Electrochemistry of modified graphene and carbon nanomaterials

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**NANYANG
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**ELECTROCHEMISTRY OF MODIFIED GRAPHENE
AND CARBON NANOMATERIALS**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY

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Electrochemistry of Modified Graphene and Carbon Nanomaterials

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Summary

This thesis investigates the various methods adopted to improve graphene and their influences on the properties of the obtained material. The study is divided into three parts: **a)**

Part 1: Influence of heteroatom functionalization on the properties of graphene, b) Part 2:

Influence of synthesis methods/conditions on the properties of graphene and c) Part 3:

Influence of structural differences on the properties of nanocarbons.

The thesis will begin by introducing graphene, its history and development over the years in **Chapter 1**. Following which, **Chapter 2** will review in depths of recently published impactful literature articles that are related to the three parts. Before proceeding, **Chapter 3** will re-emphasize the readers on the objectives of this thesis with a summarized infographical diagram of each part.

Chapters 4 – 8 will present research results that conceptualize on Part 1: Influence of heteroatom functionalization on the properties of graphene. An array of different heteroatom dopants were investigated with full-scale characterization of the doped materials. **Chapters 9 – 10** will analyze Part 2, i.e. how different synthesis methods and conditions may influence the properties of the final products. **Chapter 11** analyzes Part 3 to evaluate the properties of nanocarbons that are structurally different. Lastly, **Chapter 12** will provide an overview of the chapters and concludes the thesis.

Research articles published during PhD study

Part 1: Influence of Heteroatom Functionalization on the Properties of Graphene

1. Hwee Ling Poh, Petr Šimek, Zdeněk Sofer, Ivo Tomandl, Martin Pumera. **Boron and nitrogen Doping of Graphene via Thermal Exfoliation of Graphite Oxide in a BF₃ or NH₃ Atmosphere: Contrasting Properties.** *J. Mater. Chem. A*, 2013, **1**, 13146.
2. Hwee Ling Poh, Zdeněk Sofer, Michal Nováček, Martin Pumera. **Concurrent Phosphorus Doping and Reduction of Graphene Oxide.** *Chem. Eur. J.*, 2014, **20**, 4284.
3. Hwee Ling Poh, Petr Šimek, Zdeněk Sofer, Martin Pumera. **Sulfur-Doped Graphene via Thermal Exfoliation of Graphite Oxide in H₂S, SO₂, or CS₂ Gas.** *ACS Nano*, 2013, **7**, 5262.
4. Hwee Ling Poh, Petr Šimek, Zdeněk Sofer, Martin Pumera. **Halogenation of Graphene with Chlorine, Bromine, or Iodine by Exfoliation in a Halogen Atmosphere.** *Chem. Eur. J.*, 2013, **19**, 2655.
5. Hwee Ling Poh, Filip Šaněk, Zdeněk Sofer, Martin Pumera. **High-pressure Hydrogenation of Graphene: Towards Graphane.** *Nanoscale*, 2012, **4**, 7006.
6. Hwee Ling Poh, Zdeněk Sofer, Martin Pumera. **Graphane Electrochemistry: Electron Transfer at Hydrogenated Graphenes.** *Electrochem. Commun.*, 2012, **25**, 58.
7. Tzu Hui Seah, Hwee Ling Poh, Chun Kiang Chua, Zdeněk Sofer, Martin Pumera. **Towards Graphane Applications in Security: The Electrochemical Detection of Trinitrotoluene in Seawater on Hydrogenated Graphene.** *Electroanal.*, 2014, **26**, 62.

Part 2: Influence of Synthesis Methods/Conditions on the Properties of Graphene

8. Hwee Ling Poh, Filip Šaněk, Adriano Ambrosi, Guanjia Zhao, Zdeněk Sofer, Martin Pumera.

Graphenes prepared by Staudenmaier, Hofmann and Hummers Methods with Consequent Thermal Exfoliation Exhibit very Different Electrochemical Properties. *Nanoscale*, 2012, **4**, 3515.

9. Beng Khong Ong, Hwee Ling Poh, Chun Kiang Chua, Martin Pumera. **Graphenes Prepared by Hummers, Staudenmaier and Hofmann Methods for Analysis of TNT-Based Nitroaromatic Explosives in Seawater.** *Electroanalysis*, 2012, **24**, 2085.

10. Hwee Ling Poh, Zdeněk Sofer, Jan Luxa, Martin Pumera. **Transition Metal-Depleted Graphenes for Electrochemical Applications via Reduction of CO₂ by Lithium.** *Small*, 2014, **10**, 1529.

Part 3: Influence of Structural Differences on the Properties of Nanocarbons

11. Hwee Ling Poh, Martin Pumera. **Nanoporous Carbon Materials for Electrochemical Sensing.** *Chem. Asian J.*, 2012, **7**, 412.

12. Hwee Ling Poh, Alessandra Bonanni, Martin Pumera. **Nanoporous Carbon as a Sensing Platform for DNA Detection: The use of Impedance Spectroscopy for Hairpin-DNA based Assay.** *RSC Adv.*, 2012, **2**, 1021.

°C	Degree centigrade
wt %	Weight Percentage
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
Au-IDE	Gold Inter-Digitated Electrode
XPS	X-ray Photoelectron Spectroscopy
HR-XPS	High-resolution X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HR-TEM	High-resolution Transmission Electron Microscopy
BET	Brunauer, Emmett and Teller
EDS	Energy-dispersive X-ray spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
EA	Elemental Analysis
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
FT-IR	Fourier Transform Infrared spectroscopy
NMR	Nuclear Magnetic Resonance
PGAA	Prompt Gamma-ray Activation Analysis
EIS	Electrochemical Impedance Spectroscopy
CV	Cyclic Voltammetry
DPV	Differential Pulse Voltammetry
Bare GC	Bare Glassy Carbon
DEP	Disposable Electrical Printed
EPPG	Edge Plane Pyrolytic Graphite Electrode
CMG	Chemically Modified Graphene
CRGO	Chemically Reduced Graphene Oxide
TRGO	Thermally Reduced Graphene Oxide
ERGO	Electrochemically Reduced Graphene Oxide
HOPG	Highly Ordered Pyrolytic Graphite
DNA	Deoxyribonucleic Acid
TNT	2, 4, 6 Trinitrotoluene
CVD	Chemical Vapour Deposition
PBS	Phosphate Buffered Saline
DMF	N,N-Dimethylformamide
THF	Tetrahydrofuran
hr	Hour (time)
Min	Minutes (time)
mM	Millimolar
nm	Nanometer

Chapter 1

Introducing Graphene and its History

1.1 Introducing graphene and its history

Discoveries on graphene and graphene related materials have first begun more than 100 years ago by Prof. L. Staudenmaier. He demonstrated a solution-based preparation method to successfully obtain graphite oxides.¹ This method continues to be widely and popularly used as it produces scalable amounts of graphite oxide which was then utilized in further reactions and applications. Subsequently, only occasional scientific reports on graphene related materials surfaced.^{2,3} It is a sheet of carbon atoms bound together with double electron bonds (called a sp^2 bond) in a thin film only one atom thick as shown in fig. 1.1.

Fig. 1.1 Graphene: one-atom thick hexagonal carbon lattice network according to IUPAC definition.

Intensive research on the material soon begins where its properties, alternative synthesis methods and future applications were studied. Kanzow *et al.* derived a simple heat treatment method using thick nickel films and fullerenes to successfully generate hollow, elongated graphitic nanostructures.⁴ The material obtained possessed an interesting worm-like nanostructure which consists of multi-walled shells with an exterior diameter of ca. 300 nm.⁴ Besides characterization studies, attempts were also made to incorporate graphitic materials in various applications. An example is lithium ion batteries where Wu *et al.* reported a greener anode preparation method using graphite to replace the traditional metal catalyst such as platinum (Pt), cadmium (Cd) and nickel (Ni).⁵ Surprisingly, the synthesized graphitic anode displayed enhanced reversible lithium capacity proving graphene's potential in applications.

Eventually, a major breakthrough in the graphene research was made. Professor Andre Geim and Professor Konstantin Novoselov from the University of Manchester demonstrated the possibility of graphene as a free-standing material with several important properties (Fig. 1.2).^{6-8,9} Their ground breaking findings with regards to two dimensional graphene eventually led them to win the Nobel Prize for Physics in 2010.

Fig. 1.2 Graphene films. (A) Photograph (in normal white light) of a relatively large multilayer graphene flake on top of an oxidized Si wafer. (B) AFM image of 2 μm by 2 μm area of this flake near its edge. (C) AFM image of single-layer graphene. (D) SEM image of experimental devices prepared from FLG. (E) Schematic view of the device in (D). Reproduced with permission from ref. 6.

This immediately led to a huge explosion of research interest on this material. Numerous articles reporting on the various findings of graphene began pouring in, instantly turning graphene into the hottest research topic. Among these scientific reports, in-depth characterization studies uncovered extraordinary electronic, thermal, optical and mechanical properties that graphene possessed.⁹⁻¹² These superior characteristics soon led to graphene being integrated in a wide range of applications such as DNA biosensors,¹³ capacitors,¹⁴⁻¹⁶ gas sensors,^{17,18} nanoelectric biosensors,¹⁹ biocompatible scaffold coating for human mesenchymal stem cells (hMSCs)²⁰ and even as a conjugate with heparin for biomedical applications.²¹ With more potential applications being explored, several disadvantages soon limiting the possible usage of graphene soon became evident.

Graphene was found to possess a zero band gap energy^{22,23} which limits its ability to switch on and off as normally required in logic circuits. Hence, an urgent need to alter the

structural and chemical properties from its pristine form was required. High yield synthesis methods producing high quality graphene were also some of the limitations of graphene. This was especially true in applications requiring a large quantity and high quality graphene such as batteries and capacitors.²⁴ Other issues encountered with graphene related materials include incompatibility with biomolecules, instability in certain mediums etc.

In solution to these challenges, several approaches to modify graphene were proposed which included heteroatom functionalization of graphene,^{25,26} modifying synthesis procedures,²⁷⁻²⁹ synthesizing graphene into a structurally different form³⁰⁻³² etc. These approaches aim to alter the properties and thereby improve graphene. Hence, a full-scale characterization of the materials obtained from each approach is required to understand the influence of these approaches on the resultant properties before further implementation in future applications can be carried out.

In this thesis, the approaches to be investigated were divided into three main parts: 1) Influence of heteroatom functionalization, 2) Influence of synthesis methods/conditions and 3) Influence of structural differences. In-depth characterization studies were performed to investigate the influence of each type of modification on the properties of graphene.

In Part 1, the study focuses on the functionalization of graphene with heteroatoms, a widely practiced method to modifying graphene. In fact, several elements have been experimented as dopants and proving great success in enhancing or improving graphene's properties.³³⁻³⁵ Herein several heteroatoms were studied to gain insights on the influence of heteroatom functionalization on the characteristics of the doped graphene. The investigation involves an extensive characterization study using techniques such as SEM, TEM, XPS, Raman spectroscopy etc. Electrochemical behaviors of these resultant materials were also analyzed for their heterogeneous electron transfer (HET) rates, electrical conductivity and sheet resistivity. Electrochemical properties of these materials have significant influence on the implementation

of these materials in applications such as biosensors, capacitors, batteries and fuel cells. In this thesis, eight different heteroatom dopants were explored: boron, nitrogen, phosphorus, sulfur, chlorine, bromine, iodine and hydrogen. The results obtained revealed some interesting findings such as sulfur doped graphenes possessing electrocatalytic ability towards oxygen reduction reactions (ORRs), an important electrochemical reaction that takes in fuel cells. This implies the possibility of heteroatom doped graphene materials replacing the tradition high-cost Pt catalyst to be a metal-free ORR catalyst. The functionalized graphene was also observed to be resistant to carbon monoxide poisoning, a common problem faced with Pt catalyst. Certain heteroatom dopants were also observed to display p-type or n-type semiconducting properties when doped into graphene. Boron and nitrogen are two such examples where their resultant doped materials exhibited significant differences between their p-type and n-type effects. Experimental results for Part 1 are elaborated in Chapter 4 to Chapters 8.

In Part 2 of this study, the influence of synthesis methods/conditions on the properties of graphene will be investigated. Graphite oxide, a commonly encountered graphene related material can be synthesized from three well-known methods: Staudenmaier,¹ Hummers³⁶ and Hofmann³⁷ methods. It was frequently assumed that all three methods yield graphite oxides of similar quality and properties and hence, many simply cite the use of a single method to produce graphite oxide with no intentions to compare any contrasting properties that may exist. Herein a comparison study between Staudenmaier, Hummers and Hofmann method was performed via characterization of thermally reduced graphene oxide resulted from thermal exfoliation of graphite oxides from each method. This will provide insights on the influence of different synthesis conditions in the three methods on the properties of the resultant materials. Further detailed experimental results and discussions will be elaborated in Chapter 9.

Metal combustion in dry ice with lithium metal replacing the usual magnesium to obtain graphene was also investigated. This study was done to observe the influence of a different

reaction condition (metal for combustion reaction) on the resultant properties of the obtained transition metal-free graphenes. Similarly, full-scale characterization of the yielded materials was performed to investigate the resultant properties. The production of metal-free nanocarbons was highly desired as they were alternatives to traditional metal catalyst which were found to pose several disadvantages. Metal contaminants present in graphene were also known to influence the electrochemical properties of the graphene producing undesirable effects. Full details and discussion on this study can be found in Chapter 10.

Finally in the last part of study, the influence of structural differences on the properties of nanocarbons will be investigated. The results obtained have important implications since the existence of such structurally different nanocarbon materials is extremely common. Examples include nanoporous carbon, nanocones, carbon dots and nanoribbons. Herein investigation of nanoporous carbon properties will reveal such influence as elaborated in Chapter 11.

In the proceeding chapter, a literature review on the various experimental and theoretical studies for the three parts of this thesis will be discussed.

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Chapter 2

Literature Review

2.1	<i>Part 1: Influence of Heteroatom Functionalization on the Properties of Graphene</i>
2.1.1	<i>Group III: Metalloid boron</i>
2.1.2	<i>Group V: Pnictogen nitrogen</i>
2.1.3	<i>Group V: Pnictogen phosphorus</i>
2.1.4	<i>Group VI: Chalcogen sulfur</i>
2.1.5	<i>Group VII: Halogen chlorine</i>
2.1.6	<i>Group VII: Halogen bromine</i>
2.1.7	<i>Group VII: Halogen iodine</i>
2.1.8	<i>Hydrogen: Graphanes or hydrogenated graphenes?</i>
2.2	<i>Part 2: Influence of Synthesis Methods/Conditions on the Properties of Graphene</i>
2.3	<i>Part 3: Influence of Structural Differences on the Properties of Nanocarbons</i>

2.1 Part 1: Influence of heteroatom functionalization on the properties of graphene

The functionalization of graphene via doping with heteroatoms has long been studied as a popular method towards modifying graphene's structure and properties. Therefore, several elements were already studied as dopants such as calcium, hydrogen, boron etc. where the resultant materials were observed to possess interesting properties. In the study of Part 1, heteroatoms dopants from Group III to VII (excluding transition metals), i.e., d-block and p-block elements were investigated. These elements include boron, nitrogen, phosphorus, sulfur, chlorine, bromine, iodine and hydrogen. The unique properties of each element induced interesting characteristics and behaviors in the resultant doped graphene. Consequently, this brings about alterations in graphene's physical and electronic properties; improving the challenges that pristine graphene originally posed. The following literature review for Part 1 will investigate the various heteroatoms dopants attempted and their consequent properties in the resultant doped graphenes. The review will be presented in the sequence of the element's periodic table groupings.

2.1.1 Group III: Metalloid boron

Boron, the only nonmetal in group III is a p-type dopant capable of introducing electronic holes in the graphene structure. This resulted in a change in the carrier density of the material lowering the Fermi level to below the Dirac point and thus, affecting the material's conductivity.^{1,2} Being one electron short of carbon, boron was also observed to share several similarities with carbon.

There are numerous synthesis methods and various boron precursors available for the production of boron doped graphene materials. The more popular methods include thermal annealing of graphite/graphite oxides,³⁻⁶ chemical vapor deposition,^{7,8} and arc discharge. The boron precursors available ranged from boric acid,^{5,7} boranes,^{6,8} boron trifluoride (BF_3),³ and boron trioxide (B_2O_3).⁴ However, some of these precursors are undesirable due to their toxicity and environmentally-unfriendly effects, e.g., diborane (B_2H_6) and boron tribromide (BBR_3). The different synthesis methods were observed to produce final products with varying results and properties. For example, Shen *et al.* used boric acid precursor via thermal annealing treatment methods (Scheme 2.1) to yield boron doped graphene sheets (3.2 at. % B content) with a planar structure and a thickness of ca. 2 nm.⁴

Scheme 2.1 ORRs on boron doped graphenes. Reproduced with permission from ref. 4.

However, Wu *et al.* reported the synthesis of boron doped graphene sheets with a thickness of only ca. 0.9 nm at the edges via CVD method;⁷ further proving the resultant material to be monolayer doped graphenes. This trend of varying properties was also observed for the other properties investigated such as the types of boron-carbon interactions, boron content and defect density. Furthermore, it was observed that the boron precursor can influence the type boron-carbon interactions found in the final doped product. When boric acid was used as the boron precursor, XPS measurements showed the boron atoms existing as BC_4 , BC_3 and BC in the resultant material.⁷ However, B_2O_3 precursor produced other forms of boron-carbon bonds such as B_4C , BC_3 , BC_2O , BCO_2 in the final product.⁴ Boron doped graphenes were also studied for applications such as oxygen reduction reactions (ORRs). Lu *et al.* reported such a study where the electrocatalytic performance of the material was highly influenced by the boron content in the material (Fig. 2.1).³ It was observed that doped materials with low boron levels (23 ppm) displayed better electrocatalytic ability towards ORRs than those with high boron levels (590 ppm). Other applications investigated include capacitors where boron doped graphenes were found to exhibit good rate and stability performance.⁶

Fig. 2.1 Cyclic voltammetric scans for ORRs in air saturated 0.1 M KOH buffer of three types of boron-doped graphenes and bare GC electrode. Conditions: scan rate 100 mV/s. Reproduced with permission from ref. 3.

Theoretical studies on boron doped graphene were also conducted to observe the influence of synthesis reaction mechanism on the type of boron-carbon interactions found in the resultant material. Interesting results based on density functional theory calculations showed that boron doping via different reaction mechanism resulted in different forms of boron being doped into the graphene lattice.⁹ For example, doping via hydroboration reaction (an addition reaction, Fig. 2.2) led to the incorporation of boron as -BH_2 groups being added on top or at the edges (or zig-zag) of graphene. This implies that the density of defects/edges/zig-zag sites will affect the amount of boron doped into graphene when the mechanism is via hydroboration. On the other hand, doping via CVD methods resulted in boron being substituted into graphene as graphitic boron.⁸ Thermodynamic calculations on the reaction pathways of these two mechanisms showed that the substitution method was thermodynamically more favorable as compared to the addition reaction. This was due to the retainment of the desired aromaticity of hexagonal rings after doping and the avoidance of undesirable “deformational energy” when a sp^2 site is converted to sp^3 site after addition reaction.⁹

Fig. 2.2 (A) Hydroboration reaction: addition of a $-\text{BH}_2$ group to the $\text{C}=\text{C}$. (B) Boron substituted doping in GrB and boron addition doping in GrBH₂ and Gr(e)BH₂. Nitrogen substituted doping in GrN and nitrogen addition doping in GrNH₂ and Gr(e)NH₂. Reproduced with permission from ref. 9.

In this thesis, the boron-doped graphene materials studied were produced via thermal exfoliation methods using BF_3 as the precursor in Chapter 4. Extensive characterization based on various techniques such as XPS, SEM and Raman spectroscopy. was performed to gain insights on the material. In order to further understand the p-type doping effects brought about by boron dopants, a comparison study between p-typed (boron) doped graphene and n-type (nitrogen) doped graphene was conducted.

2.1.2 Group V: Pnictogen nitrogen

With a possession of one electron more than carbon, nitrogen is an n-type dopant in graphene. This implies that the introduction of nitrogen atoms to the graphene lattice structure results in extra electron carriers being added into graphene. This influences the electron density of the resultant material, raising the Fermi level above the Dirac point and affecting the doped material's conductivity.

Similar to boron doping, functionalization of graphene with nitrogen can be achieved through numerous different pathways. Chemical vapor deposition,^{10,11} microwave irradiation,¹² nitrogen plasma treatment^{13,14} and nitrogen ion implantation in ultra-high vacuum condition¹⁵ are just some of the methods. Regardless of the synthesis method employed, monolayer and few-layer nitrogen doped graphenes were found to be consistently achievable. Similarly, the properties and behaviors of the resultant doped materials were influenced by their methods of synthesis. The material's thickness, nitrogen content, types of nitrogen chemical states being doped and even morphologies can all be significantly affected. An example to illustrate this point is a comparison between nitrogen doped graphenes obtained via CVD method and microwave irradiation method. Using CVD method, Jin *et al.* successfully obtained large nitrogen doped monolayer graphene sheets of centimeters scale.¹⁰ Their AFM results have also shown that the resultant doped material's thickness was 10 – 12 nm. Their reported result differs significantly from the measured thickness of the nitrogen doped monolayers and few-layers graphene obtained by Lee *et al.* via microwave irradiation pathway (Fig. 2.3). The group reported an AFM measured average thickness of 1 – 3.5 nm where the thinnest spot was found to be only 1.2 nm.¹²

Fig. 2.3 Microwave-assisted graphene exfoliation and doping process from bulk graphite. Reproduced with permission from ref. 12.

The use of different nitrogen and carbon source was also observed to influence the properties of the resultant doped materials such as the type of nitrogen chemical states found in the doped graphene. Examples are two nitrogen doped graphenes obtained via similar chemical deposition methods but different precursors by Jin *et al.* and Qu *et al.* where the two resultant materials were found to possess different nitrogen species. Jin *et al.* utilized pyridine as a carbon and nitrogen source in their CVD synthesis,¹⁰ obtaining pyridinic nitrogen and quaternary nitrogen in their resultant doped material. In contrary, Qu *et al.* obtained pyridine nitrogen and pyrrolic nitrogen with methane as carbon precursor and ammonia gas as nitrogen precursor.¹¹ Nitrogen doped graphenes were often observed to consist of nitrogen existing as pyridinic N, pyrrolic N, quaternary N and nitrile N (Fig 2.4). Pyridinic N and quaternary N have sp^2 configuration¹³ and were mentioned to be responsible for electron donating effects observed in the doped graphene. Pyridinic N and pyrrolic N were also reported to be responsible for the excellent electrocatalytic ability that nitrogen doped graphenes displayed in ORRs applications.¹¹ In application studies, nitrogen doped graphenes were observed to display a reduction current

density three times higher than undoped graphenes during ORRs.¹¹ The material was also observed to be resistant to poisoning and interferences by hydrogen gas, glucose, methanol and carbon monoxide. However, the allocation of nitrogen chemical states responsible for the various properties and effects observed was still highly debatable. Other applications investigated for nitrogen doped graphenes include capacitors,¹² biosensors for glucose and glucose oxidase¹³ and reduction of hydrogen peroxide.¹³

Fig. 2.4 Types of doped nitrogen species doped found in N-doped graphene. Reproduced with permission from ref. 13.

Similar to boron, nitrogen doping can occur via a substitution reaction or an addition reaction (Fig. 2.2).⁹ The substitution reaction takes place with a nitrogen atom replacing a carbon atom in the graphene lattice, retaining the desired aromaticity of the hexagonal carbon rings while avoiding the conversion of sp^2 to defective sp^3 . On the other hand, addition reaction occurs via hydroamination reaction where $-NH_2$ groups are added either on top or at the edges of graphene. This implies that the density of defects, zig-zag sites or edges in the graphene starting material will affect the resultant level of nitrogen doped via hydroamination. To prove the n-type doping effects of nitrogen, Lazar *et al.* investigated the electronic properties of

nitrogen doped graphenes via DFT calculations.⁹ The calculated workfunction (W_f) value of nitrogen doped graphenes were observed to be lower than that of undoped graphenes indicating that a lower amount of energy was required to remove an electron from the doped graphene than from the undoped graphene. This proved that nitrogen dopant is an n-type dopant where the electron carrier concentration in graphene was increased after doping treatments.

In this thesis, a comparison study between n-type (nitrogen) and p-type (boron) doped graphenes was carried out to observe their contrasting properties. Various properties of the two materials were probed via extensive characterization studies on the resultant doped materials. Their electrical conductivities and heterogenous electron transfer rates were also investigated through electrochemical methods (Cyclic voltammetry), a study not often explored in numerous reported characterization works. Further details will be elaborated in Chapter 4.

2.1.3 Group V: Pnictogen phosphorus

Similar to nitrogen, phosphorus is another n-type dopant in group V of the periodic table. With a lower electronegativity than nitrogen and a readily available lone electron pair, phosphorus was expected to display higher electron donating ability and stronger n-type effects. However, it was notable that phosphorus atom have a larger atomic radii than nitrogen which may induce different resultant properties from those of nitrogen doped graphenes. Thus, characterization studies on phosphorus doped graphenes will prove to provide interesting results as shown in the review of the following articles.

Phosphorus doped graphenes can be synthesized through various different pathways with thermal annealing treatment method being the most common pathway undertaken. Thermal annealing treatment involves the use of a carbon source (CVD graphene, graphene oxide and graphite oxide) and a phosphorus source (usually triphenylphosphine).¹⁶⁻¹⁸ A particularly interesting synthesis method reported was a pyrolysis reaction by Latorre-Sánchez *et al.* using alginate and dihydrogen phosphate ion (H_2PO_4^-) as the carbon and phosphorus source respectively (Fig. 2.5).¹⁹ The team reported a high yield of 62 % where monolayers of phosphorus doped graphene was obtained.

Fig. 2.5 Preparation of phosphorus doped graphene. a) Addition of H_2PO_4^- to a colloidal solution of alginate at neutral pH, and recovery of the solid. b) Pyrolysis of phosphate-containing alginate at 900 °C under an Ar atmosphere, and extended sonication. A simplified structure of natural alginate composed of mannuronic (M) and guluronic (G) monosaccharides, was shown. Reproduced with permission from ref. 19.

Through thermal annealing methods, the doped phosphorus level obtained ranged from 1.16 at. %¹⁷ to 4.96 at. %.²⁰ The phosphorus doped graphenes obtained were usually thin crystalline sheets with at least 3 – 4 layers.¹⁷ The best achievement being monolayers of the doped graphene via pyrolysis with alginate as mentioned above. Regardless of the method of synthesis undertaken, doped phosphorus existed as P-C and P-O bonds (Fig. 2.6) in doped graphene. As previously mentioned, phosphorus has a larger atomic radii than nitrogen and carbon. Thus, the incorporation of larger phosphorus in the graphene lattice led to a significant increase in density of defects due to the major distortion and disruption to the perfect lattice network created by phosphorus. This was proven by the high D/G ratios measured by Raman spectroscopy of the resultant doped materials indicating the existence of large amount of defects.^{17,18,20}

Fig. 2.6 High-resolution P 2p XPS spectrum of phosphorus-doped graphene depicting P-O and P-C bonds. Reproduced with permission from ref. 18.

In applications study, phosphorus doped graphenes were found to display excellent performance for NH_3 sensing,¹⁶ as electrocatalysts for ORRs,^{17,18} photocatalysts for H_2 (g) generation from water,¹⁹ and as material in lithium ion batteries¹⁸. This may be attributed to the large amount of defects which acted as electroactive sites for electrochemical reactions to occur. It was also mentioned that the phosphorus atoms may have facilitated the adsorption of dioxygen thus aiding in the improvement of the reaction kinetics of ORRs observed.¹⁷ In the detection of NH_3 molecules, some reports have also further claimed the excellent performance to be attributed to the phosphorus doped sites acting as active sites for NH_3 molecules. Phosphorus has a lower electronegativity value (2.19, Pauling scale) than nitrogen (3.04, Pauling scale) and hence, was expected to have a more readily available lone electron pair for donating. This phenomenon was investigated and proved by Some *et al.* in a comparison study between phosphorus doped graphenes and nitrogen doped graphenes.²⁰ Their group reported back-gated graphene field effect transistor (g-FET) measurements on the two types of doped graphenes where results showed that phosphorus doped graphenes indeed exhibited much stronger n-type effect than nitrogen doped graphenes. This may be due to phosphorus having a higher nucleophilicity than nitrogen. Further investigations also showed that phosphorus was observed to be more air-stable and have much higher electron mobility within the material.

Herein we presented phosphorus doped graphenes synthesized via various methods using different phosphorus precursors. The resultant doped graphenes obtained were fully characterized and compared to contrast the differences in properties resulted from the differences in synthesis methods and precursors. Further details and discussions were elaborated in Chapter 5.

2.1.4 Group VI: Chalcogen sulfur

In group VI, sulfur is a common dopant used for the functionalization of graphene. Being electron richer than carbon, sulfur also provides n-type doping effect in graphene materials. However, it was notable that sulfur has an electronegative value (2.58, Pauling scale) close to that of carbon (2.55, Pauling scale). Hence, it will be interesting to investigate and observe the existence of any contrasting properties between sulfur doped and other n-type doped graphenes.

Similarly, thermal annealing synthesis method was also one of the most popular methods to produce sulfur doped graphenes. The thermal treatment usually takes place at temperatures ranging from 500 °C to 1050 °C in the presence of a carbon and sulfur source (Fig. 2.7).²¹⁻²⁴ The sulfur source can be solids (elemental sulfur powder,²³ benzyl disulfide²¹) or gases such as H₂S.²⁴

Fig. 2.7 Preparation of sulfur-doped graphenes. Reproduced with permission from ref. 21.

Other less commonly known synthesis methods include free radical based coupling reaction (Ullmann reaction) using tetrabromothiophene as the sulfur source.²⁵ The resultant product obtained were two to three layers of doped graphenes sheets²⁵ with some reporting success in achieving a single layer of 1 nm thickness.²⁴ EA measurements revealed that the level of S content in the resultant material was as high as 8.7 wt. % in a recent article by Yun *et al.*²³

Raman spectroscopic results have also shown that the doping process introduced large amount of defects, increasing the I_D/I_G ratio significantly as compared to the undoped graphene.^{22,25}

Fig. 2.8 High-resolution XPS scan of S 2p; inset is the scheme of S atoms incorporated into the graphene lattice. Reproduced with permission from ref. 25.

Interestingly, several articles have reported similar observations of high annealing temperatures inducing a “self-repairing” effect in the doped graphenes where the crystallinity of the sulfur doped graphene was partially restored.^{22,24} This results in a lower I_D/I_G ratio measured by Raman spectroscopy. Doped sulfur atoms were also observed to be homogeneously distributed throughout the entire doped graphene sheet as proven by EDX.^{21,25} The doped sulfur atoms were found to exist as C-S, oxidized sulfur C-SO_x-C, C-S-C and thiophene S where covalent C-S bond was observed to be the majority (Fig. 2.8).^{22,24,25}

In the study for future applications, sulfur doped graphenes were popularly investigated as a potential catalyst material for ORRs. Results showed that the doped material exhibited superior qualities such as high current density, high selectivity, excellent durability and most importantly, exceptionally high tolerance towards methanol and oxygen poisoning.^{21,24,25} It was also mentioned that the excellent performance was attributed to the C-S bonds present in the material which acted as catalytic active sites for the oxygen reduction reaction.^{21,24} The large amount of defects introduced by the dopant atom were also claimed to have contributed to the

kinetics of the reduction process.²⁵ Other applications explored include lithium ion batteries by Yun *et al.*²³ Similarly, the doped materials were also observed to be an exceptional capacitor material with high reversible capacity and kinetically fast Li ion and electron conduction. The team explained this phenomenon with reference to the defect sites present in the doped materials where these defects contributed to the extremely high reversible capacity observed. Recently, 3D graphenes were also studied as a potential material to be doped by sulfur heteroatoms in a novel work by Zhang *et al.* (Fig. 2.9).²⁶ The synthesis method involved the use of a sulfonic acid ion exchange resin which was thermally annealed at 850 °C. The resultant material was few-layers 2D sulfur doped nanographene sheets of 4 nm thickness. The interlayer spacing was measured to be 0.33 nm by high-resolution TEM (HR-TEM). Similarly, the doping procedure have also introduced defects in the structure but with high retainment of the crystallinity of the graphene as shown by the low measured I_D/I_G ratio of ca. 0.5. The S content in the material was measured to be 12.8 wt. % where the doped S atoms existed as –C-S-C, C=S and C-SO_x species with –C-S-C being the majority in the structure.²⁶ It was also observed that few oxygen functionalities were left in the structure after undergoing thermal annealing treatments. The group has also performed BET measurements to reveal the resultant doped 2D graphene possessing a large surface area (2129 m²/g) and pore volume of 1.30 cm³/g. Interestingly, this synthesis procedure was also observed to introduce a high concentration of mesopores into the resultant material where the pore size was measured to have a diameter of 2 – 6 nm. Similarly, these sulfur doped 3D graphenes also displayed excellent potential as catalyst for ORRs.

Fig. 2.9 SEM (a–c) and TEM (d–f) images of 3D sulfur-doped graphene networks. Reproduced with permission from ref. 26.

In this thesis, graphite oxides were thermally annealed at various temperatures in the presence of different sulfur sources to yield sulfur doped graphenes. The results obtained showed that sulfur doping, reduction and exfoliation of the graphite oxides have occurred simultaneously. The resultant sulfur doped reduced graphene oxides possessed few oxygen containing groups and hence, displayed excellent electrochemical properties. In addition, a comparison was made using graphite oxide starting materials synthesized via three different methods, i.e., Staudenmaier, Hofmann and Hummers. This was executed to observe any influences of the starting materials' synthesis methods on the properties of the resultant product, sulfur doped reduced graphene oxides. The comparison study was made in response to the common assumption that only the type of sulfur doping method and the sulfur source may influence the properties of sulfur doped graphenes but not the synthesis method of the carbon precursor. Full details and results can be found in Chapter 6.

2.1.5 Group VII: Halogen chlorine

Highly electronegative dopants, i.e., halogens such as chlorine (Cl), bromine (Br) and iodine (I) were also investigated as potential heteroatoms for the functionalization of graphenes. Being highly electronegative, halogens displayed a strong electron withdrawing effect and hence; p-type effects when incorporated in the graphene lattice structure. This resulted in a change in the structural properties, electrochemical behavior and electronic properties of the resultant doped as observed in the following articles reviewed.

Currently, chlorine functionalization can occur via chlorine plasma treatments,^{27,28} photochemical chlorination,^{29,30} and exposure to gaseous chlorine precursors³¹. The type of chlorine atoms or ions doping the graphene structure was highly dependent on the method of functionalization. In the photochemical synthesis pathway, graphene materials were doped via chlorine radicals formed by ultra-violet (UV) cleavage of the Cl-Cl bond (Fig. 2.10) while exposure to gaseous chlorine precursors results in chlorine ions doping the graphene lattice.

Fig. 2.10 Photochemical chlorination of graphene. Reproduced with permission from ref. 29.

In a successful demonstration by Zhang *et al.*, the group synthesized a high Cl coverage graphene with coverage of up to 45.3 %.²⁸ This gives rise to a $C_{2.2}Cl$ formula in the resultant doped graphene where 42.6 % of the carbon atoms in the graphene lattice existed as C-Cl as shown in XPS measurements. Further investigation with Hall Effect measurements revealed a decrease in its sheet resistance to $342 \Omega/\square$ and thus, an overall enhanced conductivity of the resultant material. The team had also claimed to produce chlorine doped graphenes with more

superior properties than those obtained via photochemical chlorination.²⁸ Doped chlorine atoms existed as C-Cl bonds in the graphene structure indicating the creation of defects during doping procedures. However, the crystallinity of graphene was still very much retained^{27,29} as shown by the low I_D/I_G ratio (lowest ratio: 0.16) measured.²⁸ Observations from Raman spectroscopy results also showed a transfer of electrons occurring from graphene to the highly electronegative Cl atoms thus confirming the p-type effect by chlorine dopants. Chlorine doped graphene was able to achieve monolayers as demonstrated by Li *et al.* where the monolayer was observed to have a height of 1.1 – 1.7 nm in AFM.²⁹ In the study on electronic properties of the resultant doped graphenes, ultraviolet-visible (UV-Vis) measurements coupled with DFT calculations showed a widening of the material's band gap to 1.21 eV as a result of the doping process.^{28,29} As such, chlorine doped graphenes found possible use for future applications such as solar cells.³¹ Experimental studies for solar cells application showed that chlorine doped graphenes displayed higher solar energy conversion efficiency where the charge separation and transport was highly efficient. This excellent performance was attributed to the chloride ions possessing additional charge transfer sites and the impaction of the hole carriers at the surface of the graphene.

Fig. 2.11 Schematic representation of how various adsorption configurations evolve during chlorination of graphene. Reproduced with permission from ref. 32.

In view of photochemical chlorination synthesis method, complete understanding of the mechanism of photochemical reactions with chlorine was still vague despite the numerous articles reporting on such a procedure. Yang *et al.* demonstrated an in-depth theoretical investigation on the mechanism of this synthesis method via DFT calculations.³² It was revealed that Cl atoms were first adsorbed onto the surface of graphene to form a charge-transfer complex in the initial stage following which, the Cl-graphene structure can exist as either of the two completely different structures in the second stage. The Cl-graphene charge-transfer complex can take the form of a non-bonding structure or a covalent-bonding hexagonal Cl rings (Fig. 2.11). This result has important implications on explaining the high stability observed in chlorine doped graphenes synthesized via photochemical reactions where high Cl coverage chlorine doped graphenes can exist without having Cl• radicals escaping as Cl₂ molecules.³²

Chlorine doped graphenes in the present study were synthesized via thermal annealing treatment methods in the presence of chlorine gas as the precursor. This synthesis method successfully incorporated chlorine atoms into the graphene lattice while thermally exfoliating and reducing the graphite oxide precursor simultaneously. The study was conducted as a comparison with other halogen dopants, i.e., bromine and iodine to observe the contrasting properties created by the different halogen dopants. Detailed discussions and elaborations can be found in Chapter 7.

2.1.6 Group VII: Halogen bromine

Bromine was observed to have an electronegative value of 2.96 (Pauling scale), lower than that of chlorine. In section 2.1.3, the lower electronegative phosphorus dopant was observed to display a stronger n-type doping effect than the more electronegative nitrogen of the same Group. Thus, significant differences in several properties of the resultant doped graphenes caused by the lower electronegative dopant were expected as observed in the following review.

The incorporation of bromine into the graphene lattice can occur via plasma bromination treatment,³³ solution-phase synthesis,³⁴ thermal treatment³⁵ and also through the well-known chemical bromination method.³⁶ Bromination of alkenes takes place via an addition reaction of the electrophilic bromine to the nucleophile alkene, $C=C$. This results in the cleavage of the Br-Br bond to form covalent C-Br bonds. Based on this reaction, Jankovský *et al.* have reported a recent in-depth study on bromination.³⁶ The group experimented five different reaction conditions for bromination with variations in the type of bromine precursors, the catalyst used, reaction pressure and temperatures (Fig. 2.12).

Fig. 2.12 Synthesis of brominated graphenes via five different reaction conditions. Reproduced with permission from ref. 36.

The results obtained showed that varying reaction conditions can influence the level of bromine content in the resultant doped graphene. The doped Br levels vary significantly between 0.0 wt. % (heating with reflux in the presence of liquid bromine resulted in no bromine incorporated) to 26.0 wt. % (heating with reflux in the presence of hydrobromic acid).³⁶ Homogeneous distribution of bromine atoms was observed throughout the material in the form of C-Br bonds as shown by Raman spectroscopy and XPS results. In addition, the group has also experimented with carbon precursors (graphite oxides) synthesized via two different methods: Hofmann and Hummers method which were known to produce graphite oxides with different amounts of oxygen containing groups.³⁶ Thus, it was revealed from the obtained results that bromination was affected by the concentration of reactive functional groups (e.g. epoxides) present in the starting material (carbon precursor). Higher concentrations of reactive functionalities imply that higher level of bromine can be doped into the structure. As such, the resultant doped materials were observed to possess little oxygen containing groups with high C/O ratios of 44.7 shown via XPS. Hence, this indicates that bromination with heat treatments can effectively reduce the oxygen groups in the starting material.³⁶ Solution-phase synthesis method also occurs via the bromination mechanism which involves the use of CCl_4 solution.³⁴ A bromine precursor was first dissolved in the CCl_4 solution before adding reduced graphene oxide into the solution (Fig. 2.13).

Fig. 2.13 Preparation procedures of X-RGO in CCl_4 solution. Reproduced with permission from ref. 34.

Similarly, the final product obtained contains C-Br bonds with a bromine content of 1.70 at. %. The resultant doped graphene exhibited excellent electrocatalytic ability in ORRs with a higher current density and more positive onset reduction potential.³⁴ On the other hand, plasma bromination treatment method; a more specific doping method with higher efficiency as stated by Friedrich *et al.* has reported an even higher Br concentration in their doped graphenes.³³ The group demonstrated the plasma treatment process using highly oriented pyrolytic graphite (HOPG) where up to 50 bromine atoms per 100 carbon atoms was achieved. Further theoretical studies via DFT calculations have also proved that bromine dopants provided p-type effects with a widening of the band gap in the doped materials.³⁷

The bromine doped graphenes synthesized in this thesis were performed via thermal annealing in the presence of a bromine precursor. This allows a comparison study between bromine doped graphenes and chlorine doped graphene to observe any contrasting properties. The characterization study was performed via a wide array of techniques as elaborated in Chapter 7. This comparison study was also conducted with iodine doped graphene which will be reviewed as follows.

2.1.7 Group VII: Halogens iodine

To date, the doping of graphene materials with iodine heteroatom has been rarely attempted with only few articles reporting successful doping of iodine and thus, the number of different synthesis pathways was highly limited. The more well-known articles reporting on iodine doping were executed via iodine vapor treatment methods with thermal annealing.³⁸⁻⁴² This method involves the exposure of graphene related materials to iodine vapor followed by thermal annealing treatments to obtain the resultant doped graphene (Fig. 2.14).

Fig. 2.14 Illustration of iodine doped graphene preparation. Reproduced with permission from ref. 39.

Solid iodine was used as the iodine precursor which sublimes easily at 120 °C. Several different carbon precursors have been attempted via this method such as graphene,⁴⁰ graphite oxides and activated carbon.⁴² One interesting carbon precursor attempted was camphor ($C_{10}H_{16}O$), a solid botanical derivative present in the wood of the cinnamomum camphora tree. Being recyclable and environmentally-friendly, camphor was utilized by Kalitha *et al.* to demonstrate the successful synthesis of iodine doped graphene film.³⁸ The resultant doped graphene consists of few-layers graphene sheets with an interplanar spacing of ca. 0.345 nm and an iodine content of 3.1 at. %. In the earlier review on chlorine and bromine dopants, XPS results

showed that the halogen atoms were incorporated as C-Cl and C-Br respectively in the resultant doped materials. Interestingly, iodine dopant did not follow the trend of forming covalent bonds with carbon but proceeds to form polyiodide anions instead (Fig. 2.15).

Fig. 2.15 High-resolution XPS spectrum for I 3d of iodine-doped graphene presenting two separated peaks at 619.4 eV and 63.93 eV, corresponding to I 3d_{3/2} and I 3d_{5/2}. Reproduced with permission from ref. 38.

Raman spectroscopy and XPS results revealed that iodine exists as I₃⁻ and I₅⁻ in the resultant doped graphene with no C-I bonds being formed. These polyiodide anions formed an electrostatic interaction with the graphene network without any form of covalent bonding such as C-I bonds.^{41,42} As such, the pristine sp² lattice network in the starting materials remained undamaged and retained as proven by Raman spectroscopy and XPS results.^{38,41,42} The crystallinity of the obtained doped graphene was retained as shown by I_D/I_G ratios and C/O ratios that remained unchanged after doping procedures.³⁸ Evidence of the instability of C-I bonds in graphene iodine was also observed in a report by Zbořil *et al* where the team utilized the decomposition of C-I bonds to form C-F bonds (graphene fluoride).⁴³ Results show that C-I bonds are highly unstable and can quickly decompose to carbon and iodine. Hence, iodine doped graphenes were observed to exhibit excellent electrocatalytic effects towards ORRs in further

applications studies.³⁹ The iodine doped materials were found to display a more positive onset reduction potential and higher current density with a resistance towards methanol poisoning in ORRs. It was claimed that such excellent electrocatalytic behavior was attributed to the negative polyiodide ions inducing a positive charge on the graphene via charge transfer where the positive charge was observed to promote ORRs.³⁹ One of the highest doped iodine levels reported was by Barpanda *et al.* where his group reported a 23% of iodine content in iodine doped activated carbon materials.⁴² Further investigation also revealed that the concentration of iodine in the resultant doped materials was influenced by the surface area of the carbon precursor. This observation was again reported in his article demonstrating the synthesis of iodine doped graphene using synthetic polycrystalline graphite precursor.⁴¹

In this thesis, halogen dopants (chlorine, bromine and iodine) for graphene materials were presented as a comparison study to gain insights on their contrasting properties. The iodine doped graphenes were synthesized via iodine vapor treatment methods with thermal annealing. Similarly, the resultant iodine doped graphenes were observed to also possess the polyiodides mentioned in the reviewed articles above. In addition, this thesis has included electrochemical studies of these resultant doped graphenes which were novel studies for iodine dopants. The comparison study performed showed a distinctive relationship between decreasing electronegativity (increasing atomic weight of the halogen dopants) and the resultant properties of these halogenated graphenes. Further details and discussions were elaborated in Chapter 7.

2.1.8 Hydrogen: Graphane or hydrogenated graphenes?

Earlier dopants have demonstrated doping levels to be usually less than 100 % and were still stated as successful doping examples. However, in hydrogen doping the concentration of hydrogen in the resultant doped graphenes can give rise to a completely different material obtained. Hydrogenated graphenes were defined as partially hydrogenated graphene material where the level of hydrogenation was less than 100 %. Fully hydrogenated graphene was when hydrogenation achieved 100 % to produce the resultant material known as graphanes (Fig. 2.16). Graphane, a recent popularly investigated material was reported to possess numerous superior properties and an exciting structure demonstrated in several theoretical studies.

Fig. 2.16 Left: graphane. Right: graphane molecule side and top view. Reproduced with permission from ref. 52.

As such, several attempts have been made to synthesize graphanes via hydrogen plasma treatments,⁴⁴ acid and metal reactions (producing hydrogen gas),⁴⁵ borane hydrogenation,⁴⁶ Suzuki cross-coupling reaction,⁴⁷ hydrogen radicals,⁴⁸ microwave irradiation⁴⁹ and Birch reaction.^{50,51} Unfortunately, further characterization of the resultant materials revealed that none of these materials were a C_1H_1 ratio and thus, were not graphanes. As such, graphane remained a theoretical material with experimental work still in progress.⁵² However, the reported characterization results revealed several interesting properties of these hydrogenated graphenes as elaborated in the following review.

The synthesis methods reported for hydrogenated graphenes were mainly based on the hydrogenation chemical reactions of C=C bonds. Hydrogenation of alkenes takes place in the presence of a metal catalyst where two hydrogen atoms were added to the C=C bond to form alkanes (C-C). One example was a recent study by Sofer *et al.* where his group attempted hydrogenation of graphite oxides through an acid and metal reaction.⁴⁵ Five different metals (Al, Mg, Mn, Zn and Fe) were experimented to produce hydrogen gas which was used to hydrogenate the graphite oxides. The graphite oxides precursor subsequently undergoes reduction and hydrogenation reactions to produce the resultant hydrogenated graphene materials. The group achieved a 3.93 wt. % of H in hydrogenated graphenes using Zn metal. Further XPS results also showed that the materials have undergone reduction reaction where only a small amount of oxygen functionalities were found in the resultant material. Hence, hydrogenated graphenes displayed higher heterogeneous electron transfer (HET) rates and lower electrical resistivities with the presence of lesser oxygen functionalities.⁴⁵ The group also claimed that the degree of hydrogenation of graphenes was dependent on the electrochemical potentials of the metal used. Each metal possessed unique electrochemical potentials and hence, dissolves to generate nascent hydrogen at different rates. The different gas production rates will thus, influence the amount of time allowed for simultaneous reduction reaction of graphite oxides to occur. In the case of a violent and rapid metal and acid reaction, insufficient amount of

time will be available for reduction reaction of graphenes to occur. Thus, nascent hydrogens will recombine quickly and hydrogenation of the graphite oxide will fail to occur.⁴⁵

Fig. 2.17 FT-IR spectra of the hydrogenated graphene synthesized via Zn metal and the details of C–H stretching vibration. Reproduced with permission from ref. 45.

To prove the successful hydrogenation of graphene materials, combustion elemental analysis can be employed to determine the elemental composition of the resultant doped graphenes.^{45,48,49} However, the percentage composition of H obtained includes contribution of H from functionalities such as hydroxyl and carboxyls. This implies that FT-IR measurement was the only reliable technique to prove hydrogenation via the observation of IR bands corresponding to C-H bond stretching (Fig. 2.17).^{45-48,53} IR bands that correspond to H bonded to olefinic carbon and H bonded to aromatic carbon can be observed in hydrogenated graphenes.^{46,48,53} One of the highest degree of hydrogenation reported was by Chen *et al.* where 5.27 wt. % of H was achieved.⁴⁸ The group performed a synchronized reduction and hydrogenation of graphene oxide using hydrogen radicals and ⁶⁰Co gamma rays. The resultant material was a large (micrometers) hydrogenated graphene monolayer sheet of 0.90 nm thickness. The material was also observed to possess high specific capacity and good recycling ability displaying great potential as a material for lithium ion battery application.⁴⁸ Hydrogenated graphenes were also observed to display ferromagnetism as proven by several reported theoretical and experimental studies.^{50,54,55} Theoretical studies claimed that the observed magnetism was attributed to the trigonal planar network of the structure.⁵⁴ Experimental

studies have also investigated this phenomenon through superconducting quantum interference device (SQUID) measurements where it was observed that the large extent of hydrogenation in the material attributes to the ferromagnetic behavior of the material.⁵⁰

In this thesis, high pressure and high temperature hydrogenation of graphenes was performed to synthesize hydrogenated graphenes. The resultant highly hydrogenated graphene obtained was observed to possess significantly high levels of hydrogen content. Full characterization of the materials was elaborated in Chapter 8.

2.2 Part 2: Influence of synthesis methods/conditions on the properties of graphene

In Part 2 of this thesis, the influence of synthesis methods/conditions on the properties of the resulting nanocarbon materials will be investigated. Since the discovery of graphene, numerous different synthesis methods have been explored to obtain graphene and graphene related materials such as graphite oxides. Liquid-phase exfoliation of graphite,⁵⁶⁻⁵⁹ chemical vapour deposition (CVD) growth⁶⁰⁻⁶² and unzipping of carbon nanotubes⁶³⁻⁶⁵. are some of the approaches towards obtaining graphene.

Through characterization studies on the resulted graphenes obtained via each method, it was observed that different synthesis pathways can influence the quality and properties of the resultant graphene. For example, solution-based exfoliation of graphite has been shown to produce high-quality graphenes in scalable amounts.⁶⁶ However, the majority of the product obtained possessed a multilayer structure resulting in low yields of monolayer graphenes.⁶⁷ Electrochemical exfoliation of graphite produces oxidized graphene of low quality due to the presence of large amount of defects in the structure.⁶⁸

In the study of this thesis, three well-known and established synthesis pathways to obtain graphite oxide were investigated: Staudenmaier,⁶⁹ Hummers⁷⁰ and Hofmann⁷¹ methods. Differences in reaction conditions between the three methods were summarized in table 2.2. It was often commonly assumed that the three methods produced graphite oxides of similar or negligible differences in properties. The graphite oxides obtained via the three methods were further thermally annealed to produce thermally reduced graphene oxides (TRGOs) which were then fully characterized to observe any contrasting properties. Detailed results and discussions are elaborated in Chapter 9.

Table 2.2 Comparison between Staudenmaier, Hummers and Hofmann methods.

	Staudenmaier	Hummers	Hofmann
Oxidising agent	Fuming nitric acid, con. sulfuric acid, potassium perchlorate	Con. sulfuric acid, sodium nitrate, potassium permanganate	Con. nitric acid, con. sulfuric acid, potassium perchlorate

In Part 2, the influence of synthesis condition on the properties of graphene was also investigated for the combustion reaction of magnesium metal in dry ice to obtain graphenes.⁷²⁻⁷⁴ The reaction proceeds via Eqn. 1 where magnesium metal was converted to magnesium oxide and solid CO₂ was converted to carbon.

Eqn. 1 Combustion of magnesium metal in dry ice.

The resultant material was few-layers graphene (3 – 7 layers) of varying sheet lengths of 50 nm and 300 nm with a thickness of 3.5 Å (Fig. 2.18).⁷² Raman spectroscopy measurements revealed that these materials possessed high concentration of defects and disorders at the edges.⁷³ XPS scans have also showed that these materials usually consisted of small amounts of unreacted magnesium starting material left behind by incomplete combustion.⁷⁴ In application studies, the resultant graphenes were found to display excellent high specific capacitance implying potential use as a material in capacitors.⁷³ Similar combustion synthesis method using calcium metal instead of magnesium was attempted by Zhang *et al.* where graphenes were also successfully obtained.⁷³

Fig. 2.18 TEM images of few-layer graphene. (a) Graphenes with an average length of 50–100 nm. (b) Larger size graphene sheets, average length 300 nm. (c) Crystalline graphenes with an average length of 200 nm. (d) High-resolution TEM image of few-layer graphenes, the number of layers ranging from 3–7. Inset: the electron diffraction pattern of graphenes. Reproduced with permission from ref. 72.

In this thesis, combustion of metal in dry ice was also investigated using a different metal precursor: lithium. It was previously reported that metallic impurities in graphenes can influence the electrochemistry of the materials and hence, the electrochemical properties of the resultant graphene were studied. Interestingly, the lithium impurities found in the final products did not cause undesired influences in the electrochemical behavior of the materials. Full details and results will be elaborated in Chapter 10.

2.3 Part 3: Influence of structural differences on the properties of nanocarbons

Besides graphene, extensive characterization studies were also performed for various nanocarbons of different forms and structures. Fullerenes, carbon nanotubes⁷⁵⁻⁷⁸ (single-walled, multi-walled, cup-stacked), graphene nanoribbons,⁷⁹⁻⁸¹ carbon nanocones,^{82,83} carbon nanopipettes^{84,85} and carbon nanotorus⁸⁶ are some of the examples of the nanocarbons investigated.

An example to review is carbon nanocone which have been extensively investigated and characterized. Kumar *et al.*⁸³ reported a plasma treatment approach using methane gas as a precursor to synthesize carbon nanocones with a copper cap on top (surface). SEM and TEM results revealed the carbon nanocones to have a height of 500 nm and base diameter of 150 nm as shown in fig. 2.19.⁸³

Fig. 2.19 SEM and TEM images of the typical copper-capped carbon nanocones grown on a silicon wafer. The low-magnification SEM image (a) shows the groups of the nanocones, alongside with the isolated nanostructures. The medium-magnification image (b) shows that the substrate surface between the grown nanocones is covered with small “second-generation” structures. High-magnification images show the narrow gaps formed by the closely grown nanocones. Reproduced with permission from ref. 83.

Raman spectroscopy revealed the resultant carbon nanocones to have a I_D/I_G ratio of approximately 0.5, a graphitic crystalline structure. Additional characteristics such as spectral reflectance also showed that the carbon nanocones have an efficient refractive index measurement based on Brewster angle where the calculated value was approximately 1.26 at 633 nm wavelength.⁸³ This value was approx. half of that for amorphous carbon which has a reported value of ca. 2.43. Hence, this clearly highlights that structural difference can influence the resultant properties of nanocarbons. Herein nanoporous carbon, a structurally different nanocarbon from graphene was investigated and extensively characterized. The material was also studied for its potential in biosensing applications as described in Chapter 11.

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Chapter 3

Objectives of thesis

3.1 Objectives of thesis

Since the discovery of graphene, numerous characterization studies on graphenes have been reported. Graphene was found to possess various desirable properties such as high conductivity and high tensile strength. However, the materials were also found to pose several challenges. These include zero band gap, rapid charge and discharge and a lack of synthesis methods with scalable yields etc. Hence, scientific solutions to resolve these challenges were proposed such as heteroatom functionalization of graphenes, modification of synthesis methods and conditions. These solutions were observed to influence the properties of the resultant graphenes obtained.

This thesis explores different ways of modifying graphene and carbon materials. In particular: ***a) Influence of heteroatom functionalization on the properties of graphene, b) Influence of synthesis methods/conditions on the properties of graphene*** and lastly, ***c) Influence of structural differences on the properties of nanocarbons***. Studies of the three parts were conducted as extensive characterization of the physical and electrochemical properties of the resultant materials obtained. Various techniques employed include SEM, TEM, XPS and Raman spectroscopy. Special focus on the electrochemical characteristics was made as the electrochemical behaviors of the resultant materials can determine the material's potential for important future applications such as capacitors and biosensors. The objectives of this thesis are as summarized in the infographic diagram shown below.

Objectives of thesis

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PART 1:

Influence of Heteroatom Functionalization on the Properties of Graphene

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Chapter 4

Boron and Nitrogen Doping of Graphene via Thermal Exfoliation of Graphite
Oxide: Contrasting Properties

4.1	<i>Introduction</i>
4.2	<i>Results</i>
4.2.1	<i>Properties of boron and nitrogen doped graphenes</i>
4.2.2	<i>Electrochemistry of boron and nitrogen doped graphenes</i>
4.3	<i>Discussion</i>
4.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Petr Šimek, Zdeněk Sofer, Ivo Tomandl, Martin Pumera. Boron and Nitrogen Doping of Graphene via Thermal Exfoliation of Graphite Oxide in a BF_3 or NH_3 Atmosphere: Contrasting Properties. *J. Mater. Chem. A*, 2013, **1**, 13146.

Article can be downloaded from

<http://pubs.rsc.org/en/content/articlelanding/2013/TA/c3ta12460f#!divAbstract>.

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Introduction

To kick start the series of chapters investigating Part 1 on the influence of heteroatom functionalization on the properties of graphene, we will first look at boron and nitrogen heteroatom dopants. The subsequent chapters for Part 1 will be in the sequence of the heteroatom's group in the periodic table.

As previously mentioned, boron and nitrogen atoms give p-type and n-type effects respectively when doped into a carbon-based graphene lattice. In this chapter, we have performed an in-depth study of the various properties of the two doped graphene materials. Herein we presented a scalable synthesis method to implant boron and nitrogen into the graphene lattice during thermal exfoliation of graphite oxide using boron trifluoride (BF_3) and ammonia (NH_3) gases as the dopants' precursors (Scheme 4.1). This project was presented as a comparison study between an "electron acceptor" doped graphene (boron) and an "electron donor" (nitrogen) doped graphene through an investigation of their various properties.

Moreover, previous studies on nitrogen doped graphene were usually performed using CVD or epitaxial graphene precursor which presented certain limitations in its synthesis. This further explains our desire to explore methods capable of generating gram-quantities of the doped materials. In this chapter, we have employed a wide array of standard characterization techniques such as Raman spectroscopy, high-resolution XPS (HR-XPS), prompt gamma-ray activation analysis (PGAA) and cyclic voltammetry (CV) as elaborated below.

Scheme 4.1. Fabrication of B and N doped graphene by thermal exfoliation of graphite oxide prepared in BF_3 or NH_3 atmospheres.

Results

4.2.1 Properties of boron and nitrogen doped graphenes

In this project, we have compared the properties of boron and nitrogen doped graphenes prepared by thermal exfoliating graphite oxide in gaseous BF_3 or NH_3 atmospheres at a temperature of 800°C . The graphite oxide used in this experiment was synthesized via Staudenmaier method hence, the control material in this experiment is graphene oxide (graphite oxide exfoliated in inert N_2 atmosphere) which will be labeled as ST. Boron and nitrogen doped graphenes are labeled as ST-B and ST-N respectively.

Fig. 4.1 Scanning electron micrographs of ST-B, ST-N and ST graphenes. Scale bars of 10 mm (a), 1 mm (b), 1 mm (c) and 100 nm (d).

Fig. 4.2 STEM images of ST-B and ST-N. Scale bars of 400 nm (a, b, c) and 800 nm (d).

The materials were first investigated for their morphology using SEM to observe their forms and structures. The images of each material were taken at various magnifications as shown in fig. 4.1. It could be observed that all three materials displayed structures similar to that of typical fully exfoliated graphene sheets which proves that the materials were successfully exfoliated. We have also utilized scanning transmission electron microscopy (STEM) to observe the exfoliated graphene sheets of each material. The images showed that the graphene sheets were “transparent” to the STEM electron beam causing them to be morphologically indistinguishable (Fig. 4.2).

Further assessment on the elemental composition of the materials was performed with combustible elemental CNHS/O analysis (EA). The results were shown in Table 4.1 where the values were reported as atomic weight percentages. ST was observed to contain 95.14 % of C, 1.43 % of H, 3.43 % of O and zero percentages of N and S elements. ST-N contained 90.03 % of C, 2.27 % of H, 5.76 % of O, 1.94 % of N and zero percentage of S. ST-B contained 84.83 % of C, 9.63 % of H, 5.54 % of O and zero percentages of S and N. It can be concluded that exfoliation of graphite oxide in a NH_3 atmosphere leads to the incorporation of nitrogen into the graphene structure. It was evident that thermal reduction of graphene oxide in any of the three atmospheres led to the removal of more oxygen functionalities (higher C/O ratios) than chemical reduction of graphene oxide using hydrazine (C/O ratio of 10.3)¹ or microwave reduction (C/O ratio of 2.75). Such high reduction efficiency is usually possible with only laser irradiation method.^{2,3}

Table 4.1 Relative percentages of the elemental composition of the materials determined by the combustible CNHS/O analysis method.

Materials	C (%)	H (%)	O (%)	N (%)	S (%)
ST	95.14	1.43	3.43	0	0
ST-N	90.03	2.27	5.76	1.94	0
ST-B	84.83	9.63	5.54	0	0

X-ray photoelectron spectroscopy (XPS) was used to obtain the surface elemental composition of the doped graphenes and the control material. HR-XPS spectra of N 1s peak at bond energy of ~ 400 eV (Fig. 4.3, A) shows a double peak where the 400 eV peak corresponds to amine like ($-\text{NH}-$) bonds (peak area of 51.6 %) and the 402.5 eV peak corresponds to bipolaron $=\text{NH}^+$ bond (peak area of 49.4 %).^{4,5} This proves that nitrogen was successfully incorporated into the graphene sheet. It is important to note that the bipolaron/amine ratio obtained here is significantly higher than the values recorded in previous reports. Previous findings showed that bipolaron $=\text{NH}^+$ nitrogen state was either not found or present at very low concentrations as

compared to the typical amine bond which was more commonly found.⁶⁻¹⁰

To confirm the presence of nitrogen groups in ST-N, ATR FT-IR spectrum of thermally reduced graphene oxide in nitrogen was recorded (refer to Fig. 4.3, B). The vibration band at 1590 cm^{-1} corresponds to the C=N stretching of the pyridine ring. The wavenumber of this peak is very similar to that of the graphene skeletal vibration which occurs between 1580 cm^{-1} to 1630 cm^{-1} .¹¹ However, this peak was not visible in the ATR FT-IR spectrum for ST exfoliated at the same temperature as ST-N. Hence, it can be certain that the IR band at 1590 cm^{-1} corresponds to C=N and not graphene skeletal vibration. NH_2 bending vibrational mode may account for the band at 1590 cm^{-1} but the absence of peaks at around 3250 cm^{-1} – 3500 cm^{-1} (two N-H stretching vibrations) refutes the possibility of the NH_2 group as the correct identity for the 1590 cm^{-1} band. The HR-XPS results of ST-B at $\sim 190\text{ eV}$ (B 1s) showed a noisy and inconclusive result (Fig. 4.3, C) due to concentration of boron in ST-B (140 ppm, see below) being lower than the detection limit of XPS (1000 ppm).

Fig. 4.3 HR-XPS spectra and ATR FT-IR spectrum of ST-B, ST-N and ST. (A) HR-XPS spectrum of N 1s, (B) ATR FT-IR spectroscopy of ST-N and (C) HR-XPS spectrum of ST-B for B 1s. (D–F) HR-XPS C 1s spectra of (D) ST-N, (E) ST-B and (F) ST.

High-resolution XPS measurements were carried out for the C 1s electronic state of all three materials where a single, symmetrical peak at approximately 284.5 eV with a small trailing tail (at higher binding energies) was observed. Fitting of the C 1s spectra was performed with considerations for relative sensitivity factors to identify and quantify the various carbon bonds present at the materials' surfaces. The fitted results showed that ST-N, ST-B and ST possessed similar amounts of oxygen containing groups (Fig. 4.3, D, E and F respectively). HR-XPS C 1s peaks of all three materials were fitted to show C=C bond at 284.5 eV, C-C bond at 285.5 eV, C-O bond at 286.7 eV, C=O bond at 288.2 eV, O-C=O bond at 289.5 eV and π - π interaction at 291.2

eV. ST-N, ST-B and ST graphenes possessed 68.6 %, 58.6 % and 69.3 % of C=C bonds, 14.5 %, 19.8 % and 13.2 % of C-C bonds, 6.9 %, 10.8 % and 6.5 % of C-O bonds, 2.8 %, 4.1 % and 2.5 % of C=O bonds and 2.4 %, 2.7 % and 2.2 % of O-C=O bonds respectively. The remnant of the C 1s peak corresponds to the π - π^* signal which was related to the sp^2 lattice structure of graphene. Wide scan XPS spectra of the three materials were obtained as shown in fig. 4.4. The C/O ratios calculated for the materials were 22 for ST-N, 12.5 for ST-B and 24 for ST and these values are similar to those of thermally exfoliated graphenes.¹²

Fig. 4.4 Wide scan XPS analyses of B-doped (ST-B), N-doped (ST-N) graphenes and undoped (ST) graphene.

Fig. 4.5 Prompt gamma-ray activation analysis of ST-B.

The concentration of boron in ST-B was also measured with prompt Gamma-ray Activation Analysis (PGAA) using a LWR-15 nuclear reactor.¹³ The materials were encapsulated in Teflon vials and irradiated with a thermal neutron beam at a flux rate of $\sim 3 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$.¹⁴ After three hours, a well-shielded 25 % high-purity germanium (HPGe) detector was used to obtain the spectrums. Background correction was then performed for the boron signal in the γ spectrum where the background scan was based on the measurement of an empty Teflon vial. The result obtained was as shown in fig. 4.5. The gamma lines that correspond to fluorine derived mainly from the Teflon vial and not ST-B. Using PGAA, we have established that the boron concentration in ST-B is 140 ppm. The calculated statistical uncertainty of the boron mass fraction is 20 ppm with an estimated systematic error of approximately 10 ppm. Note that typical doping levels in semiconductors are in the range of ppm.¹⁵

Fig. 4.6 Raman spectra of B-doped (ST-B), N-doped (ST-N) graphenes and graphene exfoliated in an inert atmosphere (ST).

Additional structural information can be obtained using Raman spectroscopy to examine the density of defects in the materials. The spectroscopic results show a D peak at ca. 1350 cm^{-1} and a G peak at ca. 1560 cm^{-1} which corresponds to the sp^3 defects in the sp^2 lattice and the pristine sp^2 graphene lattice structure respectively. The intensities of the D and G peaks were further expressed as D/G ratios to determine the density of defects in the structure. The Raman spectrum of each material was shown in fig. 4.6. The calculated D/G ratios for the three materials were 0.74 for ST-B, 0.32 for ST-N and 0.77 for ST. This shows that ST-N has the lowest defect density followed by ST-B and lastly, the control material ST with the largest amount of defects in its structure. The average crystallite sizes of the materials can also be calculated using the intensities of the D and G peaks and the following equation:¹⁶

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

where I_G and I_D refers to the intensity of the G and D peaks respectively. λ_{laser} is the wavelength (nm) of the laser used for Raman spectroscopic measurements. It can be observed that ST-N has the largest crystallite size of 52.3 nm, followed by ST-B with 22.6 nm and ST with the smallest crystallite size of 21.8 nm. The band that appeared at $\sim 2700 \text{ cm}^{-1}$ is a second order D peak labelled as 2D. 2D peak was present in graphene as well as in graphite.¹⁷ However, in graphite the 2D consists from two superposed peaks 2D₁ and 2D₂ while in graphene it appears as a single individual peak.¹⁷

4.2.2 Electrochemistry of boron and nitrogen doped graphenes

Fig. 4.7 Current–voltage characteristics of B-doped (ST-B), N-doped (ST-N) and undoped (ST) graphenes.

Conductivity of each material was studied using four point measurements of individual compressed tablets made from the materials. The resistivity of ST was found to be $5.2 \times 10^{-5} \Omega \text{ cm}$, $3.5 \times 10^{-5} \Omega \text{ cm}$ for ST-N and $2.2 \times 10^{-4} \Omega \text{ cm}$ for ST-B. In addition, we have also measured the current-voltage (*I*-*V*) characteristics of the materials using simple conductivity measurements performed on a gold interdigitated electrode (Au-IDE).¹⁸ The results obtained are as shown in fig. 4.7 where ST-N was found to possess the largest conductivity of all three studied materials, followed by ST and lastly, ST-B with the lowest conductivity. The electrical conductivity behaviours displayed were related to the electron donor/acceptor properties of nitrogen and boron which was further supported by the results obtained via 4-probe measurements. All three materials exhibited electrical resistance using gold probes as contacts. The results obtained is in agreement with the earlier resistivity results where the highest conductivity (lowest resistivity) was observed for the n-type doped graphene (ST-N) and the lowest conductivity (highest resistivity) was measured for p-type doped material (ST-B). We can deduce that the holes generated by boron doping act as a trap for free electrons leading to a huge decline in the mobility of free carriers and hence, a decrease in the material's conductivity. In general, the holes also exhibited lower mobility as compared to electrons. The direct measurement of the

carriers' mobility on a single sheet of exfoliated graphene was extremely complicated and only few groups reported such results. In the compact form, the material behaves like a composite of highly conductive sheet with very weak electrical interconnection to each graphene plane. The strong scattering of free carriers occurs at the graphene sheets' boundaries where the value of carrier mobility is unable to give any useful information about the material. The graphene sheets boundaries became dominant where the value of free carrier mobility on such sample is almost immeasurable.

Fig. 4.8 Cyclic voltammograms of 10 mM ferro/ferricyanide for ST-B, ST-N, ST and bare GC. Conditions: room temperature, scan rate of 100 mV s⁻¹.

From the value of HET and *I*-*V* results, we can deduce that p-type doped graphene experienced a significant decrease in free carrier mobility while nitrogen doped graphene free carriers have higher mobility. To obtain the heterogeneous electron transfer (HET) rates of ST-N, ST-B, ST and bare glassy carbon (GC) electrodes, we have performed cyclic voltammetry scans for ferro/ferricyanide probe (Fig. 4.8). The peak-to-peak separation (ΔE_{p-p}) values were found to be 220 mV, 140 mV, 240 mV and 340 mV for ST-N, ST-B, ST and bare GC electrodes, respectively. Following which, we have calculated the observed heterogeneous electron transfer rate (k_{obs}^0) of the materials through the use of the Nicholson approach.¹⁹ In this equation, ΔE_{p-p} was related to a dimensionless parameter ψ which is directly related to k_{obs}^0 . The diffusion coefficient used in the equation is $D = 7.26 \times 10^{-6}$ cm s⁻¹ for ferro/ferricyanide solution. The k_{obs}^0 values obtained

were $2.512 \times 10^{-3} \text{ cm s}^{-1}$ for ST-B, $8.051 \times 10^{-4} \text{ cm s}^{-1}$ for ST-N, $6.747 \times 10^{-4} \text{ cm s}^{-1}$ for ST and $1.755 \times 10^{-4} \text{ cm s}^{-1}$ for GC. This shows that ST-B exhibits the highest HET rate, followed by ST-N, ST and lastly GC. The sites of defects in graphene materials were known to be electrochemically more active than the other areas. Therefore, the HET results support the earlier observation made in Raman spectroscopy where ST-B and ST, the two materials with the highest defect densities as both materials have the highest amount of electroactive sites. This finding was also consistent with earlier reports on ferro/ferricyanide electrochemistry which was not known to be electrocatalyzed by either boron or nitrogen.

It is important to note that the fundamental difference between hole doped graphene (boron doped) and electron doped graphene (nitrogen doped) in electron transfer properties was perfectly demonstrated in an earlier report on the difference in the degradation of electron donor/acceptor dyes.²⁰ The results obtained in this project are completely in agreement with their findings.²⁰

Discussion

We have presented a scalable method for the incorporation of acceptor/donor dopants into the graphene sheets via exfoliation of graphite oxide in a gaseous atmosphere consisting of the dopant element. Exfoliation of graphene in BF_3 atmosphere led to the incorporation of 140 ppm of boron into the graphene lattice while exfoliation in NH_3 atmosphere led to the incorporation of ca. 2 % atomic weight of N. Extensive characterization studies have shown significant differences in the electronic properties of the materials. This further proves that electron donor doped graphenes (n-type) exhibit the highest conductivity while the electron acceptor doped graphenes (p-type) exhibit the lowest conductivity. With the possibility of the synthesis methods being able to produce highly scalable yield, these materials may have great potentials in important future applications and industrial purposes.

Experimental

Materials:

Sulfuric acid (98 %), nitric acid (fuming, 98 %), potassium chlorate (98 %), hydrochloric acid (37 %), silver nitrate (99.5 %) and barium nitrate (99.5 %) were obtained from PENTA, Czech Republic. Graphite microparticles (<50 μm) were obtained from KOOH-I-NOOR Graphite, Czech Republic. Boron trifluoride diethyl etherate, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, potassium ferrocyanide, sodium chloride and potassium chloride were purchased from Sigma-Aldrich. Deionised water was used in the preparation of all the electrolytes that were employed for any electrochemical measurement. The gases were obtained from SIAD (Nitrogen 99.9999 %, Ammonia 99.9995 %). Glassy carbon working electrode (GC), platinum auxiliary electrode (Pt) with a diameter of 3 mm and Ag/AgCl reference electrode were obtained from Autolab, The Netherlands. The gold interdigitated electrode (Au-IDE) was purchased from BAS, Inc. Tokyo.

Apparatus:

A JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) was used to acquire images under normal SEM mode and gentle-beam mode (GB). The samples were prepared by being attached onto an aluminium sample stub using a sticky conductive carbon tape. The elemental analysis was performed with Vario EL III (Elementar Analysensysteme GmbH, Germany). Calibration was performed with 5 mg of 4-aminobenzenesulfonic acid. A Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) was used for the acquirement of all X-ray photoelectron spectroscopy (XPS) measurements. Wide-range scans, high resolution C 1s scans, high resolution B 1s and high resolution N 1s scans were performed at 12.53 kV. The materials were affixed onto an aluminium XPS sample holder using a sticky conductive carbon tape with special care taken to ensure that the layer of the material was uniform throughout. The ATR FT-IR measurement was performed with ATR FT-IR

spektrometr NICOLET 6700. Diamond ATR crystal and DTGS detector were used for the measurements. The boron signal from PGAA was corrected for background signal which was measured with an empty Teflon vial. The absolute content of boron in samples was determined relative to a H_3BO_3 liquid standard of a known boron concentration. The Teflon vial containing this standard was irradiated at the same position as the graphene powder samples in the machine. Nevertheless, the difference between the volumes of the liquid standard and the powder samples led to slightly different measurement geometry. Therefore, correction for this difference was performed based on an earlier established method of dependence on the sample volume for the acquirement of the boron signal. A confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector was used to obtain Raman spectroscopic measurement. All actual measurements of the materials were performed using a 514.5 nm Ar laser, an Olympus optical microscope and a 100 $\times$ objective lens to focus the samples. Preparation of all the materials was carried out to ensure that only well-compressed and compacted samples were used for any measurements. For electrical resistivity measurements, 40 mg of the powder material were first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by the 4-probe technique using the Van der Pauw method.²¹ The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit. The measuring current was set to 10 mA. Cyclic voltammetric and conductivity measurements were performed using a microAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) which was controlled with a NOVA 1.7 software (Eco Chemie). Nova 1.7 software is published by Metrohm Autolab B.V. in support of the Metrohm Autolab's potentiostat/galvanostat equipment.

Procedures:

*Graphite oxide preparation with Staudenmaier method.*²² 87.5 mL of sulfuric acid (98 % concentration) and 27 mL of nitric acid (fuming, 98 %) were added to a reaction flask containing a magnetic stir bar. The mixture was subsequently cooled to 0 °C and 5 g of graphite were added. The mixture was then stirred vigorously to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, 55 g of potassium chlorate was slowly added to the mixture. Upon complete dissolution of the potassium chlorate, the reaction flask was loosely capped to allow the gas evolved during the reaction to escape. The mixture was then continuously stirred for 72 h at room temperature. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then dispersed in HCl (5 %) solution to remove sulfate ions and repeatedly centrifuged and dispersed repeatedly in deionized water until a negative reaction on chloride and sulfate ions (with AgNO₃ and Ba(NO₃)₂ respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Preparation of N-doped and B doped graphene. The nitrogen doped graphene was synthesized by exfoliation of Staudenmaier method's graphite oxide in ammonia atmosphere. 100 mg of graphite oxide was placed inside the quartz glass capsule connected to a magnetic manipulator and placed inside the horizontal quartz glass reactor. Before the insertion of the sample within the hot zone, the reactor was repeatedly evacuated and flushed with nitrogen. Subsequently, the nitrogen flow was switched to ammonia and the sample was inserted in the hot zone of the reactor. The sample was maintained at 800 °C for 12 minutes. An ammonia flow at 300 mL min⁻¹ was used to remove the by-products from the exfoliation process. The boron doped graphene was prepared using boron trifluoride diethyl etherate as the boron precursor. The exfoliation with BF₃·Et₂O was performed using a bubbler filled with the liquid precursor at 20 °C and 1000 mbar. Nitrogen (100 mL min⁻¹) was used as a boron precursor carrier gas and was diluted with 1

L min⁻¹ of nitrogen. The reactor was repeatedly flushed with nitrogen where the flow of the boron precursor was stabilized for 5 minutes before introducing the sample into the hot zone of the reactor. The exfoliation was performed for 12 minutes at 800 °C. The exfoliation of undoped graphene was performed under similar conditions in a nitrogen gas atmosphere (1 L min⁻¹).

Electrochemical measurements. All glassy carbon electrodes were cleaned by polishing with an alumina suspension, washed with deionized water and wiped dry prior to any usage. The materials were dispersed in a DMF solvent to create a suspension with a concentration of 0.5 mg/mL. The suspension was sonicated at room temperature for 5 min before each use. The cleaned surface of a GC electrode was modified by coating with a 1 µL aliquot of the sonicated suspension. The electrode was then left to dry under a lamp to give a layer of randomly dispersed material on the GC surface. This step was repeated three times to achieve three layers of coatings. The modified GC electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then placed into an electrochemical cell which contains the electrolyte solution and the measurements were then taken. The electrolytes used were 50 mM pH 7.4 phosphate buffer solution (PBS) as the blank buffer electrolyte and 10 mM ferro/ferricyanide which was dissolved in 50 mM pH 7.4 PBS. CV was performed in the range of + 120 mV to - 80 mV for blank buffer solution and 0 V to - 160 mV for ferro/ferricyanide electrolyte. All measurements were performed for two consecutive scans at a scan rate of 100 mV s⁻¹. Three replicates were carried out for each material and also for each electrolyte.

Conductivity measurements with Au-IDE. 1 mg/ml suspensions of the materials were prepared in deionised water. The current–voltage measurements were performed by coating 1 µL of the suspension onto the interdigitated area that bridges two gold electrode bands. The electrode was then left to dry under a lamp to obtain a randomly deposited film on the electrode. A linear sweep voltammetric measurement was then performed on the electrode at 200 mV s⁻¹ scan rate

to give I - V characteristics. Five replicates were executed for each material.

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Chapter 5

Concurrent Reduction and Phosphorus Doping of Graphene Oxide

5.1	<i>Introduction</i>
5.2	<i>Results</i>
5.2.1	<i>Properties of phosphorus doped graphenes</i>
5.2.2	<i>Electrochemistry of phosphorus doped graphenes</i>
5.3	<i>Discussion</i>
5.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Zdeněk Sofer, Michal Nováček, Martin Pumera. Concurrent Phosphorus

Doping and Reduction of Graphene Oxide. *Chem. Eur. J.*, 2014, **20**, 4284.

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Introduction

In this chapter, we will be focusing on chemically reduced graphene oxides doped with phosphorus element. Phosphorus dopant gives a n-type effect when doped into graphene. With an electronegativity lower than nitrogen, the lone electron pair on phosphorus is more readily available giving rise to a much stronger n-type effect than nitrogen. Hence, doping with the larger atomic radii phosphorus will prove to give interesting results in the properties of the doped materials. Several earlier reports have shown the successful addition of the element which was accompanied by an increase in oxygen levels of the material due to phosphorus preferential binding to oxygen.¹ However, an increase in the levels of oxygen content in materials have proved to be undesirable due to the negative charges presented by the groups causing the materials' conductivities to decrease.^{2,3} Here, we have successfully demonstrated the possibility of simultaneous phosphorus incorporation and removal of oxygen functionalities through a one step phosphorus treatment process. The resultant material was found to possess a high percentage content of phosphorus (3.65 at. %) using white phosphorus (P_4), phosphine (PH_3), sodium hypophosphite (NaH_2PO_2) and disodium hydrogen phosphite (Na_2HPO_3) as phosphorus sources. Among these precursors, sodium hypophosphite and disodium hydrogen phosphite were commonly used reducing agents. This synthesis procedure differs from earlier reported methods that utilized 1-butyl-3-methylimidazolium hexafluorophosphate,⁴ phosphoric acid,^{1,5} triethyl phosphite,⁶ phosphorus trichloride⁶ and triphenylphosphine^{7,8} as the phosphorus sources.

Results

5.2.1 Properties of phosphorus doped graphenes

The phosphorus doped graphenes were synthesized by treatment of Hofmann method's graphite oxides using various phosphorus sources to obtain reduced graphene oxides doped with phosphorus. Hence, the phosphorus doped materials were labeled as HO-P with additional information on the type of phosphorus source used. Example: HO-P: [P₄] is Hofmann graphite oxide treated with P₄ and exfoliated to yield reduced phosphorus doped graphene. The properties of these doped materials were compared against undoped graphene oxides such as HO-N (thermally exfoliated graphene under nitrogen gas atmosphere)⁹ and HO (Hofmann graphite oxide, starting material which was unexfoliated).¹⁰ Exfoliation and reduction of graphite oxides in an inert gas atmosphere was known to be the most efficient oxygen-reduction treatment methods. Hence, comparison of all HO-P with HO-N will serve as a crucial benchmark in this project. The characteristics of such materials were then studied using a wide range of techniques such as scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) measurements in different electrolytes were performed to examine properties such as heterogeneous electron transfer rates and oxygen reduction reactions.

Fig. 5.1 SEM images of all HO-P materials, HO and undoped HO-N. The scale bars are 100 nm (a), 1 mm (b), and 10 mm (c).

The morphology of the materials was examined using the SEM technique at magnifications of $\times 50,000$, $\times 6,000$ and $\times 370$ as shown in fig. 5.1. All HO-P materials and HO-N showed numerous similarities where all the materials were completely exfoliated. This indicates that phosphorus doped chemically reduced graphene oxides can be completely reduced during doping procedure. Only HO was observed to be completely unexfoliated due to the material being a graphite oxide. The poor conductivity of the material observed during SEM imaging reflects the presence of many oxygen containing groups in the HO structure.

Fig. 5.2 Raman spectra of all HO-P, HO-N and HO for comparison. A, B) Raman spectra of all the materials of study. C) Bar graph of the calculated D/G ratios for the various materials.

Further characterization was performed with Raman spectroscopy to examine the density of defects at surface level. The measurements of the materials were performed using a 514 nm wavelength laser to obtain the spectrums as shown in fig. 5.2, A and B where Raman peaks D and G were observed. Peak G ($\sim 1560 \text{ cm}^{-1}$) and D ($\sim 1350 \text{ cm}^{-1}$) corresponds to the pristine sp^2 graphene lattice structure and sp^3 defects found in the pristine sp^2 lattice respectively. The intensity of the two peaks can be expressed as a D/G ratio which reflects the density of defects found in the materials. The defect density acts as an indication of the rate of reactions that occurred at the materials' surfaces as earlier studies have proved that electrochemical reactions usually occur at sites of defects in the material. The D/G ratios are 0.93 for HO-P: $[\text{P}_4/\text{KOH}]$, 0.89 for HO-P: $[\text{P}_4]$, 0.97 for HO-P: $[\text{PH}_3]$, 1.03 for HO-P: $[\text{NaH}_2\text{PO}_2]$ and 0.95 for HO-P: $[\text{Na}_2\text{HPO}_3]$. The D/G ratios for the control materials were found to be 0.78 for HO-N and 0.83 for HO as shown in fig. 5.2, C. All phosphorus treated graphene oxides (GOs) were observed to possess higher defect densities and hence, more defects than the two control materials. This indicates that treatment of GOs with phosphorus sources introduces more defects into the materials as compared to the control materials.⁴⁻⁶ The average crystallite size (L_a) of the material can also be calculated using the intensities of the D and G peaks and the following equation:¹¹

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

where I_G and I_D refers to the intensity of the G and D peaks respectively while λ_{laser} is the wavelength (nm) of the laser used for obtaining Raman measurements. The average crystallite sizes were found to be 18.01 nm for HO-P: $[\text{P}_4/\text{KOH}]$, 18.82 nm for HO-P: $[\text{P}_4]$, 17.27 nm for HO-P: $[\text{PH}_3]$, 16.26 nm for HO-P: $[\text{NaH}_2\text{PO}_2]$ and 17.63 nm for HO-P: $[\text{Na}_2\text{HPO}_3]$. HO-N and HO has a L_a value of 21.48 nm and 20.18 nm respectively.

Fig. 5.3 Wide-range XPS spectra of all the materials for comparison. A, B) XPS spectra of HO-P, HO and HO-N. C) Bar graph of calculated C/O ratios derived from the peak intensities of the XPS spectra.

Additional information on the materials' surfaces can be analyzed with X-ray photoelectron spectroscopy (XPS) to obtain the elemental composition data. The technique acquires the elemental composition of the various major elements at their respective electronic states. The wide range XPS spectrums for all the materials were as shown in fig. 5.3, A and B. The main XPS peaks observed for all the materials are C 1s peak at 284.5 eV, O 1s peak at 534 eV. An additional P 2p peak at ca. 136 eV for observed for all phosphorus treated materials. The extent of oxidation of the materials was determined by the amount of oxygen containing groups present on the surface which was indicated by the C/O ratio calculated using the intensities of

the C 1s and O 1s peaks. The C/O ratios were observed to be 8.51 for HO-P: [P₄/KOH], 5.70 for HO-P: [P₄], 3.05 for HO-P: [PH₃], 3.02 for HO-P: [NaH₂PO₂] and 2.89 for HO-P: [Na₂HPO₃]. HO-N and HO were observed to have a ratio of 8.85 and 2.64 respectively as shown in the bar graph in fig. 5.3, C. Undoped HO-N that was exfoliated in inert nitrogen gas environment was observed to contain the least amount of oxygen containing groups as compared to phosphorus treated GOs. This may imply that exfoliation under a nitrogen gas atmosphere can result in the removal of more oxygen groups than reduction of GO with a phosphorus source. HO (graphite oxide) possessed the lowest C/O ratio and hence, the largest amount of oxygen groups. This was expected as HO did not undergo exfoliation and thermal reduction reaction resulting in a large number of oxygen groups still retained on the material's surface. In a comparison among the HO-P, the C/O ratios were found to be dependent on the type of phosphorus source used and the temperature at which the treatment occurs. The amount of oxygen containing groups was the lowest for phosphorus sources such as P₄, followed by PH₃, NaH₂PO₂ and lastly, Na₂HPO₃. The changes in the chemical procedure treatment may have led to lesser oxygen groups being removed during phosphorus reduction. This was observed in HO-P: [P₄/KOH] and HO-P: [P₄] where the latter material has a lower C/O value but it has undergone a higher treatment temperature. Interestingly, HO-P: [P₄/KOH] possessed a C/O ratio that was almost identical with that of thermally reduced HO-N. Phosphorus acts as a reducing agent in a highly reactive reaction with KOH where the white phosphorus undergoes a disproportionation reaction to generate phosphane and hypophosphite anion. This shows that such phosphorus-based reduction reactions exhibited similarly high reaction efficiency as compared to thermal shock (1000 °C) reduction reactions that was used to synthesized HO-N.

The wide-range XPS measurements have also proved the presence of P 2p (Fig. 5.3, a and B). It can be observed that only HO-P: [P₄/KOH], HO-P: [P₄] and HO-P: [PH₃] contained phosphorus after undergoing the treatment procedure. The percentage content of P 2p in the materials were 1.17 % for HO-P: [P₄/KOH], 3.65 % for HO-P: [P₄], 0.10 % for HO-P: [PH₃] and 0 %

for HO-P: [NaH₂PO₂] and HO-P: [Na₂HPO₃] (refer to Fig. 5.3, B). This indicates that only phosphorus sources, P₄ and PH₃ allows the successful incorporation of phosphorus into the materials. P₄ was also found to be a better dopant source than PH₃ as the latter gives a total P 2p content of only 0.10 %. Only hypophosphite and phosphite acted as reducing agents in the treatment process. Further fitting of the P 2p spectrums shows the presence of P-C and P-O bonds at ~ 136.0 eV and ~ 132.0 eV respectively.¹ In HO-P: [P₄/KOH], all the phosphorus existed only in the form of P-C while in HO-P: [P₄], 79.8 % of the phosphorus existed as P-C bonds and 20.2 % as P-O bonds. This shows that phosphorus treatment of the graphite oxides with white phosphorus results in the formation of mainly P-C bonds and P-O bonds as the minority.

Fig. 5.4 High-resolution XPS spectra of C 1s electronic state with fitted results.

HR-XPS measurements were also performed for the electronic state, C 1s with the results carefully fitted. The information obtained includes the type of interactions present and their respective quantitative percentages. The spectrums for the various materials were as shown in fig. 5.4. All materials except HO-P: [P₄/KOH] and HO-P: [P₄] displayed carbon and oxygen interactions at 284.5 eV for sp² hybridized carbon bonds (C=C), 285.7 eV for sp³ hybridized carbon bonds (C-C), 286.8 eV for alcohol/ether groups (C-O), 288.0 eV for carbonyl groups (C=O), 289.2 eV for carboxylic/ester groups (O-C=O) and lastly, 290.2 eV for π - π^* interactions. HO-P: [P₄/KOH] and HO-P: [P₄] which were previously found to contain the highest P 2p concentration displayed peaks for several carbon bonds and an additional C-P peak (~ 285.5 eV) as shown in fig. 5.4, A and B. The appearance of the C-P peak at 285.5 eV was also observed in previous studies.⁴ On the contrary, HO-P: [PH₃], HO-P: [NaH₂PO₂] and HO-P: [Na₂HPO₃] displayed the above mentioned carbon interactions with the absence of the C-P bond (refer to Fig. 5.4, C, D and E). The main carbon interactions detected were C=C and C-O. This may be due to an incomplete reaction with phosphorus sources resulting in an incomplete reduction of oxygen containing groups during treatment process. HO-N and HO (Fig. 5.4, F and G) also showed the carbon interactions as mentioned above with HO possessing only C=C and C-O bonds. The shape of the C 1s spectrum for HO-N was found to be similar to that of HO-P: [P₄/KOH] and HO-P: [P₄], indicating that the degree of oxidation of the materials was similar for all three materials. This was in agreement with earlier observation where the C/O ratios of these three materials were the highest and hence, they possessed the lowest oxygen content.

Fig. 5.5 ATR-IR spectrums recorded for the various materials. A) Comparison of HO with materials doped using P_4 and PH_3 as phosphorus sources. B) Comparison of HO with materials doped using NaH_2PO_2 and Na_2HPO_3 as phosphorus sources.

More information about the remaining oxygen functional group can be obtained using ATR-IR spectroscopy. Fig. 5.5, A shows that HO possessed typical oxygen functionalities like a hydroxyl group which was represented by the $-OH$ vibration at $\sim 3200\text{ cm}^{-1}$, $C-OH$ vibration at $\sim 1350\text{ cm}^{-1}$ and deformation vibration of $C-OH$ at 1060 cm^{-1} .¹² The vibrational band at ca. 950 cm^{-1} corresponds to the $C-O$ vibration of epoxide groups. Another vibration band that corresponds to oxygen functionalities is the $C=O$ vibration band of carboxylic acid at ca. 1720 cm^{-1} .^{1, 13} The Intense vibration band observed at 1620 cm^{-1} attributes to $C=C$ vibration of graphene but may also be related to the adsorbed water molecules in the material.¹³

Reduction of the GO in the presence of phosphorus resulted in the disappearance of most of these bands, leaving only a weak band at 1620 cm^{-1} which originates from $C=C$ in the graphene structure. In the case of $HO-P: [PH_3]$ where the degree of oxygen reduction was lower, the presence of weak bands at 1350 cm^{-1} and 1050 cm^{-1} that were due to the remaining unreduced $C-O$ groups could be observed. This was supported by the HR-XPS $C1s$ results shown earlier. The $-OH$ vibration band at ca. 3200 cm^{-1} was observed to show a significant decrease in its peak intensity. Reduction of the materials have also resulted in the disappearance of IR bands that arised from epoxide group stretching and $C=O$ vibration of carboxylic acid group. Other bands associated with $C-O$ vibration (1050 cm^{-1} and 1350 cm^{-1}) can still be observed for these materials but with significantly lower intensity. These conclusions were supported by earlier HR-

XPS C1s results where materials that showed a slight increase in C/O ratio which was due to the reduction of oxygen containing groups present in the materials.

5.2.2 Electrochemistry of phosphorus doped graphenes

Fig. 5.6 CV graphs for the various materials in phosphate buffer solution. Conditions: 100 mV s^{-1} , 50 mM PBS, pH 7.2.

Further investigation on the types of oxygen containing groups present in the materials can be obtained through the cyclic voltammetry technique. Epoxy, aldehyde and peroxy groups in graphene oxide has been known to undergo chemically irreversible reduction in previous studies.^{14,15} Hence, using cyclic voltammetry measurements in deoxygenated blank phosphate buffer solution (PBS); the reduction reactions of oxygen groups in the materials were studied. A reduction peak which corresponds to the reduction of the oxygen groups on the surface of the materials was observed at approximately -1200 mV. Different materials were observed to exhibit the reduction peak at slightly different reduction potentials of -1220 mV for HO-P: $[\text{P}_4/\text{KOH}]$, -1170 mV for HO-P: $[\text{PH}_3]$, -1210 mV for HO-P: $[\text{NaH}_2\text{PO}_2]$ and -1200 mV for HO-P: $[\text{Na}_2\text{HPO}_3]$ (refer to Fig. 5.6). HO displays a huge reduction peak at a much lower potential of -1350 mV. HO-P: $[\text{P}_4]$ and HO-N did not exhibit similar reduction peaks at all due to the materials possessing two of the lowest amount of oxygen functionalities on the surface. HO-P: $[\text{P}_4/\text{KOH}]$ displays an oxygen reduction peak but of a relatively small reduction current due to the presence of a low oxygen content in its structure. However, HO-P: $[\text{P}_4/\text{KOH}]$ also showed an additional oxidation peak at -1130 mV which was not found in any other materials.

Fig. 5.7 Cyclic voltammograms for the various materials measured in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Conditions: scan rate 100 mV s^{-1} , 50 mM PBS, pH 7.2.

Consequently, studies on the electrochemical activity and heterogeneous electron transfer rates of the materials were performed. The CV scans of the different materials were executed in a standard ferro/ferricyanide electrolyte solution as shown in fig. 5.7. The peak-to-peak separation (ΔE_{p-p}) between the oxidation and reduction peaks for each material was calculated as the value reflects on the electron transfer rate of the material at the surface. The ΔE_{p-p} values were 390 mV for HO-P: $[\text{P}_4/\text{KOH}]$, 440 mV for HO-P: $[\text{P}_4]$, 200 mV for HO-P: $[\text{PH}_3]$ and 290 mV for HO-P: $[\text{NaH}_2\text{PO}_2]$ and 200 mV HO-P: $[\text{Na}_2\text{HPO}_3]$. HO-N and HO have ΔE_{p-p} values of 190 mV and 440 mV respectively. All HO-P materials were observed to have larger peak-to-peak separation than HO-N. HO-P: $[\text{PH}_3]$, HO-P: $[\text{NaH}_2\text{PO}_2]$ and HO-P: $[\text{Na}_2\text{HPO}_3]$ displayed almost similar ΔE_{p-p} values. HO has the largest peak-to-peak separation due to the material possessing the highest of oxygen containing groups among all the materials. This poor electrochemical behavior observed was due to the negative charges presented by the oxygen groups (typical of graphite oxides) causing the material to display poor conductivity during CV scans.² HO-N possessed the least amount of oxygen containing groups and hence, the smallest peak separation value to be measured. The heterogeneous electron transfer rates (k_{obs}^0) were then calculated with the Nicholson approach where ΔE_{p-p} was directly related to a dimensionless parameter ψ which was eventually related to k_{obs}^0 .¹⁶ The calculated k_{obs}^0 values were 8.25×10^{-5}

cm s^{-1} for HO-P: $[\text{P}_4/\text{KOH}]$, $4.41 \times 10^{-5} \text{ cm s}^{-1}$ for HO-P: $[\text{P}_4]$, $1.17 \times 10^{-3} \text{ cm s}^{-1}$ for HO-P: $[\text{PH}_3]$, $3.44 \times 10^{-4} \text{ cm s}^{-1}$ for HO-P: $[\text{NaH}_2\text{PO}_2]$ and $1.10 \times 10^{-3} \text{ cm s}^{-1}$ for HO-P: $[\text{Na}_2\text{HPO}_3]$. HO and HO-N have k_{obs}^0 values of $4.12 \times 10^{-5} \text{ cm s}^{-1}$ and $1.29 \times 10^{-3} \text{ cm s}^{-1}$.

Table 5.1 Specific resistivity and sheet resistivity for the various HO-P materials.

Materials	Specific resistivity [$\Omega \text{ cm}$]	Sheet resistivity [$\Omega \text{ Sq}^{-1}$]
HO-P: $[\text{NaH}_2\text{PO}_2]$	7.36×10^1	1.49
HO-P: $[\text{PH}_3]$	4.23×10^{-3}	2.56×10^{-1}
HO-P: $[\text{P}_4]$	4.63×10^{-3}	5.57×10^{-1}
HO-P: $[\text{P}_4/\text{KOH}]$	1.12×10^{-2}	8.56×10^{-1}
HO-P: $[\text{Na}_2\text{HPO}_3]$	2.14×10^1	5.31×10^1

Doping of the graphite oxides with electron donating phosphorus resulted in the materials having a much higher conductivity than undoped graphene, despite both materials to have very similar C/O ratios. As such, we can assume that phosphorus acts as a n-type dopant in the materials. The increase in free charge carriers was directly reflected in the decrease of sample specific resistivities observed. Graphite oxide is an electrical insulator due to the disrupted sp^2 bonding in the graphene structure.³ The specific resistivities and sheet resistivities values measured for all materials were summarized in table 5.1. The lowest resistivity values obtained were $4.23 \times 10^{-3} \Omega \text{ cm}$ and $4.63 \times 10^{-3} \Omega \text{ cm}$ for HO-P: $[\text{P}_4/\text{KOH}]$ and HO-P: $[\text{P}_4]$ respectively. The resistivity of HO-P: $[\text{PH}_3]$ was slightly higher at $1.12 \times 10^{-2} \Omega \text{ cm}$. Materials with the lowest degree of oxygen reduction, HO-P: $[\text{NaH}_2\text{PO}_2]$ and HO-P: $[\text{Na}_2\text{HPO}_3]$ have also exhibited one of the highest resistivity values of $2.14 \times 10^1 \Omega \text{ cm}$ and $7.69 \times 10^1 \Omega \text{ cm}$, respectively.

Fig 5.8 Current–voltage characteristics of HO-P, HO-N and HO.

Similarly, the current-voltage (i/V) properties of the materials were investigated through further conductivity measurements via a gold interdigitated electrode (Au-IDE). The results obtained were as shown in fig. 5.8. HO-P: $[P_4]$ was found to exhibit the highest conductivity followed by HO-P: $[P_4/KOH]$ and HO-N. HO-P: $[PH_3]$, HO-P: $[NaH_2PO_2]$, HO-P: $[Na_2HPO_3]$ and HO exhibited similar level of conductivity which was the lowest among all the materials compared.

Discussion

We have successfully produced less oxidized phosphorus doped reduced graphene oxides, demonstrating the possibility of a phosphorus treatment process that was capable of removing oxygen groups during doping. Experimenting with the use of different phosphorus sources for doping were attempted with different reaction conditions to investigate the influence of different doping sources and conditions on the properties of the resultant materials. The electron-donating phosphorous dopant resulted in its doped materials to exhibit very high conductivities which were way higher than that of the undoped control material.

Experimental

Materials:

Graphite oxide was prepared according to Hofmann method from graphite (2-15 μm , 99.9995%, Alfa Aesar). Sulfuric acid (98 %), nitric acid (68 %), potassium chlorate (> 99 %), hydrochloric acid (37 %), silver nitrate (> 99.8 %), barium nitrate (> 99 %), sodium hydroxide (>98 %), potassium hydroxide (> 85 %), carbon disulfide (> 99.5 %) and methanol (> 99.9 %) were obtained from Penta, Czech Republic. Nitrogen (99.9999 % purity) was obtained from SIAD, Czech Republic. Sodium hypophosphite monohydrate (> 99 %) was obtained from Lach Ner (Czech Republic). Sodium phosphite dibasic pentahydrate and white phosphorus were obtained from Sigma-Aldrich, Czech Republic. Potassium phosphate dibasic, N,N-dimethylformamide (DMF), potassium ferrocyanide, sodium phosphate monobasic, potassium chloride, sodium phosphite dibasic pentahydrate and sodium chloride were obtained from Sigma-Aldrich, Singapore. Deionized water was used for the preparation of the electrolytes that were used in any electrochemical measurement. Glassy carbon working electrode (GC), platinum auxiliary electrode (Pt) with a diameter of 3 mm and Ag/AgCl reference electrode were purchased from Autolab, The Netherlands.

Apparatus:

A scanning electron microscope (JEOL 7600F field-emission, Japan) was used to obtain SEM images. The samples were attached onto an aluminum stub using a conductive carbon tape. The XPS and HR-XPS measurements were obtained using a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). All scans were performed with a 12.53 kV X-ray source. An aluminum XPS sample holder and a sticky conductive carbon tape was used to attach the XPS samples. Care was taken to ensure that a homogeneous and uniform layer of the material was attached onto the tape before the sample was placed inside the XPS

chamber for a measurement. Confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector was used for all Raman spectroscopic measurements. Silicon wafer was used for performing calibration at 0 cm^{-1} and 520 cm^{-1} to give a peak position resolution of less than 1 cm^{-1} . Raman measurements were executed using a 514.5 nm Ar laser, an Olympus optical microscope and a 100 x objective lens. The preparation of all materials involved a well-compressed and compacted material prior to any measurement. Electrochemical voltammetric measurements were performed using a microAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) and a NOVA 1.7 software (Eco Chemie). Nova 1.7 software was published by Metrohm Autolab B.V. in support of Metrohm Autolab's potentiostat/galvanostat equipment. The FT-IR measurement was performed on a FTIR spectrometer NICOLET 6700 (Thermo Scientific, USA). Diamond ATR crystal and DTGS detector were used for the measurements in the range of $4000 - 400\text{ cm}^{-1}$. For electrical resistivity measurements of graphene materials, 25 mg of the powder material was first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by the 4-probe technique using the Van der Pauw method.¹⁷ The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit. The measuring current was set to 10 mA. Conductivity measurements were performed with Au-IDE. 1 mg mL^{-1} suspensions of the materials were prepared in deionized water which was used to coat the electrode. $1\text{ }\mu\text{L}$ of the suspension was coated onto the interdigitated area and left to dry under a lamp to obtain a randomly deposited layer on the electrode's surface. Linear sweep voltammetric measurement was then performed on the electrode at a scan rate of 200 mV s^{-1} to obtain the I - V results for the materials. Five replicates were performed for each material.

Procedures:

*Graphite oxide (HO) preparation with the Hofmann method.*¹⁰ 87.5 mL of sulfuric acid (98 % concentration) and 27 mL of nitric acid (68 %) were added to a reaction flask containing a magnetic stir bar. The mixture was subsequently cooled to 0 °C and 5 g of graphite was added. The mixture was then vigorously stirred to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, 55 g of potassium chlorate was slowly added to the mixture. Upon completion dissolution of the potassium chlorate, the reaction flask was then left loosely capped to allow the gas evolved during the reaction to escape. The mixture was then continuously stirred for 72 h at room temperature. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5 %) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulfate ions (with AgNO₃ and Ba(NO₃)₂ respectively) was achieved. Graphite oxide (GO) slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Preparation of phosphorus doped materials. The reduction of GO with low valence phosphorus compounds was performed in an alkaline environment (1 M NaOH) where the compounds have the highest reduction potential (H₂PO₂⁻ and HPO₃²⁻). Reduction of HO-GO using white phosphorus was investigated under different pH environments: neutral pH and alkaline condition. In alkaline environment, white phosphorus undergoes a disproportionation reaction to form phosphane and H₂PO₂⁻ anion. In order to avoid explosive reaction of phosphane with oxygen the reaction was performed under an argon atmosphere.

Preparation of GO doped with P₄/KOH. 0.2 g of HO-GO was dispersed in 100 ml of 1 M KOH by ultrasonication and mixture was placed in 250 ml flask with argon inlet and reflux condenser. 5 g of freshly cut white phosphorus was then added into the reaction mixture. The mixture was then placed in an oil bath with vigorous stirring for 6 hours while being kept under reflux. The

reaction mixture was then subsequently cooled to room temperature and flushed with argon gas to avoid explosive reactions between phosphane and oxygen. The GO reduced with phosphorus was separated by suction filtration and repeatedly washed with water and carbon disulfide to remove any traces of unreacted white phosphorus. The final product was dried under vacuum at 60 °C for 48 hours.

Preparation of GO doped with P_4 . 0.2 g of HO-GO was dispersed in deionized water by ultrasonication and 5 g of freshly cut white phosphorus was added. The reaction mixture was then vigorously stirred and refluxed for 6 hours. The reaction mixture was cooled down where the remaining white phosphorus was then dissolved in carbon disulfide. The graphene obtained was separated by suction filtration and washed repeatedly with water and carbon disulfide to remove unreacted white phosphorus. The final product was dried under vacuum at 60 °C for 48 hours.

Preparation of GO doped with PH_3 . 20 g of freshly cut white phosphorus was placed in a reaction flask with an argon inlet and 250 ml of 5 M NaOH was added. The phosphane gas evolved from the reaction under the heating and was mixed with argon and introduced through the reflux condenser into the reaction flask with 0.2 g GO dispersed in 100 ml of deionized water. The reaction mixture was then vigorously stirred for 6 hours. The GO reduced with phosphorus was separated by suction filtration and repeatedly washed with water and carbon disulfide to remove any traces of unreacted white phosphorus formed by oxidation of phosphane. The final product was dried under vacuum at 60 °C for 48 hours.

Preparation of GO doped with NaH_2PO_2 . 0.2 g of GO was dispersed in 100 ml of 1 M NaOH by ultrasonication and 0.05 mol of $NaH_2PO_2 \cdot H_2O$ was added. The reaction mixture was refluxed for 24 hours after which, the graphene obtained was filtered using a nylon membrane (0.45 μm) and repeatedly washed with deionized water. The final product was then dried under vacuum at 60 °C for 48 hours.

Preparation of HO-GO doped with Na_2HPO_3 . 0.2 g of GO was dispersed in 100 ml of 1 M NaOH by ultrasonication and 0.05 mol of $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ was added. The reaction mixture was then refluxed for 24 hours and the graphene obtained was filtered using a nylon membrane (0.45 μm) and repeatedly washed with deionized water. The final product was then dried under vacuum at 60 $^\circ\text{C}$ for 48 hours.

Preparation of HO-N material. The thermal exfoliation of GO was carried out at 1000 $^\circ\text{C}$ for 12 minutes. GO was placed inside a porous quartz glass capsule connected to a magnetic manipulator in a vacuum tight quartz reactor under controlled atmosphere. This system provided a temperature gradient of over 1000 $^\circ\text{C min}^{-1}$. The sample was then flushed repeatedly with pure nitrogen and subsequently inserted into a preheated reactor in nitrogen (99.9999% purity) atmosphere (pressure: 100 kPa) to produce noble metal doped graphene hybrid material. The flow of the nitrogen at 1000 $\text{mL} \cdot \text{min}^{-1}$ resulted in the removal of the by-products of the reactions.

Electrochemical measurements. All glassy carbon electrodes were cleaned by polishing with an alumina suspension to renew the electrode surface then washed and wiped dry prior to any use. The materials were dispersed in DMF as the organic solvent to obtain a 0.5 $\text{mg} \cdot \text{mL}^{-1}$ suspension. The suspension was then sonicated for 5 minutes at room temperatures before every use. A cleaned GC electrode was then modified by coating with a 1 μL aliquot of the suspension and left to dry under a lamp to give a layer of randomly dispersed material on the GC surface. This process was repeated three times to obtain three layers of homogeneous coatings. EPPG electrode's surface was renewed before each measurement by polishing with the alumina suspension, washed with deionized water and wiped dry before use. The modified GC electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then placed into an electrochemical cell which contains the electrolyte solution and the measurements were then taken. The EPPG electrode will be used in place of the modified GC electrode together with the

reference and counter electrode in measurements for the EPPG electrode. The electrolytes used were 50 mM pH 7.4 phosphate buffer solution (PBS) as the blank buffer electrolyte and 10 mM Ferro/Ferricyane dissolved in PBS. All measurements were performed for two consecutive scans at a scan rate of 100 mV s^{-1} . Three measurements were carried out for each material and also for each electrolyte.

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Chapter 6

Sulfur-doped Graphene via Thermal Exfoliation of Graphite Oxide in H₂S,
SO₂ or CS₂ Atmosphere

6.1	<i>Introduction</i>
6.2	<i>Results</i>
6.2.1	<i>Properties of sulfur-doped graphenes</i>
6.2.2	<i>Electrochemistry of sulfur-doped graphenes</i>
6.3	<i>Discussion</i>
6.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Petr Šimek, Zdeněk Sofer, Martin Pumera. Sulfur-Doped Graphene via

Thermal Exfoliation of Graphite Oxide in H₂S, SO₂, or CS₂ Gas. *ACS Nano*, 2013, **7**, 5262.

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Introduction

In the group VI elements, sulfur is among the most popular choice for the doping of heteroatoms in the graphene structure. As previously mentioned in Chapter 2, sulfur was known to have an electronegative value similar to that of carbon and thus; sulfur heteroatom dopant will be an interesting case to investigate. Earlier reports on sulfur doped graphene related materials utilized synthesis methods such as mechanically mixing the individual components^{1,2} to obtain sulfur/graphene composites or heating graphene with benzyl disulfide to create sulfur-epoxy bonds in graphene.³ In this project, the n-type sulfur dopant was incorporated into the graphene structure via thermal exfoliation in the presence of various sulfur precursors, sulfur dioxide (SO₂), hydrogen sulfide (H₂S) and carbon disulfide (CS₂) (Scheme 6.1). Graphite oxides were used as the starting material. To make things more interesting, we have employed three different synthesis methods for the graphite oxides: a) Staudenmaier,⁴ b) Hofmann⁵ and c) Hummers.⁶ As such, this project will be a comparison study to investigate the influence of different synthesis methods of carbon precursors and different sulfur sources on the properties of the sulfur-doped nanocarbon materials. Further experiments on the applications of sulfur-doped materials were also conducted for oxygen reduction reactions (ORRs) where the materials were observed to display electrocatalytic ability, allowing them to be potential candidates as metal-free ORR catalyst.

Scheme 6.1 Fabrication of sulfur doped graphene by thermal exfoliation of graphite oxide prepared by Staudenmaier, Hofmann and Hummers method in CS_2 , H_2S or SO_2 atmospheres.

Results

6.2.1 Properties of sulfur-doped graphenes

The sulfur doped graphenes in this experiment were synthesized using graphite oxides as the starting material. Three different methods of synthesizing graphite oxides from graphite were employed for comparison of the final products (sulfur doped graphenes). The three methods are Staudenmaier (ST), Hofmann (HO) and Hummers (HU) methods. ST uses fuming nitric acid, sulfuric acid (H₂SO₄) and potassium chlorate (KClO₃) in its synthesis procedure to yield graphite oxide from graphite. Meanwhile, HO uses 68% nitric acid (HNO₃), H₂SO₄ and KClO₃ and HU uses a mixture of H₂SO₄, potassium permanganate (KMnO₄) and sodium nitrate (NaNO₃). Consequently, the graphite oxide obtained was placed in a quartz tube and exfoliated in atmospheres (1000 mbar) consisting of different gaseous sulfur sources (SO₂, H₂S or CS₂) at 600 °C or 1000 °C. The final products, sulfur doped graphenes were then extensively characterized using scanning electron microscopy (SEM), X-Ray photoelectron spectroscopy (XPS), Raman spectroscopy and combustible elemental analysis (EA). The sulfur doped materials were labeled according to the method by which the graphite oxide was synthesized, the sulfur source used and the temperature at which the doping procedure was carried out. Example: HO-S: [CS₂/1000 °C] is sulfur doped graphene synthesized from Hofmann method graphite oxide, doped using CS₂ source and exfoliated at 1000 °C. The control materials used in this project were graphene oxides synthesized by the three methods that were completely exfoliated in a thermal reduction reaction but not treated with any sulfur sources. They are labeled as ST, HO and HU which represents Staudenmaier thermally reduced graphene oxide (TRGO), Hofmann TRGO and Hummers TRGO respectively.

Fig. 6.1 SEM images of all the sulfur doped graphenes prepared from Hofmann, Hummers, and Staudenmaier graphite oxides. Magnification of a) x 370, b) x 6 000, c) x 10 000 and d) x 50 000. Scale bars of (a) 100 nm, (b, c) 1 µm and (d) 10 µm.

Using scanning electron microscopy (SEM), we can clearly observe the morphology and topographical differences between all the materials if present. The images of the sulfur doped graphenes were taken at various magnifications of x 370, x 6 000, x 10 000 and x 50 000 as shown in fig. 6.1. From the images, we can conclude that all the materials have been successfully exfoliated as every material presented structures that are similar to exfoliated graphene oxides where well separated sheets could be clearly seen. Thus, we can assume that different methods' starting materials (graphite oxides), the type of sulfur sources used or the reaction conditions have no major influences on the structures of the final products.

Fig. 6.2 Raman spectrums of sulfur doped graphenes and the control materials. The spectra are plotted accordance to their starting materials for comparison. D) D/G ratios from the spectrums for all the materials to be compared.

Determination of structural information such as the density of defects in the materials can be accomplished using the Raman spectroscopy technique. The recorded spectrums display a G peak (pristine sp² graphene lattice) at ~1560 cm⁻¹ and a D peak (defects in pristine sp² lattice) at ~1350 cm⁻¹. The intensities of the D and G peaks allow the calculation of the D/G ratios for each material which was an indicator of the level of electrochemical activity of the materials. This was based on earlier results where electrochemical reactions were found to most likely occur at these sites of defects. In fig. 6.2, the Raman spectra of the materials were grouped and plotted according to their starting materials used with the starting materials included as well. For ease of comparison, all the spectrums, graphs and tables will be presented in a similar manner. The obtained D/G ratios for the Staudenmaier materials were 0.77 for ST, 0.62 for ST-S: [H₂S/600 °C] and 0.69 for ST-S: [SO₂/600 °C] (refer to Fig. 6.2, A and D). Derivation of the average crystalline size of the materials can be achieved using D/G ratios and the following equation:⁷

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

The I_G/I_D is the ratio of the intensities of the D and G bands respectively and λ_{laser} refers to the laser wavelength (nm) used during Raman measurements. The L_a values obtained were 21.7 nm for ST, 27.1 nm for ST-S: [H₂S/600 °C] and 24.3 nm for ST-S: [SO₂/600 °C]. This result shows that a change in the type of sulfur source used may affect the amount of defects in the material and hence, it's resulting crystalline size. It was observed that ST possessed the highest D/G ratio as compared to the two other sulfur doped graphene oxides.

Similarly, all HO-S and HO were examined with Raman spectroscopy (refer to Fig. 6.2, B and D) where their D/G ratios were found to be 1.09, 0.84, 0.85, 0.81 and 0.91 for HO, HO-S: [H₂S/600 °C], HO-S: [SO₂/1000 °C], HO-S: [SO₂/600 °C] and HO-S: [CS₂/1000 °C] respectively. Similarly, the starting material HO displayed a higher D/G ratio as compared to all the HO-S materials. The use of H₂S and SO₂ sulfur sources resulted in similar D/G ratios of approximately 0.83 except for CS₂ which gave an exceptionally high reading of 0.91. L_a values of these materials

were calculated to be 15.4 nm, 20.0 nm, 19.7 nm, 20.8 nm and 18.5 nm for HO, HO-S: [H₂S/600 °C], HO-S: [SO₂/1000 °C], HO-S: [SO₂/600 °C] and HO-S: [CS₂/1000 °C] respectively. This indicates that HO-S graphenes have larger crystalline structures as compared to HO. HU-S materials were experimented to obtain D/G ratios of 0.97 for HU, 0.90 for HU-S: [H₂S/600 °C] and 0.99 for HU-S: [SO₂/600 °C] (Fig. 6.2, C and D). It can be observed from the results that HO-S materials were found to possess a higher amount of defects as compared to ST-S and HO-S materials. The derived average crystalline sizes were 17.3 nm for HU, 16.9 nm for HU-S: [H₂S/600 °C] and 18.5 nm for HU-S: [SO₂/600 °C]. The Raman spectroscopic results have shown that a logical trend within each type of starting material does exist. However, the comparison between sulfur doped graphenes of similar sulfur source and temperature showed no such trend. It could be clearly observed that all HO-S and HO possessed the highest D/G ratios followed by HU-S and HU and finally, ST-S and ST with the lowest D/G ratios. It should be noted that small increase of observed background in Raman spectra was due to weak photoluminescence of the sample.⁸

Fig. 6.3 Wide-range XPS spectra of ST-S, HO-S and HU-S materials. ST, HO and HU starting materials were also compared. D) Calculated C/O ratios of all materials. E) Total percentage of S 2p content present in the sulfur doped materials.

With sulfur atoms doped onto the graphene sheets, surface composition of the materials were examined to study the various functional groups present on the materials' surfaces. X-ray photoelectron spectroscopy (XPS) was utilized for this purpose to obtain the identities and quantities of the major elements present in their respective electronic states. In the wide range scans for all the materials, it can be observed that C 1s peak occurs at ~ 284.5 eV, O 1s at ~ 534 eV and S 2p at ~ 167 eV (refer to Fig. 6.3, A, B and C). An S 2p peak appeared at 167 eV for ST-S: [H₂S/600 °C] and ST-S: [SO₂/600 °C] while such a peak was not found in the ST spectrum, showing the successful incorporation of sulfur in the materials. The degree of oxidation in the material was directly reflected by the calculated C/O ratios using the intensities of the C 1s and O 1s peaks. A higher ratio indicates lesser oxygen functionalities on the surface and hence, a less oxidized material. It was found that the C/O ratio was 24.09 for ST, ST-S: [H₂S/600 °C] has a value of 13.44 and ST-S: [SO₂/600 °C] has a value of 9.30. It can be observed that ST-S materials have lower C/O ratios as compared to undoped ST (refer to Fig. 6.3, D). This shows that the exfoliation of graphite oxides in gaseous sulfur containing atmosphere resulted in the incorporation of more oxygen functionalities than exfoliation procedures carried out in nitrogen gas atmosphere. Similarly, HO-S materials showed the presence of a C 1s, O 1s and S 2p peak at binding energies identical to those reported earlier for ST-S materials. HO exhibited only a C 1s and an O 1s peak without the presence of S 2p peak, clearly indicating the successful incorporation of sulfur into the graphene sheets. The obtained C/O ratios for HO materials were 18.23 for HO, 12.61 for HO-S: [H₂S/600 °C], 10.17 for HO-S: [SO₂/1000 °C], 9.86 for HO-S: [SO₂/600 °C] and 17.02 for HO-S: [CS₂/1000 °C]. HO-S materials were also observed to have lower C/O ratios than HO. This result supports earlier conclusion that exfoliation under a gaseous sulfur atmosphere results in the inclusion of more oxygen functionalities than exfoliation in a gaseous nitrogen atmosphere. Among the different sulfur sources, CS₂ proved to give the highest C/O ratio indicating that exfoliation in a gaseous CS₂ atmosphere caused a larger

extent of elimination of the oxygen functional groups from the material's surface as compared to exfoliation in other sulfur sources. These results were in good agreement with the results obtained from the ζ -potential measurements which will be further elaborated in the next section. Likewise, HU-S materials showed C 1s, O 1s and S 2p peaks at similar binding energies of ~ 285 eV, ~ 535 eV and ~ 167 eV respectively. Presence of sulfur atoms in HU-S materials were also proven by the S 2p peak found only in HU-S materials' spectrums and not in HU's XPS spectrum. The C/O ratios were found to be 19.28 for HU, 12.19 for HU-S: [H₂S/600 °C] and 11.49 for HU-S: [SO₂/600 °C]. The trend of the starting material, HU possessing a higher C/O ratio than the HU-S doped materials was once again observed. All the materials showed a consistent trend only within the same starting material category but not within the same sulfur source or exfoliation temperature. The total S 2p content at each material's surface detected by XPS was plotted in fig. 6.3, E. The percentages obtained were 0.75 for ST-S: [H₂S/600 °C] and 0.87 for ST-S: [SO₂/600 °C] for ST materials. HO materials possessed percentages of 4.44 for HO-S: [H₂S/600 °C], 2.16 for HO-S: [SO₂/1000 °C], 2.13 for HO-S: [SO₂/600 °C] and 4.07 for HO-S: [CS₂/1000 °C]. HU materials were also found to have the following percentages of 7.03 for HU-S: [H₂S/600 °C] and 6.67 for HU-S: [SO₂/600 °C]. It was observed that HU-S materials possessed the highest sulfur content, followed by ST-S and lastly HO-S materials. Interestingly, the extent of S doping in graphene is more likely influenced by the type of graphite oxide used than on the type of sulfur source utilized. This is a significant observation as ST, HO and HU graphite/graphene oxides are frequently used interchangeably in several literatures based on the assumption that all three methods produce materials of similar properties.⁹

Fig. 6.4 High-resolution XPS spectrums of the S 2p electronic state for ST-S, HO-S and HU-S materials.

Identification and quantification of each bond type for each element was achieved through the high resolution X-ray photoelectron spectroscopic (HR-XPS) technique. Measurements were performed for a specific electronic state of each element of interest at their respective range of binding energies. HR-XPS scans were performed for S 2p and C 1s electronic states at ca. 167 eV and 284.5 eV respectively as shown in fig. 6.4 for S 2p and fig. 6.6 for C 1s. All the S 2p spectrums displayed a single broad symmetrical peak at 167 eV, indicating the existence of only one type of S bonding interaction at the surface. It can be concluded that the S 2p peak constitutes of mainly sulfur in the S⁶⁺ valence state which further indicates the presence of SO₃H group.¹⁰ These findings were also confirmed by the ζ -potential results and the ATR FT-IR spectra obtained for the materials (Fig. 6.7 and Fig. 6.5).

Fig. 6.5 ATR FT-IR spectra of HO-S: [CS₂/1000 °C] as a representative for all sulfur doped materials. The vibration bands at 1311 cm⁻¹ and 1373 cm⁻¹ corresponds to O=S=O stretching in SO₃H.¹¹

Interestingly, the presence of SO₃H group was also found on the surfaces of materials exfoliated in H₂S and CS₂ containing atmosphere. Hydrogen sulfide acts as a reducing agent in the reaction with graphite oxide where sulfur was oxidized to higher valence state and was covalently bonded to the graphene. This was confirmed by the higher C/O ratio measured by XPS and combustion elemental analysis (EA) which will be discussed later. On the contrary, sulfur dioxide acts as an oxidizing agent as much lower C/O ratios are observed for materials doped using SO₂ source. At high temperatures of 1000 °C, the exfoliation in gaseous SO₂ atmosphere led to an oxidation of the exfoliated graphene.

Fig. 6.6 High-resolution XPS spectrums of C 1s electronic state for ST-S, HO-S and HU-S materials. XPS spectrums of control materials, ST, HO and HU were included for comparison.

HR-XPS scans for the C 1s electronic state at approximately 284.5 eV were obtained for all the materials as shown in fig. 6.6. Fitting of the C 1s spectrum was performed to identify and quantify the various possible carbon bonds present on the materials' surface. It was observed that all the starting materials (ST, HU, HO) displayed six carbon interactions at 284.5 eV for C=C, 285.7 eV for C-C, 286.8 eV for C-O, 288.0 eV for C=O, 289.2 eV for O-C=O and 290.8 eV for π - π interaction. All sulfur doped materials also exhibited the six carbon bonds at similar respective binding energies. The appearance of a C-S peak was also detected at approximately 286.5 eV which was of a higher binding energy than C-O due to oxygen being more electronegative which resulted in C-O displaying stronger charging behavior. The presence of the C-S peak indicates not only the successful incorporation of sulfur during exfoliation but also implications that sulfur exists inside the lattice structure of the graphene and was covalently bonded to the graphene.

Table 6.1 Combustional elemental analysis results for all the materials.

Sample	Wt. % N	Wt. % C	Wt. % S	Wt. % H	Wt. % O
ST-S: [H ₂ S/600 °C]	< 0.1	86.27	< 0.1	1.10	12.63
ST-S: [SO ₂ /600 °C]	< 0.1	86.33	< 0.1	0.84	12.83
ST	< 0.1	93.82	< 0.1	< 0.05	6.18
HO-S: [H ₂ S/600 °C]	< 0.1	78.3	8.37	1.06	12.27
HO-S: [SO ₂ /600 °C]	< 0.1	76.54	3.69	0.90	18.87
HO-S: [CS ₂ /1000 °C]	< 0.1	80.33	7.34	1.35	10.98
HO-S: [SO ₂ /1000 °C]	< 0.1	77.01	4.12	0.95	17.92
HO	0.42	91.58	< 0.1	< 0.05	7.52
HU-S: [H ₂ S/600 °C]	0.87	72.28	11.99	1.50	13.36
HU-S: [SO ₂ /600 °C]	1.52	69.73	10.42	0.86	17.47
HU	2.11	88.57	0.97	< 0.05	8.35

Compared to high surface sensitivity of the XPS technique, the combustible elemental analysis provides information on the “bulk” composition of the materials. The EA results obtained (refer to Table 6.1) were found to be in agreement with the XPS data reported earlier. The highest sulfur content was found to be present in the materials prepared from Hummers method graphite oxide (11.99 wt. % S in HU-S: [H₂S/600 °C] and 10.42 wt. % S in HU-S: [SO₂/600 °C]). The second highest sulfur content was detected in the materials prepared from Hofmann method graphite oxide (4.12 wt. % in HO-S: [SO₂/1000 °C] and 3.69 wt. % HO-S: [SO₂/600 °C]). Higher amount of sulfur were incorporated in materials that use low valence sulfur sources during exfoliation, i.e., hydrogen sulfide and carbon disulfide. The concentrations of sulfur in HO-S materials doped with these sulfur precursors were 8.37 wt. % for HO-S: [H₂S/600 °C] and 7.34 wt. % for HO-S: [CS₂/1000 °C]. The sulfur content in ST-S materials doped using H₂S and SO₂ were below 0.1 wt. %. This can be explained by the incomplete formation of sulfur dioxide during combustion analysis. Since the sulfur dioxide formed was used for the measurement of sulfur content in the material, a slight inaccuracy may be present where actual values may be higher than the measured ones. As such, we can conclude that the incorporation of sulfur was dependent on the degree of oxidation in the graphite oxide and hence, the method of preparation of the starting material. The type of sulfur source used may also influenced the resultant sulfur content, e.g. hydrogen sulfide and carbon disulfide presents sulfur in the -2 oxidation state resulting in the material having a higher C/O ratio and also a higher amount of sulfur. These results were consistent with the observations obtained from the ζ -potential measurements for the materials.

6.2.2 Electrochemistry of sulfur-doped graphenes

Fig. 6.7 Zeta-potentials of ST-S, HO-S and HU-S materials. The control materials, ST, HU and HO are included for comparison.

The ζ -potentials of the materials were determined to examine their dispersibility in water medium (Fig. 6.7). Sulfur doped ST reduced by hydrogen sulfide and sulfur dioxide displayed slightly higher (absolute values) ζ -potential of - 40 mV and - 50 mV respectively as compared to ST (- 40 mV). This may be due to the bonding of sulfonic acid group ($-\text{SO}_3\text{H}$) to the graphene structure resulting in lesser sulfur in the materials and hence, ζ -potential was most likely to be influenced by the oxygen functionalities found in the materials instead. In the comparison with HO-S and HO materials, a different trend was observed. HO possessed a ζ -potential of + 10 mV, suggesting that the material had undergone a high extent of reduction during synthesis. At the same time, the positive potential measured may also be due to nitrogen contamination that may be present in the HO. Materials doped with H₂S and SO₂ sources were observed to have more negative potentials of - 30 mV for H₂S, - 30 mV and - 20 mV for SO₂ at 600 °C and 1000 °C respectively. The high negative potentials observed were likely to be attributed to $-\text{SO}_3\text{H}$ and oxygen groups present in the materials. HO-S: [CS₂/1000 °C] exhibited a lower ζ potential of - 10 mV even though it was earlier found to have a similar elemental composition as HO-S: [H₂S/600 °C]. HU-S materials were observed to have ζ -potentials of - 40 mV for HU-S: [H₂S/600 °C] and - 40 mV for HU-S: [SO₂/600 °C] which were similar to the

potentials measured for ST-S materials. HU displayed a lower potential of -10 mV, similar to HO. In conclusion, all sulfur doped materials exhibited higher absolute values of ζ -potentials as compared to undoped materials and hence, were more stable when dispersed in aqueous solutions. This can be explained by the presence of two functional groups: acidic -SO₃H group and unreduced oxygen groups in the materials. The presence of -SO₃H group was expected for materials exfoliated in SO₂ source but surprisingly also for H₂S source. This was proven by earlier XPS results showing the presence of -SO₃H group (refer to Fig. 6.4) where the binding energy and full width half maximum (FWHM) of the S 2p peak was similar for all the sulfur doped materials. It was interesting to note that no thiol group (-SH) was detected for materials doped with hydrogen sulfide source (~162 eV). This phenomenon was also observed in earlier studies where the use of thiol precursor as the sulfur source yielded sulfonic groups instead of thiol groups.¹⁰ Both XPS and elemental analysis results have also confirmed that higher oxygen content was present in materials doped with SO₂ source than those doped with H₂S source. This was anticipated as the SO₂ groups contain oxygen atoms that contributed to the total oxygen content while H₂S has to react with oxygen groups in the materials to form -SO₃H.

Fig. 6.8 Electrical resistivities of ST-S, HO-S, HU-S, ST, HO and HU.

Table 6.2 Conductivities of Sulfur-Doped Graphenes.

Sample	Resistivity ($\Omega\cdot\text{cm}$)
ST-S: [H ₂ S/600 °C]	5.5×10^{-5}
ST-S: [SO ₂ /600 °C]	4.1×10^{-5}
ST	5.1×10^{-5}
HO-S: [H ₂ S/600 °C]	5.9×10^{-4}
HO-S: [SO ₂ /600 °C]	5.2×10^{-4}
HO-S: [CS ₂ /1000 °C]	3.4×10^{-4}
HO-S: [SO ₂ /1000 °C]	5.9×10^{-4}
HO	3.9×10^{-4}
HU-S: [H ₂ S/600 °C]	1.0×10^{-3}
HU-S: [SO ₂ /600 °C]	1.2×10^{-3}
HU	8.0×10^{-4}

Consequently, we have also measured the resistivities of sulfur doped materials and the undoped starting materials (ST, HO and HU), refer to fig. 6.8 and table 6.2. Majority of the sulfur doped materials exhibited higher resistivities than their undoped starting materials. The higher resistivities of these doped materials may be due to the trapping of free carriers by the sulfur and oxygen functionalities in the structure. Similar observation was also reported for the graphite oxides exfoliated in the presence of halogens sources (Chapter 7).¹²

Fig. 6.9 Cyclic voltammograms for HO-S and HO materials in O₂ saturated solution of 0.1 M KOH. Conditions: scan rate of 100 mV/s.

It was previously reported that sulfur doped graphenes can act as metal-free electrocatalysts for oxygen reduction reaction.³ To investigate the electrocatalytic activity of sulfur doped materials towards oxygen reduction, we performed cyclic voltammetry measurements in 0.1 M KOH solution saturated with O₂ gas (Fig. 6.9) for HO-S, HO materials and bare GC as comparison. We observed that O₂ reduction on bare GC electrode requires a large overpotential (peak potential of - 490 mV vs. Ag/AgCl) while HO requires a lower overpotential (peak potential of - 410 mV vs. Ag/AgCl). Sulfur doped materials were observed to provide an excellent electrocatalytic surface by being able to reduce oxygen at - 410 mV for HO-S: [H₂S/600°C], - 400 mV for HO-S: [CS₂/1000°C], - 380 mV for HO-S: [SO₂/600°C], and even at only - 370 mV for HO-S: [SO₂/1000°C]. A difference in the reduction potential by 40 mV for HO (- 410 mV) and HO-S: [SO₂/1000°C] (- 370 mV) shows that sulfur doped materials do indeed provide an electrocatalytic surface for O₂ reduction reaction.

Discussion

We have demonstrated the synthesis of sulfur doped graphene materials using various graphite oxide starting materials (Staudenmaier, Hummers and Hofmann), sulfur sources and different reaction conditions to yield final products with different amounts of sulfur content. In-depth investigation was performed with different characterization techniques to understand how the variations in the reaction conditions have influenced the properties of the final products. Interesting observations such as the three undoped starting materials possessing higher defect density than the sulfur doped materials (except HU) were found. It was noteworthy that the material with the highest sulfur content was HU graphite oxide doped with H₂S at 600 °C. For the first time, we have carried out a ζ -potential measurement on the materials to study the influence of sulfur atoms on the water dispersion stability of the sulfur-doped materials. All sulfur-doped materials displayed higher (absolute value) ζ -potentials than their starting materials indicating higher dispersion stability due to the presence of –SO₃H and oxygen groups. The resistivity results obtained confirmed an interesting observation where sulfur was found to possess an electron trapping ability in the doped materials. Majority of the S-doped materials showed higher resistivities than their undoped starting materials. In conclusion, the results obtained from all the experiments have shown the possibility of sulfonic groups present on the surface of the doped materials. It can also be assumed that graphite oxides doped using SO₂ source have higher degree of oxidation than those doped with H₂S and CS₂ sources. Undoped materials exfoliated in inert N₂ atmosphere also displayed lower degree of oxidation than the SO₂ doped materials. Interestingly, we have also discovered that sulfur doped graphenes exhibited electrocatalytic behavior for oxygen reduction reaction.

Experimental

Materials:

Sulfuric acid (98 %), nitric acid (68 %), nitric acid (fuming, 98 %), potassium chlorate (98 %), potassium permanganate (98 %), hydrogen peroxide (30 %), hydrochloric acid (37 %), silver nitrate (99.5 %) and barium nitrate (99.5 %) were obtained from PENTA, Czech Republic. Carbon disulfide (99.9 %) and N,N-dimethylformamide (DMF) were obtained from Aldrich. Graphite microparticles (< 50 µm) were obtained from KOOH-I-NOOR Grafit, Czech Republic. The gases were obtained from SIAD (Nitrogen 99.9999 % and Hydrogen sulfide 99.5 %) and Linde (Sulfur dioxide 99.98 %).

Apparatus:

Scanning electron microscopic (SEM) images were acquired using a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) at 5 kV accelerating voltage. Preparation of the samples was performed by attaching the materials onto a sticky conductive carbon tape which was then mounted onto an aluminum sample stub. X-ray photoelectron spectroscopy (XPS) measurement was executed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) for the wide-range and high resolution C 1s scans at 12.53 kV. The XPS samples were prepared by attaching a uniform layer of the materials onto a conductive carbon tape which was then affixed onto an aluminum XPS sample holder. The C/O ratios were achieved from the wide-scan XPS measurements with relative sensitivity factors taken into consideration during calculations. Raman spectroscopy was performed with a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. A 514.5 nm Ar laser and an Olympus optical microscope with a 100x objective lens were used in the focusing of the samples. Calibration of the machine was carried out at 0 cm⁻¹ and 520 cm⁻¹ with a silicon wafer as reference to give a peak position resolution of less than 1 cm⁻¹. All samples were well-compressed and compacted before placing on top of a glass slip

which was positioned on a piece of glass slide before any actual measurement was carried out. The elemental analysis (CHNS-O) was performed with Vario EL III (Elementar Analysensysteme GmbH, Germany). The calibration was performed with 5 mg of 4-aminobenzenesulfonic acid. The measurements of ζ -potential were performed on Malvern Zetasizer Nano ZS. Diluted samples of 1 mg TRGO / 25 ml H₂O mass concentration were first ultrasonicated for 5 minutes and then measured in a folded capillary cell at pH 7. For electrical resistivity measurements of graphene materials, 40 mg of the powder material was first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by the 4-probe technique using the Van der Pauw method.¹³ The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit. The measuring current was set to 10 mA. The ATR FT-IR measurement was performed on Bruker IFS 66v spectrometer equipped with IR microscope Hyperion. Germanium ATR crystal and liquid nitrogen cooled MCT detector were used for the measurements. Electrochemical measurements were carried out at Autolab 302 (EcoChemie), using three electrode set-up. Glassy carbon working electrode (GC), platinum auxiliary electrode (Pt) with a diameter of 3 mm and Ag/AgCl reference electrode were obtained from Autolab, The Netherlands.

Procedures:

*Synthesis procedure of Staudenmaier graphite oxide.*⁴ The synthesis of ST-GO was performed according to the procedure reported previously. 87.5 ml of sulfuric acid (98 %) and 27 mL of nitric acid (98 %) were first cooled to 0 °C before 5 g of graphite were added to the mixture. The reaction mixture was then intensively stirred while 55 g of potassium chlorate were added over a period of 30 minutes. The reaction flask was then loosely capped to allow the escape of chlorine dioxide gas. The mixture was continuously stirred for 96 hours at room temperature and then poured into 3 L of deionized water. After decantation, the graphite oxide was re-dispersed in 5 %

hydrochloric acid. The graphite oxide was decanted from hydrochloric acid and repeatedly centrifuged and re-dispersed until a negative reaction for chloride and sulfate ions (with Ba(NO₃)₂ and AgNO₃) was observed. Graphite oxide slurry was finally dried in a vacuum oven at 60 °C for 48 hours before further use.

*Synthesis procedure of Hofmann graphite oxide.*⁵ The synthesis of HO-GO was performed according to the standard method reported in literature. 87.5 ml of sulfuric acid (98 %) and 27 mL of nitric acid (68 %) were first cooled to 0 °C before 5 g of graphite were dispersed into the reaction mixture by vigorous stirring. Keeping the reaction mixture vigorously stirred at 0 °C, KClO₃ (55 g) was then added over a period of 30 minutes. The reaction mixture was loosely capped to allow the escape of gaseous reaction products (ClO₂) and stirred at room temperature for 96 hours. Upon completion of reaction, the mixture was poured into 3 L of deionized water and decanted. The reaction product was then re-dispersed in 2 L of 5 % HCl and decanted. Graphite oxide was then repeatedly centrifuged and re-dispersed in deionized water until a negative reaction on sulfate and chloride ions (with Ba(NO₃)₂ and AgNO₃ respectively) was achieved. Graphite oxide slurry was finally dried in a vacuum oven at 60 °C for 48 hours before further use.

*Synthesis procedure of Hummers graphite oxide.*⁶ The synthesis of HU-GO was performed according to the method reported previously. 115 mL of sulfuric acid (98 %) was cooled to 0 °C and then 5 g of graphite and 2.5 g of NaNO₃ were added to the mixture. While vigorously stirred, 15 g of KMnO₄ were added over a period of two hours. The reaction mixture was then removed from the cooling bath and stirred at room temperature for 4 hours. The reaction mixture was then heated to 35 °C for 30 minutes, poured into 250 mL of deionized water and heated to 70 °C. After 15 minutes the mixture was poured into 1 L of deionized water. Unreacted KMnO₄ was decomposed with 10 % hydrogen peroxide. The reaction mixture was then decanted and

repeatedly centrifuged and re-dispersed until a negative reaction for sulfate ions (with Ba(NO₃)₂) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 hours before further use.

Synthesis procedure of sulfur doped Staudenmaier, Hummers, Hofmann materials and undoped exfoliated starting materials. All of the sulfur-doped graphene oxides were exfoliated in the same reactor as the thermally reduced graphene oxides. For every reaction, 100 mg of the graphite oxide starting material were inserted into a quartz glass capsule covered by sintered quartz glass filter facing the direction of the gas flow. The capsule was then attached to a magnetic manipulator and placed into a quartz horizontal reactor in the furnace. Before the placement of the sample into the hot zone of the reactor, the whole system was repeatedly evacuated and filled up with nitrogen. A mixture of nitrogen and sulfur precursor was used for the sulfonation process. First, the nitrogen flow (1 L/min) and the sulfur precursor (*i.e.* SO₂ and H₂S) flow (1 L/min) were stabilized for 5 minutes. Then the capsule with the sample was inserted into the furnace for 12 minutes and pulled out again at the end of the reaction. In the case of samples treated in SO₂ at 1000 °C, the exposition time was reduced to 2 minutes in order to avoid oxidation and decomposition of graphene. The 12 minutes exposure of graphene at these conditions led to a complete oxidation. The reaction with CS₂ was carried out using a bubbler filled with liquid CS₂ at a temperature of 17 °C and pressure of 1000 mbar. Nitrogen (100 mL/min) was used as a carrier gas and was diluted with 1 L/min of nitrogen before entering into the reactor. All exfoliation steps were performed under atmospheric pressure.

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Chapter 7

Halogenation and Exfoliation of Graphene with Chlorine, Bromine or Iodine

7.1 *Introduction*

7.2 *Results*

7.2.1 *Properties of halogenated graphenes*

7.2.2 *Electrochemistry of halogenated graphenes*

7.3 *Discussion*

7.4 *Experimental*

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

1. **Hwee Ling Poh**, Petr Šimek, Zdeněk Sofer, Martin Pumera. Halogenation of Graphene with Chlorine, Bromine, or Iodine by Exfoliation in a Halogen Atmosphere. *Chem. Eur. J.*, 2013, **19**, 2655.

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Introduction

Group VII elements are highly electronegative halogens that give a p-type effect when doped into graphene structures due to their strong electron withdrawing effect. In Chapter 7, we will be looking at the heteroatom doping of nanocarbon materials using halogens: chlorine, bromine and iodine. Currently, halogen doping was achieved via several pathways such as thermal annealing of graphene oxide in the presence of iodine dopant,¹ UV irradiation of the few-layer graphene in liquid chlorine/bromine² and chlorine plasma treatment of graphene.³ Methods based on UV-irradiation were especially noteworthy as they allow reversible storage of chlorine or bromine in graphene materials where the halogen atom was freed from the material upon laser irradiation or thermal treatment.² Herein we described a universal, simple and scalable method for the production of thermally reduced halogenated graphene oxides via thermal exfoliation/reduction at a temperature of 1000 °C in a gaseous halogen atmosphere (Scheme 7.1).

This project investigates not only the halogenation process but also the possible relationship between an increasing atomic number of the halogens and its influence on the properties of the halogenated materials that may exists.

Scheme 7.1 Synthesis of halogenated graphene by thermal exfoliation of graphite oxide in a halogen atmosphere.

Results

7.2.1 Properties of halogenated graphenes

Halogenated graphenes were synthesized via thermal exfoliation of graphite oxide in different gaseous halogen atmospheres (chlorine, bromine or iodine) to integrate halogen atoms into the materials. A full-scale characterization study of these materials was performed using various different techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were also employed to investigate the electrochemical behaviour of these materials. These techniques allow us to understand the properties of the halogenated graphenes such as their physical characteristics (morphology and defect density) and their electrochemical behaviours, such as the influence of the halogen atoms on the heterogeneous electron transfer (HET rate) of halogenated graphene. Doping the graphene with different halogen atoms during exfoliation allows a comparison study which may lead to the discovery of important and interesting differences which will be further elaborated below. The materials of study were TRGO-Cl, TRGO-Br, TRGO-I and TRGO-N as the control material that did not undergo halogenation but only a common exfoliation step in inert nitrogen (N_2) atmosphere. The name of the halogen found in each material's label indicates the type of halogen that material was doped with.

Scanning electron microscopy and transmission electron microscopy were first employed to study the morphology of the materials (refer to Fig. 7.1 and Fig. 7.2). The images were taken at various magnifications ranging from $370\times$ to $50,000\times$. It can be observed from the SEM images that no significant differences were noticeable between the three halogenated materials. The three halogenated graphenes resembled small-sized particles at $370\times$ magnification and were observed to consist of well-separated graphene sheets at magnification

of 10,000 × or higher. The appearance of the halogenated materials were similar to a typical graphene thermally exfoliated in inert gas atmosphere (N₂, Ar) as reported earlier.^{4,5} Hence, it can be concluded that the halogenated graphenes have successfully undergone complete exfoliation under a gaseous halogen atmosphere. Higher resolution imaging of the materials was performed with TEM to observe topographical details of single to few layers of exfoliated thermally reduced graphene oxides (TRGOs). As observed in Fig. 7.2, the morphology of the four materials appeared to be similar under the same magnifications where the TRGO sheets display a wrinkled texture throughout the entire layer. Similarly, the structures of the four materials were found to be very similar to typical single-to-few-layer graphene sheets as reported earlier⁶ which supports the conclusion from SEM images that the halogenated graphenes have been successfully exfoliated.

Fig. 7.1 SEM images of TRGO-Cl, TRGO-Br, TRGO-I and TRGO-N. Scale bars for the images are: a) 10, b) 1, c) 1 and d) 100 nm.

Fig. 7.2 TEM images of TRGO-Cl, TRGO-Br, TRGO-I and TRGO-N. Scale bars for the images are: a) 0.2 μm , b) 50 nm and c) 0.5 μm .

Important structural information such as the density of defects can be determined through the Raman spectroscopy technique. Presence of defects was demonstrated by the appearance of a D band at ca. 1350 cm^{-1} which was due to the sp^3 hybridized carbon atoms in the lattice structure while pristine sp^2 lattice carbon in the structure appears as a G band at $\sim 1560\text{ cm}^{-1}$ (refer to Fig. 7.3). The intensity of D band (intensity was normalized to G band for comparison) reflects the degree of functionalization of the material.⁷ The intensities of these bands were represented as I_D/I_G ratios to determine the density of defects present in the materials. The calculated ratios were observed to decrease with increasing atomic number of the halogens where TRGO-Cl has a ratio of 1.16, TRGO-Br of 1.09 and TRGO-I of 0.75. The control material, TRGO-N was calculated to have a ratio of 1.07.

Fig. 7.3 Raman spectra of the halogenated graphenes and control material. **A)** Raman spectrums of TRGO-Cl, TRGO-Br, TRGO-I and TRGO-N. **B)** Bar chart of the calculated I_D/I_G ratios of the halogenated graphenes. **C)** Raman spectrum of I_3^- and I_5^- of TRGO-I.

The intensities of the bands were also used to calculate the average crystalline size (L_a) of the sp^2 lattice with the equation: ⁸

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

I_G and I_D are the intensities of the D and G bands in the Raman spectrum and λ_{laser} is the wavelength of the laser in nm. The derived L_a values were 14.4 for TRGO-Cl, 15.4 for TRGO-Br, 22.3 for TRGO-I and 15.7 nm for TRGO-N. The higher I_D/I_G ratios of TRGO-Cl and TRGO-Br as compared to TRGO-N, was an indirect proof of the success functionalization of graphene with halogen atoms. However, such higher I_D/I_G ratio may also simply be due to the different effects that different halogen gas exfoliation atmosphere have on the creation of defects. Hence, additional characterization study was required to confirm such speculations. Interestingly, TRGO-I was found to possess two additional peaks at approximately 90 cm⁻¹ and 167 cm⁻¹ which were absent in the Raman spectrums of the three other TRGOs (-Cl, -Br and -N). The presence of

I_3^- in the material was confirmed by the appearance of the peak at 90 cm^{-1} and I_5^- presence was verified by the peak at 167 cm^{-1} .^[1,9,10] The existence of these peaks indicates the successful incorporation of iodine atoms in the TRGO during the exfoliation process.

Fig. 7.4 A) Wide-scan XPS spectrums of halogenated graphenes and its control material. **B)** Bar chart of the calculated C/O ratios of the three halogenated graphenes.

The identity of major surface elements and its composition can be determined through X-ray photoelectron spectroscopy. Fig. 7.4 shows the XPS spectrums of the various materials where carbon and oxygen were found to be the main elements for all four TRGOs. The presence of each halogen in their respective halogenated TRGOs was also verified by the existence of the respective halogen XPS peaks, indicating the successful incorporation of the halogens inside the materials. In the XPS spectrum for TRGO-N, only C 1s peak at 284.5 eV and the O 1s peak at 531.4 eV were observed. TRGO-Cl displayed a C 1s peak at 284.5 eV, O 1s peak at 532.5 eV and a Cl 2p peak at 200.5 eV. TRGO-Br exhibited a C 1s at 284.5 eV, O 1s peak at 532.5 eV, a Br 3p peak at 184.1 eV and a Br 3d peak at 71.5 eV. TRGO-I displayed a I 3d peak at 618.5 eV in addition to the C 1s and O 1s peaks observed at 284.5 eV and 532.5 eV respectively.

Fig. 7.5 High-resolution XPS spectra for the respective electronic states of each halogen atoms A) Br 3p for TRGO-Br, B) Br 3d for TRGO-Br, C) Cl 2p for TRGO-Cl and D) I 3d for TRGO-I.

A high resolution XPS (HR-XPS) measurement was also performed for the respective halogens' electronic state at their corresponding bond energies as shown in the Fig. 7.5. Cl 2p, Br 3p, I 3d peaks actually consisted of two peaks which were only visible upon performing a HR-XPS scan. The percentage content of the major elements (C 1s and O 1s) was calculated as C/O ratios which reflect the extent of deoxygenation of the graphite oxide during thermal exfoliation. The C/O ratios of the materials were found to be 16.77 for TRGO-Cl, 20.37 for TRGO-Br, 11.75 for TRGO-I and 18.23 for TRGO-N. It can be concluded that the amount of oxygen containing groups in halogenated TRGOs was lower than that of non-halogenated TRGO (TRGO-N) except TRGO-Br.

Fig. 7.6 HR-XPS spectra of the C 1s peak in A) TRGO-Cl, B) TRGO-Br, C) TRGO-I and D) TRGO-N. The individual C1s spectra were also fitted to different peaks to show the possible carbon bonds present in each material. Inset in (B) shows the bar chart of the total percentage of fitted C=C and C-C bonds for each material.

High-resolution XPS was also performed for the main element, C 1s peak and fitted to different peaks observe the various carbon bonds constitute the C 1s spectrum. Careful fitting of the results were executed using relative sensitivity factors to investigate the quantitative amounts of respective carbon bonds. All C 1s spectrums constitute of a large asymmetrical peak with a shoulder at higher binding energies which proposed the existence of other carbon bonds besides C=C bond. Fitting of the HR-XPS spectrum for TRGO-Cl was performed at 284.5 eV for C=C, 285.3 eV for C-C, 286.2 eV for C-Cl, 287.2 eV for C-O, 288.5 eV for C=O and 290.4 eV for π - π^* (refer to Fig. 7.6, A). TRGO-Br C1s spectrum constitute of C=C at 284.5 eV, C-C at 285.7 eV, C-Br at 286.9 eV and π - π^* at 289.4 eV. On the contrary, C1s spectrum of TRGO-I was observed to comprise of C=C at 284.5 eV, C-C at 285.4 eV, C-O at 286.2 eV, C=O at 287.2 eV, C-I at 288.8 eV¹¹ and π - π^* 290.8 eV. Non-halogenated control material (TRGO-N) was also fitted to give C=C at 284.48 eV, C-C at 285.66 eV, C-O at 286.69 eV, C=O at 287.76 eV, O-C=O at 288.90 eV and π - π^* 290.34 eV. The HR-XPS C 1s spectra of all three halogenated materials have confirmed the successful incorporation of halogen to graphene structure and the creation of the carbon-halogen bond. The combined percentages of the intensities of the carbon-carbon bonds (the sp^2 -hybridized C=C and sp^3 -hybridized C-C) were then further compared to that of the total intensities for all the carbon bonds. It can be observed that the combined percentages of these two bonds increase with increasing atomic number of the halogens from 73.1% for TRGO-Cl to 79.1% for TRGO-Br to 80.0% for TRGO-I (inset of Fig. 7.6, B). This shows that with higher atomic number halogen gases used during exfoliation, more C atoms in the TRGO were found to be bonded to other carbon atoms instead of non-carbon atoms such as halogens and oxygen.

Fig 7.7 ATR FT-IR spectra of (A) TRGO-Cl and (B) TRGO-Br where C-Cl vibration mode at 930 cm^{-1} and C-Br vibration mode at 600 cm^{-1} could be observed.

In addition to XPS measurements, attenuated total reflection infrared spectroscopy (ATR FT-IR) for TRGO-Cl and TRGO-Br were recorded (refer to Fig. 7.7). IR bands at 930 cm^{-1} and 600 cm^{-1} which corresponds to C-Cl bond in TRGO-Cl and C-Br bond in TRGO-Br respectively, could be observed. These results were in agreement with earlier findings from Rao and co-workers' report.²

The combustion elemental analysis (EA) is a useful technique to assess the amount of halogens in each halogenated graphene. A classical titrimetric analysis of halogens was performed where the material was first combusted according to Schöniger followed by a titrimetric analysis as described in experimental section to obtain the CHNS/O percentage content. TRGO-Cl contained 93.84 % (wt.) of C, 5.9 % of Cl, 0.16 % of H, 0.1% of O, 0 % of S and 0 % of N. TRGO-Br consists of 83.19 % (wt.) of C, 9.93 % of Br, 8.13 % of O, 0.53 % of H, 0 % of S and 0.22 % of N. TRGO-I consisted of 88.00 % (wt.) of C, 2.31 % of I, 9.37 % of O, 2.19 % of H, 0 % of S and 0.14 % of N. This proves that halogen atoms were indeed introduced into the graphene lattice during exfoliation in halogen gas atmosphere.

Fig. 7.8 Thermal analysis of halogenated graphenes using simultaneous thermal analysis (STA) in an oxygen atmosphere.

Fig. 7.9 Investigation on thermal stability of halogenated graphenes in argon atmosphere using X-ray fluorescence. Pre-heated materials were plotted in red while heated samples were plotted in black. Conditions: Heated to 1200 °C at a heating rate of 10 °C min⁻¹ and cooling rate of 20 °C min⁻¹.

Thermal stability of the halogenated graphenes in pure oxygen and pure argon (inert) atmospheres were studied using a similar method as Rao and coworkers.² In the pure oxygen atmosphere, the oxidation of TRGO-I begins at around 430 °C and TRGO-Br at around 450 °C. Thermogravimetric (DSC and TGA) analyses of the materials were as shown in Fig. 7.8 and Fig. 7.9. TRGO-Cl displayed significantly greater temperature stability in oxygen atmosphere where its oxidation begins at around 530 °C. Stability of the halogenated graphenes in argon atmosphere was examined with X-ray fluorescence. The materials were heated in argon atmosphere at 1200 °C where X-ray fluorescence measurements of the materials were executed before and after heating procedure (refer to Fig. 7.9). It could be observed that the concentration of iodine decreased by only about 20% while the concentration of chlorine decreased by about 90% after heating. However, bromine was completely eliminated during heat treatment.

7.2.2 Electrochemistry of halogenated graphenes

The electrochemical study of halogenated graphenes began with the conductivity measurements of the materials and the starting material (graphite oxide) using the four-probe method. It was observed that the specific resistivity of the materials were $5.5 \times 10^{-3} \Omega\cdot\text{cm}$ for TRGO-Cl, $1.8 \times 10^{-4} \Omega\cdot\text{cm}$ for TRGO-Br, 8.1×10^{-5} for TRGO-I, $3.9 \times 10^{-4} \Omega\cdot\text{cm}$ for TRGO-N and graphite oxide $3.67 \times 10^2 \Omega\cdot\text{cm}$. The difference in electronegativity of halogens and their chemical states may be attributed to the differences in the resistivity values measured. Highly electronegative chlorine may have resulted in lesser free electrons to be available in TRGO-Cl. However, this effect was much less profound for TRGO-Br due to Br having a lower electronegativity. As such, lowest electronegativity iodine results in TRGO-I to exhibit the lowest resistivity value. This observation may be due to the presence of triiodide and pentaiodide that were bonded to the graphene sheets. The lower electronegativity and high electron concentration in polyiodide results in the availability of more free electrons in the graphene sheet which led to a decrease in resistivity as observed.

Fig. 7.10 Cyclic voltammograms of halogenated and nonhalogenated graphenes. **A)** Cyclic voltammograms recorded in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. **B)** Bar chart showing the peak-to-peak values for the halogenated graphenes. **C)** Bar chart showing the HET rates of the halogenated graphenes. Conditions: scan rate 100 mV s^{-1} , background electrolyte 50 mM PBS, pH 7.2.

The heterogeneous electron transfer (HET) rates of the materials were investigated as part of the electrochemical study of the halogenated graphenes. This was crucial for the determination of the materials usefulness and effectiveness as a material in capacitors and electrochemical sensing devices. Cyclic voltammetric experiments were performed with glassy carbon electrodes modified with the materials of study. Using ferrocyanide solution, the peak-to-peak separation (ΔE_{p-p}) values for each material was measured. As shown in Fig. 7.10, the ΔE_{p-p} values were 140 mV for TRGO-Cl, 190 mV for TRGO-Br, 200 mV for TRGO-I, 260 mV for TRGO-N and 420 mV for unmodified bare GC electrode. The ΔE_{p-p} value can be observed to increase with increasing atomic number of the halogens (refer to Fig. 7.10, B). HET rates constants of the various materials can be calculated using the individual ΔE_{p-p} values via Nicholson method.¹² The HET values (k_{obs}^0) were calculated to be $2.525 \times 10^{-3} \text{ cm s}^{-1}$ for TRGO-Cl, $1.475 \times 10^{-3} \text{ cm s}^{-1}$ for TRGO-Br, $6.850 \times 10^{-4} \text{ cm s}^{-1}$ for TRGO-I, $5.063 \times 10^{-4} \text{ cm s}^{-1}$ for TRGO-N and $5.662 \times 10^{-5} \text{ cm s}^{-1}$ for bare GC electrode (refer to Fig. 7.7, C). This indicates that the HET rates of the materials were

observed to decrease with increasing atomic number of the halogens dopants for the halogenated TRGOs.

Fig. 7.11 Electrochemical impedimetric spectroscopic results of halogenated graphenes and the control material. A) Nyquist plots of the results in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution. B) Magnified view of the nyquist plots for the halogenated graphenes. C) Bar chart comparing the charge-transfer resistance of the halogenated graphenes.

The electron transfer resistance of the halogenated graphenes at the materials' surfaces can be studied using the electrochemical impedance spectroscopy (EIS) technique. This method measures the interfacial impedance towards charge transfer between the electrolyte solution and the material's surface. The EIS results were presented as nyquist plots where the diameter of the semicircular plot gives the charge transfer resistance (R_{ct}) value that we are interested in. It can be observed from Fig. 7.11, A that unmodified bare GC electrode was found to have the largest electrochemical impedance as demonstrated by the material having the largest semicircular diameter. The remaining graphenes were observed to have a much lower electrical resistance as the diameter of their Nyquist plots as much smaller. Processing of the data was performed by fitting the nyquist plots against the Randles circuit to obtain the charge transfer resistance values (R_{ct}). The fitted R_{ct} values were 46 Ω for TRGO-Cl, 408 Ω for TRGO-Br, 808 Ω for

TRGO-I, 896 Ω for TRGO-N and 5803 Ω for unmodified glassy carbon electrode. This shows that the R_{ct} increases with increasing atomic number of the halogens which supports the earlier CV results obtained.

Discussion

We have developed a pioneer synthesis method for the bulk production of halogenated (Cl, Br and I) graphenes via thermal exfoliation in halogen gas atmospheres. Detailed characterization studies of the materials such as their physical properties (morphology and density of defects), elemental composition and electrochemical reactivity (HET rates and charge transfer resistance) were performed. A direct relationship between the halogen's atomic number and the properties that these halogenated graphenes displayed was observed to exist. An example was an increasing D/G ratio with increasing atomic number of the halogen. Other properties that displayed such as a trend includes peak-to-peak separation, heterogeneous electron transfer rates and charge transfer resistance where a consistent pattern linked to the atomic number of the halogens could be found. This pioneer synthesis method of incorporation various halogens into the graphene structure will prove to be useful for various purposes such as electronic and electrochemical devices.

Experimental

Materials:

Potassium ferrocyanide, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, potassium chloride were purchased from Sigma-Aldrich. Nitric acid, sulfuric acid, hydrochloric acid, potassium chlorate was obtained from PENTA, bromine (99.5 %) and iodine (99.8 %) was obtained from Sigma-Aldrich, nitrogen gas (99.9999 %) was obtained from SIAD and chlorine (99.8 %) from Linde. Graphite was obtained from KOH-I-NOOR GRAFIT. Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions. Glassy carbon (GC) electrodes, Ag/AgCl electrode and platinum (Pt) electrode were obtained from Autolab. TEM imaging was performed using carbon coated 200 mesh lacey formvar supporting film copper grids which were purchased from Ted Pella, Inc.

Apparatus:

Scanning electron microscopy imaging was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan). The samples were prepared by randomly attaching a layer of the material onto a carbon conductive tape which was adhered onto an aluminium sample stub. The images were then obtained under the gentle-beam mode at 2 kV for various magnifications. Transmission electron microscopy measurement was performed with a JEM 1400 field-emission transmission electron microscope at 100 kV under different magnifications. The synthesized TRGOs were used directly in the preparation as suspensions of concentrations 0.5 mg ml⁻¹. The suspensions were then sonicated for five minutes to obtain a homogeneous suspension before each use. An aliquot of 3 μL of the suspension was then dropped onto a copper TEM grid laid on top of a filter paper and left to dry in a fume hood before use. Imaging was then performed under 100 kV at various magnifications. A Phoibos 100 spectrometer operating with monochromatic Magnesium X-ray source was used for the acquiring of X-ray photoelectron

spectroscopic measurements for wide-range and high-resolution scans. The materials were prepared by coating a uniform layer of the TRGOs on a sticky conductive carbon tape which was attached onto an aluminium sample holder. The measurement was then performed at 12.5 kV with a Magnesium X-ray source. Raman spectroscopy measurements were executed with a confocal micro-Raman LabRam HR machine (Horiba Scientific) with a backscattering geometry and a CCD detector. The scans were performed under a 514.5 nm Ar laser source and a X 100 objective lens mounted onto an Olympus optical microscope. Calibration of the machine was achieved with a silicon reference at 520 cm^{-1} before any measurements were performed. The materials were prepared by compressing them well between two glass slips to ensure that they are compacted before placing them on top of a glass slip which was later placed onto a glass slide. The ATR-IR measurement was performed on Bruker IFS 66v spectrometer equipped with IR microscope Hyperion. Germanium ATR crystal and liquid nitrogen cooled MCT detector were used for the measurements. Cl and Br analysis: the sample was combusted by Schöniger method. Formed Cl^- or Br^- ions were titrated by a solution of $\text{Hg}(\text{NO}_3)_2$ using sodium nitroprusside as an indicator. Iodine analysis: the sample was combusted by Schöniger method first. Iodine was determined by Leipter method described by following steps: (1) absorption of iodine in NaOH solution; (2) oxidation of various iodine forms to iodate by bromine; (3) reduction of the excessive bromine by formic acid; (4) reduction of iodate by iodine forming elemental iodine; (5) titration of iodine by a standard solution of thiosulfate. For determination of CHNS/O elemental combustible analysis system PE 2400 Series II CHNS/O from Perkin Elmer was used. For conductivity measurements of graphene related materials, 40 mg of the material was first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by the 4-probe technique using the Van der Pauw method.^[13] The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit. The simultaneous thermal analysis was performed using PT 1600 from Linseis. The measurement was carried out in oxygen atmosphere

(50 ml min⁻¹; oxygen of 99.999 % purity) or by argon (50 ml min⁻¹; argon of 99.999 % purity).

Electrochemical experiments using the cyclic voltammetric and the electrochemical impedance spectroscopic techniques were performed with a μ Autolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) controlled by the software NOVA 1.7 (Eco Chemie).

Procedures:

*Synthesis of graphite oxide using Hofmann method.*¹⁴ The preparation of graphite oxide followed a method described by Hofmann. Graphite (5 g) was added into a mixture of sulfuric acid (98 %, 87.5 ml) and nitric acid (68 %, 27 ml). Potassium chlorate (55 g) was slowly added into the mixture while cooling the resultant mixture in an ice bath. The reaction mixture was then stirred for 96 hours at room temperature. After the reaction came into completion, the mixture was poured into 3 L of deionized water and decanted. The resulting graphite oxide was then redispersed in 5 % hydrochloric acid solution and repeatedly centrifuged to remove chloride and sulfate ions. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 hours before use.

Synthesis of halogenated thermally reduced graphene oxides. The halogenated graphenes were synthesized in vacuum tight quartz glass reactor with controlled atmosphere. The reactor was equipped with porous quartz glass capsule connected to magnetic manipulator. This configuration was capable to produce the temperature gradient over 1000 °C min⁻¹. All synthesis was performed at 1000 °C for 12 minutes under 100 kPa. The 100 mg of the graphite oxide was placed into porous quartz glass capsule and the reactor was flushed several times with high purity nitrogen. Subsequently the sample was inserted into the preheated furnace with adequate atmosphere. For the chlorine doped graphene the flow of 1000 ml min⁻¹ chlorine and 1000 ml min⁻¹ nitrogen was used. For the synthesis of bromine doped graphene high purity nitrogen saturated with bromine vapor was used. The bubbler filled with bromine was kept at 10 °C to avoid condensation of bromine vapor in gas line. Nitrogen flow through bubbler was

100 ml min⁻¹ at 100 kPa. This configuration allowed us to transport 0.6 x 10⁻³ mol min⁻¹ of bromine vapors. 1000 ml min⁻¹ of nitrogen was used like carrier gas for bromine saturated nitrogen. The use of bubbler filled with iodine didn't give satisfactory results due to the low iodine vapor pressure. The flow of 1000 ml min⁻¹ of nitrogen through bubbler with iodine held on 15 °C and 100 kPa was able to transport only 4.2 x 10⁻⁶ mol min⁻¹). To obtain higher iodine concentration the graphite oxide was mixed with iodine in 1:1 mass ratio, dispersed in acetone and evaporated to dryness at room temperature. 100 mg of iodine – graphite oxide mixture was placed into quartz glass porous capsule and the reactor was flushed several times with high purity nitrogen. The exfoliation was performed with 1000 ml min⁻¹ flow of high purity nitrogen in order to remove the reaction by-products.

Synthesis of thermally reduced graphene oxides in nitrogen. The thermal exfoliation of graphite oxide was carried out at 1000 °C for 12 minutes. The graphite oxide was placed inside a porous quartz glass capsule connected to magnetic manipulator in a vacuum tight quartz reactor with controlled atmosphere. This system provided a temperature gradient of over 1000 °C min⁻¹. The sample was then flushed repeatedly with pure nitrogen and subsequently inserted to a preheated reactor in nitrogen (99.9999 % purity) atmosphere (pressure, 100 kPa). The flow of the nitrogen was 1000 mL min⁻¹, resulting in the removal of the by-products of the reactions.

Electrochemical measurements. The glassy carbon electrodes were cleaned by polishing with an alumina suspension then washed with deionised water and wiped dried before use. The synthesized TRGOs are dispersed in DMF solvent to create a suspension with a concentration of 0.5 mg ml⁻¹. The suspension was then sonicated at room temperatures for five minutes before each use. Modifying the electrodes were performed by having a 1 µL aliquot of the TRGO suspension coated onto the cleaned surface of a GC electrode which was then left under a lamp to dry to give a layer of randomly dispersed TRGO on the GC surface. This step was then repeated until three layers of coatings on the GC surface were obtained. The modified GC

electrodes, Ag/AgCl reference electrode and Pt counter electrode were then dipped into an electrochemical cell which contains the electrolyte solution (10mM $[\text{Fe}(\text{CN})_6]^{3-}$ dissolved in 50 mM pH 7.2 Phosphate buffer solution) and the measurements were started. CV measurements were taken each time before the start of every EIS measurement which was all carried out under room temperatures. CV measurements were taken for the range of potentials from +1.15 V to -0.8 V at a scan rate of 100 mV s^{-1} for two consecutive scans. This was immediately followed by an EIS measurement carried out for a range of frequencies from 10,000 Hz to 0.01 Hz. Three replicates were carried out for each TRGO.

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Chapter 8

High-pressure Hydrogenation of Graphene and its Applications in the
Electrochemical Detection of Trinitrotoluene in Seawater

8.1	<i>Introduction</i>
8.2	<i>Results</i>
8.2.1	<i>Properties of hydrogenated graphenes</i>
8.2.2	<i>Electrochemistry of hydrogenated graphenes</i>
8.2.3	<i>Application: TNT detection with hydrogenated graphenes</i>
8.3	<i>Discussion</i>
8.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Filip Šaněk, Zdeněk Sofer, Martin Pumera. High-pressure Hydrogenation of Graphene: Towards Graphane. *Nanoscale*, 2012, **4**, 7006.

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2. **Hwee Ling Poh**, Zdeněk Sofer, Martin Pumera. Graphane electrochemistry: Electron Transfer at Hydrogenated Graphenes. *Electrochem. Commun.*, 2012, **25**, 58.

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<http://www.sciencedirect.com/science/article/pii/S1388248112003803>.

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3. Tzu Hui Seah, **Hwee Ling Poh**, Chun Kiang Chua, Zdeněk Sofer, Martin Pumera. Towards Graphane Applications in Security: The Electrochemical Detection of Trinitrotoluene in Seawater on Hydrogenated Graphene. *Electroanal.*, 2014, **26**, 62.

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Introduction

Graphane or just highly hydrogenated graphenes? In Chapter 2, we have reviewed the various current methods undertaken to hydrogenate graphene related materials. From the characterization results of the final products obtained from these methods, it was concluded that they are partially hydrogenated graphenes rather than the highly anticipated graphane. As such, graphane remains a theoretical material where much experimental work is still in progress.

Herein Chapter 8, the various properties and characteristics of hydrogenated graphenes were probed. Previous experimental studies reporting on hydrogenated graphenes proved the successful incorporation of hydrogen atoms into the graphene network but failed to provide convincing evidences of the presence of C-H bonds. As such, this project successfully proves the existence of C-H in the hydrogenated materials via the ATR FT-IR and the EA techniques. This extra information allows the material to be more useful for further application as a more in-depth investigation of the material's properties is available. The method of production proposed utilized high-pressure (up to 150 bar) and high temperature (up to 500 °C) to hydrogenate graphite oxide, yielding large quantities of the hydrogenated materials crucial for applications requiring gram quantities of the materials. This production method differs from earlier reported methods such as hydrogenation of CVD graphene at low-pressure (0.1 mbar) with DC-plasma,¹ radio frequency plasma hydrogenation of highly oriented pyrolytic graphite.²

Further experiments on the actual application of hydrogenated graphenes were also attempted in this project. Electrochemical studies on the materials' heterogeneous electron transfer rates and electrical resistivities were performed via the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) techniques. Such electrochemical investigations were pilot in this project. The hydrogenated materials were also experimented as sensing platforms in the detection of 2, 4, 6-trinitrotoluene compounds (TNT). This sensing application

proves to be important due to the several environmental³⁻⁸ and security threats that TNT compounds posed to the community. Current detection methods include gas and high performance liquid chromatography and capillary electrophoresis.⁹⁻¹⁷ However, such methods proved disadvantageous as compared to electrochemical detectors in terms of rapid response time, portability, accuracy and lower cost.¹⁸ Moreover, further miniaturizations of these electrochemical analyzers can be executed to transform them into on-site detectors for swift and rapid response. The electrochemical detection of TNT was based on the reduction reaction of the three nitro groups as shown in scheme 8.1. Proof of previous success in TNT detection with carbon nanomaterials such as carbon nanotubes¹⁹, graphene nanosheets and graphene ribbons²⁰⁻²² have promoted the idea of utilizing hydrogenated materials as the sensing platform in this project. The use of hydrogenated materials as sensing platforms was pioneer in this project.

Scheme 8.1 Stepwise reduction of nitrogroups in TNT proceeds in ortho, ortho and para position vs. methyl group. Reproduced with permission from ref. 23.

Results

8.2.1 Properties of hydrogenated graphenes

High pressure/high temperature exfoliation of graphite oxide carried out in a hydrogen gas atmosphere produces a partially hydrogenated graphene. The exfoliation conditions of graphene were varied to investigate how temperature and pressure affects the material's properties through characterization studies. To date, there were no effective methods that can directly or accurately determine the hydrogenation efficiency of the materials. Most techniques such as Raman spectroscopy or conductivity measurements can only approximate the efficiency with rather high inaccuracy in the results. Analysis of the C 1s peak in X-Ray photoelectron spectroscopy (XPS) have also failed to differentiate accurately due to the narrow difference bond energy of 0.6 eV between C-H peak and C=C peak. Interestingly, chemical analysis based on the rotation/vibration modes of the bonds (infrared spectroscopy) allows a slightly greater accurate distinguishment between C-H and C=C bonds as compared to other techniques. To date, the most precise and accurate measurements on the hydrogenation efficiency was the combustible elemental analysis technique. However, no earlier reports have employed infra-red spectroscopy or combustible elemental analysis to investigate the extent of hydrogenation in the materials.^{1,2,24} This may be due to the method of synthesis employed (CVD method) resulting in insufficient amounts of the materials obtained and hence, the implementation of FT-IR and EA was impossible. With no FT-IR spectroscopy and EA results to support, any earlier claims on the hydrogenation of graphene may be least reliable and ambiguous. Herein, we have employed an array of techniques which include scanning and transmission electron microscopy (SEM, TEM), Raman spectroscopy, X-Ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and combustible elemental analysis (EA) to study the influence of varied exfoliation conditions on hydrogenation efficiency.

Two different sets of reaction conditions were investigated in this experiment: a)

constant temperature of ca. 220 °C with varied hydrogen gas pressure between 60 bars to 150 bars during exfoliation and b) constant hydrogen gas pressure at 100 bars with varied temperature between 200 °C to 500 °C during exfoliation. For the control experiment, graphene exfoliated in inert argon gas atmosphere will be used as a standard for comparison. In the following, the materials were denoted by their exfoliation temperature and gas pressure, e.g. graphene exfoliated at 100 bar hydrogen gas pressure and 350 °C will be labelled as G-H: [100 bar/350 °C].

We will first examine the hydrogenated graphenes with electron microscopy to confirm the successful exfoliation of the graphite oxides. Fig. 8.1 shows the SEM images of the control material and hydrogenated graphenes taken at three different magnifications. It can be observed from the images that all the materials have been successfully exfoliated and no observable differences was found between the various hydrogenated graphenes and the control sample.

Fig. 8.1 SEM micrographs of G-H: [60 bar/220 °C], G-H: [100 bar/200 °C], G-H: [150 bar/220 °C], G-H: [100 bar/350 °C], G-H: [100 bar/500 °C] and G-Ar: [100 bar/350 °C].

Fig. 8.2 TEM images of G-H: [60 bar/220 °C], G-H: [100 bar/200 °C], G-H: [150 bar/220 °C], G-H: [100 bar/350 °C], G-H: [100 bar/500 °C] and G-Ar: [100 bar/350 °C].

TEM imaging of all the materials of comparison were also performed as shown in fig. 8.2 to observe single to few layer sheets of graphene/graphane. It was observed that graphenes exfoliated at high temperatures of 350 °C and 500 °C (at 100 bar pressure) displayed a wrinkled appearance while other graphenes presented a much smoother texture and a straight or flat appearance. The wrinkled structure may be due to both the high concentration of heptagon/pentagon rings and the hydrogenation of graphene (note that the hydrogenated 6 member ring does not provide a 2D structure). However, no other major observable differences between the different hydrogenated graphenes and the control material were found. In conclusion, SEM and TEM have confirmed that exfoliation of graphite oxide under hydrogen atmosphere at high gas pressures occurs with similar effectiveness as that in an inert gas atmosphere.

Further investigation on the density of defects in the hydrogenated graphenes and the influence of hydrogenation conditions on the defect density was analysed through Raman spectroscopy. This technique generates two distinct peaks at ca. 1300 cm⁻¹ and ca. 1590 cm⁻¹ which corresponds to the defects in the sp² lattice network (D peak) and the sp² lattice structure (G peak) respectively. The intensities of the D and G peaks have also allowed the crystallite size of sp² graphene to be calculated according to the equation²⁵:

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

where I_G and I_D are the intensities of the D and G bands and λ_{laser} is the wavelength (nm) of the laser used in Raman.

As shown in fig. 8.3, the Raman spectra for the different materials were plotted vertically for comparison. It can be observed from fig. 8.3, A and B that the D/G ratio increases from 0.85 to 1.10 (crystallite size decreases from 19.71 to 15.23 nm) with increasing exfoliation hydrogen gas pressure from 60 bar to 150 bar (under a constant temperature of ca. 220 °C). This may be attributed to the increasing amount of defects being introduced when higher hydrogen gas pressure was used.

Fig. 8.3 Raman spectra of hydrogenated graphenes under (A) a constant temperature of 220 °C and varying hydrogen gas pressures and under (C) a constant pressure of 100 bar and varying exfoliation temperatures. The control material, G-Ar: [100 bar/350 °C] was plotted for comparison.

To ensure a reproducible and consistent Raman spectroscopic result, a total of nine measurements were taken at different spots on the material and the average of the ratios was reported. On the other hand, hydrogenation under increasing temperatures from 200 °C to 500 °C but constant gas pressure displayed a decreasing D/G ratio with increasing exfoliation temperature (Fig. 8.3, C and D). D/G ratio decreases from 0.87 for graphene exfoliated at 200 °C ($L_a = 19.26$ nm) to 0.77 for exfoliation temperature of 350 °C ($L_a = 21.76$ nm) before levelling off to 0.81 for the exfoliation temperature of 500 °C ($L_a = 20.68$ nm). G-Ar: [100 bar/350 °C] was measured to give a ratio of 0.78 ($L_a = 21.37$ nm). Hence, it can be concluded that all hydrogenated graphenes have a higher defect density than the control material. This was likely to be attributed to the fact that besides an introduction of defects into the materials during exfoliation, a partial hydrogenation of the graphene may have occurred. Besides the employment of Raman spectroscopy, XPS will also be utilized in the further exploration of the materials.

X-ray photoelectron spectroscopy is a technique suitable for the determination of the surface chemical composition of materials. The wide-scan XPS spectra of all the materials were as shown in fig. 8.4. It was evident that an increasing hydrogen gas pressure during exfoliation has a negative influence on the removal of oxygen containing groups where G-H: [150 bar/220 °C] contains significantly more oxygen containing groups than G-H: [60 bar/220 °C]. The oxygen content present in the material was reflected in the C/O ratio calculated where a high ratio indicates a low oxygen content. A sharp drop in the ratio from 7.2 to 5.0 was observed with increasing hydrogenation gas pressure from 60 bar to 150 bar (Fig. 8.4, A and B). However, an increasing exfoliation temperature resulted in easier removal of oxygen containing groups where the C/O ratio was found to increase significantly from 7.1 to 13.0 when temperature increases from 200 °C to 500 °C.

Fig. 8.4 Wide-scan XPS spectra of hydrogenated graphenes under (A) a constant temperature of 220 °C and varying hydrogen gas pressures and under (C) a constant pressure of 100 bar and varying exfoliation temperatures. The control material, G-Ar: [100 bar/350 °C] was included for comparison.

High-resolution XPS (HR-XPS) spectrums provide detailed information on the type of chemical bonds present for each electronic state of each element at the materials' surfaces. However, its accuracy in the determination of the degree of hydrogenation (and for the study of sp^3/sp^2 ratio on graphene surfaces) was still questionable due to the narrow difference in the bond energies of C=C and C-C as mentioned previously. Hence, a huge overlap of the C=C and C-C bands was expected and fitting of the spectra must be performed to clearly differentiate the

two bands. Previous reports have utilized fitting of the spectra to provide information on the quantification on the degree of hydrogenation efficiency on the graphene surfaces² and on carbon nanotubes.²⁶

Fig. 8.5 High-resolution XPS of hydrogenated graphene materials.

The HR-XPS C1s spectra for all the exfoliated graphenes were as shown in fig. 8.5.

Relative sensitivity factors were taken into consideration in the fitting of the spectra which was performed based on the bond energies of the various carbon-carbon and carbon-oxygen bonds that might be present on the materials. The fitted results were performed to give the following: C=C at 284.4 eV (red), C-C/C-H bonds at 285.1 eV (blue), C-O bonds at 286.2 eV (cyan), C=O bands at 287.4 eV (purple), O-C=O bonds at 288.7 eV (dark navy) and π - π^* interactions at 290.3 eV (green). The peak intensity for C-C/C-H bond was between 12 – 17 % of the total sum of the C 1s signals fitted for the hydrogenated materials. Fitting of the control material's (G-Ar: [100 bar/350 °C]) spectrum shows that approximately 16 % of the total C1s signal corresponds to C-C bonds. This led to the conclusion that the hydrogenation efficiency of the materials was approximately between 2 - 8 %. This finding was further confirmed with the use of the ATR FT-IR spectroscopy technique.

Fig. 8.6 ATR-IR spectra of hydrogenated graphenes and control materials. (A) Constant temperature of 220 °C and pressures of (I) 60 bar, (II) 100 bar and (III) 150 bar. (B) Constant pressure of 100 bar and varying temperatures of (I) 200 °C, (II) 350 °C and (III) 500 °C. Also shown are: (IV) G-Ar: [100 bar/350 °C], (V) graphene exfoliated at 1 bar nitrogen gas (VI) graphene exfoliated at 1 bar hydrogen gas.

Infrared spectroscopy uses a near infra-red beam that induces various stretching and bending motions of the bonds which occur at frequencies unique to the particular bond and hence, allows identification of the bonds. The C-H stretching of alkyl carbons that occurs at frequencies between 2950 cm^{-1} and 2850 cm^{-1} was found in the spectra for all the hydrogenated graphenes as shown in fig. 8.6. This stretching band was identical to earlier reports that have recorded IR spectrums for hydrogenated carbon nanotubes and fullerenes.^{26,27} However, this band was not found in the ATR FT-IR spectra for the control material and also for graphite oxides that were exfoliated nitrogen and hydrogen gas atmosphere of pressure 1 bar.

The best method to prove the presence and to measure the degree of hydrogenation efficiency of the materials was combustion elemental analysis (EA). Combustion of the starting material for this project revealed that graphite oxides contained 50.64 % of C, 20.82 % of H and 28.54 % of O. Using the results obtained from combustion elemental analysis and the infrared spectroscopic findings, it can be certain that all the H atoms in graphene oxides were bonded to the oxygen atoms present in the starting material. Graphene exfoliated in argon atmosphere was observed to have a composition of 77.67 % of C, 10.35 % of H and 11.98 % of O. Similarly, earlier ATR FT-IR results together with the EA data have proved the direct attachment of H atoms to the oxygen atoms in G-Ar: [100 bar/350 °C] to form hydroxyl groups as according to the stoichiometry of the O and H atoms. G-H: [100 bar/500 °C] exhibits an EA composition of 80.55 % of C, 11.6 % of H and 7.84 % of O. If it was assumed that all the oxygen atoms present in this graphene were bonded to hydrogen atoms to form the –OH group, it can be further concluded that the remaining 3.76 % of hydrogen was directly bonded to the carbon backbone producing graphanes structure. In fact, the O_1H_1 stoichiometry is extremely difficult to achieve and it is likely that they are presented as carboxyl and carbonyl groups with O_2H_1 or O_1H_0 stoichiometry. Hence, the deduced 3.76% of H in form of C-H bond was the lowest assumed percentage where the actual value was likely to be higher. The deduction on the existence of C-H bond in G-H: [100 bar/500 °C] was based on both the elemental analysis and the infrared spectroscopic results

which were also found to be in good quantitative agreement with the HR-XPS data. It was also important to note that a high gas pressure was required for the successful hydrogenation/exfoliation of graphene. Graphite oxides exfoliated in a hydrogen gas atmosphere at a pressure of 1 bar and temperature of 1000 °C possessed a composition of 94.25 % of C, 0 % of H and 5.75 % of O. Similarly, graphenes prepared in nitrogen (N₂) atmosphere of 1 bar pressure and at 1000 °C displayed a composition of 93.50 % of C, 0 % of H and 6.50 % of O.

8.2.2 Electrochemistry of hydrogenated graphenes

Fig 8.7 Cyclic voltammograms at various hydrogenated graphenes synthesized under (A) a constant temperature of 220 °C and varying hydrogen gas pressures and under (D) a constant pressure of 100 bar and varying exfoliation temperatures. The control materials, G-Ar: [100 bar/350 °C] and bare GC were included for comparison. Conditions of voltammetric measurements: 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 50 mM pH 7.2 phosphate buffer solution.

To investigate the heterogeneous electron transfer property of the materials, we first employed cyclic voltammetry with ferro/ferricyanide solution.²⁸ Fig. 8.7 shows the cyclic voltammograms obtained at various hydrogenated graphene surfaces as well as the control materials' (G-Ar and glassy carbon) surfaces. From the CV graphs, the peak-to-peak separation (ΔE_{p-p}) was obtained which allows heterogeneous electron transfer rates (k_{obs}^0) to be calculated using the Nicholson's approach.²⁹ The relationship between ΔE_{p-p} , k_{obs}^0 and the hydrogenation pressure and temperature was plotted as shown in fig. 8.7, B, C, E and F. It can be observed from the data that an increase in the hydrogen gas pressure led to a decrease in the heterogeneous electron transfer rate. The ΔE_{p-p} was observed to increase from 240 mV for G-H [60 bar/220 °C] to 270 mV for G-H [100 bar/200 °C] and to 270 mV for G-H [150 bar/220 °C]. Correspondingly, the HET rates were found to decrease from $8.25 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [60 bar/220 °C] to $4.83 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [100 bar/200 °C] and finally to $4.15 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [150 bar/220 °C]. The increase in the hydrogenation/exfoliation temperature led to an increase in HET rates. In the comparison between materials of varying hydrogenation temperatures, ΔE_{p-p} decreases from 270 mV for G-H [100 bar/200 °C] to 210 mV for G-H [100 bar/350 °C] and levels off afterwards. Consequently, the calculated HET rates increases from $4.83 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [100 bar/200 °C] to $9.51 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [100 bar/350 °C] and to $9.08 \times 10^{-4} \text{ cm s}^{-1}$ for G-H [100 bar/500 °C]. It was of interest to note that with increasing temperature the hydrogenation efficiency increases. Note that the control materials, bare glassy carbon surface had displayed a ΔE_{p-p} of 420 mV and k^0 of $5.66 \times 10^{-5} \text{ cm s}^{-1}$ while G-Ar possessed a ΔE_{p-p} of 180 mV and k^0 of $1.45 \times 10^{-3} \text{ cm s}^{-1}$.

To confirm the trends observed earlier, further investigations were performed with EIS. Electrochemical impedance spectroscopy (EIS) employs a small amplitude perturbation at various frequencies to investigate the electrical resistance towards heterogeneous electron transfer at the material/solution interface.³⁰ Fig. 8.8 shows the impedimetric spectra of various hydrogenated materials' surfaces and the control materials' (bare GC and G-Ar: [100 bar/350 °C]) surfaces. The influence on charge transfer resistance (R_{ct}) by the hydrogen gas pressure and

hydrogenation/exfoliation temperature was studied. The charge transfer resistance value was measured from the diameter of the semicircle of the nyquist plot.

Fig. 8.8 Electrochemical impedance spectroscopy at various hydrogenated graphenes synthesized under (A) a constant temperature of 220 °C and varying hydrogen gas pressures and under (D) a constant pressure of 100 bar and varying exfoliation temperatures. The control materials, G-Ar: [100 bar/350 °C] and bare GC were included for comparison. Conditions of voltammetric measurements: 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 50 mM pH 7.2 phosphate buffer solution.

The resistance to electron transfer at the materials' surfaces did not display a monotonical trend with an increasing gas pressure during hydrogenation (R_{ct} varied from 0.876 k Ω to 2.060 k Ω). However, an obvious trend of a decreasing R_{ct} with an increasing hydrogenation temperature was observed. The R_{ct} value decreased from 2.060 k Ω for G-H: [100 bar/200°C] to 1.100 k Ω for G-H: [100 bar/350°C] and finally to 1.098 k Ω for G-H: [100 bar/500°C]. This was in agreement with earlier results obtained from cyclic voltammetry experiments. Note that the R_{ct} of graphene (G-Ar: [100 bar/350°C]) was 0.679 k Ω and R_{ct} of bare GC was 5.803 k Ω .

The electrical conductivity of GO, hydrogenated graphene and graphene were also investigated with the results as follows. GO exhibited sheet resistivity of $2.176 \times 10^3 \Omega/\square$ and a specific resistivity of $3.67 \times 10^2 \Omega \cdot \text{cm}$; G-H: [100 bar/500 °C] has a sheet resistivity of $1.26 \Omega/\square$ and a specific resistivity of $3.6 \times 10^{-2} \Omega \cdot \text{cm}$. G-Ar: [100 bar/500 °C] possesses a sheet resistivity of $1.14 \Omega/\square$ and a specific resistivity of $2.24 \times 10^{-2} \Omega \cdot \text{cm}$. These results showed that hydrogenated graphene exhibits a larger electrical resistivity than non-hydrogenated graphene which was consistent with theoretical prediction.

8.2.3 Application: TNT detection with hydrogenated graphenes

The capabilities of hydrogenated graphenes were further explored by using them as sensing platforms in the detection of trinitrotoluene (TNT) compounds in borate buffer and in seawater.

Fig. 8.9 The cyclic voltammograms obtained for bare GC, G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] in borate buffer solution. The concentrations of TNT: A) 0 ppm, B) 20 ppm. Conditions: 20 mM borate buffer solution (pH 9.3), scan rate of 100 mV s⁻¹.

The materials of study were modified onto the surface of GC electrodes as sensing platforms to detect a range of TNT concentrations in borate buffer and seawater. A series of cyclic voltammetry measurements and differential pulse voltammetry (DPV) scans were performed and compared to find out the materials' behavior towards different concentrations of TNT in different solutions. Herein the only material of study was G-H: [100 bar/500 °C] with comparison to control materials, G-Ar: [100 bar/350 °C] and bare GC. G-H: [100 bar/500 °C] was the material of choice due to earlier findings where it was found to have the highest hydrogenation efficiency and hence, the highest hydrogen content in its structure. The CV scans were first performed to determine the three reduction peak potentials of TNT on the surface of the materials (refer to Fig. 8.9). The measurements were performed at 0 ppm and 20 ppm of TNT in pH 9.3 borate buffer. Similarly, the three major reduction peaks observed were labeled as x, y and z. Bare GC displayed three reduction peaks at – 570 mV, – 750 mV and – 950 mV. However, only two reduction peaks were observed at – 560 mV and – 770 mV for G-H: [100 bar/500 °C]

and at -540 mV and -750 mV for G-Ar: [100 bar/350 °C]. The third reduction peak for both G-H: [100 bar/500 °C] and G-Ar: [100 bar/350 °C] modified electrodes were not obvious and hence, peak x was chosen as the representative peak as it was clearly observable for all three electrode surfaces. Both G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] showed larger average peak current heights of -22.1 μA and -15.3 μA respectively, as compared to the average peak current height of -10.9 μA for bare GC. This corresponds to a marked increment of 103 % and 40 % in the average current height for G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] respectively when compared to bare GC.

Fig. 8.10 The differential pulse voltammograms obtained for (A) bare GC, (B) G-Ar: [100 bar/350 °C] and (C) G-H: [100 bar/500 °C] in borate buffer solution. Conditions: 20 mM borate buffer solution, pH 9.3. Concentration range of TNT: 0, 4, 8, 12, 16, 20 ppm.

A further study on the sensitivity of the material and the three reduction peaks were carried out via DPV. In addition, a comparison study on the sensitivities of the graphene nanomaterials was carried out with DPV. The DPV scans were performed for a range of TNT concentrations from 0 ppm to 20 ppm as shown in fig. 8.10. It can be observed that the peak current heights of the three reduction peaks increases with increasing TNT concentrations for all three electrode surfaces. As such, we proceed to perform calibration for each of the three reduction peaks for each electrode surface. In a typical calibration graph, the steeper the gradient of the graph the more sensitive the material was towards detection of the analyte. With reference to peak x, the R^2 value G-Ar: [100 bar/350 °C] (0.841) was lower than that of bare GC (0.934) which were both lower than G-H: [100 bar/500 °C] (0.985). However, G-Ar: [100 bar/350 °C] has a gradient of (−651 nA/ppm) which was much steeper than that of G-H: [100 bar/500 °C] (−182 nA/ppm). Bare GC has the least steep gradient of −110 nA/ppm as compared to the two materials. Hence, even though the R^2 value of the G-Ar: [100 bar/350 °C] was lower than both G-H: [100 bar/500 °C] and bare GC, it showed the best sensitivity towards the detection of TNT in borate buffer solution.

Fig. 8.11 Cyclic voltammograms obtained for the range of TNT concentrations for bare GC, G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] in seawater solution. The range of concentrations of TNT: A) 0 ppm, B) 20 ppm. Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (Seawater pH 6.74), scan rate of 100 mV s⁻¹.

Next, we attempt to carry out similar experimental detection procedure using actual sample, seawater as the medium for TNT to dissolve in. Prior to the DPV measurements, a series of blank CV scans (0 ppm TNT) were first performed to account for any possible electroactive compounds present in seawater that could interfere with the signals (Fig. 8.11, A). The results obtained shows that only oxygen reduction peaks at ca. -600 mV were present while any other interference was absent. CV scans were then performed at 20 ppm TNT to identify the peak potentials for the three reduction peaks as shown in fig. 8.11, B. The first two major reduction peaks (x and y) were observed at -550 mV and -730 mV for bare GC, -520 mV and -690 mV for G-Ar: [100 bar/350 °C] and -520 mV and -700 mV for G-H: [100 bar/500 °C]. The third peak (z) occurred at approximately -900 mV for bare GC but was not observable for G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C]. Similarly, peak x was chosen as the representative peak as it was clearly observable for all three electrodes. Both G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] showed larger average peak current heights of -21.7 μ A and -16.1 μ A respectively, as compared to the average peak current height of bare GC at -9.9 μ A. This corresponded to an increment of 118 % and 63 % for G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] respectively when compared to bare GC electrode.

Fig. 8.12 The DPV scans obtained over a range of TNT concentrations for (A) Bare GC, (B) G-Ar: [100 bar/350 °C] and (C) G-H: [100 bar/500 °C] in seawater solution. Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (Seawater pH 6.74). Concentration range of TNT: 0, 4, 8, 12, 16, 20 ppm.

The DPV measurements for each material were taken over a range of TNT concentrations from 0 to 20 ppm in a mixture of seawater and borate buffer solution (refer to Fig. 8.12). It can be observed that the peak current heights increase with increasing TNT concentrations for all three electrode surfaces. Moreover, the third reduction peak (z) was often not observable in several G-Ar: [100 bar/350 °C] DPV graphs (especially at lower TNT concentrations). Hence, only the peak current heights of peak x and y were further used for calibration of the materials as shown in fig. 8.13.

Fig. 8.13 The concentration dependence of TNT for bare GC, G-Ar: [100 bar/350 °C] and G-H: [100 bar/500 °C] for A) Peak x and B) Peak y in seawater solution. Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (seawater pH 6.74).

With reference to peak x, the R^2 value of bare GC (0.967) was lower than that of G-Ar: [100 bar/350 °C] (0.969), which were in turn both lower than G-H: [100 bar/500 °C] (0.975). However, the gradient of G-Ar: [100 bar/350 °C] (– 434 nA/ppm) was found to be much steeper than that of bare GC (– 196 nA/ppm), which were in turn both steeper than G-H: [100 bar/500 °C] (– 103 nA/ppm). Similarly, G-Ar: [100 bar/350 °C] displayed greatest sensitivity towards TNT detection even when its R^2 value was in between that of G-H: [100 bar/500 °C] and bare GC. Limit of detection of TNT was determined to be 400 ppb for G-Ar: [100 bar/350 °C] and 500 ppb for G-H: [100 bar/500 °C]. Limit of quantification was 1.3 ppm for G-Ar: [100 bar/350 °C] and 1.7 ppm for G-H: [100 bar/500 °C]. The results obtained proved that G-Ar: [100 bar/350 °C] exhibited greater sensitivity than G-H: [100 bar/500 °C] towards the detection of TNT in both borate buffer and seawater medium. This may possibly be due to the fact that graphene contains a larger amount of aromatic rings than hydrogenated graphene which allows favourable surface accumulation or larger concentration of analytes.

Discussion

We have successfully proved the possibility of performing hydrogenation of graphite oxide through exfoliation of graphite oxides in a hydrogen gas atmosphere under high pressure/temperature conditions. This phenomenon was fully supported by a comparison of the various characterization results between graphenes exfoliated under hydrogen and non-hydrogen gas environment where a lack of hydrogenation was observed in the latter. Further investigation on hydrogenation efficiency and the influence of the exfoliation conditions on the efficiency was also performed. It was discovered that H₂ gas pressure of 100 bar at 500 °C was the most effective reaction condition to produce hydrogenated graphene with the highest hydrogenation efficiency. The method of synthesis reported in this paper was of utmost importance due to its ability to produce scalable yield in contrast to previously published works where the yield was limited to minute amounts. The effective production of large amounts of hydrogenated graphene allows the reported method of synthesis to be useful towards the fabrication of graphane. Electrochemical studies showed that hydrogenated graphenes possessed lower heterogeneous electron transfer rates and higher charge transfer resistance as compared to graphene. This may be attributed to the hydrogenation synthesis procedure changing the electronic structure of the graphene and/or composition/structure of the electrochemically active sites in the material. Interestingly, in the TNT detection experiment; G-Ar: [100 bar/350 °C] was found to be the best sensing material as compared to G-H: [100 bar/500 °C] and bare GC due to its higher aromatic rings content. G-Ar: [100 bar/350 °C] was chosen as the representative for hydrogenated graphene due to it possessing the highest hydrogen content as compared to the other hydrogenated materials.

Experimental

Materials:

Silver nitrate, barium nitrate, nitric acid, sulfuric acid, hydrochloric acid, potassium chlorate were obtained from PENTA. Argon and hydrogen were obtained from SIAD. Graphite was obtained from KOH-I-NOOR GRAFIT. Potassium ferrocyanide, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium tetraborate decahydrate, 2,4,6-trinitrotoluene, sodium phosphate monobasic, sodium chloride, potassium chloride were purchased from Sigma-Aldrich. TNT was obtained as an analytical standard, 1000 ppm and was used as received. The seawater was collected from East Coast Park, Singapore. Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions. Glassy carbon (GC) electrodes, Ag/AgCl electrode and platinum (Pt) electrode were obtained from Autolab.

Apparatus:

SEM imaging was performed with a with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) under gentle-beam mode at 2 kV. The samples were prepared by attaching the materials onto a sticky conductive carbon tape and mounted onto an aluminium sample stub. TEM images were acquired with a JEM 1400 field-emission transmission electron microscope (JEOL, Japan) operating at 100 kV. TEM samples were prepared using 1 μL of a 0.5 mg/mL suspension of the thermally reduced graphenes dripped onto a carbon coated copper grid which was then allowed to dry at room temperature. XPS was executed with a Phoibos 100 spectrometer using a monochromatic Mg X-ray radiation source (SPECS, Germany) for the measurement of wide-scan and high resolution C 1s spectrums. The samples are attached onto a sticky conductive carbon tape that was attached to an aluminium XPS holder. Further processing of the data was performed by calculating the C/O ratios from the wide-scan XPS measurements with the use of relative sensitivity factors. The XPS samples were prepared by attaching a uniform layer of the materials onto a conductive carbon tape which was then affixed onto an

aluminium XPS sample holder. A confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector was used for the acquiring of the Raman spectrums. Measurements were performed using a 514.5 nm Ar laser and an Olympus optical microscope with a 100 x objective lens. Pre-measurement calibration was achieved with a silicon reference at 520 cm^{-1} which gives a peak position resolution of less than 1 cm^{-1} . Actual measurements were performed using well-compressed and compacted samples that were placed on top of a glass slip which was positioned on a piece of glass slide. The Fourier transform infrared spectroscopic measurements were performed using an attenuated total reflectance method on PerkinElmer Spectrum 100 system. Diamond/ZnSe was used as the ATR crystal in conjunction with a universal ATR accessory. Electrochemical experiments using the cyclic voltammetric, electrochemical impedance spectroscopic and the differential pulse voltammetry techniques were performed with a μ Autolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) controlled by the software NOVA 1.7 (Eco Chemie). For conductivity measurements of graphene related materials, 40 mg of the material were first compressed into a capsule ($\frac{1}{4}$ " diameter) under pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured with the 4-probe technique using the method according to van der Pauw.³¹ The resistivity measurement was then performed with a Keithley 6220 current source and Agilent 34970A data acquisition/switch unit.

Procedures:

*Graphite oxide preparation with Hofmann method.*³² 87.5 mL of sulfuric acid (98 %) and 27 mL of nitric acid (65 %) were added to a reaction flask (Pyrex baker with thermometer) which contains a magnetic stir bar. The mixture was then cooled by immersion into an ice bath for 30 min. 5 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and to obtain a homogeneous dispersion. While maintaining the reaction flask in the ice bath, 55 g of potassium chlorate was then slowly added into the mixture (over 30 min) in order to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon

complete dissolution of potassium chlorate, the reaction flask was left loosely capped to allow the evolution of gas and 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 hydrochloric acid (5 %) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative response towards chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Preparation of hydrogenated graphene. The high pressure synthesis of the materials was performed in a stainless steel autoclave placed in a resistive heated furnace. Approximately 0.3 g of graphite oxide was placed in a quartz glass liner inside the autoclave machine. Hydrogen gas of 99.9 % purity and argon gas of 99.996 % purity was used in the synthesis process. The autoclave was then repeatedly flushed with hydrogen or argon gas and subsequently filled with the respective gases of the desired pressure using a pressure control valve. The autoclave was heated at a rate of 5 °C min⁻¹ and the dwell time on the temperature of synthesis was 2 hours. The reaction vessel was then left to cool freely inside the furnace under room temperature.

Electrochemical, impedimetric and differential pulse voltammetric measurements. The glassy carbon electrodes were cleaned by polishing with an alumina suspension then washed with deionised water and wiped dried before use. The synthesized hydrogenated graphenes were dispersed in DMF solvent to create a suspension with a concentration of 0.5 mg ml⁻¹. The suspension was then sonicated at room temperatures for five minutes before each use. Modification of the electrodes was performed by having a 1 µL aliquot of the graphene suspension coated onto the cleaned surface of a GC electrode which was then left under a lamp to dry to give a layer of randomly dispersed G-H and G-Ar on the GC surface. This step was then

repeated until three layers of coatings on the GC surface were obtained. The modified GC electrodes, Ag/AgCl reference electrode and Pt counter electrode were then dipped into an electrochemical cell which contains the electrolyte solution (10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ dissolved in 50 mM pH 7.2 phosphate buffer solution) and the measurements were started. CV measurements were taken each time before the start of every EIS measurement which was all carried out under room temperatures. CV measurements were taken for the range of potentials from – 800 mV to + 1150 mV at a scan rate of 100 mV s^{-1} for two consecutive scans. This was immediately followed by an EIS measurement carried out for a range of frequencies from 10 000 Hz to 0.1 Hz. Three replicates were carried out for each TRGO. In the TNT experiment, cyclic voltammetry and DPV measurements were performed in 1 mL of electrolyte solution consisting of various concentrations of TNT dissolved in either 20 mM borate buffer solution or seawater solution consisting of a 9 : 1 ratio of a mixture of seawater and 200 mM borate buffer solution. The concentrations of TNT in electrolyte solutions that were used for the measurements were: 0, 4, 8, 12, 16 and 20 ppm. The borate buffer solution was prepared by dissolving sodium tetraborate decahydrate in ultrapure water to give a 20 mM borate buffer solution. The seawater solution was prepared by mixing seawater with 200 mM borate buffer solution in a 9 : 1 (seawater : borate buffer) ratio. Borate buffer is used to maintain pH 9.2 as the reduction of TNT is pH dependant.³³ All CV experiments were carried out at a scan rate of 100 mV s^{-1} . All DPV experiments were carried out at a step potential of 5 mV and modulation amplitude of 25 mV under room temperature and pressure conditions.

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PART 2:

Influence of Synthesis Methods/Conditions on the Properties of Graphene

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Chapter 9

Thermally Reduced Graphenes Prepared from Staudenmaier, Hofmann and Hummers Methods and its Application in the Electrochemical Detection of Trinitrotoluene in Seawater

9.1	<i>Introduction</i>
9.2	<i>Results</i>
9.2.1	<i>Properties of thermally reduced graphene oxides prepared from different methods</i>
9.2.2	<i>Electrochemistry of thermally reduced graphene oxides prepared from different methods</i>
9.2.3	<i>Application: TNT detection with thermally reduced graphene oxides prepared from different methods</i>
9.3	<i>Discussion</i>
9.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Filip Šaněk,^b Adriano Ambrosi, Guanjia Zhao, Zdeněk Sofer, Martin Pumera.

Graphenes prepared by Staudenmaier, Hofmann and Hummers Methods with Consequent Thermal Exfoliation Exhibit very Different Electrochemical Properties. *Nanoscale*, 2012, **4**, 3515.

Article can be downloaded from

<http://pubs.rsc.org/en/content/articlelanding/2012/NR/c2nr30490b#!divAbstract>.

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2. Beng Khong Ong, **Hwee Ling Poh**, Chun Kiang Chua, Martin Pumera. Graphenes Prepared by Hummers, Staudenmaier and Hofmann Methods for Analysis of TNT-Based Nitroaromatic Explosives in Seawater. *Electroanalysis*, 2012, **24**, 2085.

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Introduction

Besides functionalizing graphene with heteroatoms, modifying reaction conditions or employing a different synthesis method is another option to alter the properties of graphene. This led to the study of Part 2: Influence of synthesis methods/conditions on the properties of graphene.

As previously mentioned in Chapter 2, graphene and graphite oxides were some of the most common nanocarbon materials used for further applications or functionalization. Three most well-known methods to derive graphite oxides were Staudenmaier¹ (ST), Hofmann² (HO) and Hummers³ (HU) methods. Despite knowing the differences between the three methods (in terms of oxidizing agents), numerous scientists have proceeded to use graphite oxides synthesized from the three methods interchangeably; with an assumption that the final products derived will not differ in any way. In brief, these three solution-based synthesis methods differ in the oxidizing agents used. ST uses fuming nitric acid (HNO_3), concentrated sulfuric acid (H_2SO_4) and potassium chlorate (KClO_3) while HO uses concentrated HNO_3 , concentrated H_2SO_4 and KClO_3 . Lastly, HU uses concentrated H_2SO_4 instead of nitric acid, sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4). The graphite oxides obtained from all three methods were then further thermally annealed to give thermally reduced graphene oxides (TRGOs) such shown in scheme 9.1. In Chapter 9, an in-depth investigation on the various properties of the TRGOs derived from the three methods was performed. This project will be presented in the form of a comparison study to probe the influence of modified reaction conditions or different synthesis methods on the properties of the final products. The results obtained from this project will have important implications on the earlier experimental studies that based their findings on a single synthesis method with no comparison to other graphite oxides synthesis methods.

Moreover, the materials' behaviors and response towards sensing applications were also probed. This was executed to investigate if differences in synthesis methods can influence the materials' detection capabilities in sensing applications. Similar to Chapter 8, the detection of trinitrotoluene (TNT) compounds will be used for this study. The TRGOs derived from the three methods will be incorporated as sensing platforms in a similar manner as hydrogenated graphenes in the previous chapter. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) will be the electrochemical techniques utilized in this project to detect TNT.

Scheme 9.1 Schematic diagram of the procedure for the production of thermally reduced graphenes.

Results

9.2.1 Properties of thermally reduced graphene oxides prepared from different methods

Graphite oxides were prepared by treatment of graphite using three different methods as indicated in the following. Staudenmaier method¹: Fuming nitric acid, concentrated sulfuric acid and potassium chlorate. Hofmann method²: Concentrated nitric acid, concentrated sulfuric acid and potassium chlorate. Hummers method³: Concentrated sulfuric acid in the presence of sodium nitrate and potassium permanganate. Detailed elaboration of the synthesis procedure can be found in the experimental section of this chapter. The three materials of interest were abbreviated as follows, Staudenmaier: GO-ST, Hofmann: GO-HO and Hummers: GO-HU for ease of reference. The graphite oxides yielded from the three methods were then subsequently exfoliated and reduced by undergoing a thermal shock at 1000 °C in a furnace under nitrogen gas atmosphere to produce the final product, thermally reduced graphenes (Scheme 9.1). Electrochemical studies and characterization works were carried out on the three thermally reduced graphenes and the results were elaborated as follows.

Fig. 9.1 X-ray diffraction results of graphite and graphite oxide prepared by the various methods. Oxidation of graphite resulting in a large increment in the separation of the graphene layers can be observed.

Fig. 9.1 shows the X-ray diffraction (XRD) results of the starting material, graphite and the three graphite oxides. It can be observed that graphite oxides prepared from different methods showed different amounts of spacing between the graphene layers. The graphite oxide prepared using Hummers method (GO-HU) displayed the largest spacing between graphene layers (0.8133 nm) followed by Hofmann method graphite oxide (GO-HU) at 0.7226 nm. The smallest spacing was found in Staudenmaier method graphite oxide (GO-ST) at 0.7084 nm. In the XRD diffraction spectrum, the existence of the (002) diffraction line was an indication of the degree of oxidation of the graphite oxides where an absence of the (002) line signifies a complete oxidation of graphite. As observed in Fig. 9.1, the (002) diffraction line that was observed for graphite was not observed in the spectrum for GO-ST, GO-HU and GO-HO. This means that a complete oxidation of graphite to graphite oxide has occurred for all three graphite oxides synthesized from the three different methods. The XRD data was consistent with the elemental analysis (EA) obtained for the three graphite oxides.

The composition of the major elements found in GO-ST was: 58.73 % C, 23.28 % O and 17.99 % H where the C/O ratio was 2.52. Therefore, GO-ST exhibited the lowest degree of oxidation which was consistent with the XRD data obtained earlier. GO-HO have a major elemental composition of 50.64 % C, 28.54 % O and 20.82 % H with a C/O ratio 1.77. EA of GO-ST and GO-HO has also shown that sulfur and nitrogen was not detected for the two materials. However, GO-HU showed the presence of these two elements with a composition of 37.33 % C, 33.04 % O, 28.05 % H, 0.890 % N, 0.690 % S and a C/O ratio 1.12. This indicates that Hummers method produces graphite oxides with the highest degree of oxidation as it has the lowest C/O ratio among the three graphite oxides. The traces of sulfur and nitrogen in GO-HU were likely a result of covalently bonded sulfates⁴ and nitrates or adsorbed sulfuric acid and nitric acid used in the Hummers method to produce graphite oxide.

Fig. 9.2 Scanning electron microscopy images of thermally reduced graphenes. The reduced materials were Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU). Images were taken at three different magnifications.

We have also investigated the properties of the the thermally reduced graphenes of each type of graphite oxides, labeled as G-ST, G-HO and G-HU. Imaging of the three materials were performed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was observed that no significant differences in the morphologies were found among them. SEM images of each thermally reduced graphene (TR-G) at various magnifications (Fig. 9.2) displayed structures that were expected after undergoing thermal exfoliation⁵ process.

Fig. 9.3 shows TEM images of G-ST, G-HO and G-HU where all materials displayed wrinkled, single-to-few layer graphene sheets. These characteristics are typical of graphene which implies that the exfoliation procedure has effectively convert graphite oxides to graphene oxides.⁶ Similarly, the three thermally reduced graphenes displayed no major differences in their structures.

Fig. 9.3 Transmission electron microscopy images of thermally reduced graphenes. The materials were Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU). Images were taken at different magnifications.

Raman spectroscopy was also employed to determine the density of defects in the graphene sheets. Pristine sp^2 graphene lattice displays a peak in the Raman spectra at ca. 1560 cm^{-1} (*G*-band) while sp^3 defects found in the sp^2 lattice gives a signal at ca. 1350 cm^{-1} (*D*-band). The intensities of the *D* and *G* bands (*D/G* ratio) were often used for the calculation of a *D/G* ratio which acts as an indication of the degree of disorderliness in the lattice structure of the materials. The Raman spectrums for G-ST, G-HO and G-HU were as shown in Fig. 9.4 and their calculated *D/G* ratios were 0.77, 1.09 and 0.97 respectively. Using the *D* and *G* bands' intensities, the average crystallite size (L_a) of each material can be obtained according to the equation:⁷

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

where λ_{laser} is the wavelength (nm) of the laser used during Raman measurements. I_G and I_D are the intensities of the *G* and *D* bands, respectively. The resultant crystallite sizes of the materials were 21.8 nm for G-ST, 15.4 nm for G-HO and 17.3 nm for G-HU. From the Raman measurements, it can be observed that G-ST possessed the lowest density of defects.

Fig. 9.4 Raman spectrums of thermally reduced graphenes. The materials were Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU).

It was widely known that thermally reduced graphenes comprised of a small amount of oxygen functionalites on their surfaces even when majority of these functionalities were eliminated during the thermal exfoliation step.⁸ Investigation on this small amount of retained oxygen containing groups can be achieved through X-Ray photoelectron spectroscopy (XPS). This technique allows evaluation of the surface chemical composition of the materials and their respective electronic states by irradiating the material with a beam of X-rays.⁹

Fig. 9.5 X-ray photoelectron survey spectra of thermally reduced graphenes. The materials were Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU).

The XPS survey spectrums of G-ST, G-HO and G-HU were as shown in fig. 9.5. Core C 1s and O 1s peaks were clearly visible in all spectra at 285 eV and 534 eV, respectively. The C/O ratios for the materials were calculated from the spectrums and reported as follows: 24.1 for G-ST, 18.22 for G-HO and 19.27 for G-HU. High C/O ratios suggest low oxygen content in all three materials which was an indication of a successful thermal reduction/deoxygenation of the GOs. It was also observed that thermally reduced graphenes that were produced in the absence of KMnO_4 (G-ST and G-HO) presented a very different spectrum from that of G-HU which uses KMnO_4 in its synthesis. This was due to G-HU containing nitrogen functionalities in its structure which appeared as a prominent N 1s core peak that was observable only in the G-HU spectrum. This result was consistent with the earlier EA results where GO-ST, GO-HO and GO-HU; the respective starting material for each thermally reduced graphene contain the same elements as

their consequent, final product (G-ST, G-HO and G-HU). The N 1s peak in G-HU spectra accounts for 1.28 at. % of the total content in graphene. This led to the conclusion that the treatment of graphite using the Hummers method where KMnO_4 was being employed, results in the introduction of nitrogen moieties into the graphene framework. On the other hand, the Staudenmaier and Hofmann synthesis methods that use KClO_3 as an oxidizing agent does not introduce nitrogen content into the graphite oxide and its final product, thermally reduced graphenes.

Fig. 9.6 High resolution X-ray photoelectron spectrums of C 1s peak of thermally reduced graphenes. The materials were Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU).

Table 9.1 Quantitative percentages for different thermally reduced graphenes, G-ST, G-HO and G-HU for the C 1s HR-XPS spectrums. The figures were reported in percentages (%).

	C=C	C-C	C-O	C=O	O-C=O	$\pi\pi^*$
G-ST	69.3	13.2	6.5	2.5	2.2	6.2
G-HO	67.1	14.2	6.8	3.2	1.8	6.9
G-HU	67.8	14.6	6.4	3.2	1.8	6.2

High resolution X-ray photoelectron spectroscopy (HR-XPS) was utilized to explore the types of oxygen functionalities present in the three thermally reduced graphenes. Fig. 9.6 shows the HR-XPS spectrums of the C 1s peaks for G-ST, G-HO and G-HU. All spectrums showed a single peak at 284.5 eV with an asymmetrical tail at higher binding energies. Fitting was performed on each spectrum to quantify and differentiate between the five different carbon stages: sp^2 -hybridized carbon atoms (284.5 eV), sp^3 -hybridized carbon atoms (285.7 eV), the C-O of alcohol/ether groups (286.8 eV), the C=O of carbonyl groups (288.0 eV), and O-C=O of carboxy acid/ester groups (289.2 eV). A $\pi\text{-}\pi^*$ shake-up signal (290.8 eV) which was typical for sp^2 -hybridized carbon was found in all the three materials. The percentages for each carbon stage are tabulated in table 9.1 for comparison. It can be clearly observed that all three thermally reduced graphenes possessed no significant differences in their abundances of the oxygen functionalities in their structures.

9.2.2 Electrochemistry of thermally reduced graphene oxides prepared from different methods

Fig 9.7 Cyclic voltammetric results of Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods. (A) 10 mM $[\text{Fe}(\text{CN})_6]^{3-}/^{4-}$ and (B) 10 mM ascorbic acid.

The electrochemical behavior of materials is one of the key properties in determining the materials' suitability for energy storage and sensing applications. Herein we seek to investigate if different thermally reduced graphenes preparation methods may potentially influence the properties of the material such as heterogeneous electron transfer rates at the graphenic surfaces. Fig. 9.7, A shows the cyclic voltammograms of ferro/ferricyanide for bare glassy carbon, G-ST, G-HO and G-HU. It was observed that bare glassy carbon (GC) electrode displays a large peak-to-peak (ΔE_{p-p}) separation of 510 mV in the cyclic voltammetric results of ferro/ferricyanide indicating a slow heterogeneous electron transfer rate. The ΔE_{p-p} values for G-ST, G-HO and G-HU were 240 mV, 260 mV and 130 mV respectively. ΔE_{p-p} values can be translated to heterogeneous electron transfer constant (k_{obs}^0) using the Nicholson approach¹⁰ where ΔE_{p-p} was related to Ψ which eventually was related to k_{obs}^0 . The calculated k_{obs}^0 values for bare GC electrode, G-ST, G-HO and G-HU were $6.88 \times 10^{-5} \text{ cm s}^{-1}$, $2.35 \times 10^{-3} \text{ cm s}^{-1}$, $1.83 \times 10^{-3} \text{ cm s}^{-1}$ and $8.30 \times 10^{-3} \text{ cm s}^{-1}$ respectively. It can be concluded that G-HO and G-ST exhibited almost similar HET rates while G-HU (prepared with KMnO_4) displays a much faster HET rate than G-HO and G-ST.

To investigate the behavior of various thermally reduced graphenes for biosensing purposes, we studied the electrochemical response of ascorbic acid (AA) at G-ST, G-HO and G-HU surfaces (Fig. 9.7, B). Oxidation of AA at bare GC starts at 90 mV before attaining the maximum at a peak potential of 500 mV. Oxidation of AA at G-ST and G-HO begins at the same potential of -120 mV and reaches the maximum peak at 170 mV and 200 mV respectively. However, the oxidation of AA at the G-HU surface was observed to be quite different from G-ST and G-HO as three oxidation peak potentials were detected instead. The oxidation peak begins at -170 mV before reaching the first peak potential at 40 mV followed by the second peak potential at 330 mV and the third peak potential at 780 mV. These additional peaks were most likely attributed to the adsorption phenomena of AA molecules at G-HU surfaces.

9.2.3 Application: TNT detection with thermally reduced graphene oxides prepared from different methods

The difference in electrochemical behaviors observed earlier with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and ascorbic acid led to the experimenting of the three materials as sensing platforms in the application of electrochemical detection of TNT. With the use of the three thermally reduced graphenes as sensing platforms, the electrochemical behavior of TNT on each material's surface was investigated. Cyclic voltammetry was employed as the electrochemical method of detection for TNT of 20 ppm concentration prepared in 20 mM borate buffer. The reduction peak potentials of the nitro groups in TNT (refer to Fig. 9.8) can be clearly identified from the cyclic voltammograms obtained. It can be observed that three major reduction peaks account for the reduction of TNT at the surface of all three types of thermally reduced graphenes. At the surface of the bare GC electrode, reductions of TNT occurred at -530 mV and -720 mV, G-HU at -480 mV, -620 mV and -720 mV, G-ST at -520 mV, -660 mV and -750 mV and G-HO at -500 mV, -640 mV and -740 mV.

Fig. 9.8 Cyclic voltammograms of the reduction of TNT using G-HU modified, G-ST modified, G-HO modified and bare GC electrodes.

A range of TNT concentrations (0, 4, 8, 12, 16 and 20 ppm) were then explored in an attempt to calibrate the detection abilities of the different materials' surfaces. Using the differential pulse voltammetry (DPV) technique, three similar reduction peaks that were previously shown in the CV scans were also detected in the DPV results (Fig. 9.9). The three peaks were labeled according to their reduction potentials with the least negative potential (at ca. -450 mV) labeled as peak *a*, followed by the peak at ca. -550 mV as peak *b* and finally the most negative potential at ca. -650 mV as peak *c*.

Fig. 9.9 DPVs of a range of TNT concentrations for G-HU (A), G-ST (B), G-HO (C) and bare GC (D). The different concentrations of TNT: 0, 4, 8, 12, 16 and 20 ppm.

The calibration plots for all three materials were made based on the currents of the three peaks as shown in fig. 9.10. The gradient of the plots indicates the sensitivity of the materials towards the detection of TNT. From the plots, G-ST displayed the greatest sensitivities of $-0.325 \mu\text{A/ppm}$, $-0.233 \mu\text{A/ppm}$ and $-0.215 \mu\text{A/ppm}$ for peak *a*, *b* and *c*, respectively. However, the calculated R^2 values were lower as compared to G-HO and bare GC whose R^2 values were the highest for all three peaks, but their sensitivities (refer to Table 9.2) were poorer as compared to G-ST. Therefore, G-HO will be used as the main material of interest in the further investigation of the detection of TNT in seawater due to its relatively stable R^2 and sensitivity values that were achieved for all three reduction peaks. The calibration results were based on measurements from three replicates to give an average standard deviation value of 0.447 and an excellent average R^2 value of 0.952.

Fig. 9.10 Concentration dependence of G-HU, G-ST, G-HO and bare GC for peak *a* (A), peak *b* (B) and peak *c* (C).

Table 9.2. Comparison of sensitivity of the various electrochemical systems towards TNT in a 20 mM borate buffer solution.

Materials	<u>Peak a</u>		<u>Peak b</u>		<u>Peak c</u>	
	R^2	Sensitivity ($\mu\text{A/ppm}$)	R^2	Sensitivity ($\mu\text{A/ppm}$)	R^2	Sensitivity ($\mu\text{A/ppm}$)
G-HU	0.962	-0.117	0.938	-0.113	0.95	-0.105
G-ST	0.885	-0.325	0.864	-0.233	0.91	-0.215
G-HO	0.999	-0.274	0.997	-0.185	0.97	-0.135
Bare GC	0.984	-0.192	0.972	-0.068	0.99	-0.030

G-HO was employed as the main material of study due to its high linearity and sensitivity observed for all three reduction peaks as shown earlier. CV measurements were performed on G-HO and bare GC electrodes in an electrolyte solution consisting of 20 ppm TNT solution mixed in a mixture of seawater and 200 mM borate buffer solution (9:1). In the mixture, the resulting concentration of borate buffer would be 20 mM while the seawater undergone only minimal dilution. Similarly, CV scans were first performed for the two electrodes using a blank electrolyte solution to determine the presence of any background interferences in the seawater solution. A reduction peak was once again observed for the blank electrolytes which may be due to the reduction of oxygen present in the solutions (data not shown). Interestingly, no other major unknown peaks were detected in the scans which indicate an almost complete absence of interferences in the seawater that may further complicate and interfere with the electrochemical measurements. The scan results showed that the major reduction peaks for TNT in seawater occurred at – 450 mV, - 590 mV and – 690 mV for G-HO and at – 510 mV, - 670 mV and – 830 mV for bare GC electrode (refer to Fig. 9.11).

Fig. 9.11 CV of TNT in seawater at surfaces of G-HO and bare GC electrode. Scans were performed in 20 ppm TNT borate buffer and seawater mixture.

Similarly, DPV scans were also performed on TNT in seawater using G-HO and bare GC electrodes for a range of six different concentrations of TNT (0, 4, 8, 12, 16 and 20 ppm) as shown in fig. 9.12. The reduction peaks were labeled according to their potentials where the least negative potential was labeled as peak *a* (at ca. – 450 mV) followed by peak *b* (at ca. – 550 mV) and finally, peak *c* (at ca. – 700 mV). It can be observed that the currents for all the three peaks increase with increasing TNT concentrations. This indicates that the reduction of the TNT compound can still be easily detected by DPV even when the TNT compound was completely dissolved in seawater. Calibration plots based on the current height of each peak for both G-HO and bare GC were plotted as shown in fig. 9.13. From the calibration graphs obtained, a linear relationship between the TNT concentration and the peak's current height was observed for both G-HO and bare GC. G-HO was observed to display the highest sensitivity towards the detection of TNT in seawater with sensitivity values of - 0.387 $\mu\text{A/ppm}$, - 0.262 $\mu\text{A/ppm}$ and - 0.253 $\mu\text{A/ppm}$ for peaks *a*, *b* and *c*, respectively. Furthermore, a significant improvement in the sensitivity was observed for G-HO where the measured sensitivity values increased by 29 % (peak *a*), 30 % (peak *b*) and 46 % (peak *c*) as compared to the sensitivity values obtained from the TNT detections in borate buffer. The R^2 values of the three peaks for G-HO were found to be constant at ca. 0.984. The gradient of the calibration plots indicate the detection sensitivity of

the electrode systems. Therefore, G-HO was observed to possess a higher sensitivity towards TNT detection due to its steeper gradient as compared to bare GC (refer to Fig. 9.13).

Fig. 9.12 DPV of G-HO (A) and bare GC (B). Scans were performed for the TNT concentrations of 0, 4, 8, 12, 16 and 20 ppm. TNT compound was prepared in a mixture of seawater and 200 mM borate buffer (9:1).

Fig. 9.13 Calibration plots of G-HO and bare GC for peak *a* (A), peak *b* (B) and peak *c* (C). Conditions: mixture of seawater and 200 mM borate buffer solution prepared with a ratio of 9:1, pH 8.9.

Discussion

Investigation on the influence of graphite oxide preparation methods' on the properties and electrochemical behavior of thermally reduced graphenes was achieved through characterization studies and cyclic voltammetry experiments. Differing in the concentration of nitric acid and the oxidizing agent used, the three methods (Staudenmaier, Hofmann and Hummers) exhibited differences in their properties. With a different oxidation agent used during the synthesis process, Hummers methods thermally reduced graphenes was the only material found to possess nitrogen content in its structure and a faster heterogeneous electron transfer rate as compared to Staudenmaier and Hofmann methods. This clearly indicates that the method of oxidation during synthesis can influence the electrochemical properties of the resulting graphene materials and in turn affect the application of these materials in electrochemical devices. Using TNT compounds as the material of interest to be detected, the sensing capabilities of the materials were tested in borate buffer solution and seawater. The differential pulse voltammetry technique was employed as the electrochemical method of detection in this study. The results obtained proved that G-HO possessed the highest sensitivity among the thermally reduced graphenes prepared by the three methods. Even with TNT dissolved in organisms-filled seawater, G-HO proved to display even better sensitivities with increments in sensitivity values of at least 29 % and at maximum 46 % as compared to TNT in borate buffer solution. These findings showed the potential of constructing thermally reduced graphenes modified electrochemical sensors for explosive compounds.

Experimental

Materials:

Graphite microparticles (< 50 μm), sulfuric acid (98 %), sodium phosphate monobasic, potassium ferrocyanide, nitric acid (68 %), potassium chlorate (98 %), potassium permanganate (98 %), hydrogen peroxide (30 %), sodium tetraborate decahydrate, potassium phosphate dibasic, hydrochloric acid (37 %), *N,N*-dimethylformamide (DMF), acetonitrile, ascorbic acid (AA) were obtained from Sigma–Aldrich. Platinum electrode (Pt), glassy carbon (GC) and with a diameter of 3 mm and Ag/AgCl electrode were purchased from Autolab, The Netherlands. Trinitrotoluene (TNT) was purchased from Supelco Analytical (Bellefonte, PA) as an analytical standard (1000 ppm) and used as received. The seawater used in this experiment was collected at Sentosa Island, Siloso Beach (Singapore).

Apparatus:

SEM imaging was performed with a with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) under gentle-beam mode at 2 kV. The samples were prepared by attaching the materials onto a sticky conductive carbon tape and mounted onto an aluminium sample stub. TEM images were acquired using a JEM 1400 field-emission transmission electron microscope (JEOL, Japan) operating at 100 kV. Preparation of TEM samples was executed with a 0.5 mg/mL suspension of the thermally reduced graphenes. 1 μL of the suspension was dripped onto a carbon coated copper TEM grid and left to dry at room temperature. X-ray photoelectron spectroscopy was executed using a Phoibos 100 spectrometer. A monochromatic Mg X-ray radiation source (SPECS, Germany) was utilized for the measurement of survey and high resolution C 1s spectra. Relative sensitivity factors were used for the calculation of C/O ratios from the XPS survey spectra. The XPS samples were prepared by coating a uniform layer of the materials onto an adhesive carbon tape. Raman spectra

measurements were performed with a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a CCD detector. A 514.5 nm Ar laser and a 100x objective lens mounted on an Olympus optical microscope were used with the instrument. Calibration of the instrument was done with a silicon reference at 520 cm^{-1} which gives a peak position resolution of $< 1\text{ cm}^{-1}$. X-ray diffraction measurements were performed with PANalytical X'Pert PRO diffractometer, a Cu lamp and a scintillation detector. The elemental analysis was performed using Vario EL III from Elemental. Cyclic voltammetric experiments were performed using a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands). The instrument was connected to a General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). The setup for CV experiments was a three-electrode system configuration placed in a 5 mL electrochemical cell at room temperature. Pt electrode served as an auxiliary electrode and the Ag/AgCl electrode worked as the reference electrode in the setup. The electrochemical potentials reported here were with references to the Ag/AgCl reference electrode.

Procedures:

*Graphite oxide preparation with Staudenmaier method.*¹ The fuming nitric acid was prepared by distillation of a mixture of concentrated nitric acid and concentrated sulfuric acid (1:3 vol.). The nitric acid was then purified repeatedly with vacuum distillations until a negative reaction of barium nitrate with sulfate ions was achieved. The concentration of fuming nitric acid was measured with a pycnometer which was found to be 98 %. 87.5 mL of sulfuric acid (98 % concentration) and 27 mL of nitric acid (fuming) were then added to a reaction flask containing a magnetic stir bar. The mixture was then subsequently cooled by immersion in an ice bath for 30 min. 5 g of graphite was then added into the mixture with vigorous stirring motion to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask in an ice bath, 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period) in order 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 the gas evolved and the mixture was continuously stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was then poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on 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 60°C for 48 h before use.

*Graphite oxide preparation with Hofmann method.*² 87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (68%) were added to a reaction flask (pyrex baker with thermometer) containing a magnetic stir bar. The mixture was then cooled by immersion in an ice bath for 30 min. 5 g of graphite was then added to the mixture with vigorous stirring motion to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask in an ice bath, 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period) in order 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 the gas evolved and the mixture was continuously stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was then poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in hydrochloric acid (5 %) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on 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 60 °C for 48 h before use.

*Graphite oxide preparation with Hummers method.*³ 5 g of graphite, 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 two hours.

In the subsequent four hours, the reaction mixture was allowed to reach room temperature before being heated to 35 °C for 30 minutes. The reaction mixture was then poured into a flask containing 250 ml of deionized water and further heated to 70 °C. The flask temperature was then held constant for 15 minutes and later poured into 1 L of deionized water. The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3 % 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 on sulfate ion (with $\text{Ba}(\text{NO}_3)_2$) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 h before use.

Preparation of thermally reduced graphenes. Thermally reduced graphenes were obtained by thermal exfoliation/reduction of graphite oxides at 1000 °C. 0.1 g of graphite oxide was placed into a porous quartz glass capsule connected to magnetic manipulator and placed inside a vacuum tight tube furnace with controlled atmosphere. The magnetic manipulator was capable of creating a temperature gradient over 1000 °C min^{-1} . The sample was then flushed with nitrogen gas by repeated evacuation of tube furnace to remove any traces of oxygen and then quickly inserted by magnetic manipulator to preheated furnace and held in the furnace for 12 minutes. The flow of nitrogen (99.9999 % purity) during exfoliation procedure was 1000 mL min^{-1} to remove any byproducts from the exfoliation procedure.⁶

Electrochemical measurements. Cyclic voltammetry experiments were performed at a scan rate of 100 mV s^{-1} , at room temperatures with 50 mM phosphate buffer solution (PBS; pH 7.2) as the supporting electrolyte. The diffusion coefficient $D = 7.26 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used for the calculations of k_{obs}^0 .¹¹ The GC electrode surfaces were renewed by polishing with alumina particles on a polishing pad and washed with deionized (DI) water. Immobilization of the carbon materials onto the working electrode (GC) was performed by first preparing a suspension of the desired material with a concentration of 1 mg/mL in DMF with a 5 min sonication. 3 μL aliquot of

the suspension was then deposited onto the electrode surface to coat the electrode surface. The DMF solvent was then allowed to evaporate under room temperature to leave a randomly distributed film on the GC electrode surface. In the TNT detection experiment, cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) scans were performed for two different types of electrolyte solutions: TNT mixed in pH 9.3 of 20 mM borate buffer solutions and TNT mixed in a mixture of seawater and 200 mM pH 9.3 borate buffer solution prepared in a ratio of 9:1 (seawater:borate buffer) to give an electrolyte of pH 8.9. The voltammetric scans were conducted for TNT concentrations of 0 ppm, 4 ppm, 8 ppm, 12 ppm, 16 ppm and 20 ppm. The electrochemical experiments were carried out in a glass cell at room temperature using a three-electrode configuration which consisted of a platinum auxiliary electrode, Ag/AgCl reference electrode and a modified glassy carbon working electrode coated with thermally reduced graphene. All CV experiments were carried out at a scan rate of 100 mV s^{-1} . All DPV experiments were carried out at a step potential of 5 mV and modulation amplitude of 25 mV under room temperature conditions.

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Chapter 10

Transition Metal-Depleted Graphenes Prepared via Reduction of CO₂ by
Lithium

10.1	<i>Introduction</i>
10.2	<i>Results</i>
10.2.1	<i>Properties of transition metal-depleted graphenes</i>
10.2.2	<i>Electrochemistry of transition metal-depleted graphenes</i>
10.3	<i>Discussion</i>
10.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Zdeněk Sofer, Jan Luxa, Martin Pumera. Transition Metal-Depleted Graphenes for Electrochemical Applications via Reduction of CO₂ by Lithium. *Small*, 2014, **10**, 1529.

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Introduction

Combustion of magnesium metal in solid CO₂, dry ice was an exciting method to synthesize graphene materials.¹⁻² This reaction was previously attempted and reported to successfully produce few-layers graphenes. In Chapter 2, we have reviewed the properties of these graphenes to reveal that they possessed small amount of the unreacted magnesium that was left behind after the reaction process. Unfortunately, not only magnesium combustion reaction but numerous graphene synthesis pathways were also reported to produce graphenes with metallic impurities.³ Metal impurities present in graphenes were found to have dramatic influence on the electronic properties of the materials^{4,5} and may also dominate the electrochemical behavior^{3,6,7} as evident in the case of carbon nanotubes.^{8,9} Such undesirable influences on the electrochemical properties were a major setback for graphene, hindering its application as a potential material for reliable electrochemical devices.

In this chapter, we have attempted to synthesize a metal-free graphene material via similar metal combustion method but under modified reaction conditions. Pure elemental lithium metal was employed in replace of magnesium to investigate the influence of a change in reaction condition on the properties of the derived graphenes. This project also attempts to study if such a change in the combustion metal used can successfully produce the desired metal-free graphene in a simple and scalable manner.

Results

10.2.1 Properties of transition metal-depleted graphenes

The reaction between lithium (Li) and dry ice (solid state CO₂) as a carbon source led to the formation of graphene with lithium being oxidized to lithium oxide. The graphene produced has low concentrations of impurities due to all the precursors containing only traces of impurities from the start of the reaction. Furthermore, the dry ice block acts a reaction vessel and minimized the possibility of any form of impurity contamination during the reaction process. The graphene yielded from dry ice (G-CO₂) was extensively studied via various techniques such as scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The results obtained were further compared against the properties of carbon black and chemically reduced graphene (CRG). CRG contains metal impurities as it was made from natural graphite and hence, this comparison will clearly highlight the influence of impurities on the various properties of the material.

We will first assess the morphology of the materials using the SEM technique. G-CO₂ shows a few-layered structure similar to that of chemically reduced graphenes¹⁰ indicating that exfoliation of the materials did occur (refer to Fig. 10.1). The images obtained confirmed that G-CO₂ and CRG were similar morphologically.

TEM image of G-CO₂ showed the material consisting of few stacked sheets material (Fig. 10.1, D). Atomic force microscopy (AFM) image of G-CO₂ flake showed that the thickness of the separated sheet was approximately 0.8 - 0.9 nm which corresponds to single layer sheet (refer to Fig. 10.2).¹¹⁻¹³

Fig. 10.1 SEM images of G-CO₂, CRG and carbon black. Scale bars represent 1 μm. D) TEM of G-CO₂. Scale bar represents 20 nm.

Fig. 10.2 AFM results of G-CO₂ sheet. Dimension of scanned area is 1.5 μm × 1.5 μm. Height of graphene flake is 0.9 nm.

Fig. 10.3 Raman spectra of G-CO₂, CRG and carbon black. B) Calculated D/G ratios for all the materials.

Using the Raman spectroscopy technique, we can gain further insights on the surface structures of the materials. Lattice sp² carbon materials were known to exhibit a Raman spectrum with distinctive peaks at ca. 1350 cm⁻¹ and ca. 1560 cm⁻¹ which corresponds to sp³ defects (D-band) and the pristine sp² lattice (G-band) structure respectively. The intensities of the D and G bands obtained were further expressed as the D/G ratios which can provide insight into the density of defects present in the structure. The Raman spectrums measured for the materials were shown in fig. 10.3, A and their calculated D/G ratios were 0.53 for G-CO₂, 0.84 for carbon black and 1.12 for CRG (Fig. 10.3, B). It can be observed that G-CO₂ exhibit the least amount of defects followed by carbon black and lastly CRG with the highest D/G ratio and the largest amount of defects.

The average crystallite size (L_a) of the materials can be calculated using the intensities of the D and G peaks in the following equation:¹⁴

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

where λ_{laser} is the wavelength of the laser in nm. I_G and I_D are the intensities of the G and D bands respectively. The L_a sizes were 31.5 nm for G-CO₂, 19.9 nm for carbon black and 15.0 nm for CRG. It can be observed that the crystallite size increases from CRG to carbon black and lastly, G-CO₂ with the largest size. Larger crystallite size indicates a higher quality of graphene sheets which was reflected by a low D/G ratio. The quality of the material was related to the reaction condition during the reduction reaction of dry ice, CO₂ where the production of large amount of heat during reaction allows the formation of high quality graphene sheet.

Fig. 10.4 Wide-scan XPS spectrums of G-CO₂, CRG and carbon black. B) Calculated C/O intensity ratios for the materials.

Further information on the surface elemental composition can be obtained through X-ray photoelectron spectroscopy. The wide range XPS spectrums were performed from 0 eV to 1200 eV for all materials as shown in fig. 10.4. The major elemental composition of each material was obtained with relative sensitivity factors taken into considerations. It was observed that all the materials displayed a C 1s peak at 284.5 eV and O 1s peak at 534 eV except G-CO₂ which showed additional peaks for Li 1s at 56 eV, Si 2p at 107.7 eV and Si 2s at 158.7 eV. Note that the Si peaks were shifted by ca. 4 eV as compared to the binding energies of free Si atoms. This was likely due to charging effect by non-conductive amorphous silicon oxide nanoparticles present in the sample. The intensities of the peaks were then further calculated as C/O ratios which were used as an indicator on the degree of oxidation in the materials. The calculated C/O ratios were 3.53 for G-CO₂, 10.64 for carbon black and 8.71 for CRG. It can be observed that G-CO₂ has the lowest C/O ratio and hence, the highest amount of oxygen containing groups followed by CRG and carbon black with the highest C/O ratio and the least amount of oxygen containing groups (refer to Fig. 10.4, B).

Fig. 10.5 High-resolution XPS spectrums of C 1s signal for G-CO₂, CRG and carbon black. D) HR-XPS of Li 1s signal for G-CO₂.

Table 10.1 Relative percentage composition of carbon bonds in each material as determined by HR-XPS.

Material	C=C	C-C	C-O	C=O	O-C=O	π - π^*
G-CO ₂	52.7	17.9	11.8	6.0	6.2	5.4
CRG	55.6	17.3	10.0	6.2	4.5	6.4
Carbon Black	49.3	22.2	12.0	7.1	0	9.4

High resolution XPS (HR-XPS) scans were also performed for all the materials at the respective binding energies of the electronic states of each major element to gain insight on the types of bonds present at the material's surface. The HR-XPS measurements were performed for C 1s and O 1s of all materials. In addition, a Li 1s HR-XPS spectrum was also recorded for G-CO₂. Further processing of the C1s spectra was carried out with fitting of the spectrum to identify and quantify the different types of bonds that might be present (Fig. 10.5). The C1s peak was fitted at 284.5 eV for C=C, 286 eV for C-C, 287 eV for C-O, 288 eV for C=O, 289 eV for O-C=O and finally, 290 eV for π - π interactions. The relative percentage content for each bond type was as shown in table 10.1 where C=C bond remains as the major bond present in all the materials. HR-XPS spectrum for Li 1s in G-CO₂ occurred at approximately 54 eV as shown in fig. 10.5, D. It was observed that the Li 1s spectrum exhibits a significant amount of interferences from noise due to the extremely low concentration of Li present.

With the use of ultrapure starting materials such as CO₂ (99.9993 %) and Li (purity 99.9 %) impurity-free precursors, we will examine the final products to investigate if they are truly transition metal impurities free graphenes. However, even the purest materials still contains ultra-low traces of impurities in its structure. We have used inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the level of impurities in G-CO₂ and CRG. We found that G-CO₂ contains 0.67 wt. % of Li, 0.001 wt. % of Cr, < 0.001 wt. % of Mn, 0.0088 wt. % of Fe, < 0.001 wt. % of Ni, < 0.001 wt. % of Cu and 0.0058 wt. % of Pb while concentrations of Ti, V, Co, Ni is less than the

detection limit (D.L. is ca. 0.0001 wt. %). We found that CRG contains 0.093 wt. % of Fe, 0.00003 wt. % of Co, 0.0017 wt. % of Cu, 0.0018 wt. % of Ni and Mo has a concentration < D.L.

10.2.2 Electrochemistry of transition metal-depleted graphenes

Fig. 10.6 Current–voltage characteristics of G-CO₂, CRG and carbon black.

Current-voltage properties of the materials were investigated through conductivity measurements using a gold interdigitated electrode (Au-IDE).¹⁵ CRG was found to exhibit the largest conductivity followed by carbon black and G-CO₂ (refer to Fig. 10.6).

Fig. 10.7 Cyclic voltammograms of 10 mM NaHS at EPPG, G-CO₂, CRG, carbon black and bare GC electrode surfaces. Conditions: scan rate of 100 mV s⁻¹; 50 mM phosphate buffer solution at pH 7.4.

Further investigation on the influence of metallic impurities on the electrochemical behavior of the materials was carried out with cyclic voltammetry. Edge plane pyrolytic graphite (EPPG) electrode was included as a material for comparison as it was commonly known to be free from any metallic impurities in its structure. Earlier reports have shown that metallic impurities were highly catalytic towards the oxidation of HS⁻ ions as compared to sp² graphite materials.^{3,16} From the results obtained, it can be clearly observed that CRG was electrocatalytically active towards the oxidation of sulfide. From the scans, it can be seen that oxidation starts at approximately -190 mV and reaches a maximum current at 320 mV; which were much lower as compared to the EPPG electrode. The oxidation on EPPG electrode surface shows oxidation starting at -20 mV which consequently peaks at ca. 430 mV which was similar to the oxidation of sulfides for G-CO₂. Oxidation of sulfides at G-CO₂ starts at ca. 50 mV which consequently reaches the maximum at ca. 650 mV. The oxidation peak was observed to begin earliest at approximately -50 mV for carbon black which consequently peaks at 260 mV. Bare GC displays sulfide oxidation at the most positive potential of 190 mV as compared to other materials with an oxidative peak at ca. 790 mV. It was clear that the metallic impurities found in the starting material can influence the electrochemical properties of its final products.

Discussion

We have investigated the influence of metallic impurities on the properties of the materials through a comparison between materials comprising minuscule metallic impurities and materials containing significant amount of metallic impurities. Using an array of different techniques, it was discovered that the density of defects was found to be the highest in CRG while G-CO₂ has the smallest amount of defects. It was also confirmed that graphene prepared from almost impurity-free dry ice still do contain very low levels of impurities. The electrochemical behavior of G-CO₂ was observed to be independent of metallic impurities while the behavior of CRG was influenced by the metallic impurities present in its structure. Such “electrochemically active impurity-free” graphene can have useful future applications in the electrochemical devices such as sensors, supercapacitors and batteries as its performance was not affected by the presence of impurities.

Experimental

Materials:

Lithium was obtained from Alfa (99.9%), carbon dioxide in the form of dry ice (99.9993%) was obtained from Linde. Hydrochloric acid (35%) was obtained from PENTA, Czech Republic. Natural graphite (flake size, 45 μm) was donated by Asbury Carbons (Asbury, NJ). N,N-dimethylformamide (DMF), sodium hydrogen sulfide, sulfuric acid, potassium phosphate dibasic, sodium phosphate monobasic, potassium ferrocyanide, sodium chloride, potassium hydroxide and potassium chloride were obtained from Sigma-Aldrich. Ultrapure nitric acid for ICP-MS and ICP-OES analysis was obtained from J.T. Baker. Argon (purity 99.996 %) was obtained from Linde. Carbon black (Grade 5358R) was purchased from Asbury Carbons, USA. Deionized water was used for the preparation of all the electrolytes that were utilized for any electrochemical measurement. Glassy carbon working electrode (GC), edge-plane pyrolytic graphite (EPPG) electrode (diameter of 3 mm), platinum auxiliary electrode (Pt) with a diameter of 3 mm and Ag/AgCl reference electrode were obtained from Autolab, The Netherlands. The gold interdigitated electrode (Au-IDE) was purchased from BAS, Inc. Tokyo.

Apparatus:

A scanning electron microscope (JEOL 7600F field-emission, Japan) was used to obtain images under normal SEM and gentle-beam mode (GB). The samples were attached onto an aluminum sample stub using an adhesive conductive carbon tape. TEM was performed on JEOL JEM-3010 with 300 kV accelerating voltage. For investigation of graphene, the suspension was prepared in isopropanol (1 mg/mL) and ultrasonicated for 15 minutes (75 W) before use. 1 ml aliquot was dropped on a 200 mesh carbon/copper TEM grid and dried at room temperature. Bright field, dark field and SAED (selective area electron diffraction) modes were used during actual sample observation. The morphology was studied by atomic force microscopy (AFM) on NT-MTD Ntegra

Spectra from NT-MDT in a tapping mode with Si tips under ambient condition with scan rate of 1 Hz and scan line of 512. The XPS used for analysis is a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). All wide-range and high resolution scans were performed at 12.53 kV. The materials were attached onto an aluminum XPS sample holder using a sticky conductive carbon tape. Special attention was paid to ensure that a homogeneous and uniform layer of the material was attached onto the tape. Raman spectroscopic measurements were executed using a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. Calibration was performed at 0 cm⁻¹ and 520 cm⁻¹ with a silicon wafer to give a peak position resolution of less than 1 cm⁻¹. All Raman measurements of the materials were executed using a 514.5 nm Ar laser, an Olympus optical microscope and a 100x objective lens. The materials were well-compressed and compacted prior to any measurements. The concentration of impurities in G-CO₂ was measured with an optical emission spectrometer SPECTRO Arcos (SPECTRO Analytical Instruments, Germany) with radial observation of inductively coupled plasma (ICP-OES). The spectrometer features a Paschen-Runge optic mount. Spectra were measured in the range from 130 nm to 770 nm. For sample introduction, a Cyclonic spray chamber and a Modified Lichte nebulizer was used. The following ICP operating parameters were applied: generator power 1,450 W, coolant flow 13 L/min, auxiliary flow 0.8 L/min, nebulizer flow 0.8 L/min, sample aspiration rate 2 mL/min. Calibration was achieved using commercially available multi-element standard solutions (Analytika). The concentrations of all calibrated elements were 0, 0.1, 0.5, 2.0 and 10.0 mg/l, respectively. 5 mg/L Y was used as an internal standard. All measurements were performed in 4% HNO₃ as a matrix. To prepare liquid samples for ICP-OES analysis, the solid samples were weighed (approx. 5 mg) on microanalytical balance and combusted by the Schöniger method.¹⁷ After which, the closed Erlenmeyer flask was treated in an ultrasonic bath. After absorption of combustion products (at least 24 h), 0.88 mL of concentrated HNO₃ (suprapure) and 100 µL of 1 mg/mL Y standard solution were added. The liquid mixture was

quantitatively transferred from the glass flask to a plastic bottle, and made up to a final volume of 20 mL (weighed). Finally, the solution was filtered and introduced to the spectrometer system. The baseline of the ICP-OES measurements was subtracted from a blank experiment. The analysis of CRG was performed by ICP-MS using an Agilent model 7700 x ICP-MS and microwave digestions with concentrated nitric acid were performed on a Mars CEM system. Samples for ICP analysis were prepared by accurately weighing into a clean Easy Prep vessel followed by addition of 1.5 mL ultrapure HNO₃. Digestion procedure consisted of microwave treatment at 1600 W (100 %), ramping the temperature from 25 °C to 120 °C with 20 min ramping time and maintaining the final temperature of 200 °C for 15 min. Cyclic voltammetric and conductivity measurements were performed using a microAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) which was controlled using a NOVA 1.7 software (Eco Chemie). Nova 1.7 software was published by Metrohm Autolab B.V. in support of Metrohm Autolab's potentiostat/galvanostat equipment.

Procedures:

Preparation of G-CO₂. Approximately 1 g of Li metal was placed on the block of dry ice and ignited with an oxygen-hydrogen torch. The dry ice block was then covered with a second block of dry ice. The reaction proceeds spontaneously with a large amount of heat evolved until all the lithium metal reacts with the carbon dioxide. The product in the form of black powder was removed from the dry ice block and washed with diluted hydrochloric acid (10 wt. %). The product was then repeatedly decanted and ultrasonicated (15 minutes) in hydrochloric acid in order to remove the by-product (lithium oxide). The produced graphene was filtered off using nylon membrane filter (0.45 µm porosity) and washed with deionized water. Graphene was dried at 60 °C under vacuum for 48 hours prior to further use.

Synthesis procedure for CRG. Graphite oxide from natural graphite (N-GO) was prepared according to the modified Hummers method. 0.5 g of graphite, 0.5 g of NaNO₃, and 23 mL of H₂SO₄ were stirred together in an ice bath. 3 g of KMnO₄ was added slowly to the mixture at 0 °C. The solution was then heated to 35 °C and stirred for 1 h to obtain a thick paste. 40 mL of water was then added and the mixture was stirred for 30 min while raising the temperature to 90 °C. The temperature was then kept at 90 °C for 15 min and 100 mL of water was then added. 3 mL of H₂O₂ (30 %) was added slowly until gas evolution stopped and the mixture changed from dark brown to yellow color. The mixture was then filtered and washed with approximately 100 mL of warm water. The filter cake obtained was then re-dispersed in water by mechanical agitation. Centrifugation was performed at about 6, 600 × g for 15 min in water until a neutral pH of the supernatant was achieved. The GO powder was then dried in oven at 60 °C for 2 days. Dry GO powder (49.8 mg) was dispersed in ultrapure water to form a 1.0 mg mL⁻¹ colloidal solution and ultrasonicated at 150 W for 3 h. Hydrazine hydrate (2 mL, 32.1 mmol) was then added dropwise to the mixture at 47 °C and the reaction mixture was then heated up to 100 °C for 24 h. After cooling down to room temperature, the mixture was repeatedly washed with methanol and ultrapure water using centrifugation (8,000 rpm, 10 min) method. The sample pellet was then dried in oven at 60 °C for 2 d prior to any usage.

Electrochemical measurements. All glassy carbon electrodes were renewed by polishing with an alumina suspension, washed with deionized water and wiped dry prior to any usage. The materials were dispersed to create a 0.5 mg mL⁻¹ suspension using DMF as the solvent. The suspension was sonicated at room temperatures for 5 min before each use. The surface of a cleaned GC electrode was then modified by coating with a 1 µL aliquot of the suspension. The electrode was then placed under a lamp for drying to give a layer of randomly dispersed material on the GC surface. This was repeated three times to obtain three layers of homogeneous coatings. EPPG electrode's surface was renewed before each measurement by polishing with alumina suspension, washed with deionized water and wiped dry before use. The modified GC

electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then placed into an electrochemical cell which contains the electrolyte solution and the measurements were then taken. The EPPG electrode will be used in place of the modified GC electrode together with the reference and counter electrode in measurements for the EPPG electrode. The electrolytes used were 50 mM pH7.4 phosphate buffer solution (PBS) as the blank buffer electrolyte, 10 mM NaHS dissolved in the PBS. All measurements were performed for two consecutive scans at a scan rate of 100 mV s⁻¹. Three measurements were carried out for each material and also for each electrolyte.

Conductivity Measurements. 1 mg ml⁻¹ suspensions of the materials were prepared by dispersing the materials in deionized water. The current–voltage measurements were executed by coating 1 µL of the material’s suspension onto the interdigitated area between the two gold electrode bands. The electrode was then placed under a lamp to dry to obtain a randomly deposited material film on the electrode. Linear sweep voltammetric measurement was then executed on the electrode at 200 mV s⁻¹ scan rate to obtain I-V graphs. A total of five replicates were performed for each material.

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PART 3:

Influence of Structural Differences on the Properties of Nanocarbons

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Chapter 11

Nanoporous Carbon and its Application as a Sensing Platform for DNA Detection

11.1	<i>Introduction</i>
11.2	<i>Results</i>
11.2.1	<i>Properties of nanoporous carbon</i>
11.2.2	<i>Electrochemistry of nanoporous carbon</i>
11.2.3	<i>Application: DNA sensing with nanoporous carbon</i>
11.3	<i>Discussion</i>
11.4	<i>Experimental</i>

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

1. **Hwee Ling Poh**, Martin Pumera. Nanoporous Carbon Materials for Electrochemical Sensing.

Chem. Asian J., 2012, **7**, 412.

Article can be downloaded from

<http://onlinelibrary.wiley.com/doi/10.1002/asia.201100681/abstract>.

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2. **Hwee Ling Poh**, Alessandra Bonanni, Martin Pumera. Nanoporous Carbon as a Sensing

Platform for DNA detection: The use of Impedance Spectroscopy for Hairpin-DNA based Assay.

RSC Adv., 2012, **2**, 1021.

Article can be downloaded from

<http://pubs.rsc.org/en/content/articlelanding/2012/ra/c1ra00812a/unauth#!divAbstract>.

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Introduction

In the investigation of Part 3, Chapter 11 attempts to find out if nanocarbons when synthesized into a different form or structure will have their properties and electrochemical behaviors dramatically influenced. In the articles reviewed in Chapter 2, carbon nanocones were observed to possess very interesting properties revealing the possibility of a relationship between structures and properties.

To further prove the possible existence of this relationship, this chapter shall investigate the various properties and behaviors of another class of nanocarbons: nanoporous carbon. Nanoporous carbon materials include materials with pore size of up to 100 nm, thus spanning categories of microporous (0.2 - 2 nm pores), mesoporous (2 - 50 nm pores) and macroporous (50 - 1000 nm pores) materials.¹ Such materials provide many advantages over carbon nanotubes and graphene. With the size of the pores well-defined, the particles have a uniform size and therefore, its surface area, functional groups and overall structure was also well defined. Such uniform and well-defined structure was found to provide a significant advantage in terms of electrochemistry of the materials.^{2,3} Hence, the electrochemical studies conducted in this project allows us to demonstrate the dramatic improvements in electrochemical responses in nanoporous carbon materials as compared to standard graphite and carbon nanotubes electrodes. Another important factor was its low production cost as compared to CNTs and graphene,⁴ allowing it to be a potential material for various applications.

The study on this material was further extended into its application as a sensing platform in deoxyribonucleic acid (DNA) biosensors. In this work, we have pilot the use of nanoporous carbon platform for the detection of DNA hybridization and polymorphism; a novel study. The detection for DNA hybridization and polymorphism was of utmost importance as it can provide early information on the presence and the development of different genetic

diseases.⁵ As such, new analytical devices that could provide point-of-care diagnosis with rapid and sensitive responses were highly desired⁶⁻⁸ as compared to classical methods for DNA analysis.⁹ In this project, the DNA hybridization and polymorphism study was conducted using hairpin DNA probes and a series of DNA targets. Hairpin shaped DNA oligonucleotides probes (hpDNA) have a secondary DNA structure in which two regions of the same strand were complementary to each other thus, resulting in the formation of a double-stranded end and an unpaired loop.^{10,11} Due to this inherent structural constraint, hpDNA presents a higher selectivity for target recognition capabilities in the presence of single nucleotide polymorphisms (SNPs) as compared to linear DNA probes.¹²⁻¹⁴ This allows distinguishment between a complementary target and a DNA sequence with one mismatch which was correlated to the development of Alzheimer's disease. The preparation of the sensing platforms and its DNA targets to be detected were as shown in scheme 11.1.

The electrochemical Impedance Spectroscopy (EIS), an electrochemical technique capable of detecting interfacial properties at the electrode surface¹⁵ was used for this DNA bio recognition application. The use of nanoporous carbon as sensing platform and the EIS electrochemical technique is novel for the impedimetric detection of nucleic acid sequences.

Scheme 11.1 Preparation of disposable electrical printed (DEP) chips: immobilization of hairpin probe DNA and hybridization with DNA target sequences.

Results

11.2.1 Properties of nanoporous carbon

We have performed a detailed characterization study on nanoporous carbon, its electrochemical properties and examined its performance as a sensing platform for biomolecules such as DNA. Fig. 11.1 shows the TEM (Fig. 11.1, a) and SEM (Fig. 11.1, b) images of the material. The electron microscopy images showed that the nanoporous carbon consists of particles with an approximately 50 nm diameter. The nanoporous carbon material studied in this thesis was understood to have a non-crystalline nature.

Fig. 11.1 a) Transmission electron microscopy and b) Scanning electron microscopy images of nanoporous carbon.

Standard Brunauer, Emmett, Teller (BET) method was also employed to determine the pore size of the material.¹⁶ Based on the BET measurement of adsorption-desorption of nitrogen (N_2), the nanopore diameter in our nanoporous carbon samples was found to be 11.2 nm with an average pore volume of $0.6 \text{ cm}^3/\text{g}$ and a surface area of $187 \text{ m}^2 \text{ g}^{-1}$.

It was known that oxygen containing groups can influence the electrochemistry and electron transfer rates of carbon materials.¹⁷ Hence, the influence of oxygen containing groups on the materials' electrochemical behavior will be investigated through FT-IR spectroscopic

studies. Multi-walled carbon nanotubes (CNT) and graphite microparticles (Graphite) will be used as comparative materials in this experiment.

Fig. 11.2 FT-IR spectrums of nanoporous carbon, CNTs, and graphite materials. The spectrum range at around 3440 cm^{-1} and 1650 cm^{-1} corresponds to OH stretching and C=C bonds, respectively (marked in the figure).

Fig. 11.2 shows the FT-IR spectra of these materials with special focus at the range around 3440 cm^{-1} . The spectrum range at around 3440 cm^{-1} corresponds to –OH stretch and the range at around 1650 cm^{-1} corresponds to C=C stretch. The data was normalized to the C=C stretch where the ratio of the intensities of the IR bands –OH/C=C was found to be 1.84 for nanoporous carbon, 1.39 for graphite micro particles and 1.20 for CNTs.

11.2.2 Electrochemistry of nanoporous carbon

Fig. 11.3 a) Cyclic voltammetry and b) electrochemical impedance spectroscopy at graphite, nanoporous carbon, CNT and bare glassy carbon electrode surfaces. Conditions: a) 10 mM $Fe(CN)_6^{3-}$, 50 mM phosphate buffer solution (PBS) at pH 7.2, scan rate of 100 mV s^{-1} , (b) impedimetric measurements were performed from 10 kHz to 0.05 Hz with an amplitude of 10 mV.

Electrochemical study on nanoporous carbon was also executed and compared against CNT and graphite. Cyclic voltammograms of ferro/ferricyanide at the surfaces of each material were as shown in fig. 11.3, a. It can be seen that the peak-to-peak separation between the oxidation and reduction peaks was 460 mV for bare glassy carbon (GC) electrode, 600 mV for CNT, 340 mV for graphite and 130 mV for nanoporous carbon. GC electrode was used as a standard electrode for comparison. The heterogeneous electron transfer rate (k_{obs}^0) calculated from these data were $3.22 \times 10^{-5} \text{ cm/s}$, $5.09 \times 10^{-6} \text{ cm/s}$, $1.76 \times 10^{-4} \text{ cm/s}$ and $3.30 \times 10^{-3} \text{ cm/s}$ for bare GC, CNT, graphite and nanoporous carbon respectively. It can be observed that the fastest observed heterogeneous electron transfer rate (HET) was exhibited by nanoporous carbon, followed by graphite. It was important to note that the HET rate of pure CNTs was smaller than that of graphite which was consistent with earlier findings.^{18, 19}

Electrochemical impedance spectroscopy (EIS) was further employed to investigate the electrical resistance that the materials posed towards electron transfer between the electrode surface and the ferri/ferrocyanide molecules at the electrode surface. The measured impedance spectra of all four electrode surfaces were shown in fig. 11.3, b. It was obvious that the greatest electron charge transfer resistance was exhibited by CNTs (4524 Ω), followed by GC (1693 Ω), graphite (53 Ω) and nanoporous carbon with an exceptionally low resistance of 46 m Ω . These results were in agreement with the earlier data obtained from the cyclic voltammetry study. As it was mentioned earlier on, the oxygen containing groups on carbon materials influences the electrochemical behaviors of the materials. It was previously found that HET rates decrease with increasing amount of oxygen containing groups. Earlier FT-IR and electrochemical measurements showed that even though nanoporous carbon contains larger amount of oxygen functionalities than CNTs and graphite, its apparent HET rate was actually found to be faster. Hence, the electrochemical performances of nanoporous carbon can be concluded to be superior as compared to CNT and graphite despite the presence of a larger amount of oxygen containing groups on its surface.

Fig. 11.4 CVs of a) 10 mM ascorbic acid, b) 10 mM uric acid, c) 10 mM dopamine and d) 5 mM NADH at nanoporous carbon, CNT, graphite and bare GC electrode surfaces. Conditions: 50 mM phosphate buffer, pH 7.2; scan rate of 100 mV s^{-1} .

The electrochemical oxidation of biomolecules such as ascorbic acid, uric acid, dopamine and reduced nicotinamide adenine dinucleotide (NADH) were carried out for the materials of study (Fig. 11.4). Ascorbic acid (AA, Fig. 11.4, a) oxidation at the bare GC surface starts at 60 mV and reaches a maximum at 410 mV. CNT displays poorer electrochemical response with a maximum at 470 mV. However, graphite shows a lower oxidation potential of AA at 360 mV while oxidation of AA at nanoporous carbon surface starts at -90 mV before reaching the first maximum peak at 100 mV and the second maximum peak at 320 mV. The second oxidation peak was most likely attributed to the oxidation of AA at the underlying GC electrode surface. A similar trend was observed for the oxidation of uric acid (UA, Fig. 11.4, b). Oxidation of UA at both bare GC and CNT surfaces begins at 270 mV before reaching a maximum at ca. 490 mV and

580 mV respectively. Nanoporous carbon and graphite show a lower starting oxidation potential of 200 mV and reaching a maximum peak at 360 mV for nanoporous carbon and 390 mV for graphite. It can also be observed that the oxidation current measured for UA at nanoporous carbon surface was larger than that for the other materials. In the case of dopamine (DA, Fig. 11.4, c), oxidation and reduction of DA at bare GC, CNT and graphite surfaces displayed starting potentials at more extreme values than nanoporous carbon. On nanoporous carbon surface, DA displayed an oxidation peak at 380 mV and a reduction peak at 90 mV. In the oxidation of NADH, bare GC, CNT and graphite all showed a similar starting potential at 360 mV with maximum at ca. 700 mV. On the other hand, nanoporous carbon exhibits a much lower starting potential at 110 mV before reaching a maximum at 560 mV (Fig. 11.4, d).

Fig. 11.5 Differential pulse voltammetry of a) 4 mM guanine, b) 50 mM adenine, c) 100 mM cytosine and d) 100 mM thymine. The scans were performed with 50 mM phosphate buffer, pH 7.2.

Oxidation of DNA bases was also studied as a further investigation on the behavior of nanoporous carbon as an electrode material. Electrochemical DNA sensing has important implication for disease diagnostics purposes and hence, increased detection sensitivity and selectivity would prove to be highly beneficial.²⁰ Fig. 11.5 shows the DPV scans of guanine (G), adenine (A), cytosine (C) and thymine (T) at each material's surface. It was obvious from DPV voltammograms that nanoporous carbon offers significantly lower oxidation potentials for all DNA bases as compared to CNT, graphite and bare GC. The oxidation currents measured were also found to be much higher by about one order of magnitude. Guanine oxidizes at nanoporous carbon surface at 620 mV while graphite, CNT and bare GC shows the oxidation peak at around 730 mV instead. Oxidation of adenine base occurs at 850 mV for nanoporous carbon while it occurs at a higher potential of approximately 1000 mV for graphite, CNT and bare GC. It should be emphasized that nanoporous carbon displays a significantly higher oxidation current for adenine and two oxidation peaks instead of one. Graphite, CNT and bare GC exhibit poor oxidation of cytosine with a lower current measured as compared to nanoporous carbon which displayed an oxidation current of 1.41 μA (13 times of the current measured for graphite) at a lower potential of 1230 mV (compared to ca. 1300 mV for other carbon materials). Oxidation of thymine proves a similar trend like the other DNA bases where a lower oxidation potential at 1090 mV was recorded for nanoporous carbon while the other materials displayed higher oxidation potential with graphite at 1120 mV, CNT at 1130 mV and bare GC at 1130 mV. A higher oxidation current of 1.04 μA was also measured for nanoporous carbon which was 2.5 times that of graphite. The poor sensitivity of pure CNTs as a sensing platform was consistent with our previous observations.²¹

Fig. 11.6 DPV of 20 ppm of TNT at nanoporous carbon, graphite, CNT, and bare GC surfaces. Conditions: 20 mM borate buffer at a) pH 2 and b) pH 9.

Detection of 2, 4,6 trinitrotoluene (TNT) was of great importance due to frequent incidents of TNT pollution in seawater and anti-terrorism purposes.²² Herein we have studied the electrochemical response of nanoporous carbon in the detection of trinitrotoluene (TNT) using the DPV technique. Fig. 11.6 shows reduction of TNT in pH 2 and pH 9 borate buffer solution. It was obvious that nanoporous carbon provides significantly higher reduction currents of approximately 4.5 times in pH 2 buffer and by approximately 2 times in pH 9 buffer. The reduction peaks at nanoporous carbon surface occurred at more positive potentials, for example the peak potential of the reduction of the first nitro group in TNT occurred at about -240 mV for CNTs, graphite and bare GC but -180 mV for nanoporous carbon at pH 2. Similarly at pH 9, reduction occurs at -480 mV for CNT, graphite and bare GC while it occurs at -460 mV for nanoporous carbon.

11.2.3 Application: DNA sensing with nanoporous carbon

The behavior and suitability of nanoporous carbon as a sensing platform for the analysis of DNA sequences was investigated using the electrochemical impedance spectroscopy (EIS) technique. In this experiment, different nanocarbon materials were used as sensing platforms to test for the successful hybridization between a hairpin DNA probe (hpDNA) and the various hybridization targets. Through the EIS results obtained, we will be able to conclude if the hybridization was successful and deduce the identity of the target. Disposable electrical printed electrodes (DEP) were used instead of the bare GC electrodes in the setup. Bare DEP electrode and nanoporous carbon modified DEP electrode were first measured for its impedimetric which was plotted as Nyquist plots (Fig. 11.7).

Fig. 11.7 Impedimetric measurements of bare DEP-chip and nanoporous carbon modified DEP. The measurements were performed with $K_3Fe(CN)_6/K_4Fe(CN)_6$ 10mM in PBS, pH 7. Inset: Randles equivalent circuit.

The impedimetric results obtained were fitted with accordance to the Randles equivalent circuit $[R_1(Q[R_2W])]$ shown as an inset in fig. 11.7. In the circuit the electrolyte solution resistance (R_1) is in series with a parallel RC element which consists of a constant phase element (Q), the Warburg impedance (W) and the charge transfer resistance (R_2). We will be focusing on R_2 (diameter of the semicircle in the Nyquist plot) which represents the charge transfer resistance between the electrolyte solution and the material's surface.¹⁵ Hence, by monitoring the changes in R_2 we can obtain information on the identity of the target on the material's surface. From fig. 11.7, it can be observed that nanoporous carbon gives a Nyquist plot with an almost negligible semicircle as compared to the bare DEP-chip. This indicates a smaller charge transfer resistance and therefore, a higher electron transfer rate for nanoporous carbon. This result was in consistent with earlier observations which proved that nanoporous carbon has a high heterogeneous electron transfer rate in ferri/ferrocyanide solution which can be attributed to the increased surface area of the nanoporous material.

Fig. 11.8 Nyquist plots for nanoporous carbon, hpDNA, DNA target for three different hybridization experiments. A) Complementary target DNA sequences. B) Non-complementary target DNA sequences. C) Mutant target DNA sequences. Concentration of hpDNA: 10 $\mu\text{mol/L}$; concentration of DNA target: 3 nmol/L. Scans were performed in $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ 10 mM in PBS, pH 7.

In the DNA hybridization experiment, the electrode surface was first modified with the hpDNA probe. The electrode was then further modified with a target DNA (complementary, wild or mutant). An EIS scan was performed after each modification and their plots are as shown in fig. 11.8. HpDNA probe modified surface shows a much higher charge transfer resistance compared to nanoporous carbon modified DEP (larger semicircular diameter). This may be due to the negatively charged hpDNA backbone which presented an electrical repulsion between the DNA and the negatively charged $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ molecules to result in the increase of R_2 .²³ In the final electrode modification step, hpDNA modified electrodes were then further modified with target DNA sequences. Different DNA targets of the same concentration were used to observe if distinctive responses could be obtained with the nanoporous carbon platform: complementary, non-complementary and mutant (1 base-pair mismatch). Fig. 11.8, A shows that in the presence of complementary DNA target sequences (blue), an increase in R_2 was recorded. This was due to the successful hybridization of the complementary DNA target strands with the hpDNA probe, resulting in a double stranded DNA formed on the electrode surface.²³ The increased number of negatively charged phosphate groups gives rise to even greater charge repulsion and therefore, a greater charge transfer resistance.²³ However, when a non-complementary DNA target (Fig. 11.8, B) or 1-mismatch (Fig. 11.8, C) was used as the DNA target, an increase in R_2 was not observed thus confirming that hybridization between the probe and the target did not occur.

Fig. 11.9 Optimization of hpDNA concentration. Concentration range from 0.1 μmol/L to 20 μmol/L.

In order to obtain reliable EIS results, it was important to ensure that the hpDNA probe sequences have completely covered the electrode surface. This was to avoid any non-specific adsorption during hybridization which may provide a non-specific EIS signal. Hence, an optimization of the concentration of the hpDNA sequences was performed to determine the correct amount of probes to immobilize on the nanoporous carbon modified DEP.^{24,25} The impedimetric response was studied for a range of hpDNA concentrations from 0.1 μmol/L to 20 μmol/L. The results obtained were shown in fig. 11.9 where the signal was represented as a ratio between the charge transfer resistance of hpDNA modified electrode and the bare DEP electrode ($R_2 \text{ probe} / R_2 \text{ bare}$). A trend could be observed from the figure where the signal increases with increasing concentration from 0.1 μmol/L to 10 μmol/L. The highest R_2 variation, corresponds to a complete coverage of the electrode surface by the hpDNA probe which was found to be 10 μmol/L. Hence, 10 μmol/L was selected as the optimized hpDNA concentration to be immobilized on nanoporous carbon modified DEP.

Fig. 11.10 Comparison of the charge transfer resistance ratios between the different target DNA sequences: complementary, non-complementary and mutant target.

Fig. 11.10 summarizes the results obtained for the hybridization experiment with the three different DNA targets. The results were presented as a ratio of the target's charge transfer resistance relative to the probe's resistance. The discrimination between the complementary target and the sequence carrying one mismatch (mutant) was detectable at 3 nmol/L.

Discussion

Investigation on the electrochemical properties of nanoporous carbon shows that the material displays a more “superior” sensing ability in terms of lower oxidation/reduction potentials of important biomolecules and TNT. Significantly higher oxidation/reduction currents were measured for nanoporous carbon as compared to bare glassy carbon electrode, graphite microparticles and carbon nanotubes. With the excellent sensing performance witnessed for nanoporous carbon, the material was further studied for its detection capability in more complicated biomolecules such as DNA. For the first time, impedance spectroscopy was employed as the detection method of DNA hybridization and polymorphism with nanoporous carbon as the sensing platform. This experiment was demonstrated using synthetic oligonucleotides which are correlated to the development of Alzheimer’s disease. It can be concluded that with the sensing capability that nanoporous carbon exhibited in the experiments coupled with further optimization of the experiment’s protocol, the possibility of nanoporous carbon as a sensing platform can be realized for a wide array of biomolecules and other analytes.

Experimental

Materials:

Nanoporous carbon (product code: 699632), graphite (product code: 10091934), CNT (product code: 659258), sodium phosphate monobasic, potassium chlorate (98%), potassium ferrocyanide, potassium ferricyanide, sodium tetraborate decahydrate, hydrochloric acid (37%), sodium chloride, trisodium citrate, disodium hydrogen phosphate, potassium phosphate dibasic, *N,N*-dimethylformamide (DMF), ascorbic acid, uric acid, dopamine, NADH, guanine, cytosine, adenine, thymine and acetonitrile were purchased from Sigma-Aldrich. The chemicals were used as purchased. Platinum electrode (Pt), glassy carbon (GC) and with a diameter of 3 mm and Ag/AgCl electrode were purchased from Autolab, The Netherlands. Trinitrotoluene (TNT) was purchased from Supelco Analytical (Bellefonte, PA) as an analytical standard (1000 ppm) and used as received. Disposable electrical printed electrodes (DEP chips) were purchased from BioDevice Technology (EP-PP; Lot No. EPFS18), Nomi, Japan. Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions and samples. Hairpin probe oligonucleotide (hpDNA), complementary target oligonucleotide (wild), non-complementary target oligonucleotide (nc) and mutant target oligonucleotide (mutant) were pre-prepared by Sigma. Table 11.1 lists the sequences of each nucleotide used.

Table 11.1 Sequences of the hpDNA and the various targets (wild, nc and mutant).

Name	Sequence
hpDNA	5'-ATG GAG ACC AGG CGG CCG CAC ACG TCC TCC AT -3' (32 mer)
Wild	5'-ATG GAG GAC GTG TGC GGC CGC CTG GT-3' (26 mer)
nc	5'-AAA AAA AAA AAA AAA AAA AAA AA-3' (26 mer)
Mutant	5'-ATG GAG GAC GTG <u>C</u> GC GGC CGC CTG GT-3' (26 mer)

Samples and solutions for EIS measurements of hpDNA experiment:

PBS buffer, pH 7 consisted of 0.01 M phosphate and 0.1 M sodium chloride solution. A 0.01M solution mixture of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ (1:1) was used as redox marker. TSC1 buffer, pH 7 was prepared using 0.075 M trisodium citrate and 0.75 M sodium chloride. TSC2 buffer, pH 7 consisted of 0.03 M trisodium citrate and 0.3 M sodium chloride. TSC solutions were commonly used as the buffer solutions in hybridization procedures. All DNA solutions were prepared in TSC1 buffer. Nanoporous carbon was dispersed in deionized water to form a 1 mg/mL suspension. A fresh suspension was prepared monthly to ensure consistency in the results measured.

Apparatus:

Cyclic voltammetry, differential pulse voltammetry (step potential 5 mV, modulation amplitude 25 mV), electrochemical impedance spectroscopy were carried out at Autolab 302 electrochemical analyzer (Eco Chemie, The Netherlands). All EIS, CV and DPV experiments were conducted with a glassy-carbon (GC) working electrode, platinum (Pt) counter electrode and an Ag/AgCl reference electrode. TEM images were generated using a JEOL JEM-2010F field transmission electron microscope operating at 200 kV. SEM measurements were taken with a JEOL JSM-6340F scanning electron microscope. FT-IR was carried out with a Shimadzu IR Prestige ge-21. BET measurements were taken with micromeritics ASAP 2020 and the sample was degassed at 1000 °C for 5 hours before the measurement. In the hpDNA experiment, the DEP electrodes used were comprised of a three electrodes system: working electrode (carbon paste), counter electrode (carbon paste) and reference electrode (Ag/AgCl). Thermo Shaker (Model. TS-100) from BIOSAN was used in the temperature controlled incubation steps.

Procedures:

Electrochemical measurements. The GC electrodes were prepared and cleaned for use by polishing with 0.05 μm alumina powder. Nanoporous carbon, graphite and CNT were prepared as suspensions DMF at a concentration of 0.5 mg/mL and sonicated at room temperature for 5 mins to be ready for use. For all electrochemical measurements, the modified GC electrode surfaces were prepared by casting 1 μL of the prepared suspension onto the cleaned surfaces and left to dry before use. TEM measurements were carried out with a copper grid coated with 1 μL of 0.5 mg/mL suspension and left to dry at room temperature overnight. The HET rates were calculated according to Nicholson equation.²⁶

EIS measurements for hpDNA experiment. EIS measurements were performed for: 1) Bare DEP electrode. 2) Nanoporous carbon modified DEP electrode. 3) hpDNA Probe modified DEP electrode. 4) Target DNA hybridized DEP electrode. Cyclic voltammetries were performed for 1) and 2).

Preparation of nanoporous carbon modified DEP electrode for hpDNA experiment. 3 μL of nanoporous carbon suspension were deposited on the working electrode, left dry and gently washed with deionized water to remove any unabsorbed material.

Preparation of hpDNA probe modified DEP electrode for hpDNA experiment. 3 μL of the hpDNA probe solution were deposited on the nanoporous carbon modified DEP electrode and left to dry at 60 °C for 15 minutes. The electrodes were then washed in TSC2 at 25 °C under stirring for 5 minutes. The washing step was repeated twice with fresh TSC2 each time. This was to ensure that any excess or physically unabsorbed hpDNA sequences were removed from the electrode surface.

Hybridization with DNA target for hpDNA experiment. Hybridization of hpDNA probe and target DNA sequences are carried out by incubating hpDNA modified DEP electrodes in an eppendorf

tube containing the specific DNA target and left for 40 minutes at 55 °C under stirring. The electrodes were then washed in TSC2 buffer at 42 °C for 10 minutes under stirring. This was repeated twice using new TSC2 each time. The total volume used in all incubation steps was 100 μ L. A schematic of the protocol was given in scheme 11.1.

EIS and CV measurements for hpDNA experiment. All measurements were performed with the Autolab potentiostat using a mixture of $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ as the redox marker. EIS measurements were carried out for a range of frequencies from 10 KHz to 0.05 Hz with amplitude of 10mV. The results obtained were presented as Nyquist plots (Z'_{real} against $-Z''_{\text{imaginary}}$). A Randles equivalent circuit [$R_1(Q[R_2W])$] was chosen to fit the obtained.

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Chapter 12

Thesis Conclusion

Thesis Conclusion

Extensive characterization and application studies conducted on graphene revealed that graphene possessed several disadvantages. These challenges include a zero band gap, lack of synthesis methods producing quality graphene in bulk. Solutions to these challenges were explored and studied for their influence on the resultant properties of the obtained resultant graphenes which were evident via characterization studies.

Herein the proposed solutions to modify the properties of graphene were investigated. The study in this thesis was divided into three parts: a) ***Part 1: Influence of Heteroatom Functionalization on the Properties of Graphene***, b) ***Part 2: Influence of Synthesis Methods/Conditions on the Properties of Graphene*** and c) ***Part 3: Influence of Structural Differences on the Properties on Nanocarbons***.

The results obtained clearly show that the three solutions to modify the graphene have dramatic influence over every aspect of the resultant graphene obtained. These properties include density of defects, surface elemental composition, sheet resistivities and electrochemical behaviors, conductivities etc. With their electrochemical behaviors being influenced, the modified graphene's potential in future applications was also observed to be affected. These include detection of explosive nitroaromatic compounds and DNA sequences, potential materials for oxygen reduction reactions and capacitors.

Among the three parts study presented in the thesis, heteroatom functionalization of graphene is the most popular method employed by researchers. This may be due to the availability of various methods of functionalization and heteroatoms to choose from. The methods available include thermal annealing, arc discharge, plasma treatment, microwave irradiation, chemical vapor deposition where each presents different reaction efficiency. As such, the choice of method for heteroatom functionalization of graphene will be largely affected

by the actual application of the functionalized graphene. For example, functionalized graphene used for capacitors will require thermal annealing synthesis method as it is the one method that is capable of producing large scalable quantities of quality graphene that is normally not achievable via other methods of synthesis.

Currently, the research on graphene for all aspects is still in its early stage with much work in progress. Therefore, more studies and investigations need to be conducted in order to realize the ultimate goal of creating the 'super' graphene.

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Appendices

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Boron and nitrogen doping of graphene *via* thermal exfoliation of graphite oxide in a BF_3 or NH_3 atmosphere: contrasting properties

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The fabrication of graphenes doped with electron withdrawing/donating elements can be realized through the synthesis procedures reported in this paper. Doping of the graphenes occurs during the thermal exfoliation step of graphite oxide in the presence of the dopant containing gas (BF_3 or NH_3). The materials are extensively characterized by high-resolution X-ray photoelectron spectroscopy, prompt gamma-ray activation analysis and Raman spectroscopy. Their electrical and electrochemical properties related to heterogeneous electron transfer rates and oxygen reductions are investigated. The doped materials display significant differences in their electronic properties where graphenes doped by electron donating dopants exhibit the largest conductivity as compared to those doped by electron accepting dopants. The scalable method reported here is able to successfully implant B and N into the graphene lattice and hence presented important future implications for the production of these materials on an industrial scale.

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Introduction

Graphene materials have attracted the attention of many researchers due to their excellent optical, electrical, mechanical and electrochemical properties.¹ The modulation of these properties can be achieved by functionalizing graphene with heteroatoms. Graphene was functionalized with oxygen containing groups (graphene oxide),² hydrogen (graphane),³ halogens^{4–6} or nitrogen.^{7–11} These groups are able to exhibit an electron donating or withdrawing effect on the graphene backbone. This influences the electron density of graphene which translates into changes in the electronic and electrochemical properties of the material.

Here, we present a scalable method of implanting boron and nitrogen into the graphene lattice during the thermal exfoliation of graphite oxide using BF_3 and NH_3 gases as the dopants, respectively. Our objective is to present a comparison of the properties between an “electron acceptor” doped graphene (boron) and an “electron donor” (nitrogen) doped graphene. It is important to note that previous studies on the nitrogen doping of graphene typically used CVD or epitaxial graphene, and thus, such synthesis methods presented certain limitations. Here, we explored methods that are capable of generating gram-quantities

of doped materials. The resultant doped graphenes are fully characterized by Raman spectroscopy, high-resolution XPS, prompt gamma-ray activation analysis (PGAA) with their electronic and electrochemical behaviors extensively explored.

Experimental section

Materials

Sulphuric acid (98%), nitric acid (fuming, 98%), potassium chlorate (98%), hydrochloric acid (37%), silver nitrate (99.5%) and barium nitrate (99.5%) were obtained from PENTA, Czech Republic. Graphite microparticles (<50 μm) were obtained from KOOH-I-NOOR Graphite, Czech Republic. Boron trifluoride diethyl etherate, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, potassium ferrocyanide, sodium chloride and potassium chloride were purchased from Sigma-Aldrich. Deionised water was used in the preparation of all the electrolytes that were employed for any electrochemical measurement. The gases were obtained from SIAD (nitrogen 99.9999%, ammonia 99.9995%). A glassy carbon working electrode (GC), a platinum auxiliary electrode (Pt) with a diameter of 3 mm and a Ag/AgCl reference electrode were obtained from Autolab, the Netherlands. The gold interdigitated electrode (Au-IDE) was purchased from BAS, Inc., Tokyo.

Apparatus

A JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) was used to acquire images under normal SEM mode and gentle-beam mode (GB). The samples were prepared

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by attaching them onto an aluminium sample stub using sticky conductive carbon tape. The elemental analysis was performed with Vario EL III (Elementar Analysensysteme GmbH, Germany). Calibration was performed with 5 mg of 4-aminobenzenesulfonic acid. A Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) were used for the acquirement of all X-ray photoelectron spectroscopy (XPS) measurements. Wide-range scans, high resolution C 1s scans, high resolution B 1s and high resolution N 1s scans were performed at 12.53 kV. The materials were affixed to an aluminium XPS sample holder using sticky conductive carbon tape with special care taken to ensure that the layer of the material is uniform throughout. The FT-IR measurement was performed with FT-IR spectrometer NICOLET 6700. A diamond ATR crystal and a DTGS detector were used for the measurements. The boron signal from PGAA was corrected for the background signal which was measured with an empty Teflon vial. The absolute content of boron in samples was determined relative to a H_3BO_3 liquid standard of a known boron concentration. The Teflon vial containing this standard was irradiated at the same position as the graphene powder samples in the machine. Nevertheless, the difference between the volumes of the liquid standard and the powder samples led to a slightly different measurement geometry. Therefore, correction for this difference was performed based on an earlier established method of dependence on the sample volume for the acquirement of the boron signal. A confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector was used to obtain Raman spectroscopic measurements. All actual measurements of the materials were performed using a 514.5 nm Ar laser, an Olympus optical microscope and a 100 $\times$ objective lens to focus the samples. Preparation of all the materials was carried out to ensure that only well-compressed and compacted samples were used for any measurement. For electrical resistivity measurements, 40 mg of the powder material were first compressed into a capsule (1/4" diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by a 4-probe technique using the Van der Pauw method.¹² The resistivity measurements were then performed using a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit. The measuring current was set to 10 mA. Cyclic voltammetric and conductivity measurements were performed using a microAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) which was controlled with NOVA 1.7 software (Eco Chemie). The Nova 1.7 software was published by Metrohm Autolab B.V. in support of the Metrohm Autolab's potentiostat/galvanostat equipment.

Graphite oxide synthesis. The graphite-oxides were prepared according to the procedure reported previously, the Staudenmaier method.¹³ 87.5 mL of sulphuric acid (98% concentration) and 27 mL of nitric acid (fuming, 98%) were added to a reaction flask containing a magnetic stir bar. The mixture was subsequently cooled to 0 °C and 5 g of graphite were added. The mixture was then stirred vigorously to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, 55 g of potassium chlorate was slowly added to

the mixture. Upon complete dissolution of the potassium chlorate, the reaction flask was loosely capped to allow the gas evolved during the reaction to escape. The mixture was then continuously stirred for 72 h at room temperature. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then dispersed in HCl (5%) solution to remove sulphate ions and repeatedly centrifuged and dispersed in deionized water until a negative reaction on chloride and sulphate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$, respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Synthesis of N-doped and B doped graphenes. The nitrogen doped graphene was synthesized by exfoliation of Staudenmaier Graphite Oxide (ST-GO) in an ammonia atmosphere. 100 mg of graphite oxide was placed inside the quartz glass capsule connected to a magnetic manipulator and placed inside the horizontal quartz glass reactor. Before the insertion of the sample within the hot zone, the reactor was repeatedly evacuated and flushed with nitrogen. Subsequently, the nitrogen flow was switched to ammonia and the sample was inserted in the hot zone of the reactor. The sample was maintained at 800 °C for 12 minutes. An ammonia flow at 300 mL min⁻¹ was used to remove the by-products from the exfoliation process. The boron doped graphene was prepared using boron trifluoride diethyl etherate as the boron precursor. The exfoliation with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was performed using a bubbler filled with the liquid precursor at 20 °C and 1000 mbar. Nitrogen (100 mL min⁻¹) was used as a boron precursor carrier gas and was diluted with 1 L min⁻¹ of nitrogen. The reactor was repeatedly flushed with nitrogen where the flow of the boron precursor was stabilized for 5 minutes before introducing the sample into the hot zone of the reactor. The exfoliation was performed for 12 minutes at 800 °C. The exfoliation of undoped graphene was performed under similar conditions in a nitrogen gas atmosphere (1 L min⁻¹).

Cyclic voltammetry. All glassy carbon electrodes were cleaned by polishing with an alumina suspension, washed with deionized water and wiped dry prior to any usage. The materials were dispersed in a DMF solvent to create a suspension with a concentration of 0.5 mg mL⁻¹. The suspension was sonicated at room temperature for 5 min before each use. The cleaned surface of a GC electrode was modified by coating with a 1 μL aliquot of the sonicated suspension. The electrode was then left to dry under a lamp to give a layer of randomly dispersed material on the GC surface. This step was repeated three times to achieve three layers of coatings. The modified GC electrodes, a Ag/AgCl reference electrode, and a platinum counter electrode were then placed into an electrochemical cell which contains the electrolyte solution and the measurements were then taken. The electrolytes used were 50 mM pH 7.4 phosphate buffer solution (PBS) as the blank buffer electrolyte and 10 mM ferro/ferricyanide which was dissolved in 50 mM pH 7.4 PBS. CV was performed in the range of +115 mV to -80 mV for blank buffer solution and 0 V to -160 mV for ferro/ferricyanide electrolyte. All measurements were performed for two consecutive scans at a scan rate of 100 mV s⁻¹. Three replicates were carried out for each material and also for each electrolyte.

Conductivity measurements with Au-IDE. 1 mg mL⁻¹ suspensions of the materials were prepared in deionised water. The current-voltage measurements were performed by coating 1 μ L of the suspension onto the interdigitated area that bridges two gold electrode bands. The electrode was then left to dry under a lamp to obtain a randomly deposited film on the electrode. A linear sweep voltammetric measurement was then performed on the electrode at a scan rate of 200 mV s⁻¹ to give *I-V* characteristics. Five replicates were performed for each material.

Results and discussion

Boron or nitrogen doped graphenes were prepared by thermal exfoliation of graphite oxide (prepared by the Staudenmaier method denoted as ST) in a BF₃ or NH₃ atmosphere at a high temperature of 800 °C (Scheme 1). As a control experiment, we have exfoliated graphite oxide under inert gas conditions (N₂) to be used as a comparison. These graphenes were consequently denoted as ST-B, ST-N and ST (boron is denoted by B and nitrogen is denoted by N).

The materials were first investigated for their morphology using the scanning electron microscopy technique (SEM) to confirm that exfoliation of the materials has occurred. The microscope images at various magnifications of 370 $\times$, 3000 $\times$, 10 000 $\times$ and 70 000 $\times$ are shown in Fig. 1. It could be observed

from the images that all three materials displayed structures similar to that of typical fully exfoliated graphene sheets, indicating an effective and successful exfoliation step of the materials. The thermal exfoliation of graphene oxide typically provides few layer graphene with close to 100% yield, which is favourable when compared with *i.e.* exfoliation of graphite by sonication.¹⁴ In addition, we have performed scanning transmission electron microscopy (STEM) of exfoliated sheets. Graphene sheets were “transparent” to the electron beam and they were morphologically indistinguishable (Fig. 2).

To further assess the elemental composition of the doped graphene materials, a combustible CNHS/O analysis was performed with the results shown in Table 1. ST was found to contain the following elements in atomic weight percentages: 95.14% of C, 1.43% of H and 3.43% of O and concentrations of N and S were found to be zero. ST-N contained 90.03% of C, 2.27% of H, 5.76% of O, 1.94% of N and the concentration of S was found to be zero. ST-B contained 84.83% of C, 9.63% of H, 5.54% of O and concentrations of S and N were found to be zero. It can be concluded that exfoliating graphite oxide in NH₃ led to the incorporation of nitrogen into the graphene lattice. From this data, it is evident that thermal reduction of graphene oxide in any of the atmospheres described above leads to a higher C/O ratio than the chemical reduction of graphene oxide using hydrazine (C/O ratio of 10.3)¹⁵ or microwave reduction (C/O ratio of 2.75). Such high reduction efficiency is also typical of the laser irradiation method.^{16,17}

XPS analysis was used to provide insight into the surface elemental composition (C, O, N) of the doped graphenes as well

Scheme 1 Fabrication of B and N doped graphenes by thermal exfoliation of graphite oxide prepared in BF₃ or NH₃ atmosphere.

Fig. 1 Scanning electron micrographs of B (ST-B) and N (ST-N) doped graphenes as well as graphene exfoliated in an inert gas atmosphere (ST) prepared from Staudenmaier graphite oxides by exfoliation in BF₃ and NH₃ gases. Scale bars of 10 μ m (a), 1 μ m (b), 1 μ m (c) and 100 nm (d).

Fig. 2 STEM images of B (ST-B) and N (ST-N) doped graphenes prepared from Staudenmaier graphite oxides by exfoliation in BF_3 and NH_3 gases. Scale bars of 400 nm (a, b, c) and 800 nm (d).

Table 1 Relative percentages of the elemental composition of the materials determined by the combustable CNHS/O analysis method

Materials	C (%)	H (%)	O (%)	N (%)	S (%)
ST	95.14	1.43	3.43	0	0
ST-N	90.03	2.27	5.76	1.94	0
ST-B	84.83	9.63	5.54	0	0

as that of the control (inert gas exfoliated) material. HR-XPS spectra of the N 1s peak at energy ~ 400 eV (Fig. 3A) shows a distinctive double peak where the 400 eV peak corresponds to amine-like ($-\text{NH}-$) bonds (peak area of 51.6%) and the 402.5 eV peak corresponds to the bipolaron $=\text{NH}^+$ -bond (peak area of 49.4%).^{18,19} These data clearly show that nitrogen was successfully integrated into the graphene sheet as a dopant atom. Notably, the bipolaron/amine ratio reported here is significantly higher than in all previous reports where the bipolaron $=\text{NH}^+$ -nitrogen state was either not found or present at very low concentrations as compared to the typical amine bond which was more commonly found.^{7–11}

To confirm the presence of nitrogen groups, FTIR-ATR spectra of thermally reduced graphene oxide in nitrogen were recorded (see Fig. 3B). The vibration band at 1590 cm^{-1} , assignable to the $\text{C}=\text{N}$ stretching of the pyridine ring, was observed. The wavenumber of this peak is very close to that of the graphene skeletal vibration which occurs at around $1580\text{--}1630\text{ cm}^{-1}$.²⁰ However, this peak was not visible in the spectrum for the control material, ST, which was exfoliated at the same temperature. The NH_2 bending vibrational mode could also be a possible candidate for the appearance of the band at 1590 cm^{-1} . However, the absence of peaks at around $3250\text{--}3500\text{ cm}^{-1}$ (two

N-H stretching vibrations) refutes the possibility of the NH_2 group as the correct identity for the 1590 cm^{-1} band. The HR-XPS peak at ~ 190 eV (boron) showed a noisy and inconclusive result (Fig. 3C) due to the low level boron doping of graphene (140 ppm, see below) which was much lower than the possible detection limit that XPS can achieve (1000 ppm).

High-resolution XPS measurements were carried out for the C 1s electronic state of all three materials to display a single, symmetrical peak at approximately 284.5 eV with a small trailing tail at a much higher binding energy. Fitting of the C 1s spectra was performed with considerations for relative sensitivity factors to identify and quantify the various carbon interactions present on the materials' surfaces. Analysis of the fitted results showed that N- and B-doped graphenes as well as ST exhibit similar amounts of oxygen containing groups (Fig. 3D–F, respectively). HR-XPS C 1s peaks of all three materials were fitted to give a $\text{C}=\text{C}$ bond at 284.5 eV, a $\text{C}-\text{C}$ bond at 285.5 eV, a $\text{C}-\text{O}$ bond at 286.7 eV, a $\text{C}=\text{O}$ bond at 288.2 eV, a $\text{O}-\text{C}=\text{O}$ bond at 289.5 eV and the $\pi-\pi$ interaction at 291.2 eV. ST-N, ST-B and ST graphenes contain 68.6%, 58.6% and 69.3% of $\text{C}=\text{C}$ bonds, 14.5%, 19.8% and 13.2% of $\text{C}-\text{C}$ bonds, 6.9%, 10.8% and 6.5% of $\text{C}-\text{O}$ bonds, 2.8%, 4.1% and 2.5% of $\text{C}=\text{O}$ bonds and 2.4%, 2.7% and 2.2% of $\text{O}-\text{C}=\text{O}$ bonds, respectively. The remnant of the C 1s peak corresponds to the $\pi-\pi^*$ signal which is related to the sp^2 lattice of graphene. Low-resolution (wide scan) XPS spectra of the three materials were performed as shown in Fig. 4. The C/O ratios obtained for the materials are 22 for ST-N, 12.5 for ST-B and 24 for ST and these figures correspond to those for thermally exfoliated graphenes.²¹

The concentration of boron in ST-B was also measured by means of prompt gamma-ray activation analysis (PGAA) using a LWR-15 nuclear reactor.²² The samples were encapsulated in Teflon vials and irradiated with a thermal neutron beam at a flux of $\sim 3 \times 10^6\text{ n cm}^{-2}\text{ s}^{-1}$.²³ A well-shielded 25% HPGe detector was used to obtain the spectra after 3 hours. A background correction was then performed for the boron signal in the γ spectrum where the background scan was based on the measurement of an empty Teflon vial. The γ spectra of the sample is shown in Fig. 5. The gamma lines that correspond to fluorine originate mainly from the Teflon vial and not from the materials to be investigated. Using PGAA, we can establish that the boron concentration in ST-B is 140 ppm. The calculated statistical uncertainty of this boron mass fraction is 20 ppm, where the estimated systematic error is approximately 10 ppm. Note that the typical doping in semiconductors is in the ppm level.²⁴

Additional structural information on the materials can be obtained using Raman spectroscopy to examine the density of defects in the graphene oxides. Spectroscopic measurements were carried out using a 514.5 nm Ar laser to obtain a D peak at approx. 1350 cm^{-1} and a G peak at approx. 1560 cm^{-1} which correspond to the sp^3 defects in the sp^2 lattice and the pristine sp^2 lattice structure, respectively. The intensities of the D and G peaks are further expressed as a D/G ratio to demonstrate the density of defects and hence the degree of disorders in the structure. Raman spectra of ST-B, ST-N and ST were recorded and are shown in Fig. 6. The D/G ratios for the three graphene

Fig. 3 Chemical analyses of the B and N doped graphenes. (A) HR-XPS spectra of N 1s of N-doped graphene; (B) FTIR spectroscopy of N-doped graphene proved the existence of a pyridine ring in the system; (C) HR-XPS spectra of B 1s of B-doped graphene; (D–F) HR-XPS of C 1s of (D) N-doped graphene, (E) B-doped graphene and (F) graphene exfoliated in an inert atmosphere.

oxides were calculated to give values of 0.74 for ST-B, 0.32 for ST-N and 0.77 for the control material, ST. This indicates that ST-N has the lowest density of defects, followed by ST-B and lastly the control material ST with the largest amount of defects in the structure. The average crystallite sizes of the three materials can also be calculated using the intensities of the D and G peaks in the following equation:²⁵

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

where I_G and I_D refer to the intensities of the G and D peaks, respectively, while λ_{laser} is the wavelength of the laser used for Raman spectroscopic measurements in nm. It can be concluded that ST-N has the largest crystallite size of 52.3 nm, followed by ST-B with a size of 22.6 nm and ST with the smallest crystallite

size of 21.8 nm. The band at $\sim 2700 \text{ cm}^{-1}$ is the second order D peak, labelled as 2D. A 2D peak is present in graphene as well as in graphite;²⁶ however, in graphite, the 2D consists of two superposed peaks 2D₁ and 2D₂, while in graphene, there is a single individual peak.²⁶

The conductivity of the resulting doped materials was studied using four point measurements of compressed tablets made from the materials. The resistivity of ST was measured to be $5.2 \times 10^{-5} \Omega \text{ cm}$, $3.5 \times 10^{-5} \Omega \text{ cm}$ for ST-N and $2.2 \times 10^{-4} \Omega \text{ cm}$ for ST-B. Correspondingly, we have recorded the I - V characteristics of the materials through simple conductivity measurements on a gold interdigitated electrode (Au-IDE).²⁷ The results are shown in Fig. 7 where ST-N was found to exhibit the largest conductivity of all three studied materials, followed by ST and lastly ST-B which exhibits the lowest conductivity.

Fig. 4 Wide scan XPS analyses of B-doped (ST-B), N-doped (ST-N) graphenes and undoped (ST) graphene.

Fig. 5 Prompt gamma-ray activation analysis of B-doped graphene.

These electrical conductivity behaviours are related to the electron donor/acceptor properties of nitrogen and boron which were further confirmed by the results found using the 4-probe measurements.

All investigated samples exhibit ohmic behavior using gold probes as contacts. The higher slope of the I/V characteristic for the n-type doped graphene is in agreement with the resistivity measurement where the highest conductivity was observed for the n-type doped graphene (ST-N) and the lowest conductivity and adequate highest resistivity measured for the p-type doped material (ST-B). On the basis of this observation, we can

Fig. 6 Raman spectra of B-doped (ST-B), N-doped (ST-N) graphenes and graphene exfoliated in an inert atmosphere (ST).

suppose that boron directly substitutes carbon. On the basis of the rigid band model, we can deduce that generated holes act as a trap for free electrons and we can suppose a strong decrease of free carrier mobility and conductivity. Generally, this led to a decrease of material conductivity. In general, holes also exhibit lower mobility compared to electrons. The direct measurement of carrier mobility on a single sheet of exfoliated graphene is extremely complicated and only a few groups have reported such measurement. In the compact form, the material behaves like a composite of a highly conductive sheet with very weak electrical interconnection of each graphene plane. The strong

Fig. 7 Current-voltage characteristics of B-doped (ST-B), N-doped (ST-N) and undoped (ST) graphenes.

scattering of free carriers occurs on the graphene sheet boundaries and the value of carrier mobility is unable to give any significant information about the material and graphene sheet boundaries became dominant and the value of free carrier mobility on such a sample is almost immeasurable.

From the value of HET and the I/V characteristic, we can deduce a significant decrease of free carrier mobility for p-type doped samples and the highest mobility of free carriers for nitrogen doped graphene.

Heterogeneous electron transfer properties are of great importance for electrochemical sensing, energy storage and electrochemical energy generation. We have investigated the heterogeneous electron transfer (HET) on ST-N, ST-B and ST modified glassy carbon (GC) electrodes for the ferro/ferricyanide probe (Fig. 8). The peak-to-peak separations were found to be 223 mV, 139 mV, 236 mV and 335 mV for ST-N, ST-B, ST and bare GC electrodes, respectively. As such, the measured ΔE_{p-p} values can be employed for the calculation of the observed heterogeneous electron transfer rate (k_{obs}^0) through the use of the Nicholson approach.²⁸ In this equation, ΔE_{p-p} is related to a dimensionless parameter Ψ which is eventually related to k_{obs}^0 . The diffusion coefficient used is $D = 7.26 \times 10^{-6} \text{ cm s}^{-1}$ for the ferro/ferricyanide electrolyte. The calculated k_{obs}^0 values are $2.512 \times 10^{-3} \text{ cm s}^{-1}$ for ST-B, $8.051 \times 10^{-4} \text{ cm s}^{-1}$ for ST-N, $6.747 \times 10^{-4} \text{ cm s}^{-1}$ for ST and $1.755 \times 10^{-4} \text{ cm s}^{-1}$ for GC. This indicates that ST-B exhibits the fastest transfer (HET) rate, followed by ST-N, ST and finally GC. This result is in agreement with the earlier observation made by Raman spectroscopy where ST-B and ST, the materials with the two highest defect densities showed that the density of defects do play a role in influencing the HET rates. This is consistent with previous findings on ferro/ferricyanide electrochemistry which was not known to be electrocatalyzed by either boron or nitrogen.

It is important to mention that the fundamental difference between a hole doped graphene (boron doped) and electron doped graphene (nitrogen doped) is clearly displayed through its electron transfer properties. This was previously beautifully

demonstrated through an example where the difference in degradation of electron donor/acceptor dyes can be observed.²⁹ Our results are fully supported by this work.²⁹

Conclusion

We have demonstrated a scalable method for implanting acceptor/donor dopants into graphene sheets *via* exfoliation of graphite oxide in a corresponding element containing gaseous atmosphere. Boron doping in the BF_3 atmosphere led to the incorporation of 140 ppm of B into the lattice while doping in the NH_3 atmosphere led to the incorporation of $\sim 2\%$ atomic weight of N. The materials were extensively characterized by X-ray photoelectron spectroscopy, prompt gamma-ray activation analysis and Raman spectroscopy. Doped materials exhibit significant differences in their electronic properties, showing that electron donor doped graphenes exhibit the largest conductivity while the electron acceptor doped graphenes exhibit the lowest conductivity. The doping of materials during thermal exfoliation in various atmospheres is a highly scalable methodology that has important future applications for industrial purposes.

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Fig. 8 Heterogeneous electron transfer of B and N-doped graphenes. (A) Cyclic voltammograms of 10 mM ferro/ferricyanide for B-doped (ST-B), N-doped (ST-N) and undoped (ST) graphene surfaces. (B) Oxygen reduction in a blank 50 mM pH 7.4 phosphate buffer solution for the various surfaces. Conditions: room temperature, scan rate of 100 mV s^{-1} .

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Graphene

Concurrent Phosphorus Doping and Reduction of Graphene Oxide

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Abstract: Doped graphene materials are of huge importance because doping with electron-donating or electron-withdrawing groups can significantly change the electronic structure and impact the electronic and electrochemical properties of these materials. It is highly important to be able to produce these materials in large quantities for practical applications. The only method capable of large-scale production is the oxidative treatment of graphite to graphene oxide, followed by its consequent reduction. We describe a scalable method for a one-step doping of graphene with

phosphorus, with a simultaneous reduction of graphene oxide. Such a method is able to introduce significant amount of dopant (3.65 at. %). Phosphorus-doped graphene is characterized in detail and shows important electronic and electrochemical properties. The electrical conductivity of phosphorus-doped graphene is much higher than that of undoped graphene, owing to a large concentration of free carriers. Such a graphene material is expected to find useful applications in electronic, energy storage, and sensing devices.

Introduction

Graphene materials possess numerous interesting and useful characteristics, such as optical, electrical, mechanical, and electrochemical properties.^[1] These properties make graphene useful for energy storage and biosensing, hence the increasing demand for, and importance of, graphene materials in these fields. However, the application of these materials is often difficult, owing to the various limitations presented by the material itself, such as a zero band gap,^[2] and electrochemical properties resembling those of graphite.^[3] Various syntheses of graphene result in a low mass yield, which is often a constraint for applications or further reactions that require gram quantities of the graphene materials. Doping of graphene with heteroatoms has proved to be a new strategy to produce scalable amounts of metal-free material with improved electronic properties and catalytic behavior. Doping with heteroatoms, such as nitrogen,^[4–6] boron,^[4,7] and halogen atoms^[8,9] has been attempted in earlier studies. In this study, we have focused on the doping of graphite oxide with phosphorus atoms to produce chemically reduced graphene oxides doped with elemental phosphorus, which is incorporated into the final product. Several researchers have demonstrated the successful addition of phosphorus accompanied by an increase in oxygen content

in the material, owing to the preference for phosphorus to bind to oxygen during the doping process.^[10] An increase in the number of oxygen-containing groups has proved to be undesirable because the negative charge presented by these groups causes the conductivity of the materials to decrease.^[11,12] Herein, we have successfully shown the possibility of simultaneously incorporating phosphorus into the material and removing oxygen from the material during a one-step phosphorus-treatment process. The resultant material was found to possess a high percentage content of phosphorus (3.65 at. %) when P_4 , PH_3 , NaH_2PO_2 , and Na_2HPO_3 were used as phosphorus sources in the doping process, with sodium hypophosphite and phosphite representing commonly used reducing agents. This synthetic method is different from earlier reported methods, which utilized 1-butyl-3-methylimidazolium hexafluorophosphate,^[13] phosphoric acid,^[10,14] triethyl phosphite,^[15] phosphorus trichloride,^[15] and triphenylphosphine^[16,17] as the phosphorus sources.

Results and Discussion

The treatment of Hofmann graphite oxides was carried out by using various phosphorus sources, and performed under different reaction conditions, in an attempt to dope these materials with phosphorus atoms. The doped materials are reduced graphene oxides (RGOs) and are denoted as HO-P, followed by the phosphorus source used and the condition at which the doping procedure was carried out, for example, HO-P:[P_4 /KOH]. These phosphorus-doped materials were then compared with both undoped graphene oxides that were thermally exfoliated under nitrogen gas (TRGO, HO-N),^[18] and the starting material (unexfoliated) Hofmann graphite oxide (HO).^[19] Thermal exfoliation or reduction of graphene oxide is one of the most efficient oxygen-reduction treatments of graphite oxide,

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Figure 1. Scanning electron microscopy images of phosphorus-doped graphenes prepared from Hofmann graphite oxides, the starting material HO, and the undoped TRGO (HO-N) exfoliated in a nitrogen atmosphere. The scale bars are 100 nm (a), 1 μ m (b), and 10 μ m (c).

therefore, HO-N serves as an important benchmark. The characteristics of such materials were then investigated by using various techniques, such as scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) in both wide-scan and high-resolution modes. An in-depth study was also carried out with cyclic voltammetry methods, in different electrolytes, to examine properties, such as heterogeneous-electron-transfer rates and oxygen-reduction reactions.

The morphology of the materials was studied by using SEM techniques at various magnifications ($\times 50\,000$, $\times 6\,000$, and $\times 370$) as shown in Figure 1. All HO-P materials and HO-N showed various similarities when the materials were completely exfoliated. This result shows that phosphorus-doped chemically reduced graphene oxides can be successfully reduced under a phosphorus environment. Only HO was observed to be different; this difference is due to the material being a graphite oxide and hence, completely unexfoliated and non-conductive with the presence of many oxygen-containing groups.

Further characterization of the materials was performed with Raman spectroscopy to investigate the density of defects at surface level. Raman spectroscopic measurements of the materials were performed by using a 514 nm wavelength laser to obtain the spectra shown in Figure 2, A and B, in which peaks D and G can be observed. Raman peaks G ($\approx 1560\text{ cm}^{-1}$) and D ($\approx 1350\text{ cm}^{-1}$) refer to the pris-

tine sp^2 graphene network lattice and sp^3 defects found in the pristine sp^2 lattice, respectively. The intensity of the two peaks can be further calculated as a D/G ratio, which represents the density of defects found in the materials. The defect density can act as an indication of the rate of reactions occurring at the surface of the materials because earlier studies have shown that electrochemical reactions take place at defect sites. The calculated D/G ratios are 0.93 for HO-P:[P_4 /KOH], 0.89 for HO-P:[P_4], 0.97 for HO-P:[PH_3], 1.03 for HO-P:[NaH_2PO_2], and 0.95 for HO-P:[Na_2HPO_3]. The D/G ratios for the control materials are 0.78 for HO-N and 0.83 for HO, as shown in Figure 2, C. All phosphorus-treated graphene oxides (GOs) were found to possess higher defect densities and, therefore, more defects,

Figure 2. Raman spectra of the phosphorus-doped and undoped reduced graphene oxides. A, B) Raman spectra of RGOs doped by using various phosphorus sources. Spectra of undoped TRGO (HO-N) and starting material, HO, were also compared. C) Bar graph of the derived D/G ratios for the various materials.

than their undoped or unexfoliated counterparts. This finding indicates that treatment of GOs with phosphorus sources introduces defects into the materials.^[13–15] The average crystallite size of each material can also be calculated by inputting the intensities of the D and G peaks into the following equation:^[20]

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

L_a denotes average crystallite size, I_G and I_D refer to the intensity of the G and D peaks, respectively. λ_{laser} is the wavelength of the laser used for obtaining Raman measurements in nm. The average crystallite sizes are calculated to be 18.01 nm for HO-P:[P₄/KOH], 18.82 nm for HO-P:[P₄], 17.27 nm for HO-P:[PH₃], 16.26 nm for HO-P:[NaH₂PO₂], and 17.63 nm for HO-P:[Na₂HPO₃]. HO-N and HO have a L_a size of 21.48 nm and 20.18 nm, respectively.

The surface of the materials can be analyzed with X-ray photoelectron spectroscopy (XPS) to obtain elemental composition data. XPS utilizes a focused X-ray beam on the material to acquire the elemental composition of various elements in their respective electronic states. A wide-range XPS scan was first performed to detect the elements that are present on the surface of the material, as shown in Figure 3, A and B. The major XPS peaks observed are a C 1s peak at 284.5 eV, a O 1s peak at 534 eV, for all materials, and an additional P 2p peak at approximately 136 eV for the phosphorus-treated GOs. The extent of oxidation of the materials is determined by the amount of oxygen-containing groups available on the surface, indicated by the C/O ratio, which is calculated by the intensities of the C 1s and O 1s peaks. The C/O ratios were found to be 8.51 for HO-P:[P₄/KOH], 5.70 for HO-P:[P₄], 3.05 for HO-P:[PH₃], 3.02 for HO-P:[NaH₂PO₂], and 2.89 for HO-P:[Na₂HPO₃].

The control materials, HO-N and HO, were found to have a ratio of 8.85 and 2.64, respectively, as shown in Figure 3, C. Undoped HO-N, exfoliated in an inert nitrogen-gas environment, was observed to contain the fewest oxygen-containing groups on comparison with the phosphorus-treated GOs. This finding may imply that exfoliation under a nitrogen-gas atmosphere can result in the removal of more oxygen groups than the reduction of GO with a phosphorus source. Unexfoliated HO possessed the lowest C/O ratio and the largest amount of oxygen groups. This result was expected because HO did not undergo the exfoliation process, which is a thermal reduction reaction, and therefore, a large number of oxygen groups were still present on the surface. On comparison of the phosphorus-treated materials, the C/O ratios were found to be dependent on the type of phosphorus source used and the temperature at which the treatment occurred. The number of oxygen-containing groups is lowest when phosphorus sources, such as P₄, followed by PH₃, NaH₂PO₂, and lastly, Na₂HPO₃ are used. The changes in the chemical procedure of the treatment may also result in fewer oxygen groups being removed during phosphorus reduction, as shown for HO-P:[P₄/KOH] and HO-P:[P₄], for which the latter material has a lower C/O ratio, but was treated at a higher temperature. It is noteworthy (Figure 3, C) that phosphorus-doped and simultaneously reduced HO-P:[P₄/KOH] material was reduced to give a C/O ratio that is almost identical to that of thermally reduced HO-N. Phosphorus acts as a reducing agent in a highly reactive reaction with KOH, in which the white phosphorus undergoes a disproportionation reaction, generating phosphane and a hypophosphite anion. Therefore, phosphorus-based reduction reactions exhibit similarly high reaction efficiencies compared with thermal-shock (1000 °C) reduction reactions.

Figure 3. Wide-range XPS spectra. A, B) XPS spectra of phosphorus-doped RGOs, undoped TRGOs, and starting material HO. C) Bar graph of calculated C/O ratios derived from the peak intensities of the XPS spectra.

XPS measurements show the presence of P 2p (Figure 3). It can be clearly observed in Figure 3, A that only HO-P:[P₄/KOH], HO-P:[P₄], and HO-P:[PH₃] contain phosphorus after the treatment process. The percentage content of P 2p in the treated materials are 1.17% for HO-P:[P₄/KOH], 3.65% for HO-P:[P₄], 0.10% for HO-P:[PH₃], and 0% for HO-P:[NaH₂PO₂] and HO-P:[Na₂HPO₃] (Figure 3, B). This indicates that only treatment methods that use P₄ and PH₃ as the phosphorus sources result in successful incorporation of phosphorus into the materials. P₄ was also observed to be a better dopant source than PH₃ because the latter gave a total P 2p content of only 0.10%. Hypophosphite and phosphite only act as reducing agents in the treatment process. Further fitting of

the spectra results shows the presence of P–C and P–O bonds at ≈ 136.0 and ≈ 132.0 eV, respectively.^[10] In HO-P:[P₄/KOH], all of the doped phosphorus existed only in the form of P–C bonds, whereas for HO-P:[P₄], 79.8% of the phosphorus existed as P–C bonds and 20.2% as P–O bonds. This shows that phosphorus treatment of the graphite oxides results in the formation of P–C bonds as the majority and P–O bonds as the minority when pure white phosphorus is used as the phosphorus source during treatment.

HR-XPS measurements were also performed for the electronic state C 1s, with careful fitting of the results, to obtain information on the type of interactions present and their respective percentages. The spectra for the various materials are as shown in Figure 4. All materials, except HO-P:[P₄/KOH] and HO-P:[P₄], display standard carbon and oxygen interactions at 284.5 eV for sp²-hybridized carbon bonds (C=C), 285.7 eV for sp³-hybridized carbon bonds (C–C), 286.8 eV for alcohol/ether groups (C–O), 288.0 eV for carbonyl groups (C=O), 289.2 eV for carboxylic/ester groups (O–C=O), and lastly, 290.2 eV for π – π^* interactions between carbon atoms. HO-P:[P₄/KOH] and HO-P:[P₄], which were previously found to contain the highest P 2p content, display peaks for several carbon interactions and an additional C–P peak (≈ 285.5 eV) as shown in Figure 4, A and B. The occurrence of the C–P peak at 285.5 eV was also observed in earlier studies.^[13] On the other hand, HO-P:[PH₃], HO-P:[NaH₂PO₂], and HO-P:[Na₂HPO₃] displayed standard carbon interactions with the absence of the C–P bond as observed in Figure 4, C, D, and E. The major carbon interactions detected were C=C and C–O bonds. This may be due to an incomplete reaction with phosphorus sources and hence, incomplete reduction of the oxygen-containing groups during the treatment process. The control materials, HO-N and HO (Figure 4, F and G), also showed standard carbon interactions as mentioned above, with HO possessing only C=C and C–O bonds. The shape of the C 1s

spectra for HO-N was found to be similar to that of HO-P:[P₄/KOH] and HO-P:[P₄], indicating that the extent of oxidation of the materials is similar for all three materials. This finding is in agreement with the earlier observation that the C/O ratios of these three materials are the highest, therefore, they possess the lowest oxygen content.

More information about the remaining oxygen functional groups could be obtained from FTIR spectroscopy. Figure 5 A shows the comparison of HO-P:[P₄/KOH], HO-P:[P₄], and HO-P:[PH₃] with unreduced HO. Unreduced HO possesses typical oxygen functionalities, such as hydroxyl groups, which are represented by the –OH vibration at ≈ 3200 cm^{–1}, C–OH vibration

Figure 4. High-resolution XPS spectra of C 1s electronic state with fitted results. A) HO-P:[P₄/KOH], B) HO-P:[PH₃], C) HO-P:[P₄], D) HO-P:[NaH₂PO₂], E) HO-P:[Na₂HPO₃], F) HO-N, and G) HO.

Figure 5. FTIR spectra recorded for various materials. A) Comparison of HO with phosphorus-doped RGOs by using P_4 and PH_3 as phosphorus sources. B) Comparison of HO with phosphorus-doped RGOs by using NaH_2PO_2 and Na_2HPO_3 as phosphorus sources.

at $\approx 1350\text{ cm}^{-1}$, and deformation vibration of C–OH at 1060 cm^{-1} .^[21] The vibrational band observed at approximately 950 cm^{-1} is related to the C–O vibration of epoxide groups. Another vibration band that is related to oxygen functionalities is the C=O vibration band, originating from carboxylic acid functionalities, at around 1720 cm^{-1} .^[22] The intense vibration band observed at 1620 cm^{-1} originates from the C=C bond in graphene, and can also be related to the adsorbed water molecules.^[22] Reduction of the GO in the presence of phosphorus resulted in the disappearance of most of these bands, leaving only a weak band at 1620 cm^{-1} , originating from C=C bonds in the graphene structure. In the case of HO-P:[PH_3], in which the degree of reduction is lower, weak bands at 1350 cm^{-1} and 1050 cm^{-1} that are due to the remaining unreduced C–O groups could be observed. This was also confirmed by the HR-XPS C 1s spectrum. HO-P:[NaH_2PO_2] and HO-P:[Na_2HPO_3] were previously observed by XPS to have undergone a lower degree of reduction compared with HO, as shown in Figure 5 B. The –OH vibration band located at around 3200 cm^{-1} displayed a significant decrease in its peak intensity. Reduction of the

materials also resulted in the loss of vibration bands that arise from epoxide-group stretching and C=O vibration of carboxylic acid groups. Other bands associated with C–O vibration (1050 cm^{-1} and 1350 cm^{-1}) can still be observed in these samples, but with significantly lower intensity. These conclusions can be supported by earlier HR-XPS C 1s results, in which a slight increase in C/O ratio was due to the reduction of oxygen-containing groups.

Further insight into the types of oxygen-containing groups present in the material could be obtained through cyclic voltammetry. It is known that epoxy, aldehyde, and peroxy groups in graphene oxide undergo chemically irreversible reduction.^[23,24] Thus, the electrochemical activity of the doped materials in deoxygenated blank phosphate buffer solution (PBS) was studied by using cyclic voltammetry. A reduction peak, which corresponds to the reduction reaction of the oxygen groups on the surface of the materials, was observed at approximately -1200 mV . Different materials displayed the reduction peak at the slightly different reduction potentials of -1220 mV for HO-P:[P_4/KOH], -1170 mV for HO-P:[PH_3], -1206 mV for HO-P:[NaH_2PO_2], and -1200 mV for HO-P:[Na_2HPO_3] (Figure 6). The control material, HO, exhibits a huge reduction peak at a much lower potential of -1345 mV . HO-P:[P_4] and HO-N did not show similar reduction peaks to the other materials because they possess the fewest surface oxygen groups. HO-P:[P_4/KOH] displays an oxygen reduction peak, but of a relatively small current due to the presence of a low oxygen content.

Figure 6. Cyclic voltammograms for the various materials in phosphate buffer solution. Conditions: 100 mV s^{-1} , 50 mM PBS , pH 7.2.

Consequently, we carried out studies on the electrochemical activity, such as heterogeneous-electron-transfer rates, because such properties are crucial for applications, such as energy storage and biosensing. Electrochemical properties, such as peak-to-peak separation and heterogeneous-electron-transfer rates can be determined through cyclic voltammetric (CV) measurements. The CV scans of the different materials were performed in a standard ferro/ferricyanide electrolyte solution as shown in Figure 7. The peak-to-peak separation (ΔE_{p-p}) between the oxidation and reduction peaks for each material was calculated because this value provides information on the

Figure 7. Cyclic voltammograms for phosphorus-doped graphenes, recorded in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Conditions: scan rate 100 mV s^{-1} , 50 mM PBS, pH 7.2.

electron-transfer rate of the material. The $\Delta E_{\text{p-p}}$ values obtained were 391 mV for HO-P:[P_4 /KOH], 437 mV for HO-P:[P_4], 195 mV for HO-P:[PH_3], 286 mV for HO-P:[NaH_2PO_2], and 200 mV HO-P:[Na_2HPO_3]. The control materials have a $\Delta E_{\text{p-p}}$ value of 188 mV and 442 mV for HO-N and HO, respectively. Phosphorus-doped reduced graphene oxides have larger peak-to-peak separation compared with the undoped materials. The three undoped materials, HO-P:[PH_3], HO-P:[NaH_2PO_2], and HO-P:[Na_2HPO_3], displayed similar $\Delta E_{\text{p-p}}$ values. Unexfoliated HO has the largest peak-to-peak separation, owing to the material possessing the largest amount of oxygen-containing groups. This poor electrochemical behavior is due to the negative charges presented by the oxygen groups, typical of graphite oxides, as well as their poor conductivity.^[11] HO-N, with the fewest oxygen-containing groups, exhibited the smallest peak-separation value. The heterogeneous electron transfer rates (k_{obs}^0) were then calculated by using the Nicholson approach in which $\Delta E_{\text{p-p}}$ is related to a dimensionless parameter, Ψ , which is eventually related to k_{obs}^0 .^[25] The calculated electron-transfer rates are $8.25 \times 10^{-5} \text{ cm s}^{-1}$ for HO-P:[P_4 /KOH], $4.41 \times 10^{-5} \text{ cm s}^{-1}$ for HO-P:[P_4], $1.17 \times 10^{-3} \text{ cm s}^{-1}$ for HO-P:[PH_3], $3.44 \times 10^{-4} \text{ cm s}^{-1}$ for HO-P:[NaH_2PO_2], and $1.10 \times 10^{-3} \text{ cm s}^{-1}$ for HO-P:[Na_2HPO_3]. The control materials, HO and HO-N, have k_{obs}^0 values of $4.12 \times 10^{-5} \text{ cm s}^{-1}$ and $1.29 \times 10^{-3} \text{ cm s}^{-1}$.

Doping with electron-donating phosphorus resulted in much higher conductivities than those of undoped graphene, despite a very similar C/O ratio. On the basis of the rigid-band model applied for semiconducting materials, we can conclude that phosphorus acts as an n-type dopant. The increase of free charge carriers is directly reflected in the decrease of sample specific resistivities. The starting material, graphite oxide, is an electrical insulator because of the disrupted sp^2 bonding in the graphene backbone.^[26] The specific resistivities of all samples are summarized in Table 1, together with the values of sheet resistivity. The lowest resistivity is obtained with HO-P:[P_4 /KOH] and HO-P:[P_4], with values of $4.23 \times 10^{-3} \Omega \text{ cm}$ and $4.63 \times 10^{-3} \Omega \text{ cm}$, respectively. The resistivity of HO-P:[PH_3] was slight-

Table 1. Measured specific resistivity and sheet resistivity for the various phosphorus-doped RGOs.

Material	Specific resistivity [$\Omega \text{ cm}$]	Sheet resistivity [$\Omega \text{ Sq}^{-1}$]
HO-P:[NaH_2PO_2]	7.36×10^1	1.49
HO-P:[PH_3]	4.23×10^{-3}	2.56×10^{-1}
HO-P:[P_4]	4.63×10^{-3}	5.57×10^{-1}
HO-P:[P_4 /KOH]	1.12×10^{-2}	8.56×10^{-1}
HO-P:[Na_2HPO_3]	2.14×10^1	5.31×10^1

ly higher at $1.12 \times 10^{-2} \Omega \text{ cm}$. Samples that undergo the lowest degree of reduction, HO-P:[NaH_2PO_2] and HO-P:[Na_2HPO_3], also exhibited high resistivities of $2.14 \times 10^1 \Omega \text{ cm}$ and $7.69 \times 10^1 \Omega \text{ cm}$, respectively. Similarly, the conductivity properties of the materials were investigated through further conductivity measurements by using a gold interdigitated electrode (Au-IDE). The results are as shown in Figure 8. HO-P:[P_4] was found to exhibit the highest conductivity of all the materials investigated, followed by HO-P:[P_4 /KOH] and HO-N. HO-P:[PH_3], HO-P:[NaH_2PO_2], HO-P:[Na_2HPO_3], and HO exhibited similar conductivity, which was the lowest of the materials investigated. For this reason there are several I-V curves that overlap at the lowest conductivity levels (Figure 8).

Figure 8. Current-voltage characteristics of phosphorus-doped RGOs, undoped TRGO, and starting material (HO).

Conclusion

We have successfully synthesized phosphorus-doped reduced graphene oxides, demonstrating a phosphorus treatment process that is capable of removing oxygen groups during the doping procedure. The use of different phosphorus sources for doping was attempted, together with different reaction conditions, in order to investigate the impact of different doping conditions on the characteristics and properties of the resultant materials. The electron-donating phosphorous-doped materials exhibited very high conductivity, higher than that of the undoped control materials.

Experimental Section

Materials

Graphite oxide was prepared according to the Hofmann method^[19] from graphite (2–15 μm , 99.9995 %, Alfa Aesar). Sulfuric acid (98 %), nitric acid (68 %), potassium chlorate (> 99 %), hydrochloric acid (37 %), silver nitrate (> 99.8 %), barium nitrate (> 99 %), sodium hydroxide (> 98 %), potassium hydroxide (> 85 %), carbon disulfide (> 99.5 %), and methanol (> 99.9 %) were obtained from Penta, Czech Republic. Nitrogen (99.9999 % purity) was obtained from SIAD, Czech Republic. Sodium hypophosphite monohydrate (> 99 %) was obtained from Lach Ner (Czech Republic). Sodium phosphite dibasic pentahydrate and white phosphorus were obtained from Sigma-Aldrich, Czech Republic. Potassium phosphate dibasic, *N,N*-dimethylformamide (DMF), potassium ferrocyanide, sodium phosphate monobasic, potassium chloride, sodium phosphite dibasic pentahydrate, and sodium chloride were obtained from Sigma-Aldrich, Singapore. Deionized water was used for the preparation of the electrolytes that were used in any electrochemical measurement. Glassy-carbon (GC) working electrode and platinum auxiliary electrode (Pt), with a diameter of 3 mm, and Ag/AgCl reference electrode were purchased from Autolab, The Netherlands.

Apparatus

A scanning electron microscope (JEOL 7600F field-emission, Japan) was used to obtain SEM images. The samples were attached onto an aluminum stub by using a conductive carbon tape. The XPS and HR-XPS measurements were obtained by using a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). All scans were performed with a 12.53 kV X-ray source. An aluminum XPS sample holder and a sticky conductive carbon tape was used to attach the XPS samples. Care was taken to ensure that a homogeneous and uniform layer of the material was attached onto the tape before the sample was placed inside the XPS chamber for a measurement. Confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector was used for all Raman spectroscopic measurements. Silicon wafer was used for performing calibration at 0 cm^{-1} and 520 cm^{-1} to give a peak position resolution of less than 1 cm^{-1} . Raman measurements were executed by using a 514.5 nm Ar laser, an Olympus optical microscope and a 100 $\times$ objective lens. The preparation of all materials involved a well-compressed and compacted material prior to any measurement. Electrochemical voltammetric measurements were performed by using a microAutolab TypeIII electrochemical analyzer (Eco Chemie, The Netherlands) and a NOVA 1.7 software (Eco Chemie). Nova 1.7 software is published by Metrohm Autolab B.V. in support of Metrohm Autolab's potentiostat/galvanostat equipment. The FTIR measurement was performed on a FTIR spectrometer NICOLET 6700 (Thermo Scientific, USA). Diamond ATR crystal and DTGS detector were used for the measurements in the range of 4000–400 cm^{-1} . For the electrical resistivity measurements of graphene materials, 25 mg of the powder material was first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by a 4-probe technique using the Van der Pauw method.^[27] The resistivity measurements were then performed with a Keithley 6220 current source and Agilent 34970 A data acquisition/switch unit. The measuring current was set to 10 mA. Conductivity measurements were performed with Au-IDE. 1 mg mL^{-1} suspensions of the materials were prepared in deionized water, which was used to coat the electrode. 1 μL of the suspension was coated onto the interdigitat-

ed area and left to dry under a lamp to obtain a randomly deposited layer on the electrode's surface. Linear-sweep voltammetric measurement was then performed on the electrode at a scan rate of 200 mV s^{-1} to obtain the I-V (current-voltage) characteristics for the materials. Five replicates were performed for each material.

Synthetic procedure for phosphorus-doped GOs

The reduction of GO with low-valence phosphorus compounds was performed in an alkaline environment (1 M NaOH), in which the compounds have the highest reduction potential (H_2PO_2^- and HPO_3^{2-}). Reduction of HO-GO by using white phosphorus was investigated under different pH environments: neutral pH and alkaline conditions. In an alkaline environment, white phosphorus undergoes a disproportionation reaction to form phosphane and a H_2PO_2^- anion. To avoid the explosive reaction of phosphane with oxygen the reaction was performed under an argon atmosphere.

Reduction of GO with NaH_2PO_2

GO (0.2 g) was dispersed in 1 M NaOH (100 mL) by ultrasonication and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (0.05 mol) was added. The reaction mixture was heated at reflux for 24 h, after which time the graphene obtained was filtered by using a nylon membrane (0.45 μm) and repeatedly washed with deionized water. The final product was then dried under vacuum at 60 °C for 48 h.

Reduction of HO-GO with Na_2HPO_3

GO (0.2 g) was dispersed in 1 M NaOH (100 mL) by ultrasonication and $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ (0.05 mol) was added. The reaction mixture was then heated at reflux for 24 h and the graphene obtained was filtered by using a nylon membrane (0.45 μm) and repeatedly washed with deionized water. The final product was then dried under vacuum at 60 °C for 48 h.

Reduction of GO with P_4

HO-GO (0.2 g) was dispersed in deionized water by ultrasonication and freshly cut white phosphorus (5 g) was added. The reaction mixture was then vigorously stirred and heated at reflux for 6 h. The reaction mixture was cooled and the remaining white phosphorus was then dissolved in carbon disulfide. The graphene obtained was separated by suction filtration and washed repeatedly with water and carbon disulfide to remove unreacted white phosphorus. The final product was dried under vacuum at 60 °C for 48 h.

Reduction of GO with P_4/KOH

HO-GO (0.2 g) was dispersed in 1 M KOH (100 mL) by ultrasonication and the mixture was placed in 250 mL flask with an argon inlet and reflux condenser. Freshly cut white phosphorus (5 g) was then added into the reaction mixture. The mixture was then placed in an oil bath with vigorous stirring for 6 h, while being kept under reflux. The reaction mixture was then subsequently cooled to room temperature and flushed with argon gas to avoid explosive reactions between phosphane and oxygen. The GO reduced with phosphorus was separated by suction filtration and repeatedly washed with water and carbon disulfide to remove any traces of unreacted white phosphorus. The final product was dried under vacuum at 60 °C for 48 h.

Reduction of GO with PH₃

Freshly cut white phosphorus (20 g) was placed in a reaction flask with an argon inlet and 5 M NaOH (250 mL) was added. The phosphane gas evolved from the reaction under heating and was mixed with argon and introduced through the reflux condenser into the reaction flask with GO (0.2 g) dispersed in deionized water (100 mL). The reaction mixture was then vigorously stirred for 6 h. The GO reduced with phosphorus was separated by suction filtration and repeatedly washed with water and carbon disulfide to remove any traces of unreacted white phosphorus formed by oxidation of phosphane. The final product was dried under vacuum at 60 °C for 48 h.

Synthetic procedure for HO

The graphite oxide was prepared according to the procedures reported previously. Graphite oxide preparation with the Hoffman method^[9]: Sulfuric acid (98% concentration, 87.5 mL) and nitric acid (68%, 27 mL) were added to a reaction flask containing a magnetic stir bar. The mixture was subsequently cooled to 0 °C and graphite (5 g) was added. The mixture was then vigorously stirred to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, potassium chlorate (55 g) was slowly added to the mixture. Upon completion dissolution of the potassium chlorate, the reaction flask was left loosely capped to allow the gas evolved during the reaction to escape. The mixture was then continuously stirred for 72 h at room temperature. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solution to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulfate ions (with AgNO₃ and Ba(NO₃)₂, respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Synthetic procedure for HO-N

The thermal exfoliation of GO was carried out at 1000 °C for 12 min. GO was placed inside a porous quartz glass capsule connected to a magnetic manipulator in a vacuum-tight quartz reactor, under controlled atmosphere. This system provided a temperature gradient of over 1000 °C min⁻¹. The sample was then flushed repeatedly with pure nitrogen and, subsequently, inserted into a preheated reactor in a nitrogen (99.9999% purity) atmosphere (pressure: 100 kPa) to produce a noble-metal-doped graphene hybrid material. The flow of the nitrogen at 1000 mL min⁻¹ resulted in the removal of the by-products of the reactions.

Cyclic Voltammetry

All glassy-carbon electrodes were cleaned by polishing with an alumina suspension to renew the electrode surface then washed and wiped dry prior to any use. The materials were dispersed in DMF as the organic solvent to obtain a 0.5 mg mL⁻¹ suspension. The suspension was then sonicated for 5 min at room temperatures before every use. A cleaned GC electrode was then modified by coating with a 1 µL aliquot of the suspension and left to dry under a lamp to give a layer of randomly dispersed material on the GC surface. This process was repeated three times to obtain three layers of homogeneous coatings. The modified GC electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then placed into an electrochemical cell which contains the electrolyte solution and the measurements were then taken. The elec-

trolytes used were 50 mM pH 7.4 phosphate buffer solution (PBS) as the blank buffer electrolyte and 10 mM ferro/ferricyane dissolved in PBS. All measurements were performed for two consecutive scans at a scan rate of 100 mV s⁻¹. Three measurements were carried out for each material and also for each electrolyte.

Keywords: conductivity · doping · graphene · phosphorus

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Sulfur-Doped Graphene *via* Thermal Exfoliation of Graphite Oxide in H₂S, SO₂, or CS₂ Gas

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ABSTRACT Doping of graphene with heteroatoms is an effective way to tailor its properties. Here we describe a simple and scalable method of doping graphene lattice with sulfur atoms during the thermal exfoliation process of graphite oxides. The graphite oxides were first prepared by Staudenmaier, Hofmann, and Hummers methods followed by treatments in hydrogen sulfide, sulfur dioxide, or carbon disulfide. The doped materials were characterized by scanning electron microscopy, high-resolution X-ray photoelectron spectroscopy, combustible elemental analysis, and Raman spectroscopy. The ζ -potential and conductivity of sulfur-doped graphenes were also investigated in this paper. It was found that the level of doping is more dramatically influenced by the type of graphite oxide used rather than the type of sulfur-containing gas used during exfoliation. Resulting sulfur-doped graphenes act as metal-free electrocatalysts for an oxygen reduction reaction.

KEYWORDS: graphene · doping · sulfur · gas phase · electrochemistry

Graphene in its pure state has been shown to exhibit many interesting materials properties that are useful for electronic and electrochemical application, such as nanoelectronics and electrode surfaces (*i.e.*, oxygen reduction reaction or electrocatalysis).^{1–7} However, the suitability of the material for these applications is limited by the fact that pristine graphene exhibits zero band gap⁸ and that its electrochemical behavior resembles that of graphite.⁹ Doping of graphene with various atoms, such as transition metals,^{10,11} halogens,^{12–14} hydrogen,¹⁵ nitrogen,^{16–20} or sulfur²¹ can change the electron density²² in the graphene sheet and provide an electrocatalytic surface in the material at the same time.

Sulfur doping of graphene is of particular interest as the resulting materials are expected to have a wider band gap due to the electron-withdrawing character of sulfur. Previous studies have successfully produced elemental sulfur/graphene composites by mechanically mixing the individual components^{23,24} or heating graphene with benzyl disulfide where the creation of sulfur-epoxy bonds in graphene was proposed

to exist.²¹ Here we have employed different sulfur doping strategies and we investigated to what extent they influence the composition of the final product. We used graphite oxide as a starting material, which was then thermally exfoliated in a sulfur-containing gaseous environment (Scheme 1). Graphite oxide was prepared using three different classical methods, such as Staudenmaier,²⁵ Hofmann,²⁶ and Hummers²⁷ and further exfoliated at high temperature in SO₂, H₂S, and CS₂ gas atmosphere. Interestingly, we observed that the type of graphite oxide used for sulfur doping brought about a greater effect on the properties of the final product as compared to the type of the sulfur-containing gas used for exfoliation. We show that sulfur-doped graphenes show electrocatalysis for the oxygen reduction reaction, which is of high industrial importance, and make them ideal candidates for metal-free oxygen reduction electrocatalysts.

RESULTS AND DISCUSSION

To prepare sulfur-doped graphenes, graphite was first oxidized to graphite oxide with (a) fuming nitric acid, H₂SO₄, and KClO₃

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Scheme 1. Fabrication of sulfur-doped graphene by thermal exfoliation of graphite oxide prepared by Staudenmaier, Hofmann, and Hummers method in CS_2 , H_2S , or SO_2 atmospheres.

(Staudenmaier method (ST)), (b) 68% HNO_3 , H_2SO_4 , and KClO_3 (Hofmann method (HO)), or (c) H_2SO_4 , KMnO_4 , and NaNO_3 mixture (Hummers method (HU)). Consequently, the material was placed in a quartz tube and exfoliated in SO_2 , H_2S , or CS_2 atmospheres (1000 mbar) at 600 or 1000 °C. The resulting materials were then extensively characterized using scanning electron microscopy (SEM), high-resolution X-ray photoelectron spectroscopy (HR-XPS), Raman spectroscopy, and combustible elemental analysis. Its other properties such as ζ -potential and conductivity were also investigated. The materials discussed in this paper are labeled in accordance with the reaction conditions and types of materials used; that is, HO-S: [CS_2 /1000 °C] signifies sulfur-doped graphene prepared from Hofmann graphite oxide exfoliated in CS_2 atmosphere at 1000 °C. The thermally reduced graphene oxide (TRGO) starting materials that are not doped with sulfur will be indicated as ST, HO, and HU which represents Staudenmaier TRGO, Hofmann TRGO, and Hummers TRGO, respectively.

Materials Characterization. The following sections will further elaborate in detail the findings obtained for these materials using various characterization techniques such as scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Comparison will also be made with non-sulfur-doped graphene oxides (ST, HU, and HO) which act as the control materials in this paper.

Characterization of the materials was first carried out using SEM to observe the morphology and

topographical details. Imaging of the materials was carried out at various magnifications of 370 $\times$, 6000 $\times$, 10 000 $\times$, and 50 000 $\times$, as shown in Figure 1. It was observed from the obtained images that all of the materials have been successfully exfoliated as the images presented structures that are similar to exfoliated graphene oxides where separated sheets of sulfur-doped graphene oxides could be clearly observed. Comparison between different starting materials, sulfur sources, or reaction conditions showed that no major structural differences could be visually observed from the different conditions that were executed to generate the materials.

Further structural information such as the density of defects in the materials can be accomplished using Raman spectroscopy technique through the determination of the G (related to pristine sp^2 graphitic layer) bands at $\sim 1560\text{ cm}^{-1}$ and D (related to defect in sp^2 lattice) bands at $\sim 1350\text{ cm}^{-1}$ in the spectrum. The presence of defects in the pristine graphene structure is crucial in affecting the electrochemical behavior of the materials as earlier studies have shown that such reactions are most likely to occur at these sites of defects which are characterized to be of a sp^3 nature. Using the green Ar laser source at 514 nm, a Raman spectrum which shows the presence of a D and G band is recorded. The density of defects can be represented by a calculated D/G ratio of the intensity of the D band to the intensity of the G band where this ratio is an indication of the degree of disorder in the structure. Figure 2 shows the Raman spectra for corresponding sulfur-doped as well as for undoped (graphite oxide exfoliated in argon atmosphere) graphenes. The calculated D/G ratios for the Staudenmaier materials are 0.77 for the undoped ST thermally reduced graphene oxide, 0.62 for sulfur-doped Staudenmaier graphene oxide using the H_2S source at 600 °C (labeled as ST-S: [H_2S /600 °C]), and 0.69 for ST-S: [SO_2 /600 °C] (refer to Figure 2A,D). The formation of defects in these ST graphene oxides may be partially attributed to the sulfur that is being doped onto the graphene oxide surfaces. Derivation of the average crystalline size (L_a) of the materials can also be possible through the use of the D/G ratios in the equation as follows:²⁸

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

The I_G/I_D is the ratio of the intensities of the G and D bands, respectively, and λ_{laser} refers to the laser wavelength (nm) used in the measurement of the Raman spectrum (i.e., 514 nm). The calculated L_a values are 21.7 nm for ST, 27.1 nm for ST-S: [H_2S /600 °C], and 24.3 nm for ST-S: [SO_2 /600 °C]. This result shows that a change in the sulfur-containing gas environment during exfoliation of the graphene oxide may affect the density of defects in the material and hence its resulting crystalline size. It was observed that undoped ST

Figure 1. Scanning electron micrographs of sulfur-doped graphenes prepared from Hofmann, Hummers, and Staudenmaier graphite oxides by exfoliation in sulfur-containing gas at various temperatures. Magnification of (A) 370 $\times$, (B) 6000 $\times$, (C) 10 000 $\times$, and (D) 50 000 $\times$. Scale bars of 100 nm (A), 1 μ m (B,C), and 10 μ m (D).

possesses the highest D/G ratio as compared to the two other sulfur-doped graphene oxides.

Similarly, Raman spectroscopic measurements were also performed to obtain D/G band intensities for sulfur-doped graphene oxides using Hofmann synthesized graphite oxides as the starting material (as shown in Figure 2B,D). The measured D/G ratios are 1.09, 0.84, 0.85, 0.81, and 0.91 for HO, HO-S: [H₂S/600 °C], HO-S: [SO₂/1000 °C], HO-S: [SO₂/600 °C], and HO-S: [CS₂/1000 °C], respectively. Once again, the undoped thermally reduced graphene oxide (HO) displays a

higher D/G ratio as compared to the S-doped HO materials where similar phenomenon was also observed in the case of ST materials. The use of H₂S and SO₂ sources as the dopant resulted in similar D/G ratios of approximately 0.83, except for CS₂, which gives an exceptionally high reading of 0.91 among the three different sulfur-doping sources. Average crystalline sizes of these materials were calculated to be 15.4, 20.0, 19.7, 20.8, and 18.5 nm for HO, HO-S: [H₂S/600 °C], HO-S: [SO₂/1000 °C], HO-S: [SO₂/600 °C], and HO-S: [CS₂/1000 °C], respectively. This result shows that

Figure 2. Raman spectra of sulfur-doped graphenes prepared from (A) Staudenmaier, (B) Hummers, and (C) Hofmann graphite oxides by exfoliation in sulfur-containing gas at various temperatures, as stated in the figure. Raman spectra of control materials exfoliated in inert gas are also shown. (D) D and G band intensity ratios.

sulfur-doped Hofmann graphene oxides have a larger crystalline structure as compared to non-sulfur-doped Hofmann graphene oxides. Sulfur-doping treatments were also performed on graphite oxides produced from Hummers method to give D/G ratios of 0.97 for HU, 0.90 for HU-S: $[\text{H}_2\text{S}/600^\circ\text{C}]$, and 0.99 for HU-S: $[\text{SO}_2/600^\circ\text{C}]$ (refer to Figure 2C,D). It can be observed from the results that sulfur-doped Hummers graphene oxides are found to consist of a higher amount of defects as compared to ST and HO sulfur-doped materials. D/G ratios were also used for the derivation of the average crystalline sizes, which are calculated to be 17.3 nm for HU, 16.9 nm for HU-S: $[\text{H}_2\text{S}/600^\circ\text{C}]$, and 18.5 nm for HU-S: $[\text{SO}_2/600^\circ\text{C}]$. The Raman measurements obtained showed that the D/G ratio only displays a logical trend within each type of graphene oxide used for sulfur-doping treatments. However, a noncoherent trend exists between different types of graphene oxides that were doped under similar conditions. It could be clearly observed that all doped and undoped Hofmann graphene oxides possess the highest D/G ratios followed by HU graphene oxides (doped and undoped) and, finally, doped and undoped ST graphene oxides having the lowest D/G ratios of the three different types of materials. It should be noted that a small increase of background in Raman spectra is due to weak photoluminescence of the sample.²⁹

Exfoliation of the three types of graphite oxides under different sulfur gaseous environments was performed in an attempt to successfully dope the materials' surfaces with sulfur. Therefore, it is crucial to study the surface composition of the materials to investigate

Figure 3. Wide-range XPS spectra of sulfur-doped graphenes prepared from (A) Staudenmaier, (B) Hummers, and (C) Hofmann graphite oxides by exfoliation in sulfur-containing gas at various temperatures, as stated in the figure. XPS spectra of control materials exfoliated in inert gas are also shown. (D) C 1s and O 1s (sensitivity factor corrected) ratios in particular graphenes. (E) Percentage of S 2p signal in total count of wide-angle XPS spectra.

the various functionalities present on the surface in order to determine the successful incorporation of sulfur into the materials. X-ray photoelectron spectroscopy utilizes a focused X-ray beam to irradiate the materials surface, obtaining the chemical composition information of the elements present *via* their respective electronic states. This measurement is presented as a form of a wide-range spectrum for the different materials, as shown in Figure 3, where the C 1s peak occurs at ~ 284.5 eV, O 1s at ~ 534 eV, and S 2p at ~ 167 eV. Figure 3A shows the XPS spectra of the ST and sulfur-doped ST materials where the presence of C and O could be clearly observed for all three materials. The existence of the S 2p peak at 167 eV for ST-S: $[\text{H}_2\text{S}/600^\circ\text{C}]$ and ST-S: $[\text{SO}_2/600^\circ\text{C}]$ coupled with the absence of the S 2p peak in the ST spectrum shows successful doping of the materials with sulfur. Further information on the degree of oxidation of the material can be obtained through the calculation of the C/O ratios with relative sensitivity factors taken into consideration. The intensities of the C 1s and O 1s peaks allow the derivation of a C/O ratio where a higher ratio indicates lesser oxygen functionalities on the surface and, hence, a more reduced material. Calculation of the C/O ratios shows that ST possesses a ratio of 24.09; ST-S: $[\text{H}_2\text{S}/600^\circ\text{C}]$ has a value of 13.44, and ST-S: $[\text{SO}_2/600^\circ\text{C}]$ has a value of 9.30. It was observed that

sulfur-exfoliated Staudenmaier graphene oxides have a lower C/O ratio as compared to undoped ST (refer to Figure 3D). This shows that the exfoliation of graphene oxides under a sulfur-containing gas environment results in the addition of oxygen functionalities on the materials' surfaces as compared to exfoliation under nitrogen gas environment. Further wide spectra XPS measurements were also carried out on HO graphite oxides exfoliated under a sulfur gaseous environment to investigate their respective C/O ratios.

As shown in Figure 3C, the spectra of sulfur-doped HO materials display the presence of a C 1s, O 1s, and S 2p peak at similar respective binding energies as the peaks shown earlier for sulfur-doped ST materials. The control material HO once again exhibits only a C 1s and an O 1s peak, and hence, the absence of the S 2p is a clear indication of the successful incorporation of sulfur into the exfoliated HO graphene oxides. The calculated C/O ratios for HO materials are 18.23 for HO, 12.61 for HO-S: [H₂S/600 °C], 10.17 for HO-S: [SO₂/1000 °C], 9.86 for HO-S: [SO₂/600 °C], and 17.02 for HO-S: [CS₂/1000 °C]. It can be observed from these values that all sulfur-doped HO graphene oxides have lower C/O ratios than the control material HO (refer to Figure 3D). This indicates that exfoliation under a sulfur gaseous environment results in the inclusion of more oxygen functionalities onto the graphene oxides surfaces as compared to a nitrogen gaseous environment. This phenomenon was also observed earlier for ST materials where the control material, ST, was found to have a much higher C/O ratio than its sulfur-doped counterparts. Among the four doped HO graphene oxides, doping of the graphene oxide using CS₂ as the sulfur source proved to have the highest C/O ratio. This indicates that exfoliation of HO graphite oxide in a CS₂ gaseous environment results in a larger extent of elimination of the oxygen moieties from graphene oxide's surface as compared to exfoliation in other sulfur sources. These results are in good agreement with the results obtained from ζ -potential measurement, which will be further elaborated in a later section. Wide-range XPS scans for doped and undoped HU graphene oxides were recorded, as shown in Figure 3B, where the C 1s, O 1s, and S 2p peaks are observed at binding energies of $\sim$ 285, $\sim$ 535, and $\sim$ 167 eV, respectively, similar to the values reported earlier for HO and ST materials. Presence of a S 2p peak in the spectra for sulfur-doped HU as compared to the absence of a S 2p peak in undoped HU graphene oxide is evidence of the successful incorporation of sulfur during exfoliation of the material. Calculation of the intensities of the C 1s and O 1s peaks gives the following C/O ratios (refer to Figure 3D) of 19.28 for HU, 12.19 for HU-S: [H₂S/600 °C], and 11.49 for HU-S: [SO₂/600 °C]. Similarly, undoped graphene oxides possessed higher C/O ratios than their sulfur-doped counterparts, where this same trend was observed for HO and ST materials.

Figure 4. High-resolution XPS spectra of the S 2p signal of sulfur-doped graphenes prepared from (A) Staudenmaier, (B) Hummers, and (C) Hofmann graphite oxides by exfoliation in sulfur-containing gas at various temperatures. XPS spectra of control materials exfoliated in inert gas are also shown.

This shows that the phenomenon of an addition of oxygen functionalities in the materials during exfoliation occurred not only for HO and ST but also for HU materials. Similarly, no obvious trend could be observed in the comparison between different graphene oxides exfoliated under similar sulfur environment and conditions.

A more significant observation was realized in the comparison within each type of graphene oxides, such as Staudenmaier, Hummers, and Hofmann, as discussed in the earlier section. The intensities of the S 2p peaks are plotted in the form of a bar graph, as shown in Figure 3E, as a percentage of the total number of counts collected during the XPS measurement. The total amount of S is calculated as a percentage of the total elemental composition at the materials' surfaces. The percentages are reported to be 0.75 for ST-S: [H₂S/600 °C] and 0.87 for ST-S: [SO₂/600 °C] for ST materials. HO materials are observed to have percentages of 4.44 for HO-S: [H₂S/600 °C], 2.16 for HO-S: [SO₂/1000 °C], 2.13 for HO-S: [SO₂/600 °C], and 4.07 for HO-S: [CS₂/1000 °C]. HU materials were also recorded to have the following percentages of 7.03 for HU-S: [H₂S/600 °C] and 6.67 for HU-S: [SO₂/600 °C]. It could be observed that sulfur-doped Hummers materials possessed the highest sulfur content, followed by sulfur-doped Staudenmaier and last Hofmann materials. It is of interest to highlight that the extent of S doping in graphene is more dependent on the type of graphite oxide used than on the type of sulfur gas atmosphere utilized during synthesis. This is of great significance as ST, HO, and HU graphite/graphene oxides are frequently used interchangeably in several reports in the literature without any emphasis on the fact that they are actually very different materials.³⁰

Figure 5. High-resolution XPS spectra of C 1s signal of sulfur-doped graphenes prepared from Staudenmaier (ST), Hummers (HU), and Hofmann (HO) graphite oxides by exfoliation in sulfur-containing gas at various temperatures. XPS spectra of control materials exfoliated in inert gas are also shown.

Crucial information on the types of oxygen and sulfur-containing groups present in each material is important in the characterization of the materials. It allows a complete understanding of the synthesis process and how each functional group is incorporated into the materials' surfaces during the synthesis step. The identification of these functionalities can be achieved through a high-resolution X-ray photoelectron spectroscopic measurement for a specific electronic state of the element of interest at their respective range of binding energies. HR-XPS scans were performed for S 2p and C 1s electronic states at approximately 167 and 284.5 eV, respectively, for all of the materials, as shown in Figure 4 (for sulfur-bonded species *via* S 2p signal) and Figure 5 (for carbon-bonded species *via* C 1s signal). High-resolution XPS scans were obtained for the sulfur-doped

graphene oxides at the S 2p electronic state, as shown in Figure 4, at the binding energy of approximately 167 eV. HR-XPS measurements were carried out for sulfur-doped ST materials, sulfur-doped HU, and sulfur-doped HO, as shown in Figure 4A–C, respectively. All of the S 2p spectra show a single broad symmetrical peak at the position 167 eV, indicating the existence of a single type of S bonding interaction in the structure. With the S 2p peak's maximum intensity positioned at 167 eV, this peak can be concluded to be attributed to the presence of sulfur in the S^{6+} valence state, which indicates the presence of a SO_3H group.³¹ These observations were also confirmed by the ζ -potential measured and the FT-IR spectra obtained for the materials (Figure 6 and Supporting Information Figure S1, respectively). Interestingly, the presence of SO_3H group was also observed

Figure 6. Zeta-potentials of sulfur-doped graphenes prepared from Staudenmaier (ST), Hummers (HU), and Hofmann (HO) graphite oxides by exfoliation in sulfur containing gas at various temperatures. Values of ζ -potential of control materials exfoliated in inert gas are also shown.

for samples exfoliated in H₂S and CS₂ atmosphere (see Figure S1, Supporting Information). In this case, the hydrogen sulfide acts as a reducing agent in the reaction with graphite oxide where sulfur is oxidized to higher valence state and is covalently bonded to the graphene. This observation is confirmed by the higher C/O ratio measured by XPS and combustion elemental analysis, which will be discussed later. On the other hand, the sulfur dioxide acts as an oxidizing agent as much lower C/O ratios are observed on samples exfoliated in SO₂ atmosphere. At high temperatures (1000 °C), the exfoliation in SO₂ atmosphere led to an oxidation of exfoliated graphene.

HR-XPS scans were also performed for the C 1s electronic state at approximately 284.5 eV to investigate the types of oxygen- and sulfur-containing groups present on the surface of these materials (Figure 5). Fitting of the C 1s spectrum was carefully performed to identify and quantify the various possible carbon interactions that may be present on the material's surface. It was observed that all undoped reduced graphene oxides (ST, HU, HO) display six carbon interactions at 284.5 eV for C=C, 285.7 eV for C–C, 286.8 eV for C–O, 288.0 eV for C=O, 289.2 eV for O–C=O, and 290.8 eV for π – π interactions. The spectrum is often shown as a symmetrical peak at 284.5 eV, which corresponds to C=C interaction and a trailing tail shape at higher binding energy which depicts the π – π interaction (refer to Figure 5). On the other hand, all sulfur-doped graphene oxides also exhibited all six carbon interactions that were previously observed for undoped graphene oxides at their respective binding energies that are similar to the values reported above. The appearance of a C–S peak was also detected at approximately 286.5 eV, which is of a lower energy than the C–O interaction due to oxygen being more electronegative which results in C–O displaying stronger charging behavior. The presence of the C–S peak indicates not only the successful inclusion of sulfur

during exfoliation but also implications that the S exists inside the lattice structure of the graphene and is covalently bonded to the graphene.

Compared to high surface sensitivity of XPS, the combustible elemental analysis gives information about the “bulk” composition of material. The results obtained from elemental analysis measurements are in agreement with the data obtained from XPS. The highest concentration of sulfur content was found to be present in the samples prepared from graphite oxide prepared by the Hummers method (11.99 wt % S in HU-S: [H₂S/600 °C] and 10.42 wt % S in HU-S: [SO₂/600 °C]). The second highest concentration of sulfur was detected in the samples prepared from GO according to Hofmann method (4.12 wt % in HO-S: [SO₂/1000 °C] and 3.69 wt % HO-S: [SO₂/600 °C]). Higher incorporation of sulfur was observed for samples exfoliated in atmospheres with low valence sulfur compounds—hydrogen sulfide and carbon disulfide. The concentrations of S in HO-GO exfoliated with these sulfur precursors were 8.37 wt % for HO-S: [H₂S/600 °C] and 7.34 wt % for HO-S: [CS₂/1000 °C]. The concentration of sulfur in ST-GO exfoliated in H₂S and SO₂ atmosphere was below 0.1 wt %. This observation can be explained by the incomplete formation of sulfur dioxide during combustion analysis. Sulfur dioxide formed during the combustion process is used for measurement of sulfur concentration within the sample. On the basis of this observation, we can make some general conclusions that the incorporation of sulfur is dependent on the degree of GO oxidation and, hence, the method of preparation of the GO. Sulfur precursors used during exfoliation have also significantly influenced the resultant composition percentages of graphene. Reactions with hydrogen sulfide and carbon disulfide with sulfur in the oxidation state 2– results in the material having a higher C/O ratio and also a higher concentration of sulfur. A complete list of the results from elemental analysis can be obtained in Table S1 (Supporting Information). These results are consistent with the observations obtained from the ζ -potential measurements for the materials.

Dispersions of TRGOs in water were analyzed by measuring their ζ -potential (Figure 6). Sulfur-doped ST reduced by hydrogen sulfide and sulfur dioxide exhibited slightly higher (in absolute values) ζ -potential (–38 and –45 mV, respectively) compared to the TRGO in nitrogen (–35 mV). This could be due to the bonding of sulfonic acid group (–SO₃H) to the graphene framework. As the concentration of sulfur in the materials is low (refer to XPS and elemental analysis results), ζ -potential is most likely to be influenced by the oxygen functionalities found in the materials. In the comparison within sulfur-doped and undoped HO TRGOs, a different trend can be observed. Undoped TRGO that is exfoliated in an inert gas atmosphere exhibited a very distinct ζ -potential of +9 mV,

TABLE 1. Numerical Data of Conductivities of Sulfur-Doped Graphenes

Sample	Resistivity (Ωcm)
ST-S: [$\text{H}_2\text{S}/600^\circ\text{C}$]	5.5×10^{-5}
ST-S: [$\text{SO}_2/600^\circ\text{C}$]	4.1×10^{-5}
ST: [$\text{N}_2/1000^\circ\text{C}$]	5.1×10^{-5}
HO-S: [$\text{H}_2\text{S}/600^\circ\text{C}$]	5.9×10^{-4}
HO-S: [$\text{SO}_2/600^\circ\text{C}$]	5.2×10^{-4}
HO-S: [$\text{CS}_2/1000^\circ\text{C}$]	3.4×10^{-4}
HO-S: [$\text{SO}_2/1000^\circ\text{C}$]	5.9×10^{-4}
HO: [$\text{N}_2/1000^\circ\text{C}$]	3.9×10^{-4}
HU-S: [$\text{H}_2\text{S}/600^\circ\text{C}$]	1.0×10^{-3}
HU-S: [$\text{SO}_2/600^\circ\text{C}$]	1.2×10^{-3}
HU: [$\text{N}_2/1000^\circ\text{C}$]	8.0×10^{-4}

suggesting a very high degree of GO reduction in the material. The positive potential measured may be attributed to nitrogen contamination in the HO. TRGOs exfoliated in H_2S and SO_2 were observed to have more negative potentials of -34 mV for H_2S and -26 and -20 mV for SO_2 at 600 and 1000 $^\circ\text{C}$, respectively. The highly negative potentials observed were likely to be attributed to $-\text{SO}_3\text{H}$ and oxygen groups present in the materials. Sulfur-doped HO in CS_2 exhibits lower ζ -potential of -9 mV even though it possessed similar elemental composition as HO doped by H_2S (according to XPS and elemental analysis results). Sulfur-doped HU was observed to have ζ -potentials (-38 mV for H_2S and -42 mV for SO_2) that were similar to those measured for sulfur-doped ST TRGOs. Undoped HU has a lower potential of -8 mV, similar to that of undoped HO. In conclusion, sulfur-doped TRGOs always exhibit higher values of ζ -potentials as compared to undoped TRGOs and, therefore, are more stable when dispersed in aqueous solutions. This behavior can be explained by the presence of two groups: acidic $-\text{SO}_3\text{H}$ group and unreduced oxygen groups. The presence of $-\text{SO}_3\text{H}$ group was expected for GO reduced in SO_2 but comes as a surprise in the case of H_2S . Earlier XPS results have shown the presence of $-\text{SO}_3\text{H}$ group (refer to XPS results Figure 4) where the position and fwhm of the S 2p peak were the same for all sulfur-doped samples. The peaks were centered at 166.3 eV, which suggests oxidized sulfur with a valence of 6+. It is interesting to note that no thiol group ($-\text{SH}$) was detected for GO reduced with hydrogen sulfide (~ 162 eV). Similarly, the preference to create sulfonic groups and not thiol groups was observed on carbon chain when doping with thiol precursor as shown in earlier studies.³¹ Both XPS and elemental analysis results have confirmed that a higher concentration of oxygen was present in GO reduced by SO_2 than in GO

Figure 7. Electrical resistivity of sulfur-doped graphenes prepared from Staudenmaier (ST), Hummers (HU), and Hofmann (HO) graphite oxides by exfoliation in sulfur-containing gas at various temperatures. The values of resistivity of control materials exfoliated in inert gas are also shown.

Figure 8. Cyclic voltammograms for undoped and sulfur-doped graphenes in O_2 saturated solution of 0.1 M KOH. Conditions: scan rate of 100 mV/s.

reduced by H_2S . This observation was anticipated as the SO_2 groups contain oxygen atoms that contributed to the oxygen content while H_2S has to react with oxygen groups in GO in order to form $-\text{SO}_3\text{H}$.

Consequently, we have measured the resistivity of sulfur-doped graphene oxides as well as undoped graphene oxides exfoliated in inert gas atmosphere (refer to Table 1 and Figure 7). Majority of the sulfur-doped samples showed higher resistivity than their undoped counterparts that were reduced in nitrogen atmosphere. The increase in their resistivities can be attributed to the trapping of free carriers by the sulfur and oxygen functionalities. Such similar influence on the resistivity was also observed for the GO exfoliated in the presence of halogens.¹³

It has been previously reported that sulfur-doped graphenes can act as metal-free electrocatalysts for oxygen reduction.²¹ In order to investigate electrocatalytic activity of sulfur-doped graphene toward oxygen reduction, we performed cyclic voltammetry of solution saturated with O_2 in 0.1 M KOH (Figure 8). We have found that O_2 reduction on a bare glassy carbon electrode requires large overpotentials (peak potential of -492 mV vs Ag/AgCl); undoped graphene (HO)

results in lower overpotentials required (peak potential of -411 mV vs Ag/AgCl). Sulfur-doped graphenes provided excellent electrocatalytic surfaces, being able to reduce oxygen at -405 mV for HO-S: [H₂S/600 °C], -397 mV for HO-S: [CS₂/1000 °C], -380 mV for HO-S: [SO₂/600 °C], and even only -370 mV for HO-S: [SO₂/1000 °C]. The shift of reduction potential by 40 mV from -411 to -370 mV from undoped graphene to S-doped graphene shows that sulfur-doped graphenes provide electrocatalytic surface of O₂ reduction reaction.

CONCLUSION

Doping of graphene with sulfur was made possible using various sulfur sources and reaction conditions to give final products with different amounts of sulfur content. This synthesis procedure was carried out with three main graphite oxide sources: Staudenmaier, Hummers, and Hofmann. We have investigated the physical and chemical properties of these materials in an attempt to understand how the variation in the reaction conditions has impacted the final outcome of these materials. Physical properties of these materials were studied using scanning electron microscopic technique where all of the sulfur-doped graphene oxides were found to be fully exfoliated, similar to the undoped graphene oxides. Raman spectroscopy results showed that all undoped graphene oxides possessed higher defect density than their sulfur-doped counterparts with the exception of HU. S-doped HO materials were also found to have the highest amount of defects followed by HU and eventually ST materials. XPS measurements and elemental combustible analysis have shown that HU has the highest sulfur content followed by HO and finally ST materials. The ζ -potential measurements showed that sulfur doping has a significant effect on the water dispersion

stability of the sulfur-doped GO. All sulfur-doped materials exhibit higher (absolute value) ζ -potentials than their undoped counterparts. Especially, ST and HU S-doped GO treated with SO₂ have good dispersion stability (ζ -potential over -40 mV, generally considered limit for "good stability"). This is in accordance with the expectations that the sulfur is present as a $-\text{SO}_3\text{H}$ group. The ζ -potential is determined both by the type of graphite oxide starting material and by the exfoliation atmosphere. Especially S-doped HO and HU exhibited strong increase of their ζ -potentials as compared to undoped HO and HU. There is also a good correlation between the concentration of sulfur and the increase of ζ -potential. The concentration of sulfur in S-doped ST, as evaluated from the XPS, was lowest of the graphite oxides, and the corresponding shift of ζ -potential was least significant. The resistivity measurements confirmed the electron trapping ability of the sulfur dopant. Majority of the S-doped GO materials show higher resistivity than their undoped counterparts. However, the absolute values are still determined by the oxidation method rather than by the exfoliation atmosphere. The combustible elemental analysis is in good agreement with the XPS results. It confirmed that the highest concentration of sulfur was found for S-doped HU materials. The concentrations of sulfur also correspond with the ζ -potential results and the possibility of a sulfonic group present on the surface of the graphene oxides. The concentration of oxygen is also in accordance with the XPS results and suggests that graphite oxides treated with SO₂ have a higher degree of oxidation than those exfoliated in more reducing atmospheres (N₂, H₂S, CS₂). We have demonstrated that sulfur-doped graphenes exhibit electrocatalytic behavior for oxygen reduction reaction.

EXPERIMENTAL PROCEDURE

Materials. Sulfuric acid (98%), nitric acid (68%), nitric acid (fuming, 98%), potassium chlorate (98%), potassium permanganate (98%), hydrogen peroxide (30%), hydrochloric acid (37%), silver nitrate (99.5%), and barium nitrate (99.5%) were obtained from PENTA, Czech Republic. Carbon disulfide (99.9%) and *N,N*-dimethylformamide (DMF) were obtained from Aldrich. Graphite microparticles (<50 μm) were obtained from KOOH-I-NOOR Grafit, Czech Republic. The gases were obtained from SIAD (nitrogen 99.9999% and hydrogen sulfide 99.5%) and Linde (sulfur dioxide 99.98%).

Apparatus. Scanning electron microscopic (SEM) images were acquired using a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) at 5 kV accelerating voltage. Preparation of the samples was performed by attaching the materials onto a sticky conductive carbon tape which was then mounted onto an aluminum sample stub. X-ray photoelectron spectroscopy (XPS) measurement was executed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) for the wide-range and high-resolution C 1s scans at 12.53 kV. The XPS samples were prepared by attaching a uniform layer of the materials onto a conductive carbon tape which was then affixed onto an

aluminum XPS sample holder. The C/O ratios were achieved from the wide-scan XPS measurements with relative sensitivity factors taken into consideration during calculations. Raman spectroscopy was performed with a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. A 514.5 nm Ar laser and an Olympus optical microscope with a 100 $\times$ objective lens were used in the focusing of the samples. Calibration of the machine was carried out at 0 and 520 cm^{-1} with a silicon wafer as reference to give a peak position resolution of less than 1 cm^{-1} . All samples were well-compressed and compacted before placing on top of a glass slip which was positioned on a piece of glass slide before any actual measurement was carried out. The elemental analysis (CHNS-O) was performed with Vario EL III (Elementar Analysensysteme GmbH, Germany). The calibration was performed with 5 mg of 4-aminobenzenesulfonic acid. The measurements of ζ -potential were performed on Malvern Zetasizer Nano ZS. Diluted samples of 1 mg of TRGO/25 mL of H₂O mass concentration were first ultrasonicated for 5 min and then measured in a folded capillary cell at pH 7. For electrical resistivity measurements of graphene materials, 40 mg of the powder material was first compressed into a capsule (1/4 in. diameter) under a pressure of 400 MPa for 30 s. The resistivity of

the resulting capsule was measured by a four-probe technique using the Van der Pauw method.³² The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit. The measuring current was set to 10 mA. The FT-IR measurement was performed on Bruker IFS 66v spectrometer equipped with IR microscope Hyperion. Germanium ATR crystal and liquid nitrogen cooled MCT detector were used for the measurements. Electrochemical measurements were carried out at Autolab 302 (EcoChemie), using a three-electrode setup. Glassy carbon working electrode (GC), platinum auxiliary electrode (Pt) with a diameter of 3 mm, and Ag/AgCl reference electrode were obtained from Autolab, The Netherlands.

Synthesis Procedure of Staudenmaier Graphite Oxide²⁵. The synthesis of ST-GO was performed according to the procedure reported previously. First, 87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (98%) were first cooled to 0 °C before 5 g of graphite was added to the mixture. The reaction mixture was then intensively stirred while 55 g of potassium chlorate were added over a period of 30 min. The reaction flask was then loosely capped to allow the escape of chlorine dioxide gas. The mixture was continuously stirred for 96 h at room temperature and then poured into 3 L of deionized water. After decantation, the graphite oxide was redispersed in 5% hydrochloric acid. The graphite oxide was decanted from hydrochloric acid and repeatedly centrifuged and redispersed until a negative reaction for chloride and sulfate ions (with Ba(NO₃)₂ and AgNO₃) was observed. Graphite oxide slurry was finally dried in a vacuum oven at 60 °C for 48 h before further use.

Synthesis Procedure of Hofmann Graphite Oxide²⁶. The synthesis of HO-GO was performed according to the standard method reported in literature. First, 87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (68%) were first cooled to 0 °C before 5 g of graphite was dispersed into the reaction mixture by vigorous stirring. Keeping the reaction mixture vigorously stirred at 0 °C, KClO₃ (55 g) was then added over a period of 30 min. The reaction mixture was loosely capped to allow the escape of gaseous reaction products (ClO₂) and stirred at room temperature for 96 h. Upon completion of reaction, the mixture was poured into 3 L of deionized water and decanted. The reaction product was then redispersed in 2 L of 5% HCl and decanted. Graphite oxide was then repeatedly centrifuged and redispersed in deionized water until a negative reaction on sulfate and chloride ions (with Ba(NO₃)₂ and AgNO₃, respectively) was achieved. Graphite oxide slurry was finally dried in a vacuum oven at 60 °C for 48 h before further use.

Synthesis Procedure of Hummers Graphite Oxide²⁷. The synthesis of HU-GO was performed according to the method reported previously. First, 115 mL of sulfuric acid (98%) was cooled to 0 °C and then 5 g of graphite and 2.5 g of NaNO₃ were added to the mixture. While vigorously stirred, 15 g of KMnO₄ was added over a period of 2 h. The reaction mixture was then removed from the cooling bath and stirred at room temperature for 4 h. The reaction mixture was then heated to 35 °C for 30 min, poured into 250 mL of deionized water, and heated to 70 °C. After 15 min, the mixture was poured into 1 L of deionized water. Unreacted KMnO₄ was decomposed with 10% hydrogen peroxide. The reaction mixture was then decanted and repeatedly centrifuged and redispersed until a negative reaction for sulfate ions (with Ba(NO₃)₂) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 h before further use.

Synthesis Procedure of Sulfur-Doped Staudenmaier, Hummers, and Hofmann Graphite Oxide. All of the sulfur-doped graphene oxides were exfoliated in the same reactor as the thermally reduced graphene oxides. For every reaction, 100 mg of the graphite oxide starting material was inserted into a quartz glass capsule covered by sintered quartz glass filter facing the direction of the gas flow. The capsule was then attached to a magnetic manipulator and placed into a quartz horizontal reactor in the furnace. Before the placement of the sample into the hot zone of the reactor, the whole system was repeatedly evacuated and filled up with nitrogen. A mixture of nitrogen and sulfur precursor was used for the sulfonation process. First, the nitrogen flow (1 L/min) and the sulfur precursor (i.e., SO₂ and H₂S) flow

(1 L/min) were stabilized for 5 min. Then the capsule with the sample was inserted into the furnace for 12 min and pulled out again at the end of the reaction. In the case of samples treated in SO₂ at 1000 °C, the exposition time was reduced to 2 min in order to avoid oxidation and decomposition of graphene. The 12 min exposure of graphene at these conditions led to a complete oxidation. The reaction with CS₂ was carried out using a bubbler filled with liquid CS₂ at a temperature of 17 °C and pressure of 1000 mbar. Nitrogen (100 mL/min) was used as a carrier gas and was diluted with 1 L/min of nitrogen before entering into the reactor. All exfoliation steps were performed under atmospheric pressure.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Additional figures and table as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Sulphur Doped Graphene *via* Thermal Exfoliation of Graphite Oxide in H₂S, SO₂ or CS₂ gas

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Figure S1. To confirm the presence of sulphonic group, FT-IR spectra of sulphonated graphenes were recorded using ATR attachment. Spectrum of HO TRGO reduced in CS₂ was selected as an example. The vibration bands 1311 cm⁻¹ and 1373 cm⁻¹ (O=S=O in SO₃H stretching) determine the SO₃H groups on the graphene sheets.¹

Table S1. Combustible elemental analysis of the samples

Sample	Wt.% N	Wt.% C	Wt.% S	Wt.% H	Wt.% O
ST-S: [H ₂ S/600°C]	< 0.1	86.27	< 0.1	1.10	12.63
ST-S: [SO ₂ /600°C]	< 0.1	86.33	< 0.1	0.84	12.83
ST [N ₂ /1000°C]	< 0.1	93.82	< 0.1	< 0.05	6.18
HO-S: [H ₂ S/600°C]	< 0.1	78.30	8.37	1.06	12.27
HO-S: [SO ₂ /600°C]	< 0.1	76.54	3.69	0.90	18.87
HO-S: [CS ₂ /1000°C]	< 0.1	80.33	7.34	1.35	10.98
HO-S: [SO ₂ /1000°C]	< 0.1	77.01	4.12	0.95	17.92
HO [N ₂ /1000°C]	0.42	91.58	< 0.1	< 0.05	7.52
HU-S: [H ₂ S/600°C]	0.87	72.28	11.99	1.50	13.36
HU-S: [SO ₂ /600°C]	1.52	69.73	10.42	0.86	17.47
HU [N ₂ /1000°C]	2.11	88.57	0.97	< 0.05	8.35

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Halogenation of Graphene with Chlorine, Bromine, or Iodine by Exfoliation in a Halogen Atmosphere

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Dedicated to Professor Joseph Wang on the occasion of his 65th birthday

Abstract: Nanoarchitectonics on graphene implicates a specific and exact anchoring of molecules or nanoparticles onto the surface of graphene. One such example of an effective anchoring group that is highly reactive is the halogen moiety. Herein we describe a simple and scalable method for the introduction of halogen (chlorine, bromine, and iodine) moieties onto the

surface of graphene by thermal exfoliation/reduction of graphite oxide in the corresponding gaseous halogen atmosphere. We characterized the halogenated graphene by using various tech-

Keywords: electrochemistry • graphene • halogenation • reduction

niques, including scanning and transmission electron microscopy, Raman spectroscopy, high-resolution X-ray photoelectron spectroscopy, and electrochemistry. The halogen atoms that have successfully been attached to the graphene surfaces will serve as basic building blocks for further graphene nanoarchitectonics.

Introduction

Graphene has recently attracted considerable attention due to its interesting chemical, physical, and materials properties.^[1] The chemical modification of graphene is an important method for modifying its properties and can significantly influence their eventual electrical,^[2] electrochemical,^[3] and chemical^[4] behavior. Such modifications can serve two purposes: 1) to fabricate graphenes with enhanced properties for future applications, which often include electrochemical sensing^[5] and energy storage^[6] systems and 2) to perform further modification procedures on the attached groups—nanoarchitectonics.^[7] Graphene has been recognized as an attractive material in nanoarchitectonics devices, which operate according to the functionalities attached to the graphene backbone, such as biomolecules, nanoparticles, or other carbon nanostructures. There are several potential groups for the functionalization of graphene, including halogens, which can be readily incorporated onto the graphene structure. There are several ways to incorporate such groups

onto the surface of graphene, such as thermal annealing of graphene oxide in the presence of iodine dopant,^[8] UV irradiation of few-layer graphene in liquid chlorine/bromine,^[9] and chlorine plasma treatment of graphene.^[10] Methods based on UV irradiation are especially noteworthy as they allow the reversible storage of chlorine or bromine in graphene materials; the halogen is freed from the material upon laser irradiation or thermal treatment.^[9] This phenomenon was confirmed by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy, which are ideal characterization tools for investigating the extent of halogenation of graphenes.^[9]

Herein, we describe a universal, simple, and scalable method for the halogenation of graphene with chlorine, bromine, or iodine by thermal exfoliation/reduction of graphite oxide in a halogen gas atmosphere. This method is based on the bulk preparation of graphite oxide from graphite by oxidation in the presence of nitric acid and a strong oxidizing agent followed by exfoliation of the graphite oxide to thermally reduced graphene oxide (TRGO) under temperature shock at 1000 °C in a gaseous halogen atmosphere (Scheme 1).

Results and Discussion

Halogenated graphenes were prepared by thermal exfoliation of graphite oxide in different gaseous halogen atmospheres (chlorine, bromine, or iodine) in an attempt to incorporate halogen atoms onto the materials. A full-scale characterization of these materials was performed by using an array of different techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM),

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Scheme 1. Synthesis of halogenated graphene by thermal exfoliation of graphite oxide in a halogen atmosphere.

X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). These methods have provided information on the properties of the halogenated graphenes, such as their physical characteristics (morphology and density of defects) and their electrochemical behavior, for example, the influence of halogenation on the heterogeneous electron transfer (HET) rate of the halogenated graphene. The incorporation of different halogen atoms onto the graphene backbone during exfoliation may lead to important and interesting differences in the materials and electrochemical characteristics; these will be elaborated in detail in the following sections.

Electron microscopy: The morphologies of the materials were studied by SEM and TEM. The SEM images shown in Figure 1 depict the halogenated graphenes prepared by exfoliation in various gases (labeled accordingly as TRGO-X; TRGO=thermally reduced graphene oxide and X=Cl, Br, or I). TRGO-Cl, TRGO-Br, and TRGO-I were imaged at various magnifications ranging from $370\times$ to $50000\times$. It can be seen in Figure 1 that there are no significant differences between the three materials.

All three materials resemble small-sized particles at a low magnification of $370\times$ that are made up of well-separated sheets of TRGO, as observed at a magnification of $10000\times$ or higher. Their appearance is similar to that of a typical graphene thermally exfoliated in an inert gas atmosphere

Figure 1. SEM images of A) TRGO-Cl, B) TRGO-Br, C) TRGO-I, and D) TRGO-N. The scale bars for the micrographs are: a) 10, b) 1, c) 1, and d) $100\mu\text{m}$.

(N₂, Ar)^[11,12] and therefore the SEM images confirm the successful exfoliation of graphite oxide in a gaseous halogen atmosphere. We have also performed an exfoliation of graphite oxide in an inert nitrogen gas atmosphere (labeled as TRGO-N) to be used as a control for comparison purposes. The structures observed in Figure 1 are similar to those of well-exfoliated TRGOs reported previously. This shows that the four TRGOs have undergone complete exfoliation during the preparation process. Higher-resolution images of the materials were collected by TEM to observe the topographical details of a single to a few layers of exfoliated TRGO under a high voltage. As shown in Figure 2, the morphologies of the four TRGOs (Cl, Br, I, and N) appear to be similar under the same magnifications, the sheets of TRGOs exhibiting a wrinkled texture throughout the entire layer. The structures of the four materials appear to be very similar to typical single-to-few-layer graphene sheets reported earlier,^[3] indicating successful exfoliation of the graphite oxide to yield halogenated graphenes.

Raman spectroscopy: Important structural information of halogenated graphenes, such as the density of defects, can be determined by Raman spectroscopic measurements. The presence of defects is indicated by the appearance of a D band at approximately 1350 cm⁻¹, which is attributed to the sp³-hybridized carbon atoms in the network, whereas pristine sp² lattice carbon atoms in the network appear as a G band at approximately 1560 cm⁻¹ (see Figure 3). The intensity of the D band gives (with intensities normalized to the G band) an indication of the degree of functionalization of the material.^[13] The intensities of these bands can be represented as I_D/I_G ratios, which can be used to determine the density of the defects present in the materials. The calculated ratios were found to decrease with increasing atomic number of the halogen such that TRGO-Cl has a ratio of 1.16, TRGO-Br a ratio of 1.09, TRGO-I a ratio of 0.750, and the control material, TRGO-N, a ratio of 1.07. The intensities of the bands are also useful for calculating the average crystalline size (L_a) of the sp² lattice^[14] by using Equation (1) in which I_G and I_D are the intensities of the Raman D and G bands and λ_{laser} is the wavelength of the laser in nm.

$$L_a = 2.4 \times 10^{-10} \lambda_{\text{laser}}^4 (I_G/I_D) \quad (1)$$

The derived crystallite sizes are 14.4 nm for TRGO-Cl, 15.4 nm for TRGO-Br, 22.3 nm for TRGO-I, and 15.7 nm for TRGO-N. The higher I_D/I_G ratio of TRGO-Cl and TRGO-Br compared with TRGO-N can be used as an indirect proof of the successful functionalization of graphene with halogen atoms. However, it is also possible that the higher I_D/I_G ratio may simply be a result of the effect of different gas atmospheres used during exfoliation on the crea-

Figure 2. TEM images of A) TRGO-Cl, B) TRGO-Br, C) TRGO-I, and D) TRGO-N. The scale bars for the images are: a) 0.2 μm, b) 50 nm, and c) 0.5 μm.

Figure 3. Raman spectra of the halogenated and nonhalogenated graphenes. A) Raman spectra of TRGO-Cl, TRGO-Br, TRGO-I, and the control TRGO-N. B) Bar chart showing the I_D/I_G ratios of the halogenated graphenes. C) Raman spectrum of I₃⁻ and I₅⁻ of TRGO-I.

tion of defects in the graphene sheets. Therefore additional characterization was required and is described in the following sections. Furthermore, it is of great interest to note that TRGO-I was found to possess two additional peaks at approximately 90 and 167 cm⁻¹ that are absent in the Raman spectra of TRGO-Cl, TRGO-Br, and TRGO-N. The presence of I₃⁻ in the material leads to the appearance of the peak at 90 cm⁻¹ and the presence of I₅⁻ gives rise to the peak at 167 cm⁻¹.^[8,15,16] The emergence of these peaks indicates the successful incorporation of iodine atoms into the TRGO during the exfoliation procedure.

X-ray photoelectron spectroscopy: The incorporation of halogen atoms onto the graphene backbone can be determined through the use of X-ray photoelectron spectroscopy. The wide-scan XPS spectra (Figure 4) show carbon and oxygen as the main elements in the four TRGOs along with the respective halogens in the corresponding halogenated TRGOs. The XPS spectrum for TRGO-N shows only the C1s peak at 284.5 eV and the O1s peak at 531.4 eV. TRGO-Cl exhibits the C1s peak at 284.5 eV, the O1s peak at 532.5 eV, and the Cl2p peak at 200.5 eV. TRGO-Br shows the C1s peak at 284.5 eV, the O1s peak at 532.5 eV, as well as the Br3p peak at 184.1 eV and the Br3d peak at 71.5 eV. TRGO-I shows the I3d peak at 618.5 eV in addition to the standard C1s and O1s peaks observed at 284.5 and 532.5 eV, respectively. The presence of these halogen peaks indicates the successful halogenation of the TRGOs during the exfoliation of the materials.

High-resolution XPS measurements were also carried out on the halogen TRGOs, as shown in Figure 5. The Cl2p, Br3p, and I3d peaks in fact consist of two peaks, which are clearly visible in the high-resolution XPS spectra. The percentage contents of the major elements, C1s and O1s, were calculated and are presented as C/O ratios, which indicate the extent of deoxygenation of the graphite oxide during the thermal exfoliation. The C/O ratios are 16.77 for TRGO-Cl,

Figure 4. A) Wide-scan XPS spectra of halogenated and nonhalogenated graphenes. B) Bar chart showing the C/O ratios in the three halogenated graphenes.

Figure 5. High-resolution XPS spectra of the respective electronic states of the halogen atoms. A) Br3p of TRGO-Br, B) Br3d of TRGO-Br, C) Cl2p of TRGO-Cl, and D) I3d of TRGO-I.

20.37 for TRGO-Br, 11.75 for TRGO-I, and 18.23 for TRGO-N. Thus, the amount of oxygen in the halogenated TRGOs is less than that in the nonhalogenated TRGO, except in the case of TRGO-Br.

High-resolution XPS was also carried out on the main element C1s peak to observe the fine detail in the C1s spectra. More detailed analysis of the C1s peak was performed by

careful fitting of the spectra by using relative sensitivity factors to investigate the possible presence of different carbon bonds contributing to the C1s peak and their relative amounts. The C1s spectra show an asymmetrical peak with a shoulder at higher-binding energies, which suggests the existence of other carbon bonds besides the C=C bond. Fitting of the HR-XPS spectrum for TRGO-Cl was performed at 284.5 eV for C=C, 285.3 eV for C-C, 286.2 eV for C-Cl, 287.2 eV for C-O, 288.5 eV for C=O, and 290.4 eV for π - π^* (as shown in Figure 6A). The TRGO-Br C 1s spectrum was

other carbon atoms and thus less of them are bonded to non-carbon atoms such as halogens and oxygen.

Infrared spectroscopy: In addition to XPS, the FTIR spectra of TRGO-Cl and TRGO-Br were recorded (see Figure S1 in the Supporting Information). The spectrum of the former exhibits a vibration at 930 cm^{-1} , which indicates the presence of a C-Cl bond in TRGO-Cl, and the spectrum of the latter shows a vibration at 600 cm^{-1} , which is indicative of a C-Br bond in TRGO-Br. Note that our results are in agreement with the findings of Rao and co-workers.^[9]

Elemental analysis: The “classical” elemental analysis is an appropriate tool for assessing the amount of halogen in halogenated graphenes. We performed classical titrimetric analysis of halogens (samples were first combusted according to the Schöniger method and then subjected to titrimetric analysis as described in the Experimental Section). The CHNS/O content was determined by elemental combustible analysis. The TRGO-Cl contains 93.84% (wt) of C, 5.9% of Cl, 0.16% of H, 0.1% of O, 0% of S, and 0% of N, the TRGO-Br contains 83.19% (wt) of C, 9.93% of Br, 8.13% of O, 0.53% of H, 0% of S, and 0.22% of N, and the TRGO-I contains 88.00% (wt) of C, 2.31% of I, 9.37% of O, 2.19% of H, 0% of S, and 0.14% of N. This demonstrates that during the thermal exfoliation process in a gaseous halogen atmosphere, the halogen is indeed introduced into the graphene lattice.

Conductivity measurements: Conductivity experiments were performed on both the starting materials and the halogenated samples by using a four-probe method. It was found that the specific resistivities of TRGO-Cl, TRGO-Br, TRGO-I, TRGO-N, and graphite oxide are 5.5×10^{-3} , 1.8×10^{-4} , 8.1×10^{-5} , 3.9×10^{-4} , and $3.67 \times 10^2\ \Omega\text{ cm}$. The reason for the differences in conductivity could be due to the differences in the electronegativity of the halogens and their chemical states. The high electronegativity of chlorine leads to a decrease in the concentration of free electrons and in their trapping. This effect is much less profound in the case of bromine due to its lower electronegativity. The iodine-doped graphene exhibits very low resistivity. This effect can be related to the presence of tri- and penta-iodide bonded to the graphene sheets. The lower electronegativity and high electron concentration in polyiodide leads to an injection of additional electrons into the graphene sheet accompanied by a decrease in the resistivity.

Thermal stability: The thermal stabilities of the halogenated graphenes in pure oxygen and pure argon (inert atmosphere) were investigated, in a similar manner to Rao and co-workers.^[9] The halogenated graphenes exhibit different stability towards oxidation. In oxygen, the oxidation of TRGO-I and TRGO-Br starts at around 430 and 450°C, respectively (for the corresponding thermogravimetric analyses (DSC and TGA), see Figure S2 in the Supporting Information). TRGO-Cl exhibits significantly greater stability in

Figure 6. High-resolution XPS spectra of the C1s peak in A) TRGO-Cl, B) TRGO-Br, C) TRGO-I, and D) TRGO-N. Fittings of the individual C1s spectra show the possible carbon bonds present in the graphene. Inset in (B) shows the bar chart of the total percentage of fitted C=C and C-C bonds for each graphene.

also fitted to reveal the following carbon interactions: C=C at 284.5 eV, C-C at 285.7 eV, C-Br at 286.9 eV, and π - π^* at 289.4 eV. On the other hand, the C 1s spectrum of TRGO-I was found to comprise C=C at 284.5 eV, C-C at 285.4 eV, C-O at 286.2 eV, C=O at 287.2 eV, C-I^[17] at 288.8 eV, and π - π^* at 290.8 eV. The nonhalogenated control, TRGO-N, was also fitted to reveal C=C at 284.48 eV, C-C at 285.66 eV, C-O at 286.69 eV, C=O at 287.76 eV, O-C=O at 288.90 eV, and π - π^* at 290.34 eV (Figure 6D). The high-resolution XPS spectra of the C1s peak for all three halogenated materials confirm the successful incorporation of halogen onto the graphene backbone and the creation of the C-X bond. It is of interest to calculate the combined percentages of the intensities of the carbon-carbon bonds (the sp^2 -hybridized C=C and sp^3 -hybridized C-C bonds) and to compare them with that of the total intensities for all carbon bonds. It was observed that the total percentage of these two bonds increases with increasing atomic number of the halogen from 73.1% for TRGO-Cl to 79.1% for TRGO-Br and to 80.0% for TRGO-I (Figure 6B, inset). This indicates that following exfoliation with higher atomic number halogen gases, more carbon atoms in the TRGO are bonded to

oxygen, its oxidation starting at around 530°C. The stabilities of the halogenated graphenes in argon were measured by X-ray fluorescence; the samples were heated in argon at 1200°C and the halogen concentrations were measured before and after the heating procedure (see Figure S3). Following the heat treatment, the concentration of iodine decreased by only about 20%, the concentration of chlorine decreased by about 90%, and bromine was completely eliminated.

Electrochemistry: One of the main applications of graphenes is for electrochemical sensing and energy storage purposes. For such applications, it is of considerable interest to be able to establish the rate of heterogeneous electron transfer (HET) in the materials to determine the effective and usefulness of these materials in devices. Cyclic voltammetric (CV) experiments were performed on TRGO-modified glassy carbon (GC) electrodes in ferrocyanide in an attempt to study the HET rates at the surfaces of the materials. For such purposes, the potential difference between the oxidation and reduction waves, ΔE_{p-p} (peak-to-peak separation), of the molecular probes is typically used for comparison. As shown in Figure 7A, the peak-to-peak separations are 143 mV for TRGO-Cl, 190 mV for TRGO-Br, 202 mV for TRGO-I, 257 mV for TRGO-N, and 424 mV for unmodified bare GC. Thus, the value of ΔE_{p-p} increases with increasing atomic number of the halogen, as depicted in Figure 7B. The HET rate constants of the various halogenated graphenes were calculated from ΔE_{p-p} by the Nicholson method.^[18] The HET values (k_{obs}^0) are 2.525×10^{-3} , 1.475×10^{-3} , 6.850×10^{-4} , 5.063×10^{-4} , and $5.662 \times 10^{-5} \text{ cm s}^{-1}$ for TRGO-Cl, TRGO-Br, TRGO-I, TRGO-N, and bare GC, respectively (see Figure 7C). These results indicate that the HET rates at the surfaces of the materials decrease with increasing atomic number of the halogen in the halogenated TRGOs.

The heterogeneous electron transfer resistance of the halogenated graphenes can also be investigated by electrochemical impedance spectroscopy (EIS), which measures the interfacial impedance towards charge transfer between the electrolyte solution and the electrode surface. The results are presented as a Nyquist plot in which the diameter of the semicircular plot gives the electrical impedance, known as the charge-transfer resistance (R_{ct}). The Nyquist plots for the halogenated graphenes, TRGO-N, and bare GC electrodes are shown in Figure 8A; the unmodified glassy carbon electrode was found to have the largest electrochemical impedance, as demonstrated by the largest semicircular diameter. The four TRGOs were found to have a much smaller electrical resistance (the diameters of the Nyquist plots of the individual TRGOs are shown in detail in Figure 8B). Further analysis of the impedance data was carried out by performing a fitting against the Randles circuit to obtain the charge-transfer resistance values. The R_{ct} values are 46 Ω for TRGO-Cl, 408 Ω for TRGO-Br, 808 Ω for TRGO-I, 896 Ω for TRGO-N, and 5803 Ω for the unmodified glassy carbon electrode. This indicates that the

Figure 7. Cyclic voltammograms of halogenated and nonhalogenated graphenes. A) Cyclic voltammograms recorded in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. B) Bar chart showing the peak-to-peak values for the halogenated graphenes. C) Bar chart showing the HET rates of the halogenated graphenes. Conditions: scan rate 100 mV s^{-1} , background electrolyte 50 mM PBS, pH 7.2.

charge-transfer resistance increases with increasing atomic number of the halogen, which is in agreement with the CV results reported above.

Conclusion

We have developed the first scalable and simple bulk method for the preparation of halogenated (chlorine, bromine, and iodine) graphenes by thermal exfoliation in gaseous halogen atmospheres. Detailed examinations of the materials, starting from their physical properties (such as morphology and density of defects) to their elemental composition, and finally to the electrochemical reactivity (HET rates and charge-transfer resistance), were executed. From some of the results obtained, it can be seen that a direct relationship exists between the halogen atomic number and the properties of the halogenated graphenes. In the Raman

Figure 8. Electrochemical impedance spectroscopic analysis of halogenated and nonhalogenated graphenes. A) Nyquist plots of the graphenes in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$: ■ TRGO-Br, ● TRGO-Cl, ▲ TRGO-N, ▼ TRGO-I, and ◆ bare GC. B) Magnified view of the Nyquist plots of the halogenated graphenes: ■ TRGO-Br, ● TRGO-Cl, and ▲ TRGO-I. C) Bar chart showing the charge-transfer resistance of the halogenated graphenes. Conditions: background electrolyte 50 mM PBS, pH 7.2.

spectroscopic analysis, the I_D/I_G ratio increases with increasing atomic number of the halogen. Interestingly, clear trends linked to the atomic number of the halogen in the TRGOs were also observed for the electrochemical properties, such as the CV peak-to-peak separation, HET rates, and charge-transfer resistance. This method of incorporation of various halogens into the graphene backbone will find application in graphene nanoarchitectonics for various purposes, including electronic and electrochemical devices.

Experimental Section

Materials: Potassium ferrocyanide, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, and potassium chloride were purchased from Sigma-Aldrich. Nitric acid, sulfuric acid, hydrochloric acid, and potassium chlorate were obtained from PENTA, bromine (99.5%) and iodine (99.8%) were obtained from Sigma-Aldrich, nitrogen gas (99.9999%) was obtained from

SIAD, and chlorine (99.8%) from Linde. Graphite was obtained from KOH-I-NOOR GRAFIT. Deionized water with a conductivity of 18.2 MΩ cm was used in the preparation of the solutions. Glassy carbon (GC), Ag/AgCl, and platinum (Pt) electrodes were obtained from Autolab. TEM imaging was performed by using carbon-coated 200 mesh Lacey Formvar supporting film copper grids, which were purchased from Ted Pella.

Apparatus: SEM imaging was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan). TEM was performed with a JEM 1400 field-emission transmission electron microscope at 100 kV under different magnifications. A Phoibos 100 spectrometer operating with a monochromatic magnesium X-ray source was used to acquire wide-scan and high-resolution X-ray photoelectron spectra. Raman spectroscopy was performed with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific) with a backscattering geometry and a CCD detector. The scans were performed under a 514.5 nm argon laser source and with an X 100 objective lens mounted on an Olympus optical microscope. Cyclic voltammetric and electrochemical impedance spectroscopy were performed with a μAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) controlled by the NOVA 1.7 software (Eco Chemie). Nova 1.7 software is published and designed by Metrohm Autolab B.V. to be compatible in support of Metrohm Autolab's potentiostat/galvanostat.

Synthesis of graphenes: The halogenated graphenes were synthesized by the oxidation of graphite to graphite oxide and consequent exfoliation in halogen or nitrogen atmospheres. The procedures are described in detail in the following paragraphs.

Synthesis of graphite oxide: Graphite oxide was prepared following the method described by Hofmann.^[20] Graphite (5 g) was added to a mixture of sulfuric acid (98%, 87.5 mL) and nitric acid (68%, 27 mL). Potassium chlorate (55 g) was slowly added while cooling the resultant mixture in an ice bath. The reaction mixture was then stirred for 96 h at room temperature. After completion of the reaction, the mixture was poured into deionized water (3 L) and decanted. The resulting graphite oxide was then redispersed in 5% hydrochloric acid solution and repeatedly centrifuged to remove chloride and sulfate ions. The graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 h before use.

Synthesis of thermally reduced halogenated graphene oxides: The halogenated graphenes were synthesized in a vacuum-tight quartz glass reactor in a controlled atmosphere. The reactor was equipped with a porous quartz glass capsule connected to a magnetic manipulator. This configuration is capable of producing a temperature gradient of over 1000 °C min⁻¹. All syntheses were performed at 1000 °C for 12 min under a pressure of 100 kPa. Graphite oxide (100 mg) was placed in a porous quartz glass capsule and the reactor was flushed several times with high purity nitrogen. Subsequently, the sample was inserted into the preheated furnace under the selected atmosphere. For the chlorine-doped graphene, a flow of 1000 mL min⁻¹ chlorine and 1000 mL min⁻¹ nitrogen was used. For the synthesis of the bromine-doped graphene, a flow of 1000 mL min⁻¹ of high purity nitrogen saturated with bromine vapor was used. The bubbler filled with bromine was kept at 10 °C to avoid condensation of bromine vapor in the gas line. The nitrogen flow through the bubbler was 100 mL min⁻¹ at 100 kPa. This configuration allowed us to transport 0.6×10^{-3} mol min⁻¹ of bromine vapor. In the case of iodine, the use of a bubbler filled with iodine did not give satisfactory results due to the low vapor pressure of iodine; a flow of 1000 mL min⁻¹ of nitrogen through a bubbler with iodine maintained at 15 °C and 100 kPa was able to transport only 4.2×10^{-6} mol min⁻¹. To obtain a higher iodine concentration, the graphite oxide was mixed with iodine in a 1:1 mass ratio, dispersed in acetone, and evaporated to dryness at room temperature. The iodine/graphite oxide mixture (100 mg) was placed in a quartz glass porous capsule and the reactor was flushed several times with high purity nitrogen. The exfoliation was performed with a 1000 mL min⁻¹ flow of high purity nitrogen to remove reaction byproducts.

Exfoliation of thermally reduced graphene oxides in nitrogen: The thermal exfoliation of the dry precursor was carried out at 1000 °C for 12 min by placing the graphite oxide inside a porous quartz glass capsule connected to a magnetic manipulator in a vacuum-tight quartz reactor under

a controlled atmosphere. This system provided a temperature gradient of over $1000^{\circ}\text{C}\cdot\text{min}^{-1}$. The sample was then flushed repeatedly with pure nitrogen and subsequently inserted in a preheated reactor under an atmosphere of nitrogen (99.9999% purity, pressure, 100 kPa). The flow of nitrogen was $1000\text{ mL}\cdot\text{min}^{-1}$, which resulted in the removal of byproducts from the reactions.

Preparation of samples for scanning electron microscopic measurements:

The samples were prepared by randomly attaching a layer of the material onto a carbon conductive tape, which was adhered to an aluminium sample holder. The images were then obtained by using the gentle-beam mode at 2 kV for various magnifications.

Preparation of samples for transmission electron microscopic measurements:

The synthesized TRGOs were used directly in the preparations as suspensions with concentrations of $0.5\text{ mg}\cdot\text{mL}^{-1}$. The suspensions were then sonicated for 5 min to obtain a homogeneous suspension before each use. An aliquot of $3\text{ }\mu\text{L}$ of the suspension was then dropped onto a copper TEM grid laid on top of filter paper and left to dry in a fume hood before use. Imaging was then performed at 100 kV at various magnifications.

Preparation of samples for X-ray photoelectron spectroscopy: The materials were prepared by coating a uniform layer of the TRGOs on a sticky conductive carbon tape, which was attached to an aluminum sample holder. The measurements were then performed at 12.5 kV with a magnesium X-ray source.

Preparation of samples for Raman spectroscopy: Calibration of the spectrometer was achieved by using a silicon reference at 520 cm^{-1} before any measurements were performed. The materials were prepared by compressing them well between two glass slips to ensure that they were compacted before placing them on top of a glass slip, which was later placed on a glass slide.

Infrared spectroscopy: FTIR spectra were recorded with a Bruker IFS 66v spectrometer equipped with an IR microscope Hyperion. A germanium ATR crystal and liquid-nitrogen-cooled MCT detector were used for the measurements.

Elemental analysis: For the analysis of the chlorine and bromine samples, the samples were combusted by using the Schöniger method. The Cl^{-} or Br^{-} ions formed were titrated against a solution of $\text{Hg}(\text{NO}_3)_2$ using sodium nitroprusside as indicator. For the analysis of iodine samples, the sample was first combusted by using the Schöniger method. The amount of iodine was determined by the Leipter method according to the following steps: 1) Iodine formed by sample combustion was dissolved in NaOH solution, 2) the various forms of iodine were oxidized to iodate by bromine, 3) excess bromine was reduced by formic acid, 4) iodate was reduced by iodine to form elemental iodine, and 5) titration of iodine by a standard solution of thiosulfate. For the CHNS/O elemental analysis, a Perkin–Elmer PE 2400 Series II CHNS/O instrument was used.

Conductivity measurements: For conductivity measurements of the graphene materials, the material (40 mg) was first compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured by the four-probe technique using the Van der Pauw method.^[19] The resistivity measurements were then performed by using a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit.

Thermogravimetry: The simultaneous thermal analysis was performed by using a PT 1600 instrument from Linseis. The measurements were performed under an atmosphere of oxygen ($50\text{ mL}\cdot\text{min}^{-1}$; oxygen of 99.999% purity) or argon ($50\text{ mL}\cdot\text{min}^{-1}$; argon of 99.999% purity). Argon ($50\text{ mL}\cdot\text{min}^{-1}$) was used to purge the balance system in all experiments. The heating rate was $10\text{ K}\cdot\text{min}^{-1}$.

Preparation of samples for the electrochemical measurements: The glassy carbon electrodes were cleaned by polishing with an alumina suspension and then washed with deionized water and wiped dry before use. The synthesized TRGOs were dispersed in DMF solvent to create a suspension with a concentration of $0.5\text{ mg}\cdot\text{mL}^{-1}$. The suspension was then sonicated at room temperatures for 5 min before each use. The electrodes were modified by coating the cleaned surface of a GC electrode with a $1\text{ }\mu\text{L}$ aliquot of the TRGO suspension, which was then left under a lamp

to dry to give a layer of randomly dispersed TRGO on the GC surface. This step was repeated until the GC surface had received three layers of coatings. The modified GC electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then dipped into an electrochemical cell containing the electrolyte solution (10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ dissolved in 50 mM pH 7.2 phosphate buffer solution) and the measurements were started. CV measurements were taken before the start of every EIS measurement at room temperature. CV was performed in the range $+1.15$ to -0.8 V at a scan rate of $100\text{ mV}\cdot\text{s}^{-1}$ for two consecutive scans. This was immediately followed by an EIS measurement carried out in the frequency range of 10000 to 0.01 Hz. Three measurements were carried out for each TRGO.

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Supporting Information

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Halogenation of Graphene with Chlorine, Bromine, or Iodine by Exfoliation in a Halogen Atmosphere

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Figure S1. FTIR spectra of (A) TRGO-Cl and (B) TRGO-Br with characteristic C-Cl vibration at 930 cm⁻¹ and C-Br vibration at 600 cm⁻¹.

Figure S2. Thermal analysis of halogenated graphenes using STA in an oxygen atmosphere.

Figure S3. Investigation of thermal stability of halogenated graphenes in Ar atmosphere. X-ray fluorescence spectra of as prepared (red line) and thermally treated (to 1200 °C, no dwell, 10 °C.min⁻¹ heating rate, 20 °C.min⁻¹ cooling rate; black line) halogenated graphenes.

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PAPER

High-pressure hydrogenation of graphene: towards graphane†

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The conversion of graphene to graphane is of high importance from a technological and scientific point of view. We present here a scalable method for the hydrogenation of graphene based on thermal exfoliation of graphite oxide in a hydrogen atmosphere under high pressure (60–150 bar) and temperature (200–500 °C). This method does not require a plasma source and is able to produce gram quantities of the material. The properties of the resultant hydrogenated graphene were studied by scanning and transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and combustible elemental analysis techniques. Sheet and specific resistance of the graphene and hydrogenated graphene were measured. This scalable synthesis method has great potential to serve as a pathway towards the mass production of graphane.

Introduction

Graphene is currently one of the highly researched materials. The idea of incorporating a single-atom thick¹ conductive sheet with excellent thermal conductivity, fast heterogeneous electron transfer, and a huge surface area into functional devices has quickly found its way to physicists, chemists and materials scientists.^{2–5} Graphane is a hydrogenated analogue of graphene consisting of sheets of sp³ bonded carbon atoms which could be an interesting alternative material to graphene. The theoretical explanation for the existence of graphane has surfaced several years ago⁶ and experimental attempts for preparation of the material have begun in 2009.⁷ It is expected that graphane will behave similar to an electrical insulator that possesses a huge surface area and high C : H ratio with potential use for hydrogen storage.⁸ Partial hydrogenation of graphene is anticipated to result in the opening of the graphene bandgap which allows the material to have huge implications towards the fabrication of atomically thin transistors⁹ or electrochemical devices.¹⁰ In addition, graphane can be used as an anticorrosion protective layer for metallic structures.

Currently, few publications reporting on the preparation of graphanes and their resulting properties are available. One of the earliest reports showed that such graphanes were achieved through the hydrogenation of CVD graphene in low-pressure (0.1 mbar) hydrogen–argon mixture with DC-plasma.⁷ Plasma hydrogenation at pressures of ~2 mbar to produce graphanes was also carried out on CVD graphene with a reported

hydrogenation efficiency of <10%.¹¹ Similar results were obtained with multilayer graphene prepared from mechanically cleaved highly oriented pyrolytic graphite using radio frequency plasma hydrogenation, which was executed to produce graphanes with a reported efficiency of ~17%.¹² It is of interest to mention that through the execution of theoretical calculations, it was discovered that single-sided hydrogenated graphene is thermodynamically stable to have a coverage of maximum of ~12%.¹³ The above-mentioned methods were carried out with minute amounts of graphene, prepared either by CVD growth or mechanical cleavage. Although these methods are certainly important towards the study on the fundamental chemistry of graphene/graphane, the need for scalable methods to produce bulk quantities of graphane is still greatly in demand. Herein we propose one such straightforward method where the use of high-pressure (up to 150 bar) and temperature (up to 500 °C) in the hydrogenation of graphite oxide is capable of yielding large quantities of partially hydrogenated graphane sheets.

Experimental section

SEM imaging was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) in gentle-beam mode at 2 kV. The samples were prepared by attaching the materials onto a sticky conductive carbon tape and mounting it on an aluminium sample stub. TEM images were acquired with a JEM 1400 field-emission transmission electron microscope (JEOL, Japan) operating at 100 kV. TEM samples were prepared using 1 µL of a 0.5 mg mL^{−1} suspension of the thermally reduced graphenes dripped onto a carbon coated copper grid which was then allowed to dry at room temperature. XPS was executed with a Phoibos 100 spectrometer using a monochromatic Mg X-ray radiation source (SPECS, Germany) for the measurement of wide-scan and high resolution C 1s spectra. The samples were attached onto a sticky conductive carbon tape that was attached

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to an aluminium XPS holder. Further processing of the data was performed by calculating the C/O ratios from the wide-scan XPS measurements with the use of relative sensitivity factors. The XPS samples were prepared by attaching a uniform layer of the materials onto a conductive carbon tape which was then affixed onto an aluminium XPS sample holder. A confocal micro-Raman LabRam HR instrument (Horiba Scientific) in back-scattering geometry with a CCD detector was used for acquiring Raman spectra. Measurements were performed using a 514.5 nm Ar laser and an Olympus optical microscope with a 100 $\times$ objective lens. Pre-measurement calibration was achieved with a silicon reference at 520 cm⁻¹ which gives a peak position resolution of less than 1 cm⁻¹. Actual measurements were performed using well-compressed and compacted samples that were placed on top of a glass slip which was positioned on a piece of glass slide. The Fourier transform infrared spectroscopic measurements were performed using an attenuated total reflectance method on a PerkinElmer Spectrum 100 system. Diamond/ZnSe was used as the ATR crystal in conjunction with a universal ATR accessory. For conductivity measurements of graphene related materials, 40 mg of the material were first compressed into a capsule (1/4" diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured with a 4-probe technique using the method of van der Pauw.¹⁴ The resistivity measurements were then performed with a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit.

The graphene oxide that was used for the synthesis of partially hydrogenated graphane was prepared according to the Hofmann method that had previously been reported.¹⁵ 87.5 mL of sulphuric acid (98%) and 27 mL of nitric acid (65%) were added to a reaction flask (Pyrex baker with thermometer) which contains a magnetic stir bar. The mixture was then cooled by immersing it into an ice bath for 30 min. 5 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and to obtain a homogeneous dispersion. While maintaining the reaction flask in the ice bath, 55 g of potassium chlorate was then slowly added to the mixture (over 30 min) in order to avoid a sudden increment in temperature and the formation of the explosive chlorine dioxide gas. Upon complete dissolution of potassium chlorate, the reaction flask was left loosely capped to allow the evolution of gas and 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%) solution to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative response towards chloride and sulphate ions (with AgNO₃ and Ba(NO₃)₂, respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

The high pressure synthesis of the materials was performed in a stainless steel autoclave placed in a resistive heating furnace. Approximately 0.3 g of graphite oxide was placed in a quartz glass liner inside the autoclave machine. Hydrogen gas of 99.9% purity and argon gas of 99.996% purity were used in the synthesis process. The autoclave was then repeatedly flushed with hydrogen or argon gas and subsequently filled with the respective gases of the desired pressure using a pressure control valve. The autoclave was heated at a rate of 5 °C min⁻¹ and the dwell time on the temperature of synthesis was 2 hours. The reaction vessel

was then left to cool freely inside the furnace under room temperature.

Results and discussion

The presented method uses a high pressure/high temperature exfoliation procedure on graphite oxide carried out in a hydrogen gas atmosphere, which results in the material being partially hydrogenated. We have also studied the influence of temperature and pressure on the properties of the resulting hydrogenated graphene sheets by systematically varying the exfoliation conditions of graphite oxides. Before further discussions on the characterization results are elaborated, one should ask himself the fundamental question: which method is the most appropriate in determining the hydrogenation efficiency of the materials? Previously, it was correctly stated that "it is quite difficult to measure the percentage of hydrogen content in graphene films by most surface analytical techniques".¹¹ Indeed, these methods can only provide indirect and/or approximate information on the hydrogen coverage of the materials. An example of such a method that provides indirect information is Raman spectroscopy or conductivity measurements. There is no accurate method including X-ray photoelectron spectroscopy (XPS) which is based on the analysis of the C 1s peak to provide some information on the presence of the C–H bond. However, the narrow difference between bond energies of C–H and C=C bonds (difference of only 0.6 eV) makes any accurate conclusion on hydrogen coverage impossible. In contrast, chemical analysis based on the rotation/vibration modes of the bonds (infrared spectroscopy) allows C–H and C=C bonds to be distinguished with greater certainty. To date, the most precise and accurate measurements on the hydrogenation efficiency can only be derived by the classical combustible elemental analysis technique. It is also of interest to note that none of the earlier reports have utilised infrared spectroscopy or combustible elemental analysis to analyse the extent of hydrogenation in the materials.^{7,11,12} This is likely due to the fact that the graphanes were synthesized from minute amounts of graphene grown by the CVD method and hence, the small amount of material available is unsuitable for the implementation of the mentioned techniques. The lack of evidence derived from the FT-IR spectroscopy and elemental analysis implies that any earlier claims on the hydrogenation of graphene are least reliable and ambiguous. Herein, all available materials and chemical analysis methods were employed to investigate the effect on hydrogenation efficiency under varied exfoliation conditions. These methods include scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and combustible elemental analysis (EA).

Two different sets of reaction conditions were employed to study the influence of hydrogen pressure and exfoliation temperature on the properties of the materials. In the first experiment, the temperature was held constant at approximately 220 °C while the hydrogen gas pressure was varied between 60 and 150 bar during the exfoliation process. In the second experiment, the hydrogen gas pressure was held constant at 100 bar while the exfoliation temperature was varied from 200 to 500 °C instead. For the control experiment, graphene exfoliated

in an inert gas (argon) atmosphere will be used for comparison with the hydrogenated graphenes. In this paper, the materials will be denoted by their exfoliation conditions in terms of temperature and gas pressure, *e.g.* graphene exfoliated under 100 bar hydrogen gas pressure at 500 °C will be labelled as G-H: [100 bar/500 °C].

As unexfoliated graphite oxide was used as the starting material in this project, we will first examine the exfoliated/hydrogenated graphenes (final product) with electron microscopy to confirm the successful exfoliation of the graphite oxides. Fig. S1 (see ESI†) shows the SEM images of the control sample and graphenes hydrogenated under different pressures and temperatures taken at different magnifications. It can be clearly observed from the SEM images that exfoliation of the graphite oxides has successfully taken place and that no observable differences between the various hydrogenated graphenes and the control sample can be noted. TEM imaging of the hydrogenated graphene sheets (as well as control graphene exfoliated in Ar) was also performed as shown in Fig. S2 (see ESI†) to observe single to few layer sheets of graphene/graphane. It was observed that graphenes exfoliated under high temperatures of 350 °C and 500 °C (at 100 bar pressure) exhibit a wrinkled appearance when compared to other graphenes which showed a much smoother texture and a straight or flat appearance. Wrinkling of graphene can be both due to the high concentration of heptagon/pentagon rings in the wrinkle or the hydrogenation of graphene (note that the hydrogenated 6 member ring does not exhibit a 2D structure). However, no other major difference between the different hydrogenated graphenes and the control sample is observable through TEM. In summary, SEM and TEM results have confirmed that effective exfoliation of graphite oxide under hydrogen atmosphere at high gas pressures occurs in a similar manner as that in an inert gas atmosphere.

Consequently, we have investigated the density of defects in the hydrogenated graphenes and the influence of the hydrogenation conditions on such density of defects using Raman spectroscopy analysis. The Raman spectroscopic technique generates two distinct peaks at $\sim 1300\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$ which correspond to defects in the sp^2 lattice network (D peak) and the sp^2 hybridized carbon (G peak), respectively. Using the ratio of the intensities of the D and G peaks, it is also possible to calculate the crystallite size of sp^2 graphene according to the equation:¹⁶

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

where I_G and I_D are the intensities of the D and G bands and λ_{laser} is the wavelength of the laser in nm.

As shown in Fig. 1, the Raman spectra are presented for the range of wavenumbers from 1000 cm^{-1} to 3000 cm^{-1} for comparison between the different graphite oxides. It can be clearly observed from Fig. 1A (top part) that the D/G ratio increases from 0.85 to 1.10 (crystallite size decreases from 19.71 to 15.23 nm) with increasing exfoliation gas pressure from 60 bar to 150 bar (under a constant temperature of $\sim 220\text{ °C}$). This may be due to the increasing amount of defects being introduced when higher hydrogen gas pressure is used during exfoliation/hydrogenation of the graphite oxides. This relationship is demonstrated in a graphical plot shown in Fig. 1A (bottom part). Moreover, it is important to note that special care was taken to

ensure that a reproducible and consistent result was obtained for the Raman spectroscopic characterization by calculating an average ratio from a total of nine measurements which were taken at different positions on the specimen. In Fig. 1B, the Raman spectra of graphenes hydrogenated under increasing temperatures from 200 to 500 °C but at a constant gas pressure of 100 bar are presented. It was found that the D/G ratio decreases with increasing exfoliation temperature from 0.87 for graphene exfoliated at 200 °C (crystallite size: 19.26 nm) to 0.77 for an exfoliation temperature of 350 °C (crystallite size: 21.76 nm) before levelling off to 0.81 for the exfoliation temperature of 500 °C ($L_a = 20.68\text{ nm}$). Graphene exfoliated in an argon atmosphere was measured to give a D/G ratio of 0.78 ($L_a = 21.37\text{ nm}$). Therefore, it was discovered that all hydrogenated graphenes have a higher density of defects than graphenes exfoliated in argon. This is likely due to the fact that in addition to the introduction of defects into the materials during the exfoliation process (demonstrated by the control sample exfoliated in an Ar atmosphere), a partial hydrogenation of the graphene may have occurred. Since Raman spectroscopy is an indirect method for the investigation of the density of hydrogenated sites, the hydrogenation efficiency of the materials will be further explored with an alternative technique, XPS.

X-ray photoelectron spectroscopy (XPS) is a useful method for the determination of the chemical composition at the surface of the materials. Herein, a wide-scan XPS measurement is performed to determine if any possible removal of the oxygen containing groups from the graphite oxide surfaces during exfoliation/hydrogenation may have occurred. The wide-scan XPS spectra of graphenes exfoliated under increasing gas pressures (constant temperature) and graphenes exfoliated under increasing temperatures (constant gas pressure) are shown in Fig. S3A and B,† respectively. It is evident that an increasing gas pressure applied during exfoliation has a negative influence on the removal of oxygen containing groups, where G-H: [150 bar/220 °C] contains significantly more oxygen containing groups than G-H: [60 bar/220 °C]. The oxygen content in the material is reflected in the C/O ratio calculated, where a sharp decrease in the ratio from 7.2 to 5.0 was observed with increasing hydrogenation gas pressures from 60 to 150 bar (Fig. S3A†). The increasing temperature of exfoliation (constant pressure of 100 bar) resulted in a greater ease in the removal of oxygen containing groups where the C/O ratio was found to increase significantly from 7.1 to 13.0 when the temperature increases from 200 to 500 °C.

High-resolution XPS spectra provide detailed information on the type of chemical bonds present between the atoms that are useful for the chemical analysis at the surface of the materials. However, its application in the determination of the degree of hydrogenation (and for the study of the sp^3/sp^2 ratio on graphene surfaces) is still questionable due to the narrow difference in the bond energies of C=C and C–C bonds as mentioned earlier. Therefore, a strong overlap of the C=C and C–C bands is expected where fitting of the spectra must be performed to clearly separate the bands. Such a fitting has previously been reported to provide information on the quantification of the degree of hydrogenation efficiency on the graphene surfaces¹² as well as on carbon nanotubes.¹⁷ The high-resolution C 1s XPS spectra for all the exfoliated graphenes are shown in Fig. S4.† Relative

Fig. 1 Raman spectra of hydrogenated graphenes under (A) a constant temperature of $\sim 220^\circ\text{C}$ and pressures of (a) 60, (b) 100 and (c) 150 bar and under (B) a constant pressure of 100 bar and varying temperatures of (a) 200, (b) 350 and (c) 500°C . Also shown are Raman spectra of graphite oxide exfoliated in an Ar atmosphere (d).

sensitivity factors were considered in the fitting of the spectra which was executed in accordance with the bond energies of the various possible carbon–carbon and carbon–oxygen bonds that could be present in the materials. Fitting of the results was performed with the bond energy of C=C at 284.4 eV (red), C–C/C–H bonds at 285.1 eV (blue), C–O bonds at 286.2 eV (cyan), C=O bands at 287.4 eV (purple), O–C=O bonds at 288.7 eV (dark navy) and π – π^* interactions at 290.3 eV (green). The intensity of the C–C/C–H bond was between 12 and 17% of the total sum of the C 1s signals fitted for the hydrogenated graphenes. Percentage of the C–C bonds obtained from the fitting for the control sample's (exfoliated in argon) spectrum was found to account for approximately 16% of the total C 1s signal. Further confirmation of the C–H bonds can be accomplished by the use of IR spectroscopy.

Infrared spectroscopy utilizes a near infra-red beam to induce the various stretching and bending motions of the bonds that occur at frequencies unique to the particular bond and thus, is able to act as a form of identification. The C–H stretching of alkyl carbons occurs at frequencies from 2950 to 2850 cm^{-1} and was found to be present in the spectra for all the hydrogenated graphenes as shown in Fig. 2. The presence of this stretching

band is identical to that in the recorded spectra for hydrogenated carbon nanotubes and fullerenes that were previously reported.^{17,18} However, this was not observed in the same region of the FT-IR spectra for the control sample where the graphenes are exfoliated in an argon environment and also for the graphite oxides that were used as the starting materials.

The best approach in proving the presence and to measure the degree of hydrogenation efficiency of the materials will be to conduct a combustion elemental analysis. It was revealed that the starting material for this project, graphite oxides, contained 50.64% of C, 20.82% of H and 28.54% of O. With the combination of the data from the combustion elemental analysis and the results obtained from infrared spectroscopy, it can be ascertained that all the H atoms in graphene oxides are bonded to the oxygen atoms present in the starting material, graphene oxides. Graphene exfoliated in argon was found to have a composition of 77.67% of C, 10.35% of H and 11.98% of O. Similarly, earlier FT-IR results coupled with the elemental analysis data have proved the direct attachment of H atoms to the oxygen atoms in G-Ar: [100 bar/350 °C] to form hydroxyl groups, according to the stoichiometry of O and H atoms. Graphene exfoliated under high pressure/temperature in a

Fig. 2 FT-IR spectra of hydrogenated graphenes under (A) a constant temperature of ~ 220 °C and pressures of (a) 60, (b) 100 and (c) 150 bar and under (B) a constant pressure of 100 bar and varying temperatures of (a) 200, (b) 350 and (c) 500 °C. Also shown are Raman spectra of graphite oxide exfoliated in (d) an Ar atmosphere, (e) hydrogen and (f) a hydrogen atmosphere at a pressure of 1 bar.

hydrogen gas atmosphere (G-H: [100 bar/500 °C]) displays a composition of 80.55% of C, 11.6% of H and 7.84% of O. If it was assumed that all the oxygen atoms present in this graphene were bonded to hydrogen atoms to form the -OH stoichiometry, it can be further deduced that the remaining 3.76% of hydrogen is bonded directly to the carbon backbone to give graphanes. In fact, the O_1H_1 stoichiometry is extreme and it is likely that there are carboxyl and carbonyl groups present with O_2H_1 or O_1H_0 stoichiometry; therefore the deduced 3.76% of H in the form of C–H bond is the lowest assumption and the real amount is likely to be higher. This deduction on the existence of the C–H bond in G-H: [100 bar/500 °C] was supported by both the elemental analysis results and the infrared spectroscopic data which were also in good quantitative agreement with the HR-XPS data. It is also of importance to note that a high gas pressure is required for the successful hydrogenation reaction of graphene. Graphite oxides exfoliated in a hydrogen gas atmosphere at a pressure of 1 bar and temperature of 1000 °C possessed an elemental composition of 94.25% of C, 0% of H and 5.75% of O. Similarly, graphenes prepared in a N_2 atmosphere of 1 bar pressure at 1000 °C exhibited an elemental composition of 93.50% of C, 0% of H and 6.50% of O.

We investigated the conductivity of GO, hydrogenated graphene and graphene. GO exhibited a sheet resistivity of $2.176 \times 10^3 \Omega \square^{-1}$ and specific resistivity of $3.67 \times 10^2 \Omega \text{ cm}$; G-H: [100 bar/500 °C] has a sheet resistivity of $1.26 \Omega \square^{-1}$ and specific resistivity of $3.6 \times 10^{-2} \Omega \text{ cm}$; G-Ar: [100 bar/500 °C] possesses a sheet resistivity of $1.14 \Omega \square^{-1}$ and specific resistivity of $2.24 \times 10^{-2} \Omega \text{ cm}$. These values showed that hydrogenated graphene exhibits a larger resistivity than non-hydrogenated graphene which is consistent with the theoretical prediction.

Conclusions

In summary, we have successfully proved that exfoliation of graphite oxides in a hydrogen gas atmosphere under high pressure/temperature conditions can result in a hydrogenation of the graphenes. This was fully supported by an observation of a lack of hydrogenation in graphenes exfoliated under similar conditions but in a non-hydrogen gas environment. Further understanding of the materials was realised through an investigation of the impact of the reaction conditions on the hydrogenation efficiency of the materials. The method using a H_2 pressure of 100 bar at 500 °C was found to be the most efficient reaction condition towards the synthesis of hydrogenated graphene. The synthesis method presented in this paper is of utmost importance due to its scalable capability (in contrast to previously published work where the yield is in limited minute amounts) and thus, effectively producing large amounts of the hydrogenated graphene end product which can be useful towards the fabrication of graphane.

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Electronic Supplementary Information

High-Pressure Hydrogenation of Graphene: Towards Graphane

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Figure S1. SEM micrographs of (A) G-H: [60 bar/220 °C], (B) G-H: [100 bar/200 °C], (C) G-H: [150 bar/220 °C], (D) G-H: [100 bar/350 °C], (E) G-H: [100 bar/500 °C] and (F) G-Ar: [100 bar/350 °C]. Scale bars (a) 10 μm , (b) 1 μm and (c) 100 nm.

Figure S2. TEM images of (A) G-H: [60 bar/220 °C], (B) G-H: [100 bar/200 °C], (C) G-H: [150 bar/220 °C], (D) G-H: [100 bar/350 °C], (E) G-H: [100 bar/500 °C] and (F) G-Ar: [100 bar/350 °C]. Scale bars (a) 200 nm, (b) 50 nm.

Figure S3. Survey XPS spectra of hydrogenated graphenes under (A) constant temperature of ~220 °C and pressure of (a) 60, (b) 100 and (c) 150 bar and under (B) constant pressure of 100 bar and varying temperature of (a) 200, (b) 350 and (c) 500 °C. Also shown XPS spectra of graphite oxide exfoliated in Ar atmosphere (d).

Figure S4. High-resolution XPS of hydrogenated graphene materials.

Graphane electrochemistry: Electron transfer at hydrogenated graphenes

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ABSTRACT

Graphane, the hydrogenated derivate of graphene is a highly novel material in the field of two dimensional nanocarbon related research. Preparation of hydrogenated graphene is achieved via a high-pressure/high-temperature (up to 150 bar and 500 °C) thermal exfoliation procedure of graphite oxide. We investigated the properties of the materials via voltammetry and electrochemical impedance spectroscopy to establish the electron transfer rates of hydrogenated graphenes to compare against non-hydrogenated graphene. Understanding the electrochemistry of graphane is crucial towards the exploration of the materials for future practical applications.

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1. Introduction

Graphane, the hydrogenated analogue of graphene, has attracted significant attention in the recent years [1]. It consists of sheets of sp^3 hybridised carbon in a lattice network which is expected to serve as an outstanding material for hydrogen storage or as a protection against corrosion. Partial hydrogenation of graphene is expected to result in the opening of the band gap with strong implication as a material for electronic devices [2].

The structure and synthesis procedure of graphane was predicted theoretically in 2007 [3] and from 2009, there were only few attempts to prepare graphane sheets via hydrogenation of graphene. Low pressure (mbar or lower) hydrogenation in a plasma of individual graphene sheets was attempted by various groups [1,4,5] with a limited yield of the graphane material. We have recently developed a high-yield scalable method for the fabrication of gram quantities of hydrogenated graphane via high-pressure/high-temperature exfoliation of graphite oxide [6].

Electrochemical properties of hydrogenated graphenes have not been investigated. Herein we wish to investigate how the heterogeneous electron transfer progresses on the hydrogenated graphenes as compared to that of graphene.

2. Experimental section

2.1. Materials and apparatus

Potassium ferrocyanide, *N,N*-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, potassium chloride were purchased from Sigma-Aldrich. Nitric acid, sulphuric acid, hydrochloric acid, and potassium chlorate were obtained from PENTA, argon and hydrogen were obtained from SIAD. Graphite was obtained from KOH-I-NOOR GRAFIT. Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions. Glassy carbon (GC) electrodes, Ag/AgCl electrode and platinum (Pt) electrode were obtained from Autolab. Electrochemical experiments using cyclic voltammetric and electrochemical impedance spectroscopic techniques were performed with a μAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) controlled by the software NOVA 1.7 (Eco Chemie).

2.2. Hydrogenation of graphene

We followed the method of hydrogenation as described earlier [6]. The graphene oxide that was used for the synthesis of partially hydrogenated graphane was prepared according to the Hofmann method that has previously been reported [7]. 87.5 mL of sulphuric acid (98%) and 27 mL of nitric acid (65%) were added to a reaction flask (Pyrex baker with thermometer) which contains a magnetic stir bar. The mixture was then cooled by immersion into an ice bath for 30 min. 5 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and to obtain a homogeneous dispersion. While maintaining the reaction flask in the

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ice bath, 55 g of potassium chlorate was then slowly added into the mixture (over 30 min) in order to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon complete dissolution of potassium chlorate, the reaction flask was left loosely capped to allow the evolution of gas and 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 deionised water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions to remove sulphate ions and repeatedly centrifuged and redispersed in deionised water until a negative response towards chloride and sulphate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use. The high pressure synthesis of the materials was performed in a stainless steel autoclave placed in a resistive heated furnace. Approximately 0.3 g of graphite oxide was placed in a quartz glass liner inside the autoclave machine. Hydrogen gas of 99.9% purity and argon gas of 99.996% purity were used in the synthesis process. The autoclave was then repeatedly flushed with hydrogen or argon gas and subsequently filled with the respective gases of the desired pressure using a pressure control valve. The autoclave was heated at a rate of 5 °C min⁻¹ and the dwell time on the temperature of synthesis was 2 h. The reaction vessel was then left to cool freely inside the furnace under room temperature.

2.3. Electrochemical measurements

The glassy carbon electrodes were cleaned by polishing with an alumina suspension then washed with deionised water and wiped dry before use. The synthesized hydrogenated graphenes are dispersed in DMF solvent to create a suspension with a concentration of 0.5 mg·mL⁻¹. The suspension was then sonicated at room temperature for 5 min before each use. Modifying the electrodes was performed by having a 1 µL aliquot of the graphene suspension coated onto the cleaned surface of a GC electrode which was then left under a lamp to dry to give a layer of randomly dispersed G–H and G–Ar on the GC surface. This step was then repeated until three layers of coatings on the GC surface were obtained. The modified GC electrodes, Ag/AgCl reference electrode and Pt counter electrode were then dipped into an electrochemical cell which contains the electrolyte solution (10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ dissolved in 50 mM pH 7.2 phosphate buffer solution) and the measurements were started. CV measurements were taken each time before the start of every EIS measurement which was all carried out under room temperatures. CV measurements were taken for the range of potentials from –800 mV to +1150 mV at a scan rate of 100 mV·s⁻¹ for two consecutive scans. This was immediately followed by an EIS measurement carried out for a range of frequencies from 10 000 Hz to 0.1 Hz. Three replicates were carried out for each TRGO.

Further processing of the data was performed using the Nicholson method [8] to calculate the heterogeneous electron transfer rates of the materials.

3. Results and discussion

We prepared various hydrogenated graphenes at different temperatures and pressures in order to investigate i) how pressure and ii) how temperature of the hydrogenation process influence the electrochemical properties of the resulting materials. The first set of hydrogenated graphenes was prepared at a constant temperature of approximately 200 °C and varied pressures of 60, 100 and 150 bar. The second set of hydrogenated graphenes was prepared at a constant pressure of 100 bar and varied temperatures of 200, 350 and 500 °C. The hydrogenated graphenes are denoted in the text according to their preparation conditions, i.e. hydrogenated graphene at 100 bar/500 °C is denoted as G–H: [100 bar/500 °C]. We have also prepared graphene in inert argon

atmosphere as the control material for comparative purposes (denoted as G–Ar: [100 bar/350 °C]).

To investigate the heterogeneous electron transfer properties, we first employed cyclic voltammetry using ferro/ferricyanide probe [9]. Fig. 1 shows the cyclic voltammograms obtained at various hydrogenated graphene surfaces as well as the control materials' (G–Ar and glassy carbon) surfaces. From the peak-to-peak separation (ΔE_{p-p}) of the voltammetric responses, it is possible to calculate the heterogeneous electron transfer rates (k^0), using Nicholson's approach [8]. The dependence of ΔE_{p-p} and k^0 of hydrogenated graphene surfaces on the hydrogenation pressure and temperature is plotted as shown in Fig. 1. From the analysis of the voltammetry data, it can be clearly observed that an increase in the hydrogenation pressure leads to a decrease in the heterogeneous electron transfer rate. The ΔE_{p-p} increases from 243 mV for G–H [60 bar/220 °C] to 266 mV for G–H [100 bar/200 °C] and to 273 mV for G–H [150 bar/220 °C]. Consequently, the calculated HET rates decreased from 8.25×10^{-4} cm s⁻¹ for G–H [60 bar/220 °C] to 4.83×10^{-4} cm s⁻¹ for G–H [100 bar/200 °C] and finally to 4.15×10^{-4} cm s⁻¹ for G–H [150 bar/220 °C]. The increase in the hydrogenation temperature leads to an increase in HET rates. The ΔE_{p-p} decreases from 266 mV for G–H [100 bar/200 °C] to 212 mV for G–H [100 bar/350 °C] and levels off afterwards. Correspondingly, the calculated HET rates increase from 4.83×10^{-4} cm s⁻¹ for G–H [100 bar/200 °C] to 9.51×10^{-4} cm s⁻¹ for G–H [100 bar/350 °C] and to 9.08×10^{-4} cm s⁻¹ for G–H [100 bar/500 °C]. It is of interest to note that with increasing temperature the hydrogenation efficiency increases [6]. Therefore a fundamental theoretical study should be carried out to provide deep insight into the correlation between the hydrogen coverage and electrochemical activity of the hydrogenated graphenes. Note that the control experiment using a bare glassy carbon surface had exhibited a ΔE_{p-p} of 424 mV and k^0 of 5.66×10^{-5} cm s⁻¹ while G–Ar shows a ΔE_{p-p} of 178 mV and k^0 of 1.45×10^{-3} cm s⁻¹.

Next we turn to another independent technique to confirm the trends observed earlier. Electrochemical impedance spectroscopy (EIS) is a technique which employs small amplitude perturbation at various frequencies for use in an investigation on the resistance towards heterogeneous electron transfer at the electrode/solution interface [10]. Fig. 2 shows the impedimetric spectra of various hydrogenated surfaces as well as that of the control materials' (glassy carbon and G–Ar) surfaces. Again, we studied how the charge transfer resistance (R_{ct}) is influenced by varying the hydrogenation pressure under the constant temperature (Fig. 2, left panel) and hydrogenation temperature under constant pressure (Fig. 2, right panel). The resistance to electron transfer did not show a monotonic trend with an increasing pressure during hydrogenation (R_{ct} varied from 0.876 kΩ to 2.060 kΩ) while a clear trend of a decreasing R_{ct} with an increasing temperature of hydrogenation was observed. The R_{ct} decreased from 2.060 kΩ for G–H: [100 bar/200 °C] to 1.100 kΩ for G–H: [100 bar/350 °C] and to 1.098 kΩ for G–H: [100 bar/500 °C]. This is consistent with the earlier data obtained from cyclic voltammetry experiments. Note that the R_{ct} of graphene (G–Ar: [100 bar/350 °C]) is 0.679 kΩ and the R_{ct} of GC is 5.803 kΩ.

4. Conclusion

We have for the first time investigated the electrochemical behaviour of hydrogenated graphene synthesized under various pressures and temperatures for comparison. We have showed that hydrogenation of graphene (towards graphane) results in a decrease in the observed heterogeneous electron transfer rates as measured by cyclic voltammetry and an increase in the charge transfer resistance as measured by impedance spectroscopy as compared to graphene. This is likely due to the fact that hydrogenation changes the electronic structure of graphene and/or composition/structure of the electrochemically active sites in the material.

Fig. 1. Cyclic voltammograms at various hydrogenated graphenes and graphene. Left panels: data related to the behaviour of hydrogenated graphenes when the hydrogenation pressure is increased while the hydrogenation temperature is held constant. Right panels: data related to the behaviour of hydrogenated graphenes when the hydrogenation temperature is increased while the hydrogenation pressure is held constant. Conditions of voltammetric measurements: 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 50 mM pH 7.2 phosphate buffer solution.

Fig. 2. Electrochemical impedance spectroscopy at various hydrogenated graphenes and graphene. Left panel: data related to the behaviour of hydrogenated graphenes when the hydrogenation pressure is increased while the hydrogenation temperature is held constant. Right panel: data related to the behaviour of hydrogenated graphenes when the hydrogenation temperature is increased while the hydrogenation pressure is held constant. Conditions of voltammetric measurements: 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 50 mM pH 7.2 phosphate buffer solution.

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Towards Graphane Applications in Security: The Electrochemical Detection of Trinitrotoluene in Seawater on Hydrogenated Graphene

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Abstract: With greater security and humanitarian concerns, the pressing need to develop fast and sensitive point-of-care explosives detectors has never been more pronounced. Electrochemical detectors facilitate accurate and swift detection of these explosive traces to provide opportunities for preemptive measures. Sensitivity of the electrode material is one of the many important factors in the development of an effective and efficient electrochemical detector. Herein, we present study on the ap-

plicability of graphene and hydrogenated graphene for the detection of TNT in seawater. Graphene was found to display a higher sensitivity than hydrogenated graphene and could be an ideal material for the detection of TNT in seawater. This is likely due to the fact that graphene contains a larger amount of aromatic rings than hydrogenated graphene, enabling larger preconcentration. These findings are of high importance to the application of graphene-based materials for explosives detection.

Keywords: Graphane • Graphene • Trinitrotoluene (TNT) • Seawater • Security

1 Introduction

Security and safety is one of the main concerns of modern civilizations. The detection of explosives is of high importance due to both security (terrorism) and environmental (leakage of ammunition spoiling natural waters) threats. 2,4,6-trinitrotoluene (TNT) is one of the main components present in explosive ordinances. TNT is classified as both toxic to the environment and a possible human carcinogen by the United States Environmental Protection Agency and Agency for Toxic Substances and Disease Registry. TNT contamination of groundwater and seawater comes from a variety of sources such as unexploded mines, munitions manufacturing and storage facilities. Extensive research has been done on the toxicological effects of TNT on soil [1], animals and humans [2–6]. The results from animal testings have shown that haemolytic anaemia, liver and gill damage, reduced testis size and increased mortality rates are some of the observable symptoms upon exposure to TNT. Moreover, studies done on humans have shown a slight prevalence of cases of cataract formation, spleen and liver enlargement as a result from TNT exposure.

Leakages from munitions into ground or seawater could pose a huge problem for the populations and wildlife living around such areas, affecting their health through contaminated food and water supply. Also, leakages that stem from underwater ammunition could expose their presence in the surrounding body of water. Hence, the development of point-of-care detectors for TNT in ground or seawater is vital to prevent casualties by the swift identification of potential problem sites for decontamination.

Explosives detection has been of great interest to the research community, with a multitude of methods devised for this purpose such as gas and high performance liquid chromatography and capillary electrophoresis [7–15]. One of the many methods that have been garnering a greater interest in recent years is that of electrochemical methods. This is due to the rapid response time, portability, accuracy and lower cost that electrochemical analysers can offer as compared to other laboratory based analytical techniques [16]. Further miniaturizations of these electrochemical analysers are becoming a reality through the use of advanced scientific engineering technologies to eventually allow such devices to be used as on-site detectors.

The study on the electrochemical detection of TNT is based on its reduction process. The reduction of TNT proceeds through a step-wise reduction of three nitro groups [17], which could be achieved via electrochemical methods, such as cyclic voltammetry and differential pulse voltammetry [17]. Such reduction of $-\text{NO}_2$ groups starts at *ortho* position (vs. methyl group), continues in *ortho* position for the second $-\text{NO}_2$ group and finally the remaining $-\text{NO}_2$ group in *para* position is reduced (see Scheme 1 [17]). In order to improve the sensitivity of the detection, various types of sensing platforms have been

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Scheme 1. Stepwise reduction of nitrogroups in TNT proceeds in *ortho*, *ortho* and *para* position vs. methyl group [17].

applied. These include carbon nanomaterials such as carbon nanotubes [18], graphene nanosheets and graphene ribbons [19,20,22].

As such, it is important to continue in the effort of incorporating novel graphene-based nanomaterials as sensing platforms to achieve better detection sensitivity. Our group has previously assessed a range of graphene-based materials for their sensing abilities towards the detection of explosives in seawater [21,22]. In this work, hydrogenated graphene is utilized for the first time as a sensing platform for TNT. The partial hydrogenation of graphene was performed based on a thermal exfoliation method of graphite oxide in a highly pressurized hydrogen atmosphere [23]. This attempt could also potentially offer a deeper insight into a scalable synthesis of pure graphene, which is a fully hydrogenated graphene [24]. Here, we aim to characterize and compare the electrochemical sensing capabilities of graphene and hydrogenated graphene towards the detection of TNT in seawater.

2 Experimental

2.1 Apparatus

All electrochemical experiments were performed using μ Autolab type III instrument (Ecochemie, the Netherlands) connected to a computer and controlled by NOVA 1.8. All experiments were carried out at room temperature using a three-electrode system in a glass cell. Glassy carbon electrode (3 mm in diameter), platinum auxiliary electrode (3 mm in diameter) and Ag/AgCl reference electrode were obtained from CHInstruments. After each successive measurement, the glassy carbon electrodes were polished with 0.05 μ m alumina polishing powder on a polishing pad.

2.2 Reagents and Materials

N,N-Dimethylformamide (DMF) was obtained from Merck. 2,4-Dinitrotoluene (2,4-DNT) and sodium tetraborate decahydrate were obtained from Sigma Aldrich. 2,4,6-trinitrotoluene (TNT) was obtained from Supelco Analytical, Sigma-Aldrich unless otherwise stated. The seawater was collected from East Coast Park, Singapore.

2,4-DNT was prepared as a 1000 ppm bulk solution in acetonitrile. TNT was obtained as an analytical standard, 1000 ppm, and was used as received. The borate buffer solution was prepared by dissolving sodium tetraborate

decahydrate in ultrapure water to give a 20 mM borate buffer solution. The seawater solution was prepared by mixing seawater with 200 mM borate buffer solution in a 9:1 (seawater:borate buffer) ratio. Borate buffer is used to maintain pH 9.2; the reduction of TNT is pH dependent [25].

2.3 Methods

The graphene samples were first prepared in DMF to obtain a suspension with a concentration of 1 mg/mL and were dispersed under ultrasonication for 30 minutes. Before each coating, the solution was placed under ultrasonication for 5 minutes to ensure uniform dispersion. A 1 μ L droplet of the graphene sample coating solution was carefully deposited onto the active surface of the glass carbon electrode and left to dry under a lamp before each experiment. Triplicates were performed for each concentration step with each material.

2.4 Procedures

2.4.1 Graphite Oxide Preparation According to the Hofmann Method [26]

The graphite oxide that was used for thermal reduction in this paper was prepared according to the Hofmann method. 27 mL of nitric acid (65%) and 87.5 mL of sulfuric acid (98%) were added to a Pyrex beaker that contained a thermometer and a magnetic stir bar. The mixture was then cooled in an ice bath for 30 minutes. 5 g of graphite was then carefully added to the mixture under vigorous stirring, to obtain a homogenous dispersion whilst preventing agglomeration. 55 g of potassium chlorate was then added to the mixture over a period of 30 minutes, to prevent both a sudden spike in temperature and the formation of explosive chloride dioxide gas. Then, the mixture was stirred for 96 hours at room temperature whilst the beaker was loosely capped to allow for the evolution of gases. The resultant mixture was then poured into 3 L of deionized water and then decanted. The solid obtained was then first dispersed in 5% HCl solution to remove sulfate ions. It was then repeatedly centrifuged and re-dispersed in deionized water until a negative response towards both chloride and sulfate ions [with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$, respectively] were achieved. The slurry was then left to dry in a vacuum oven for 48 hours before being used in the next step.

2.4.2 Thermally Reduced Graphite Oxide Preparation in Hydrogen Atmosphere [G-H]

Synthesis of this material was performed in a stainless steel autoclave machine in a resistive heating furnace as described. Approximately 0.3 g of graphite oxide, prepared using Hofmann's method, was placed in a quartz glass liner inside the autoclave machine. The machine was then repeatedly flushed with hydrogen gas to evacuate the chamber before being filled with hydrogen gas at 100 bar. The machine was then heated to 500 °C at a rate of 5 °C/min and the material was left to dwell within the chamber for a period of 2 hours at 500 °C and 100 bar. The vessel was then left to cool down to room temperature before the material was extracted for use.

2.4.3 Thermally Reduced Graphite Oxide Preparation in Argon Atmosphere [G-Ar]

Synthesis of this material was performed in a stainless steel autoclave machine in a resistive heating furnace as described. Approximately 0.3 g of graphite oxide, prepared using Hofmann's method, was placed in a quartz glass liner inside the autoclave machine. The machine was then repeatedly flushed with argon gas to evacuate the chamber before being filled with argon gas at 100 bar. The machine was then heated to 350 °C at a rate of 5 °C/min and the material was left to dwell within for a period of 2 hours at 350 °C and 100 bar.

2.5 Electrochemistry

2.5.1 2,4-Dinitrotoluene Electrochemistry

Cyclic voltammetry (CV) measurements were performed in 10 mL of electrolyte solution consisting of various concentrations of 2,4-DNT dissolved in a pH 9.3, 20 mM borate buffer solution. The concentrations of 2,4-DNT electrolyte solutions that were used for the measurements were: 0, 4, 8, 12, 16 and 20 ppm.

2.5.2 2,4,6-Trinitrotoluene Electrochemistry

Cyclic voltammetry and differential pulsed voltammetry (DPV) measurements were performed in 1 mL of electrolyte solution consisting of various concentrations of TNT dissolved in either 20 mM borate buffer solution or seawater solution consisting of a 9:1 ratio of a mixture of seawater and 200 mM borate buffer solution. The concentrations of TNT in electrolyte solutions that were used for the measurements were: 0, 4, 8, 12, 16 and 20 ppm.

All CV experiments were carried out at a scan rate of 100 mVs⁻¹. All DPV experiments were carried out at a step potential of 5 mV and modulation amplitude of 25 mV under room temperature and pressure conditions.

3 Results and Discussion

TNT-based explosives usually contain impurities of smaller nitroaromatic compounds such as 2,4-dinitrotoluene and 2,6-dinitrotoluene. The electrochemical reductions of these smaller compounds provide distinct step-wise reduction peaks similar to TNT. Therefore, the electrochemical reduction of 2,4-DNT (in borate buffer) was conducted prior to the detection of TNT (in borate buffer and seawater) to provide a convenient introductory insight into the sensing capabilities of hydrogenated graphene (G-H) and graphene (G-Ar). The performances of the graphene nanomaterials were compared against that of bare GC with CV and DPV electrochemical methods; conducted in a standard borate buffer prior to actual detection in seawater.

3.1 Electrochemical Detection of 2,4-DNT in Borate Buffer Solution

The cyclic voltammetric measurements for bare GC, G-Ar and G-H modified electrodes were carried out in a borate buffer solution containing 2,4-DNT in a concentration range of 0, 4, 8, 12, 16 and 20 ppm (Figure 1). The reduction of 2,4-DNT afforded two major reduction peaks, labelled peak *a* and *b*, respectively. It was observed that an increase in concentration resulted in an increase in the reduction peak heights for both peaks, for all three electrodes. One should note peak at ~-600 mV at blank buffer (black line) which corresponds to the reduction of oxygen in the sample. We intentionally did not remove oxygen dissolved in buffer or seawater as we intend to develop point-of-care sensor for sense-and-act application.

The two reduction peaks were located at -651 and -828 mV for bare GC, -651 and -797 mV for G-H and -656 and -797 mV for G-Ar. For the ease of comparison, peak *a* was chosen as the representative peak for discussion. Both G-Ar and G-H showed larger average peak current heights of -27.4 and -21.2 μA, respectively, as compared to the average peak current height of bare GC at -14.4 μA. This corresponded to a marked increment of 90% and 47% in average peak current height for G-Ar and G-H, respectively, when compared to bare GC.

3.2 Electrochemical Detection of TNT in Borate Buffer Solution

Since the electrochemical detection of 2,4-dinitrotoluene successfully provided two obvious reduction peaks as expected, subsequent evaluations on the performances of the two graphene nanomaterials for the detection of TNT were performed. Cyclic voltammetry measurements were initially performed to determine the three reduction peak potentials of TNT on the graphene nanomaterials. The CV scans were carried out at 0 ppm and 20 ppm of TNT under similar experimental conditions to that for 2,4-DNT, as shown in Figure 2. The reduction of TNT provided three major reduction peaks, labeled *x*, *y* and *z*. Bare

Fig. 1. The cyclic voltammograms obtained for a range of 2,4-DNT concentrations for A) bare GC, B) G-Ar and C) G-H in borate buffer solution. Conditions: 20 mM borate buffer solution (pH 9.3), scan rate of 100 mVs^{-1} . Concentration range of 2,4-DNT: 0, 4, 8, 12, 16, 20 ppm.

GC gave three reduction peaks at -566 , -749 and -950 mV . However, the graphene nanomaterials provided only two reduction peaks at -556 and -768 mV for G-H and at -543 and -752 mV for G-Ar. The third reduction

Fig. 2. The cyclic voltammograms obtained for the range of TNT concentrations for bare GC (black), G-Ar (red) and G-H (blue) in borate buffer solution. The concentrations of TNT: A) 0 ppm, B) 20 ppm. Conditions: 20 mM borate buffer solution (pH 9.3), scan rate of 100 mVs^{-1} .

peak for both G-H and G-Ar modified electrodes was not obvious. For comparison, peak *x* was chosen as the representative peak as it was clearly observable on all three electrodes. Both G-Ar and G-H showed larger average peak current heights of $-22.1 \mu\text{A}$ and $-15.3 \mu\text{A}$, respectively, as compared to the average peak current height of bare GC at $-10.9 \mu\text{A}$. This corresponded to a marked increment of 103 % and 40 % in average peak current height for G-Ar and G-H respectively, when compared to bare GC.

As cyclic voltammetry technique was unable to elucidate the three reduction peaks of TNT with the graphene nanomaterials, a more sensitive electrochemical method, differential pulse voltammetry, was applied for subsequent analyses. In addition, a comparison study on the sensitivities of the graphene nanomaterials was carried out with DPV. DPV scans were performed on TNT in borate buffer solution for a range of concentrations starting from 0 ppm to 20 ppm as depicted in Figure 3. The voltammograms provided three obvious reduction peaks

Fig. 3. The differential pulse voltammograms obtained for the range of TNT concentrations for (A) bare GC, (B) G-Ar and (C) G-H in borate buffer solution. Conditions: 20 mM borate buffer solution, pH 9.3. Concentration range of TNT: 0, 4, 8, 12, 16, 20 ppm.

for TNT. Moreover, it was observed that with increasing TNT concentrations, the peak current heights of the three reduction peaks increased for all three electrodes.

Calibration curves for each of the three distinct TNT reduction peaks were recorded. In a typical calibration curve, the steeper the slope of the curve, the more sensi-

tive the material is to the detection of the analyte. In reference to peak x, the R^2 value of G-Ar (0.841) was lower than that of bare GC (0.934), which was in turn both lower than G-H (0.985). However, the slope of G-Ar (-651 nA/ppm) was much steeper than that of G-H (-182 nA/ppm), which was in turn both steeper than bare GC (-110 nA/ppm). Therefore, even though the R^2 value of the G-Ar is lower than both the G-H and bare GC, it showed the best sensitivity towards the detection of TNT in borate buffer solution.

3.3 Electrochemical Detection of TNT in Seawater

We then focused our attention to the main aim, which is to determine the suitability and sensitivity of these two graphene nanomaterials for the detection of TNT in seawater with bare GC acting as the control. Since seawater solution differ from standard buffer solutions, measurements were first performed using CV to determine the

Fig. 4. The cyclic voltammograms obtained for the range of TNT concentrations for bare GC (black), G-Ar (red) and G-H (blue) in seawater solution. The range of concentrations of TNT: A) 0 ppm, B) 20 ppm. Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (Seawater pH 6.74), scan rate of 100 mV s^{-1} .

three reduction peak potentials for each graphene nano-material.

Prior to the analyses, a series of blank CV scans (0 ppm TNT) were performed with seawater to account for any possible electroactive compounds present in seawater that could interfere with the measurements (Figure 4A). The measurements highlighted the absence of such interferences, with only oxygen reduction peaks at ~ -600 mV.

Subsequently, CV scans were performed with 20 ppm TNT to identify the peak potentials for each of the three electrodes, as shown in Figure 4B. Three reduction peaks were observed for the reduction of TNT, which are labeled as *x*, *y* and *z*. The first two major reduction peaks (*x* and *y*) were observed at -550 and -734 mV for bare GC, -516 and -691 mV for G-Ar and -518 and -703 mV for G-H. The third reduction peak (*z*) occurred at approximately -900 mV for bare GC but was not observable for G-Ar and G-H. For comparison, peak *x* was chosen as the representative peak as it was clearly observable for all three electrodes. Both G-Ar and G-H showed larger average peak current heights of -21.7 μ A and -16.1 μ A, respectively, as compared to the average peak current height of bare GC at -9.9 μ A. This corresponded to a marked increment of 118% and 63% for G-Ar and G-H, respectively when compared to bare GC.

A more in-depth comparison of the sensitivities of the three electrodes for the detection of TNT in seawater solution was then carried out using DPV. The scans were performed in a range of TNT concentrations (0 ppm to 20 ppm) in seawater solution for all three electrodes, as depicted in Figure 5. It was observed that with increasing TNT concentrations, the peak current heights increased for all three electrodes as well. Further comparisons were conducted with calibration curves (Figure 6) generated from the peak current heights obtained from the DPV scans in Figure 5.

Several G-Ar DPV voltammograms, especially those at lower TNT concentrations, were found to show no observable presence of a third reduction peak in seawater measurements. Therefore, in this comparison study, the third reduction peaks for all three electrodes were not taken into consideration. The calibration curves were only plotted based on the first two TNT reduction peak heights. In reference to peak *x*, the R^2 value of bare GC (0.967) was lower than that of G-Ar (0.969), which was in turn both lower than G-H (0.975). However, the slope of G-Ar (-434 nA/ppm) was much steeper than that of bare GC (-196 nA/ppm), which were in turn both steeper than G-H (-103 nA/ppm). Therefore, even though the R^2 value of G-Ar was in between that of G-H and bare GC, in the presence of seawater, G-Ar again displayed a greater sensitivity towards TNT detection as compared to the other two electrodes. Limit of detection of TNT determined for G-Ar was 400 ppb and for G-H was 500 ppb. Limit of quantification is 1.3 ppm for G-Ar and 1.7 ppm for G-H.

The results obtained were coherent to the findings gathered from the measurements performed in borate

Fig. 5. The differential pulse voltammograms obtained for the range of TNT concentrations for (A) bare GC, (B) G-Ar and (C) G-H in seawater solution. Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (Seawater pH 6.74). Concentration range of TNT: 0, 4, 8, 12, 16, 20 ppm.

buffer solution in the previous section, whereby G-Ar exhibited a greater sensitivity than G-H towards the detection of TNT. On another note, we have previously found that the heterogeneous electron transfer at hydrogenated

Fig. 6. The concentration dependence of TNT for bare GC and G-Ar for A) Peak x B) Peak y in seawater solution. Bare GC (black), G-Ar (red) and G-H (blue). Conditions: 9:1 ratio mixture of seawater and 200 mM borate buffer solution (Seawater pH 6.74).

graphene towards ferro/ferricyanide is similar to that of graphene [22]. We have also demonstrated that graphene could be beneficial towards the detection of biomarkers [27]. Nevertheless, the enhanced sensitivity of G-Ar over G-H is possibly due to the fact that graphene contains a larger amount of aromatic rings than hydrogenated graphene, which enables favorable surface accumulation or larger preconcentration of analytes.

4 Conclusions

In summary, the electrochemical detection of TNT has been investigated with graphene and hydrogenated graphene as potential sensing platforms. Graphene showed a higher sensitivity than hydrogenated graphene in the detection of TNT in both standard borate buffer and seawater solution. Future work in this research direction

could include newer graphene-based materials to be tested for their sensitivity towards the detection of TNT.

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PAPER

Graphenes prepared by Staudenmaier, Hofmann and Hummers methods with consequent thermal exfoliation exhibit very different electrochemical properties

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Large-scale fabrication of graphene is highly important for industrial and academic applications of this material. The most common large-scale preparation method is the oxidation of graphite to graphite oxide using concentrated acids in the presence of strong oxidants and consequent thermal exfoliation and reduction by thermal shock to produce reduced graphene. These oxidation methods typically use concentrated sulfuric acid (a) in combination with fuming nitric acid and KClO₃ (Staudenmaier method), (b) in combination with concentrated nitric acid and KClO₃ (Hofmann method) or (c) in the absence of nitric acid but in the presence of NaNO₃ and KMnO₄ (Hummers method). The evaluation of quality and applicability of the graphenes produced by these various methods is of high importance and is attempted side-by-side for the first time in this paper. Full-scale characterization of thermally reduced graphenes prepared by these standard methods was performed with techniques such as transmission and scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. Their applicability for electrochemical devices was further evaluated by means of cyclic voltammetry techniques. We showed that while Staudenmaier and Hofmann methods (methods that do not use potassium permanganate as oxidant) generated thermally reduced graphenes with comparable electrochemical properties, the graphene prepared by the Hummers method which uses permanganate as oxidant showed higher heterogeneous electron transfer rates and lower overpotentials as compared to graphenes prepared by the Staudenmaier or Hofmann methods. This clearly shows that the methods of preparations have dramatic influences on the materials properties and, thus, such findings are of eminent importance for practical applications as well as for academic research.

Introduction

Research on graphene is currently of great interest to the scientific community due to the many exceptional properties that graphene and graphene related materials possess.^{1–6} There are various methods towards the preparation of graphene related materials, such as adhesive tape-exfoliation of graphite,¹ chemical vapour deposition (CVD) growth,⁷ unzipping of carbon nanotubes⁸ and other methods that are based on the exfoliation of graphite oxide.⁹ In the applications where gram quantities of such materials are needed, solution-based oxidative treatment of graphite to graphite oxide and consequent thermal exfoliation of graphite oxide is more popular as compared to the tape exfoliation or CVD growth methods. Such applications include electrochemical energy storage or sensing.^{5,10}

There are three main methods of solution-based preparation of graphite oxide which serves as a precursor for thermal exfoliation and these include the Staudenmaier method¹¹ (ST) involving fuming nitric acid, concentrated sulfuric acid and potassium chlorate (KClO₃), the Hofmann method¹² (HO) involving concentrated nitric acid, concentrated sulfuric acid and KClO₃ and the Hummers method¹³ (HU) which uses concentrated sulfuric acid instead of nitric acid, NaNO₃ and KMnO₄. Herein we wish to investigate the extent to which the use of various “standard” oxidation methods of graphite (*i.e.* Staudenmaier, Hofmann and Hummers), to graphite oxide (GO) followed by a thermal exfoliation process, leading into thermally reduced graphene (see Scheme 1) may influence the materials properties, such as morphology, density of defects, amount of oxygen containing groups on the surface as well as heterogeneous electron transfer rates (HET rates). We believe that these findings have important implications on the electrochemical applications of graphene. Characterization studies on the resultant graphenes and the reaction byproducts were performed with techniques such as scanning and transmission electron microscopy (SEM and TEM), Raman spectroscopy, high-resolution X-ray

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Scheme 1 Schematic diagram of the procedure for the production of thermally reduced graphenes. An oxidative treatment of graphite using (a) fuming nitric acid and H_2SO_4 in the presence of KClO_3 (Staudenmaier method) or (b) 68% nitric acid and H_2SO_4 in the presence of KClO_3 (Hofmann method) or (c) H_2SO_4 in the presence of KMnO_4 and NaNO_3 (Hummers method) was performed to generate graphite oxides which were consequently thermally exfoliated to thermally reduced graphenes. These thermally reduced graphenes are labelled in the following text as G-ST (Staudenmaier method), G-HO (Hofmann method) and G-HU (Hummers method).

photoelectron spectroscopy (XPS), elemental analysis, X-ray diffraction and cyclic voltammetry (CV). In this paper, we showed that there are no major differences between the thermally reduced graphenes that are produced by the Staudenmaier method and those that are produced from the Hofmann method (both use KClO_3 and nitric acid). However, the Hummers method (employing KMnO_4) produced thermally reduced graphenes which are found to possess very different properties and electrochemical characteristics from those produced using the Staudenmaier and Hofmann methods.

Experimental

Materials

Graphite microparticles ($<50\ \mu\text{m}$), sulfuric acid (98%), nitric acid (68%), potassium chlorate (98%), potassium permanganate (98%), hydrogen peroxide (30%), hydrochloric acid (37%),

N,N-dimethylformamide (DMF), potassium phosphate dibasic, sodium phosphate monobasic, potassium ferrocyanide, and ascorbic acid (AA) were purchased from Sigma-Aldrich. Glassy carbon (GC) and platinum electrode (Pt) with a diameter of 3 mm and Ag/AgCl electrode were obtained from Autolab, The Netherlands.

Apparatus

A JEM 1400 field-emission transmission electron microscope (JEOL, Japan) operating at 100 kV was used to acquire TEM images. For TEM measurements, $1\ \mu\text{L}$ of a $0.5\ \text{mg mL}^{-1}$ suspension of the thermally reduced graphenes was dripped onto a carbon coated copper TEM grid and allowed to dry under room temperature. X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) for the measurement of survey and high resolution C 1s spectra. Relative sensitivity factors were used for the evaluation of C/O ratios from survey spectra XPS measurements. XPS samples were prepared by coating a carbon tape with a uniform layer of the materials under study. Raman spectra were obtained by using a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a CCD detector, a 514.5 nm Ar laser and a $100\times$ objective mounted on an Olympus optical microscope. The calibration is initially made using a silicon reference at $520\ \text{cm}^{-1}$ which gives a peak position resolution of less than $1\ \text{cm}^{-1}$. All voltammetric experiments were performed on a $\mu\text{Autolab}$ type III electrochemical analyzer (Eco Chemie, The Netherlands) controlled by the General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). The elemental analysis was performed with Vario EL III (Elementar Analysensysteme GmbH, Germany). The X-ray diffraction was measured with a PANalytical XPert PRO diffractometer with a Cu lamp and a scintillation detector.

Voltammetric experiments were performed in a 5 mL electrochemical cell at room temperature with a three-electrode system configuration. The platinum electrode served as an auxiliary electrode and the Ag/AgCl electrode served as the reference electrode. All electrochemical potentials reported in this paper are with reference to the Ag/AgCl reference electrode.

Procedures

Graphite oxide preparation with the Staudenmaier method.¹¹

The fuming nitric acid was prepared by distillation of a mixture of concentrated nitric acid and concentrated sulfuric acid (1 : 3 vol). The nitric acid was then purified repeatedly with vacuum distillations until a negative reaction of barium nitrate with sulfate ions was achieved. The concentration of fuming nitric acid was measured with a pycnometer which was found to be 98%. 87.5 mL of sulfuric acid (98% concentration) and 27 mL of nitric acid (fuming) were then added to a reaction flask containing a magnetic stir bar. The mixture was then subsequently cooled by immersion in an ice bath for 30 min. 5 g of graphite was then added into the mixture with vigorous stirring motion to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask in an ice bath, 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period)

in order 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 the gas evolved and the mixture was continuously stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was then poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on 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 60 °C for 48 h before use.

Graphite oxide preparation with the Hofmann method.¹² 87.5 mL of sulfuric acid (98%) and 27 mL of nitric acid (68%) were added to a reaction flask (Pyrex beaker with thermometer) containing a magnetic stir bar. The mixture was then cooled by immersion in an ice bath for 30 min. 5 g of graphite was then added to the mixture with vigorous stirring motion to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask in an ice bath, 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period) in order 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 the gas evolved and the mixture was continuously stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was then poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on 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 60 °C for 48 h before use.

Graphite oxide preparation with the Hummers method.¹³ 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 two hours. In the subsequent four hours, the reaction mixture was allowed to reach room temperature 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 then poured into 1 L of deionized water. The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% 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 on sulfate ion (with $\text{Ba}(\text{NO}_3)_2$) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 60 °C for 48 h before use.

Thermally reduced graphenes. Thermally reduced graphenes were obtained by thermal exfoliation/reduction of graphite oxides 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 sample 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 byproducts from the procedure.¹⁶

Cyclic voltammetry. Cyclic voltammetry experiments were performed at a scan rate of 100 mV s⁻¹ with 50 mM phosphate buffer solution (PBS; pH 7.2) as the supporting electrolyte. The k_{obs}^0 values were determined using the method developed by Nicholson²⁰ which relates ΔE_p to a dimensionless parameter, ψ , and consequently to k_{obs}^0 . The roughness factor was not taken into account in this case. The diffusion coefficient $D = 7.26 \times 10^{-6}$ cm² s⁻¹ for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used for calculations.¹⁴ The GC electrode surfaces were renewed by polishing with 0.05 mm alumina particles on a polishing pad and washed with deionized (DI) water. Immobilization of the carbon materials onto the working electrode (GC) was performed by first preparing a suspension of the desired material with a concentration of 0.5 mg mL⁻¹ in DMF with a 5 min sonication. A 1 μL aliquot of the suspension was then deposited onto the electrode surface. The coating was then allowed to dry at room temperature before a new aliquot was deposited. This was repeated until 3 layers of coatings were deposited onto the electrode surface. The DMF solvent was then allowed to evaporate under room temperature to leave a randomly distributed film on the GC electrode surface.

Results and discussion

Graphite oxides were prepared by treatment of graphite using three different methods as indicated in the following. Staudenmaier method:¹¹ fuming nitric acid, concentrated sulfuric acid and KClO_3 . Hofmann method:¹² concentrated nitric acid, concentrated sulfuric acid and KClO_3 . Hummers method:¹³ concentrated sulfuric acid in the presence of NaNO_3 and KMnO_4 . Details of the experimental procedure can be found in the Experimental section. The graphite oxides produced from the different methods are labeled as follows, Staudenmaier: GO-ST, Hofmann: GO-HO and Hummers: GO-HU. The graphite oxides yielded from the three methods were then subsequently exfoliated and reduced by undergoing a thermal shock at 1000 °C in a furnace under nitrogen gas atmosphere to produce the final product, thermally reduced graphenes (Scheme 1). Electrochemical studies and characterization works were carried out on the three thermally reduced graphenes and the results are elaborated in the following sections.

Materials characterization

First, we characterized the graphite oxides prepared by oxidation of graphite using Staudenmaier, Hofmann and Hummers methods. Fig. 1 shows the X-ray diffraction (XRD) results of the starting material, graphite and the three graphite oxides. It can be observed that graphite oxides prepared from different

Fig. 1 X-ray diffraction of graphite and graphite oxide prepared by the various methods. The large increment in the separation of the graphene layers due to the oxidation of graphite can be clearly observed.

methods showed a variation in the spacing between the graphene layers. The graphite oxide prepared using the Hummers method (GO-HU) exhibits the largest distance between graphene layers (0.8133 nm) followed by the Hofmann method graphite oxide (GO-HO) at 0.7226 nm. The smallest spacing was found to be possessed by the Staudenmaier method graphite oxide (GO-ST) at 0.7084 nm. In the XRD diffraction spectrum, the presence of the (002) diffraction line is an indication of the degree of oxidation of the graphite oxides where an absence of the (002) line implies a complete oxidation of graphite. As observed in Fig. 1, the (002) diffraction line that was observed for graphite completely disappeared for GO-ST, GO-HU and GO-HO. This implies that a complete oxidation of graphite to graphite oxide has occurred for all three graphite oxides regardless of the different methods of preparation. The data from XRD were consistent with that obtained from an elemental analysis that was performed on the three graphite oxides. The composition of the major elements found in GO-ST was as follows: 58.73% C, 23.28% O and 17.99% H where the C/O ratio is 2.52 resulting in GO-ST exhibiting the lowest degree of oxidation which was consistent with the XRD data obtained earlier. Hofmann method graphite oxide (GO-HO) gave a major elemental composition of 50.64% C, 28.54% O and 20.82% H with a C/O ratio of 1.77. Elemental analysis of GO-ST and GO-HO has also indicated that sulfur and nitrogen were not detected for the two materials. However, the Hummers method prepared graphite oxide showed the presence of these two elements; GO-HU was found to contain 37.33% C, 33.04% O, 28.05% H, 0.890% N, and 0.690% S with a C/O ratio of 1.12, which indicates that the Hummers method produces graphite oxides with the highest degree of oxidation as it possesses the lowest C/O ratio among the three graphite oxides. It is therefore important to re-emphasize that GO-HU displays the largest interlayer spacing and also the highest degree of oxidation among all the materials. The observed traces of sulfur and nitrogen in GO-HU are likely to be due to the covalently bonded sulfates¹⁵ and nitrates or adsorbed sulfuric acid and nitric acid found on Hummers method produced graphite oxide.

Consequently, we investigated the properties of the final products, the thermally reduced graphenes, labeled as G-ST,

G-HO and G-HU. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were carried out for the three materials to observe that no major differences in the morphologies were observed among them. SEM images of each thermally reduced graphene (TR-G) at various magnifications (Fig. 2) showed structures that were expected after the thermal exfoliation⁹ process with no significant morphological differences between these three materials. Fig. 3 shows TEM micrographs of G-ST, G-HO and G-HU where all materials displayed wrinkled, single-to-few layer graphene sheets which are typical of graphene, indicating an effective exfoliation of the graphite oxides to give graphenes.¹⁶ In addition, no major visible differences in the TEM images could be deduced for the three thermally reduced graphenes.

Raman spectroscopic measurements were also carried out to obtain important structural information which is essential for determining the density of defects in the graphene sheets. The pristine sp^2 graphene lattice exhibits a signal in the Raman spectra at $\sim 1560\text{ cm}^{-1}$ (G-band) while sp^3 defects in the sp^2 lattice give a prominent signal at $\sim 1350\text{ cm}^{-1}$ (D-band). The ratio between the D and G band intensities (D/G ratio) is often used as an indication of the degree of disorder in a carbon structure. The Raman spectra of G-ST, G-HO and G-HU are shown in Fig. 4 where their D/G ratios were found to be 0.77, 1.09 and 0.97, respectively. Using the D and G band intensities, it is also possible to calculate the average crystallite size (L_a) using eqn (1):¹⁷

$$L_a = 2.4 \times 10^{-10} \times \lambda_{\text{laser}}^4 \times I_G/I_D \quad (1)$$

where λ_{laser} is the laser wavelength in nm, and I_G and I_D are the intensities of the Raman G and D bands, respectively. The resultant calculated crystallite sizes of the three graphene oxides were 21.8 nm for G-ST, 15.4 nm for G-HO and 17.3 nm for G-HU. It should be re-emphasized that G-ST and G-HO differ only in the concentration of the nitric acid used (fuming for G-ST (98%) vs. concentrated for G-HO (68%)) while G-HU differs

Fig. 2 Scanning electron micrographs of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods at different magnifications. Scale bars are 50 μm (top), 2 μm (middle) and 200 nm (bottom).

Fig. 3 Transmission electron micrographs of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods at different magnifications. Scale bars are 500 nm (top) and 100 nm (bottom).

from the other two methods in the type of oxidizing agent used (KMnO_4 for G-HU and KClO_3 for G-ST and G-HO). From the Raman measurements, it can be concluded that thermally exfoliated GO prepared using the Staudenmaier method is capable of producing graphene oxide with the lowest density of defects.

It is known that thermally reduced graphenes bear a small amount of oxygen containing groups on their surfaces as the majority of them are eliminated during the thermal exfoliation process.¹⁸ Since a small amount of oxygen containing groups are still retained on the TR-G, it is therefore vital to investigate the type of oxygen functionalities of these groups through the use of X-ray photoelectron spectroscopy (XPS). This technique is capable of evaluating the surface chemical composition of materials and their electronic states by irradiating the material with a beam of X-rays.¹⁹ The XPS survey spectra of G-ST, G-HO and G-HU are shown in Fig. 5 where the peaks of core C 1s and O 1s are clearly visible in all spectra at energies of 285 and 534 eV, respectively. The C/O ratios for the three materials are calculated from the spectra and are as follow: 24.1 for G-ST, 18.22 for G-HO and 19.27 for G-HU. High C/O ratios imply low oxygen content in all three graphite oxides and this is evidence of a successful thermal reduction/deoxygenation of the GOs. It could also be clearly observed from the XPS results that thermally reduced graphenes that are produced in the absence of KMnO_4 (G-ST and G-HO) presented much different spectra from that of G-HU which uses KMnO_4 , where the latter was found to contain nitrogen functionalities. A prominent N 1s core peak was observable in the G-HU spectra but not in the spectra of the two other materials. This finding is consistent with the earlier elemental analysis results shown where graphite oxides (GO-ST, GO-HO and GO-HU), the respective precursors of each thermally reduced graphene, contain the same elements as their consequent, final product. The N 1s peak in G-HU spectra corresponds to a 1.28 atomic % of the total content in graphene which leads to the conclusion that the treatment of graphite with the Hummers method where KMnO_4 is being utilized yields in the introduction of nitrogen moieties into the graphene framework. In contrast, the Staudenmaier and Hofmann methods

Fig. 4 Raman spectra of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods.

which use KClO_3 as an oxidising agent, do not introduce nitrogen content into the graphite oxide and its consequent product, thermally reduced graphene.

Following which, high resolution X-ray photoelectron spectroscopy (HR-XPS) was employed to bring insight into the types of oxygen containing groups that are present in the three thermally reduced graphenes. Fig. 6 shows the detailed HR-XPS of each C 1s signal of G-ST, G-HO and G-HU where all the spectra showed a single peak at 284.5 eV with an asymmetrical tail at higher energies. Careful curve fitting was performed on each C 1s spectrum to quantitatively differentiate the five different carbon stages: sp^2 -hybridized carbon atoms (284.5 eV), sp^3 -hybridized carbon atoms (285.7 eV), the C–O of alcohol/ether groups (286.8 eV), the C=O of carbonyl groups (288.0 eV), and O–C=O of carboxy acid/ester groups (289.2 eV). Also present is the

Fig. 5 Wide-scan X-ray photoelectron spectra of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods.

π - π^* shake-up signal (290.8 eV) which is typical for sp^2 -hybridized carbon and is found in all the three thermally reduced graphenes. A quantitative comparison on the abundance of various oxygen containing groups at the surface of each TR-G is given in Table 1. It is clear from HR-XPS spectra that the three thermally reduced graphenes possess no significant differences in their abundances of the oxygen containing groups.

To summarize, the comparison of each thermally reduced graphene is predominantly on the appearance of a distinctive N 1s signal in XPS spectra indicating an incorporation of nitrogen into the G-HU framework even though earlier characterization results have proved the materials to be strikingly similar. Interestingly, the electrochemical properties dramatically differ among G-ST/G-HO vs. G-HU as described below.

Fig. 6 High resolution X-ray photoelectron spectra of the C 1s peak of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods.

Electrochemical properties

Electrochemistry is one of the key properties of graphene-based materials energy storage and sensing applications. In this paper, we seek to determine if the differences in the methods of

Table 1 Quantitative comparison of high-resolution X-ray photoelectron spectra of the C 1s core level for different thermally reduced graphenes, G-ST, G-HO and G-HU

	C=C	C-C	C-O	C=O	O-C=O	π - π^*
G-ST	69.3	13.2	6.5	2.5	2.2	6.2
G-HO	67.1	14.2	6.8	3.2	1.8	6.9
G-HU	67.8	14.6	6.4	3.2	1.8	6.2

preparation of thermally reduced graphenes may influence the properties of the material such as heterogeneous electron transfer rates at the graphenic surfaces. Fig. 7A shows the cyclic voltammograms of a standard electrochemical probe, ferro/ferricyanide, for bare glassy carbon (green line), G-ST (black line), G-HO (blue line) and G-HU (red line). It was observed that the cyclic voltammetry of ferro/ferricyanide at the bare glassy carbon (GC) electrode surface results in a large peak-to-peak (ΔE_{p-p}) separation of 508 mV which indicates a slow heterogeneous electron transfer rate. The calculated ΔE_{p-p} values for G-ST, G-HO and G-HU are 236, 258 and 134 mV respectively. ΔE_{p-p} values can be translated to a heterogeneous electron transfer constant (k^0_{obs}) using the Nicholson approach²⁰ (see Experimental part for details) and the resultant k^0_{obs} values for the bare GC electrode surface, G-ST, G-HO and G-HU are $6.88 \times 10^{-5} \text{ cm s}^{-1}$, $2.35 \times 10^{-3} \text{ cm s}^{-1}$, $1.83 \times 10^{-3} \text{ cm s}^{-1}$ and $8.30 \times 10^{-3} \text{ cm s}^{-1}$ respectively. From the cyclic voltammetric measurements obtained, it can be concluded that G-HO and G-ST exhibit similar HET rates while G-HU (prepared with KMnO_4) exhibits a much faster HET rate than G-HO and G-ST.

To investigate the utility of the various thermally reduced graphenes for biosensing, we studied the electrochemical response of ascorbic acid (AA) molecules at G-ST, G-HO and

G-HU surfaces (Fig. 7B). Oxidation of AA at bare GC starts at 90 mV before reaching the maximum at a peak potential of 502 mV. Oxidation of AA at G-ST and G-HO begins at the same potential of -118 mV and reaching the maximum at 167 and 207 mV, respectively. On the other hand, the oxidation of AA at the G-HU surface was observed to behave much differently where three peak potentials were detected. The oxidation peak starts at -165 mV before reaching the first peak potential at 40 mV followed by the second peak potential at 332 mV and the third peak potential at 782 mV. These additional peaks are most likely attributed to the adsorption phenomena of AA molecules at G-HU surfaces.

Conclusion

We have compared the properties and electrochemical performance of thermally reduced graphenes prepared from graphite oxidized with three methods (Staudenmaier, Hofmann and Hummers). The three methods differ in the choice of oxidation agents used to yield graphite oxide which was subsequently exfoliated with a thermal shock at 1000 °C. The resulting thermally reduced graphenes exhibited similar properties except for G-HU prepared from the Hummers oxidation method, where it was found to possess unique characteristics such as higher heterogeneous electron transfer rate and the presence of nitrogen in the graphene backbone. Most importantly, little differences in the electrochemical performances were observed for graphenes prepared from oxidation by fuming nitric acid and by concentrated nitric acid, whilst a much greater difference in the electrochemical response was detected when KMnO_4 was used as the oxidation agent for graphite (Hummers method). This clearly shows that the type of the oxidation method utilized has profound influence on the electrochemical properties of the resulting graphene materials which in turn has eminent implications for any application of graphene in electrochemical devices.

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Fig. 7 Electrochemical behavior of thermally reduced graphenes resulting from exfoliation of graphite oxides prepared by Staudenmaier (G-ST), Hofmann (G-HO) and Hummers (G-HU) methods. (A) Cyclic voltammograms of 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and (B) cyclic voltammograms of 10 mM ascorbic acid. Conditions: scan rate 100 mV s^{-1} , background electrolyte 50 mM PBS, pH 7.2.

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Graphenes Prepared by Hummers, Staudenmaier and Hofmann Methods for Analysis of TNT-Based Nitroaromatic Explosives in Seawater

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Abstract

The detection of TNT and related nitroaromatic compounds in seawater is of great interest. Electrochemical techniques can be applied for detection purposes since nitroaromatic compounds contain easily reducible nitro groups. In this study, we investigate the performance of thermally reduced graphenes prepared by three different oxidative methods: Hummers, Staudenmaier and Hofmann methods with consequent thermal exfoliation. The Hofmann method-based graphene was found to exhibit the highest sensitivity in detecting TNT electrochemically. Extended study on the detection of TNT in seawater using the graphene material provided significant improvements in the detection sensitivity. These findings will have profound impacts on the detection of nitroaromatic explosives in seawater.

Keywords: Nitroaromatic explosives, TNT-based nitroaromatic explosives, Hofmann method, Staudenmaier method, Hummers method, Graphene, Biosensors

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1 Introduction

The use of the nitro-substituted aromatic explosive 2,4,6-trinitrotoluene (TNT) for military and industrial applications has led to environmental contaminations with harmful effects on human beings such as anemia, carcinogenic, hepatic effect, and mutagenic [1–5]. TNT tends to pose environmental threats since it often leaks into the ground water at sites of explosions or ammunition storage areas [6–8]. The contaminated ground water, even at a low concentration, will then flow into the sea, affecting marine life and therefore, indirectly impacting human beings through the food chains. Apart from that, the presence of underwater ordnances also leads to leakage of explosive compounds into the sea. Hence, it is crucial to develop devices and methods that are able to rapidly and efficiently detect TNT at a low concentration with high sensitivity.

A number of different methods have been developed for TNT analysis, such as liquid and gas chromatography, Raman spectroscopy, immunoassay techniques and electrochemical methods [9–15]. Among these methods, the electrochemical methods are particularly well suited for the development of fast, portable and resilient devices for detection of TNT in water/aqueous medium [2]. The TNT contains three nitroaromatic groups which can be individually reduced via a six-electron transfer route [16,17]. The electrode materials that has been investigated

for detection of TNT, since the last few decades, include glassy carbon as well as more innovative materials such as modified glassy carbon, modified gold, mercury/gold-amalgam, carbon nanotube or graphene-based electrodes [18–22]. Electrochemical methods have proven to be an excellent approach towards the detection of TNT at a very low concentration, in terms of parts per million (ppm) and parts per billion (ppb) [2, 22–29]. Even though several nanocarbon electrodes were used, such as nanoporous carbon [30], carbon nanotubes [22] or graphene [21], so far the most sensitive system involved carbon nanotubes surfaces [22]. The electrochemical measurements of TNT can be carried out with techniques such as differential pulse or square-wave voltammetry using various electrodes.

It is of interest to investigate the use of graphene-based materials, given its outstanding physical and electronic properties. The only study on the use of graphene for detection of explosives was on the influence of single-, few- and multi-layered graphene on the sensing performance [21]. It was shown that, in a similar manner to other compounds [31,32], there is a small difference between single-, few- and multi-layered graphenes. On another note, we wish to study a different aspect of graphenes as materials for detectors. Graphenes can be prepared chemically, in principle, by three major oxidative methods, mainly the Hummers, Staudenmaier and Hofmann methods. Here we wish to investigate whether the preparation methods

of graphenes will have any influences on the sensor response. Earlier reports have shown that graphite oxides prepared by the Hummers, Staudenmaier and Hofmann methods can be thermally exfoliated and reduced by thermal shock to produce thermally reduced graphene oxides (TRGOs), which exhibit different electrochemical properties due to their differences in the C/O ratios [33]. In this study, the three TRGOs will be denoted as follows: G-HU for Hummers method, G-ST for Staudenmaier method and G-HO for Hofmann method. Indeed, glassy carbon electrodes modified with TRGOs prepared by the three different methods exhibit different levels of sensitivities in the detection of both 2,4-dinitrotoluene (which is a degradation product of TNT)[34] and TNT. Calibrations of the results were further executed to determine the material that gives the highest sensitivity in detecting TNT in seawater.

2 Experimental

2.1 Materials

2,4-Dinitrotoluene (2,4-DNT) and sodium tetraborate decahydrate were obtained from Sigma Aldrich (St. Louis, MO). Acetonitrile and *N,N*-dimethylformamide (DMF) was obtained from Merck (Singapore). Trinitrotoluene (TNT) was purchased from Supelco Analytical (Bellefonte, PA) as analytical standard in diluted form (1000 ppm) and used as received. The seawater was collected at Sentosa Island, Siloso Beach (Singapore).

2.2 Apparatus

All electrochemical experiments were performed using a μ Autolab type III instrument (Ecochemie, the Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems Version 4.9 software. The experiments were carried out at room temperature using a three-electrode system in a glass cell. Glassy carbon electrode (3 mm in diameter), platinum auxiliary electrode (3 mm in diameter) and Ag/AgCl (with porous Teflon tip) reference electrode were obtained from CH instruments (Austin, TX). Prior to measurements, glassy carbon electrodes were cleaned by polishing with 0.05 μ m alumina polishing powder on a polishing pad.

2.3 Procedures

2.3.1 Graphite Oxide Preparation Using the Hummers Method [35]

2.5 g of sodium nitrate and 5 g of graphite were stirred with 115 mL of sulfuric acid (98%). The mixture was cooled in an ice bath. 15 g of potassium permanganate was then added with vigorous stirring over a period of 2 h. The reaction mixture was allowed to reach room temperature for 4 h before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask con-

taining 250 mL of deionized water and heated to 70 °C. After ensuring the temperature was constant for 15 min, the mixture was then poured into 1 L of deionized water. 3 % hydrogen peroxide was added to remove the unreacted potassium permanganate and manganese dioxide. After which, the reaction mixture was allowed to settle and decant. The graphite oxide obtained was then purified by repeated centrifugation and redispersing in deionized water until a negative reaction on sulfate ion (with $\text{Ba}(\text{NO}_3)_2$) was obtained. Lastly, graphite oxide slurry was dried in a vacuum oven at a temperature of 60 °C for 48 h before use.

2.3.2 Graphite Oxide Preparation Using the Staudenmaier Method [36]

The fuming nitric acid was prepared by distillation of a mixture of concentrated sulfuric acid and concentrated nitric acid (3:1 vol). Then the nitric acid was purified repeatedly with vacuum distillations until a negative reaction of barium nitrate with sulfate ions was obtained. The concentration of fuming nitric acid was measured using a pycnometer which was found to be 98%. After which, 27 mL of nitric acid (fuming) and 87.5 mL of sulfuric acid (98% concentration) were added to a reaction flask with stirring. The mixture was then cooled in an ice bath for 30 min. Then 5 g of graphite was added into the mixture with vigorous stirring to obtain a homogeneous dispersion and prevent agglomeration. In order to prevent a sudden increment in temperature and the formation of explosive chlorine dioxide gas, 55 g of potassium chlorate was slowly added to the mixture over a 30 min period while maintaining the reaction flask in the ice bath. Then the reaction flask was loosely capped to allow the escape of the gas evolved upon the complete dissolution of potassium chlorate. The mixture was continuously stirred vigorously for another 96 h at room temperature. After which, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions in order to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on sulfate and chloride ions (with $\text{Ba}(\text{NO}_3)_2$ and AgNO_3 respectively) was obtained. Lastly, graphite oxide slurry was dried in a vacuum oven at 60 °C for 48 h before use.

2.3.3 Graphite Oxide Preparation Using the Hofmann Method [37]

27 mL of nitric acid (68%) and 87.5 mL of sulfuric acid (98%) were added to a flask (Pyrex beaker with thermometer) containing a magnetic stir bar. Then the mixture was cooled by immersion of the flask in an ice bath for 30 min. After which, 5 g of graphite was added to the mixture with vigorous stirring to obtain a homogenous dispersion and prevent agglomeration. In order to prevent a sudden increment in temperature and the formation of explosive chlorine dioxide gas, 55 g of potassium

chlorate was slowly added to the mixture over a 30 min period while maintaining the reaction flask in the ice bath. Then the reaction flask was loosely capped to allow the escape of the gas evolved upon the complete dissolution of potassium chlorate. The mixture was continuously stirred vigorously for another 96 h at room temperature. After which, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solutions in order to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on sulfate and chloride ions (with $\text{Ba}(\text{NO}_3)_2$ and AgNO_3 respectively) was obtained. Lastly, graphite oxide slurry was dried in a vacuum oven at 60°C for 48 h before use.

2.3.4 Thermal Exfoliation of Graphite Oxides

Thermally reduced graphenes were obtained by thermal reduction/exfoliation of graphite oxides at 1000°C . 0.1 g of the desired graphite oxide was placed into a porous quartz glass capsule which was connected to a magnetic manipulator. Then it was placed inside a vacuum tight tube furnace with controlled atmosphere. The magnetic manipulator is able to create a temperature gradient over $1000^\circ\text{C min}^{-1}$. Then the sample was flushed with nitrogen gas by repeated evacuation of the tube furnace to remove any traces of oxygen. It was then quickly inserted by the magnetic manipulator to a preheated furnace and held in the furnace for 12 min. The flow of nitrogen (99.9999% purity) during the exfoliation procedure was 1000 mL min^{-1} to remove any by-products from the procedure [38].

2.3.5 Electrochemistry

Immobilization of the desired graphene oxide onto the working glassy carbon (GC) electrode was performed by first preparing a suspension of the thermally reduced graphene oxide with a concentration of 0.5 mg/mL in DMF with a 5 min sonication. A $1\text{ }\mu\text{L}$ aliquot of the suspension was then deposited onto the GC electrode surface and the coating was left to dry under a lamp before a new aliquot was deposited. This was repeated until 3 layers of coatings were deposited onto the GC electrode surface. The DMF solvent was allowed to evaporate under a lamp to leave a randomly distributed film on the GC electrode surface. 2,4-DNT was prepared as a 1000 ppm bulk solution dissolved in acetonitrile. Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) were performed in 8 mL of electrolyte solution consisting of various concentrations of 2,4-DNT mixed in a pH 9.3 of 20 mM borate buffer solution. The borate buffer solution was prepared by dissolving sodium tetraborate decahydrate in deionized water to give the desired concentration. The concentrations of 2,4-DNT electrolyte solutions that were used for the measurements were: 0, 4, 8, 12, 16 and 20 ppm . CV and DPV scans were also performed for another two different types of electrolyte solutions: TNT

mixed in pH 9.3 of 20 mM borate buffer solutions and TNT mixed in a mixture of seawater and 200 mM pH 9.3 borate buffer solution prepared in a ratio of 9:1 (seawater : borate buffer) to give an electrolyte of pH 8.9. The voltammetric scans were conducted for TNT concentrations of 0 ppm, 4 ppm, 8 ppm, 12 ppm, 16 ppm and 20 ppm . The electrochemical experiments were carried out in a glass cell at room temperature using a three-electrode configuration which consisted of a platinum auxiliary electrode, Ag/AgCl reference electrode and a modified glassy carbon working electrode coated with thermally reduced graphene oxide. All CV experiments were carried out at a scan rate of 100 mVs^{-1} . All DPV experiments were carried out at a step potential of 5 mV and modulation amplitude of 25 mV under room temperature conditions.

3 Results and Discussion

3.1 Electrochemical Measurements of 2,4-DNT in Borate Buffer

The cyclic voltammetry (CV) of 2,4-DNT (20 ppm , in 20 mM borate buffer) was performed on four different types of electrodes – bare glassy carbon electrode (bare GC), Hummers method (G-HU) TRGO-, Staudenmaier method (G-ST) TRGO- and Hofmann method (G-HO) TRGO-modified glassy carbon electrodes. Before the start of any measurements, cyclic voltammetric scans were performed in a blank electrolyte containing only the borate buffer solution to determine the occurrence of any background interferences. The measurements for all the four types of electrode surfaces showed a reduction peak which was due to the presence of oxygen in the solution (data not shown). Figure 1 shows the major reduction peaks of the nitro groups for the different electrode surfa-

Fig. 1. Cyclic voltammograms of 2,4-DNT using G-HU modified, G-ST modified, G-HO modified and bare GC electrodes. Conditions: 20 mM borate buffer, pH 9.3; scan rate of 100 mVs^{-1} . Concentration of 2,4-DNT: 20 ppm .

Fig. 2. Differential pulse voltammograms of various concentrations of 2,4-DNT for G-HU (A), G-ST (B), G-HO (C) and bare GC (D). Conditions: 20 mM borate buffer, pH 9.3. Concentrations of 2,4-DNT: 0, 4, 8, 12, 16 and 20 ppm.

ces. It can be observed that the reductions occurred at -636 and -806 mV for bare GC while the potentials for the TRGOs shifted slightly, where the reductions with G-HU occurred at -674 and -804 mV, G-ST at -644 and -773 mV, and G-HO at the potentials of -653 and -785 mV (all potentials are stated vs. Ag/AgCl).

Differential pulse voltammetry (DPV) was performed on 2,4-DNT for the four different modified electrodes at concentrations of 0, 4, 8, 12, 16 and 20 ppm as shown in Figure 2. It could be observed that the potentials of the reduction peaks obtained from the DPV scans coincided with those from the CV scans acquired earlier on. For clarity purposes, these reduction peaks were labeled as peaks *a* and *b*, for the peaks with the least and the most negative potentials, respectively (refer to Figure 2). From the DPV scans obtained, the peak current heights for the peaks *a* and *b* increased with increasing concentrations of 2,4-DNT for all the four electrode surfaces. Concentration dependences have secured an average R^2 value of

0.935 and an average standard deviation value of 0.525 which were based on measurements from three replicates. The slopes of the calibration curves also indicate the sensitivity of the electrode systems towards the detection of 2,4-DNT in the buffer solution. From Table 1, it can be concluded that G-ST has the highest sensitivity and R^2

Table 1. Comparison of sensitivity of the various electrochemical systems towards 2,4-DNT in a 20 mM borate buffer solution.

Materials	Peak <i>a</i>		Peak <i>b</i>	
	R^2	Sensitivity ($\mu\text{A/ppm}$)	R^2	Sensitivity ($\mu\text{A/ppm}$)
G-HU	0.853	-0.151	0.878	-0.101
G-ST	0.942	-0.210	0.951	-0.112
G-HO	0.927	-0.151	0.963	-0.106
Bare GC	0.979	-0.130	0.983	-0.075

Fig. 3. Concentration dependence of G-HU, G-ST, G-HO and bare GC for peak *a* (A) and peak *b* (B). Conditions: 20 mM borate buffer, pH 9.3.

value for peak *a*, as well as the highest sensitivity in the calibration for peak *b*.

3.2 Electrochemical Measurements for TNT in Borate Buffer

The electrochemical behavior of TNT on the different TRGOs modified electrodes was subsequently investigated. The CV scans for TNT (20 ppm, in 20 mM borate buffer) were performed to determine the reduction peak potentials of the nitro groups (refer to Figure 4). It can be observed that the reduction of TNT gave rise to the occurrence of three major reduction peaks for the three types of TRGOs. With the bare GC, reductions occurred at potentials of -532 and -721 mV, G-HU at -475 , -619

and -721 mV, G-ST at -517 , -660 and -751 mV and G-HO at -495 , -638 and -744 mV.

We further investigated the utility of DPV technique for detection of TNT on the three graphene materials at different concentrations of TNT (0, 4, 8, 12, 16 and 20 ppm) as shown in Figure 5. It can be observed that the reduction peaks obtained from the DPV measurements coincided with the three peaks from the earlier CV scans. The three major peaks are labeled according to their reduction potentials where the least negative potential (at approximately -450 mV) is labeled as peak *a*, followed by the peak at approximately -550 mV as peak *b* and finally the most negative potential at approximately -650 mV as peak *c*. Calibration plots based on the currents of these three peaks were conducted separately as shown in Figure 6. The slopes of the calibration curves indicate the sensitivity of the electrode system towards the detection of TNT in the solution. From the calibration curves, G-ST showed the highest sensitivities of -0.325 , -0.233 and -0.215 $\mu\text{A}/\text{ppm}$ for peak *a*, *b* and *c*, respectively. However, the R^2 values were lower as compared to the other TRGOs. G-HO and bare GC accounted for the highest R^2 values for all three peaks, but in turn were poor in their sensitivities (refer to Table 2) as compared to G-ST. Hence, G-HO will be used to further investigate the detection of TNT in seawater due to its relatively stable R^2 and sensitivity figures that were achieved on all three reduction peaks. Overall, the calibration results were based on measurements from three replicates to give an excellent average R^2 value of 0.952 and an average standard deviation value of 0.447.

Fig. 4. Cyclic voltammograms of TNT using G-HU modified, G-ST modified, G-HO modified and bare GC electrodes (A). Conditions: 20 mM borate buffer, pH 9.3; scan rate of 100 mV s^{-1} . Concentration of TNT: 20 ppm.

3.3 Electrochemical Measurements of TNT in Seawater

The electrochemical detection of TNT has important implications due to the several reported incidents of frequent TNT seepage into seawater from sources such as factories and military ammunition holding grounds. The

Fig. 5. Differential pulse voltammograms of various concentrations of TNT for G-HU (A), G-ST (B), G-HO (C) and bare GC (D). Conditions: 20 mM borate buffer, pH 9.3. Different concentration of TNT: 0, 4, 8, 12, 16 and 20 ppm.

severe impacts brought about by TNT on the environment have made the detection of this explosive compound a pressing issue for health and military purposes. The study on the detection of TNT in seawater will be carried out with G-HO due to its high linearity and sensitivity observed for all three reduction peaks as shown in the earlier results. Cyclic voltammetric measurements were performed on only G-HO and bare GC electrodes in an electrolyte solution consisting of 20 ppm TNT solution mixed in a mixture of seawater and 200 mM borate buffer prepared in a ratio of 9:1, such that the resulting concentration of borate buffer would be 20 mM while the seawater underwent only minimal dilution. Likewise, CV scans were performed for the two electrodes using a blank electrolyte solution to determine any background interferences in the seawater solution. Similarly, a reduction peak was once again observed for the blank electrolytes which may be attributed to the reduction of oxygen present in the solutions (data not shown). Interestingly, no other major unknown peaks were observed from the scans which implied an almost complete

absence of interferences in the seawater that could further complicate and interfere with the electrochemical measurements. It can be observed from the scans that the major reduction peaks for TNT in seawater occurred at potentials of -451 , -591 and -693 mV for G-HO and at -512 , -673 and -833 V for bare GC (see Figure 7).

Differential pulse voltammetry was also performed on TNT in seawater using G-HO and bare GC electrodes at six different concentrations of TNT (0, 4, 8, 12, 16 and 20 ppm) as shown in Figure 8. The three major reduction peaks observed in the scans were labeled according to their potentials where the least negative potential was labeled as peak *a* (at approximately -450 mV) followed by peak *b* (at approximately -550 mV) and the most negative potential as peak *c* (at approximately -700 mV). It can be clearly observed that the currents of all the three peaks increased with increasing TNT concentrations, which implied that the reduction of the TNT compound was still easily detectable by the DPV technique even though the TNT compound was dissolved in seawater. The current height measured for the three reduction

Fig. 6. Concentration dependence of G-HU, G-ST, G-HO and bare GC for peak *a* (A), peak *b* (B) and peak *c* (C). Conditions: 20 mM borate buffer, pH 9.3.

Table 2. Comparison of sensitivity of the various electrochemical systems towards TNT in a 20 mM borate buffer solution.

Materials	Peak <i>a</i>		Peak <i>b</i>		Peak <i>c</i>	
	R^2	Sensitivity (μA/ppm)	R^2	Sensitivity (μA/ppm)	R^2	Sensitivity (μA/ppm)
G-HU	0.962	−0.117	0.938	−0.113	0.957	−0.105
G-ST	0.885	−0.325	0.864	−0.233	0.910	−0.215
G-HO	0.999	−0.274	0.997	−0.185	0.977	−0.135
Bare GC	0.984	−0.192	0.972	−0.068	0.990	−0.030

peaks were further utilized in the plotting of the calibration curves for the individual peaks as shown in Figure 9. From the calibration curves obtained, a linear relationship between the TNT concentration and the peak's current was observed for both G-HO and bare GC. G-HO was found to display the highest sensitivity towards the detection of TNT in seawater with sensitivity values of -0.387 , -0.262 and -0.253 μA/ppm for peaks *a*, *b* and *c*, respectively. Moreover, a significant improvement in the

Fig. 7. Cyclic voltammograms of TNT in seawater using G-HO and bare GC. Conditions: mixture of seawater and 200 mM borate buffer solution prepared in a ratio of 9:1, pH 8.9; scan rate of 100 mVs^{-1} . Concentration of TNT: 20 ppm.

Fig. 8. Differential pulse voltammograms of G-HO (A) and bare GC (B). Conditions: mixture of seawater and 200 mM borate buffer solution prepared with a ratio of 9:1, pH 8.9. Different concentration of TNT: 0, 4, 8, 12, 16 and 20 ppm.

Fig. 9. Concentration dependence of G-HO and bare GC for peak *a* (A), peak *b* (B) and peak *c* (C). Conditions: mixture of seawater and 200 mM borate buffer solution prepared with a ratio of 9:1, pH 8.9.

sensitivity was observed on G-HO, where the measured sensitivity values increased by 29% (peak *a*), 30% (peak *b*) and 46% (peak *c*) when compared to the sensitivity

values obtained from TNT detections in borate buffer. The R^2 values of the three peaks for G-HO remained constant at approximately 0.984. The slopes of the cali-

bration curves indicate the detection sensitivity of the electrode systems and this implied that G-HO possessed a higher sensitivity towards TNT detection due to its steeper slope as compared to bare GC (refer to Figure 9).

4 Conclusions

Differential pulse voltammetry technique coupled with modified glassy carbon electrodes using TRGOs prepared from Hummers, Staudenmaier and Hofmann oxidation methods has allowed for the successful detection and quantification of TNT at a low reduction potential with high detection sensitivity. G-HO was proven to display the highest sensitivity among the TRGOs prepared by the three methods. Significant improvements were observed for the detection of TNT in seawater as compared to TNT in borate buffer solution where increments in sensitivity values of at least 29% and at maximum 46% were achieved. These findings will have profound influences towards the construction of modified electrochemical sensors for explosive compounds. It is expected that graphene substrates prepared by various methods will demonstrate very different sensing properties for detection of explosives in sea water. Research in this direction is in progress in our laboratory.

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Transition Metal-Depleted Graphenes for Electrochemical Applications via Reduction of CO₂ by Lithium

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Graphene has immense potential for future applications in the electrochemical field, such as in supercapacitors, fuel cells, batteries, or sensors. Graphene materials for such applications are typically fabricated through a top-down approach towards oxidation of graphite to graphite oxide, with consequent exfoliation/reduction to yield reduced graphenes. Such a method allows the manufacture of graphenes in gram/kilogram quantities. However, graphenes prepared by this method can contain residual metallic impurities from graphite which dominate the electrochemical properties of the graphene formed. This dominance hampers their electrochemical application. The fabrication of transition metal-depleted graphene is described, using ultrapure CO₂ (with benefits of low cost and easy availability) and elemental lithium by means of reduction of CO₂ to graphene. This preparation method produces graphene of high purity with electrochemical behavior that is not dominated by any residual transition metal impurities which would dramatically alter its electrochemical properties. Wide application of such methodology in industry and research laboratories is foreseen, especially where graphene is used for electrochemical devices.

1. Introduction

There has been immense interest in the application of graphene in electrochemical storage and sensing devices. The properties of graphene, such as high conductivity, large surface area, and fast heterogeneous electron transfer are the main driving force, coupled with the low cost of graphene production.^[1–7] These properties suit graphene to applications in supercapacitors, batteries, fuel cells, and sensors.^[8–10] For such applications, gram quantities of graphene are often

required. Top-down fabrication methods of reduced graphenes are typically used with cheap and readily available graphite as the precursor. Graphite is oxidized using a mixture of strong mineral acids and oxidants (chlorate or permanganate)^[11–13] to form graphite oxide, with subsequent exfoliation and chemical reduction to give graphene.^[14] It is typically assumed that graphite is a pure material and thus reduction results in graphenes which are also of high purity grade. However, it was discovered that graphite, being a mineral, contains a significant amount of impurities which remain in the final product, graphene.^[15] Such impurities may not significantly change, i.e., thermal conductivity properties, but they can have dramatic influence on electronic properties of graphenes formed by such a method^[16,17] and may dominate the electrochemical properties of the graphene^[15,18,19] in very similar manner to the case of carbon nanotubes.^[20,21] Such dramatic influences on the electrochemical properties of graphene by residual impurities is a major problem for mass production of reliable electrochemical devices. As such, we have explored an alternative route of fabrication of graphene using pure, readily available and cheap greenhouse gas, CO₂ as the reaction precursor.^[22] The CO₂ is reduced by

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a pure elemental metal, lithium; such a reduction reaction of CO₂ to carbon by metals was previously realized where Mg burns in CO₂ to create MgO and carbon powder.^[22] This reaction was later utilized to produce graphene materials.^[23] Similarly, lithium was combusted in a solid CO₂ to yield Li₂O and carbon powder. This reaction was used recently for creation of graphene from greenhouse gas. Magnetite (Fe₃₊δO₄; δ = 0.127) was reported as another reducing agent capable of reducing CO₂ to carbon powder.^[24] NH₃BH₃ was used as a CO₂ fixation agent at conditions of less than <100 °C and pressures at 2.96 MPa to fix carbon with consequent graphenization of the composite to form graphene oxide/boron oxide nanocomposites.^[25]

We employed reduction of CO₂ in solid form (dry ice) with ultrapure elemental lithium to fabricate graphene materials that exhibit a high degree of purity and act as electrochemical-impurity-free materials.

2. Results and Discussions

We fabricated graphene from CO₂ by reducing it with an elemental metal, lithium. The reaction of lithium with dry ice (solid-state CO₂) as a source of carbon where lithium was oxidized to lithium oxide which resulted in the formation of graphene. The lithium metal was first ignited by means of a hydrogen–oxygen torch, which caused the subsequent reaction to take place spontaneously. The low concentration of impurities is due to the fact that all reactants contain only traces of impurities and that the dry-ice block functions as a reaction vessel. Therefore, with reaction conditions under complete control, possibility of impurity contamination is minimized. The degree of purity and the material properties of the graphene prepared from CO₂ were compared with those of carbon black and chemically reduced graphene (CRG) that contain metal impurities that arise from natural graphite. The comparison of the materials was carried out using several techniques such as scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), atomic force microscopy (AFM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence, and electrochemical methods such as cyclic voltammetry and conductivity measurements.

First, we assessed the morphology of the materials using SEM. Graphene produced from CO₂ (G-CO₂) showed a few-layered structure that is similar to that of chemically reduced graphenes.^[14] Meanwhile, amorphous carbon (control sample) exhibited a typical irregular amorphous shape (Figure 1). SEM confirmed that morphologically, G-CO₂ and CRG are similar materials. TEM of G-CO₂ showed a material made up of a few stacked sheets (Figure 1D). AFM of a G-CO₂ flake showed that the thickness of the materials is close to 0.8–0.9 nm, which corresponds to a single-layer sheet.^[26–28] Further insight into the morphologies of the graphenes at nanoscale level was performed with Raman spectroscopy. sp² carbon materials are known to exhibit a Raman spectrum with distinctive peaks at ca. 1350 and 1560 cm^{−1} which correspond to sp³ defects (D band) and the pristine sp² lattice (G band) structure, respectively. The intensities of the

D and G bands can provide insight into the density of defects in the graphene lattice. The Raman spectra measured for the materials are shown in Figure 2. The calculated D/G ratios for the materials are 0.53 for G-CO₂, 0.84 for carbon black, and 1.12 for CRG (Figure 2D). It can be clearly observed that G-CO₂ possessed the least defects followed by carbon black and lastly, CRG which had the highest D/G ratio and the largest amount of defects. The average crystallite size (*L_a*) of the materials can be obtained with the intensities of the D and G bands using the following Equation (1):^[29]

$$L_a = 2.4 \times 10^{-10} \times \gamma_{\text{laser}}^4 \times I_G / I_D \quad (1)$$

where λ_{laser} is the wavelength of the laser in nanometers and *I_G* and *I_D* are the intensities of the G and D bands, respectively. The calculated sizes are 31.5 nm for G-CO₂, 19.9 nm for carbon black, and 15.0 nm for CRG. It can be observed that the crystallite size increases from CRG to carbon black and lastly, to G-CO₂ which has the largest size. Larger crystallite size indicates higher quality of graphene sheets. The high quality of graphene is related to the low D/G ratio and the large crystallite size is related to the reaction conditions during the reduction reaction of CO₂. The reaction produces a large amount of heat which favored the formation of high-quality graphene sheets.

Further information on the surface chemistry of the materials such as the elemental composition can be obtained with X-ray photoelectron spectroscopy. Wide-range XPS spectra were recorded from 0–1200 eV for all materials, as shown in Figure 3. The percentage elemental composition was obtained with relative sensitivity factors taken into consideration. It can be observed that all the materials display a C 1s peak at 284.5 eV and O 1s peak at 534 eV, except for G-CO₂ which showed additional peaks for Li 1s at 56 eV, Si 2p at 107.7 eV, and Si 2s at 158.7 eV. Note that Si 2p peak was shifted by ca. 4 eV which was most likely due to the charging of nonconductive amorphous silicon oxide nanoparticles present in the sample. In terms of electrochemical measurements, silicon oxide is an electrochemically inert material with no influence on the effective electrochemical activity of the materials. The intensities of the peaks were then further calculated as C/O ratios, which are commonly used as an indication of the degree of oxidation of a material. The C/O ratios are 3.53 for G-CO₂, 10.64 for carbon black, and 8.71 for CRG. G-CO₂ has the lowest C/O ratio and thus, the highest amount of oxygen-containing groups followed by CRG and carbon black with the highest C/O ratio and the smallest number of oxygen-containing groups.

High-resolution XPS (HR-XPS) measurements were also performed for all the materials at the respective binding energies of the electronic states of each element of interest. This gives insight into the type of binding interactions of each element in its respective environment. The HR-XPS scans were carried out for C 1s and O 1s of all three materials. In addition, a Li 1s spectrum was also recorded for G-CO₂. Further processing of the C1s spectra was carried out where fitting of the spectrum was performed to identify and quantify the different types of bonding arrangement (Figure 4). The C1s

Figure 1. Morphological characterization. SEMs of A) G-CO₂, B) CRG, and C) carbon black. Scale bars represent 1 μ m. D) TEM of G-CO₂. Scale bar represents 20 nm. E,F) AFM of G-CO₂ sheet with height profile. Dimension of scanned area is 1.5 $\times$ 1.5 μ m. Height of graphene flake is 0.9 nm.

peak can be fitted to resolve into various binding energies at 284.5 eV for C=C, 286 eV for C-C, 287 eV for C-O, 288 eV for C=O, 289 eV for O-C=O, and 290 eV for π - π^* interactions. The relative content for each respective bond type is as shown in **Table 1**. The C=C bond was observed to be the most significant bond type among all the materials. HR-XPS was also performed for Li 1s of G-CO₂ at approximately 54 eV (Figure 4D). The Li 1s spectrum exhibits significant noise interferences due to the extremely low concentration of Li present in the G-CO₂.

Current-voltage characteristics of the materials were investigated through conductivity measurements using a gold interdigitated electrode (Au-IDE).^[30] CRG was found to exhibit the largest conductivity of all the studied materials, followed by carbon black and then G-CO₂ (**Figure 5**).

This project focuses on the possibility of fabricating transition metal-impurity-depleted graphenes for future applications. High purity grade starting materials such as CO₂ (99.9993 %) and Li (purity 99.9 %) were used for the

fabrication process. However, ultralow traces of impurities was still detected in these highly pure materials. We used inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine level of impurities in CRG and graphene prepared from CO₂. We found that G-CO₂ has a content of 0.67 wt% of Li, 0.001 wt% of Cr, <0.001 wt% of Mn, 0.0088 wt% of Fe, <0.001 wt% of Ni, <0.001 wt% of Cu, and 0.0058 wt% of Pb concentrations of Ti, V, Co, Ni were < D.L. (D.L. = detection limit; ca. 0.0001 wt%). We found that CRG has a content of 0.093 wt% of Fe, 0.00003 wt% of Co, 0.0018 wt% of Ni, 0.8311 wt% of Mn, and Mo is present in a concentration < D.L.

Further investigation was carried out on the potential influence of metallic impurities on the electrochemical behavior of graphene prepared from CO₂. Edge-plane pyrolytic graphite (EPPG) electrode was included as a control material for comparison as it is commonly known to be free from any metallic impurity on its surface. It is well

Figure 2. Raman spectra of A) G-CO₂, B) CRG, and C) carbon black. D) D- and G-band intensity ratios.

known that metallic impurities contributed catalytic behavior towards the oxidation of HS⁻ ions as compared with sp² graphite materials.^[15,31] It is apparent that CRG is electrocatalytically active towards the oxidation of sulfide as shown in the cyclic voltammetric scan (**Figure 6**). It could be observed from the figure that the start of the oxidation at approximately -90 mV and attains its maximum current at 320 mV. These values are much lower than those for the EPPG electrode. The oxidation on EPPG electrode exhibits oxidation starting at -21 mV, which consequently peaks at ca. 433 mV, similar to the oxidation of sulfides for G-CO₂. Oxidation of sulfides at G-CO₂ starts at ca. 46 mV, which consequently peaks at ca. 650 mV. Oxidation of the sulfide groups was observed to begin earliest at approximately -45.8 mV for carbon black and consequently peaked at 255 mV. Bare glassy carbon (GC) displays sulfide oxidation at the most

Figure 3. Wide-scan XPS spectra of A) G-CO₂, B) CRG, and C) carbon black. D) C/O intensity ratios.

positive potential of 194 mV, as compared to other materials, and has an oxidative peak at ca. 789 mV. It is clear that CRG prepared from graphite contains residual metallic impurities which dominate its electrochemical properties while for graphene prepared from CO₂, the electrochemistry is not dominated by metallic impurities.

3. Conclusion

We have investigated the influence of metallic impurities on the properties of graphene nanomaterials through a comparison between metallic-impurity-containing materials and materials strongly depleted in content of such impurities. The properties that were examined included physical properties such as the density of defects, surface chemical composition, and electrochemical characteristics. The density of defects in the materials was found to be the highest for CRG while G-CO₂ has the smallest number of defects. It was determined that graphene prepared from CO₂ contained very low levels of impurities. Electrochemistry of graphene prepared by reduction of CO₂ was not dominated by residual metallic impurities while electrochemistry of CRG was dominated by these metallic impurities. Such “electrochemically active

Figure 4. High-resolution XPS spectra of C 1s signal of A) G-CO₂, B) CRG, and C) carbon black. D) HR-XPS of Li 1s signal for G-CO₂.

impurity-free” graphene should find a wide range of applications in the electrochemical domain, such as in sensors, supercapacitors, and batteries, as its performance is not skewed by the presence of impurities.

4. Experimental Section

Materials: Lithium was obtained from Alfa (99.9 %), carbon dioxide in the form of dry ice (99.9993 %) was obtained from Linde. Hydrochloric acid (35 %) was obtained from PENTA, Czech Republic. Natural graphite (flake size, 45 μm) was donated by Asbury Carbons (New Jersey, USA). *N,N*-dimethylformamide (DMF), sodium hydrogen sulfide, sulfuric acid, potassium phosphate dibasic, sodium phosphate monobasic, potassium ferrocyanide, sodium chloride, potassium hydroxide, and potassium chloride were obtained from Sigma–Aldrich. Ultrapure nitric acid for ICP-MS and ICP-OES analysis was obtained from J. T. Baker. Argon (purity 99.996 %) was obtained from Linde. Carbon black (Grade 5358R) was purchased from Asbury Carbons. Deionized water was used for the preparation of all the electrolytes that were utilized for any electrochemical measurement. The glassy carbon working electrode (GC), edge-plane pyrolytic graphite (EPPG) electrode (diameter of 3 mm), platinum auxiliary electrode (Pt) with a diameter of 3 mm and Ag/AgCl reference electrodes were obtained from Autolab, The Netherlands. The gold interdigitated electrode (Au-IDE) was purchased from BAS, Inc. Tokyo.

Apparatus: A scanning electron microscope (JEOL 7600F field-emission, Japan) was used to obtain images under normal SEM and gentle-beam mode (GB). The samples were attached to an aluminum sample stub by using adhesive conductive carbon tape. For XPS analysis a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany) were used. All wide-range and high-resolution scans were performed at 12.53 kV. The materials were attached to an aluminum XPS sample holder by using sticky conductive carbon tape. Special attention was paid to ensure that a homogeneous and uniform layer of the material was attached onto the tape. Raman spectroscopic measurements were executed using a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in back-scattering geometry with a charge-coupled device (CCD) detector. Calibration was performed at 0 and 520 cm^{-1} with a silicon wafer to give a peak-position resolution of less than 1 cm^{-1} . All Raman measurements of the materials were executed using a 514.5 nm Ar laser, an Olympus optical microscope, and a 100 $\times$ objective lens. The materials were well-compressed and compacted prior to any measurements. The concentration of impurities in G-CO₂ was measured with an optical emission spectrometer SPECTRO Arcos (SPECTRO Analytical Instruments, Germany) with radial observation of inductively coupled plasma. The spectrometer features a Paschen-Runge optic mount. Spectra were measured in the range from 130–770 nm. For sample introduction, a cyclonic spray chamber and a modified Lichte nebulizer were used. The following ICP operating parameters were applied: generator power 1450 W, coolant flow 13 L min^{-1} , auxiliary flow 0.8 L min^{-1} , nebulizer flow 0.8 L min^{-1} , sample aspiration rate 2 mL min^{-1} . Calibration was achieved using

Table 1. Relative percentage composition of carbon bonds in respective materials as determined by HR-XPS.

Material	C=C	C–C	C–O	C=O	O–C=O	π – π^*
G-CO ₂	52.7	17.9	11.8	6.0	6.2	5.4
CRG	55.6	17.3	10.0	6.2	4.5	6.4
Carbon black	49.3	22.2	12.0	7.1	0	9.4

Figure 5. Current–voltage characteristics of G- CO_2 , CRG, and carbon black.

commercially available multielement standard solutions (Analytika). The concentrations of all calibrated elements were 0, 0.1, 0.5, 2.0, and 10.0 mg L^{-1} , respectively. 5 mg L^{-1} Y was used as an internal standard. All measurements were performed in 4 % HNO_3 as a matrix. To prepare liquid samples for ICP-OES analysis, the solid samples were weighed (approximately 5 mg) on a micro-analytical balance and combusted by the Schöniger method.^[25] Afterwards, the closed Erlenmeyer flask was treated in an ultrasonic bath. After absorption of combustion products (at least 24 h), 0.88 mL of concentrated HNO_3 (suprapure) and 100 μL of 1 mg mL^{-1} Y standard solution were added. The liquid mixture was quantitatively transferred from the glass flask to a plastic bottle, and made up to a final volume of 20 mL (weighed). Finally, the solution was filtered and introduced to the spectrometer system. The baseline of the ICP-OES measurements was subtracted from a blank experiment. The analysis of CRG was performed by ICP-MS using an Agilent model 7700x ICP-MS and microwave digestions with concentrated nitric acid were performed on a Mars CEM system. Samples for ICP analysis were prepared by accurately weighing into a clean Easy Prep vessel followed by addition of 1.5 mL ultrapure HNO_3 . Digestion procedure consisted of microwave treatment at 1600 W (100 %), ramping the temperature from 25 °C to 120 °C with 20 min ramping time, and maintaining the final temperature of 200 °C for 15 min. TEM was performed on Jeol JEM-3010

Figure 6. Cyclic voltammograms of 10 mM NaHS at EPPG, G- CO_2 , CRG, carbon black, and bare GC electrode surfaces. Conditions: scan rate, 100 mV s^{-1} ; buffer, phosphate 50 mM, pH 7.4.

with 300 kV accelerating voltage. For investigation of graphene, the suspension was prepared in isopropanol (1 mg mL^{-1}) and ultrasonicated for 15 min (75 W) before use. A 1 mL aliquot was dropped onto a 200 mesh carbon/copper TEM grid and dried at room temperature. Bright field, dark field, and selective-area electron-diffraction (SAED) modes were used during actual sample observation. The morphology was studied by atomic force microscopy (AFM) on NT-MTD Ntegra Spectra from NT-MDT in tapping mode with Si tips under ambient conditions, with scan rate of 1 Hz and scan line of 512. Cyclic voltammetric and conductivity measurements were performed using a microAutolab Type III electrochemical analyzer (Eco Chemie, The Netherlands) which was controlled using NOVA 1.7 software (Eco Chemie). Nova 1.7 software is published by Metrohm Autolab B.V. in support of Metrohm Autolab's potentiostat/galvanostat equipment.

Synthesis Procedure of G- CO_2 : An about 1 g piece of Li metal was placed on the block of dry ice and, after its ignition with an oxygen–hydrogen torch, covered by another dry-ice block. The reaction proceeded spontaneously with a large amount of heat evolved until all the lithium metal reacted with the carbon dioxide. The product in the form of black powder was removed from the dry-ice block and washed with diluted hydrochloric acid (10 wt%). The product was then repeatedly decanted and ultrasonicated (15 min) in hydrochloric acid to remove the by-product (lithium oxide). The produced graphene was filtered off using nylon membrane filter (0.45 μm porosity) and washed with deionized water. Graphene was dried at 60 °C under vacuum for 48 h prior to further use.

Synthesis Procedure for CRG: Graphite oxide from natural graphite (N-GO) was prepared according to a modified Hummers method: 0.5 g of graphite, 0.5 g of NaNO_3 , and 23 mL of H_2SO_4 were stirred together in an ice bath. 3 g of KMnO_4 were added slowly to the mixture at 0 °C. The solution was then heated to 35 °C and stirred for 1 h to obtain a thick paste. 40 mL of water were then added and the mixture was stirred for 30 min while raising the temperature to 90 °C. The temperature was then kept at 90 °C for 15 min and 100 mL of water were then added. 3 mL of H_2O_2 (30 %) were added slowly until gas evolution stopped and the mixture changed from dark brown to yellow. The mixture was then filtered and washed with approximately 100 mL of warm water. The filter cake obtained was then redispersed in water by mechanical agitation. Centrifugation was performed at about 6, 600 $\times g$ for 15 min in water until a neutral pH of the supernatant was achieved. The GO powder was then dried in oven at 60 °C for 2 days. Dry GO powder (49.8 mg) was dispersed in ultrapure water to form a 1.0 mg mL^{-1} colloidal solution and ultrasonicated at 150 W for 3 h. Hydrazine hydrate (2 mL, 32.1 mmol) was then added dropwise to the mixture at 47 °C and the reaction mixture heated up to 100 °C for 24 h. After cooling to room temperature, the mixture was repeatedly washed with methanol and ultrapure water using centrifugation (8000 rpm, 10 min) method. The sample pellet was then dried in oven at 60 °C for 2 days prior to usage.

Cyclic Voltammetry: All glassy carbon electrodes were renewed by polishing with an alumina suspension, washing with deionized water, and wiping dry prior to usage. The materials were dispersed to create a 0.5 mg mL^{-1} suspension with DMF as the solvent. The suspension was sonicated at room temperature for 5 min before each use. The surface of a cleaned GC electrode was then modified by coating with a 1 μL aliquot of the suspension. The electrode was then placed under a lamp for drying to give a layer of

randomly dispersed material on the GC surface. This procedure was repeated three times to obtain three layers of homogeneous coating. The EPPG electrode's surface was renewed before each measurement by polishing with the alumina suspension, washing with deionized water, and wiping dry. The modified GC electrodes, Ag/AgCl reference electrode, and platinum counter electrode were then placed into an electrochemical cell that contained the electrolyte solution and the measurements were then taken. The EPPG electrode was used in place of the modified GC electrode together with the reference and counter electrode in measurements for the EPPG electrode. The electrolytes used were 50 mM pH 7.4 phosphate-buffer solution (PBS) as the blank buffer electrolyte, with 10 mM NaHS dissolved in the PBS. All measurements were performed for two consecutive scans at a scan rate of 100 mV s⁻¹. Three measurements were carried out for each material and also for each electrolyte.

Conductivity Measurements: 1 mg mL⁻¹ suspensions of the materials were prepared by dispersing the materials in deionized water. The current–voltage measurements were executed by coating 1 µL of the material suspension onto the interdigitated area between the two gold electrode bands. The electrode was then placed under a lamp to dry and obtain a randomly deposited material film on the electrode. Linear sweep voltammetric measurement was then executed on the electrode at 200 mV s⁻¹ scan rate to obtain *I*–*V* graphs. A total of five replicates was performed for each material.

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Nanoporous Carbon Materials for Electrochemical Sensing

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Abstract: Nanoporous carbon materials are highly important materials for a wide array of applications. Here we show that nanoporous carbon can act as highly active materials for electrochemical sensing. We observed that nanoporous carbon material exhibits a faster heterogeneous electron transfer than graphite and pure carbon nanotubes. Nanoporous carbon exhibits a superior electrochemical performance for sensing of important biomarkers such as dopamine, ascorbic acid, uric acid, NADH, DNA bases, and forensic-related compounds such as nitroaromatic explosives.

Keywords: cyclic voltammetry • electrochemistry • electron transfer • nanoporous carbon • sensors

Introduction

Carbon materials are very popular as electrodes in electrochemical devices due to their low cost, high conductivity, and fast electron transfer rates.^[1–5] Carbon electrodes are used on all scales in many application areas, from electrodes for steel fabrication to energy storage devices and sensors.^[1–10] There has been much research done on carbon nanotubes and graphene nanomaterials, both in electrochemical sensing and energy storage areas.^[7,11] Another class of nanostructured materials, such as nanoporous carbon materials has been exploited almost exclusively in the area of energy storage.^[12,13] Interestingly and surprisingly, nanoporous carbon materials for electrochemical sensing applications remained somehow on the fringes of the interests of researchers,^[14] even though such materials could potentially improve tremendously the electrochemical response.

Nanoporous carbon materials include materials with pore sizes up to 100 nm, thus spanning categories of microporous (0.2–2 nm pores), mesoporous (2–50 nm pores), and macroporous (50–1000 nm pores) materials.^[15] Such materials provide many advantages over carbon nanotubes and graphene because the size of the pores is well defined and the pore-containing carbon particles have a uniform size, and therefore the surface area, the functional groups, and the overall structure is well defined. Because nanoporous carbon materials are usually prepared from biomass, their preparation is cost effective, especially when compared to carbon nanotubes (CNTs) and graphene.^[16] The confinement of molecules in nanopores is of significant benefit for electrochemistry.^[17] The probability that an electron is transferred be-

tween the molecule and the electrode surface depends on two factors: 1) the frequency at which molecule encounters the surface and 2) the success rate of electron transfer between a molecule and the surface.^[18] It has been shown by random walk theory that a molecule explores one small region of space very thoroughly during diffusion before wandering off. It has also been shown that when a molecule enters a pore in the electrode, the concentration profile of this molecule and product is very different from a standard disk electrode facing an open semi-infinite solution.^[17] This leads to a higher occurrence of molecule–electrode surface encounters and consequently to higher voltammetric currents. A similar phenomenon has been previously demonstrated with Pt nanoporous surfaces, where the presence of a high surface-to-volume ratio and exclusive geometry of nanoporous structures allow the electrolyte molecules to stay for longer periods of time on the electrode surface through a confinement effect.^[19] Thus, the reactant molecules can undergo the respective reactions more efficiently to give a higher redox current. Here we wish to demonstrate that nanoporous carbon materials result in an enhanced performance of the electrochemical responses as compared to standard graphite and carbon nanotube electrodes.

Results and Discussion

We have subjected nanoporous carbon to detailed materials analysis before investigating its electrochemical properties. Figure 1 shows electron microscopy images in transmission (Figure 1a) and scanning modes (Figure 1b). The electron microscopy images show that nanoporous carbon consists of particles with a diameter of approximately 50 nm. We have not observed pores in the TEM images due to the non-crystalline nature of the carbon material. We used the standard Brunauer–Emmett–Teller (BET) method to determine the pore size.^[20] Based on BET measurement of adsorption–desorption of N₂, the pore diameter in our nanoporous carbon

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Figure 1. a) TEM and b) SEM images of nanoporous carbon.

samples was 11.2 nm, with an average pore volume of $0.6 \text{ cm}^3 \text{ g}^{-1}$ and a surface area of $187 \text{ m}^2 \text{ g}^{-1}$.

It is well known that oxygen-containing groups can influence the electrochemistry of carbon materials.^[21] Thus, to have a clearer picture of the potential influence of oxygen-containing groups during comparative electrochemical studies, we have performed fourier transform infrared (FTIR) spectroscopic measurements of nanoporous carbon as well as of multiwalled carbon nanotubes and graphite microparticles, of which the latter two were used as comparative materials.

Abstract in Czech: Nanoporezní materiály na bázi uhlíku nacházejí využití v mnoha oblastech. V tomto článku ukážeme jejich výhody pro použití v oblasti electrochemického stanovení látek. Heterogenní přenos elektronu mezi nanoporezním uhlíkem a solutem je velmi rychlý. Použití tohoto typu uhlíku je velmi výhodné pro stanovení dopaminu, vitamínu C, kyseliny močové, NADH, DNA bází a nitroaromatických látek.

Figure 2. FTIR spectra of nanoporous carbon, CNTs, and graphite. Areas of interest around 3440 cm^{-1} and 1650 cm^{-1} , which correspond to OH stretching and C=C bonds, respectively, are marked.

Figure 2 shows representative FTIR spectra of these materials. The main focus of interest is the spectrum range at around 3440 cm^{-1} , which corresponds to $-\text{OH}$ stretch, and the range at around 1650 cm^{-1} , which corresponds to C=C stretch. We normalized the data to C=C stretch and we found that the ratio of $-\text{OH}$ to C=C intensity is 1.84 for nanoporous carbon, 1.39 for graphite microparticles, and 1.20 for CNTs. The influence of oxygen-containing groups on the electrochemical response will be discussed below.

Figure 3. a) Cyclic voltammetry and b) electrochemical impedance spectroscopy at nanoporous carbon, CNT, graphite, and bare glassy carbon electrode surfaces. Conditions: 10 mM $\text{Fe}(\text{CN})_6^{3-}$, 50 mM phosphate buffer solution at pH 7.2; in (a), a scan rate of 100 mV s^{-1} was employed; in (b), impedimetric measurements were performed from 10 kHz to 0.05 Hz with an amplitude of 10 mV.

We carried out a comparative electrochemistry study of nanoporous carbon with CNT and graphite samples. First we carried our experiments using the well-established redox couple ferro/ferricyanide. Cyclic voltammograms of the ferro/ferricyanide couple are shown in Figure 3a.

It can be seen that the peak-to-peak separation for oxidation and reduction is 460 mV for a bare glassy carbon (GC) electrode (used for comparison as it represents the standard electrode surface), 596 mV for CNTs, 335 mV for graphite, and 129 mV for nanoporous carbon. The calculated k_0^{obs} from these data is $3.22 \times 10^{-5} \text{ cm s}^{-1}$, $5.09 \times 10^{-6} \text{ cm s}^{-1}$, $1.76 \times 10^{-4} \text{ cm s}^{-1}$, and $3.30 \times 10^{-3} \text{ cm s}^{-1}$ for bare GC, CNTs, graphite, and nanoporous carbon, respectively. It is clear that the highest observed heterogeneous electron transfer (HET) rate was exhibited by nanoporous carbon, followed by graphite. It should be noted that the HET rate of pure CNTs is lower than that of graphite; this is consistent with previous findings.^[22,23]

Further confirmation of the above-mentioned results was carried out by using an independent electrochemical technique, electrochemical impedance spectroscopy (EIS). EIS measurements were used to investigate the resistance of the materials to electron transfer between ferri/ferricyanide at the electrode surface. Impedance spectra of all four materials are shown in Figure 3b. It is apparent that the highest electron charge transfer resistance was exhibited by CNTs (4524 Ω), followed by GC (1693 Ω) and graphite (53 Ω), while nanoporous carbon exhibit an exceptionally low resistance (46 m Ω). These results are consistent with our data obtained by cyclic voltammetry. As mentioned above, the oxygen-containing groups on carbon materials have a certain influence on the electrochemical response; it was previously found that the HET rate constant decreases with an increasing amount of oxygen-containing groups. It can be concluded from FTIR and electrochemical measurements that even though nanoporous carbon contains a larger amount of oxygen-containing groups than CNTs and graphite, its apparent HET rate is faster. Therefore, the electrochemical performance of nanoporous carbon is superior to CNTs and graphite despite the presence of a larger amount of oxygen-containing groups on its surface.

Next, we investigated the electrochemical oxidation of the biologically important markers ascorbic acid (AA), uric acid (UA), dopamine (DA), and the reduced form of nicotina-

Figure 4. Cyclic voltammograms of a) 10 mM ascorbic acid, b) 10 mM uric acid, c) 10 mM dopamine, and d) 5 mM NADH at nanoporous carbon, graphite, CNT, and bare GC electrode surfaces. Conditions: 50 mM phosphate buffer, pH 7.2; scan rate of 100 mV s⁻¹.

mid adenine dinucleotide (NADH; see Figure 4). Oxidation of AA (Figure 4a) at bare GC originates at 56 mV and reaches maximum at 414 mV. CNTs exhibit a poorer electrochemical response with a maximum at 471 mV. On the other hand, graphite shows a lower oxidation potential of AA at 361 mV while oxidation of AA at nanoporous carbon starts at -86.1 mV, reaches a first maximum at 94.5 mV and then a second maximum at 318 mV. The second peak most likely corresponds to the oxidation on the underlying GC electrode. A similar trend was observed for UA (Figure 4b). UA oxidation at both bare GC and CNTs begins at 272 mV before attaining a maximum at approximately 494 mV and 582 mV, respectively. Graphite and nanoporous carbon display a lower starting oxidation potential at 198 mV, which was followed by a maximum at 360 mV for nanoporous carbon and 390 mV for graphite. It was also clearly observed that the oxidative current of UA at nanoporous carbon is larger than that of the other carbon materials. In the case of DA (Figure 4c), oxidation and reduction of this compound at bare GC, CNTs, and graphite exhibit starting potentials at more extreme values as compared to those of nanoporous carbon. DA at nanoporous carbon exhibits an oxidation peak at 379 mV and a reduction peak at 86 mV. Oxidation of NADH at bare GC, CNTs, and graphite occurs at a similar starting potential of 357 mV with a maximum at approximately 700 mV, while nanoporous carbon provides a much lower starting potential at 111 mV before attaining a maximum at 557 mV (Figure 4d).

We further investigated the behavior of nanoporous carbon as electrode material for oxidation of DNA bases because electrochemical DNA sensing is of high importance

Figure 5. Differential pulse voltammetry of a) 4 μM guanine, b) 50 μM adenine, c) 100 μM cytosine, and d) 100 μM thymine. Conditions: 50 mM phosphate buffer, pH 7.2.

for disease diagnostics and an increased sensitivity and selectivity would be highly beneficial.^[24] Figure 5 shows differential pulse voltammograms (DPVs) of guanine (G), adenine (A), cytosine (C), and thymine (T). It is apparent from the DPVs that nanoporous carbon offers significantly lower oxidation potentials for all DNA bases when compared to

CNTs, graphite, and bare GC, with dramatically (by about one order of magnitude) increased currents. More specifically, the oxidation potential of guanine at nanoporous carbon is 616 mV while graphite, CNTs, and bare GC give peaks at around 729 mV. Oxidation of adenine occurs at 851 mV for nanoporous carbon while it occurs at around 1000 mV for graphite, CNTs, and bare GC. It should be highlighted that although nanoporous carbon exhibits significantly enhanced oxidation currents for adenine, it also results in double peaks being formed; this may have a detrimental effect on further analysis. Graphite, CNTs, and bare GC display a poor oxidation of cytosine and low currents when compared to nanoporous carbon, which gives an

oxidation current of 1.41 μA (13 times the current measured for graphite) at a lower potential of 1226 mV (compared to ca. 1300 mV for other carbon materials). Oxidation of thymine shows a similar trend to the other DNA bases, with a lower oxidation potential of 1087 mV for nanoporous carbon, while the other materials display higher oxidation potentials ranging between 1122 mV and 1132 mV. A larger current of 1.04 μA was also measured for nanoporous carbon; this value was 2.5 times that of graphite. The low sensitivity of pure CNTs is consistent with our previous observations.^[25]

The detection of 2,4,6-trinitrotoluene (TNT) is of high importance from the viewpoints of environmental remediation and anti-terrorism measures.^[26] We investigated whether nanoporous carbon provides improved electrochemical responses when compared to other carbon-based materials for detection of TNT in a similar fashion as it did for DNA bases. Figure 6 shows the reduction of TNT at pH 2 (a) and pH 9 (b). It is clear that nanoporous carbon provides significantly enhanced reduction currents; values are about 4.5 times higher in buffer of pH 2 and approximately two times higher in buffer of pH 9. Peak potentials on nanoporous carbon are shifted noticeably toward positive potentials; for example, the peak potential of the first reduced nitro group shifts from about -238 mV (for CNTs, graphite, and bare GC) to -178 mV (for nanoporous carbon) at pH 2, and less profoundly at pH 9, from -480 mV (for CNT, graphite, and bare GC) to -455 mV (for nanoporous carbon).

Figure 6. Differential pulse voltammetry of 20 ppm of 2,4,6-trinitrotoluene at nanoporous carbon, graphite, CNT, and bare GC surfaces. Conditions: 20 mM borate buffer at a) pH 2 and b) pH 9.

Conclusions

Our investigations on the electrochemical properties of nanoporous carbon reveal that this material consistently shows a “superior” sensing performance in terms of lower oxidation/reduction potentials of important biomarkers and forensic-related compounds and significantly increased currents when compared to bare glassy carbon electrode, graphite microparticles, and carbon nanotubes. We wish to emphasize here that the nanoporous carbon exhibits an excellent performance for sensing of a wide range of analytes and thus we would like to suggest that such nanoporous carbon materials could not only be excellent for energy storage application but also for electrochemical sensing applications.

Experimental Section

Instrumentation

Cyclic voltammetry (CV), differential pulse voltammetry (DPV; step potential 5 mV, modulation amplitude 25 mV), and electrochemical impedance spectroscopy (EIS) measurements were carried out using an Autolab 302 electrochemical analyzer (Eco Chemie, The Netherlands). All CV, DPV, and EIS experiments were conducted with a glassy carbon (GC) working electrode, a platinum (Pt) counter electrode, and an Ag/AgCl reference electrode. TEM images were generated using a JEOL JEM-2010F field transmission electron microscope operated at 200 kV. SEM images were taken using a JEOL JSM-6340F scanning electron microscope. FT-IR spectroscopy was carried out with a Shimadzu IR Prestige ge-21 spectrometer. BET measurements were done using a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer, and the sample was degassed at 1000 °C for 5 h before the measurement.

Chemicals

All chemicals were purchased in highest commercially available purity from Sigma–Aldrich, Singapore.

Procedures

The GC electrodes were prepared and cleaned for use by polishing with 0.05 µm alumina powder. As-purchased nanoporous carbon (#699632), graphite (#10091934), and CNTs (#659258; all Sigma–Aldrich) were prepared as suspensions in *N,N*-dimethylformamide (DMF) at a concentration of 0.5 mg mL^{−1} and sonicated for 5 min at room temperature prior to use. For all electrochemical measurements, modified GC electrode surfaces were prepared by casting 1 µL of the prepared suspension onto the cleaned surfaces and leaving them to dry before use. For TEM measurements, samples were prepared by coating a copper grid with 1 µL of 0.5 mg mL^{−1} suspension, followed by drying overnight at room temperature. The HET rates were calculated as previously described by Nicholson.^[27]

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PAPER

Nanoporous carbon as a sensing platform for DNA detection: The use of impedance spectroscopy for hairpin-DNA based assay

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Nanoporous carbons represent well defined materials with large surface area, defined porosity, high electrical conductivity and fast heterogeneous electron transfer rates. These materials are seldom used for sensing and even more rarely for biosensing. We for the first time show the application of nanoporous carbon using electrochemical impedance spectroscopy technique to detect DNA hybridization and polymorphism. Our findings demonstrated the proof of concept of using nanoporous carbon in nucleic acid analysis, being able to detect the presence of a single nucleotide polymorphism.

Introduction

The demand for new materials in the electrochemical detection of biomolecules has increased considerably in the last few years.^{1–4} This is due to the enormous need for new analytical devices for point-of-care diagnosis which can provide rapid and sensitive responses.^{5–7} The detection of DNA hybridization and polymorphism is becoming a very important issue in biomedical field since it can provide early information on the presence and the development of different genetic diseases.⁸ DNA biosensors are the ideal candidate for this purpose since they fulfil the requirements for a fast and reliable response, while at the same time being more affordable and easier to handle for the general user, as compared to the classical methods for DNA analysis.⁹

Electrochemical Impedance Spectroscopy (EIS) is a rapid, non-destructive method which can be used for the characterization of different kinds of materials.^{10,11} Being able to detect interfacial properties at the electrode surface, EIS has become an increasingly powerful tool for highly sensitive detection of biorecognition events.^{12,13}

Carbon materials have been used in biosensing schemes as electrode materials due to their high electrical conductivity, fast electron transfer rates, well established chemistry and affordability. There has been significant research carried out using carbon-based materials such as graphite,¹⁴ carbon paste,¹⁵ carbon nanotubes¹³ and graphene¹⁶ as electrode platforms for biosensing. However, another type of carbon nanostructured material remains completely unexplored for biosensing applications. This material is nanoporous carbon. Nanoporous carbons are termed carbon structures with pores of less than 100 nm, spanning across areas of microporous (pores of 0.2–2 nm), mesoporous (pores of 2–50 nm) and macroporous (50–1000 nm

pores) carbons.¹⁷ Such materials are well established, have high surface area and well defined structure. Surprisingly, they found most of the applications in the energy storage area,^{18,19} but a little attention was given to their sensing properties.^{20,21} Earlier works on the detection of nucleic acids and proteins such as thrombin with mesoporous carbon using fluorescence emission techniques has been reported^{22,23} but the use of electrochemical sensing methods are still yet to be fully explored. Even though nanoporous carbon materials exhibit very fast heterogeneous electron transfer rates and high surface area, they have not been used for electrochemical nor impedimetric DNA sensing.

In this work we used for the first time a nanoporous carbon platform for the detection of DNA hybridization and polymorphism by electrochemical impedance spectroscopy. Hairpin shaped oligonucleotides were used as DNA probes to be immobilized on the electrode surface. A hairpin-DNA (hpDNA) is a secondary DNA structure in which two regions of the same strand are complementary to each other, thus resulting in the formation of a double-stranded end and an unpaired loop.^{24,25} Due to this inherent structural constraint, hpDNA presents a higher selectivity for target recognition capabilities in the presence of single nucleotide polymorphisms (SNPs) as compared to linear DNA probes.^{26–28} The developed platform was able to distinguish between a complementary target and a sequence with one mismatch which is correlated to the development of Alzheimer's disease. Our findings demonstrated a novel application of nanoporous carbon as sensing platform for the impedimetric detection of nucleic acid sequences.

Experimental

Materials

Disposable electrical printed electrodes (DEP chips) were purchased from BioDevice Technology (EP-PP; Lot No. EPFS18), Nomi, Japan. Potassium ferricyanide ($K_3Fe(CN)_6$),

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Table 1 Sequences of the hpDNA and the various targets (wild, nc and mutant)

Name	Sequence
hpDNA	5'-ATG GAG ACC AGG CGG CCG CAC ACG TCC TCC AT -3' (32 mer)
Wild	5'-ATG GAG GAC GTG TGC GGC CGC CTG GT-3' (26 mer)
nc	5'-AAA AAA AAA AAA AAA AAA AAA AA-3' (26 mer)
Mutant	5'-ATG GAG GAC GTG <u>C</u> GC GGC CGC CTG GT-3' (26 mer)

potassium ferrocyanide ($K_4Fe(CN)_6$), hydrochloric acid, sodium chloride (NaCl), trisodium citrate ($Na_3C_5H_6O_7$), disodium hydrogen phosphate ($Na_2H_2PO_4$) and nanoporous carbon (Lot No. 699632; pore size: 11.2 nm) were used as received from Sigma (singapore). Nanoporous carbon was in detail characterized in our previous publication.²¹ Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions and samples. Hairpin probe oligonucleotide (hpDNA), complementary target oligonucleotide (wild), non-complementary target oligonucleotide (nc) and mutant target oligonucleotide (mutant) were pre-prepared by Sigma. Table 1 lists the sequences of each nucleotide used.

Samples and solutions

PBS buffer, pH7 consisted of 0.01 M phosphate and 0.1 M sodium chloride solution. A 0.01 M solution mixture of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (1 : 1) was used as redox marker. TSC1 buffer, pH 7 was prepared using 0.075 M trisodium citrate and 0.75 M sodium chloride. TSC2 buffer, pH 7 consisted of 0.03 M trisodium citrate and 0.3 M sodium chloride. TSC solutions are commonly used as the buffer solutions in hybridization procedures. All DNA solutions were prepared in TSC1 buffer. Nanoporous carbon was dispersed in deionized water to form a 1 mg mL⁻¹ suspension. A fresh suspension is prepared monthly to ensure consistency in the results measured.

Apparatus

Impedimetric and cyclic voltammetric measurements were carried out using Autolab 302 electrochemical analyzer (Eco Chemie, The Netherlands) operated by the GPES software. The DEP electrodes used were comprised of a three electrodes system: working electrode (carbon paste), counter electrode (carbon paste) and reference electrode (Ag/AgCl). Thermo Shaker (Model. TS-100) from BIOSAN was used in the temperature controlled incubation steps.

Procedure

EIS measurements were performed for: 1) Bare DEP electrode. 2) Nanoporous carbon modified DEP electrode. 3) hpDNA Probe modified DEP electrode. 4) Target DNA hybridized DEP electrode. Cyclic voltammetries were performed in steps 1 and 2.

Specific details on the preparations, modifications and hybridization of the DEP electrode at each step is further described in the respective sections below.

Preparation of nanoporous carbon modified DEP electrode

3 μL of nanoporous carbon suspension were deposited on the working electrode, left to dry and gently washed with deionized water to remove any unabsorbed material.

Preparation of hpDNA probe modified DEP electrode

3 μL of the hpDNA probe solution were deposited on the nanoporous carbon modified DEP electrode and left to dry at 60 °C for 15 min. The electrodes were then washed in TSC2 at 25 °C under stirring for 5 min. The washing step was repeated twice with fresh TSC2 each time. This was to ensure that any excess or physically unabsorbed hpDNA sequences were removed from the electrode surface.

Hybridization with DNA target

Hybridization of hpDNA probe and target DNA sequences are carried out by incubating hpDNA modified DEP electrodes in an eppendorf tube containing the specific DNA target and left for 40 min at 55 °C under stirring. The electrodes were then washed in TSC2 buffer at 42 °C for 10 min under stirring. This was repeated twice using new TSC2 each time. The total volume used in all incubation steps was 100 μL. A schematic of the protocol is given in Scheme 1.

EIS and CV measurements

All measurements were performed with the Autolab potentiostat using a mixture of $K_3Fe(CN)_6/K_4Fe(CN)_6$ as the redox marker. EIS measurements were carried out for a range of frequencies from 10 KHz to 0.05 Hz with amplitude of 10 mV. The results obtained were presented as Nyquist plots (Z' against $-Z''$). A Randles equivalent circuit [$R_1(Q[R_2W])$] was chosen to fit the obtained data.

Scheme 1 Preparation of DEP chips: immobilization of hairpin probe DNA and hybridization with DNA target sequences.

Fig. 1 Comparison of impedimetric measurements between bare DEP-chip (purple color) and nanoporous carbon modified DEP-chip (black color). Measurements were performed in $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ 10 mM in PBS, pH 7. Inset: Randles equivalent circuit.

Results and discussion

The behavior and suitability of nanoporous carbon as sensing platform in the analysis of DNA sequences was studied using electrochemical impedance spectroscopy as the detection technique. The bare electrode surface was first modified with nanoporous carbon and the impedimetric signal was recorded. In Fig. 1 the Nyquist plots obtained for the bare DEP chip (purple color) and the nanoporous carbon modified electrode (black color) are represented.

The Randles equivalent circuit $[R_1(Q[R_2W])]$ used for the data fitting is given in the inset. In the circuit the electrolyte solution resistance (R_1) is in series with a parallel RC element. This consists of a constant phase element (Q), the Warburg impedance (W) and the charge transfer resistance (R_2). We focus on R_2 (diameter of the semicircle in the Nyquist plot) which denotes the charge transfer resistance of the redox marker between the solution and the electrode surface.^{10,11} Therefore, by monitoring the changes in R_2 we can obtain information about the different steps of the biosensing. From Fig. 1 it is clear that the nanoporous carbon gives a much smaller and almost negligible semicircle in the Nyquist plot as compared to the bare DEP-chip, indicating a lower charge transfer resistance and higher electron transfer rate for nanoporous carbon. This result is in agreement with earlier works where nanoporous carbon was found to have a fast heterogeneous electron transfer rate in the presence of the same redox marker.²¹ This behavior can be due to the increased surface area of the nanoporous material.

After the impedimetric characterization, the electrode surface was modified with hairpin DNA probe (hpDNA) sequences. Nyquist plot obtained for EIS measurements are shown in Fig. 2A, B and C (red color). A much higher charge transfer resistance compared to nanoporous carbon modified DEP-chip (larger diameter in the Nyquist plot) was observed. This increase is generated by the introduction of an additional layer which carries a negatively charged DNA backbone. The repulsion between the latter and the negatively charged redox marker $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ results in the increase of R_2 .²⁹

Detection of DNA sequences involves the final step of the protocol: hybridization of the hairpin DNA probes with target

Fig. 2 Nyquist plot for nanoporous carbon (black), hpDNA (red), DNA target (blue) for three different hybridization experiments. A) Complementary target DNA sequences. B) Non-complementary target DNA sequences. C) Mutant target DNA sequences. Concentration of hpDNA: $10 \mu\text{mol L}^{-1}$; concentration of DNA target: 3 nmol L^{-1} . Measurements were performed in $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ 10 mM in PBS, pH 7.

DNA sequences. Different target DNA molecules at the same concentration were used to observe if distinctive responses could be obtained with the nanoporous carbon platform: complementary, non-complementary and mutant (1 base-pair mismatch). Fig. 2A shows that in the presence of complementary DNA target sequences (blue color), an increase in R_2 is recorded. This is because upon addition of the complementary target DNA strands, hybridization between the target and the probe DNA sequences occurs and a double stranded DNA is formed on the electrode surface.²⁹ The formation of this double layer, together with the increased number of negatively charged phosphate groups gives rise to greater like-charge repulsion towards the

Fig. 3 Optimization of hpDNA concentration. Concentration range from 0.1 $\mu\text{mol L}^{-1}$ to 20 $\mu\text{mol L}^{-1}$.

redox marker and therefore, a greater charge transfer resistance.²⁹ When either a non-complementary sequence (blue color in Fig. 2B) or a sequence with 1-mismatch (blue color in Fig. 2C) was employed in the hybridization step, the above mentioned increase in R_2 was not observed, thus confirming that hybridization did not take place.

In order to obtain reliable EIS measurements, it is crucial to ensure that the hpDNA probe sequences have completely covered the electrode surface. This is to avoid any non-specific adsorption during the hybridization step which would provide a non-specific signal. Hence, an optimization of the concentration of the hpDNA sequences was performed to determine the amount of probes to immobilize on the nanoporous carbon modified DEP-chip.^{30,31} The impedimetric response was studied using a hpDNA concentration range from 0.1 $\mu\text{mol L}^{-1}$ to 20 $\mu\text{mol L}^{-1}$. The obtained results are shown in Fig. 3. The signal is represented as the ratio between the charge transfer resistance of hpDNA modified electrode and the bare electrode ($R_2 \text{ probe} / R_2 \text{ bare}$). A trend could be observed in Fig. 3, where the signal increases with increasing concentration from 0.1 $\mu\text{mol L}^{-1}$ and 10 $\mu\text{mol L}^{-1}$. The highest R_2 variation, corresponding to the electrode surface full coverage was obtained at 10 $\mu\text{mol L}^{-1}$ hpDNA. Therefore this value was selected as the optimized hpDNA concentration to be immobilized on nanoporous carbon modified DEP-chips.

Fig. 4 summarizes results obtained in the hybridization experiment with three different DNA target sequences. Signal

Fig. 4 Comparison of the charge transfer resistance ratios between the different target DNA sequences: complementary, non-complementary and mutant target.

is given as the variation of the target charge transfer resistance relative to the probe one. The discrimination between the completely complementary target and the sequence carrying one mismatch was detectable at 3 nmol L^{-1} .

Conclusions

The impedimetric detection of DNA hybridization and polymorphism was realized for the first time on nanoporous carbon material. The feasibility of nanoporous carbon as sensing platform was demonstrated in the analysis of synthetic oligonucleotides which can be correlated to the development of Alzheimer's disease. After further optimization of the experimental protocol, the incorporation of nanoporous carbon in bioanalytical devices can be considered, in order to develop a universal platform with the general purpose of biomolecule detection.

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