Chemical modification of graphenes : synthesis and electrochemistry

Wong, Colin Hong An

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Chemical Modification of Graphenes: Synthesis and Electrochemistry

WONG HONG AN COLIN

School of Physical and Mathematical Sciences

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Summary

Graphene has been touted as the next “wonder material” for various applications, owing to its excellent properties. The development of novel graphene materials enables hitherto unavailable characteristics for electrochemical applications, while in-depth and systematic study of graphene materials is necessary to understand its electrochemistry. Hence, new synthesis methods were explored using carbon nanotubes as a precursor to produce graphene materials, with analysis on the types of products formed and the effect of residual metallic impurities. A novel method for the reduction of graphene oxide nanoribbons was demonstrated to afford graphene nanoribbons with superior properties than those using conventional chemical reduction. The synthesis of graphene materials using rapid microwave treatment was also studied to provide insight on the influence of the precursor graphite oxide, with the procedure then being modified to successfully synthesize sulfur-doped materials that exhibited electrocatalytic activity. On the other hand, comprehensive investigations on current synthetic procedures were also conducted, revealing the impact of different methods on the levels of metallic impurity contamination of the graphene materials. The choice of graphite source was also shown to have varying, compounding effects on the properties of the resulting graphite oxides and graphene materials. Different techniques for the transfer of CVD graphene were compared in order to determine the most suitable method to obtain graphene films for electrochemical applications. These studies thus serve the dual purpose of expanding the synthetic toolbox available for graphene production as well as provide insight on the suitability of graphene materials for various electrochemical applications.

List of Publications (reverse chronological order)

1. **Wong, C. H. A.**; Sofer, Z.; Klímová, K.; Pumera, M. Microwave exfoliation of graphite oxides in H₂S plasma for the synthesis of sulfur-doped graphenes as oxygen reduction catalysts. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31849–31855.
2. Ambrosi, A.; Chua, C. K.; Latiff, N. M.; Loo, A. H. L.; **Wong, C. H. A.**; Eng, A. Y. S.; Bonanni, A.; Pumera, M. Graphene and its electrochemistry – an update. *Chem. Soc. Rev.* **2016**, *45*, 2458–2493.

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3. **Wong, C. H. A.**; Pumera, M. Electrochemical delamination and chemical etching of chemical vapor deposition graphene: Contrasting properties. *J. Phys. Chem. C* **2016**, *120*, 4682–4690.
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5. **Wong, C. H. A.**; Sofer, Z.; Pumera, M. Geographical and geological origin of natural graphite heavily influence the electrical and electrochemical properties of chemically modified graphenes. *Chem.-Eur. J.* **2015**, *21*, 8435–8440.

Highlighted as “Hot Paper,” selected as back cover.

6. **Wong, C. H. A.**; Sofer, Z.; Kubešová, M.; Kucera, J.; Matejková, S.; Pumera, M. Synthetic routes contaminate graphene materials with a whole spectrum of unanticipated metallic elements. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 13774–13779.
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reduction/exfoliation of graphite oxide and the influence of precursor graphite oxide. *Carbon* **2014**, 77, 508–517.

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9. **Wong, C. H. A.**; Chua, C. K.; Khezri, B.; Webster, R. D.; Pumera, M. Graphene oxide nanoribbons from the oxidative opening of carbon nanotubes retain electrochemically active metallic impurities. *Angew. Chem. Int. Edit.* **2013**, 52, 8685–8688.

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10. Pumera, M.; **Wong, C. H. A.** Graphane and hydrogenated graphene. *Chem. Soc. Rev.* **2013**, 42, 5987–5995.

Selected as inside back cover.

11. **Wong, C. H. A.**; Pumera, M. Unscrolling of multi-walled carbon nanotubes: towards micrometre-scale graphene oxide sheets. *Phys. Chem. Chem. Phys.* **2013**, 15, 7755–7759.

CHAPTER 1

OBJECTIVES OF THESIS

Chapter 1 – Objectives of thesis

Graphene is the latest carbon allotrope to gain significant research attention, ever since the pioneering research on its isolation and characterization that subsequently earned Geim and Novoselov the 2010 Nobel Prize in Physics. Due to graphene possessing a slew of excellent and unique traits, particularly its electrical and electronic properties, graphene and its derivatives are slated to become important materials for the fabrication of electrochemical devices.

Defined as a single carbon layer of graphite, graphene has a deceptively simple structure. Coupled with the ready availability of graphite from both natural and synthetic sources, one might be led to assume that there is easy access to graphene for practical applications. However, producing bulk quantities (both in terms of mass as well as area) of graphene has proven to be nowhere nearly as straightforward as simple repetitive peeling away at large amounts of graphite. In response to this, the scientific community has developed an astonishingly huge catalogue of methods to produce graphene, to make the harnessing of graphene a commercial and industrial reality.

Unfortunately, not all graphene is created equal. The downside of having many synthesis procedures at our disposal is that the different reaction conditions, precursors, and post-processing methods lead to graphene materials that are chemically modified differently. Strictly speaking, most of these synthesis methods do not actually produce pristine graphene, despite the best efforts of researchers. These differences among the final graphene materials produced, subtle or not, can have drastic consequences for electrochemical applications. Hence, it is imperative that the synthesis methods are studied rigorously, to assess how they affect the properties of the graphene materials thus obtained. This leads us to two general research directions, which will be outlined below.

Research direction 1: Exploring recent and novel graphene synthesis methods

The production of bulk quantities of graphene today is mostly carried out through the initial oxidation of graphite to produce graphite oxide, followed by its reduction to yield graphene materials in the form of reduced graphene oxides. Graphene materials derived from graphite typically maintain the lateral dimensions of the parent graphite flakes. The harsh oxidative conditions used to produce graphite oxide, coupled with additional processing (e.g. ultrasonication) is often able to “cut up” graphite flakes into smaller pieces, but it is not possible to control the size and shape of GO sheets.

Recently, carbon nanotubes have been used for the synthesis of graphene materials, with the final product being graphene nanoribbons: essentially long and thin sheets of graphene. By virtue of their high length-to-width ratios, more numerous edge sites, and opportunity for tuning their electronic structures through their widths, graphene nanoribbons are able to exhibit different properties from graphene. Using carbon nanotubes as a precursor to produce graphene nanoribbons thus presents a promising approach to develop novel materials for electrochemical applications.

The use of microwaves has been gaining popularity in organic syntheses as a means to provide energy to the reaction system, ensuring more even heating as well as much faster reaction completion. This technique has also been recently employed for the reduction/exfoliation of graphene oxides, yielding a material similar to that obtained using thermal reduction. As a relatively new method, microwave exfoliation deserves further study to understand its potential for graphene materials.

Projects following this research direction will be elaborated in Chapters 3 and 4 of this thesis.

Chapter 1 – Objectives of thesis

Research direction 2: Understanding the effects of current synthesis methods on the properties of chemically modified graphenes

A vast number of applications for graphene have been put forward, owing to its unique and marvelous properties; the methods available for the synthesis of graphene and its derivatives are similarly diverse. For better or worse, various methods produce chemically modified graphenes (CMGs), imbued with different properties that deviate from pristine graphene. Despite such differences, many of these CMGs, particularly the reduced graphene oxides, are able to approach the nature of pristine graphene sufficiently to be considered for various applications.

Hence, it is important to carefully study how the different synthesis methods affect the properties of the resulting CMGs, rather than just writing them off as “imperfect graphene.” Fundamental studies documenting the variations in the properties of CMGs resulting from the different ways in which they are fabricated would allow for more robust comparison of the synthesis methods. This would be helpful in highlighting not only any shortcomings but also the advantages of using a particular chosen route to obtaining graphene.

Projects following this research direction will be elaborated in Chapters 5 and 6 of this thesis.

CHAPTER 2

A BRIEF HISTORY OF GRAPHENE: DISCOVERY AND SYNTHESIS METHODS

2.1 Introduction

2.1.1 Graphene and its discovery

2.1.2 The early days of graphene: graphite and graphite oxide

2.2 Approaching graphene: reduced graphene oxides

2.2.1 Chemical reduction of GO

2.2.2 Thermal reduction of GO

2.2.3 Electrochemical reduction of GO

2.3 Bottom-up synthesis of graphene

2.3.1 Total organic syntheses of graphene

2.3.2 Graphene epitaxy on SiC

2.3.3 Chemical vapour deposition of graphene

2.4 References

2.1 – INTRODUCTION

2.1.1 Graphene and its discovery

The allotrope of carbon known as graphene consists of a plane of sp^2 carbon atoms in an extended hexagonal honeycomb structure. The definition as given by IUPAC states that a graphene layer is “a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size.”¹ It joins a host of other graphitic carbon allotropes that have been extensively studied, starting with the readily available and naturally abundant graphite and followed by nanocarbons such as fullerenes and carbon nanotubes (CNTs).² While these other allotropes are exceptional materials in their own rights, graphene is notable for conceptually being the basic building block of all other forms of graphitic materials (Figure 1), causing graphene to be dubbed “the mother of all graphitic forms.”² The concept of graphene was first put forward by Wallace in 1947, when he considered the band structure of “a monolayer of graphite” in his investigations into the electronic properties of graphite.³ Conventional wisdom at that time, however, dismissed the possibility of the existence of 2D crystals, owing to their supposed thermodynamic instability. Boehm *et al.* introduced the term “graphene” in their formulation of rules for naming graphite intercalation compounds in 1986.⁴ Although studies on graphitic thin films have existed since the 1960s, unambiguous identification of individual graphene layers did not arrive until four decades later, using transmission electron microscopy (TEM) techniques.⁵⁻⁷ In 2004, Novoselov and Geim finally catapulted graphene to the forefront of scientific research worldwide by not only isolating a free-standing, monocrystalline graphene film, but also detailing its remarkable electronic properties and hinting at its possible tunability for a

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slew of electronic applications.⁸ Ever since this isolation of free-standing graphene and the subsequent unearthing of its many unique and unprecedented physical and chemical properties, there has been a tremendous influx of researchers into the field.^{2, 8-10} For example, graphene possesses remarkably high charge carrier mobilities even at low temperatures, and is a promising material for the fabrication of room-temperature ballistic transistors.² The resistivity of graphene ($\sim 1 \times 10^{-6} \Omega\cdot\text{cm}$) was found to be significantly lower than silver, the next lowest resistivity material known at room-temperature. The basal plane of graphene sheets is chemically unreactive compared to the edges, but its reactivity can be tailored by introducing defects in the plane, or changing the number of sheets in the material. Despite the seeming simplicity of graphene's structure, the material has shown to be promising for wide array of potential applications, including but not limited to solar cells,¹¹ touch screen displays,¹² protective coatings,¹³ and electrochemical-sensing.¹⁴

Many of these outstanding properties and applications are attributable only to free-standing, pristine graphene films, as these are easily obtainable through mechanical cleavage of graphite (in particular, highly ordered pyrolytic graphite, or HOPG). In this method, repeated peeling off graphite layers from HOPG using adhesive tape ultimately leads to a single graphene layer, which can then be studied for research purposes.^{8, 10} The term "pristine graphene" usually refers to graphene monolayers as per the IUPAC definition: a single layer of the graphite structure; nothing more, and nothing less. This implies that the graphene is free from defects, heteroatomic doping, and impurities. Although the mechanical cleavage method yields graphene samples of the highest quality, such monolayer graphene crystallites are scattered throughout the substrate, with most of the sample consisting of thick graphite flakes. It is also unthinkable to even

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consider scaling up this method to produce bulk quantities of pristine graphene for commercial applications.

As a response to the issue of scalability, numerous alternative methods have been proposed and carried out to produce graphene samples. These methods are broadly classified into either top-down or bottom-up approaches. In the top-down approach, graphitic structures are already inherent in the parent material, and such fabrication procedures involve isolating individual graphene sheets from the precursors, similar in principle to the mechanical cleavage method. In contrast, the bottom-up approach attempts to build graphene from small organic molecules, either through catalytic growth on suitable substrates or traditional organic syntheses. For both top-down and bottom-up approaches, many of these methods do not produce pristine graphene, but instead yield graphene analogues possessing additional functional groups, defects, or metal-based dopants. Such graphene analogues can be collectively termed as chemically modified graphenes (CMGs),¹⁵ regardless of whether the inclusion of these additional heteroatoms is intentional (to impart desirable properties to the graphene material) or not. Examples of CMGs include functionalized graphene, graphene oxide (GO), and reduced graphene oxides (RGOs). RGOs are typically formed from the reduction of oxygen-containing groups in GO by various procedures,^{16, 17} and even though the complete removal of oxygen from the material is exceedingly rare, RGOs are often able to closely approach the nature of pristine graphene for practical applications. Examples of various routes to produce RGOs are provided in Figure 2. As such, the scientific community generally uses the term “graphene” to encompass both pristine graphene as well as layered graphitic materials with a low degree of residual heteroatomic contamination, such as RGOs and exfoliated graphites.

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Figure 1. Graphene, visualized as the basic building block for higher dimension graphitic materials such as (a) buckyballs, (b) CNTs, and (c) graphite. Reproduced from Reference 2.

Figure 2. Schematic of the production of RGOs. Graphite oxide can be reduced directly by (A) thermal means, or (B) exfoliation into graphene oxide followed by reduction (C) chemically, or (D) electrochemically, to yield varying types of RGOs. Reproduced from Reference 11.

*Chapter 2 – A brief history of graphene: discovery and synthesis methods***2.1.2 The early days of graphene: graphite and graphite oxide**

The most fundamental method of obtaining graphene from graphite, “peeling off” graphene layers from a bulk graphite material, involves overcoming the weak van der Waals forces between adjacent layers in graphite. This was the basis of many early applications of graphite as a marking material, even though intimate knowledge of the lamellar structure of graphite did not come until centuries later. Indeed, the word “graphite” has its etymology in the ancient Greek word *γράφω* (gráfo, “to write”), tagged onto the suffix *-ite* used for minerals, and first coined by A. G. Werner in 1789. Similarly, the easy slippage of graphite’s layers combined with an ultralow atomic-scale friction (“superlubricity”) allows its application as a dry lubricant.¹⁸ The high stability of graphite under normal conditions resulted in a general lack of knowledge of the chemistry of graphite until Brodie exposed graphite to fuming nitric acid and potassium chlorate in 1859, and obtained a substance that he called “graphic acid,” which decomposed under thermal treatment to form what he believed to be a new form of carbon with an “atomic weight of 33”, proposing to call it “Graphon.”¹⁹ In truth, this “graphic acid” was the first experimental observation of graphite oxide documented. The Brodie method produced GO over 4 successive treatment cycles, and thus presented a large opportunity for improvement. In 1898, Staudenmaier modified the Brodie method by adding concentrated sulfuric acid to the reaction mixture, increasing its acidity, and adding KClO_3 in stages over the duration of the reaction.²⁰ The product obtained was similar to Brodie GO in terms of chemical composition and appearance, with the advantage of being obtainable in a single reaction vessel.

Even after such improvements, the Staudenmaier method still required reactions times of a week or more, required the use of fuming nitric acid (Hofmann replaced this

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with concentrated HNO_3 in 1937, reducing the danger of explosion significantly^{21, 22}), and resulted in the formation of significant amounts of toxic ClO_2 gas. The search for more efficient oxidation methods resulted in Hummers and Offeman developing a procedure utilizing potassium permanganate and sodium nitrate in concentrated sulfuric acid in 1958.²³ The Hummers method overcame many hazards in the Staudenmaier and Hofmann methods through the use of lowered reaction temperatures and the generation of HNO_3 in situ, as well as reducing reaction times to a mere two hours.

The most recent addition to these methods was demonstrated by Tour's group in 2010, which eliminated the use of NaNO_3 (and by proxy, the generation of toxic nitrogen oxides).²⁴ Instead, phosphoric acid was introduced, which purportedly played a role in creating fewer defects in the graphene basal planes. Furthermore, the extent of oxidation as well as the final yield of GO were higher than in the Hummers method. However, permanganate oxidation of graphite using the Hummers method (with or without slight modifications) still remains the most commonly used method to synthesize GO to date.²⁵⁻²⁷

2.2 – APPROACHING GRAPHENE: REDUCED GRAPHENE OXIDES

Out of all the oxidation procedures listed above, only the Tour method can be considered an outcome of the “graphene gold rush;” the majority of graphite oxidation procedures predate the 2004 watershed graphene study by several decades. Graphite has an interlayer distance of 3.35 to 3.44 Å, depending on the orientation and crystallinity of the sample.^{28, 29} The introduction of oxygen moieties between the layers during the oxidation of graphite to GO greatly increases this spacing to between 6 and 12 Å with increasing humidity, simultaneously weakening the van der Waals forces between adjacent layers.^{30, 31} This causes GO to be exfoliated far more easily into individual sheets than the analogous exfoliation of graphite to graphene, but the resulting GO sheets are highly insulating due to the presence of oxygen species disrupting the conductive sp^2 network, making it unsuitable for applications where high electron and electrical conductivities are required.¹⁶

It did not take the scientific community long to figure out that the removal of oxygen-containing groups from GO would, in theory, restore the sp^2 system and give rise to graphene. With the birth of a new subfield dedicated to advancing reduction techniques to obtain graphene from GO, a wide range of procedures to obtain RGOs have since been developed, and can be broadly classified into one of three methods: chemical, thermal, and electrochemical reduction.^{16, 32} Despite the varying properties of RGOs depending on the oxidation and reduction methods used, they are often able to achieve comparable performance to pristine graphene devices for many applications, and still remain highly important CMG materials today due to their comparative ease of production scalability.

2.2.1 Chemical reduction of GO

The removal of oxygen functionalities on GO via chemical processing is the most diverse family of reduction methods, due to the vast number of chemical reagents in the organic chemistry toolbox that are readily available in synthetic laboratories all over the world. It is widely acknowledged that the oxygen groups on GO comprise epoxides and hydroxyls on the basal plane, as well as ketones, quinones, and a small amount of carboxylic acids along the edges.^{33, 34} Reagents commonly chosen for the reduction of GO were, therefore, chosen based on their ability to remove such functional groups in “traditional” organic chemistry, and early examples include hydrazine and sodium borohydride.³⁵⁻³⁷ The reduction can be monitored visually in solution as the originally yellow GO solution turns black (Figure 3).³⁸ Reduction methods involving hydrohalic acids,^{39, 40} thio-compounds,^{41, 42} amines,^{43, 44} and metal-acid mixtures^{45, 46} have also been reported, as well as “greener” approaches using environmentally friendly molecules such as amino acids⁴⁷ and plant extracts.⁴⁸ As these methods differ in their reactivity towards different functional groups, they also vary greatly in their reduction efficiencies, as exhibited by the resultant RGOs.³² The selective removal of hydroxyl groups was also shown to be possible, using an ethanethiol–aluminium chloride complex.⁴⁹

While the empirical reduction of GO to RGO using chemical means is readily verified experimentally (such as tracking carbon-to-oxygen atomic ratios, measuring conductivity, using infrared spectroscopy to determine the presence of IR-active functional groups, etc.), how the reduction occurs is not always clear. For example, conventional organic chemistry wisdom forbids the reduction of carboxyl and carbonyl groups by LiAlH_4 beyond the corresponding alcohol; however, the removal of hydroxyl groups was demonstrated to occur on oxidized graphene materials.^{50, 51} Attempts to

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elucidate the reaction mechanism of hydrazine reduction of GO, using model reactions with small conjugated molecules both experimentally and theoretically, often do not agree with each other.⁵²⁻⁵⁴ Such phenomena, coupled with the non-stoichiometric nature of GO, make it difficult to discern the exact mechanisms of these reduction processes.

Figure 3. Chemical reduction of GO, showing colour change of the GO solution from yellow to black for RGO. Reproduced from Reference 38.

2.2.2 Thermal reduction of GO

Although the exact structure of GO is debatable, what is certain is that the oxygen functionalities residing on the surface of GO are sensitive to storage conditions, such as light, atmosphere, and temperature.⁵⁵ As such, one strategy for the reduction of GO is through exposure to elevated temperatures, causing the thermal decomposition of oxygen-containing groups. It is generally known that the thermal decomposition of oxygen-containing groups on GO produces gases such as CO_2 , CO, and H_2O , assuming GO consists only of carbon, hydrogen, and oxygen atoms. In reality, the gaseous products evolved during thermal treatment of GO include sulfur-containing molecules, such as COS, CS_2 , linear sulfur compounds, and thiophene, due to the presence of sulfuric acid in

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the oxidizing mixture.⁵⁶ The vaporization of oxidized carbon atoms on GO at high temperatures also releases more complex molecules, such as benzene, acetone, long chain alkanes, and bi-cyclic compounds, depending on the exfoliation pressure and atmosphere.⁵⁶ Regardless of the identity of the gases formed, this outgassing during rapid heating creates high pressure buildup between the layers of GO,⁵⁷ which then forces the layers apart and exfoliates the resultant RGO.⁵⁸ This makes thermal annealing a convenient method to obtain RGO directly from GO in a single step. However, it comes at the expense of sheet quality: thermal RGO has been shown to be highly defective due to considerable mass loss in the form of combusting carbon atoms,⁵⁸ leaving behind smaller-sized, wrinkled graphene sheets with holes scattered throughout the lattice.⁵⁹ Typical structures of thermal RGO as seen under SEM are shown in Figure 4.

Computational studies have shown that it is possible to eliminate certain oxygen species on GO without the formation of defects by heating the material past a critical dissociation temperature (T_c).⁵³ The impetus for heating GO at relatively low temperatures is to prevent the combustion of carbon atoms in the immediate vicinity of the oxygen-containing groups, which would otherwise create large amounts of defects in the graphene sheet due to holes, adatoms, and other multi-layered structures.⁶⁰ According to calculations, more stable groups such as epoxides and carbonyls could only be removed at a T_c as high as 1730 °C, while reactive carboxyls could be reduced at temperatures as low as 100–150 °C. Experimentally, it would appear that deoxygenation occurs more readily than simulations predict; most oxygen-containing groups were shown to be removed at a relatively low temperature of 200 °C, while annealing at 1000 °C produced highly conductive RGO with a C/O ratio of 14.^{61, 62}

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Figure 4. Thermally reduced graphene oxide, as seen under (left) scanning electron microscopy and (right) scanning transmission electron microscopy. Scale bars represent 1 μm in both cases.

Microwave reduction of GO is related to thermal annealing in that the buildup of pressure from outgassing also drives exfoliation, but the origin of heating follows a slightly more complex mechanism. This method will be discussed in more detail in Chapter 4.

2.2.3 Electrochemical reduction of GO

Regardless of the oxidation method chosen to oxidize graphite to GO, inherently electroactive oxygen species are present on the surface of GO.⁶³ These oxygen functionalities can be targeted by electrochemical reduction in suitable buffer solutions, which eliminates the need for potentially hazardous reducing agents to prepare RGO from GO. Electrochemical reduction of GO is typically performed by the deposition of a GO film onto a suitable substrate, using it as the working electrode in an electrochemical cell, followed by the application of a cathodic potential. Removal of the majority of electro-active oxygen functionalities on the GO film generally occurs around -1 V (against the saturated calomel electrode),⁶⁴⁻⁶⁶ although more electrochemically unreactive groups like carboxyls require around -2 V . Driving the electroreduction

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process by applying more negative potentials results in more complete removal of oxygen-containing groups;⁶⁷ however, the integrity of the GO/RGO film can be compromised at strongly reducing potentials due to H₂ gas evolution from the electrolysis of water. Although electrochemical reduction of GO is promising due to the ability to tune the amount of oxygen-containing groups present, it is not as scalable as other reduction methods and, thus, is likely to be suitable only for niche electrochemical applications.

2.3 – BOTTOM-UP SYNTHESIS OF GRAPHENE

Despite the advantages of top-down methods to synthesize graphene through the reduction of GO, they generally suffer one main drawback: the size and quality of the RGOs obtained is intrinsically linked to the starting material used. Top-down approaches cannot create graphene sheets with larger dimensions than their precursors, and “cutting-up” graphene sheets to a particular uniform size also cannot yet be reliably achieved. Nanographenes prepared from top-down methods additionally suffer from poorly defined edges and/or structures.⁶⁸ In contrast, bottom-up approaches use small, well-defined carbon-containing molecules as a starting material, and attempt to build up graphene structures through the formation of carbon-carbon bonds. The most common bottom-up approaches used today include total organic syntheses, epitaxy on silicon carbide, and chemical vapour deposition.

2.3.1 Total organic syntheses of graphene

As the name implies, this approach exploits organic chemistry knowledge to construct graphene by using small molecules as the template, or as a monomer unit that can be polymerized in a controllable fashion. Müllen’s group has been particularly active on this front, synthesizing graphene-like molecules of sizes up to 222 carbon atoms, representing 37 benzene units combined in a planar, hexagonal structure (Figure 5).⁶⁹ This method was later adapted to synthesize graphene nanoribbons as well.⁷⁰⁻⁷² However, this method is fundamentally limited by the solubility limits of larger organic precursors, which cause the formation of 3D product molecules in solution.⁷³ Difficulty in isolating the graphene molecules for additional characterization of properties has also

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Figure 5. Chemical structures of graphene molecules synthesized from oligophenylene precursors. Reproduced from Reference 66.

largely restricted such synthetic methods to fabricate graphene for observational experiments only; however, the ability to synthesize atomically precise graphene molecules (and, thus, precisely tailored electrical and electronic properties) cannot be ignored. Additional progress is expected to be made to allow the application of graphene molecules in working devices.

2.3.2 Graphene epitaxy on SiC

Silicon carbide is a semiconducting material currently undergoing extensive research efforts for applications in high-frequency and high-voltage devices.⁷⁴ When heated to high temperatures (up to 2000 °C is relatively common today), silicon atoms sublime from the material surface, leaving behind a carbon-rich top layer that can form graphene under controlled growth conditions. Early attempts to graphitize SiC under vacuum conditions resulted in a highly corrugated surface, consisting of discontinuous and disordered graphene domains (Figure 6b), which is detrimental to device performance due to the scattering of charge carriers in the conductive graphene

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layer.^{75, 76} Significant progress was made in 2009 when it was demonstrated that sublimation in an inert Ar atmosphere, which suppressed sublimation of Si, allowed graphitization of SiC to proceed at far higher temperatures.⁷⁷ Under these conditions, a predominantly monolayer of graphene is produced instead, which is continuous over the steps and terraces of the underlying SiC. The graphene produced is also of very high quality, with individual crystallite sizes in the hundreds of microns. However, the existence of bilayer and trilayer graphene at the edges of the terraces still contributes to charge carrier scattering. High substrate (SiC) cost, high temperature growth conditions, and small SiC wafer dimensions are some of the other factors currently prohibiting more extensive applications of epitaxial graphene.

Figure 6. Evolution of the surface of SiC during sublimation of Si. (a) SiC surface before heating, showing a staircase with atomic steps. (b) Graphitized SiC under vacuum conditions, showing extensive discontinuity. (c) Graphitized SiC under high-pressure Ar atmosphere, showing a continuous, predominantly monolayer graphene growth on SiC. G_1 , G_2 , and G_3 represent monolayer, bilayer, and trilayer graphene regions respectively. Adapted from Reference 74.

2.3.3 Chemical vapour deposition graphene

Currently, by far the most promising method to achieve large-area, high quality graphene films is using CVD methods. In this approach to growing graphene, a substrate (almost always a metal catalyst foil) is first heated and annealed to clean the catalyst surface, as well as to modify catalyst morphological properties, such as grain size and roughness. A hydrocarbon source is then introduced into the chamber and decomposes thermally on the heated substrate, paving the way for one of two graphene growth mechanisms (Figure 7).⁷⁸ As such, the catalyst substrate not only lowers the activation energy for the decomposition reaction, but also determines the mechanism through which graphene is deposited. In the first mechanism, carbon has a high solubility in the chosen substrate at elevated temperatures, which causes carbon atoms to dissolve into the substrate and form a solid solution near the surface of the substrate. Examples of substrates that fall under this category include metal catalysts such as Ni,^{79, 80} Fe,⁸¹ Co,⁸² and Pd.⁸³ Upon cooling of the setup, solubility of carbon decreases and carbon atoms segregate out of the substrate, forming graphene on the surface.^{84, 85} As this process is dependent on carbon solubility, careful control of thermodynamic factors (such as cooling rate) is paramount in determining the number of layers of graphene formed on the substrate surface.^{80, 86}

In contrast, substrates with low carbon solubility follow a different mechanism for the growth of graphene. As carbon is unable to dissolve appreciably, carbon atoms instead form nucleation sites, which expand laterally as more carbon atoms are deposited on the substrate and migrate toward the nucleation sites, with new carbon atoms attaching themselves at the graphene edges. Since this process occurs entirely on the surface of the substrate, termination of graphene growth occurs when the surface is

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entirely covered by the graphene layer; this mechanism is thus referred to as “self-limiting surface deposition” as the end result is predominantly a graphene monolayer (> 95%).⁸⁷ Examples of substrates that follow this growth mechanism include Cu (thus far, the only metal observed in this category),⁸⁸ Ge (semimetal),⁸⁹ and sapphire (insulator).⁹⁰

Other than the choice of substrate, there are a variety of additional factors that can affect the quality, size, and number of graphene layers that are grown using CVD. Although many types of carbon precursors have been used, including gas, liquid, and even solid carbon sources, all these sources are in the gaseous state before approaching the substrate surface, and a major factor in reducing the energy required for the deposition to occur is the strength of the C–H bond.^{91, 92} The base pressure in the reaction chamber prior to graphene growth should be kept low to minimize the amount of impurities and residual oxygen (which would contaminate graphene), and could possibly increase the quality of graphene grown by enhancing the smoothness of the substrate during the initial annealing process.⁹³ The temperature at various regions in the reactor also affects the resulting graphene significantly in several ways. For instance, the number of graphene nucleation sites is lower when temperature is kept high (> 1035 °C), which leads to large individual domain sizes; unfortunately, at these temperatures coupled with very low pressures, evaporation of the substrate could cause roughness and decrease the resulting graphene film quality.⁷⁸

CVD techniques are also able to integrate well with roll-to-roll processes already used industrially, allowing the production of continuous CVD graphene films of enormous sizes (a 100-m-long film was reported in 2013).^{12, 94} These graphene films were shown to maintain excellent optical and electrical properties, thus showing great promise for the continuous production of transparent conducting films for commercial

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applications in the near future. However, CVD graphene films are polycrystalline in general, with grain boundaries formed when graphene growing from different nucleation sites meet each other. As such, control over the amount of nucleation sites formed is a key factor in growing large, single crystals of graphene.⁹⁵ Somewhat counter-intuitively, growing graphene in the presence of oxygen on the surface of Cu has produced the largest CVD-grown single crystal graphene to date, with individual domains repeatedly exceeding 1 cm in diameter after prolonged growth.⁹⁶ It was postulated that oxygen on the surface of the Cu substrate was able to passivate Cu active sites, thus reducing the amount of nucleation sites formed. Graphene films grown this way were demonstrated to have comparable electrical quality to mechanically exfoliated graphene, despite grown in the presence of O.

An additional hurdle for the application of CVD graphene is the relative immaturity of the methods available to directly grow graphene on insulating substrates. A consequence of this is that CVD graphene has to be transferred from the (typically metal) substrate onto another target substrate for practical applications. This is achieved through either wet transfer methods (e.g. chemical etching of metal with or without polymer support, electrochemical delamination) or dry transfer methods (e.g. thermal release tape, pressure-sensitive adhesive), although wet transfer mediated by poly(methyl methacrylate) (PMMA) as the polymer support is currently the most commonly used method. PMMA has proven to be a reliable support for the transfer of nanomaterials due to its flexibility, transparency, excellent wetting capability, and solubility in readily available organic solvents such as acetone; the key steps in this transfer method are shown in Figure 8.⁹⁷ The effect of different wet transfer methods on the properties of CVD graphene films will be discussed in greater detail in Chapter 6.

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Figure 7. Mechanism of CVD graphene growth on substrates with high carbon solubility (e.g. Ni) and low carbon solubility (e.g. Cu). Reproduced from Reference 78.

Figure 8. Schematic of the wet transfer method of nanotubes, mediated by PMMA. Reproduced from Reference 97.

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CHAPTER 3

GRAPHENE NANORIBBON MATERIALS DERIVED FROM THE OXIDATIVE OPENING OF CARBON NANOTUBES

- 3.1 Oxidative opening of carbon nanotubes: unscrolling vs. unzipping**
- 3.2 Electrochemistry of graphene oxide nanoribbons from the oxidative unzipping of carbon nanotubes**
- 3.3 Graphene nanoribbons from the reduction of graphene oxide nanoribbons using lithium aluminium hydride**
- 3.4 Materials and methods**
- 3.5 References**

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The results and findings in this chapter were published in the following manuscripts:

3.1 Wong, C. H. A.; Pumera, M. Unscrolling of multi-walled carbon nanotubes: towards micrometre-scale graphene oxide sheets. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7755–7759.

3.2 Wong, C. H. A.; Chua, C. K.; Khezri, B.; Webster, R. D.; Pumera, M. Graphene oxide nanoribbons from the oxidative opening of carbon nanotubes retain electrochemically active metallic impurities. *Angew. Chem. Int. Edit.* **2013**, *52*, 8685–8688.

3.3 Wong, C. H. A.; Pumera, M. Highly conductive graphene nanoribbons from the reduction of graphene oxide nanoribbons with lithium aluminium hydride. *J. Mater. Chem. C* **2014**, *2*, 856–863.

*Chapter 3 – Graphene nanoribbon materials derived from the oxidative opening of carbon nanotubes***Background**

The obvious first step to be taken before a material can be studied is its production in sufficient amounts as per experimental requirements, and this often presents a problem in graphene preparation. Methods yielding high quality pristine graphene like mechanical exfoliation often produce minute quantities, while bulk synthesis procedures tend to introduce structural defects into the graphitic sp^2 plane.¹ As a result, current synthesis methods are often a balance between the quality of material and scalability. Even though the chemical modification of graphitic materials does not provide pristine graphene samples, it is still a frequently used route since it does not require the use of sophisticated equipment and can produce large quantities of material. Common precursors to preparing graphene with this method include graphite and its oxides,² graphite nanofibres,³⁻⁵ and carbon nanotubes (CNTs).⁶

Naturally, the choice of graphitic precursor affects the structure (and properties) of the resulting graphene material. Considering the lamellar structure of graphite, wherein individual graphene layers are stacked on top of each other, it is easy to visualize the formation of isolated sheets if the layers can be separated from each other. This separation is commonly achieved using a variety of exfoliation methods, such as oxidation and intercalation, by increasing the interlayer distance to weaken or overcome the π -stacking existing between adjacent graphene sheets (a summary of these methods have been discussed in Chapter 1). Similarly, graphite nanofibres can be exfoliated between adjacent sheets to yield graphene nanosheets or even graphene quantum dots.^{3, 7, 8} These differ from graphite-derived graphene sheets only in the lateral dimensions of the sheets obtained. For CNTs, however, the end products are not immediately discernible by intuition. The analogous separation of multi-walled CNTs

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(MWCNTs) into individual CNTs does not occur under these exfoliation conditions, possibly due to the constrained nature of nested nanotubes not permitting expansion to overcome interlayer van der Waals forces. Instead, treating MWCNTs with oxidizing agents first produces oxidized nanotubes, which can then be “sliced” laterally (yielding “pipes”^{9, 10}) or longitudinally,⁶ depending on the conditions used. Current literature widely acknowledges that permanganate oxidation of MWCNTs results in the formation of long and thin nanoribbons due to longitudinal slicing, also known as “unzipping.”⁶ Subsequent reduction of these graphene oxide nanoribbons (GONRs) can then produce graphene nanoribbons (GNRs).

In this Chapter, we explore three different aspects of graphene materials derived from CNTs: (1) the formation of alternative graphene structures during permanganate oxidation of CNTs, (2) the effect of residual metallic impurities on the electrochemistry of GONRs, and (3) the use of lithium aluminium hydride as a novel reducing agent for GONRs to GNRs.

3.1 – OXIDATIVE OPENING OF CARBON NANOTUBES: UNSCROLLING VS. UNZIPPING

Introduction

CNTs are interesting precursors to graphene materials because of their high length to width ratio. MWCNTs can occur in either the *Russian Doll* or *Scroll* form.^{11, 12} *Scroll* MWCNTs consist of rolled up sheets of graphitic sp^2 carbon as opposed to the nested concentric shells found in *Russian Doll* MWCNTs; an illustration of their different structures is given in Figure 1. While the cross-sectional cutting of CNTs has been documented previously and yields short “pipes”,^{9, 10} the longitudinal “unzipping” of CNTs has recently been reported by multiple groups, using different methods involving oxidation,⁶ metal nanoparticles,¹³ hydrogenation,¹⁴ intercalation-exfoliation,¹⁵ plasma etching,¹⁶ and electrical rupturing.¹⁷ This unzipping process leads to long, thin nanoribbons with functionalization dependent on the method of preparation. In the oxidation method of unzipping, the mechanism proposed first involves the formation of a manganate ester on the external wall of the CNT, followed by a dione. This causes strain at the adjacent sites and renders them more susceptible to subsequent oxidation. Propagation of this process continues longitudinally along the CNT wall until the bond-angle strain is finally relieved upon complete unzipping of the tube into the nanoribbon.⁶

Conceptually, both *Russian Doll* and *Scroll* MWCNTs should be able to undergo this mechanism to afford nanoribbons, since the only difference in the external structure of the two models is the exposed edge of the sheet resulting from the final turn of the scroll. Indeed, work on the oxidative opening of MWCNTs has only reported nanoribbon formation thus far.^{18, 19} However, it has been noted that the edge of graphene layers has

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a higher reactivity than the basal plane, which may result in preferential initial oxidation at the edge sites.²⁰⁻²² Herein, we report the oxidative unscrolling of MWCNTs to afford large sheets of oxidized multilayer graphene, in contrast to previously reported nanoribbon formation.

Figure 1. 3D and end-on representations of *Russian Doll* (top) and *Scroll* (bottom) MWCNTs. The choice of nanotube type subjected to oxidative treatment leads to different products from the opening process.

Results and Discussion

MWCNTs were exposed to oxidative conditions according to the Tour method; briefly, this involved sulfuric acid treatment followed by oxidation with KMnO_4 . The oxidised material was isolated, dried, and subsequently characterized. To investigate their morphological properties, scanning electron microscopy (SEM) was performed on the materials. SEM images of the MWCNTs before and after oxidation are shown in Figure 2.

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Figure 2. SEM images of MWCNTs before (left) and after oxidation (right) at magnifications of 40k and 150k for top and bottom images respectively. Scale bars represent 100 nm in all images.

SEM analysis showed that most of the starting material MWCNTs had an average external diameter of approximately 135 nm. Upon oxidation, the material's morphology was visibly changed and displayed evidence of nanotube exfoliation, having a flakier appearance than the original MWCNTs. Also clearly present were residual MWCNTs that were not successfully exfoliated but show visible signs of damage on the walls as a result of the oxidative treatment.

X-ray photoelectron spectroscopy (XPS) techniques are often used to probe the surface elemental composition of a material, and the extent of surface oxidation of the nanotubes after treatment can be easily inferred from the ratio of C to O as obtained from survey scans. XPS wide spectra of the two materials (Figure 3) showed significant differences, where the relative C1s and O1s signal intensities indicated a decrease in C/O ratio from 13.8 to 2.86 after oxidation. This confirmed that the new material was highly oxidized compared to the starting MWCNTs, having a C/O ratio similar to that of graphite oxide.²³

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Although SEM micrographs excel at displaying the three-dimensional topography of a bulk sample, it does so only at the surface, as is apparent from Figure 2. Scanning transmission electron microscopy (STEM) uses higher electron beam energies and is thus able to penetrate a sample that is sufficiently thin, enabling it to reveal information regarding the deeper layers of a material as well as characterization of individual nanomaterials. Thus, STEM was employed to further characterize the oxidized nanotubes, expecting to find evidence of nanotube unzipping into nanoribbons as past studies have described.^{6, 24, 25} However, as the STEM images (Figure 4) show, what we obtained was entirely different. Apart from the expected residual MWCNT bundles/clusters, we did not find any of the abovementioned nanoribbons. Instead, large exfoliated stacks of sheets with either dimension in the μm -scale were seen throughout the sample. Even taking into consideration MWCNTs with the largest diameters ($\sim 260\text{ nm}$) found occasionally in our starting material, these findings cannot be accounted for using the longitudinal unzipping model, where Russian Doll MWCNTs are unzipped to afford oxidized nanoribbons with widths approximately 3 times their original diameters ($L_c = \pi D$, where L_c is the circumference of the nanotube and D is its diameter). This strongly suggests that the MWCNTs used were of a different type.

Indeed, observations of *Scroll* MWCNTs have been reported since their initial description as “graphite whisker scrolls” by Bacon, although *Russian Doll* MWCNTs are far more common.^{12, 26, 27} The appearance of large sheets after oxidation implied that the MWCNTs used were *Scroll* type, while the lack of nanoribbon formation suggests that progressive longitudinal unzipping along the outer nanotube wall did not occur. Instead, oxidation at the final external turn of the scroll is likely to have occurred

Chapter 3 – Graphene nanoribbon materials derived from the oxidative opening of carbon nanotubes preferentially relative to the wall surface, due to the presence of numerous edge sites (which have higher reactivity than CNT walls, as previously noted²⁰⁻²²) in the former.

Figure 3. XPS wide spectra for (A) MWCNT before oxidative treatment and (B) MWCNT after oxidation showing C1s and O1s peaks, normalized to C1s peak intensity.

Figure 4. STEM images of unscrolled MWCNT. Scale bars represent 1 µm. Bottom: magnified image of the boxed region, showing multilayer sheet structure. Scale bar represents 100 nm.

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This initial oxidation increases dramatically the interlayer distance between adjacent planes near the edge in a similar fashion to the oxidation of graphite to graphite oxide.²⁸ Further oxidation between the wall surfaces near the original site is then facilitated, causing a literal “unscrolling” of the MWCNTs into large, flat sheets of graphene oxide.

Unlike nanoribbons in which the aspect ratio is very high, the unscrolled nanotubes were observed as sheets with widths and lengths in the same order of magnitude as each other. Additionally, many sheets were only approximately quadrilaterals with parallel sides. These factors made it more difficult to discern the direction in which the sheets were originally rolled up in their *Scroll* MWCNT form. Even so, it is worth noting that many of the sheets showed long stretches of clean, straight edges, and these may correspond to the length of the original MWCNTs before unscrolling.

Correlation between diameter of MWCNTs and the size of unscrolled sheets can be inferred using the formula for the length of an Archimedean spiral (of which scrolls are a type of) in polar coordinates. For the few largest MWCNTs observed with external/internal diameters of approximately 260/100 nm, the corresponding maximum sheet length is 132 μm . In contrast, the largest sheets observed had lengths of up to 16 μm , and this initially seemed highly incompatible with our calculated values. However, as was previously visible in Figure 4, we also noted that the sheets always occurred in stacks of multiple (5 and above) layers. On top of this, STEM dark-field images (Figure 5) showed that the sheets in a single stack had highly similar edge features. As a result, it is unlikely that individual sheets from different nanotubes stacked together in the solvent; instead, the sheets were more conceivably unscrolled from a single MWCNT.

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Ultrasonication is also known to have a negative effect on the flake size.²⁹ Consideration of these factors would make our sheet sizes consistent with the calculated unscrolled total lengths.

Figure 5. (A) STEM dark-field image of a single stack of unscrolled MWCNT. Inset: zoomed in features of boxed region, in dark-field (red) and bright-field (blue) modes. (B) STEM dark-field image of two stacks of unscrolled MWCNT.

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Conclusion

We have demonstrated that the oxidative treatment of *Scroll* MWCNTs with permanganate leads to oxidized sheets, as compared to the more commonly seen nanoribbons resulting from *Russian Doll* nanotubes. The process seems to be an unscrolling of the MWCNTs layer by layer rather than an unzipping mechanism, and is proposed to occur due to preferential first oxidation at the edge sites rather than the CNT walls. These unscrolled sheets are large in size, easily exceeding 10 μm in length and possess relatively smooth edge features.

Contributions:

C. H. A. Wong and M. Pumera conceptualized the project. C. H. A. Wong conducted the experiments. C. H. A. Wong and M. Pumera wrote the manuscript.

3.2 – ELECTROCHEMISTRY OF GRAPHENE OXIDE NANORIBBONS FROM THE OXIDATIVE UNZIPPING OF CARBON NANOTUBES

Introduction

Graphene nanoribbons are commonly synthesized using carbon nanotubes (CNTs) as a precursor via the oxidative opening of the nanotubes into elongated ribbons. However, CNTs contain significant amounts of metallic impurities even after purification. Herein, we show that these impurities persist at parts-per-million levels after oxidative opening of CNTs to graphene oxide nanoribbons and heavily influence the electrochemical behaviour of the resulting material. This may have negative impacts on the range and effectiveness of potential applications suitable for graphene materials.

For practical applications, especially in the areas of electronics and electrosensing, bulk quantities of material are necessary for device fabrication, which makes scalable methods of graphene production more favoured. To date, methods to synthesize gram-scale quantities of graphene at lower cost generally utilize the chemical modification of graphite followed by exfoliation and/or reduction to obtain single- or few-layered graphene sheets.³⁰ For instance, a common route towards the preparation of graphene involves the preliminary oxidation of graphite to varying degrees. This oxidized product (termed graphite oxide) can be subsequently reduced via thermal,^{31, 32} chemical,^{33, 34} or electrochemical methods^{35, 36} to obtain graphene-like materials. Unfortunately, this route is typically hampered by the inevitable introduction of defects (and possibly heteroatoms) into the sp^2 carbon plane, and the resulting materials do not have the same degree of crystallinity as true, pristine graphene.³⁰

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A variant of the IUPAC defined graphene (“polycyclic aromatic hydrocarbon of quasi infinite size”)³⁷ is the graphene nanoribbon, which retains the sp^2 carbon plane but has an elongated structure and thus a high aspect ratio. GNRs were found to have adjustable band gaps inversely proportional to their widths, while they can be either semiconducting or metallic based on their edge orientations (zigzag or armchair).³⁸⁻⁴⁰ These properties make them excellent candidates for constructing tuneable semiconducting devices. Although a variety of preparation methods for GNRs exist, CNTs are convenient precursors since they have intrinsically high aspect ratios to begin with and are easily obtained commercially or grown in a laboratory. Such a route involves the opening of CNTs through several means, examples of which have been covered in the previous section. The oxidative unzipping method was pioneered by Tour and co-workers and used permanganate oxidation in acidic conditions, with the mechanism proposed to proceed initially through manganate ester formation, which then oxidizes further to the dione. Subsequent permanganate oxidation eventually leads to the longitudinally unzipped nanotube. Further optimization and modification of this reaction was carried out in a later work, which showed that the degree of unzipping, exfoliation, oxidation and amount of defects could be adjusted as desired.¹⁸ In a step analogous to the reduction of graphite oxide to obtain graphene materials, these graphene oxide nanoribbons (GONRs) then undergo a chemical reduction process to give GNRs.

Current methods of CNT production require the use of metal catalysts, whether through arc discharge, chemical vapour deposition, or laser ablation methods. These catalysts remain embedded in the CNTs post-production in the form of metallic impurities.^{41, 42} Furthermore, it is widely acknowledged by the scientific community that these residual impurities are extremely difficult to remove, even though much progress

Chapter 3 – Graphene nanoribbon materials derived from the oxidative opening of carbon nanotubes has been made in the purification of CNTs.⁴²⁻⁴⁴ These impurities have tremendous influence on the electrochemical,⁴⁵⁻⁴⁸ redox,^{49, 50} toxicological,^{51, 52} and electronic⁵³ properties of CNTs. We have also previously demonstrated that metallic impurities inherent in parent graphites persist in the final reduced graphene product, interfering greatly with the electrochemical responses of the materials.⁵⁴ It is thus unsettling that, with regard to the GNR synthesis methods using CNTs described above, no effort was made to characterize or quantify any residual metallic impurities present, despite it being a common knowledge that their parent CNT material typically contains significant amounts of residual metal catalyst.

Herein, we investigate the amount of metallic impurities in multiwalled carbon nanotubes (MWCNTs), as well as the reaction product GONRs, after exposure to the oxidative procedure commonly used to open nanotubes. We show that these impurities persist in the opened nanotubes despite the harsh oxidative conditions used, which are typically regarded as being sufficient in eliminating metal-based impurities (Figure 6). Additionally, these impurities are present in amounts that evidently affect the electrochemical properties of the GONRs.

Figure 6. Schematic for the preparation of GONRs via the oxidative unzipping of CNTs. Metallic impurities inherent in the starting CNTs persist in the GONRs even after chemical treatment.

Results & Discussion

MWCNTs were exposed to oxidative conditions following the procedure laid out by Tour and co-workers.⁶ In this method, treatment of MWCNTs with concentrated sulfuric acid is followed by oxidation via KMnO_4 . The isolated product obtained was highly dispersible in water and DMF due to a large increase in the amount of oxygen containing groups. X-ray photoelectron spectroscopy (XPS) measurements (Figure 7) affirmed this, showing a significant decrease in the C/O ratio from 8.99 to 2.39 as calculated from the relative C1s and O1s signal intensities. The morphology of the MWCNTs observed using scanning electron microscopy was visibly different before and after treatment, showing a highly expanded material as expected after oxidative treatment (Figure 8a). Scanning transmission electron microscopy utilizes electron beams of higher intensity and allows the imaging of a material's individual layers. It can be seen that the GONRs exhibit clean, smooth edges (Figure 8b).

We started our investigation for residual metallic nanoparticles by analyzing the starting MWCNTs and the opened GONRs using inductively coupled plasma mass spectrometry (ICP-MS) for common metallic impurities. The MWCNTs showed the presence of residual metals, particularly Co, Fe, and Ni. This is despite the description of the MWCNTs as already being “cleaned” by the manufacturer. Exposure to the oxidation procedure in acidic conditions above decreased the concentrations of all three metals, most notably in Co (5463.3 ppm to 193.2 ppm) and Ni (100.2 ppm to 13.0 ppm). Fe content showed a more modest decrease from 379.5 ppm to 314.0 ppm. Such levels of decrease in metal contents were similarly observed previously in the oxidation of graphite using the Hummers method, which also used permanganate oxidation in sulfuric acid.⁵⁴

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Figure 7. XPS wide spectra of (a) MWCNTs before oxidation and (b) GONRs. Data shown is normalized to C1s peak intensity.

Figure 8. Electron microscopy imaging of materials. a) SEM images of MWCNTs (left) and GONRs (right) with a highly expanded structure. b) STEM images of GONRs, showing smooth and clean edges.

The effect of metallic impurities on the electrochemical properties of carbon nanotubes has been well documented.^{45-48, 55} Oxidation of sulfide groups is sensitive

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towards catalytic metal impurities, and this effect is seen in the lowering of its oxidation potential towards more negative values. We have previously shown that the electrocatalytic oxidation of sulfides at carbon nanotube surfaces can be attributed to the presence of Ni-based impurities.⁵⁶ Cyclic voltammetry experiments were conducted in the presence of 10 mM NaHS on MWCNT, GONR, and NiO nanoparticle modified electrodes (Figure 9a). Edge-plane pyrolytic graphite (EPPG, representative of graphitic edge and defect sites in carbon materials)⁵⁷ and bare, unmodified GC electrodes served as control experiments to provide a basis of comparison. The voltammograms showed that oxidation of the sulfide group on a GC electrode produces a peak at approximately +0.68 V, while the corresponding value on the EPPG electrode was +0.51 V. Experiments with Fe₃O₄ and Co₃O₄ nanoparticle modified electrodes did not show any catalytic activity towards the oxidation of HS⁻. The MWCNT modified electrode gave a highly electrocatalytic oxidation peak around 0 V, which as previously mentioned arises from residual metallic impurities, even at the ppm level. What is of greater concern is that despite a tenfold decrease in the Ni content to less than 13 ppm after exposure to oxidative treatment, GONRs still showed electrocatalytic behavior towards the oxidation of HS⁻, with both the GONR and NiO modified GC electrodes exhibiting oxidative peaks around +0.25 V as well as highly similar voltammetric profiles. This is striking evidence that even the harsh oxidative and acidic conditions used in the unzipping reaction are unable to sufficiently remove metal-based impurities to render them electrochemically inactive.

The electrocatalytic effect of metallic impurities in the oxidation of hydrazine has also been previously reported.^{45, 58} Since the NaHS experiments were a clear indicator of electrocatalytic activity due to the presence of residual Ni-based impurities, our next

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course of action was to search for signs of similar activity with hydrazine in both the starting MWCNTs as well as the GONRs obtained. Figure 9b shows cyclic voltammetry measurements in the presence of 5 mM hydrazine using the same electrode setups used in the NaHS investigation.

Figure 9. Cyclic voltammetry profiles in the presence of a) 10 mM NaHS, and b) 5 mM hydrazine, on MWCNT, GONR, NiO nanoparticle modified GC electrodes as well as bare GC and EPPG electrodes. The suffix “x” denotes the number of times the current values of the CV was scaled to for ease of comparison. Conditions: scan rate, 100 mV s⁻¹; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl.

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Oxidation of hydrazine on bare GC and EPPG electrodes represented the non-electrocatalytic control case and occurred at similar potentials (+0.80 V). In contrast, the MWCNT modified electrode gave a first oxidation wave beginning at +0.08 V with a peak at +0.58 V and can be attributed to the presence of Ni-based impurities since it is in the same region as the peak corresponding to first oxidation at a NiO modified electrode (beginning at +0.12 V, peak at +0.53 V). The second oxidation peak in both cases arises from the underlying GC electrode surface; such behaviour is typical of heterogeneous electrode surfaces and could arise from incomplete coverage of the GC electrode with the deposited materials. As for the electrode modified with GONRs, a much broader peak with oxidation commencing at +0.03 V was observed, and constituted both Ni-catalyzed oxidation of hydrazine as well as the uncatalyzed reaction on the underlying GC surface. This may conceivably be due to the lowered Ni content in the nanoribbons as compared to the MWCNT starting material.⁵⁴ Nevertheless, it is evident and paramount that the lowered Ni content in GONRs after oxidative treatment in acidic conditions, once again, manifests itself in the electrocatalytic oxidation of hydrazine.

Conclusion

Thus, we have demonstrated that the oxidative opening of multiwalled carbon nanotubes cannot eliminate metallic impurities, despite the relatively harsh conditions used, although the metal content is indeed lowered. For the MWCNTs used as well as the GONRs derived from them, residual metals (demonstrated in the form of Ni-based impurities) still heavily influence the electrochemical behaviour of the materials as shown in the oxidation of HS^- and hydrazine. This phenomenon occurs even at the extremely low amounts (ppm level) detected. It is likely that the presence of metallic

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impurities affects more than just the electrochemical properties of opened nanotubes, which would be of concern when the purity of the material is important in its applications, for example in biomedical uses and the fabrication of nanoscale electronic devices. It is reasonable to propose that all reports on the applications of graphene-based materials should also include accurate measurements of the existing levels of metallic impurities.

Contributions:

C. H. A. Wong and M. Pumera conceptualized the project. C. H. A. Wong and C. K. Chua synthesized the materials. C. H. A. Wong conducted microscopy, XPS, and voltammetry experiments. B. Khezri conducted ICP–MS experiments. C. H. A. Wong and M. Pumera wrote the manuscript. All authors contributed to discussions.

3.3 – GRAPHENE NANORIBBONS FROM THE REDUCTION OF GRAPHENE OXIDE NANORIBBONS USING LITHIUM ALUMINIUM HYDRIDE

Introduction

Research efforts in graphene have recently turned towards a more specialized variant: graphene nanoribbons (GNRs), which have a high aspect ratio (relationship between length and width) and can even be quasi-one-dimensional if the width is narrow enough (<10 nm).⁵⁹ GNRs can exhibit many variable characteristics; the edge-type (armchair or zigzag) can determine if the nanoribbon is semiconducting or metallic,³⁹ the band gap of nanoribbons is dependent on their widths,⁴⁰ and half-metallic GNRs possess electric-field dependent magnetic properties.⁶⁰ These examples of tunability in combination with the superior properties intrinsic to graphene materials make GNRs obvious candidates for next-generation nanoelectronic devices.⁶¹

As the large-scale production of CNTs with desired geometric parameters (i.e. length, thickness, external and internal diameters) is already a reality today, synthesis of GNRs via the unzipping of CNTs is currently the most convenient as well as most promising method. In particular, the oxidative unzipping method covered in the previous sections is favoured due to the advantages of high yields (up to 100%) and the ability to acquire nanoribbons of particular widths as determined by the parent CNTs. This unzipping process yields graphene oxide nanoribbons (GONRs), which are insulating in nature and have to be reduced subsequently in order to obtain GNRs.

This reduction of GONRs is typically carried out through chemical reduction,⁶ thermal annealing,^{3, 62} or a combination of both.⁶³ Thus far, hydrazine has surprisingly been the dominant reducing agent whenever chemical reduction was utilized.⁶⁴⁻⁶⁶ The

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analogous reduction of graphene oxide (GO) to reduced graphene oxide (rGO) with hydrazine has been shown to have a side effect of introducing aromatic N₂-moieties into the graphitic sp² plane, causing considerable changes to its electronic and chemical properties.⁶⁷ On the other hand, reduction of GO to rGO has been shown to occur using a wide array of reducing agents, including but not limited to sodium borohydride,^{68, 69} carbon monoxide,⁷⁰ hydroquinone,³³ potassium hydroxide,⁷¹ and even larger molecules, such as saccharides⁷² and proteins.⁷³ Our group recently showed that lithium aluminium hydride (LAH) can also be utilized for the reduction of GO, with noticeably different properties observed in comparison to its hydrazine-reduced counterpart.⁷⁴ In this study, we synthesized GNRs through the reduction of GONRs using both LAH and hydrazine, and compare their resultant properties via scanning transmission electron microscopy (STEM), Raman spectroscopy, cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and current-voltage measurements. We demonstrate that GNRs obtained from the reduction of GONRs using LAH show significantly higher conductivity than their N₂H₄-reduced counterparts, with values close to that of pristine CNTs, as well as faster heterogeneous electron transfer rates. These LAH-reduced GNRs are also free from nitrogen doping and its complications.

Results & Discussion

The initial unzipping of multi-walled carbon nanotubes (MWCNTs) was carried out using the procedure pioneered by Kosynkin et al. with slight modifications.⁶ This method involves the treatment of MWCNTs with sulfuric acid followed by permanganate oxidation, which results in the longitudinal unzipping of the nanotube walls. Scanning

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transmission electron micrographs of the product revealed the successful formation of graphene oxide nanoribbons (GONRs) with smooth edges and high aspect ratio as shown in Figure 10a. These GONRs were then chemically reduced with LiAlH_4 to produce graphene nanoribbons (LAH-GNRs); reduction utilizing the more traditional reagent hydrazine was also carried out to obtain hydrazine-reduced graphene nanoribbons (N_2H_4 -GNRs) in order to allow comparison their properties. As can be seen from their STEM images, both LAH-GNRs and N_2H_4 -GNRs (Figure 10b and 10c respectively) retain the high aspect ratio of their GONR precursor, though possessing a slightly more wrinkled appearance.

Raman spectroscopy is commonly used to glean information regarding the degree of disorder in graphene materials, where the relative D-band and G-band peak intensities (I_D/I_G) reflect the general density of defects in the sp^2 lattice.⁷⁵ Figure 11 shows the Raman spectra of the materials involved in this study. Three prominent signals were observed in all materials, namely the D-band ($\sim 1345\text{ cm}^{-1}$, defect related), G-band (1575 cm^{-1} , representing the sp^2 lattice), and 2D-band (2700 cm^{-1} , second order overtone of the D band).⁷⁶ After oxidative unzipping of the MWCNTs into GONRs, the I_D/I_G ratio increased from 0.08 to 0.96 due to extensive oxidation occurring on the pristine nanotube walls, which decreases the average sp^2 domain size. Unzipping of MWCNTs into GONRs also generates a large number of edge sites compared to the starting material, which also accounts for the increase in D-band intensity.⁷⁶ Reduction of the GONRs via LAH and hydrazine led to further increases in the I_D/I_G ratios to 1.30 and 1.21, respectively, consistent with previous works on both reduced graphene oxides and reduced GONRs.^{6, 77} An explanation of this behaviour was proposed to be the formation of graphitic domains during reduction that are smaller in size, but more num-

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Figure 10. STEM images of a) GONR, b) LAH-GNR, and c) N_2H_4 -GNR. Scale bars represent 100 nm in all images.

Figure 11. Raman spectra of MWCNTs, GONRs, LAH-GNRs and N_2H_4 -GNRs, normalized to G-band intensity.

-erous, than in graphene oxide.^{77, 78} Average crystallite sizes (L_a) as derived from the I_D/I_G ratios gave 12.9 nm for LAH-GNRs and 13.9 nm for N_2H_4 -GNRs, which shows that the two reduction methods are highly similar in the graphitization of GONRs.

The influence of defect density on the electrochemical performances of the materials was investigated through cyclic voltammetry experiments, carried out in the presence of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ (Figure 12). The electron transfer in this redox couple is known to be sensitive to surface sites;⁷⁹ in particular, Compton and co-workers showed that

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edge-sites are responsible for anomalously fast electron transfer.⁵⁷ Peak-to-peak separation (ΔE_p) values are an indicator of this phenomenon, with smaller ΔE_p values corresponding to faster heterogeneous electron transfer (HET) rates, and is generally desirable for electrochemical sensing applications. Glassy carbon (GC) electrodes modified with MWCNTs showed a ΔE_p of 290 mV for the ferro/ferricyanide probe, which is equivalent to an observed HET constant (k_{obs}^0) of $3.22 \times 10^{-4} \text{ cm s}^{-1}$. Modifying the GC electrode with GONRs decreased ΔE_p to 223 mV ($k_{obs}^0 = 8.19 \times 10^{-4} \text{ cm s}^{-1}$) due to the introduction of numerous defects and edge sites onto the material surface as seen from the increase in I_D/I_G ratio from 0.08 (MWCNTs) to 0.96 (GONRs). However, this increase in electrochemical performance (in terms of HET rates) is modest, due to repulsive interactions between surface oxygen groups on the GONRs and negatively charged $[\text{Fe}(\text{CN})_6]^{4-/3-}$ ions. Reduction of GONRs led to the removal of these oxygen-containing groups as well as a further increase in defects and edge sites, which resulted in drastically lowered ΔE_p values as expected for both LAH-reduced and N_2H_4 -reduced GNRs. LAH-GNRs displayed slightly better electrochemical performance ($\Delta E_p = 107 \text{ mV}$, $k_{obs}^0 = 4.48 \times 10^{-3} \text{ cm s}^{-1}$) than N_2H_4 -GNRs ($\Delta E_p = 112 \text{ mV}$, $k_{obs}^0 = 3.96 \times 10^{-3} \text{ cm s}^{-1}$), and is related to the slight difference in I_D/I_G ratios of the two materials (1.30 vs. 1.21).

The relative performances of LAH and N_2H_4 in the removal of oxygen-containing groups in GONRs were also probed via X-ray photoelectron spectroscopy, which can reveal not only the chemical composition of the material surface but also the types of chemical groups present. Analysis of the materials' XPS wide spectra (Figure 13a) showed that oxidative unzipping of MWCNTs led to a decrease in the atomic C/O ratio from 20.42 to 2.25, indicating extensive oxidation. Subsequent reduction via LAH increa-

Figure 12. Cyclic voltammograms for 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ on MWCNT, GONR, LAH-GNR, and N_2H_4 -GNR modified GC electrodes. Conditions: scan rate, 100 mV s^{-1} ; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl.

-sed the C/O ratio to 8.60, while hydrazine-mediated reduction resulted in a C/O ratio of 8.67. High-resolution XPS (Figure 13b) was also carried out on the GONRs, LAH-GNRs and N_2H_4 -GNRs to investigate the types of oxygen-containing groups present on the materials as well as their relative amounts. The $\text{C}1\text{s}$ signal of GONRs displayed four main peaks centred at 284.5 eV (graphitic $\text{sp}^2 \text{C}$), 286.0 eV ($\text{sp}^3 \text{C}$, hydroxyl, and epoxy groups), 288.1 eV (carbonyl), and 289.8 eV (carboxyl). The large amount of carbonyl groups observed is consistent with the CNT unzipping mechanism via buttressing ketones that has been proposed.^{6, 80} Upon reduction, the $\text{C}1\text{s}$ spectra of both LAH-GNRs and N_2H_4 -GNRs showed significant changes as compared to their precursor GONRs. Deconvolution of these signals resulted in six components for both samples: 284.5 eV ($\text{sp}^2 \text{C}$), 285.6 eV ($\text{sp}^3 \text{C}$), 286.6 eV (hydroxyl & epoxy), 287.9 eV (carbonyl), 289.4 eV (carboxyl) and 291.2 eV ($\pi-\pi^*$ shaking interactions). Relative amounts of these components are detailed in Table 1. Key features include a vast increase in the amount of $\text{sp}^2 \text{C}$ in both GNR samples

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indicating a restoration of the graphitic π -network, as well as highly similar values obtained for the individual components after reduction. This, in combination with the C/O ratios obtained above in the XPS wide spectra, shows that the two reduction methods do not differ much in their ability to reduce oxygen-containing groups on GONRs.

However, it has been noted in multiple studies that the reduction of graphene oxide and GONRs with hydrazine inevitably incorporates nitrogen into the sp^2 carbon lattice.^{6, 81, 82} The analogous Li-doping of LAH-GNRs was also a concern due to lithium's high binding energy to graphene lattices, which leads to an increased reactivity of monolayer graphene.⁸³ We did not observe any contaminating Li present in the XPS analysis of our obtained LAH-GNRs. In contrast, N_2H_4 -GNRs were observed to possess an atomic nitrogen concentration of 3.8%. Ruoff and co-workers suggested that the hydrazine adducts are pyrazoline or pyrazole groups depending on whether additional heat treatment was present, and showed that such N-doping affects the material's electronic structure greatly.⁶⁷ Additionally, these pyrazole groups are proposed to form at edge and defect sites on the graphene material. This implies that N-doping resulting from the hydrazine-mediated reduction of GONRs (which have naturally high numbers of edge sites) to GNRs is even more unavoidable, and is likely to increase further with decreasing nanoribbon width. The presence of these additional functional groups may induce unwanted side reactions on the material surface, which would be undesirable for applications such as biomedical nanocomposites and electrochemical sensors. By using LAH as a reducing agent instead of hydrazine, this problem is obviously circumvented, while yielding GNRs that are similar in terms of types and amounts of oxygen-containing functionalities.

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The two reduction methods were further compared through solid-state ATR-FTIR studies to look for any possible differences in functional groups remaining on the GNRs, and the spectra for all four materials (MWCNTs, GONRs, and both GNRs) are given in Figure 14. The starting MWCNTs showed a predominantly featureless FTIR spectrum, while oxidative unzipping introduced a myriad of oxygen-based functionalities onto the GONRs. An intense, broad feature spanning 2300–3700 cm^{-1} was observed corresponding to O–H stretching from carboxylic acids, alcohols, and adsorbed H_2O ; signals at 1720 and 1615 cm^{-1} were due to C=O stretching from carboxylic acids and ketones, respectively; the band at 1420 cm^{-1} originated from O–H bending; epoxy group C–O–C stretching accounted for signals at 1280, 1220 and 870 cm^{-1} ; and alcohol C–O stretching led to signals at 1165 and 1040 cm^{-1} . Exposure of these GONRs to LAH and N_2H_4 resulted in the removal of these functional groups, as is apparent from the spectra of both LAH-GNRs and N_2H_4 -GNRs, with both materials showing strikingly similar profiles. This once again demonstrates that these reduction methods are on par with each other in removing oxygen-based functionalities.

Although XPS and ATR-FTIR data showed that both LAH and N_2H_4 reduce GONRs to approximately the same extent and types of functionalities, it is necessary to note that the underlying reduction mechanisms of each reagent are noticeably different. Several studies have proposed mechanisms for hydrazine-mediated reduction of epoxides; in general they suggest hydrazine attacking one of three possible carbon atoms: 1) the carbon atom directly attached to the epoxide, 2) alpha carbon, or 3) beta

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Figure 13. a) XPS wide spectra of MWCNTs, GONRs, LAH-GNRs, and N₂H₄-GNRs, normalized to C1s peak intensity. b) High resolution XPS C1s core spectra of GONRs, LAH-GNRs, and N₂H₄-GNRs.

Table 1. Relative amounts of components in deconvoluted high resolution C1s core spectra of GONRs, LAH-GNRs, and N₂H₄-GNRs.

	% composition of C1s signal		
	GONR	LAH-GNR	N ₂ H ₄ -GNR
C=C	7.7	60.0	57.9
C–C	41.8	19.0	20.3
C–O	42.3	9.3	9.5
C=O	8.2	4.6	5.1
O–C=O	–	4.8	4.7
π–π*	–	2.3	2.6

Figure 14. Solid state ATR-FTIR spectra of MWCNTs, GONRs, LAH-GNRs, and N₂H₄-GNRs.

carbon to the epoxide, forming a hydroxyl and a hydrazino group (–HNNH₂).^{77, 84, 85} H-atom transfer from the hydrazino group to the hydroxyl releases both groups as H₂O and diazene (N₂H₂). While this is plausible for the deoxygenation of epoxides, no reaction pathways were determined for hydrazine-mediated reduction of GO for hydroxyl, carbonyl, or carboxyl groups.⁸⁵ Additionally, GONRs obtained via unzipping of CNTs have a high proportion of carbonyl groups, which are also unlikely to be removed via Wolff-Kishner type reactions due to the low basicity and temperature of the reduction reaction.

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The presence of N-doping and absence of C–H stretching modes in N₂H₄-GNRs are also in disagreement with Wolff-Kishner reduction. This essentially implies that the complete mechanism for hydrazine-mediated reduction of oxidized graphene materials is still not understood, inevitably hampered by the highly heterogeneous structure of GO.

LAH operates via a hydride-transfer mechanism, displacing a highly electronegative element adjacent to a carbon atom. For reduction of oxygen functionalities, LAH first transfers one hydride (H⁻) anion to an electron-deficient carbon atom, forming a C–H bond and an ion of the form AlH₃OR⁻. Subsequent workup with a suitable proton source releases the aluminium moiety as a salt, while the final organic component is an alcohol. In the case of GO, this occurs in the reduction of epoxides, carbonyls, and carboxylic acid groups to the corresponding alcohols. Although the mechanism seems straightforward enough, this line of classical organic chemistry understanding of LAH does not allow the reduction of such functionalities beyond the alcohol. As such, it is unclear why no signals arising from hydroxyl functionalities were observed in the ATR-FTIR spectrum of LAH-GNRs. Since research on LAH-mediated reduction of large, heterogeneous substrates like GO and GONRs is still in its infancy, the chemical pathways are not well understood, as is the case with hydrazine-mediated reduction.

While the mechanisms of both reduction methods remain unclear, physical differences between the GNRs in the form of solubility properties were easily observable. Suspensions of MWCNTs, GONRs, LAH-GNRs and N₂H₄-GNRs were prepared at a concentration of 1 mg mL⁻¹ in *N,N*-dimethylformamide (DMF), a polar aprotic solvent commonly used to disperse graphene materials. The suspensions were ultrasonicated for 30 min and left to stand for extended periods of time. As seen from Figure 15a, all

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four materials were well dispersed in DMF immediately after sonication. After 3 days (Figure 15b) the MWCNTs settled completely, GONRs and LAH-GNRs remained well dispersed, while N_2H_4 -GNRs were partially settled. It took 5 days for N_2H_4 -GNRs to settle completely. However, even after being left to stand for 1 month (Figure 15c), LAH-GNRs still remained highly dispersed in DMF with no observable differences in the appearance of the solution. This implies that the structure of LAH-GNRs possess a larger amount of polar moieties than that of N_2H_4 -GNRs, and hydroxyl groups are a distinct possibility when one considers the classical LAH reduction mechanism. Once again, it is unclear why these polar moieties do not show up in the ATR-FTIR spectra of LAH-GNRs. Since LAH-GNRs are stable in polar DMF over time even without the use of additional surfactants, they possess a distinct advantage over N_2H_4 -GNRs in solution-processed applications, such as thin-film devices.

Previously, our group showed that the reduction of graphene oxide using LAH generated CH_2-OH functionalities from the reduction of carboxylic acid groups, causing noticeable bands in the region of $2800-3000\text{ cm}^{-1}$.⁷⁴ The occurrence of C-H stretching modes could also have originated from the reduction of C=C double bonds conjugated with C=O groups to CH_2-CH_2 moieties, and these insulating moieties were inferred to be likely cause of the LAH-reduced material's low conductivity.⁷⁴ In contrast, the C-H stretching modes are clearly not present in the FTIR spectrum of our current work LAH-GNRs.

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Figure 15. Digital photographs of MWCNTs, GONRs, LAH-GNRs and N_2H_4 -GNRs dispersed in DMF a) immediately after 30 min ultrasonication, b) left to stand for 3 days, and c) 1 month. Dispersions were prepared at a concentration of 1 mg mL^{-1} .

This may be due to the difference in the procedures used for the oxidation of graphite and the unzipping of MWCNTs. In light of the absence of insulating C–H moieties, we next carried out current-voltage measurements on an interdigitated gold

Chapter 3 – Graphene nanoribbon materials derived from the oxidative opening of carbon nanotubes electrode (Au-IDE) to provide qualitative conductivity comparison for the materials used in this work, with the results shown in Figure 16. MWCNTs displayed ohmic behaviour with the highest I/V slope of 58.6 mA V^{-1} , while GONRs were observed to be insulating as expected of oxidized graphene materials, with a practically horizontal profile on the scale shown and exhibiting a slope of only 0.03 mA V^{-1} .⁷⁷ Reduction of GONRs by LAH saw conductivity being restored greatly, with LAH-GNRs presenting a slope of 50.5 mA V^{-1} , approaching that of the parent MWCNTs. N_2H_4 -GNRs also showed restored conductivity but to a lesser extent with a slope of 38.9 mA V^{-1} , indicating that LAH was more effective in restoring conductivity to GONRs after a reduction procedure. The lowered conductivity of N_2H_4 -GNRs is consistent with previous literature: studies have shown that conductivity of hydrazine-reduced GO is significantly lower than pristine graphene.⁸⁶⁻⁸⁸ Other works on N-doped graphenes suggest that the introduction of foreign N atoms creates scattering centers that decreases conductivity of the graphene lattice.^{89, 90}

Figure 16. Current-voltage profiles of MWCNTs, GONRs, LAH-GNRs, and N_2H_4 -GNRs, measured after material deposition on an Au-IDE.

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This makes LAH-GNRs significantly more efficient materials for nanoelectronic applications in which conductivity is paramount, such as nanowires for molecular-scale computers and flexible screen displays.

Conclusion

In this study we have shown that lithium aluminium hydride is an efficient reducing agent to obtain graphene nanoribbons, showing performance (in terms of amounts and types of functional groups reduced) on par with hydrazine, which is the most commonly used reducing agent for oxidized graphene materials. Reduction of GONRs with LAH instead of hydrazine also yields a material with superior conductivity, better electrochemical performance, as well as being free from nitrogen doping and the resulting possible complications (e.g. increased reactivity). Additionally, LAH-GNRs remain soluble in DMF over long periods of time, making them easier to handle for solution-processing techniques. These factors pave the way for LAH-reduced GNRs to be used in practical applications in which hydrazine-reduced GNRs are otherwise unsuitable.

Contributions:

C. H. A. Wong and M. Pumera conceptualized the project. C. H. A. Wong conducted the experiments. C. H. A. Wong and M. Pumera wrote the manuscript.

3.4 – MATERIALS AND METHODS

Materials

MWCNTs were obtained from BuckyUSA, USA, as well as Sigma-Aldrich, Singapore. Sulfuric acid (95–98% w/v), hydrochloric acid (37% w/v), *N,N*-dimethylformamide, tetrahydrofuran, methanol, lithium aluminium hydride, sodium sulfate, potassium hexacyanoferrate(III), phosphate buffer powder, sodium hydrogen sulfide (anhydrous), and nickel(II) oxide nanopowder were obtained from Sigma-Aldrich, Singapore. Hydrogen peroxide, hydrazine hydrate, and hydrazine dihydrochloride were obtained from Alfa Aesar, Singapore. Fuming nitric acid (>90%), ultrapure nitric acid (for ICP-MS analysis sample preparation) and potassium permanganate were obtained from J.T. Baker. Diethyl ether was obtained from RCI LabScan, Thailand. Ethanol was obtained from Merck, Singapore. Deagglomerated alpha alumina powder (0.05 μm) was purchased from Struers, Singapore. Glassy carbon (GC) working electrodes, Ag/AgCl reference electrode, and Pt auxiliary electrode were obtained from CH Instruments, USA. Edge plane pyrolytic graphite (EPPG) electrode was obtained from ALS, Japan.

Apparatus

A JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) was used to acquire the SEM images using gentle-beam mode at 2.0 or 5.0 kV at a working distance of 5.8 mm. The solid samples were immobilized atop a carbon tape on an aluminium SEM holder for analyses. Scanning transmission electron microscopy (STEM) images were acquired at 30.0 kV at a working distance of 8.3 mm. The sample for STEM

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was prepared by depositing 1 μL of the material suspension (1 mg mL^{-1} in DMF) onto a carbon film coated copper TEM grid (Ted Pella) and allowed to dry in air.

Raman spectra were obtained with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific, Japan) with an Ar ion laser (excitation wavelength 514.5 nm) beam in backscattering geometry with a CCD detector, measuring from 1000 to 3000 cm^{-1} . The crystallite size (L_a) of the sp^2 lattice was calculated using the equation:

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

where λ is the wavelength of the laser in nm, I_G and I_D are the intensities of the Raman G and D bands respectively.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Phoibos 100 spectrometer (SPECS, Germany) with a monochromatic Mg X-ray source. Relative sensitivity factors were used for evaluation of C/O ratios from wide spectra XPS measurements. The samples for XPS were prepared by coating carbon tape with a uniform layer of the materials studied.

Inductively coupled plasma mass spectrometry elemental analysis was conducted using an Agilent model 7700x ICP-MS, while microwave digestions in concentrated HNO_3 were carried out in a CEM-MARS 5 system. Samples for ICP analysis were prepared by accurately weighing the materials into a clean Easy Prep vessel followed by the addition of 1.5 mL of ultrapure HNO_3 . Digestion of the samples was carried out with microwave treatment at 1,600 W (100%), with temperature ramping from 25°C to 120°C over 20 min and maintaining at 120°C for 15 min.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy measurements were performed using a PerkinElmer Spectrum 100 spectrometer with a

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universal ATR accessory. Materials tested were sampled in the solid state without further sample preparation. A diamond/ZnSe crystal was used as the ATR crystal.

Procedures

Oxidation of MWCNTs (for both unscrolling and unzipping, Sections 3.1 and 3.2) was adapted from the Tour method.⁶ 50 mg of MWCNTs was stirred in 50 mL concentrated H₂SO₄ for 12 hr at room temperature. KMnO₄ (250 mg) was then added to the reaction mixture and stirred for 1 hr. The mixture was then heated at 55 °C for 30 min and the reaction monitored by sampling a few drops of the reaction mixture into an Eppendorf tube containing 1 mL of deionized water. A red hue in the test solution signalled reaction completion due to the formation of Mn(IV). A few drops of the reaction mixture was also added to a separate Eppendorf tube with 1 mL of water and 2–3 drops of H₂O₂ and ultrasonicated; a dark yellow or brown colour as well as high dispersibility of the solid indicated reaction completion. The reaction temperature was then raised to 70 °C, allowed to stabilize, and then cooled to room temperature. The mixture was poured into 150 mL of ice water containing 2 mL of 27% H₂O₂ and then filtered through a RC membrane (0.22 µm). The solid residue was stirred in 50 mL H₂O for 30 min and ultrasonicated for 15 min. HCl (37%, 6 mL) was added and the mixture filtered again (RC, 0.22 µm). The residue was stirred in 50 mL ethanol for 30 min and ultrasonicated for 15 min. 50 mL of ether was added and the mixture filtered through a PTFE membrane (0.22 µm). The solid residue was washed with ether (2 x 25 mL) and dried in an oven at 50 °C for 4 days before use. Similar procedures were used for the synthesis of GONRs in Section 3.3, except that the scale was increased to 300 mg of starting MWCNTs.

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For the reduction of GONRs by lithium aluminium hydride, GONRs (100 mg) were stirred in dry THF (60 mL) and ultrasonicated for 3 h. LAH (400 mg) was then added to the reaction mixture portion-wise in a 0 °C ice bath until bubbling was no longer observed. The reaction mixture was then transferred drop-wise into a solution of LAH (1600 mg) in dry THF (60 mL) at 0 °C, and then allowed to stir under reflux for 24 h. The reaction was quenched with saturated sodium sulfate, followed by addition of 1 M HCl at 0 °C until a clear solution was obtained. The mixture was filtered over a PTFE membrane (0.22 µm), the residue washed with copious amounts of ultrapure water, then dried in an oven at 60 °C for 5 days to afford LAH-reduced graphene nanoribbons (LAH-GNRs).

For the reduction of GONRs by hydrazine, GONRs (100 mg) were stirred in ultrapure water (100 mL) and ultrasonicated for 3 h. Hydrazine hydrate (4 mL) was added drop-wise at 47 °C, after which it was heated to 80 °C for 24 h. The reaction was allowed to cool to room temperature, filtered over a PTFE membrane (0.22 µm), and the residue washed repeatedly with methanol and ultrapure water. The solid was then dried in an oven at 60 °C for 5 days to afford hydrazine-reduced graphene nanoribbons (N₂H₄-GNRs).

The maximum length of an unscrolled MWCNT was determined using the general equation of an Archimedean spiral in polar coordinates:

$$r = a + b\theta$$

where r is the distance of a point on the curve from the origin, a is the internal diameter of the nanotube, b is related to the interlayer distance d by $d = 2\pi b$, and θ is the angle travelled in radians. The integral for the length of an arc in a curve:

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$$L = \int_0^{2n\pi} \sqrt{r^2 + \left(\frac{dr}{d\theta}\right)^2} d\theta$$

where n is the number of layers (as deduced from the external diameter, internal diameter and interlayer distance d) was then solved to attain the length of an unscrolled MWCNT of a certain internal and external diameter. The value of d used in calculations was 0.344 nm.⁹¹

Cyclic voltammetry experiments were carried out on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). Electrochemical experiments were carried out in a 5 mL electrochemical cell at room temperature with a three-electrode configuration (Ag/AgCl as the reference, Pt as the auxiliary). Cyclic voltammetry experiments were conducted at a scan rate of 100 mV s⁻¹ with 5 mM hydrazine, 10 mM NaHS, and 10 mM [Fe(CN)₆]^{4-/3-} as molecular probes, in a supporting electrolyte of 50 mM phosphate buffer solution (pH 7.4). All CV data shown are first scans of the experiment, unless otherwise stated. All electrochemical potentials in this paper are stated versus the Ag/AgCl reference electrode (plastic tube, silver wire in 3.0 M KCl). GC and EPPG electrode surfaces were renewed before each measurement/modification by polishing for 2 min on a polishing pad with alumina slurry, and then washed with deionized water of resistivity not less than 18.2 M Ω cm (Milli-Q, Millipore). Suspensions of MWCNTs, GONRs, and NiO nanoparticles were prepared with a concentration of 5 mg mL⁻¹ in DMF with 30 min sonication (Section 3.2). Suspensions of MWCNTs, GONRs, LAH-GNRs, and N₂H₄-GNRs were prepared with a concentration of 1 mg mL⁻¹ in DMF with 30 min sonication (Section 3.3). Modification of GC electrode surfaces with these materials was performed by

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depositing a 1 μL aliquot of the suspension onto the electrode, after which the solvent was evaporated under a sun lamp for 20 min. The suspensions were sonicated for an additional 1 min before each deposition to ensure homogeneity.

k_{obs}^0 values were calculated according to the Nicholson method⁹² relating ΔE_p values to a dimensionless kinetic parameter ψ , leading to k_{obs}^0 via the equation:

$$k_{obs} = \psi \left[D_O \pi \nu \left(\frac{nF}{RT} \right)^{1/2} \right] \left(\frac{D_R}{D_O} \right)^{\alpha/2}$$

where D_O and D_R are the diffusion coefficients for potassium ferricyanide and potassium ferrocyanide respectively at 298 K,⁹³ ν is the scan rate in V s^{-1} , n is the number of electrons transferred, F is the Faraday constant, R is the ideal gas constant, T is the temperature in K and α is the transfer coefficient (0.5).

Current-voltage (I/V) measurements were carried out by first depositing 1 μL of the material suspension (1.0 mg mL^{-1} in ethanol) onto interdigitated gold electrodes (Au-IDE) with a gap of 10 μm . The solvent was then evaporated off under a sun lamp for 20 min to leave a randomly deposited film on the interdigitated area. I-V curve data were obtained using linear sweep voltammetry (scan rate 20 mV s^{-1}).

3.5 – REFERENCES

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CHAPTER 4

MICROWAVE IRRADIATION IN THE SYNTHESIS OF CHEMICALLY MODIFIED GRAPHENES

- 4.1 Microwave reduction/exfoliation of different types of graphite oxides under low pressure conditions**
- 4.2 Microwave exfoliation of graphite oxides in the presence of hydrogen sulfide**
- 4.3 Materials and methods**
- 4.4 References**

Chapter 4 – Microwave irradiation in the synthesis of chemically modified graphenes

The results and findings in this chapter were published in the following manuscripts:

4.1 Wong, C. H. A.; Jankovský, O.; Sofer, Z.; Pumera, M. Vacuum-assisted microwave reduction/exfoliation of graphite oxide and the influence of precursor graphite oxide. *Carbon* **2014**, 77, 508–517.

4.2 Wong, C. H. A.; Sofer, Z.; Klímová, K.; Pumera, M. Microwave exfoliation of graphite oxides in H₂S plasma for the synthesis of sulfur-doped graphenes as oxygen reduction catalysts. *ACS Appl. Mater. Interfaces* **2016**, 8, 31849–31855.

Background

One-step synthesis of high quality graphene at gram-scale quantities is important for industrial applications, e.g. in electrochemistry for sensing and energy storage. Currently, thermal reduction/exfoliation of GO is a typical method of choice. However, it has the drawback of requiring specialized equipment for rapid thermal shock. A recent alternative method, microwave-assisted exfoliation, usually suffers from poor reduction of graphite oxide and thus low C/O ratios. The mechanism of exfoliation in microwave (MW) reduction of GO is driven by the buildup of interlayer pressure from gases, similar to thermal annealing. The core difference is MW irradiation does not directly remove oxygenated species on GO because the oxidized regions lack extensive conjugated π -networks for efficient absorption and dissipation of microwaves.¹ Instead, MW irradiation is absorbed and dissipated by conjugated graphene islands, which then causes a superheating of these regions, triggering the thermal deoxygenation of adjacent GO sites.² These newly-deoxygenated sites then become effective MW absorbers themselves, leading to a cascade reaction and subsequent rapid reduction of the entire GO. This process leads to two significant advantages of MW reduction over standard thermal annealing: firstly, the GO is heated more uniformly; secondly, RGO can be obtained in a fraction of the time required for thermal annealing.

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4.1 – MICROWAVE REDUCTION/EXFOLIATION OF DIFFERENT TYPES OF GRAPHITE OXIDES UNDER LOW PRESSURE CONDITIONS

Introduction

For use in electrochemical sensors where gram-scale quantities of material are necessary, chemical oxidation of graphite to GO followed by a reduction process is often used as it is both more cost-efficient and scalable than other currently available methods.³ However, this pathway leads to the introduction of extensive defects in the graphene plane along with the presence of residual oxygenated species, which make the resultant materials' properties differ from pristine graphene. Hence, such materials are loosely referred to as "reduced graphene oxides" rather than graphene. Despite their different natures, reduced graphene oxides still possess remarkably similar characteristics to pristine graphene, and are suitable for many of the latter's applications.⁴

After solution-based oxidation of graphite to GO, it is commonly exposed to thermal treatment, which has the dual effect of reducing oxygen content as well as exfoliating the material. These effects arise from the thermal decomposition of oxygen-containing groups on GO, directly removing them from the graphene plane in the form of gaseous products, which also cause enormous interlayer pressure build-up resulting in exfoliation of the individual sheets.⁵ Extensive structural damage in the graphene is expected in the form of vacancies and topological defects due to the decomposition of oxygen-containing groups, though these defects have the side effect of increasing heterogeneous electron transfer (HET) rates, which generally leads to better electrochemical performance.^{6, 7} The final product is termed thermally reduced

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graphene oxide (TRGO), a highly expanded, fluffy black powder with worm-like or accordion structures.^{8, 9}

Microwave irradiation has been utilized in multiple studies to facilitate the reduction of GO.¹⁰⁻¹⁴ This is possible to carry out in aqueous media, organic media, as well as in ionic liquids.¹⁰⁻¹² Solid-state reduction of GO has been achieved without other agents,^{13, 14} while reduction in the presence of additional microwave susceptors (e.g. graphene and graphene nanosheets) can enhance localized heating and facilitate exfoliation.^{1, 15} The absorption of microwave irradiation by GO rapidly creates regions of high temperature within the material analogous to thermal shock treatment in the production of TRGO, and highly similar worm-like/accordion structures have been identified in reduced graphene oxide after microwave irradiation.¹⁵ Thus, it is expected that microwave-exfoliated graphenes will bear many similar properties to TRGO, but can be obtained at a fraction of the time needed for TRGO. In addition, the microwave exfoliation procedure can be performed in a simple, ubiquitous commercial microwave oven. These factors of time, cost, and ease of access make microwave irradiation a very promising route towards the synthesis of reduced graphene oxides. However, current methods using microwave exfoliation of GO in an ambient air atmosphere result in C/O ratios of 1.39–3.60,^{1, 13-15} while TRGO typically exhibits a C/O ratio of ~20.⁷ It has been shown that with increasing C/O ratio, the electrochemical performance in terms of heterogeneous electron transfer (HET) rates increases.^{7, 16} Therefore, it is important to develop microwave exfoliation methods capable of fabricating exfoliated graphene with high C/O ratios and fast HET rates. However, research efforts on the solid-state microwave exfoliation of GO have focused only on the tuning of microwave treatment parameters (e.g. duration of irradiation or amount of additives) rather than the type of

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GO used. To the best of our knowledge, all existing studies on the dry, microwave-assisted production of reduced graphene oxides have been carried out only on GO prepared using the commonly used Hummers' method. This severely limits the scope of the investigation, since GOs synthesized using different methods differ significantly in their structures and types of functionalization, which can alter the final reduced materials' properties.

Herein, we subject three different types of graphite oxides to microwave exfoliation in closed, evacuated environments. The subsequent exfoliation environments during irradiation are unique to each graphite oxide prepared by different oxidation procedures. This is because graphite oxides exhibit different structures and contain different oxygen containing groups, depending on the oxidation method used to generate them. At the beginning of exfoliation formation of plasma is initiated, followed by the release of gases (H_2O , CO_2 , as well as simple and complex organic molecules).¹⁷ As previously stated, such gases are specific to individual graphite oxides.¹⁷ The exfoliated materials obtained are characterized systematically using scanning transmission electron microscopy (STEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), combustion elemental analysis, Fourier-transform infrared spectroscopy, cyclic voltammetry, and specific resistivity measurements. We show that the obtained graphene materials vary significantly in their properties as a result of their different parent graphite oxides, and may be related to the composition and amounts of volatile exfoliation products. Voltammetric characterization using cyclic voltammetry shows that our microwave-vacuum exfoliated graphenes are suitable for electrochemical applications, showing highly similar electrochemical performance to the more commonly used TRGO.

*Chapter 4 – Microwave irradiation in the synthesis of chemically modified graphenes***Results and Discussion**

Three different graphite oxides (GOs) were synthesized using Hummers, Staudenmaier, and Hofmann methods, sealed and evacuated in quartz ampoules, then exposed to microwave radiation for 3 min (see Experimental Section for full procedure). Such microwave treatment of solid-phase GO has the dual effect of reducing the oxygen-containing groups present and exfoliating the resultant material.^{13, 14} Initial plasma formation and the intense evolution of gases in the ampoule were observed during irradiation, as well as a large expansion in the volume of the materials. Formation of microwave plasma led to rapid initial heating of graphene oxide and exfoliation, arising from the evolution of gaseous exfoliation products. The plasma was quenched by the evolved gases and subsequent heating is related to microwave absorption by newly-formed graphene regions, further facilitating exfoliation and gas release. The resulting microwave-vacuum exfoliated graphenes MVG-HU, MVG-ST, and MVG-HO (from their graphite oxide precursors HU-GO, ST-GO, and HO-GO synthesized using Hummers, Staudenmaier, and Hofmann methods, respectively) were obtained from the ampoules as black powders with fluffy appearances. High temperature thermal reduction of GO yields a similar highly expanded material (termed thermally reduced graphene oxide, or TRGO), due to interlayer pressure build up from the evolution of gases originating from the thermal decomposition of oxygen-containing groups.⁸ As such, a sample of TRGO was also studied for the purpose of comparison.

Scanning transmission electron microscopy (STEM) was performed to investigate the morphologies of the MVGs and TRGO, with the micrographs shown in Figure 1. As was the case with TRGO, all MVGs were observed as single- or few-layer sheets with a highly wrinkled appearance, although MVG-HU sheets showed a higher extent of

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stacking as well as less wrinkling. Such wrinkled features correspond to the introduction of both physical and chemical defects into the graphene sp^2 lattice, which can be studied using Raman spectroscopy. Primary features in the Raman spectra of the materials (Figure 2) are the D-band at $\sim 1350\text{ cm}^{-1}$ corresponding to defects in the sp^2 lattice, and the G-band at $\sim 1575\text{ cm}^{-1}$ representing the sp^2 lattice itself. The relative peak intensities of these bands, referred to as I_D/I_G ratios, are often used to indicate the amount of disorder in the material. I_D/I_G ratios of 0.76, 0.88, and 0.93, and 1.12 were calculated for MVG-HU, MVG-ST, MVG-HO, and TRGO respectively; these correspond to crystallite sizes (L_a) of 22.1, 19.0, 17.9 and 15.1 nm. These results show that microwave exfoliation of GO under initial evacuation produces materials similar to TRGO but with less disorder in the graphitic plane.

The main consideration when gauging the effectiveness of a procedure to produce reduced graphene oxides is its ability to remove oxygen-containing species from GO. This parameter is typically investigated using X-ray photoelectron spectroscopy

Figure 1. STEM images of (a) MVG-HU, (b) MVG-ST, (c) MVG-HO, and (d) TRGO. Scale bars represent 100 nm in all images.

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(XPS), which reveals not only the surface elemental composition of a material but also the types of bonding present in these species. Atomic C/O ratios for the materials can be calculated from their XPS survey spectra (Figure 3) and we obtained C/O ratios of 10.5, 6.23, and 11.6 for MVG-HU, MVG-ST, and MVG-HO respectively. For comparison, GOs synthesized using similar methods in a separate study had C/O ratios of 2.05 (Hummers), 2.47 (Staudenmaier), and 2.71 (Hofmann).¹⁸ The large differences in C/O ratios before and after microwave treatment indicated that dry bulk reduction of GO occurred successfully, in stark contrast to a previous study that required the additional use of ammonium carbonate to facilitate reduction of a Hummers-method GO to a similar degree (XPS-determined C/O ratio ~10 compared to 10.5 in our current work).¹⁹ However, TRGO gave a C/O ratio of 18.2, which is significantly higher than any of the MVGs. It is known that high temperature thermal shock exfoliation (> 1000 °C) used to produce TRGO causes decomposition of oxygen-containing groups as well as sublimation of the carbon backbone itself, which creates vacancies and topological defects in the lattice.²⁰ Thus, the more effective removal of oxygen species in TRGO is likely to be related to its higher defect density as compared to the MVGs.

High-resolution C 1s spectra of the MVGs (Figure 4) revealed highly similar profiles to that of TRGO, with C=C bonds comprising the majority of the C 1s signal (60–67%) for all four samples, providing further evidence that microwave treatment of graphite oxides successfully removes most of the oxygen-containing species present. A recent study by our group showed that microwave exfoliation of graphite oxides in the presence of H₂ plasma flow yielded hydrogenated graphenes with almost identical C/O ratios and composition of oxygen-containing groups remaining.²¹ In contrast, there are

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Figure 2. Raman spectra of MVGs and TRGO normalized to G-band intensity.

Figure 3. XPS wide spectra for MVGs and TRGO, depicting relative C/O peak intensities. Data is normalized to C 1s peak intensity.

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Figure 4. XPS high-resolution C 1s core spectra of MVGs and TRGO.

Table 1. Relative amounts of components in deconvoluted XPS high-resolution C 1s core spectra of MVGs and TRGO.

% composition of C 1s signal				
	MVG-HU	MVG-ST	MVG-HO	TRGO
C=C	67.3	59.8	61.6	68.6
C–C	15.6	18.6	18.9	13.2
C–O	8.0	10.6	8.5	7.9
C=O	3.5	4.5	3.8	3.2
O=C–O	2.3	3.9	2.5	2.3
π – π^*	3.3	2.6	4.8	4.8

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small but noticeable differences in the types and amounts of oxygen species remaining on the current MVGs as shown in Table 1. MVG-ST contained the highest total amount of carbon-bonded oxygen species (epoxy, carbonyl, and carboxyl) of 19.0%, as compared to 13.8% and 14.8% for MVG-HU and MVG-HO respectively. This once again shows that MVG-ST was not reduced as effectively as MVG-HU and MVG-HO by vacuum-assisted microwave treatment, as seen previously from their C/O ratios.

Evidently, the removal of oxygen-containing groups from ST-GO is suppressed when compared to HU-GO and HO-GO. The procedure employed in this study involved evacuation followed by sealing of the reaction ampoule, ensuring an initial vacuum environment within the vessel. Upon microwave treatment, large amounts of gaseous products from the decomposition of oxygen-containing groups are released. These gases comprise mainly CO, CO₂, and H₂O when GO undergoes incomplete reduction with significant amounts of oxygen groups still bound to the graphene plane.²² More complete removal of oxygen species creates a wider array of gaseous products, and as the different oxidation procedures create different types of oxygen functionalities on the graphite oxides,¹⁸ the identities of the gaseous products formed post-decomposition as well as their relative amounts are unique to the oxidation method.¹⁷ The volatile exfoliation products of HU-GO and HO-GO are qualitatively similar to each other, consisting primarily of CO₂/COS, acetone, and simple aromatic cycles with 1 or 2 benzene rings. In contrast, thermally exfoliating ST-GO not only results in simple compounds like acetone and benzene, but also a much larger variety of non-aromatic cyclic compounds and an array of substituted aliphatic alkenes.¹⁷ The exfoliation products of ST-GO also show a distinct lack of CO₂ or COS, which have far higher O:C ratios (which implies more efficient removal of oxygen) as compared to other simple

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organic molecules. Since exfoliation atmospheres are known to affect the removal of oxygen species from GOs, these differences in volatile exfoliation products may account for the suppressed deoxygenation noted in the case of MVG-ST.

Combustion elemental analyses were also carried out on the MVGs as well as their starting GOs to determine any changes in elemental composition, allowing us to investigate the effect of microwave irradiation on different GOs. A summary of these results is as shown in Table 2. Large decreases in oxygen content were observed after the graphite oxides underwent microwave treatment to produce MVGs, exhibiting final C/O ratios ranging from 5.73 to 7.10 as determined by elemental analysis. These values are factors of 2 to 3 higher than reported by Ruoff and co-workers (2.75), which to the best of our knowledge is the only study done thus far on dry microwave exfoliation-reduction of graphite oxide that includes combustion elemental analysis data.¹³ Oxygen removal during the irradiation procedure was coupled with the loss of hydrogen in a roughly 1:1 ratio in terms of at.% for MVG-HU (H loss: 17.60%; O loss: 20.19%) and MVG-ST (H loss: 10.91%; O loss: 11.59%). However, MVG-HO showed very different behaviour, with oxygen content decreasing far more than hydrogen content (H loss: 7.54%; O loss: 17.83%), giving final H and O compositions of 13.28% and 10.71% respectively. Assuming H was bonded to O in the most extreme 1:1 stoichiometry (i.e. hydroxyl groups), this still resulted in a hydrogen excess of 2.57%, which may indicate hydrogenation of the graphene lattice. In reality, this hydrogen excess is likely to be even higher since the presence of oxygen containing groups with higher O:H stoichiometries like carboxyls (2:1) and carbonyls (1:0) was observed in the XPS C 1s spectrum previously.

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Table 2. Elemental compositions (in atomic %) of GOs and MVGs as determined by combustion elemental analysis.

Material	% N	% C	% S	% H	% O
HU-GO	0.89	37.33	0.69	28.05	33.04
MVG-HU	1.35	73.60	1.75	10.45	12.85
ST-GO	-	58.73	-	17.99	23.28
MVG-ST	-	80.91	0.32	7.08	11.69
HO-GO	-	50.64	-	20.82	28.54
MVG-HO	-	76.01	-	13.28	10.71

Thermal decomposition of highly energetic bulk GO has been shown to rapidly evolve gaseous products;²³⁻²⁶ as such, safety of the exfoliation procedure is an important concern. Based on elemental composition changes, as well as the measured mass loss from 0.3 g HO-GO after microwave exfoliation, the maximum pressure in the ampoule was calculated to be around 13.0 atm for an ampoule with a volume of 20 mL. This calculation assumed CO₂, CO, and H₂O as the only gaseous products. In reality, the internal pressure should be significantly lower because CO₂, CO, and H₂O as the sole products represents the most extreme scenario. These calculations are corroborated very well by a recent study on the thermochemistry of GO decomposition, in which the overpressure using our conditions (0.3 g GO, 20 mL vessel volume) is estimated to be only 7.5 atm.²⁶ The quartz ampoules utilized in this study are commonly used for relatively high pressures (up to several tens of atm), and we did not observe any exploding ampoules during our experiments. Hence, for gram-scale production of MVGs using this exfoliation procedure, a corresponding increase in ampoule size would be sufficient. For these large batches, scaling up the ampoule volume to 1 L for every 10 g of GO results in a maximum estimated internal pressure of 8.7 atm. To further ensure the safety of the procedure for larger batches, the ampoules can be fitted with pressure

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relief valves. Thus, we can infer that batch sizes of about 10–20 g of GO can be used with larger sizes of ampoules, without relatively complicated design modifications.

To glean additional information on residual functional groups remaining on the MVGs, Fourier-transform infrared spectroscopy was conducted and the spectra are shown in Figure 5. Intensive C–H stretching that manifested as twin peaks at 2800–3000 cm^{-1} was observed for MVG-HU, as well as weaker C–H stretches for MVG-ST and MVG-HO (Figure 5b). This implies that hydrogenation occurred for all three MVGs to a small extent under the conditions used in this work, with the hydrogen atoms originating from the GO samples themselves (since exfoliations were carried out in closed, evacuated environments) rather than an external source. Small peaks noted in the spectra of MVG-HU and MVG-ST at 1750 cm^{-1} are attributed to C=O stretching from residual carboxylate groups. Also observed in the FTIR spectra for MVG-HU and MVG-HO was a signal around 1620 cm^{-1} corresponding to C=C skeletal vibrations of graphitic domains, consistent with re-aromatization of the basal plane after removal of oxygen functionalities. This same signal was extremely weak in MVG-ST, which suggests that the graphene network was restored to a far lesser degree than in MVG-HU and MVG-HO, and would understandably have negative implications on its resistivity.

Owing to differences in the C/O ratios of the MVGs in the XPS studies, as well as differences in their FTIR spectra, resistivity measurements of the MVGs were also performed. MVG-HU, MVG-ST, and MVG-HO were found to have specific resistivities of 5.19×10^{-4} , 1.97×10^{-3} , and $2.99 \times 10^{-4} \text{ } \Omega\cdot\text{cm}$, respectively, showing an inverse correlation with their C/O ratios, as expected since the presence of oxygen functionalities on graphene materials is known to have an insulating effect;²⁷ MVG-ST has a distinctly higher resistivity than MVG-HU and MVG-HO due to its much lower C/O ratio. The

Figure 5. FTIR spectra of MVGs. (a) Overall spectra of all MVGs, with boxed region showing C–H stretching. (b) Close-up spectra of MVGs.

measured resistivities are typical of values observed on TRGO materials, but significantly higher than that of pristine graphene.²⁸ These differences are related to lower C/O ratios and also formation of C–H bonds in our MVGs. The remaining oxygen functionalities and hydrogen covalently bonded to the graphene backbone induce a splitting of graphene bandgap and the formation of local traps for free carriers. This subsequently led to observation of higher resistivities compared to TRGO.

Electrochemical studies in the form of cyclic voltammetry experiments were also carried out to assess the materials' suitability for electrochemical sensing applications. The heterogeneous electron transfer (HET) rate of a material is an indicator of its performance as an electrochemical sensor, and can be calculated from the peak-to-peak separation (ΔE_p) values in the presence of a suitable redox probe. The $[\text{Fe}(\text{CN})_6]^{4-/3-}$

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system is a well-known standard in electrochemistry, and is understood to be sensitive to surface defects as well as oxygenated sites.^{29, 30} Voltammetric responses of glassy carbon (GC) electrodes modified with MVGs recorded in the presence of the $[\text{Fe}(\text{CN})_6]^{4-}/^{3-}$ redox couple are as shown in Figure 6a; the responses of a TRGO-modified GC electrode and a bare GC electrode to the same system are also provided. The ΔE_p of the bare GC electrode was 405 mV (Figure 6b), leading to an observed HET rate (k_{obs}^0) of $6.81 \times 10^{-5} \text{ cm s}^{-1}$. Modification of the GC electrode with all three MVGs lowered ΔE_p to 160, 108, and 119 mV (corresponding to dramatically improved k_{obs}^0 values of 1.77×10^{-3} , 4.38×10^{-3} , and $3.43 \times 10^{-3} \text{ cm s}^{-1}$) for MVG-HU, MVG-ST, and MVG-HO respectively. For comparison, the TRGO-modified electrode showed a ΔE_p of 127 mV ($k_{obs}^0 = 2.97 \times 10^{-3} \text{ cm s}^{-1}$), which is similar to the responses observed for the MVGs. MVG-HU's lower k_{obs}^0 is likely due to its far lower defect density than TRGO, while MVG-ST and MVG-HO

Figure 6. (a) Cyclic voltammograms for 10 mM $[\text{Fe}(\text{CN})_6]^{4-}/^{3-}$ on MVG-modified GC electrodes, as well as comparative voltammograms for TRGO-modified GC electrode and bare GC electrode. Conditions: scan rate, 100 mV s^{-1} ; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl. (b) Peak-to-peak separation values for MVG-modified GC electrodes, TRGO-modified GC electrode, and bare GC electrode.

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actually showed faster HET rates than TRGO despite possessing lower C/O ratios and densities of defects. These results imply that the microwave exfoliation procedure employed in this work can yield graphene materials with better electrochemical performance as compared to TRGO.

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Conclusion

Graphite oxides synthesized using three commonly used oxidation methods (Hummers, Staudenmaier, and Hofmann) were successfully reduced and exfoliated using a dry microwave procedure in a sealed, evacuated quartz glass ampoule. This was readily performed in the absence of other agents and media to assist reduction. The procedure initially creates vacuum environments in the ampoules, followed by gaseous atmospheres unique to each type of graphite oxide (due to different decomposition products) and, consequently, leads to microwave-vacuum exfoliated graphenes with varying densities of defects, elemental compositions and resistivities. Evidence of hydrogenation was observed in the FTIR spectra of the MVGs. In spite of these differences, the MVGs obtained show highly similar electrochemical behaviour to more commonly employed TRGO, with two MVGs even surpassing the performance of TRGO. Due to its distinct advantages over thermal exfoliation in terms of convenience, cost, and duration, this microwave reduction-exfoliation method is promising for the bulk production of graphene materials for electrochemical sensing applications.

Contributions:

Z. Sofer and M. Pumera conceptualized the project. O. Jankovský synthesized the materials and conducted combustion elemental analyses and FTIR experiments. C. H. A. Wong conducted microscopy, Raman, XPS, and voltammetry experiments. C. H. A. Wong, Z. Sofer, and M. Pumera wrote the manuscript. All authors contributed to discussions.

4.2 – MICROWAVE EXFOLIATION OF GRAPHITE OXIDES IN THE PRESENCE OF HYDROGEN SULFIDE

Introduction

Graphene has been suggested to be the next disruptive technology in various fields, owing to its interesting properties as well as the relative ease of synthesis of graphene and its modified analogues.³¹⁻³⁵ In its pristine form, graphene has no band gap, although it may take on p-type semiconducting properties under ambient conditions, due to adsorbed species such as oxygen and water.³⁶ Such heteroatomic doping presents opportunities for tuning the band gap in graphene, thus increasing the types of potential applications that graphene materials would be suitable for.^{37, 38} For example, the doping of carbon nanomaterials can change their electrochemical properties significantly, bestowing upon them catalytic activities towards many important electrochemical reactions, such as the oxygen reduction reaction in fuel cells.³⁹⁻⁴⁴ Commercial fuel cells rely heavily on platinum-based catalysts to overcome the slow kinetics of the oxygen reduction reaction;^{45, 46} unfortunately, Pt-based catalysts suffer from low stability (especially under alkaline conditions),⁴⁷ and are expensive due to the rarity of Pt.⁴⁸

Doping graphene with sulfur has been shown to increase its electrocatalytic activity towards the reduction of H_2O_2 , proposed to arise from the creation of more active sites for electrocatalytic reduction to occur.⁴⁹ S-doping of graphene was also able to confer upon it catalytic activity in the oxygen reduction reaction.^{28, 50, 51} Herein, we report the efficient synthesis of S-doped graphenes from the microwave-assisted reduction/exfoliation and simultaneous doping of different graphite oxides through

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exposure to H₂S plasma during the microwave exfoliation procedure. The degree of exfoliation of the parent graphite oxide after microwave irradiation was found to be linked to the extent of S-doping, which subsequently played a key role in the catalysis of the oxygen reduction reaction.

Results and Discussion

Sulfur-doped microwave-exfoliated graphenes (MWS) were synthesized by subjecting various graphite oxides to microwave radiation in the presence of H₂S. This treatment simultaneously exfoliates and thermally reduces the graphene materials, while also incorporating sulfur (from the microwave dissociation of H₂S plasma) into the graphene lattice. S-doped MW-exfoliated graphenes obtained in this microwave exfoliation method from Hummers, Staudenmaier, and Hofmann graphite oxide precursors were termed as HU-MWS, ST-MWS, and HO-MWS, respectively. The resulting materials had the appearance of black, fluffy powders, reminiscent of thermally reduced graphene oxides. To further study their morphology at the microscopic level, scanning electron microscopy (SEM) was employed, which revealed an abundance of wormlike/accordion structures typical of microwave-exfoliated graphenes (Figure 7). It was observed that ST-MWS possessed significantly larger particle sizes, with many regions of the material existing as thickly stacked layers. HU-MWS and HO-MWS had similar wormlike morphologies that exhibited a greater degree of exfoliation as well as more wrinkled sheets than ST-MWS. Such highly corrugated features imply the presence of disordered structures in HU-MWS and HO-MWS, which can be investigated using Raman spectroscopy (Figure 8). The G mode ($\sim 1580\text{ cm}^{-1}$) arises from bond stretching from sp² carbon atoms in the graphene lattice, while the D mode ($\sim 1350\text{ cm}^{-1}$) is caused

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Figure 7. SEM images of HU-MWS, ST-MWS, and HO-MWS at 5 000 × magnification (a–c, respectively; scale bar represents 1 μm), 15 000 × magnification (d–f, respectively; scale bar represents 1 μm), and 50 000 × magnification (g–i, respectively; scale bar represents 100 nm).

Figure 8. Raman spectra of MWS samples normalized to G-band intensity.

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by disorder in the lattice, and its intensity is proportional to the density of defects.^{52, 53}

Indeed, the Raman spectra of the materials revealed that HU-MWS and HO-MWS had significantly more disorder, with I_D/I_G ratios of 0.95 and 0.85, respectively (in contrast, ST-MWS had a ratio of 0.63). Also note the presence of the 2D band ($\sim 2700\text{ cm}^{-1}$) only in ST-MWS; this mode is known to emerge with less disorder and disappear upon loss of interlayer bonding,^{54, 55} once again supporting that ST-MWS has less defects than HU-MWS and HO-MWS, as well as exhibiting a more thickly stacked structure.

Next, we sought to determine the extent of sulfur doping in each MWS sample. X-ray photoelectron spectroscopy (XPS) was employed to determine the chemical composition of the materials studied, with carbon and oxygen as the main elements present in the wide spectra (Figure 9a). Carbon-to-oxygen ratios of the MWS samples calculated from XPS data were 9.01, 11.7, and 8.73 for HU-MWS, ST-MWS, and HO-MWS, respectively; similar ratios of 8.93, 13.11, and 8.71 were obtained using combustion elemental analysis. Small amounts of sulfur were also detected in the materials, determined by XPS as 1.25, 0.49, and 0.95 at.% for HU-MWS, ST-MWS, and HO-MWS, respectively. The corresponding values using combustion elemental analysis were 1.11, 0.62, and 0.86 at.%, respectively; these results show that both methods of elemental analysis were in good agreement with each other. The significantly lower extent of S-doping in ST-MWS (approximately half the amount observed in other MWS samples) is likely due to its lower degree of exfoliation, which would hinder the penetration of H_2S plasma into the layers. This was corroborated in the high resolution XPS S 2p spectra of the MWS samples (Figure 9b), which revealed C–S–C type bonding ($2p_{1/2}$ and $2p_{3/2}$ transitions at 163.8 and 165.3 eV, respectively) as well as C–SO_x–C groups (sulfones, sulfonates, and sulfates, ranging from 167.6–168.9 eV for the $2p_{3/2}$ transition).⁵⁶⁻⁵⁸ All

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three MWS samples showed similar amounts of sulfur in the form of sulfur oxides, but ST-MWS had significantly less sulfur bound only to carbon atoms. This discrepancy is most likely to arise from the less extensive exfoliation in ST-MWS hampering the formation of sulfur ring clusters connecting adjacent graphene sheets at the edges, while S-doping in the form of sulfur oxides at the edges of graphene was not impeded.⁵⁹

Figure 9. (a) XPS wide spectra of MWS samples with data normalized to C 1s peak intensity. Boxed area indicates the region in which the S 2p signal is located. (b) XPS high resolution S 2p spectra of MWS samples.

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The electrochemical performance of the MWS materials were then assessed using cyclic voltammetry experiments using the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox probe (Figure 10a). The electron transfer in this redox probe is sensitive to the amount of defects present in graphene materials; edge sites in graphene exhibit extremely fast electron transfer kinetics,⁶⁰ while thermal reduction/exfoliation of GO creates defects with a high proportion of edge sites. Peak-to-peak separation (ΔE_p) values of the cyclic voltammogram are an indicator of heterogeneous electron transfer (HET) rates of the electrode surface; lower ΔE_p values correspond to faster HET. An unmodified glassy carbon (GC) electrode served as the control and showed a ΔE_p of 351 mV in the presence of $[\text{Fe}(\text{CN})_6]^{4-/3-}$. GC electrodes modified with HU-MWS and HO-MWS gave very similar voltammograms as well as ΔE_p readings of 149 and 137 mV, respectively, indicating a large improvement in HET rates over the unmodified GC electrode. The corresponding ΔE_p value for a ST-MWS modified GC electrode was 225 mV, which is still an improvement over the unmodified electrode, albeit a more modest one. In essence, HU-MWS and HO-MWS exhibited better electrochemical performance than ST-MWS due to their higher defect densities; it is unlikely that the small amount of sulfur doping played any significant role in altering the MWS materials' electron transfer kinetics towards the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ probe. Current-voltage measurements were also performed on the MWS materials to gauge their conductivities (Figure 10b). ST-MWS was the most conductive sample with a I/V slope of 43.4 mA V⁻¹, while HU-MWS and HO-MWS once

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Figure 10. (a) Cyclic voltammograms for 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ on MWS-modified GC electrodes, as well as comparative voltammograms for a bare GC electrode. Conditions: scan rate, 100 mV s^{-1} ; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl. (b) Current-voltage profiles of MWS samples, measured after material deposition on an Au-IDE.

again displayed highly similar values, with I/V slopes of 32.1 and 33.3 mA V^{-1} , respectively. The increased conductivity in ST-MWS resulted from its lower oxygen content, as oxidized species are known to disrupt the conductive π -network in graphene materials.²⁷ Slight contribution from S-doping may be present, as sulfur oxides and sulfur ring clusters increase resistivity by trapping free charge carriers.²⁸ The C/(O+S) atomic ratios (using XPS data) of HU-MWS, ST-MWS, and HO-MWS were 7.99, 11.1, and 7.98, respectively, which correlates well with the virtually identical I/V profiles of HU-MWS and HO-MWS, as well as the increased conductivity seen in ST-MWS.

It has been previously shown that sulfur-doped graphenes can act as catalysts for the oxygen reduction reaction.^{28, 50, 51} Sulfur atoms in C–S–C and C–SO_x–C (sulfur oxides) bonding conformations as well as small sulfur ring clusters are postulated to be the active catalytic sites.⁵⁹ Linear sweep voltammograms of MWS-modified electrodes in air-saturated 0.1 M KOH are given in Figure 11. A small cathodic peak can be seen in the voltammetric response of a bare GC electrode arising from the reduction of oxygen at an

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onset potential of -304 mV. Modification of the electrode with ST-MWS resulted in a slightly larger current magnitude but the same onset potential of -297 mV, showing that ST-MWS was only slightly catalytic towards the oxygen reduction reaction. The onset potential recorded at the electrode modified with HU-MWS (which had the highest amount of sulfur content) was -254 mV, while the corresponding value at HO-MWS was -261 mV. Cathodic current peak heights were also observed to increase with increasing sulfur content. These results show positive correlation between the extent of sulfur doping and the catalytic activity of MWS materials towards the oxygen reduction reaction. For comparison against commercially available catalysts, the voltammetric response at an electrode modified with Pt/C was also recorded, which had a reduction onset potential of -149 mV. Despite the more negative onset potentials at MWS-modified electrodes than Pt/C for the same mass loading, it is noteworthy that the peak current at HU-MWS was more than twice that of Pt/C, and HU-MWS outperforms Pt/C when the applied potential is more negative than -333 mV. Similarly, the catalytic performance of HO-MWS exceeds that of Pt/C at potentials more negative than -354 mV. This suggests that HU-MWS and HO-MWS may be better alternatives to Pt/C as catalysts for the oxygen reduction reaction in niche electrochemical systems where the applied potential already crosses the threshold value.

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Figure 11. Linear sweep voltammograms for air-saturated 0.1 M KOH on MWS modified GC electrodes, as well as comparative voltammograms for Pt/C-modified and bare GC electrodes.

Conclusion

The simultaneous reduction and exfoliation using microwave irradiation of three different graphite oxides (Hummers, Staudenmaier, and Hofmann) was successfully carried out in the presence of H_2S gas, which resulted in sulfur doping of the materials to varying extents. The types and amounts of S-doping were affected mainly by the degree of exfoliation, with more exfoliated samples showing higher amounts of non-oxidized sulfur species. Variations in the amounts of defects in the materials were observed to affect their electrochemical properties, with more defective MWS samples exhibiting better electrochemical performance. The presence of both sulfur and oxygen species were seen to have a negative effect on the conductivities of the MWS samples. These materials were shown to possess catalytic activity towards the oxygen reduction reaction, with a positive correlation between the amount of S-doping and the reduction in overpotentials required. Under certain conditions, HU-MWS and HO-MWS show

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better performance than commercial Pt/C in the catalysis of the oxygen reduction reaction.

Contributions:

Z. Sofer and M. Pumera conceptualized the project. Z. Sofer and K. Klímová synthesized the materials and conducted combustion elemental analyses. C. H. A. Wong conducted microscopy, Raman, XPS, and voltammetry experiments. C. H. A. Wong and M. Pumera wrote the manuscript. All authors contributed to discussions.

4.3 – MATERIALS AND METHODS

Materials

Graphite (2–15 μm , 99.99995%) was obtained from Alfa Aesar, Germany. *N,N*-dimethylformamide, phosphate buffer powder, potassium hydroxide, and potassium hexacyanoferrate(III) were obtained from Sigma-Aldrich, Singapore. Sulfuric acid (98%), nitric acid (65%), nitric acid (fuming, >98%), potassium chlorate (98%), potassium permanganate (98%), hydrogen peroxide (30%), hydrochloric acid (37%), sodium nitrate (99.5%), silver nitrate (99.5%) and barium nitrate (99.5%) were obtained from PENTA, Czech Republic. Nitrogen gas (99.9999%) and hydrogen sulfide gas (99.5%) was obtained from SIAD, Czech Republic. Deagglomerated alpha alumina powder (0.05 μm) was purchased from Struers, Singapore. Glassy carbon (GC) working electrodes, Ag/AgCl reference electrode and Pt auxiliary electrode were obtained from CH Instruments, USA.

Apparatus

A JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) was used to acquire scanning STEM images at an acceleration voltage of 30 kV and a working distance of 8.3 mm, and SEM images at 5.0 kV at a working distance of 5.8 mm. The samples for STEM were prepared by depositing 1 μL of each material suspension (1 mg mL^{-1} in DMF) onto a lacey carbon/Formvar copper TEM grid (Ted Pella) and allowed to dry in air. The samples for SEM were prepared by immobilizing the graphene materials onto a carbon tape on an aluminum SEM holder for analyses.

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Raman spectra were obtained with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific, Japan) with an Ar ion laser (excitation wavelength 514.5 nm) beam in backscattering geometry with a CCD detector, measuring from 1000 to 3000 cm^{-1} . I_D/I_G ratios were averaged over 8 measurements for each material. The crystallite size (L_a) of the sp^2 lattice was calculated using the equation:

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

where λ is the wavelength of the laser in nm, I_G and I_D are the intensities of the Raman G and D bands respectively.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Phoibos 100 spectrometer (SPECS, Germany) with a monochromatic Mg X-ray source. Relative sensitivity factors were used for evaluation of C/O ratios from wide spectra XPS measurements. The samples for XPS were prepared by coating carbon tape with a uniform layer of the materials studied.

Specific resistivities of MVGs were measured by first compressing 40 mg each of the materials into a capsule (diameter 63.5 mm) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was then measured according to the van der Pauw method with a 4-probe technique, using a home-made system with a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit.

Elemental analyses were performed with a Vario EL III Element Analyzer (Elementar Analysensysteme GmbH, Germany). Analysis was performed in CHNS/O mode. A microbalance MX5 (Mettler Toledo) was used for precise weighing of samples (1.5–2.5 mg per single sample analysis). The accuracy of CHNS determination is better than 0.10 wt.% abs. Internal calibration was performed using 5 mg of 4-amino-benzenesulfonic acid.

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FTIR measurements were performed on FTIR spectrometer NICOLET 6700 (Thermo Scientific, USA). Diamond ATR crystal and DTGS detector were used for the measurements in the range of 400–4000 cm^{-1} .

Procedures

Graphite oxide preparation using Staudenmaier method⁶¹

87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (fuming, 98%) were added to a reaction flask, and the mixture was then cooled in an ice bath for 30 min. 5 g of graphite was then added into the mixture with vigorous stirring to avoid agglomeration and obtain a homogeneous dispersion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period, in ice bath) to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of gas evolved. The mixture was then stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5% w/w) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction for chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Graphite oxide preparation using Hofmann method^{62, 63}

87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (68%) were added to a reaction flask, and the mixture was then cooled in an ice bath for 30 min. 5 g of graphite

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was then added to the mixture with vigorous stirring to avoid agglomeration and obtain a homogeneous dispersion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period, in ice bath) to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of gas evolved. The mixture was then stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5% w/w) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction for chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Graphite oxide preparation using Hummers method⁶⁴

5 g of graphite and 2.5 g of sodium nitrate were stirred with 115 mL of sulfuric acid (98%). The mixture was then cooled in an ice bath. With vigorous stirring, 15 g of potassium permanganate was then added over a period of 2 h. The reaction mixture was allowed to reach room temperature (over 4 h) before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask containing 250 mL of deionized water and further heated to 70 °C. After holding the temperature constant for 15 min, the mixture was poured into 1 L of deionized water. The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% (w/w) hydrogen peroxide. The reaction mixture was then allowed to settle and decanted. The graphite oxide obtained was then purified by repeated centrifugation and redispersing in

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deionized water until a negative reaction for sulfate ion (with $\text{Ba}(\text{NO}_3)_2$) was achieved.

Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Microwave exfoliation of graphite oxides in vacuum

Graphite oxides synthesized above were each placed in separate quartz glass ampoules (300 mg) and evacuated to a base pressure of 5×10^{-5} mbar with an oil diffusion pump. During the evacuation procedure the graphite oxide was heated to 60 °C to remove any traces of moisture. The quartz glass ampoule was sealed off in vacuo with an oxygen-hydrogen flame. The ampoules were placed inside the microwave reactor and irradiated for 3 minutes (1 kW, 2.45 GHz). Quartz glass does not absorb microwave radiation and the resultant heating of GO is only related to the direct absorption of radiation itself and not by secondary heating of exfoliated material from the reaction vessel. This secondary heating effect is commonly observed when standard labware glass (like Pyrex glass) is utilized. Formation of plasma was observed inside the evacuated ampoule during the start of the exfoliation procedure, which was then accompanied by the intense evolution of large amounts of gases. The pressure increase led to the quenching of plasma discharge a few seconds after the start of exfoliation procedure. The ampoule was then broken to retrieve their respective microwave-vacuum exfoliated graphenes (MVGs).

Preparation of thermally reduced graphene oxide

Graphite oxides prepared using the Hofmann method was subjected to thermal reduction/exfoliation at 1000 °C. 0.1 g of graphite oxide was placed into a porous quartz glass capsule connected to a magnetic manipulator and placed inside a vacuum tight tube furnace with controlled atmosphere. The magnetic manipulator is capable of

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creating a temperature gradient over $1000\text{ }^{\circ}\text{C min}^{-1}$. The reactor was then flushed with nitrogen gas by repeated evacuation of the tube furnace to remove any traces of oxygen and then quickly inserted by the magnetic manipulator to a preheated furnace and held in the furnace for 12 minutes. The flow of nitrogen (99.9999% purity) during the exfoliation procedure was 1000 mL min^{-1} to remove any by-products from the procedure.

Estimation of pressure in ampoules due to microwave exfoliation

The pressure was calculated using the rounded empirical formula of HO-GO and MVG-HO, $\text{C}_{51}\text{H}_{21}\text{O}_{29}$ and $\text{C}_{76}\text{H}_{13}\text{O}_{11}$ respectively, as determined through elemental analysis (Table 2 in main text). Based on the empirical formulae as well as the measured reduction of mass of 47% after microwave treatment, the exfoliation process can be written as the following equation:

Slight equation imbalance (loss of 0.5 O atoms) is treated as negligible as this is an approximation. It is also assumed that all H escapes as H_2O , and CO_2/CO ratios were determined through linear combination of the remaining C and O atoms.

From the above equation, microwave exfoliation of 0.3 g HO-GO can be shown to result in the formation of approximately 1.98 mmol H_2O (36 mg), 0.82 mmol CO_2 (36 mg), and 2.73 mmol CO (77 mg) for a total of 5.53 mmol of gaseous products. The ideal gas equation was used to calculate gas pressures. At $T = 573.15\text{ K}$, initial GO mass of 0.3 g, and a vessel volume of 20 mL, the total pressure would be 13.0 atm. (300 $^{\circ}\text{C}$, or 573.15 K, was the typical temperature measured using a contact thermometer on ampoule surface after microwave treatment.)

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For a 10 g batch of HO-GO in an ampoule of volume 1 L at 573.15 K, the corresponding pressure would be approximately 8.7 atm using the same calculation methods as above.

Similar results can be expected for the other MVG samples.

Microwave treatment of graphite oxides with hydrogen sulfide

Graphite oxides (250 mg) synthesized above were each placed in separate quartz glass microwave reactors (500 mL) and the reactors repeatedly evacuated and flushed with nitrogen. The reactor was filled with H₂S and the pressure was reduced to 10 mbar. The GO was subsequently exfoliated by exposure to microwave radiation (2.45 GHz, 1 kW) for 30 s. This initial exfoliation led to significant increase of pressure. The microwave reactor was then flushed with H₂S and the graphene treated with H₂S plasma for another 3 minutes at a pressure of 10 mbar. The flow rate of H₂S was 100 mL min⁻¹. Lastly, the reactor was evacuated and filled with nitrogen. The resulting S-doped graphene was removed from the reactor, redispersed in acetone and separated by suction filtration. The S-doped graphene was then dried under vacuum for 48 hours at 50 °C before use.

Characterization of samples

Cyclic voltammetry experiments were carried out on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). Electrochemical experiments were carried out in a 5 mL electrochemical cell at room temperature with a three-electrode configuration (Ag/AgCl as the reference, Pt as the auxiliary). Cyclic voltammetry experiments were conducted at

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a scan rate of 100 mV s^{-1} with 10 mM ferro/ferricyanide as the analyte in a supporting electrolyte of 50 mM phosphate buffer solution (pH 7.4). All CV data shown are first scans of the experiment, unless otherwise stated. The supporting electrolyte was purged with nitrogen for 20 min before electrochemical measurements. Linear sweep voltammetry experiments for oxygen reduction reaction were conducted at a scan rate of 100 mV s^{-1} with 10 mM air-saturated KOH as the analyte. All electrochemical potentials in this paper are stated versus the Ag/AgCl reference electrode (plastic tube, silver wire in 3.0 M KCl). GC electrode surfaces were renewed before each measurement/modification by polishing for 2 min on a polishing pad with alumina slurry, and then washed with deionized water of resistivity not less than $18.2 \text{ M}\Omega \text{ cm}$ (Milli-Q, Millipore).

Suspensions of TRGO, MVGs, S-doped graphenes, and Pt/C were prepared with a concentration of 1 mg mL^{-1} in DMF with 30 min sonication. Modification of GC electrode surfaces with these materials was performed by depositing a $1 \text{ }\mu\text{L}$ aliquot of the suspension onto the electrode, after which the solvent was evaporated under a sun lamp for 20 min. The suspensions were sonicated for an additional 1 min before each deposition to ensure homogeneity.

k_{obs}^0 values were calculated according to the Nicholson method⁶⁵ relating ΔE_p values to a dimensionless kinetic parameter ψ , leading to k_{obs}^0 via the equation:

$$k_{obs} = \psi \left[D_O \pi \nu \left(\frac{nF}{RT} \right)^{1/2} \right] \left(\frac{D_R}{D_O} \right)^{\alpha/2}$$

where D_O and D_R are the diffusion coefficients for potassium ferricyanide and potassium ferrocyanide respectively at 298 K,⁶⁶ ν is the scan rate in V s^{-1} , n is the number of

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electrons transferred, F is the Faraday constant, R is the ideal gas constant, T is the temperature in K and α is the transfer coefficient (0.5).

Current-voltage (I/V) measurements were carried out by first depositing 2 μL of the material suspension (1.0 mg mL^{-1} in ethanol) onto interdigitated gold electrodes (Au-IDE) with a gap of 10 μm . The solvent was then evaporated off under a sun lamp for 20 min to leave a randomly deposited film on the interdigitated area. I/V curve data were obtained using linear sweep voltammetry (scan rate 20 mV s^{-1}).

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CHAPTER 5

FUNDAMENTAL STUDIES ON CHEMICALLY MODIFIED GRAPHENES: THE ROLES OF SYNTHETIC PROCEDURES AND CHOICE OF STARTING GRAPHITE MATERIAL

- 5.1 Inadvertent contamination of CMGs with metallic impurities as a result of synthetic procedures
- 5.2 Choice of graphite source and its influence on the properties of derived CMGs
- 5.3 Materials and methods
- 5.4 References

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The results and findings in this chapter were published in the following manuscripts:

5.1 **Wong, C. H. A.**; Sofer, Z.; Kubešová, M.; Kucera, J.; Matejková, S.; Pumera, M.

Synthetic routes contaminate graphene materials with a whole spectrum of unanticipated metallic elements. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 13774–13779.

5.2 **Wong, C. H. A.**; Sofer, Z.; Pumera, M. Geographical and geological origin of natural graphite heavily influence the electrical and electrochemical properties of chemically modified graphenes. *Chem.-Eur. J.* **2015**, *21*, 8435–8440.

Background

Graphene is well-poised to revolutionize many industries due to its multitude of exceptional properties. A vast majority of these properties were based on studying pristine graphene, obtained from the mechanical exfoliation of graphite.¹⁻⁶ Current synthetic methods are not yet able to produce pristine graphene in commercially viable quantities for applications; for example, bulk quantities of graphene would be required as electrode materials for electrochemical applications.⁷ Until industrial-level production of truly pristine graphene becomes a reality (*if at all*), practical electrochemical applications of graphene are mostly limited to the broad class of graphene analogues, collectively known as chemically modified graphenes (CMGs).⁸ The defining feature of CMGs is that they possess additional elements and functional groups, covalently attached to individual sheets of graphene in the material. The presence of this heteroatomic contamination cause CMGs to deviate from the observed properties of pristine graphene; nevertheless, CMGs are still useful for intended practical applications of graphene, due to their relative ease of production and handling compared to pristine graphene. A heavily utilized class of CMGs comprises graphite oxide and its reduced derivatives, often termed as reduced graphene oxides (RGOs).⁹ A brief history of GO and RGOs and their various methods of syntheses were covered in Chapter 2; we additionally noted that the term “graphene” is often used for CMGs with low amounts of residual heteroatomic contamination, despite them not strictly being graphene.

We previously observed the pivotal role of metallic impurities in dominating the electrochemical responses at GONR-modified electrodes in Chapter 3, and the source of these impurities was postulated to be the CNT starting materials (or more accurately, residual metal catalysts from CNT growth procedures).¹⁰ These metallic impurities are

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extremely challenging to remove, even after exposure to strong oxidative or reductive conditions, ultrasonication, and Cl_2 at 1000 °C.^{10, 11} Similar arguments can be made for CMGs produced from “tainted” graphite or chemical vapour deposition methods.¹¹⁻¹⁵ It is thus tempting to circumvent the issue of residual metals by employing extremely pure starting materials, such as extensively purified CNTs and graphite sources, or CNTs grown without the use of metal catalysts.^{16, 17} However, the implicit assumption in this “solution” is that there are no further sources of contamination.

With regard to the synthesis of RGOs, a colossal amount of research has gone into documenting the different properties of graphene materials synthesized using various combinations of oxidation and reduction methods on graphite starting materials.^{9, 18-20} Our group has contributed to this effort in understanding the effects that different oxidation methods have on the oxygen composition and electrochemical properties of the resulting reduced graphene oxides.^{21, 22} The scientific community has, thus far, treated graphite as a constant and homogeneous starting material, largely ignoring a key step in the synthesis process. In reality, the truth is often not so simple, and graphite is no exception: it can exhibit varying properties depending on its quality and crystallinity.

In this Chapter, we seek to address current lapses in graphene literature in two specific oversights: (1) that synthetic procedures in the manufacture of CMGs are not actually benign in introducing impurities to the CMGs, and (2) that the properties of CMGs can be influenced by the choice of parent graphite material used for synthesis.

5.1 – INADVERTENT CONTAMINATION OF CMGS WITH METALLIC IMPURITIES AS A RESULT OF SYNTHETIC PROCEDURES

Introduction

Although the large scale fabrication of pristine graphene is not yet a reality, various methods have been developed to synthesize graphitic carbon materials that closely approach the properties of pristine graphene. One such route involves the initial oxidation of graphite to GO, followed by its reduction to yield RGO. Recently, the oxidative procedure has been successfully scaled up towards industrial levels, utilizing a continuous stirred tank reactor process capable of yielding 2 kg of GO per day from a single setup.²³ The RGO subsequently obtained showed excellent electrical conductivity and surface area on par with RGO synthesized using more controlled laboratory procedures.

Several conditions and reagents for the oxidation of graphite to GO have been studied, which can be broadly classified as chlorate-based: Brodie,²⁴ Staudenmaier,²⁵ and Hofmann^{26, 27} methods, or permanganate-based: Hummers²⁸ method. The Hummers approach is presently the most commonly used procedure to obtain GO, though many variations with small modifications exist. For the reduction step, methods available encompass thermal annealing, electrochemical reduction,²⁹ and chemical reduction. The last category itself is highly varied, using a plethora of traditional reducing agents such as hydrazine,³⁰ sodium borohydride,³¹ and lithium aluminium hydride;³² more unconventional, “greener” agents like reducing sugars³³ and tea solution³⁴ have been used as well. The wide selection of oxidising and reducing agents offers practically

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unlimited combinations of procedures to synthesize RGOs from graphite, with large differences in the RGO material properties in each case.³⁵

The presence of residual metallic impurities in graphene is a known problem, many of which are able to dramatically alter the electronic and electrochemical properties of graphene.^{12, 36, 37} It is often falsely assumed in the graphene community that these impurities are sufficiently removed during the conversion of graphite to RGOs, and has little or no effect on the final material's properties. On the contrary, metallic impurities inherent in the parent graphite are retained in the resultant chemically reduced graphenes, at levels widely considered to be "trace" and "negligible" but still enough to exert significant influence on the electrochemical responses of RGOs.¹¹ Thus, proper quantization of the metallic impurities present in RGOs is paramount to ensure that the levels of contamination do not have adverse impacts on a specific use that a RGO is intended for. Unfortunately, this characterization is almost always never performed despite the potential consequences. This situation is reminiscent of the state of carbon nanotube (CNT) research about a decade ago, during which many ground-breaking properties, such as electrocatalytic effects, were initially ascribed to CNTs; these were later proven to arise from the presence of residual metallic catalyst impurities within them. The dominant effects of metallic impurities in CNT have been extensively documented in many areas, including electrocatalysis,³⁸⁻⁴³ toxicity studies,^{44, 45} or sorption properties of CNTs.⁴⁶ In the case of CNTs, metallic impurities observed were remnants of catalyst nanoparticles, the presence of which was crucial for successful growth of CNTs. These impurities ultimately proved difficult to remove from the CNT materials.^{47, 48} For graphene materials prepared from graphite, it is generally assumed that the final graphene materials are free from metallic impurities because no

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catalyst is used; otherwise, the impurities originate from inclusions in the starting graphite.¹²

Herein, we demonstrate that ultrapure-certified graphite is contaminated to varying extents by the chemical agents used during synthetic processing to RGO by comprehensively studying the metallic impurity contamination levels in several RGOs synthesized using a combination of the procedures most commonly used in literature today. The materials are analysed at each stage of synthesis (i.e. before oxidation, after oxidation, and after reduction), thereby revealing how different routes of synthesis affect the metallic element concentrations (Figure 1). We show that contamination occurs during the oxidation and reduction procedures themselves, at levels significant enough to alter the electrochemical behaviour of RGOs, thus highlighting the importance of proper characterization of metal impurities. The origin of many of these metallic elements can be traced back to the oxidizing and reducing agents used during synthesis, with important implications on the potential applications that RGOs are slated for.

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Figure 1. Common synthesis methods for the preparation of reduced graphene oxides using graphite as a starting material, which ultimately leads to varying contamination arising from impurities within the chemical agents used. Grey spheres represent carbon atoms, red spheres represent oxygen atoms, and other colours represent metallic impurities.

Results and Discussion

It has been shown that even trace amounts of metallic impurities originating from the starting graphite are able to influence the electrochemical responses of reduced graphene oxides.¹¹ To minimize this effect, we used nuclear reactor grade graphite as the starting material due to its extremely high purity. Neutron activation analysis (NAA) was used as the primary method to determine the levels of impurities present in our materials due to its accuracy and robustness.⁴⁹ Additionally, since the materials being studied can be irradiated directly, true bulk analysis of the material can be performed, as well as eliminating the possibility of contamination during sample

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preparation for analysis. While the amount of metallic impurities in the nuclear graphite was zero according to the enclosed ICP-MS certification, NAA of the nuclear graphite detected the presence of six trace metals, four of which had a concentration well below 1 ppm by mass (Table 1). The NAA data as well as ICP-MS certification confirmed our starting graphite's high purity, and also served as a basis for assessing changes in metal concentrations after subsequent oxidation and reduction procedures.

To study the evolution of metallic impurities incorporated during the synthetic procedures, graphite oxide (GO) was first prepared using a modified Hummers method, which is the most common oxidation method currently used for GO production. This procedure eliminated most of the original metallic impurities in the starting graphite; however, trace amounts of 7 new metals and 2 metalloids were observed (total of 11 metallic elements). Hereafter, metals and metalloids will be collectively referred to as metallic elements. Additionally, the concentration of manganese increased drastically from 0.14 ppm to 2290 ppm (Table 1). Indeed, the Hummers method is known to result in considerable amounts of residual manganese due to the use of permanganate oxidant.⁵⁰⁻⁵² This Hummers GO (HU-GO) was subsequently reduced to yield reduced graphene oxides (HU-RGOs) using three different methods: thermal treatment (HU-TRGO), sodium borohydride (HU-NaBH₄), and hydrazine (HU-N₂H₄). An abundance of Mn-based impurities were also observed in the resultant materials, with HU-TRGO showing the highest Mn content (5700 ppm) while the Mn concentrations in HU-NaBH₄ and HU-N₂H₄ were 3800 ppm and 3000 ppm of Mn, respectively. Our group has shown previously that Mn-based impurities exert an influence on the electrocatalysis of the oxygen reduction reaction at carbon electrode surfaces.⁵³ We verified this phenomenon once again by recording linear sweep voltammograms of glassy carbon (GC) electrodes

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Table 1. Elemental concentrations of metals and metalloids (parts-per-million by mass) present in nuclear graphite, HU-GO, and HU-RGOs and their expanded uncertainties (coverage factor $k=2$), as determined by NAA. Values below the detection limit of the NAA procedure are also shown. These values, and to a lesser extent the uncertainties, vary as a function of the matrix composition, including non-metal and non-metallloid elements.

Element	Elemental concentration [ppm]				
	Graphite	HU-GO	HU-TRGO	HU-NaBH ₄	HU-N ₂ H ₄
Ag	< 0.12	< 0.06	< 0.11	2.22 ± 0.17	1.90 ± 0.17
Al	5.2 ± 1.6	< 60	< 110	310 ± 70	420 ± 80
As	< 0.03	0.056 ± 0.012	1.08 ± 0.12	< 1	< 17
Ba	< 3	< 7	< 9	19 ± 5	570 ± 40
Ce	< 0.3	< 0.1	< 0.3	5.9 ± 0.4	1.20 ± 0.17
Co	< 0.01	0.157 ± 0.013	6.2 ± 0.4	2.17 ± 0.16	1.42 ± 0.10
Cr	< 0.4	1.82 ± 0.15	50 ± 4	5.2 ± 0.4	9.2 ± 0.7
Cs	< 0.03	0.028 ± 0.008	< 0.15	< 0.03	< 0.05
Cu	< 1.2	130 ± 40	< 200	< 200	< 400
Fe	< 18	82 ± 6	270 ± 20	123 ± 12	144 ± 16
Hf	< 0.03	< 0.01	0.055 ± 0.014	0.33 ± 0.05	0.26 ± 0.02
In	0.016 ± 0.002	< 0.1	< 0.8	0.63 ± 0.12	1.97 ± 0.14
K	< 30	820 ± 60	2410 ± 180	< 1400	< 10000
La	0.031 ± 0.004	< 0.004	< 0.3	< 0.15	< 2
Mn	0.14 ± 0.02	2290 ± 160	5700 ± 400	3800 ± 300	3000 ± 200
Na	1.0 ± 0.3	96 ± 7	138 ± 10	7600 ± 500	420 ± 70
Sb	< 0.009	0.012 ± 0.003	< 0.3	0.068 ± 0.016	0.37 ± 0.04
Sc	< 0.002	0.0017 ± 0.0004	0.011 ± 0.001	0.021 ± 0.002	0.024 ± 0.002
Ta	< 0.013	< 0.006	0.26 ± 0.02	0.066 ± 0.006	0.038 ± 0.004
Th	< 0.04	< 0.013	< 0.03	0.059 ± 0.013	< 0.04
V	0.059 ± 0.014	< 1.8	< 5	< 5	9 ± 2
Zn	< 0.8	< 150	3.0 ± 0.8	114 ± 8	169 ± 12

modified with HU-RGOs in the presence of air-saturated KOH, with an unmodified GC electrode serving as a representation of non-catalytic response (Figure 2). The oxygen reduction onset potential at the non-catalytic bare GC electrode was at -265 mV. The onset potential on HU-RGO-modified GC electrodes were clearly shifted towards more positive potentials, with HU-TRGO showing the largest shift (onset potential of -121 mV) as a result of its high Mn concentration. A similar but slightly less positive value (-135 mV) was noted for HU-N₂H₄. Comparatively, the onset potential at the MnO₂-modified

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electrode was -92 mV. Intriguingly, the corresponding onset potential for HU- NaBH_4 was -226 mV despite possessing a higher Mn content than HU- N_2H_4 . This is most likely due to the relative inefficiency of borohydride reduction and exfoliation compared to thermal treatment and hydrazine. Scanning electron microscopy (Figure 3) showed that HU- NaBH_4 existed primarily as large areas of stacked sheets, in contrast to the highly exfoliated, wrinkled structures seen in HU-TRGO and HU- N_2H_4 . This is consistent with other studies, in which the surface areas of NaBH_4 -reduced RGOs are distinctly lower than that of hydrazine-reduced RGOs.^{30, 54-56} As a result, a large proportion of the Mn-based impurities in HU- NaBH_4 would have been sheathed in between these stacked sheets, rendering them surface-inaccessible and thus leading to the greatly reduced catalytic effect observed.

While the incorporation of manganese-based impurities was expected due to the usage of permanganate oxidant, contamination with elements not typically associated with the synthesis process was also observed. In addition to residual Na, K, and Mn as expected due to the use of potassium permanganate and sodium nitrate during the oxidation procedure, new metallic elements (As, Co, Cr, Cs, Cu, Fe, Sb, and Sc) were also introduced into the HU-GO sample after the oxidative treatment. The origin of most of these elements is likely to be the synthesis reagents themselves; inductively coupled plasma optical emission spectrometry (ICP-OES) of KMnO_4 and NaNO_3 used showed the presence of 8 metallic elements (Ca, Co, Cr, Cu, Fe, Ni, Pb, Zn) as seen from Table 2. Similarly, the three reductive processes subsequently used to obtain HU-RGOs introduced 3 to 9 new trace metallic impurities, depending on the reduction method used (Table 1). The concentrations of certain metals also increased post-reduction. For example, iron concentrations within HU-TRGO, HU- NaBH_4 , and HU- N_2H_4 were

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determined to be 270 ppm, 123 ppm, and 144 ppm respectively, while there was 82 ppm of Fe in HU-GO (no Fe was detected in the starting graphite).

To determine whether these Fe impurities would influence the electrochemical properties of HU-RGOs, we employed cumene hydroperoxide (CHP) as a molecular pro-

Figure 2. Linear sweep voltammograms for air-saturated 0.1 M KOH on HU-RGO modified GC electrodes, as well as comparative voltammograms for bare and MnO₂-modified GC electrodes.

Figure 3. SEM images of a) HU-TRGO, b) HU-NaBH₄, and c) HU-N₂H₄. HU-NaBH₄ visibly shows a far lesser extent of exfoliation than HU-TRGO or HU-N₂H₄.

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Table 2. Elemental concentrations of metals and metalloids (parts-per-million by mass) present in synthetic reagents used in oxidation and reduction, as determined by ICP-OES. A null value indicates that the elemental concentration was below the detection limit of the ICP-OES procedure.

Concentration of elements [ppm]								
	KMnO ₄	NaNO ₃	KClO ₃	NaBH ₄	N ₂ H ₄	HNO ₃	HCl	H ₂ SO ₄
B	41.7	-	-	265734.6	-	0.01	0.004	0.004
Ba	-	-	-	-	-	-	0.02	0.03
Ca	13.1	-	-	-	-	0.04	0.5	0.07
Co	2.5	2.5	0.6	4.4	8.5	-	0.05	0.05
Cr	47.9	5.1	3.2	-	4.3	-	0.03	0.03
Cu	-	14.6	-	7.3	25.6	-	0.09	-
Fe	22.4	7.6	1.9	-	-	0.01	0.1	0.07
Mg	-	-	-	1275.7	-	-	0.05	0.01
Mn	289445.5	-	-	-	-	-	-	-
Ni	9.3	7.6	1.9	-	8.5	-	0.02	0.02
Pb	84.7	27.2	12.1	19.0	46.9	-	0.1	0.2
Zn	4.4	4.4	0.6	-	-	0.02	0.02	0.03

Figure 4. Cyclic voltammograms for 10 mM CHP on HU-RGO-modified GC electrodes, as well as comparative voltammograms for bare and Fe₃O₄-modified GC electrodes. The suffix “x” denotes the number of times the current values of the CV was scaled for ease of comparison. Conditions: scan rate, 100 mV s⁻¹; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl.

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-be, which is known to undergo catalytic reduction in the presence of iron.¹¹ As can be seen from the cyclic voltammograms (CVs) in Figure 4, the non-catalytic reduction of CHP occurs on a bare GC electrode, giving rise to a reduction peak in the region of -830 mV. For GC electrodes modified with HU-RGOs, we noted a trend of decreasing reduction potential with increasing Fe content. The electrode modified with HU-TRGO (highest Fe content) exhibited a reduction peak drastically shifted to -457 mV, while those of HU-N₂H₄ (second highest) and HU-NaBH₄ (lowest) were -566 mV and -606 mV, respectively. For comparison, the catalytic reduction of CHP by Fe₃O₄ nanoparticles was found to occur at -496 mV, which is in the same region as HU-TRGO. Hence, it is evident that different reduction procedures (encompassing both thermal and chemical means) unintentionally introduce different amounts of trace Fe impurities into HU-RGOs, with varying influence on their electrochemical properties dependent on the level of contamination.

Further to the above results, we sought to investigate the changes in impurities originating from the oxidation procedure itself by employing another two oxidation procedures, Staudenmaier and Hofmann methods, to first synthesize two other graphite oxides (ST-GO and HO-GO respectively) and then following a uniform reduction procedure. NAA of ST-GO revealed 11 different trace metallic elements, which is numerically similar to that in HU-GO, though the identities of several elements were different (Table 3). HO-GO had the highest contamination with a total of 15 metallic elements. The decreased amounts (both in terms of types as well as concentrations) of impurities in ST-GO compared to HO-GO can be attributed to the use of fuming nitric acid in the Staudenmaier method, which is much more corrosive and thus better able to

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remove metallic impurities than the concentrated nitric acid utilized in the Hofmann method.

A standard thermal reduction was then applied to ST-GO, HU-GO, and HO-GO to obtain ST-TRGO, HU-TRGO, and HO-TRGO respectively. Thermal reduction was chosen as this procedure was found to introduce the least amount of new trace impurities into the HU-RGOs studied above. This can be understood to occur because thermal reduction does not require any additional solution processing, thus eliminating further contamination from reagents and experimental work-up. NAA of the TRGOs (Tables 1 and 3) showed that thermal reduction of the GOs resulted in a general increase in the concentrations of metallic elements of around an order of magnitude, with only slight differences in the identities of metallic contaminants. On the basis of NAA measurements, the widest range of contamination from metallic elements was found in ST-TRGO. However, unlike the previous case in which the NAA detection limits in HU-RGOs were similar regardless of reduction method, the detection limits for certain elements in ST-TRGO, HU-TRGO, and HO-TRGO showed much larger variance. For example, the detection limit of nickel using NAA ranged from 800 ppm in ST-TRGO to 20000 ppm in HU-TRGO; these detection limits are also far too high for meaningful trace detection of Ni-based impurities. Consequently, ICP-OES was also carried out on the TRGOs, which obtained Ni concentrations of 7.0 ppm, 14.0 ppm, and 20.6 ppm in ST-TRGO, HU-TRGO, and HO-TRGO, respectively. Once again, the origin of these nickel impurities can be traced back to the reagents used during synthesis (Table 2). Nickel-based substrates have been demonstrated to play a pivotal role in the electrocatalytic oxidation of hydrazine, sometimes in tandem with iron compounds.^{10, 57, 58} CVs of a bare GC electrode (non-catalytic) in the presence of hydrazine showed a small oxidation wave beginning at +151

mV (Figure 5). In contrast, distinctly earlier oxidation waves were noted for the TRGO-modified electrodes, with onset potentials correlated to Ni content(+100 mV, +64 mV, and +53 mV for ST-TRGO, HU-TRGO, and HO-TRGO respectively) and similar to the response shown by NiO-modified electrodes (+65 mV).

Table 3. Elemental concentrations of metals and metalloids (parts-per-million by mass) present in ST-GO, ST-TRGO, HO-GO, and HO-TRGO and their expanded uncertainties (coverage factor k=2), as determined by NAA. Values below the detection limit of the NAA procedure are also shown. These values, and to a lesser extent the uncertainties, vary as a function of the matrix composition, including non-metal and non-metalloid elements.

Element	Elemental concentration [ppm]			
	ST-GO	ST-TRGO	HO-GO	HO-TRGO
Ag	0.038 ± 0.011	< 0.12	< 0.03	< 0.5
Al	< 4	57 ± 5	< 12	< 150
As	0.60 ± 0.06	0.83 ± 0.09	< 0.06	< 0.1
Ca	< 50	4500 ± 1600	< 30	< 7
Ce	< 0.06	< 0.4	2.5 ± 0.3	< 0.9
Co	0.058 ± 0.005	8.1 ± 0.8	0.33 ± 0.02	1.49 ± 0.11
Cr	0.94 ± 0.08	69 ± 5	0.72 ± 0.08	42 ± 3
Cs	< 0.005	< 0.05	0.188 ± 0.004	< 0.08
Fe	8.3 ± 1.5	340 ± 30	16 ± 4	260 ± 30
In	< 0.02	0.153 ± 0.013	0.013 ± 0.004	0.076 ± 0.016
K	360 ± 30	60 ± 20	240 ± 20	450 ± 100
La	< 0.008	< 0.1	0.022 ± 0.004	0.080 ± 0.016
Mn	0.62 ± 0.06	5.9 ± 0.4	3.1 ± 0.2	97 ± 7
Mo	< 0.6	4.4 ± 0.8	< 0.6	< 7
Na	3.5 ± 0.3	31 ± 2	12.1 ± 0.9	44 ± 4
Pt	< 0.6	< 5	< 0.6	75 ± 6
Sb	0.042 ± 0.004	0.19 ± 0.02	0.040 ± 0.006	0.12 ± 0.03
Sc	< 0.01	< 0.004	0.0015 ± 0.0002	< 0.007
Se	0.34 ± 0.03	< 0.4	< 0.14	< 1
Ta	< 0.003	< 0.06	0.019 ± 0.004	< 0.1
V	< 0.12	18.2 ± 1.3	0.37 ± 0.07	2.6 ± 0.3
W	< 0.07	3.7 ± 0.3	< 0.07	< 1
Zn	0.69 ± 0.11	3.5 ± 1.1	2.0 ± 0.2	< 6

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Figure 5. Cyclic voltammograms for 5 mM hydrazine on TRGO-modified GC electrodes, as well as comparative voltammograms for bare and NiO-modified GC electrodes. The suffix “x” denotes the number of times the current values of the CV was scaled for ease of comparison. Conditions: scan rate, 100 mV s⁻¹; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl.

The results discussed above indisputably show that metallic impurities are introduced during both oxidation and reduction procedures in the synthesis of RGOs, and the identities of the impurities are not easily anticipated unless thorough elemental analyses on the materials as well as reagents are carried out. While we have only examined how these metallic impurities can impact the electrochemical responses of RGOs, it is important to keep in mind that other properties can be affected as well. For metallic elements with higher levels of contamination, potassium doping is known to have profound effects on the electronic properties of graphene,^{59, 60} while the presence of aluminium on graphene greatly increases its affinity for gases such as N₂O and CO.^{61, 62} Additionally, graphene films have been envisaged to function as water desalination systems, due to the potential of tuning pore sizes to allow permeation or rejection of

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different ions.⁶³ However, the leaching of impurities from within the graphene membrane itself may be a potential problem, considering the World Health Organization guideline values for chromium and arsenic in drinking water are a mere 50 ppb and 10 ppb respectively.⁶⁴ We also emphasize our use of exceedingly pure nuclear graphite as the starting material in this work, to exclude contribution of contamination from inherent impurities. In reality, the synthesis of RGOs typically utilizes natural or synthetic graphite, which is more economically feasible. Unfortunately, these graphites possess far higher levels of initial metallic contamination (which remain in significant amounts even after purification), thus compounding the issues highlighted.

Conclusion

We have tracked the changes in the concentrations of metallic elements present in several graphene materials at each stage of synthesis, which were prepared using three different oxidation methods as well as three different reduction methods. The synthetic procedures were found to vary significantly in terms the types of impurities introduced as well as the extent of contamination, and the origin of these metallic elements can be traced back to the reagents used for oxidation and reduction of the materials involved. These impurities are highly active in the catalysis of an array of electrochemical reactions, being able to dramatically alter the electrochemical responses of reduced graphene oxides as shown in our investigations. As metallic impurities are able to affect many other properties of graphene materials, their implications are wide-reaching, potentially impacting many proposed applications of graphene materials.

Contributions:

C.H.A. Wong and M. Pumera designed research. C.H.A. Wong, Z. Sofer, M. Kubešová, J. Kucera, and S. Matejková performed research. M. Kubešová, J. Kucera, and S. Matejková contributed new reagents/analytic tools. C.H.A. Wong, Z. Sofer, M. Kubešová, J. Kucera, S. Matejková, and M. Pumera analyzed data. C.H.A. Wong and M. Pumera wrote the paper.

5.2 – CHOICE OF GRAPHITE SOURCE AND ITS INFLUENCE ON THE PROPERTIES OF DERIVED CMGS

Introduction

The conversion of graphite to GO is typically carried out using the chlorate-based Brodie,²⁴ Hofmann,^{26, 27} and Staudenmaier²⁵ methods, or the permanganate-based Hummers method.²⁸ The general method outlined by Hummers is the most commonly used method for the synthesis of GO today, usually with small modifications in the conditions used. The oxidation of graphite to GO using such a modified Hummers method has been shown to be diffusion controlled and hence follows a front-like reaction progression, commencing from the edge of the graphite flake and slowly working towards the center.⁶⁵ With this knowledge, it should be immediately obvious that the reaction progress is highly dependent on the graphite used. Graphite in itself exhibits different properties depending on the variety used, despite being traditionally treated as a homogeneous material with a well understood structure, and can be first classified as either natural or synthetic.⁶⁶ The former is defined by IUPAC as a natural mineral “consisting of graphitic carbon regardless of its crystalline perfection,” and can thus be further divided into amorphous, flake, or vein graphite.^{67, 68} Amorphous graphite is cryptocrystalline and unlikely to be suitable for electrochemical applications due to its low purity, crystallinity and conductivity.⁶⁶ Natural flake graphite is macro-crystalline and mined from ores of 5–40% graphite by weight, and thus requires additional processing and purification to reach levels of purity suitable for commercial sale. Vein graphite (also known as lump graphite) is the purest (generally >90% “as found”) as well as most highly crystalline form of graphite found in nature, formed from the direct deposition of

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graphitic carbon from a geologic fluid. While this rare form of graphite can be found in many locations, it is mined in commercial quantities only in Sri Lanka. On the other hand, synthetic graphites are produced from the heat-induced graphitization of carbon precursors, and yields graphite powders with variable properties depending on the raw materials and graphitization temperature used. Typically, synthetic graphite can be produced at higher purities than natural graphite through careful choice of the carbon precursors, although recent improvements in flake graphite purification have enabled the production of ultra-pure natural graphite (>99.97% carbon).⁶⁹ Synthetic graphite is also more expensive, with a price of 7000–20000 USD per metric ton in 2012 (prices for natural graphites ranged from 850–1800 USD per metric ton during the same period), while possessing lower crystallinity than natural flake or vein graphite.⁷⁰ As a result, the use of natural graphite remains highly relevant for many applications.

In light of the multitude of variable properties that different natural graphites display, the choice of graphite is paramount during the synthesis of CMGs with desired properties. Commercial suppliers usually obtain their natural graphite from a number of geographical sources, with the source of each lot changing depending on availability and economic factors. However, the geological processes that form natural graphites differ from deposit to deposit, especially in the case of flake graphite, which forms as a seam mineral in between (or alongside) rock sequences. This leads to natural graphites from different deposits differing widely in terms of defects, inclusions, and impurities, with consequences in their reactivity towards chemical treatment. Herein we show that natural graphites obtained from different geographical sources display marked variations in their responses to chemical oxidation as well as subsequent reduction

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procedures, with distinct implications on the electrochemical and electrical properties of the resulting CMGs.

Results & Discussion

To examine the influence of geographical and geological origin on the properties of graphite and the resulting GOs, four natural graphite samples from different mines were obtained for use in our investigations. These graphites were from Český Krumlov, Czech Republic (G-CZE), Bogala Mine, Sri Lanka (G-LKA and G-LKB), and Lynx Mine, Zimbabwe (G-ZWE). The Sri Lankan samples were both vein graphites, while G-CZE and G-ZWE were flake graphites. A sample of synthetic graphite (G-SYN) was similarly studied to serve as a material for comparison. All five graphites were highly crystalline as evidenced by their X-ray powder diffraction patterns (Figure 6). These samples were further characterized using Raman spectroscopy (Figure 7a), with the peaks of interest being the D-band at $\sim 1350\text{ cm}^{-1}$ and the G-band at $\sim 1575\text{ cm}^{-1}$; the relative intensities of these peaks (I_D/I_G ratio) is an indicator of the density of defects present in the graphites.⁷¹ All four natural graphites were found to have low defect densities of 0.05, 0.06, 0.04, and 0.03 (for G-CZE, G-LKA, G-LKB, and G-ZWE, respectively), which correspond to respective average sp^2 domain sizes (L_a) of 366, 300, 420, and 510 nm (Table 1). G-SYN had a comparatively higher I_D/I_G ratio of 0.12 ($L_a = 139\text{ nm}$). Subsequently, oxidation of graphite samples to GOs was carried out using a modified Hummers' method, causing a dramatic broadening of the G-band as well as an increase in the intensity of the D-band across all samples (Figure 7b). These changes can be attributed to a large increase in disorder during the oxidation process from the generation of multiple types of oxygen functionalities as well as a larger number of edge

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sites.^{72, 73} Despite the differences in defect densities among the starting graphites, the resultant GOs exhibited Raman spectra that were virtually indistinguishable from each other (including the GO derived from synthetic graphite), with I_D/I_G ratios falling within a small range of 0.91 to 0.94 (with L_a ranging from 18.0 nm to 18.4 nm).

Figure 6. X-ray powder diffraction patterns of graphite samples. Samples were measured as received. Data have been normalized to 002 peak intensity.

Figure 7. Raman spectra of (a) graphites, and (b) graphite oxides, normalized to G-band intensity.

Table 1. Relative intensities of D- and G-bands in graphites and graphite oxides and corresponding average crystallite sizes.

	Graphite (G)		Graphite oxide (GO)	
	I_D/I_G	L_a/nm	I_D/I_G	L_a/nm
CZE	0.05	366	0.94	18.0
LKA	0.06	300	0.92	18.3
LKB	0.04	420	0.93	18.1
ZWE	0.03	510	0.93	18.1
SYN	0.12	139	0.91	18.4

While the data obtained from Raman spectroscopy suggested that the GOs were highly similar in terms of their defect densities, it does not offer any insight into the extent to which the individual GOs are oxidized. X-ray photoelectron spectroscopy (XPS) was therefore utilized to glean information on the extent of oxidation as well as types of elements and chemical bonding present in the starting graphites and their derived GOs. Analysis of the recorded XPS wide spectra (Figure 8a) showed that the graphite samples varied significantly in their initial oxygen contents, with their C/O ratios ranging from 13.6 in G-ZWE to 22.4 in G-CZE (Table 2). Silicon impurities were also observed in trace amounts (0.44 – 1.54 at.%) for the natural graphites; no silicon was detected in the synthetic graphite sample. Based on this information, G-CZE was the purest natural graphite both in terms of carbon purity and amount of Si contamination, followed by G-LKB, G-LKA, and finally G-ZWE.

An identical Hummers oxidation procedure was then carried out on each graphite and the XPS spectra of the resulting GOs recorded (Figure 8b). C/O ratios decreased greatly across all materials after conversion to GO (Table 2), with GO-CZE being the most oxidized sample (C/O = 1.92) and GO-ZWE being the least oxidized (C/O = 2.27). No relationship was found between starting graphite defect density and extent of oxidation of GO as suggested by a previous study.⁷⁴ Instead, a direct correlation between

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starting natural graphite purity and extent of oxidation in the resultant GO was observed. Small quantities of sulfur and nitrogen were also present in the GOs, arising from covalently bonded organosulfates, inorganic sulfates, and/or residual adsorbed sulfuric and nitric acid during synthesis.^{22, 75-77} These sulfur and nitrogen species were present in amounts also correlated to the extent of oxidation, which implies that penetration of chemical reagents (during Hummers oxidation) into the graphite layers occurred more readily with higher purity of the natural graphite, resulting in a more oxidized product. Similarly, elimination of silicon impurities was observed in all natural graphite samples upon conversion to GO, with the exception of GO-ZWE, which was also the least oxidized GO. Evidently, natural graphites with different geographical origins yield GOs with varying extents of oxidation, and may be related to the differing elemental purities of the starting graphite. In comparison, GO-SYN was found to be oxidized to a lesser extent than most of the GOs derived from natural graphites, despite its parent synthetic graphite having a high C/O ratio of 20.2.

Figure 8. XPS wide spectra of a) graphites and b) graphite oxides. Values were normalized to C 1s peak intensities.

Table 2. Carbon-to-oxygen atomic ratios and amounts of other elements present in graphite and graphite oxide samples as derived from XPS.

	graphite (G)		graphite oxide (GO)			
	C/O	Si%	C/O	N%	S%	Si%
CZE	22.4	0.44	1.92	1.06	2.30	<DL
LKA	16.8	0.91	2.07	0.58	1.27	<DL
LKB	18.4	0.89	1.99	0.85	1.63	<DL
ZWE	13.6	1.54	2.27	<DL	0.76	1.30
SYN	20.2	<DL	2.18	0.77	0.74	<DL

These observed differences in extent of oxidation would conceivably impact the electrochemical behaviours of GOs as electroensing materials. Voltammetric characterization of the GOs in the form of cyclic voltammetry was carried out by recording the electrochemical responses of GOs in the presence of the iron(II)/iron(III) redox couple (Figure 9). Being a positively charged probe, the approach of $\text{Fe}^{2+/3+}$ cations to the electrode surface is favoured by the presence of oxygen species due to attractive electrostatic interactions, thus facilitating electron transfer between the electrode surface and the probe. This phenomenon becomes apparent in the peak-to-peak separation (ΔE_p) values of the measured voltammograms, where lower ΔE_p corresponds to faster heterogeneous electron transfer. GC electrodes modified with GO-CZE (most oxidized) gave an average ΔE_p value of 557 mV; in contrast, the corresponding value for GO-ZWE (least oxidized) was 703 mV, an increase of 146 mV. ΔE_p values for the Sri Lankan vein graphites-derived GO-LKA (626 mV) and GO-LKB (647 mV) fell in between, in line with their intermediate levels of oxidation as compared to GO-CZE and GO-ZWE. Further experiments were conducted using the ferro/ferricyanide redox system, which has negatively charged redox species due to the presence of cyanide ligands. In contrast

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to $\text{Fe}^{2+/3+}$ cations, $[\text{Fe}(\text{CN})_6]^{4-/3-}$ anions undergo repulsive interactions with surface-bound oxygen species, and is expected to show the opposite trend in ΔE_p values as compared to the iron(II)/iron(III) system. For GOs derived from natural graphites, the voltammograms recorded in the presence of ferro/ferricyanide (Figure 10) generally showed greater ΔE_p with increasing oxidation, with values ranging from 374 mV (GO-ZWE) to 431 mV (GO-CZE). However, the GC electrodes modified with GO derived from synthetic graphite (GO-SYN) was found to have the largest ΔE_p of 464 mV despite possessing the second lowest extent of oxidation among the GOs. The poor electron transfer kinetics at GO-SYN modified GC electrodes in both $\text{Fe}^{2+/3+}$ as well as $[\text{Fe}(\text{CN})_6]^{4-/3-}$ systems may be an indicator of its unsuitability as an electrode material for electrochemical applications.

In addition to differences in the overall oxidation state of the GOs, the types and relative amounts of carbon-bound oxygen functionalities present can also be determined from high-resolution C 1s core XPS (Figure 11). At first glance, the high resolution spectra cursorily show that the GOs derived from Sri Lankan graphites as well as synthetic graphite had similar types of carbon-bound oxygen species, while the GOs from Czech Republic and Zimbabwe graphites were more varied in their compositions. Deconvolution of the high-resolution C 1s signals generally showed C=C sp^2 bonding at 284.6 eV, C–C and C–O (sp^3 , epoxy, hydroxyl) forming a combination peak at 285.8 eV, C=O (carbonyl) at 287.8 eV, and O=C–O (carboxyl) bonding at 289.6 eV. Briefly, the amount of C=C ranged from 6.0 to 11.6%, sp^3 C from 32.0 to 40.6%, carbonyls from 41.4 to 52.4%, and carboxyls from 6.5 to 10.2%; a summary of the relative amounts of these components is given in Table 3. These differences in carbon-bound oxygen environments, in addition to differing overall C/O ratios, are likely to affect the response of the GOs

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Figure 9. Electrochemical performance of GO-modified GC electrodes in the presence of iron(II)/iron(III) ions. (a) Cyclic voltammograms for 5 mM Fe^{2+/3+}; conditions: scan rate, 100 mV s⁻¹; background electrolyte, 0.1 M HClO₄ (pH 0.72); reference electrode, Ag/AgCl. (b) Peak-to-peak separation values for GO-modified GC electrodes in the Fe^{2+/3+} system.

Figure 10. Electrochemical performance of GO-modified GC electrodes in the presence of ferro/ferricyanide ions. (a) Cyclic voltammograms for 10 mM [Fe(CN)₆]^{4-/3-}; conditions: scan rate, 100 mV s⁻¹; background electrolyte, 50 mM phosphate buffer solution (pH 7.4); reference electrode, Ag/AgCl. (b) Peak-to-peak separation values for GO-modified GC electrodes in the [Fe(CN)₆]^{4-/3-} system.

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Figure 11. High resolution XPS C 1s core spectra of graphite oxides.

Table 3. Relative amounts of components in deconvoluted high resolution C1s core spectra of GOs.

	% composition of C 1s signal			
	C=C	C-C + C-O	C=O	O=C-O
GO-CZE	11.6	39.1	42.8	6.5
GO-LKA	6.3	32.0	52.4	9.3
GO-LKB	6.0	33.5	50.7	9.8
GO-ZWE	7.8	40.6	41.4	10.2
GO-SYN	7.8	33.8	49.6	8.8

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towards subsequent processing, in particular chemical-based ones.

As GOs are highly oxidized and electrically insulating by nature, a reduction process is typically employed to remove oxygen species from GOs, converting them to reduced graphene oxides (RGOs). The creation of more extensive C=C sp^2 networks during the deoxygenation of GO restores electrical conductivity, making RGOs suitable for electrical applications. We subjected the GOs to a standard chemical treatment with hydrazine and studied the changes that occurred post-reduction. No significant differences were observed in the defect densities of the RGOs during Raman spectroscopy (Figure 12); I_D/I_G ratios of the RGOs fell within a range of 1.11 to 1.17, which represent L_a values of 14.4 to 15.1 nm. The higher amount of defects and smaller crystallite sizes in RGOs than GOs has been previously rationalized by the formation of numerous graphitic domains during reduction, but which are smaller in size than those in GO.^{30, 78} Despite possessing similar defect densities, the RGOs were found to have starkly different responses to the reduction procedure as determined by XPS analysis (Figure 13). RGO-CZE was the most reduced natural graphite-derived sample with a C/O ratio of 7.74, followed by RGO-LKA (7.22), RGO-LKB (6.45), and finally RGO-ZWE (3.73). RGO-SYN had a C/O ratio of 6.61, similar to that of RGO-LKB. The effect of reduction efficiency on the electrical conductivities of the RGOs was studied by conducting current-voltage (I/V) measurements on an interdigitated gold electrode (Au-IDE) as shown in Figure 14. All five RGOs exhibited ohmic behaviour, but with significantly different conductivities as determined by the slope of their I/V profiles. The most reduced natural graphite-derived sample, RGO-CZE, possessed the highest I/V slope of 20.2 mA V⁻¹, while the least reduced (RGO-ZWE) had the lowest slope of 1.0 mA V⁻¹. RGO-LKA and RGO-LKB had intermediate conductivities as shown by their slopes of 15.2

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and 6.6 mA V^{-1} , respectively. The comparative I/V slope for RGO-SYN was 7.9 mA V^{-1} . These I/V values correspond directly with the trend of increasing conductivity with increasing reduction efficiency, and also demonstrate that RGOs synthesized from graphites with different geographical origins ultimately display highly different conductivities.

Figure 12. Raman spectra of reduced graphene oxides, normalized to D-band intensity.

Figure 13. (a) XPS wide spectra and (b) high resolution C 1s core spectra of reduced graphene oxides.

Figure 14. Current–voltage profiles of RGOs, measured after material deposition on a Au-IDE.

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Conclusion

We have demonstrated that the oxidation of natural graphites with different geographical and geological origins leads to graphite oxides that, while possessing similar defect densities, actually exhibit significant variance in their extents of oxidation and types of carbon-bound oxygen species, and may be related to the different elemental purities of the starting natural graphites. These parameters were shown to exert influence on the electrochemical behaviours of the GOs. Furthermore, differences in reductive efficiency were observed when the GOs were subsequently reduced by chemical means. The resultant reduced graphene oxides showed large differences in their conductivities as a result of their different extents of reduction.

Contributions:

C. H. A. Wong, Z. Sofer, and M. Pumera conceptualized the project. Z. Sofer provided the various graphites. C. H. A. Wong synthesized the materials and conducted the experiments. C. H. A. Wong and M. Pumera wrote the manuscript. All authors contributed to discussions.

*Chapter 5 – Fundamental studies on chemically modified graphenes***5.3 – MATERIALS AND METHODS**Materials

For Section 5.1, graphite (99.9995 %, 2-15 μm) was obtained from Alfa Aesar, Germany. Sulfuric acid (98%), nitric acid (68%), nitric acid (fuming, >98.5%) potassium chlorate (>99%), potassium permanganate (>99.5%), hydrogen peroxide (30%), sodium nitrate (>99.5%), hydrochloric acid (37%), hydrazine monohydrate (99%), silver nitrate (99%), and barium nitrate (99%) were obtained from PENTA, Czech Republic. Nitrogen (99.9999 %) was obtained from SIAD, Czech Republic. Sodium borohydride (99%) was obtained from Sigma-Aldrich, Czech Republic. For Section 5.2, the natural graphite termed as G-CZE was obtained from KOH-I-NOOR GRAFIT, Czech Republic. Natural and synthetic graphites termed as G-LKA, G-LKB, G-ZWE and G-SYN were obtained from Graphite Týn, Czech Republic. Sulfuric acid (98%), sodium nitrate, and methanol were obtained from Sigma-Aldrich, Singapore. For both Sections 5.1 and 5.2, *N,N*-dimethylformamide, phosphate buffer powder, potassium hydroxide, iron(II,III) oxide nanopowder, nickel(II) oxide nanopowder, potassium hexacyanoferrate(III), perchloric acid, and iron(III) chloride hexahydrate were obtained from Sigma-Aldrich, Singapore. Potassium permanganate was obtained from J.T. Baker. Hydrogen peroxide (35%), hydrazine hydrate, hydrazine dihydrochloride and manganese(IV) oxide powder were obtained from Alfa Aesar, Singapore. Barium chloride dihydrate was obtained from QR&C. Ethanol was purchased from Merck, Singapore. Deagglomerated alpha alumina powder (0.05 μm) was purchased from Struers, Singapore. Glassy carbon (GC) working electrodes, Ag/AgCl reference electrode and Pt auxiliary electrode were obtained from CH Instruments, USA.

Apparatus

A JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) was used to acquire the SEM images at 5.0 kV and a working distance of 5.7 mm. The solid samples were immobilized onto a carbon tape on an aluminium SEM holder for analyses.

Raman spectra were obtained with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific, Japan) with an Ar ion laser (excitation wavelength 514.5 nm) beam in backscattering geometry with a CCD detector, measuring from 1000 to 3000 cm^{-1} . The crystallite size (L_a) of the sp^2 lattice was calculated using the equation:

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

where λ is the wavelength of the laser in nm, I_G and I_D are the intensities of the Raman G and D bands respectively.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Phoibos 100 spectrometer (SPECS, Germany) with a monochromatic Mg X-ray source. Relative sensitivity factors were used for evaluation of C/O ratios from wide spectra XPS measurements. The samples for XPS were prepared by coating carbon tape with a uniform layer of the materials studied.

ICP-OES measurements were performed with Spectro ARCOS (SPECTRO Analytical Instruments, Germany). The spectrometer used the Paschen-Runge configuration with an optimized Rowland circle polychromator, measuring simultaneously in the broad spectral range of 130–770 nm using 32 linear CCD detectors. The detection limits reach the ppb levels for the elements determined.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy measurements were performed using a PerkinElmer Spectrum 100 spectrometer with a

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universal ATR accessory. Materials tested were sampled in the solid state without further sample preparation. A diamond/ZnSe crystal was used as the ATR crystal.

Procedures

Graphite oxide preparation using Staudenmaier method²⁵

87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (fuming, 98%) were added to a reaction flask, and the mixture was then cooled in an ice bath for 30 min. 5 g of graphite was then added into the mixture with vigorous stirring to avoid agglomeration and obtain a homogeneous dispersion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period, in ice bath) to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of gas evolved. The mixture was then stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5% w/w) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction for chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Graphite oxide preparation using Hofmann method^{26, 27}

87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (68%) were added to a reaction flask, and the mixture was then cooled in an ice bath for 30 min. 5 g of graphite was then added to the mixture with vigorous stirring to avoid agglomeration and obtain

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a homogeneous dispersion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period, in ice bath) to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of gas evolved. The mixture was then stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5% w/w) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction for chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Graphite oxide preparation using Hummers method²⁸

For Section 5.1, 5 g of graphite and 2.5 g of sodium nitrate were stirred with 115 mL of sulfuric acid (98%). The mixture was then cooled in an ice bath. With vigorous stirring, 15 g of potassium permanganate was then added over a period of 2 h. The reaction mixture was allowed to reach room temperature (over 4 h) before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask containing 250 mL of deionized water and further heated to 70 °C. After holding the temperature constant for 15 min, the mixture was poured into 1 L of deionized water. The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% (w/w) hydrogen peroxide. The reaction mixture was then allowed to settle and decanted. The graphite oxide obtained was then purified by repeated centrifugation and redispersing in deionized water until a negative reaction for sulfate ion (with $\text{Ba}(\text{NO}_3)_2$)

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was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

For Section 5.2, graphite (200 mg) was stirred with sulfuric acid (9.2 mL, 98%) in an ice bath until an even dispersion was obtained. Sodium nitrate (200 mg) was then added to the mixture and stirred for 1 h. Potassium permanganate (1200 mg) was slowly added portionwise at 0 °C (ice bath), after which the reaction mixture was heated to 35 °C and stirred for 1 h. Deionized water (16 mL) was then added dropwise while ensuring that the reaction mixture temperature did not exceed 90 °C. The reaction was then heated to 90 °C and stirred for 30 min. Deionized water (40 mL) was then added to the mixture and hydrogen peroxide (35%) added to remove unreacted potassium permanganate and manganese dioxide. The reaction mixture was then allowed to settle and decanted. The graphite oxide obtained was then purified by repeated centrifugation and redispersing in deionized water until a negative reaction for sulfate ion (with BaCl₂) was achieved. The graphite oxide slurry obtained was then dried in a vacuum oven at 30 °C for 4 days before use.

Thermal reduction of graphite oxide

Graphite oxides prepared using the procedures above were subjected to thermal reduction/exfoliation at 1000 °C. 0.1 g of graphite oxide was placed into a porous quartz glass capsule connected to a magnetic manipulator and placed inside a vacuum tight tube furnace with controlled atmosphere. The magnetic manipulator is capable of creating a temperature gradient over 1000 °C min⁻¹. The reactor was then flushed with nitrogen gas by repeated evacuation of the tube furnace to remove any traces of oxygen and then quickly inserted by the magnetic manipulator to a preheated furnace and held

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in the furnace for 12 minutes. The flow of nitrogen (99.9999% purity) during the exfoliation procedure was 1000 mL min^{-1} to remove any by-products from the procedure.

Sodium borohydride reduction of graphite oxide

Graphite oxide prepared using Hummers method (500 mg) was dispersed in 500 mL of deionized water by ultrasonication (400 W, 30 min). The suspension was alkalized to pH 10 with 1 M NaOH, and 5 g of NaBH₄ was added to the suspension. The reaction mixture was heated at 80 °C with vigorous stirring for 1 hour. The reaction mixture was allowed to cool to room temperature, after which the reduced graphene oxide was separated by suction filtration, repeatedly washed with deionized water, and dried in a vacuum oven at 50 °C for 48 hours.

Hydrazine reduction of graphite oxide

For Section 5.1, graphite oxide prepared using Hummers method (500 mg) was dispersed in 500 mL of deionized water by ultrasonication (400 W, 30 min). The suspension was alkalized to pH 10 with 1 M KOH, and 5 mL of hydrazine hydrate was added to the suspension. The reaction mixture was heated under reflux for 24 hours. After cooling down to room temperature, the reduced graphene oxide was separated by suction filtration, repeatedly washed with deionized water, and dried in a vacuum oven at 50°C for 48 hours.

For Section 5.2, graphite oxide (50 mg) was stirred in ultrapure water (50 mL) and ultrasonicated for 3 h. Hydrazine hydrate (2 mL) was added dropwise at 47 °C, after which it was heated to 80 °C for 24 h. The reaction was allowed to cool to room temperature, filtered over a PTFE (0.22 µm) membrane, and the residue washed

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repeatedly with methanol and ultrapure water. The solid was then dried in an oven at 60 °C for 5 days to afford reduced graphene oxide.

Characterization of samples

Samples of nuclear graphite, graphite oxides, and reduced graphene oxides prepared by various procedures were packed for irradiation into disk-shaped polyethylene (PE) capsules with a 25 mm diameter made by sealing of PE foils with 0.2 mm thickness. Irradiations were carried out in the LVR-15 experimental reactor of the Research Centre Řež, Ltd. within the CANAM infrastructure (MŠMT Project No. 2011019). Short time irradiations (1 min) were carried out in channel H1 using a pneumatic transport system with a transport time of 3.5 s. Long-time irradiations were done in channel H8 for 3 h. Thermal neutron fluence rates in both channels were $3\text{--}4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. For k_0 standardization, bare triple-monitor method was used for determination of neutron flux parameters in the irradiation channels. For this purpose, newly developed monitors for short-time⁷⁹ and long-time irradiations⁸⁰ were employed. Gamma-ray spectra of samples and monitors were measured with coaxial HPGe detectors (relative efficiency 21 % to 78 %, FWHM resolution 1.80 keV to 1.85 keV, both for the 1332.5 keV photons of ^{60}Co) interfaced to a Canberra Genie 2000 gamma-spectrometer. Decay times, counting times, and counting geometry were selected according to sample activities and half-lives of radionuclides present to optimize detection limits of as many elements as possible. The measurements were evaluated with Kayzero for Windows software package. For verification of results, standard reference materials of the U.S. National Institute of Standards and Technology (NIST SRMs), namely NIST SRM 1547

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Peach Leaves, NIST SRM 2711 Montana Soil, and NIST SRM 1633b Coal Fly Ash were co-analysed with the samples, and showed excellent agreement with the NIST certified values. The difference between matrix composition of the materials in this study and that of NIST SRMs does not invalidate the proof of accuracy due to matrix independence of neutron activation analysis.

For graphite and graphene sample decomposition a procedure based on Schöniger oxidation was used.⁸¹ A precisely weighted sample of 5 mg was wrapped in ash-free nitrocellulose paper and burned in a flask (filled with pure oxygen) with Pt sample holder. The burning products were decomposed by prolonged ultrasonication and heating with ICP grade nitric acid. After this procedure the sample solution was diluted with deionized water ($R = 18.2 \text{ M}\Omega$) to obtain a concentration of nitric acid of around 1% and used for analysis. Blank experiments were performed with ash-free cellulose paper in order to subtract the amount of impurities introduced by sample preparation. The calibration of spectrometer was performed with certified ICP-OES elements standards in 2% HNO_3 and 2% HNO_3 -2% HCl matrixes; Y was used as an internal standard.

Voltammetry experiments were carried out on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). Electrochemical experiments were carried out in a 5 mL electrochemical cell at room temperature with a three-electrode configuration (Ag/AgCl as the reference, Pt as the auxiliary). Linear sweep voltammetry experiments were conducted at a scan rate of 100 mV s^{-1} with 10 mM air-saturated KOH as the analyte. Cyclic voltammetry experiments were conducted at a scan rate of 100 mV s^{-1} with 10

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mM cumene hydroperoxide or 5 mM hydrazine as the molecular probes in a supporting electrolyte of 50 mM phosphate buffer solution (pH 7.4). All CV data shown are first scans of the experiment, unless otherwise stated. All electrochemical potentials in this paper are stated versus the Ag/AgCl reference electrode (plastic tube, silver wire in 3.0 M KCl). GC electrode surfaces were renewed before each measurement or modification by polishing for 2 min on a polishing pad with alumina slurry, and then washed with deionized water of resistivity not less than 18.2 M Ω cm (Milli-Q, Millipore).

Suspensions of graphene materials and metal oxide nanoparticles were prepared with a concentration of 1 mg mL⁻¹ in DMF with 30 min sonication. Modification of GC electrode surfaces with these materials was performed by depositing a 1 μ L aliquot of the suspension onto the electrode, after which the solvent was evaporated under a sun lamp for 20 min. The suspensions were sonicated for an additional 1 min before each deposition to ensure homogeneity.

Current-voltage (I/V) measurements were carried out by first depositing 1 μ L of the material suspension (1.0 mg mL⁻¹ in ethanol) onto interdigitated gold electrodes (Au-IDE) with a gap of 10 μ m. The solvent was then evaporated off under a sun lamp for 20 min to leave a randomly deposited film on the interdigitated area. I-V curve data were obtained using linear sweep voltammetry (scan rate 20 mV s⁻¹).

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CHAPTER 6

ELECTROCHEMICAL STUDIES ON CHEMICAL VAPOUR DEPOSITION GRAPHENE

- 6.1 Effect of transfer procedures on the electrochemical properties of CVD graphene
- 6.2 Materials and methods
- 6.3 References

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The results and findings in this chapter were published in the following manuscripts:

6.1 Wong, C. H. A.; Pumera, M. Electrochemical delamination and chemical etching of chemical vapor deposition graphene: Contrasting properties. *J. Phys. Chem. C* **2016**, *120*, 4682–4690.

*Chapter 6 – Electrochemical studies on chemical vapour deposition graphene***Background**

Among the many paths towards the synthesis of graphene materials, bulk production is achieved primarily through top-down methods, starting with readily available graphitic precursors such as graphite or CNTs. The relative ease to scale up production to industrial levels has resulted in a general preference for top-down graphene synthesis methods for electrochemical applications, at least during most of the first decade of intensive research in the graphene field.¹ We have similarly explored top-down methods in the previous Chapters. On the other side of the same coin, bottom-up approaches attempt to produce graphene from small, carbon-containing molecules. A highly promising bottom-up method is chemical vapour deposition (CVD), in which carbon sources are decomposed over a metal catalyst foil, followed by the growth of graphene via the diffusion of elemental carbon either out of the metal catalyst or along its surface, depending on the metal used.² The number of layers and quality of graphene formed can be tuned by adjusting parameters, such as the type of metal catalyst, pressure, size of hydrocarbon molecules in the feedstock, and temperature.³⁻⁵

Recent advancements in CVD techniques for the growth of graphene have enabled access to large-area and high-quality graphene film for various applications. The key step in determining the quality of the final graphene films is the transfer process to desired substrates, with the goal of minimizing the amount of structural and chemical modification to the film. Multiple methods exist for this transfer process, with each method differing in the extent to which the graphene film is altered. These alterations in structure and composition are invariably propagated into the electrochemical properties of the resultant graphene films. In this Chapter, we seek to understand how different

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transfer techniques impact the properties of CVD graphene films, in order to recommend the most suitable contemporary procedure for electrochemical applications.

6.1 – EFFECT OF TRANSFER PROCEDURES ON THE ELECTROCHEMICAL PROPERTIES OF CVD GRAPHENE

Introduction

The unique physical, mechanical, chemical, and electrical properties of graphene have led to massive amounts of research poured into exploiting the two-dimensional material in various applications.⁶⁻⁸ Examples of these applications include energy generation and storage, electronics, inhibitive coatings, nanocomposites, and electrochemical sensing.⁹⁻¹⁵ The most promising method to date for the fabrication of large-area, single- or few-layer graphene sheets for electrical and electronic applications is chemical vapour deposition (CVD) on metal foils, with recent advances in the technique allowing the scalable production of high-quality graphene sheets at industrial levels.¹⁶⁻²⁰ However, CVD-grown graphene sheets subsequently need to undergo a transfer process from the metal catalyst foil onto desired substrates for application, and this transfer inevitably causes chemical and mechanical damage to the graphene film.^{21, 22} As such, the transfer process can be regarded as the critical step in enabling the application of CVD graphene, leading to the devotion of much current research towards the improvement of this process.²³ Contemporary transfer methods typically involve the initial spin-coating of a polymer support onto the graphene film, followed by the removal of the metal substrate via chemical etching (using reagents such as iron-based salts, acids, or ammonium persulfate); however, contamination of the graphene film with metallic impurities can occur due to an incomplete etch, as well as from the etching solution itself.²⁴ These metallic impurities were shown to exert considerable influence on the electrochemical properties of the graphene films produced. Transition metal

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impurities have also been theoretically predicted to significantly alter the electronic, magnetic, and optical properties of graphene films that these impurities are embedded in, which can be detrimental to the performance of electronic devices.²⁵⁻²⁷ Examples of alternative methods to alleviate or circumvent this contamination include the use of thermal release tape in roll-to-roll or hot press processes, electrostatic discharge, and electrochemical delamination.^{22, 28, 29}

The first demonstrated form of electrochemical delamination harnessed the reduction of water to produce hydrogen bubbles at the graphene/Cu interface, which results in the separation of the graphene layer from the copper foil substrate, leaving the polymer/graphene film floating on the surface of the electrolyte.³⁰ Advantages of using bubbling delamination include extremely fast delamination as well as the recyclable use of the metal catalyst. The vigorous bubbling observed during electrochemical bubbling delamination can, unfortunately, cause mechanical damage to the graphene film, resulting in the degradation of its conductivity.³¹ This concern led to the development of other electrochemical delamination methods utilizing potentials below the threshold of hydrogen production, thus avoiding the formation of hydrogen bubbles.³² In these procedures, the formation of a thin metal oxide layer and its subsequent removal by reduction, coupled with gentle mechanical forces induced by a gradual immersion technique, serve as the driving force behind delamination.³³ Another form of electrochemical delamination involves the application of highly positive potentials (as opposed to negative potentials used in bubbling delamination), creating oxidizing conditions that lead to the dissolution of the metal foil.³⁴ However, this obviously leads to the inevitable destruction of the metal catalyst, besides the possibility of oxidative damage to the graphene film.

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The performance of CVD graphene films fabricated using different growth conditions varies greatly, due to differences in their grain size, number of layers, and coverage.³⁵ It has been demonstrated that performing the same transfer technique on different sources of CVD graphene can cause considerably different levels of metallic contamination.³⁶ Variations in the initial quality of CVD graphene films are compounded further by the plethora of transfer methods available that further damage and/or modify the graphene layers, culminating in graphene films with significantly different electrical and electronic properties. Furthermore, there is scant data available in current literature regarding the electrochemical properties of CVD graphene films, which is important when considering these films as electrode materials for electrochemical sensing applications. Herein, we used several contemporary transfer procedures to obtain four different multilayer graphene films and characterized the differences in their morphologies, defects, and chemical compositions. The effect of these differences on the electrochemical performance of the graphene films was then investigated in detail by studying their responses towards several electrochemical probes. We show that different electrochemical delamination and chemical etching procedures can ultimately result in graphene films with significantly different voltammetric profiles, in part due to parasitic electrocatalytic effects brought about by residual metal-based contamination, thus impacting the types of electrosensing applications that the films are suitable for.

*Chapter 6 – Electrochemical studies on chemical vapour deposition graphene***Results and Discussion**

For the application of graphene as electrode materials, multilayer graphene is often preferable to monolayer graphene due to overall conductivity improving with an increasing number of graphene layers.^{28, 37, 38} We investigate in the following section the influence of electrochemical delamination and chemical etching methods on the properties of graphene. Multilayer graphene grown via CVD on nickel foils (G/Ni) were chosen for analysis in this study. Several delamination and etching methods were then carried out on G/Ni to obtain graphene films for subsequent characterization (see Figure 1 for scheme). The first method chosen was electrochemical bubbling delamination, in which hydrogen bubbles evolving at the Ni surface as a result of the reduction of water provide the force to delaminate the graphene film.³⁰ In our setup we used an alkaline electrolyte (1.0 M NaOH) to avoid partial etching of the Ni foil.³⁹ Due to the possibility that such hydrogen bubbles may induce macroscopic tearing of the graphene film, bubble-free electrochemical delamination conditions were also studied. In this method, initial oxidation of the metal surface at the G/Ni interface, followed by its subsequent removal via reduction, provides the driving force for delamination.^{32, 33} This was achieved by holding the cathodic G/Ni film at a less negative potential than the bubbling method, thus precluding the macroscopic formation of bubbles. For chemical etching methods, we performed traditional etching using FeCl_3 to dissolve the metal foil, as well as etching with an acidic solution of HCl with added H_2O_2 .⁴⁰ The latter method ensures that additional metallic contaminants are not introduced as part of the etching procedure. Poly(methyl methacrylate) (PMMA) was first spin-coated onto G/Ni samples and then subjected to electrochemical delamination or chemical etching methods as described above. After washing, the G/PMMA films were immobilized (graphene side

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Figure 1. Scheme showing the general method used to obtain graphene films using different electrochemical delamination and etching techniques.

Figure 2. SEM images of (a) G-EC/B, (b) G-EC/BF, (c) G-FeCl₃, and (d) G-HCl/H₂O₂ films at 1000 x magnification. Scale bars represent 10 μm in all images.

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up) and dried on glass cover slips without the removal of PMMA and analysed directly. This “reverse transfer” route allowed access to the graphene film side that was exposed to the various treatment conditions, as well as circumventing any possible contamination or structural damage that may occur during subsequent post-treatment using standard graphene film transfer methods.⁴¹ Graphene films obtained using electrochemical bubbling delamination, bubble-free delamination, FeCl_3 etching and $\text{HCl}/\text{H}_2\text{O}_2$ etching were designated as G-EC/B, G-EC/BF, G- FeCl_3 , and G- $\text{HCl}/\text{H}_2\text{O}_2$, respectively. It should be noted that the transfer size of these electrochemical delamination and chemical etching techniques is in principle fully scalable, limited only by the mechanical strength of the polymer film in supporting its own weight during handling. It has been shown that using a rolling-coater instead of a spin-coater as well as reinforcing the PMMA layer with an additional polymer substrate can allow the successful transfer of 14-inch graphene films using chemical etching, while stacks obtained using hot lamination rolling have been demonstrated to be suitable for electrochemical bubbling delamination.^{42, 43}

To investigate the quality of the prepared graphene materials, scanning electron microscopy (SEM) was first conducted to determine whether the different delamination/etching methods had any visible effect on the graphene film surfaces. SEM images (Figure 2) of the graphene films showed typical multilayer graphene structures, without any obvious structural differences in their morphologies. These observations were supported by Raman spectroscopy, where the graphene samples showed a two-component 2D peak at $\sim 2700\text{ cm}^{-1}$, which is a prominent feature of multilayer graphene samples.⁴⁴ All four films also possessed a strong, sharp G signal centred at 1580 cm^{-1} arising from the vibration of sp^2 sites, as well as a small D peak at $\sim 1365\text{ cm}^{-1}$, which is

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related to defects in the lattice and edge sites. The amount of disorder in graphene materials can be inferred from the relative amplitudes of the D and G peaks, and we obtained D/G ratios of 0.043, 0.038, 0.048, and 0.052 for G-EC/B, G-EC/BF, G-FeCl₃, and G-HCl/H₂O₂, respectively. Based on the integrated intensities of the D and G signals, average crystallite sizes (L_a) of the graphene films were calculated to be 230 nm for G-EC/B, 303 nm for G-EC/BF, and 195 nm for both G-FeCl₃ and G-HCl/H₂O₂. These results cursorily suggest that electrochemical delamination methods create fewer defects in the graphene film than chemical etching methods, possibly due to the difference in the amounts of time that the films were exposed to the various treatment conditions. For instance, bubbling and bubble-free electrochemical delamination could be completed within 1 min and 30 min, respectively, while etching in FeCl₃ and HCl required up to 12 h and 2 h, respectively. Even though G-HCl/H₂O₂ was etched for a far shorter duration than G-FeCl₃, it had a slightly higher D/G ratio, likely because the HCl/H₂O₂ etching solution is more aggressive than FeCl₃. Furthermore, the innate formation of oxygen bubbles arising from the decomposition of hydrogen peroxide could lead to mechanical damage of the graphene film, causing an increase in the number of defects. To further examine the effects of the different treatment procedures, X-ray photoelectron spectroscopy (XPS) was employed to glean information on the surface chemical composition of the graphene films. Analysis of the XPS wide spectra (Figure 4a) revealed the presence of oxygen as the only non-carbon element present on the graphene film surfaces, with G-EC/BF and G-EC/B possessing the highest atomic C/O ratios of 29.7 (3.3 at.% O) and 19.0 (5.0 at.% O), showing that electrochemical delamination methods resulted in negligible oxidation of the graphene surface. The amount of oxygen in G-FeCl₃ and G-HCl/H₂O₂ were noticeably higher, with C/O ratios of 10.4 (8.8 at.% O) and 7.6 (11.6 at.% O),

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respectively. This trend was the same as that observed for density of defects, indicating that the defects introduced by the various delamination and etching procedures are primarily oxidative in nature.

The electrochemical properties of the graphene films were then studied using cyclic voltammetry in the presence of various analytes. The $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox couple has been extensively studied, and has been shown to be sensitive to the surface sites of the electrode, owing to its electron transfer occurring through an inner-sphere mechanism.⁴⁵ In particular, edge-sites have been demonstrated to be responsible for fast electron transfer, while the presence of oxygenated species has the opposite effect due to electrostatic repulsion with negatively charged ferro/ferricyanide complexes.^{46, 47} Cyclic voltammograms at the four different graphene films were recorded in the presence of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and are shown in Figure 5a. The response at a glassy carbon (GC) electrode modified with graphite was also included for comparison. Using the peak-to-peak separations (ΔE_p) of the redox signals as an indicator of the rate of heterogeneous electron transfer (HET), it can be seen that G-EC/B had the smallest ΔE_p of 364 mV, corresponding to an observed HET constant (k_{obs}^0) of $1.19 \times 10^{-4} \text{ cm s}^{-1}$, while the ΔE_p of G-EC/BF was slightly larger at 391 mV ($k_{obs}^0 = 8.23 \times 10^{-5} \text{ cm s}^{-1}$). For the chemically etched graphene films (which possessed noticeably higher oxygen contents than the electrochemically delaminated films), ΔE_p values were 439 mV ($k_{obs}^0 = 4.29 \times 10^{-5} \text{ cm s}^{-1}$) and 753 mV ($k_{obs}^0 = 6.04 \times 10^{-7} \text{ cm s}^{-1}$) for G-FeCl₃ and G-HCl/H₂O₂, respectively. Comparing these results with that obtained for the graphite-modified GC electrode ($\Delta E_p = 429 \text{ mV}$; $k_{obs}^0 = 4.91 \times 10^{-5} \text{ cm s}^{-1}$), only the electrochemically delaminated films G-EC/B and G-EC/BF gave better electrochemical performance, while the response at G-

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Figure 3. Raman spectra of graphene films, normalized to the G-band intensity.

Figure 4. XPS wide spectra of graphene films, normalized to the C 1s peak intensity.

FeCl₃ was similar to that of the graphite-modified electrode. Evidently, the significantly higher oxygen content in G-HCl/H₂O₂ was detrimental towards its observed HET rate; indeed, a general trend of smaller k_{obs}^0 with increasing oxygen content was observed for the graphene film electrodes with the exception of G-EC/B, which had a larger k_{obs}^0 than G-EC/BF despite the latter containing the least amount of oxygen (3.3 at.% vs 5.0 at.%). However, noting that G-EC/B had more defects (and by extension, more edge-sites) than

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G-EC/BF, it is plausible that the contribution towards faster electron transfer arising from edge-sites plays a more significant role than a decrease in performance caused by electrostatic repulsion, at low levels of oxygenated species present. This may also imply that for the application of multilayer graphene as electroensing materials, using electrochemical bubbling delamination is advantageous over bubble-free delamination as the former method is much faster, while the slightly higher amount of defects induced in the graphene film is conveniently beneficial towards electron transfer rates.

Although the defects induced by bubbling delamination were beneficial in the case of multilayer graphene films, we caution that this may not hold true for monolayer graphene films typically grown on copper foils. Preliminary experiments showed that the electrochemical performance of a monolayer graphene film obtained by bubbling delamination was significantly worse than a film obtained by FeCl_3 etching (Figure 6). This is due to mechanical damage causing a certain amount of discontinuity in the monolayer graphene film; indeed, the formation of pores on the graphene film due to trapped hydrogen bubbles from bubbling delamination at the graphene/Cu interface has been demonstrated to have a drastic effect on the final graphene film's sheet resistance.⁴⁸ Multilayer graphene films are more unlikely to experience the same increases in sheet resistance after bubbling delamination, as the mechanical damage occurs mainly on the surface of the graphene film in contact with the electrolyte. The underlying graphene layers are thus able to maintain overall conductivity of the film since they are relatively undamaged by the delamination procedure. Comparing the electrochemical performance at monolayer and multilayer graphene films in the presence of the ferro/ferricyanide probe, the monolayer films showed peak current

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Figure 5. Electrochemical performance of graphene films and a graphite-modified GC electrode in the presence of ferro/ferricyanide ions. (a) Cyclic voltammograms for 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$. (b) Peak-to-peak separations for graphene films in the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ system.

Figure 6. Cyclic voltammograms recorded at monolayer G-EC/B and monolayer G-FeCl₃ for 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$.

values an order of magnitude lower than the multilayer films, as well as far slower electron transfer kinetics; the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ was not even observed at monolayer G-EC/B. These findings reinforce the fact that multilayer

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graphene films are more suitable than monolayer graphene films as electrode materials for electrosensing applications.

The “whole-film”-type delamination observed in the electrochemical delamination methods, coupled with their non-destructive nature, allows the completion of the procedure to be verified with ease. This is not the case with chemical etching, where conclusion of the etching step can only be assessed visually by the dissolution of the metal foil. Unfortunately, even after the foil has apparently dissolved completely, islands of residual metal from the foil inevitably remain on the graphene surface.^{24, 49, 50} It was recently shown that increasing the etching time from 8 h to 72 h can considerably reduce the amount of residual metal impurities, but this comes at a cost of the graphene layer integrity.³⁶ We examined the effect of etching time on the electrochemical performance of both G-FeCl₃ and G-HCl/H₂O₂ by carrying out prolonged etching; separate samples of G/Ni were etched in FeCl₃ for 24 h and 48 h (in comparison to the original 12 h), as well as in HCl/H₂O₂ for 3 h and 4 h (in comparison to the original 2 h). Subsequent CV experiments in the presence of [Fe(CN)₆]^{4-/3-} showed that increasing the duration of etching had an adverse effect on the electron transfer kinetics at G-FeCl₃ films (Figure 7a); quadrupling the etching time from 12 h to 48 h led to increased ΔE_p from 439 mV to 988 mV, as well as noticeably lowered peak current values. Similar trends were observed for G-HCl/H₂O₂ films (Figure 7b), though the decrease in electrochemical performance in terms of ΔE_p was not as apparent. These results show that increasing the duration of etching with the express intent of removing residual metal impurities is not feasible, as it has the unfortunate side effect of substantially degrading the graphene film’s electrochemical performance.

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Figure 7. Electrochemical performance of chemically etched graphene films after prolonged etching, recorded in the presence of 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$. (a) Cyclic voltammograms recorded at graphene films etched in FeCl_3 for 12 h, 24 h, and 48 h. (b) Cyclic voltammograms recorded at graphene films etched in $\text{HCl}/\text{H}_2\text{O}_2$ for 2 h, 3 h, and 4 h.

Additionally, chemical wet etching in iron-based etchants such as FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ has been demonstrated to introduce Fe impurities into the graphene film, which dramatically influences the material's electrochemical response towards various analytes.^{24, 36} In particular, the electro-reduction of peroxides is known to be catalysed by the presence of Fe-based impurities.⁵¹⁻⁵⁴ The electrochemical responses of the graphene films towards cumene hydroperoxide (CHP) was further investigated using cyclic voltammetry and compared against the signal observed at a Fe_3O_4 -modified GC electrode, which showed a prominent reduction peak at approximately -0.50 V vs. Ag/AgCl (Figure 8). The reduction of CHP did not occur on G-EC/B and G-EC/BF films in the scanned potential window; this was unsurprising as their delamination procedures did not involve the use of any Fe-based reagents. On the other hand, G- FeCl_3 gave a strong, electrocatalytic response at -0.52 V, which is strikingly similar to the value observed for the Fe_3O_4 -modified electrode. It should be noted that the presence of such

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Fe impurities does not necessarily pose a problem in electroanalysis, as they can be exploited for their electrocatalytic properties in the detection of peroxides.⁵⁵ Indeed, the magnitude of the reduction peak current of CHP on G-FeCl₃ was found to be appreciably higher than that of the Fe₃O₄-modified GC electrode. However, we noted that G-HCl/H₂O₂ also showed a reduction signal in the same region, albeit much smaller in amplitude. This result was counter-intuitive since the etchant used for G-HCl/H₂O₂ did not involve Fe-based reagents. Control CV experiments conducted in the absence of CHP revealed that G-HCl/H₂O₂ possessed an inherent reduction peak at -0.55 V; such a feature was not observed in analogous control experiments involving G-FeCl₃ (Figure 9a). This inherent peak was also found to decrease considerably with each successive scan (Figure 9b). Taking into account that G-HCl/H₂O₂ possessed the highest oxygen content among the graphene films, we conclude that the inherent signal arose from the reduction of electro-reducible oxygen species residing on the surface of G-HCl/H₂O₂. The existence of this parasitic peak severely limits the potential window that G-HCl/H₂O₂ can be used for electrochemical detection applications.

Metal-based impurities in carbon nanomaterials have also been reported to be highly active in the electro-oxidation of hydrazine.⁵⁶⁻⁵⁹ As the graphene films used in this study were originally grown on Ni foil, it is possible that contamination of the graphene film with residual Ni could occur.²⁴ We recorded the electrochemical responses of the graphene films in the presence of hydrazine, with a NiO-modified GC electrode serving as the representation of the Ni-based electrocatalytic response (Figure 10). The NiO-modified electrode exhibited three oxidation signals at +0.47 V, +0.97 V, and +1.33 V (vs. Ag/AgCl); control experiments showed that the first two oxidation peaks can be

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Figure 8. Cyclic voltammograms recorded at graphene films and a Fe_3O_4 -modified GC electrode, in the presence of 10 mM CHP.

Figure 9. (a) Cyclic voltammograms recorded at G- FeCl_3 and G-HCl/ H_2O_2 films, in the presence of 10 mM CHP (solid lines) and in blank buffer solution (dotted lines). (b) Three successive scans of G-HCl/ H_2O_2 in blank buffer solution.

attributed to the oxidation of hydrazine, while the final, most positive signal was found to be inherent to the NiO-modified electrode itself (Figure 11a). For the electrochemically delaminated graphene films, a large oxidation signal commencing at +0.20 V and peaking at approximately +1.30 V was observed for both G-EC/B and G-EC/BF, and was verified to correspond to the oxidation of hydrazine (Figure 11b). In add-

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Figure 10. Cyclic voltammograms recorded at graphene films and a NiO-modified GC electrode, in the presence of 5 mM hydrazine. Inset shows a zoomed-in portion of the CV recorded at G-HCl/H₂O₂.

ition to this primary oxidation signal, a small oxidation wave was noticed at +0.40 V, with current amplitudes roughly 1–1.5% of the main oxidation peak intensity. This smaller signal is likely due to the oxidation of hydrazine at residual Ni-based impurities, implying that electrochemical delamination does not lead to a completely clean detachment of graphene from the metal catalyst foil.³⁶ No significant differences between G-EC/B and G-EC/BF films could be observed in their responses towards hydrazine. For G-FeCl₃, the oxidation of hydrazine did not manifest as a discernible peak over the potential range scanned, but instead as a wave commencing at the same region as previously recorded for G-EC/B and G-EC/BF. The implications of this observation are twofold: firstly, etching in FeCl₃ for the studied duration (12 h) is sufficient to remove Ni-based impurities from the surface of graphene to an extent where they are rendered electrochemically benign. Secondly, the electron transfer kinetics at G-FeCl₃ is slower than those at the electrochemically delaminated graphene films. A similar oxidation

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wave was seen in the voltammogram of G-HCl/H₂O₂, except for the appearance of a secondary signal occurring at +1.05 V (Figure 10, inset), which is in the same region as the second oxidation peak originally seen at the NiO-modified electrode. This led us to believe that the signal at +1.05 V was also caused by Ni-based impurities. To test this hypothesis, we carried out a separate etch of PMMA/G/Ni in HCl/H₂O₂ with a reduced duration of etching (1 h compared to the original 2 h) to obtain an incompletely etched sample with more residual Ni, denoted as G-HCl/H₂O₂-Ni. Repeating the hydrazine experiments with G-HCl/H₂O₂-Ni, we found a marked increase in the oxidation signal current at +1.05 V, which now formed a distinctly visible peak (Figure 11c). Intriguingly, this was accompanied by the appearance of the first oxidation peak at +0.47 V as well, further supporting that residual Ni-based impurities similar to NiO were responsible for the oxidation of hydrazine at these two potentials. While extending the duration of etching in HCl/H₂O₂ can conceivably reduce the amount of Ni-based impurities, prolonged exposure to the etchant is, as we previously determined, detrimental to the electrochemical performance of the graphene film.

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Figure 11. (a) Cyclic voltammograms recorded at a NiO-modified GC electrode, in the presence of 5 mM hydrazine (solid line) and in blank buffer solution (dotted line). CV of bare GC in blank buffer is included for comparison. (b) Cyclic voltammograms recorded at G-EC/B and G-EC/BF, in the presence of 5 mM hydrazine (solid lines) and in blank buffer solution (dotted lines). Inset shows a zoomed-in portion of the CVs recorded at G-EC/B and G-EC/BF, in both the presence and absence of hydrazine. (c) Cyclic voltammograms recorded at G-HCl/H₂O₂ in the presence of 5 mM hydrazine (solid line) and in blank buffer solution (dotted line). CV of G-HCl/H₂O₂-Ni and NiO-modified GC electrode in the presence of hydrazine are included for comparison.

Conclusion

To conclude, we have prepared multilayer graphene films using two electrochemical delamination techniques along with two chemical etching techniques, and compared their properties in terms of morphology, structural integrity, and elemental purity. While there were no visually significant differences in their morphologies, graphene films obtained via electrochemical delamination were found to possess less defects as well as lower oxygen contents than those obtained via chemical etching. We examined the effect of these differences on their electrochemical properties by studying their responses towards several analytes. It was found that the graphene films had heterogeneous electron transfer rates faster than or similar to a graphite-modified glassy carbon electrode, with the exception of G-HCl/H₂O₂. The faster electron transfer observed at G-EC/B compared to G-EC/BF was postulated to be defect related, while the poor performance of G-HCl/H₂O₂ was likely due to its noticeably higher oxygen content. Prolonged exposure of graphene films to chemical etchants was found to be highly detrimental towards their electrochemical performance. The influence of residual metal impurities was also studied, revealing that electrochemically delaminated graphene films showed almost no parasitic electrocatalytic effects arising from either Fe or Ni impurities, while G-FeCl₃ displayed electrocatalytic behaviour towards the reduction of cumene hydroperoxide due to Fe contamination. Inherent electro-reducible oxygen species residing on the surface of G-HCl/H₂O₂ limits its potential window when used for electrosensing applications, while its observed electrocatalytic activity in the oxidation of hydrazine was attributed to residual Ni impurities. Unless the inclusion of metallic impurities is expressly desired for the electrocatalytic detection of specific compounds, we suggest that multilayer graphene

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films delaminated using electrochemical bubbling are most suitable as electrode materials because the procedure can be completed extremely fast, the resulting film has the fastest electron transfer kinetics among the methods studied, and is free from parasitic effects.

Contributions:

C. H. A. Wong and M. Pumera conceptualized the project. C. H. A. Wong conducted the experiments. C. H. A. Wong and M. Pumera wrote the manuscript.

6.2 – MATERIALS AND METHODS

Materials

Ni foils (25 μm thickness) with CVD-grown graphene films were purchased from Graphene Laboratories Inc. *N,N*-dimethylformamide, phosphate buffer powder, graphite powder, sodium hydroxide, iron(III) chloride hexahydrate, potassium hexacyanoferrate(III), iron(II,III) oxide nanopowder, and nickel(II) oxide nanopowder were obtained from Sigma-Aldrich, Singapore. Poly(methyl methacrylate) powder, cumene hydroperoxide, and hydrazine dihydrochloride were obtained from Alfa Aesar, Singapore. Chloroform was obtained from Fisher Chemical. Deagglomerated alpha alumina powder (0.05 μm) was purchased from Struers, Singapore. Glassy carbon (GC) working electrodes, Ag/AgCl reference electrode and Pt auxiliary electrode were obtained from CH Instruments, USA.

Apparatus

A JEOL 7600F Field-Emission Scanning Electron Microscope (JEOL) was used to acquire the SEM images at 5.0 kV at a working distance of 4.4 mm. The G/PMMA films were immobilized onto a carbon tape on an aluminum SEM holder for analyses.

Raman spectra were obtained with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific, Japan) using an argon ion laser beam ($\lambda = 514.5 \text{ nm}$) employing backscattering geometry with a CCD detector. *D/G* ratios were averaged over 8 measurements for each material.

X-ray photoelectron spectroscopy (XPS) was performed using a Phoibos 100 spectrometer (SPECS, Germany) with a monochromatic Mg X-ray source. Relative

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sensitivity factors were used for evaluation of C/O ratios from wide spectra XPS measurements. The crystallite size (L_a) of the sp^2 lattice was calculated using the equation:

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

where λ is the wavelength of the laser in nm, and I_G and I_D are the integrated intensities of the Raman G and D bands respectively.⁶⁰

Procedures

Poly(methyl methacrylate) (PMMA, 50 mg mL⁻¹ in chloroform) was spin-coated onto both sides of the graphene/Ni samples (2000 rpm, 90 s). For samples to be etched in FeCl₃ solution, one side of the graphene/Ni samples were carefully polished with fine abrasive paper to expose the Ni foil to the etching solution, before spin-coating PMMA onto the graphene film on the other side. The samples were then cured at 175 °C for 30 min and left to cool to room temperature before being subject to delamination or etching methods as elaborated below.

For “bubbling” delamination, PMMA/G/Ni stacks were immersed in a solution of NaOH (1.0 M) and held at a potential of –3.5 V in a 2-electrode system, with a Pt wire as the counter electrode. “Bubbling” delamination was typically complete within 1 min. For “bubble-free” delamination, PMMA/G/Ni stacks were gradually immersed in NaOH (1.0 M) and held at a potential of –2.5 V; complete delamination usually occurred within 15 min. After delamination, the G/PMMA films were carefully transferred into deionized water for rinsing. This rinsing was repeated seven times to ensure the removal of excess NaOH. After rinsing, the G/PMMA films were placed on clean glass cover slips with the

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graphene film facing up, and then dried at 120 °C for 30 min before use in subsequent experiments.

For etching in FeCl_3 , PMMA/G/Ni stacks were immersed in a solution of FeCl_3 (0.1 g mL^{-1}) until the Ni foil was completely dissolved (typically within 12 h). The resulting G/PMMA films were then transferred into deionized water for rinsing. This rinsing was repeated seven times to ensure the removal of excess FeCl_3 . After rinsing, the G/PMMA films were placed on clean glass cover slips with the graphene film facing up, and then dried at 120 °C for 30 min before use in subsequent experiments.

For etching in $\text{HCl}/\text{H}_2\text{O}_2$, PMMA/G/Ni stacks were immersed in an etching solution comprising HCl and H_2O_2 in water. The final concentrations of HCl and H_2O_2 were 2.0 M and 1.0 M, respectively. The setup was then heated to and maintained at 45 °C until the Ni foil was completely dissolved (typically within 2 h). The resulting G/PMMA films were then transferred into deionized water for rinsing. This rinsing was repeated seven times to ensure the removal of excess etching solution. After rinsing, the G/PMMA films were placed on clean glass cover slips with the graphene film facing up, and then dried at 120 °C for 30 min before use in subsequent experiments.

Cyclic voltammetry experiments were carried out on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). Electrochemical experiments were carried out in a custom made 3 mL electrochemical cell at room temperature with a three-electrode configuration (Ag/AgCl as the reference, Pt as the auxiliary). Cyclic voltammetry experiments were conducted in the presence of 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$, 5 mM hydrazine, or 10 mM cumene hydroperoxide, at a scan rate of 100 mV s^{-1} in a supporting electrolyte of 50 mM

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phosphate buffer solution (pH 7.4). All CV data shown are first scans of the experiment, unless otherwise stated. The supporting electrolyte was purged with nitrogen for 20 min before electrochemical measurements. All electrochemical potentials in this paper are stated versus the Ag/AgCl reference electrode (plastic tube, silver wire in 3.0 M KCl). GC electrode surfaces were renewed before each measurement/modification by polishing for 2 min on a polishing pad with alumina slurry, and then washed with deionized water of resistivity not less than 18.2 MΩ cm (Milli-Q, Millipore). Graphite suspensions were prepared with a concentration of 1 mg mL⁻¹ in dimethylformamide with 30 min sonication. Fe₃O₄ and NiO nanopowder suspensions were prepared with a concentration of 5 mg mL⁻¹ in dimethylformamide with 30 min sonication. Modification of GC electrode surfaces with graphite or metal oxides was performed by depositing a 1 μL aliquot of the suspension onto the electrode, after which the solvent was evaporated under a sun lamp for 20 min. The suspensions were sonicated for an additional 1 min before each deposition to ensure homogeneity.

k_{obs}^0 values were calculated according to the Nicholson method⁶¹ relating ΔE_p values to a dimensionless kinetic parameter ψ , leading to k_{obs}^0 via the equation:

$$k_{obs} = \psi \left[D_O \pi \nu \left(\frac{nF}{RT} \right)^{1/2} \right] \left(\frac{D_R}{D_O} \right)^{\alpha/2}$$

where D_O and D_R are the diffusion coefficients for potassium ferricyanide and potassium ferrocyanide respectively at 298 K,⁶² ν is the scan rate in V s⁻¹, n is the number of electrons transferred, F is the Faraday constant, R is the ideal gas constant, T is the temperature in K and α is the transfer coefficient (0.5).

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CHAPTER 7

CONCLUSION AND EPILOGUE

7.1 Conclusion

7.1.1 Exploring recent and novel graphene synthesis methods

7.1.2 Understanding the effects of current synthesis methods on the properties of chemically modified graphenes

7.2 Epilogue

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7.1 – CONCLUSION

Graphene has taken the world by storm ever since the initial demonstration of its remarkable physical, chemical, electrical, and electronic properties. Outstanding in its own right and yet flexible enough to be modified to overcome its weaknesses, it is no wonder that graphene is a strong candidate to be the next disruptive technology, especially in the electronics industry. The ever-growing catalogue of methods through which graphene materials can be synthesized and modified is a testament to the perceived importance of the graphene's role in the present as well as the future.

Hence, the first research direction in this project focused on investigating new methods for the production of graphene materials. Recent procedures that utilize carbon nanotubes as the precursor were studied to provide fundamental understanding of an alternative reaction product, the material's electrochemical properties, as well as adding our own entry to the synthetic toolbox. At the same time, the use of ubiquitous microwave ovens for the synthesis and modification of graphenes was demonstrated, thus presenting a step forward in making graphene more easily accessible.

While the rapid development of synthesis and modification methods is beneficial because it can hasten the entry of graphene into general consumer applications, there are nuances that cannot be overlooked, inevitably present in graphene materials produced by different methods. Subtle changes in properties can have significant impacts on the electrochemical and electronic applications of graphene, making it important to have in-depth comparisons of commonly utilized procedures today. This formed the basis of the second research direction.

7.1.1 Exploring recent and novel graphene synthesis methods

Conceptually equivalent in structure to rolled-up sheets of graphene, carbon nanotubes have recently been employed in the production of graphene nanoribbons. The oxidative opening of multi-walled carbon nanotubes was studied as a key synthetic method toward the fabrication of graphene nanoribbons in Chapter 3. Permanganate oxidation of MWCNTs was found to produce oxidized nanoribbons only when *Russian Doll* nanotubes were used; in the case where *Scroll* nanotubes were oxidatively opened, large sheets were generated instead, providing an alternative synthetic pathway towards graphene oxide sheets. The mechanism was proposed to involve an initial oxidation of the final edge of the nanotube, followed by turn-by-turn unscrolling due to oxidation of the walls, which increases interlayer distance and weakens van der Waals forces between adjacent walls. When harsh oxidative unzipping is carried out on *Russian Doll* nanotubes, residual metallic impurities were demonstrated to remain embedded in the GONRs. These electrochemically active impurities heavily influenced the electrochemical behaviours of the materials despite the low amounts (ppm level) detected. As such metallic impurities are known to have an impact on more than just electrochemical properties, proper characterization of the amounts of existing impurities should be carried out on graphene materials before considering their applications. The reduction of GONRs to GNRs using lithium aluminium hydride was then shown to be on par to the analogous popular reduction with hydrazine, in terms of extent of reduction and types/amounts of residual oxygen species. However, LAH-GNRs proved to possess superior properties to N_2H_4 -GNRs, exhibiting better conductivity, electrochemical performance, and long-term dispersibility in DMF. LAH-GNRs were also free from N-doping and its associated complications.

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The use of microwave irradiation as a rapid tool for synthesizing as well as modifying graphene materials was the focus of Chapter 4, which began by studying the outcome of reducing and exfoliating three different types of GO in a dry microwave procedure, within a sealed and evacuated environment. Outgassing products from thermal decomposition of oxidized species on GO then created gaseous atmospheres within the sealed vessels. These atmospheres were unique to the type of GO, leading to exfoliated graphenes with different amounts of defects, elemental compositions, and resistivities. Incidental hydrogenation was also observed. The resulting microwave-exfoliated graphenes displayed equal to or better electrochemical performance than thermally reduced graphene oxide, and can be obtained in a fraction of the duration and cost. The microwave procedure was then modified to accommodate a flow of hydrogen sulfide gas, which formed H_2S plasma upon microwave irradiation and permitted the incorporation of sulfur into the materials. S-doped graphenes thus obtained showed varying elemental compositions, conductivities, as well as amount of defects, leading to differences in their electrochemical performances. The samples were then shown to be catalytic towards the reduction of oxygen in alkaline media, with higher amounts of S-doping corresponding to increased catalytic activity.

7.1.2 Understanding the effects of current synthesis methods on the properties of chemically modified graphenes

Rather than further expanding the list of novel methods of graphene production, this research direction sought to bring new insight and understanding within the boundaries of synthetic methods currently available through systematic comparison of contemporary procedures as well as fundamental studies on the resulting graphene materials. In Chapter 5, the evolution of metallic impurity contents was tracked primarily using the extremely accurate and robust method of neutron activation analysis. Starting with ultrapure graphite to exclude contribution from inherent impurities, three different oxidation methods were used to obtain graphite oxides, which were subsequently reduced with three different reduction methods. An alarmingly diverse range of metallic impurities were found to be introduced at each stage of graphene material synthesis, and were shown to alter the electrochemical responses of graphene materials toward several analytes. The origins of the metallic impurities were traced back to the reagents used for the oxidation and reduction procedures, showing that various synthetic procedures contaminate graphene materials differently. Separately, the choice of graphite source was shown to impact the extents and types of oxidation after exposure to a standard Hummers method oxidation, despite the resulting graphite oxides possessing similar defect densities. These differences then exerted influence in the electrochemical behaviours of the GOs. Furthermore, when these GOs were reduced using hydrazine, significant disparities in reductive efficiencies were observed, with the RGOs showing highly contrasting conductivities as a consequence.

Graphene grown using chemical vapour deposition requires additional processing to transfer the graphene film onto a suitable substrate. Although not strictly part of the

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graphene synthesis procedure, the transfer process has been acknowledged to be a critical step in governing the properties of the final graphene film. Four such transfer methods, two based on electrochemical delamination and two using wet chemical etching, were investigated for their effects on multilayer graphene films in Chapter 6. Electrochemical delamination methods were generally superior to chemical etching methods, resulting in graphene films that had less defects, lower oxygen contents, better electrochemical performance, as well as much shorter transfer times. EC-delaminated films showed almost no parasitic electrocatalytic effects, while chemically etched films suffered limited potential windows arising from significant metallic contamination and the presence of electro-reducible oxygen species. In particular, EC-delamination under bubbling conditions was suggested to be the most suitable transfer method for multilayer graphene films due to extremely fast delamination, and the resulting film also had the best electrochemical performance.

7.1 – EPILOGUE

More than a decade on, intensive research efforts into graphene have continued to shed light on its excellent properties as well as potential applications. The meteoric rise in the number of publications on graphene reached a peak in 2015 as seen in Figure 1; although there are signs of it slowing down in 2016 (based on incomplete data), the absolute output remains high. For comparison, the number of publications on carbon nanotubes was at an all-time high of ~16 000 in 2015 and ~9000 as of 1 Aug 2016. This is indicative of the graphene field reaching a mature stage, and graphene-based products have already entered the market, first in the form of graphene inks and later in nanocomposites, thermal pastes, and conductive coatings. Graphene “light bulbs” are also slated to be commercially available in the very near future.

Figure 1. Number of yearly publications with “graphene” as the topic in the period of 2000 to 2016 (partial). Source: Web of Science™

It is currently not appropriate to decide whether top-down or bottom-up production methods are “better” as the graphene materials synthesized show different

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properties, which enables graphene materials to be applied to various orthogonal applications. For example, RGO powders can be easily processed into dispersions for spray-coating or pressed into electrode materials, while ultrathin graphene films are applicable in flexible and transparent electronics. New fabrication methods for graphene and their continuous optimization have also contributed to sharp decreases in the price of the material, which is currently the main barrier to entry. Batch production of graphene (both in the form of RGOs as well as continuous graphene films using CVD techniques) in impressive amounts has also been demonstrated successfully, making it just a matter of time before economically feasible production of graphene at industrial scales happens. Until then, research efforts to develop novel graphene synthesis methods as well as fully understand their properties will remain vital, in order to bring graphene one step closer to everyday applications.