Inherent Electrochemistry of Molybdenum vs. Tungsten Transition Metal Dichalcogenides

The achievements of MoS₂ as a viable catalyst for electrochemical applications such as hydrogen evolution drive the search for analogues amongst similar layered TMD materials. Along with their proliferation as catalysts in electrochemistry, it is essential to acquire fundamental knowledge of their inherent electrochemical properties, which are not well studied at present. Also, the impact of the chemical exfoliation treatments on the TMDs is examined. Towards these ends, we carry out a systematic investigation of the TMDs using cyclic voltammetry as a suitable technique for examining the electrochemistry of layered materials like graphenes²⁶ and TMDs.²⁷

The voltammograms of all bulk and exfoliated TMDs are displayed in Figure 13.4, each characterized by their distinctive oxidation peaks. Of note is the incidence of varying peak shapes and positions suggesting involvement of numerous species. Also, the inherent processes corresponding to these must involve chemically irreversible oxidations. This is evidenced in MoSe₂ by the large peaks observed during the initial oxidative sweep and which virtually disappear from subsequent scans. However for WS₂ and to a lesser extent in WSe₂, these peaks significantly diminish in height after the first oxidative sweep but broad peaks may still be observed even after two oxidation cycles. A further comparison with a previous report on MoS₂ shows that the recurrence of broad waves is likely characteristic only of tungsten and not molybdenum dichalcogenides, highlighting the possible difference in oxidation routes occurring between the two TMD elements.²⁸ It is also interesting to note an increase in oxidation potential in the order from WSe₂ < MoSe₂ < WS₂ < MoS₂. These dissimilarities must again originate from the different reactants and products involved during electrochemical oxidation, and the solubility of their products can also play an important role.²⁹ One possibility resulting in

this difference identified earlier from XPS is the larger presence of surface oxides in exfoliated MoSe_2 compared to similarly treated tungsten materials prior to any electrochemical treatment. XPS measurements after electro-oxidation confirm significant dissolution of MoSe_2 material with a corresponding decrease in the Mo(VI) signal. Tungsten dichalcogenides in comparison maintain similar compositions after electro-oxidation. Hence, the soluble products formed from MoSe_2 electro-oxidation are immediately lost, but small amounts of insoluble oxides remain on tungsten TMD surfaces after electrochemical treatment. Examples could include tungsten oxide precipitates reported in WSe_2 .²⁹ These could subsequently detach gradually during potential cycling especially from hydrogen evolution induced at negative potentials, and therefore appear as broad waves that decrease with each cycle. Considering the intrinsic HER catalytic activity of TMDs, it is also important to note possible delamination of surface material if strongly reducing potentials are applied.

Figure 13.4. Cyclic voltammograms illustrating inherent electrochemistry of transition metal dichalcogenides in their bulk states (a-c), and as exfoliated in methyl lithium (d-f) and butyl lithium (g-i). All scans start at 0.0 V vs. Ag/AgCl, and arrows indicate the

starting scan direction. First scans are labelled red, followed by second scans in blue and third scans in grey. Conditions: supporting electrolyte of 50 mM PBS at pH 7.2; scan rate: 100 mV s⁻¹.

We then scrutinized the significance of different peak potentials that occur for TMD electro-oxidations depending on exfoliation treatment. MoSe₂ voltammetry is found to depend strongly on whether it exists as the bulk material, after MeLi treatment, or after exfoliation with BuLi. With only few other reports on MoS₂ available,^{27,28,30} very little else is known about the general inherent electrochemistry of TMDs. They however cite typical oxidation processes analogous to those observed in our voltammetry of MoSe₂, WS₂ and WSe₂. In particular, two oxidation peaks were first reported by Chorkendorff *et al.*; a small peak at *ca.* 0.7 V and a notably larger peak at higher anodic potentials.²⁷ The two peaks were correlated to oxidation of the *edge* plane which requires a lower overpotential and oxidation of the *basal* plane that necessitates application of a higher potential.²⁹ It then follows that peak potentials should increase after exfoliation in our case as more basal plane surfaces are revealed, which is indeed the trend observed for both tungsten dichalcogenides. The same general trend follows for MoSe₂ only for voltammetric runs started in the anodic direction, with the exception of an unusually low oxidation potential of the MeLi-treated product. Such a negative effect from MeLi treatment, however, can arise from the passivation and inactivation of TMD layers due to by-products of the exfoliation reaction. The lithium intercalation mechanism is known to occur *via* a radical process, with lithium diffusion into the layers followed by combination of the corresponding radical moiety; the resulting butyl radical is observed to form octane as the final dimerization product in the BuLi case.^{1,31} It stands to reason that MeLi treatment correspondingly results in methyl radicals, but which are

considerably more reactive and are known to attack oxides particularly prevalent in exfoliated MoSe₂.³² Hence, the presence of more surface oxide in MoSe₂ inadvertently lends itself to passivation from MeLi.

This knowledge further explains differences in the oxidation potentials of MoSe₂ materials depending on whether an initial anodic or cathodic sweep (Figure 13.5) was performed; higher peak potentials are seen from a starting anodic scan for both forms of exfoliated MoSe₂, while the reverse is true for the bulk. We can infer from XPS that the initial reduction sweep causes surface oxides in MeLi and BuLi-exfoliated MoSe₂ to undergo dissolution. This then reveals the original underlying MoSe₂ surface as validated by the position of the Se 3d_{5/2} and 3d_{3/2} peaks (Figure 13.6) at 54 eV and 55 eV, respectively.^{6,18} Subsequent reversal of the potential sweep towards the anodic direction then results in a peak at approximately 0.6 V (Figure 13.5 d and g), and is thus likely to account for oxidation of MoSe₂ itself (Figure 13.6). This peak is always observed as a small pre-wave, and also justifies the unusually low oxidation potential of the MeLi material with its passivated/inactive oxide surfaces. Instead, bulk MoSe₂ has at least three visible peaks at *ca.* 0.6 V, 0.8 V and 1.2 V, of which the 1.2 V peak dominates if a cathodic sweep is performed first. Unlike its tungsten counterpart, the Se 3d peak of MoSe₂ appears at a higher binding energy after electro-oxidation (Figure 13.6), suggesting formation of a new selenium species that might explain this peak observed at high potential. Overall, the absence of such peculiar behavior in tungsten dichalcogenides again stems from the insolubility of its oxides and probable higher resistance to electro-oxidation.²⁹

Figure 13.5. Cyclic voltammograms illustrating inherent electrochemistry of transition metal dichalcogenides in their bulk states (a-c), and as exfoliated in methyl lithium (d-f) and butyl lithium (g-i). All scans start at 0.0 V vs. Ag/AgCl, and arrows indicate the starting scan direction. First scans are labelled red, followed by second scans in blue and third scans in grey.

Figure 13.6. High resolution X-ray photoelectron spectra of the chalcogen Se 3d and S 2p peaks for BuLi-exfoliated TMDs after electrochemical pre-treatments, illustrating the shift in binding energy only for MoSe₂ after electrochemical oxidation.

Despite the involvement of numerous convoluting aspects such as different electroactivities of edge vs. basal planes, surface oxides and their solubilities, a key interest remains in identifying the electrochemical redox processes responsible for the observations. Under similar conditions, the voltammetry of molybdenum and tungsten oxides show irreversible oxidation peaks only for the IV oxides and not in the VI oxides. A sharp oxidation for molybdenum(IV) oxide is observed at 0.7 V close to those of MoSe₂, whereas oxidation of tungsten(IV) oxide occurs at a slightly lower potential with a low and broad peak-shape interestingly similar to tungsten dichalcogenides. These may serve as evidence for the proposed irreversible oxidation of metal centers from their +4 to +6 oxidation states,^{27,28} or otherwise as conclusive proof of oxide participation. The identities of products may also be postulated based on thermodynamic stabilities at their observed potentials. At strongly anodic potentials above ~1.0 V vs. Ag/AgCl, constituent elements would exist at their highest oxidation states and include species such as: MoO₄²⁻, WO₃(s), HSO₄⁻ and HSeO₄⁻ under acidic conditions or MoO₄²⁻, WO₄²⁻, SO₄²⁻ and SeO₄²⁻ at neutral to basic pH,^{29,33,34} and a combination of the above products likely result.

Thus far, we have shown that all the TMDs studied exhibit inherent electrochemistry, each bearing their specific set of characteristics. In addition to conventional wisdom on the effects of basal and edge planes,^{27,28,29} we further propose that surface oxides can dictate the inherent electrochemistry of chemically exfoliated TMDs, and are also influenced by their differing solubilities. Due to the greater solubility of oxides in MoSe₂, more erratic behavior is observed which we attribute to the redox reactions of MoSe₂ itself. Despite that their intricate redox mechanisms cannot be entirely elucidated at present, a more pressing concern for the immediate future is that inherent electrochemistry of TMDs can pose limitations on many related applications.

One foremost constraint that they will likely pose is to limit their own use as electrode materials in various fields such as sensing and electrocatalysis, which we study in depth next.

13.2.3. Inherent Electrochemistry of TMDs Limits Potential Window of Common Redox Analytes

In recent years, the majority of electrochemical applications involving TMDs are centered almost chiefly on HER catalysis. To address the relative shortfall in this aspect, we firstly explore the possibility of other potential applications such as ORR. Heterogeneous electron transfers at these surfaces are also investigated towards a redox analyte commonly used in electrochemical sensing. More importantly, effects and implications of the previously discussed inherent TMD electrochemistry are further studied in their contexts.

The heterogeneous electron transfer (HET) rate of an electrode material is a parameter of paramount importance and determines its suitability for electrochemical and biological sensing devices. An intrinsically fast HET rate is preferable for a prospective electrode material as it effectively lowers the overpotential required for an electrochemical reaction. Cyclic voltammetry is firstly performed within the typical potential region for ferro/ferricyanide, as a redox couple commonly employed for electrochemical sensing purposes. HET rate constants are then calculated based on the classical Nicholson approach,³⁵ with larger separations between the anodic and cathodic peaks relating to slower HET rates. A first observation in the voltammograms is that in addition to the reversible peaks of the ferro/ferricyanide couple appearing from -0.2 V to 0.5 V vs. Ag/AgCl, characteristic waves due to the inherent electrochemistry of the TMDs dominate their voltammetry particularly during the first scan and occur at similar potentials as seen in the preceding section. Hence, immediate extraction of HET

information from the initial scan cycle may be unreliable and calculations are performed using data from the subsequent scans instead as shown in Figure 13.7a-c. Peaks from inherent TMD electroactivity are considerably diminished from the second scan onwards, allowing for clear observation of the ferro/ferricyanide redox couple. Peak separations are presented in Figure 13.7g, from which the observed HET rate constants (k_{obs}^0) can be calculated. Two distinct trends were observed. The first is a dependence on the metal/chalcogen constituents of the TMDs irrespective of their chemical treatment, where MoSe_2 typically exhibits the fastest HET and decreases in the order: $\text{MoSe}_2 > \text{WSe}_2 > \text{WS}_2$.

Figure 13.7. Electrochemical activities of the ferro/ferricyanide redox probe and the oxygen reduction reaction (ORR) on metal dichalcogenide catalysts. (a-c) Cyclic voltammograms for $\text{Fe}(\text{CN})_6^{3-/4-}$ on bulk and exfoliated MoSe_2 , WS_2 and WSe_2 ; conditions: 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 50 mM PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s^{-1} ; only second scans are shown. (d-f) Oxygen reduction reaction on bulk and exfoliated MoSe_2 , WS_2 and WSe_2 ; conditions: 0.1 M KOH, scan rate: 50 mV s^{-1} . (g) Peak

separations for the ferro/ferricyanide redox probe on TMD surfaces. (h) Peak reduction potentials for the ORR. Error bars correspond to standard deviations based on triplicate measurements. Green shaded regions designate the potential range where the analyte investigated is active, whereas red regions indicate the presence of inherent electroactivity from the TMD. Potentials are with respect to the Ag/AgCl reference electrode.

It is unsurprising that this trend corresponds to their electrical conductivities (Figure 13.8), as it is a leading determinant of the observed HET at an electrode surface. On one extreme, all WS₂ materials showed irreversible k_{obs}^0 values lower than the quasi-reversible limit which we determine to be $6.3 \times 10^{-6} \text{ cm s}^{-1}$ at the scan rate used,³⁶ and are thus unsuitable for electrochemical sensing. On the other hand, BuLi-exfoliated MoSe₂ has the highest k_{obs}^0 value of $9.17 \times 10^{-4} \text{ cm s}^{-1}$ better than that of conventional GC electrodes at $2.78 \times 10^{-4} \text{ cm s}^{-1}$. This leads to the observation of the exfoliation method as a secondary factor influencing HET rate. Materials demonstrated improved HET rates after BuLi exfoliation compared to their MeLi-treated counterparts, followed by the bulk materials with the slight exception of bulk WSe₂. Such an improvement in HET may be correlated with the increase in surface area as a direct consequence of the exfoliation process as shown earlier. Overall, combined effects of a high conductivity and increased surface area result in BuLi-exfoliated MoSe₂ exhibiting the fastest HET rate.

Figure 13.8. Current-voltage curves of transition metal dichalcogenides in their a) bulk unexfoliated state, and after treatment in b) methyl lithium, and c) butyl lithium. Conductance measurements were performed on a gold interdigitated array electrode by deposition of a 2.0 μL suspension of the relevant material (1 mg mL^{-1} in deionised water) onto the interdigitated region. Detailed procedure is described in Chapter 3.

The oxygen reduction reaction is subsequently studied with its key importance in fuel cell technologies.³⁷ Two reduction peaks near -0.4 and -0.9 V vs. Ag/AgCl corresponding to the two-step reduction process of O_2 are observed. In addition to the appearance of inherent oxidation waves at positive potentials, we now also note the incidence of inherent reduction peaks, especially in BuLi-exfoliated MoSe_2 and WSe_2 within the potentials highlighted in red (*ca.* -0.8 V to -1.0 V) in Figures 13.7d and f. Closer examination of the inherent reductions reveals a sharp faradaic process for MoSe_2 and a drawn out wave in the case of WSe_2 but altogether not in WS_2 , allowing us to deduce that these inherent reductions must involve selenides, likely in forming compounds such as HSe^- based on the potentials in which they occur.^{33,34}

For the purposes of studying the electrocatalysis of oxygen reduction, we focus only on the reduction peak at about -0.4 V vs. Ag/AgCl. As collated in Figure 13.7h, the lowest reduction peak potential occurs for Pt/C at about -0.33 V vs. Ag/AgCl, agreeing with the use of Pt-based catalysts as the current state-of-the-art in proton exchange

membrane fuel cells.³⁷ Unlike the case of ferro/ferricyanide catalysis, neither TMD compositions nor the chemical exfoliation methods have any obvious effect on ORR, and MoSe₂ materials (-0.44 V, -0.45 V and -0.46 V for BuLi-exfoliated, bulk and MeLi-treated MoSe₂ respectively) show just a marginal improvement in their reduction peak potentials from GC electrodes at -0.47 V likely due to their higher intrinsic conductivities. No other relation is discernible, specifically within tungsten dichalcogenides. As such, the only factor for enhancement of ORR catalysis in TMDs currently known is that of size effects.³⁸

We can thus conclude that there is a strong dependence of TMD compositions and the choice of chemical exfoliation method on ferro/ferricyanide catalysis due to differences in electrical conductivity and surface area, but such effects are less distinct for the ORR. In addition, inherent electrochemistry characteristic of the various TMDs are shown to occur within both anodic and cathodic potentials of ± 1.2 V for common analytes (ferrocyanide and aqueous dissolved oxygen) as model systems. Inherent TMD electroactivities within the same potential window of an analyte may limit applications if caution is not exercised, especially if there is a lack of controls to distinguish analyte from inherent electrode activity. Therefore, these new insights can effectively provide recourse to the future use of TMDs in sensing and catalysis applications.

13.2.4. Hydrogen Evolution Reaction: Strong Dependence on Metal/Chalcogen Composition and Exfoliation Method

In stark contrast to the ORR, the HER efficiency is seen to have strong dependencies on the chemical exfoliation route and TMD composition. Linear sweep HER measurements were performed in N₂-saturated 0.5 M sulfuric acid at a low scan rate of 2 mV s⁻¹ for bulk and exfoliated TMDs, with their polarization curves shown in

Figure 13.9a-c. Polarization curves for bare GC electrodes, and finely dispersed platinum-on-carbon as the best known HER electrocatalyst are also demonstrated for reference. We observe the lowest onset potential of approximately -0.13 V vs. RHE for MoSe₂ after BuLi-treatment against a significantly poorer -0.29 V vs. RHE for the bulk material. This low onset potential is very similar to that recently reported for MoSe₂ nanosheets,¹⁸ and also for MoS₂ nanoparticles.³⁹ For a tenable evaluation of catalytic performance across the literature, however, the overpotential at a current density of 10 mA cm⁻² is used instead. At this increased level of H₂ production, a comparison of the overpotential between different TMDs (Figure 13.9f) reveals a first trend: MoSe₂ materials always performed best followed by WS₂ and WSe₂. Interestingly, there is also a second dependence on the choice of chemical intercalant used; BuLi-exfoliated catalysts always showed an improvement from the bulk, while MeLi treatment of the TMDs results in poorer catalysis. Overall, BuLi-exfoliated MoSe₂ was the most efficient HER catalyst (-0.36 V vs. RHE) followed by the unexfoliated bulk (-0.53 V) and MeLi-treated MoSe₂ (-0.66 V) at greater reducing overpotentials. It is much expected that the HER efficiency increases after BuLi treatment due to the concomitant effects of: (1) an abundance of active edge sites from the exfoliation of layers,^{40,41} (2) phase transition to the more catalytic 1T polymorph due to electron transfer from the C-Li bond in butyl lithium^{1,42} and (3) a reduction in the potential barrier for electron hopping with a decreasing number of layers.¹⁷ In terms of more convenient parameters, this enhancement in HER efficiency is clearly correlated with BuLi exfoliation due to the surface area increase determined earlier. With MeLi however, any effect from increased surface area is effectively negated by passivation of TMD surfaces from reactive methyl radicals,³² mirroring our observations in their inherent electrochemistry. This is also reflected in their typically lower conductivity values as previously seen.

Tafel analysis was subsequently executed for the HER polarization curves to elucidate the electrochemical mechanisms (Figure 13.9d), with their values tabulated in Figure 13.9e. The mechanism of the hydrogen evolution on different TMD surfaces can be understood from the rate determining steps as such:

1. Volmer adsorption step: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ $b \approx 120 \text{ mV/dec}$
2. Heyrovsky desorption step: $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$ $b \approx 40 \text{ mV/dec}$
3. Tafel desorption step: $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$ $b \approx 30 \text{ mV/dec}$

In the well-known MoS_2 analogue, both the metallic 1T phase and active edge sites are known to be electrocatalytic for HER, with prior reports showing the lowest Tafel slopes for metallic MoS_2 at typically 40 mV/dec,^{1,43} agreeing with the Volmer-Heyrovsky mechanism. In comparison, edge-rich nanosheets show a slightly higher Tafel slope of 55-60 mV/dec.⁴⁰ We observe in our case a Tafel slope of 126 mV/dec on bare GC electrodes, indicating adsorption as the slow step in contrast to the most catalytic Pt/C with a value of 32 mV/dec corresponding to the Tafel reaction. The broad trend we observed for both tungsten dichalcogenides is the Volmer adsorption mechanism as the limiting step with slopes generally close to its 120 mV/dec theoretical value.

The highest catalytic efficiencies however were consistently seen in MoSe_2 , with Tafel slopes ranging significantly lower at an average of 65 mV/dec for the bulk and also after BuLi exfoliation, whereas a 96 mV/dec value was obtained for the MeLi-treated material. Since experimental Tafel slopes are a direct outcome of surface HER mechanisms, it is thus prudent to consider surface compositions of the catalysts. Constituent elements of the TMDs themselves may first contribute to their varying HER performance, in addition to possible negative effects of insoluble surface oxides from tungsten dichalcogenides. Though this is deterministic of different TMDs, the surface metal-to-chalcogen ratios instead represent a potential point of control in improving

HER efficiency. We see from XPS that only MoSe₂ materials exhibit chalcogen-deficient surfaces. Their surface compositions are MoSe_(2-x), where $x = 0.6$ and 0.7 for Bulk and MeLi-treated MoSe₂ respectively, with the BuLi-treated material being most deficient in selenium at $x = 1.3$. This is in agreement with Mo edge sites shown to have a lower energy barrier for hydrogen evolution in MoS₂,^{27,44} and also recently with colloidal MoSe₂ having unsaturated Se-edges⁴⁵ and vacancies.¹⁶ The chalcogen deficiency in our case is likely to have arisen from surface oxidation shown previously from XPS and SEM-EDS, and intriguingly enhances the overpotential and Tafel slope. Again, the poorer slope after MeLi treatment supports our proposition of surface passivation by methyl radicals. Overall, the 65 mV/dec value that we see for exfoliated MoSe₂ is improved from that of *pure* MoSe₂ nanosheets at 101 mV/dec,¹⁸ and free MoS₂ nanoparticles at 94 mV/dec.³⁹ Thus, HER efficiencies of TMDs are observed to be profoundly dependent on the metal-to-chalcogen composition which determines the intrinsic free energy for adsorption of atomic hydrogen, and also the exfoliation method employed that in turn influences the catalytic edge sites and polymorphs.

Figure 13.9. Electrochemical activity of the hydrogen evolution reaction (HER) on metal dichalcogenide catalysts. Polarization curves (a-c) for HER on bulk and exfoliated MoSe₂, WS₂ and WSe₂. Bare glassy carbon electrodes and platinum on carbon catalyst are also shown for comparison. Conditions: 0.5 M H₂SO₄, scan rate: 2 mV s⁻¹. (d) Tafel plot for the HER. (e) Tabulated values for the Tafel slope; dotted lines at 120 and 30 mV/dec correspond to the Volmer and Tafel mechanisms, respectively. (f) Overpotentials for HER at 10 mA cm⁻² current density. Error bars correspond to standard deviations based on triplicate measurements. Overpotentials are with respect to the formal potential of the reversible hydrogen electrode.

Another point of interest is the presence of pre-waves seen only in some materials such as MoSe₂ and WS₂ after BuLi exfoliation. These waves can result from either chemical or physical processes; first is the inherent TMD electroactivity as

outlined previously, while the second is varying catalytic efficiencies of HER on different sites such as edge and basal planes. Chemically irreversible reductions were observed only in some materials, noted by their disappearance after the initial HER measurement with no apparent effects on the subsequent HER efficiency. However, the charges passed within these HER pre-waves do not necessarily correspond with the charges measured from inherent reductions and are usually far greater by about two orders of magnitude. Therefore, while the inherent electrochemistry of the TMDs is a probable cause of HER pre-waves wherever they arise, differences in catalytic activities of TMD surfaces may also be an important contributing factor,⁴⁰ such as the enhanced catalysis at edge sites against basal planes with their sluggish kinetics. Nonetheless as shown, the effects of TMD composition and exfoliation method can still be accurately investigated by evaluating materials at a suitably high current density to avoid misinterpretation from inherent electroactivity.

13.3. Conclusions

A comprehensive investigation into the effects of chemical exfoliation of TMDs (MoSe_2 , WS_2 , WSe_2) was performed and their properties examined with consideration towards various electrochemical aspects and applications. Strong dependences on the TMD composition and chemical exfoliation route are found to exist due to changes in properties such as surface area and electrical conductivity. All TMDs investigated possess inherent electrochemical activity, and their characteristics are influenced by their compositions, with molybdenum exhibiting greater variation over tungsten TMDs. Inherent electroactivities can pose limitations for their current use as electrocatalysts and also electrode materials in other applications. Voltammetric studies reveal that possible complications may arise in many areas such as sensing and catalysis, even for

common redox reactions within a relatively small potential window of ± 1 V and over a wide range of pH. In summary, care must be taken when exploiting TMD materials for any electrochemical purpose, as activity of the electrode material itself may convolute data obtained and result in erroneous interpretations. Therefore, an awareness of characteristic TMD electrochemistry is particularly crucial for the development of HER catalysts and useful outcomes may be achieved with application of this new knowledge. This is especially relevant in electrochemical sensing where heterogeneous electron transfer rates can be accurately determined at TMD surfaces, and also in HER catalysis where highly efficient hydrogen production can be accomplished by the careful choice of TMD composition and exfoliation routes.

13.4. Detailed Experimental Procedures

The exfoliation of TMDs was carried out by suspension of 15 mmol of a bulk TMD powder in 20 mL of 1.6 M methyl lithium in diethyl ether and 20 mL of 1.6 M n-butyl lithium in hexane. The solution is then stirred for 72 h at 25 °C under argon atmosphere. The Li-intercalated material is separated by suction filtration under argon atmosphere and the intercalation compound was washed several times with hexane (dried over Na). The separated TMD with intercalated Li was subsequently placed in water (100 mL) and repeatedly centrifuged (18 000 g). The final obtained materials were dried in a vacuum oven at 50 °C for 48 h prior to further use.

Surface areas were measured using adsorption of methylene blue. About 0.1 g of each TMD material (weighed exactly to within ± 0.01 mg) was dispersed in 70 mL of deionized water by ultrasonication (400 W, 30 minutes). To the suspension was added 1 mM aqueous solution of methylene blue and then filled to 100 mL. Concentration of unabsorbed methylene blue was determined by UV-Vis spectroscopy at $\lambda_{\text{max}} = 665$ nm

(Cary 50, Agilent). For the calculation of surface areas, the value of 0.13 nm^2 per methylene blue molecule was used.¹³ Above procedures were performed by our collaborators (Z. Sofer, P. Simek).

Aqueous dispersions of transition metal dichalcogenide (TMDs) catalysts were prepared by the author in deionized water at a 1.0 mg mL^{-1} concentration with ultrasonication for 1 h to obtain a well-dispersed suspension. The dispersion process was most efficient for butyl lithium exfoliated materials as indicated by the intense change of solution color which continued to remain stable after approximately 15 min of sonication. Bulk materials require longer periods of more than 40-50 min, with only slight increase in color intensities. Suspensions of bulk TMDs are unstable and agglomeration is almost immediate. 5 μL aliquots of the dispersion inks were then drop-casted on GC electrodes immediately after sonication and dried, giving a catalyst loading of $70.7 \text{ }\mu\text{g cm}^{-2}$ per electrode. GC electrode surfaces were renewed prior to new measurements by polishing with a $0.05 \text{ }\mu\text{m}$ alumina particle slurry on a polishing pad and thoroughly washed with deionized water.

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Chapter 14 –

Conclusions and Future Outlook

This thesis titled “Graphene, Chemically Modified Graphenes, and Two-Dimensional Layered Materials – Electrochemical Fundamentals and Applications” focused on the use of electrochemical methods and materials characterisation techniques to study both the fundamental and applied aspects of graphene and its related materials.

In **Part I**, fundamental and experimental aspects of graphene and CMGs were discussed. Graphene oxide (GO), or graphite oxide when in the bulk state, is an important intermediate in the “top-down” approach to graphene production. It can then be reduced through thermal shock treatment, with chemical reductants, or electrochemically by application of a sufficiently reducing potential. While the prevailing knowledge at the time was that GO can only be irreversibly reduced, a chance observation led to our discovery that some oxygen groups specific to permanganate-GOs instead exhibit reversible electrochemistry. X-ray photoelectron spectroscopy and pH studies suggested that hydroquinones/quinones might be involved. Although GO is also one of the most extensively studied CMG materials, there remains some dispute between its proposed structural models. Thus, a second study was undertaken to chemically label the different oxygen group types in the GOs, which established the most significant differences as: (1) quinonyl species making up the majority of carbonyl groups in permanganate-oxidised GO compared to chlorate-oxidised GO which comprised mainly of aliphatic ketones/aldehydes, and (2) carboxylic acids being low in permanganate-GO and virtually non-existent in chlorate-GO, contrary to conventional wisdom that carboxylic groups are inherently responsible for the acidity of GO. A further study was carried out to investigate the electrochemistry of colloidal GOs, which determined that an acidic environment, small particle size (~ 50 nm), and high concentration (~ 1 mg mL⁻¹) are required for direct voltammetric detection. In

preparation for studies on the heterogeneous electron transfer kinetics at CMG-modified electrodes, the reliability of the drop-casting method for electrode preparation was also examined. Adsorption and thin-layer effects due to porosity were not observed to influence the normal diffusion profile of graphene-modified electrodes. Additionally, the apparent porosity can be controlled at a low level by use of multiple aliquots of a less concentrated dispersion.

Part II moved towards understanding the physical and chemical properties that influence the heterogeneous electron transfer at various CMG materials. This aspect focused primarily on reduced and hydrogenated graphenes. Graphene produced from the thermal reduction of graphite oxide was first investigated, either in the presence or absence of elemental potassium. Despite a higher oxygen-content in the potassium-reduced GO, its HET towards ferrocyanide was improved likely as a result of the potassium forming complexes with inherent oxygen groups, and thus reducing the repulsion of the negatively-charged ferrocyanide. Subsequent research on hydrogenated graphenes explored two diverse approaches, either through gaseous hydrogenation or through the liquid-phase method based on the well-known Birch reduction. In general, the gaseous approach by a microwave-generated hydrogen plasma produced hydrogenated graphene with a lower hydrogen content (8-19 at.%), but less residual oxygen due to excellent deoxygenation from the microwave process. This resulted in their better HET rates than hydrogenated graphenes from the Birch reduction which gave significantly higher hydrogen contents (11-37 at.%) but also higher amounts of residual oxygen groups. Comparatively, an increased density of defects arising from sheet edges and edge-like defects was seen to be a more influential factor that enhanced the HET. Partial hydrogenation of graphene was not found to significantly impact the HET, either positively or negatively, but as with the most hydrogenated

graphenes (*e.g.* from the Birch reduction using potassium and water), electrical conductivity due to sp^2 conjugation might have been disrupted. We can therefore postulate that complete hydrogenation, if achieved in future, would consequently cause sluggish HET.

Part III further included the study of two groups of graphene-related nanomaterials and their use in scientifically-relevant and industrial applications, namely chemically-functionalized graphene oxide and transition metal dichalcogenides (TMDs). GO was functionalized with *o*-phenylenediamine which increased the electrochemical capacitance by two orders of magnitude up to 191 F g^{-1} . As a potential supercapacitor material, the prerequisite electrical conductivity was also increased, which we suggest to be from extended sp^2 conjugation due to the phenazine adduct formed between edge quinones and *o*-phenylenediamine. A bright green fluorescence was also observed particularly from the smallest fragments of the functionalized GO attributed to localisation of sp^2 domains. Based on the results, other forms of GO functionalization may possibly be used in future for similar applications like supercapacitors or as fluorescent labels in biosensing. Layered TMD nanomaterials (MoSe_2 , WS_2 , WSe_2) were also studied with special emphasis on their catalysis of the hydrogen evolution reaction. The chemical exfoliation method strongly influenced the resulting material and electrochemical properties. After exfoliation treatment with *n*BuLi, MoSe_2 demonstrated quasireversible HET rates to ferrocyanide, faster than bare glassy carbon unlike all other studied TMDs. Its catalysis of the HER was also the best with a low overpotential of -0.36 V vs. RHE (at -10 mA cm^{-2} current density), and a Tafel slope of $\sim 65 \text{ mV/dec}$.

Graphite is an abundant natural resource that has been exploited for centuries, but *graphene* was only first isolated very recently in 2004 and shown to possess a myriad of useful properties. The ensuing surge in scientific interest within the decade or so that followed was then touted by some to be the *golden age* of materials science. A large number of academic institutions and commercial entities alike pursued research in a great variety of potential graphene applications ranging from energy generation and storage, to electronics, sensors, and nanomedicine. However, others have also argued that graphene has not quite lived up to its epithet as the new wonder material (perhaps considering the economic returns that might have yet to realise). Nevertheless, it is indisputable that there is now greater knowledge on the fundamental structures and physical properties of graphenes and other layered nanomaterials, and more importantly that we have come a long way in developing the methods to study and exploit them. As scientists are turning their attentions to discover or create new graphene analogues and nanomaterials, the technical knowledge and expertise garnered over the years can only serve us well in the quest for novel applications or solutions that these materials may provide in future.

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