Electrochemical studies of carbon nanotubes, graphenes and layered nanomaterials

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ELECTROCHEMICAL STUDIES OF CARBON
NANOTUBES, GRAPHENES AND LAYERED
NANOMATERIALS**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY

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GRAPHENES AND LAYERED NANOMATERIALS

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**Electrochemical Studies of Carbon
Nanotubes, Graphenes and Layered
Nanomaterials**

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“There’s a way to do it better — find it.”

This quote was attributed to the inventor and research laboratory pioneer Thomas A. Edison, which is the one that close to my heart and guided me through all my PhD study. Looking at this four years journey, it is not only about that PhD certificate, experiments and experience, but also about to explore the meaning of life, the way how I think about it and the way how I do it, just like the words from Thomas A. Edison, *“There’s a way to do it better — find it.”*

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Table of Contents

	Page
Acknowledgement	i
Table of contents	ii-iii
Abstract	iv
List of publications	v-vii
Thesis organization	xiii-ix
List of abbreviations	x
Chapter 1 Objectives and Introduction	1-24
<i>In this Chapter, the objectives of the thesis, history and general properties of carbon nanotubes, graphenes and layered nanomaterials would be outlined.</i>	
Chapter 2 Literature review	25-54
<i>In this Chapter, the properties of carbon nanotubes and graphenes as well as the effects of the impurities and doping, and the electrochemistry performance of 3D layered nanomaterial were reviewed.</i>	
Objective 1: Electrochemical studies on effects of impurities and doping of carbon nanotubes and graphenes	
Chapter 3 Influence of carbonaceous impurities on electrochemistry of carbon nanotubes and graphenes	55-80
<i>In this Chapter, the influence of carbonaceous impurities on the electrochemistry of carbon nanotubes and graphenes towards detection of important analytes was studied.</i>	
Chapter 4 Influence of metallic impurities on electrochemistry of carbon nanotubes and graphenes	81-120
<i>In this Chapter, the influence of metallic impurities on the electrochemistry of carbon nanotubes and graphenes towards oxygen reduction reaction was studied.</i>	

Chapter 5	Influence of doping of graphenes	121-160
	<i>In this Chapter, the influence of doping of nitrogen and boron into graphenes were studied.</i>	
Objective 2: Electrochemical studies of 3D layered nanomaterials		
Chapter 6	Electrochemical studies of 3D layered nanomaterials	161-188
	<i>In this Chapter, the electrocatalytic properties of 3D layered nanomaterials towards either oxygen reduction reaction or hydrogen evolution reaction were studied.</i>	
Chapter 7	Conclusion and Epilogue	189-196
	<i>In this Chapter, a summary of the findings in this PhD thesis and a future perspective for this area of research were described.</i>	
	Appendices	197

Abstract

This thesis investigates the influence of impurities, doping and 3D structure on the properties of the nanocarbons and layered nanomaterials. The study mainly focusing on two objectives, *a) Objective 1: Electrochemical studies on effects of impurities and doping of carbon nanotubes and graphenes, and b) Objective 2: Electrochemical studies on 3D layered nanomaterials.*

The thesis will begin by introducing the history and development of carbon nanotubes, graphenes and layered nanomaterials. Then the structures, fundamental properties and some electrochemical properties of the aforementioned nanomaterials were introduced. Later on, a literature review will be shown to reader for the recent development that relates to the objectives.

After the introduction on recent progress that relates to the objectives, detailed results of the purposed objectives will be presented to reader. For **objective 1**, the effects of the carbonaceous impurities, metallic impurities and doping will be shown by varying different factors of the samples and indicate that both of the impurities and doping can influence the properties of the sample nanocarbons. In case of **objective 2**, the popular layered nanomaterials were coated/grown onto the 3D support and the electrochemical studies were performed and showing their electrocatalytic properties toward important reactions such as oxygen reduction reactions and hydrogen evolution reactions.

List of publications

1. Lu Wang, Adriano Ambrosi, Martin Pumera, Metal-Free” Catalytic Oxygen Reduction Reaction on Heteroatom-Doped Graphene is Caused by Trace Metal Impurities, *Angew. Chem. Int. Ed.* **2013**, 52, 13818. **VIP paper by Wiley (at least 2 reviewers judged this paper as very important). Highlighted as Cover.**
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13. Lu Wang, Zdenek Sofer, Jan Luxa, Martin Pumera, $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ Solid Solutions as Three-Dimensional Electrodes for Hydrogen Evolution Reaction. *Adv. Mater. Interfaces*, **2015**, DOI: 10.1002/admi.201500041.
14. Lu Wang, Colin Hong An Wong, Bahareh Kherzi, Richard D. Webster, Martin Pumera, So-Called “Metal-Free” Oxygen Reduction at Graphene Nanoribbons is in fact Metal Driven, *ChemCatChem*, **2015**, DOI: 10.1002/cctc.201500262.
15. Lu Wang, Chun Kiang Chua, Bahareh Khezri, Richard D. Webster, Martin Pumera, Remarkable electrochemical properties of electrochemically reduced graphene oxide towards oxygen reduction reaction are caused by residual metal-based impurities, *Electrochem. Commun.* **2016**, 62, 17.

Thesis organization

This thesis includes **seven (7) Chapters**. The general ideas and intentions of this thesis will be presented in **Chapter 1**. Meanwhile, **Chapter 1** will also provide general introduction to electrochemistry properties of nanocarbon and layered nanomaterials and the effects of electrochemistry properties that caused by either impurities or doping of the mentioned nanomaterials. In **Chapter 2**, the further discussion on previous works, which relate to the effects in electrochemistry properties of carbonaceous impurities, metallic impurities and doping for aforementioned nanocarbons, such as, carbon nanotubes (CNTs), graphenes, and graphene nanoribbons (GNRs), will be shown to reader. Meanwhile, the previous studies on electrochemistry properties of 3D coated layered nanomaterials, including graphenes and transition metal dichalcogenides (TMDs), will also be presented to reader. A collection of scientific research towards the purposes that established in **Chapter 1** will be shown in **Chapter 3-6**, to let reader further understand the aims and motivations of this thesis.

In detail, **Chapter 3** will present the effects on electrochemistry properties of carbonaceous impurities within carbon nanotubes (CNTs), and graphenes. Similar to **Chapter 3**, **Chapter 4** will discuss the influence of metallic impurities on electrochemistry properties of CNTs, graphenes, and GNRs. Then the studies on effects of heteroatom doped graphenes will be shown in **Chapter 5**. Subsequently, interesting electrochemical studies on 3D coated graphenes and TMDs is presented in **Chapter 6**.

A conclusion and perspective of the work presented in this thesis will be shown in **Chapter 7**.

The published version of the results shown in **Chapter 3-6** are shown in **Appendices**.

Index of Abbreviations

°C	Degree centigrade
at%	Atomic percentage
BPPG	Basal Plane Pyrolytic Graphite
CrG	Chemically Reduced Graphene Oxide
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
DMF	<i>N,N</i> -Dimethylformamide
EDX	Energy Dispersive X-ray Spectroscopy
ErG	Electrochemically Reduced Graphene Oxide
EPPG	Edge Plane Pyrolytic Graphite
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
GC	Glassy Carbon
GeO	Graphene Oxide
GiO	Graphite Oxide
HOPG	Highly Ordered Pyrolytic Graphite
hr	Hour (time)
LSV	Linear Sweep Voltammetry
min	Minute (time)
mM	Millimolar
nm	Nanometer
PBS	Phosphate Buffer Solution
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
wt%	Weight Percentage

Chapter 1

Objectives and Introduction

1.1	<i>Objectives of the thesis</i>
1.2	<i>Discovery of carbon nanotubes, graphenes and layered nanomaterials</i>
1.3	<i>General properties of carbon nanotubes, graphenes and layered nanomaterials</i>
1.4	<i>Electrochemistry properties of carbon nanotubes, graphenes and layered nanomaterials</i>

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1.1 Objectives of the thesis

Recently, nanocarbons and layered nanomaterials attracted more and more attentions, and considered to be the poster child in nanotechnology area. The nanocarbons and layer structured nanomaterials in this thesis mainly include carbon nanotubes (CNTs), graphenes and transition metal dichalcogenides (TMDs). As the unique structure of these nanomaterials, they usually have large surface area and some specific electrochemistry properties. The detailed discussion will be presented in following paragraphs.

Earlier studies showed that the carbon nanomaterials, such as carbon nanotubes, graphenes, and graphene nanoribbons (GNRs) have remarkable electrocatalytic properties and claimed as their own inherent properties without any further studies. Since then, the defect sites and edge planes are considered as the active sites which are responsible for the enhancement of observed electrochemical behaviors. In this case, the defects information can be obtained from Raman spectrum and a I_D/I_G ratio, which can generally represent the ratio of defects over graphitic structure in unit area, is always to be calculated and compared. However, it is not sufficient to explain that the defects and edges are the only factor for less catalytic electrochemical behaviors for some analytes or reactions. Then the detailed discussion will be presented later to show that the actual causes of those inherent properties are the impurities or doping of the materials, such as carbonaceous impurities, metallic impurities and heteroatom doping. Therefore, it is important to compare the electrochemical behaviors of carbon nanomaterials modified electrode with similar electrode that modified with appropriate impurities and relative “pure” reference materials.

Similar to graphene's structure, layered transition metal dichalcogenides (TMDs), another group of layered nanomaterials, whose formula is MX_2 , where M is a transition metal (i.e., Mo, and W) from groups 4-10 and X is a chalcogen (i.e., S, and Se), recently showed promising electrocatalytic properties in clean energy production area. However, there are several kinds of TMDs, ranging from true metal (i.e., NbS_2 , and VSe_2), to semi-metals (i.e., TiSe_2 , and WTe_2), to semiconductors (i.e., MoS_2 , and WS_2), to insulators (i.e., HfS_2). Unfortunately, most of the layered nanomaterials were studied under 2D conditions which basically based on the drop cast method prepared electrode and not much study had been done on 3D conditions/samples. Compared with the 2D conditions, on 3D conditions/samples, a much larger surface area (with same dipped volume to electrode) would be provided which is preferred in case of energy production and storage area. Then the detailed discussion will be presented later to show the studies of layered nanomaterials under 3D conditions.

Therefore, this project has two objectives aiming at addressing and improving the mentioned research areas. The two objectives are shown in Figure 1.1 and detailed discussion will be shown in **Chapter 2**.

Figure 1.1 Challenges and objectives for this project.

Objective 1: Electrochemical studies on effects of impurities and doping of carbon nanotubes and graphenes

Carbon nanomaterials, such as carbon nanotubes (CNTs), graphenes, and graphene nanoribbons (GNRs), showed excellent properties, especially for the electrical conductivity which make them able to be used as an electrode substrate and studied via voltammetric methods. The aforementioned carbon nanomaterials showing promising electrocatalytic properties, higher sensitivity, lower detection limits and enhanced signals, but only little explanation has been given to explain these excellent electrochemical properties.

Later studies showed that the defect sites and edge planes in carbon nanomaterials are acting as active sites for those excellent electrochemistry properties. However, it is still not sufficient to explain all those behaviors and there are always some exceptions. Then these exceptions were found to be influenced by the impurities within the materials. These impurities were mainly coming from two sources, one is added during manufacturing process, and the other one is coming together with the starting materials. These impurities can contribute up to 2 wt% of the materials and some of these impurities, such as Ni, Co, Fe, Mn, and amorphous carbon can strongly influence the electrochemistry properties of the material and show electrocatalytic properties towards some analytes or reactions. Unlike impurities which are not intend to add, doping is another type of “impurities” that is added into materials on purpose. Doping to carbon nanomaterials means introducing foreign atoms (i.e., N, S, B, and P) to the carbon structure, which can do either positive or negative influence to the doped materials on electrochemistry properties. It has already been shown that, the doped carbon nanomaterials, such as nitrogen doped CNTs, sulfur doped graphenes, and

nitrogen doped GNRs were electrocatalytic to some important reactions, for instance, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER).

As such, it is important to investigate the actual reason for the electrocatalytic properties that performed by carbon nanomaterials. In addition, such amount of the impurities (few wt% of the material) clearly indicates the lacking of an efficient purification method that can effectively remove the impurities shown in materials.

The research direction for this objective will be shown in **Chapter 3** to **Chapter 5**.

Objective 2: Electrochemical studies of 3D coated layered nanomaterials

Nanocarbons, such as, carbon nanotubes (CNTs), graphenes, and graphene nanoribbons (GNRs), showed promising electrocatalytic properties in the field of energy storage and energy production, for instance, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Layered transition metal dichalcogenides (TMDs), such as MoS₂, MoSe₂, WS₂, and WSe₂, exhibited excellent electrocatalytic properties towards HER. However, most of the previous studies are focusing on the nanomaterials under 2D conditions. The studies on electrochemistry of 3D coated layered nanomaterials (i.e., graphene and TMDs) with larger active surface area remain unclear.

As such, it is necessary to carry on further study on such potential layered nanomaterials under 3D conditions in electrochemistry area. Since under 3D conditions, the product and electrolyte could be influenced by not only the deposited catalysts but also the structure of 3D support, such as produced H₂ gas was trapped in porous structure of the foam which may further result in a decreasing surface area during the measurement. Furthermore, in such fast developing nanotechnology area, the electrochemistry properties of these high potential layered nanomaterials will be important and necessary to explore as much as possible.

The electrochemical studies on 3D coated layered nanomaterials are shown in **Chapter 6.**

1.2 Discovery of carbon nanotubes, graphenes and layered nanomaterials

The buckminsterfullerene C_{60} was first discovered by Smalley and co-workers in 1985, this brand new C_{60} consists of 32 faces and 60 vertices.¹ However, after several attempts, these carbon spherical structures exhibited really poor electrical conductivity which makes them impossible to be considered as a kind of potential material for electrode surface.² This entire situation has been changed since 1991 when Iijima re-discovered the carbon nanotubes (CNTs).³ Even though CNTs were considered as a tubular structured fullerene that the walls are hexagonal carbon⁴, they do have one of the most important property that fullerene does not have, excellent electrical conductivity, which makes CNTs able to be considered as a material for electrode surface⁵. Subsequently, the single wall CNTs were discovered in 1993⁶ which can be generally described as seamlessly “rolled-up” graphite sheets.

Graphene, which was first described by Boehm *et al.* in 1986 as a single graphite-like layer of carbon with infinite size.⁷ Then the term “graphene” has been used as description of, for instance, graphite layers, carbon sheets, and carbon layers. After 11 years, the IUPAC has formally defined the term “graphene” as “a single carbon layer of graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size”.⁸ However, because of graphene’s thermodynamically instability^{9,10}, it will convert itself to some other carbon nanostructures, such as CNTs and fullerenes under ambient conditions. Therefore, graphene was considered as a hypothetical material until Geim and Novoselov successfully obtained the graphene via micromechanical exfoliation of highly oriented pyrolytic graphite¹¹ and open the new gate of research work on graphenes.

Graphene nanoribbons (GNRs) which were first introduced in 1996 by Fujita and co-workers as a theoretical model.¹² Similar to graphene, GNRs can be considered as ultra-thin width strips of graphene which also consist of sp^2 hybridized carbon framework. Consequently, the real GNRs were successfully synthesized from graphite in 2008 by Li *et al.*¹³ and later in 2009, Both Tour's group¹⁴ and Dai's group¹⁵ showed their methods to synthesis GNRs from unzipping CNTs. The research gate of GNRs will not be opened without these scientists' great contributions and recently works on GNRs have already been shown lot of remarkable properties.¹⁶⁻¹⁹

Figure 1.2 General representative structures for carbon nanotube, graphene and graphene nanoribbon.

Since 400 C.E., When the Mayans first obtained dyes by using layered clays, people start looking into the properties of layered materials. Since then, the layered materials start

to be studied in scientific area, to find out the laminar structures of layered material, to understand the properties of layered material, and eventually to exfoliate three dimensional layered materials into individual two dimensional few layers or single layer nanomaterials, where the term “nano” refers to the thickness magnitude of the exfoliated layers.

Layered material can be defined as solid with weak out-of-plane, van der Waals bonds but strong in-plane chemical bonds.²⁰ Such material consists of two dimensional platelets which are weakly stacked to form a three dimensional structure. The most famous example of the layered materials is graphite which basically consists of weakly stacked monolayer graphenes. Not only atomically thin hexagonal sheet graphenes²¹⁻²³ belong to family of layered nanomaterials, but also some transition metal dichalcogenides (TMDs),^{24,25} which consist of a metal atom plane together with two planes of chalcogen and have near identical structures, are members of family of layered nanomaterials.

Two dimensional layered nanomaterials have attracted vast amount of interest due to their unique structure dependent chemical and physical properties, and their potential applications. The properties of these layered nanomaterials can be tailored via both chemical and physical treatments. Layered nanomaterials, such as graphenes, GNRs, and TMDs have showed promising properties towards the field of sensing²⁶⁻³² energy storage³³⁻³⁷ and energy production³⁸⁻⁴⁵.

1.3 General properties of carbon nanotubes, graphenes and layered nanomaterials

Since the discovery of carbon nanotubes (CNTs), graphenes, and graphene nanoribbons (GNRs), due to their exceptional electronic, mechanical, and physical properties, they have attracted vast amount of attentions from industrial and scientific communities.

Carbon nanotubes, which can be considered as rolled up graphene sheets, can be either metallic or semiconducting which mainly depend on the angle at which the graphene sheets are rolled (e.g. zigzag, armchair and chiral structure)⁴⁶ and the electrical conductivity of CNTs was reported as 1,000x higher than the copper wires.⁴⁷ In addition, CNTs also exhibit excellent thermal stability up to 2800 °C under vacuum condition and perform much better thermal conductivity than diamond and graphite under ambient condition.⁴⁸ On the other hand, CNTs are also known as a kind of material with high stiffness and mechanical strength which are caused by the strong sp^2 covalent bonds between carbon atoms and make the CNTs can afford strain up to 25 GPa without fracture or deformation.⁴⁹

Graphene can be considered as a single graphite layer which consists of sp^2 hybridized carbon atoms in a hexagonal lattice. Similar to CNTs, graphene is another allotrope of carbon and exhibit unique properties, such as excellent thermal and electrical conductivity, mechanical strength, optical transparency, and large surface area ($2630 \text{ m}^2\text{g}^{-1}$).^{22,50} The high electrical conductivity of graphene is mainly caused by the delocalization of π bonds, which result in high electronic mobility of graphene at room temperature and also can afford much higher current density than copper.^{51,52,53} The thermal conductivity of graphene has been reported as approximately $5,000 \text{ Wm}^{-1}\text{K}^{-1}$, which performs way much better than other

carbon allotropes, such as CNTs and diamond.⁵⁴ The high optical transparency (absorb 2.3% of visible light) of graphenes also perform remarkably based on the atomically thin single layer graphene.⁵⁵ The properties of graphene can be easily tailored by chemical functionalization, such as doping with heteroatoms.^{56,57,58}

Even though graphene exhibits excellent electronic properties, the zero bandgap still limits its potential applications in digital electronics.^{59,60} Graphene nanoribbons (GNRs) which can be considered as strips of graphenes with width of less than 50 nm.^{14,15} Unlike graphenes, GNRs are semiconductors which have a tunable bandgap that can be tailored by the edge (zigzag or armchair) and width of ribbon.^{61,62,63} In addition, the zigzag GNRs are always metallic and armchair GNRs can be either semiconductor or metallic.⁶⁴ Thus, the developing in GRNs also opened a new gate for the applications of graphenes in the field of electronic devices.

As mentioned previously, transition metal dichalcogenides (TMDs) which have the chemical formula MX_2 , where M is a transition metal (i.e., Mo and W) and X is a chalcogen (i.e., S and Se), consist of similar layered structure (van der Waals force between each layer) to graphene and showed promising properties in lubrication, catalysis and photovoltaic.^{65,66} Popular examples of TMD including MoS_2 and WS_2 which contain sandwich-like layered structure where a metal sub-layer located in the middle and two chalcogen sub-layer located above and below the metal layer and covalently bonded with each other, and have Van der Waals force between each layer. Such special layered structure make the exfoliation become possible and the obtained single/few layer TMDs can be obtained by exfoliation of bulk TMDs.

Such atomically thin TMD layers provide much more and interesting properties than the bulk TMDs.^{67,68}

1.4 Electrocatalytic properties of carbon nanotubes, graphenes and layered nanomaterials

The remarkable physical and chemical properties shown by the carbon nanomaterials also build a bright future in the field of electrochemistry and attract vast amount of attentions from scientific community to utilize them in electroanalysis.

Since 1996, Britto *et al.* first demonstrated the application of CNTs in electrocatalyzing dopamine with an electrode made from a CNTs paste⁶⁹ and perform a faster and redox electrochemical behavior which compared with a graphite electrode. Not only dopamine showed interesting electrochemical behavior, but also ascorbic acid showed a quasi-reversible electrochemical behavior where only showed irreversible signal on graphite electrode. In addition, this work pioneered the methodology that using layered carbon nanomaterials modified electrode.

Then in 2002, Wang *et al.* applied a new methodology to study the electrochemistry properties of CNTs which modified glassy carbon (GC) electrode with CNTs. The CNTs were first to prepared in suspensions with non-polar organic solvent like dimethylformamide due to their highly hydrophobic properties. Then 1 μ L of the prepared suspensions was directly casted onto the GC electrode, the formed suspension layer was allowed to evaporate and resulting in a layer of sample onto the GC electrode.

Later on, more and more good news have been reported to support carbon nanomaterials, such as CNTs, graphenes, and GNRs are the new generation electrocatalysis for lots of important analytes and reactions, such as epinephrine,⁷⁰ insulin,⁷¹ hydroquinone,^{72, 73} homocysteine,⁷⁴ nucleic acids,⁷⁵ nitric oxide,⁷⁶ N-acetylcysteine,⁷⁷

serotonin,⁷⁸ acetaminophen,^{14, 79} carbohydrates,⁸⁰ uric acid,⁸¹ glucose,⁸² hydrazine,⁸³ hydrogen peroxide,⁸⁴ L-glutathione,⁸⁵ trinitrotoluene,⁸⁶ NADH,⁸⁷ carbamazepine,⁸⁸ hydrogen sulfide,⁸⁹ morphine,⁹⁰ oxygen reduction reaction (ORR)⁹¹⁻⁹⁸ and hydrogen evolution reaction (HER).^{99,100} However, such remarkable electrochemistry properties were not really detailed explained and usually considered as their inherent electrochemistry properties.

In order to investigate the reason behind these remarkable electrochemical properties, Compton *et al.* performed the measurement with edge (EPPG) and basal (BPPG) plane pyrolytic graphite electrodes and found that EPPG performs similar to CNTs' electrochemical behavior which indicates that the electrocatalytic properties shown by CNTs were actually caused by the edge-like (defect) structure in CNTs.¹⁰¹ This result also extend to other carbon nanomaterials, such as graphenes.

Defect structures in carbon nanomaterials can enhance the electrocatalytic properties is a good reason for the shown remarkable electrocatalytic properties, but it is still sufficient to explain everything, there are always exceptions that cannot be well explained by defects of the materials. Therefore, the further studies were carried on, and found that there are always significant amount of residual metallic impurities present in the materials. The results indicate that these residual metallic impurities within the material can dramatically enhance the electrocatalytic properties toward analytes and reactions, such as hydrogen peroxide¹⁰², hydrazine¹⁰³, and oxygen reduction reaction¹⁰⁴⁻¹⁰⁶.

Apart from the metallic impurities, carbonaceous impurities were present in the material which can also affect the electrochemical properties of the materials. Pumera *et al.*

showed that carbonaceous impurities, such as amorphous carbon can enhance the electrocatalytic properties by providing large amount of edge plane that can act as active sites for samples.¹⁰⁷

Similar to impurities, doping is another way to tailor the electrical properties of the materials, such as nitrogen doped CNTs,¹⁰⁸ phosphorus doped graphenes¹⁰⁹ and nitrogen doped GNRs⁴⁰. Unlike impurities which are contaminated not on purpose, doping is adding the foreign atoms to the material on purpose. Such doping method can change the electron density of the material which can further tailor the electrochemical properties of the material as well.³⁶

Since the exfoliation of layered transition metal dichalcogenides (TMDs) become possible, more and more TMDs were exfoliated such as MoS₂ and WS₂ which exhibit remarkable electrocatalytic properties, especially for hydrogen evolution reaction (HER).¹¹⁰⁻¹¹⁴ However, such energy related reaction occurs on the surface of the material which in this case a large active surface area is preferred. In order to provide a large surface area, a 3D porous support (i.e., Ni foam and carbon foam) can be used as substrate and provide a large surface condition with coated layered nanomaterials. Moreover, nanocarbons such as graphenes also exhibit attractive electrochemical properties towards energy related reaction, oxygen reduction reaction (ORR).¹¹⁵ Therefore, a study on electrochemistry properties of 3D coated layered nanomaterial would be interesting and useful.

In this project, the influence of carbonaceous and metallic impurities on electrochemistry of carbon nanomaterials (i.e., CNTs, graphenes and GNRs) were further

studied and extended to other important analytes and reactions. The effects of carbonaceous and metallic impurities in carbon nanomaterials were present in **Chapter 3** and **Chapter 4**, respectively. Then the effects of heteroatom doped graphene were shown in **Chapter 5**. Furthermore, electrochemical studies of 3D coated layered nanomaterials were shown in **Chapter 6**.

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Chapter 2

Literature review

2.1	<i>Fundamental electrochemical properties of carbon nanotubes and graphenes</i>
2.2	<i>Influence of impurities on electrochemistry of carbon nanotubes and graphenes</i>
2.2.1	<i>Carbonaceous impurities</i>
2.2.2	<i>Metallic impurities</i>
2.2.3	<i>Doping</i>
2.3	<i>Electrochemical studies of 3D layered nanomaterials</i>

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2.1 Fundamental electrochemical properties of carbon nanotubes and graphenes

Carbon nanomaterials, such as carbon nanotubes (CNTs), graphenes, and graphene nanoribbons (GNRs), have showed remarkably structure induced properties and attract vast amount of interest from both industrial community and scientific community. Figure 2.1 shows some carbon nanomaterials and the area of their potential applications.

Figure 2.1 Some potential electrochemical applications of carbon nanomaterials.

Graphene can be considered as atomically thin two dimensional sp^2 bonded carbon sheet which is generally a single layer of graphite. Such unique structure make graphene exhibits remarkable properties in both physical and chemical field, such as, excellent thermal¹ and electrical conductivity²⁻⁴, mechanical strength⁵, optical transparency⁶, large surface area^{7,8} and remarkable electrochemical properties⁹. The carbon nanotubes (CNTs) can be considered as rolled up graphene sheets and perform excellent electron conductivity and fast

heterogeneous electron transfer rate at the end of tubular structure.¹⁰ Then for graphene nanoribbons (GNRs) which are basically strips of graphenes with tunable width depended bandgap.¹¹⁻¹³ All of these aforementioned nanocarbons exhibit unique properties in the field of electrochemical sensing, supercapacitors, batteries and fuel cells.¹⁴⁻³² The exhibited electrochemical properties are strongly influenced by the structure (defects), functional groups, carbonaceous impurities and metallic impurities.³³⁻⁴¹

Structurally speaking, both of CNTs and GNRs can be considered as different forms of graphene; CNTs can be considered as rolled-up graphenes along different directions, and GNRs can be considered as strips of graphenes, which all contain both edge plane (defect) and basal plane carbon structure. As Compton *et al.* have already showed the measurement with edge (EPPG) and basal (BPPG) plane pyrolytic graphite electrodes and found that EPPG performs similar to CNTs' electrochemical behavior which indicates that the electrocatalytic properties shown by CNTs were actually caused by the edge like structures in CNTs. This result further confirmed that the edge sites (defects) are much more electroactive than the basal plane of carbon structure and can also extend this result to other nanocarbons, such as graphenes and GNRs.

In case of the influences of various functional groups, the functional groups of nanocarbons can be considered as the oxygen containing groups at the edge sites/defects of the carbon nanostructure. It has been already proved that the oxygen containing groups can either enhance the heterogeneous electron transfer rate^{40,42} or inhibit the heterogeneous electron transfer rate³⁹. On the other side, the oxygen containing groups can not only affect the heterogeneous electron transfer rate, but also can influence the adsorption and desorption

of molecules. It has been shown by Pumera *et al.* that, in case of graphene, the adsorption of β -nicotinamide adenine dinucleotide (NAD^+) can be strongly influenced by the carboxylic groups which usually present on the edge site or defect of the graphene framework.⁴³

Although several factors have been shown can influence the electrochemistry properties of the carbon nanomaterials, there are always some instances that the response of nanocarbon modified electrode behaves quite different from the previous findings. Even compared with both edge plane pyrolytic graphite (EPPG) electrode and basal plane pyrolytic graphite (BPPG) electrode.⁴⁴ Such result implies that apart from the electroactive site that produced by edge site (defects), there should be another factor that can influence the electrochemistry properties of the nanocarbons: the presence of impurities.

2.2 Influence of impurities on electrochemistry of carbon nanotubes and graphenes

It will not be surprise to say CNTs contains impurities, as in order to prepare CNTs the arch evaporation based growth or chemical vapour deposition (CVD) would be employed, and the target carbon structure will be formed on the metal catalysts (i.e., Ni, Fe, Co, Mo and their mixtures). During this synthesis process, the diffusion of dissociated carbon from the precursor will not only form the tubular structure, but also enclose the metal catalysts into the nanotubes and present as metallic impurities.^{45,46} Moreover, during this synthesis process, some other kind of nanocarbon can be formed as well, such as nanographite⁴⁷ and amorphous carbon⁴⁸ which can be considered as carbonaceous impurities. The prepared CNTs can contain up to 30 wt% of carbonaceous impurities as well as metallic impurities.^{49,50}

Meanwhile, the GNRs which commonly synthesized via chemically unzipping CNTs into nanoribbons by applying permanganate to CNTs.⁵¹ During this treatment, one side of CNTs was oxidized and unzipped, and lots of manganese based impurities will also be introduced as metallic impurities. Additionally, since GRNs were prepared from CNTs, most of the impurities present in CNTs will also transfer to the prepared GNRs.

It is well known that, even the graphite contains significant amount of metallic impurities with up to 2 wt% of the material, which means the nanocarbons (i.e., graphene) that employ graphite as starting material will contaminated with these metallic impurities at the beginning. The most widely used method to prepare the graphene is to chemically oxidize graphite into graphite oxide (GiO) and the prepared graphite oxide can be mechanically, thermally, chemically and electrochemically treated into the reduced graphene oxide (rGO).

In order to oxidize the graphite, several methods can be applied, such as Staudenmaier method⁵² (using potassium chlorate and sulphuric acid), Hofmann method⁵³ (using fuming nitric acid and non-fuming nitric acid), and Hummers method⁵⁴ (using potassium permanganate and sodium nitrate) which mainly differ on used oxidizing agent. Due to the highest oxygenated level and faster synthesis process, Hummers method is the most popular method for preparing GiO. However, Hummers method also comes with a problem which will introduce a significant amount of manganese based impurities (thousands of ppm)³⁶ into the prepared GiO. Then in order to obtain the rGO, the GiO can be reduced by several methods, apart from the mechanically, thermally and electrochemically reduction which will not add more impurities, the chemically reduction, especially with hydrazine will also accidentally introduce the nitrogen into the prepared rGO and the final product rGO will also be contaminated with all mentioned impurities.

Therefore, the aforementioned nanocarbons do contain a significant amount of the impurities and all of these impurities can be divided into two distinct classes: carbonaceous impurities and metallic impurities. The influence of the present impurities on electrochemistry properties of the nanocarbons will be reviewed in the sub-chapters.

2.2.1 Carbonaceous impurities

Carbon based impurities, such as nanographite and amorphous carbon are hard to be completely removed due to the similarity in their elemental compositions. There are some purification methods were that can be applied to CNTs, for instance, ultrasonication assisted microfiltration⁴⁷ and conventional acid washing treatment⁴⁸, and the 90% purified CNTs can be obtained⁵⁰.

Figure 2.2 Schematic representation of CNTs and nanographite impurities. Reproduced from reference 57.

On the other hand, the present carbonaceous impurities also provide better reactivity owing to the defects and dangling bonds of impurities (Figure 2.2). It has been showed that

the edge sites (defects) perform faster heterogeneous electron transfer than the basal plane of the carbon structure.^{55,56}

In order to study how carbonaceous impurities are able to influence the electrochemistry properties of the carbon nanomaterials, such as CNTs. The impurity free CNTs (CNT-pure) were employed with controlled amount of carbonaceous impurities, and the electrochemistry performance can be then measured. Since the carbonaceous impurities, such as nanographite contains significant higher amount of edge sites than CNT-pure, which can also be considered as the higher amount of electroactive sites were added into the CNT-pure. As such, the results evidently indicate that, the enhanced heterogeneous electron transfer rate was observed along with the increasing amount of nanographite introduced.⁵⁷ In addition, the CNT-pure with 25 wt% of nanographite showed similar heterogeneous electron transfer to the CNT-pure with 100 wt% of nanographite. This result also indicates that even the presence of 25 wt% of nanographite can govern the electrochemical performance of CNTs.⁵⁷ Furthermore, it has been shown that, CNTs can contain 10-40 wt% of the nanographitic impurities⁴⁹ which implies the observed electrochemical performance was strongly influenced by the present carbonaceous impurities. Several reports have showed that the observed electrochemical response of a wide range of analytes, such as hydroquinone,⁵⁸ signal transducers and enzyme co-factors,⁵⁹ azo compounds⁶⁰ and organic hydrazines⁶¹ can be actually caused by the present carbonaceous impurities.

Similarly, another type of carbonaceous impurities, amorphous carbon can also be studied in same method by introducing varies amount of amorphous carbon into the CNT-pure. In this case, a poorly graphitized carbon black was employed to mimic the amorphous

carbon impurities.⁶² Same result was obtained; the heterogeneous electron transfer rate was enhanced with the increasing amount of introduced amorphous carbon impurities. A 16x higher heterogeneous electron transfer rate was observed after 30 wt% of amorphous impurities were introduced to the CNT-pure. Additionally, from the previous reports, the amorphous carbon impurities in carbon nanomaterials also play the domain electrocatalytic roles (Figure 2.3) in acetaminophen,^{63,64} cytochrome *c*,⁶⁵ hydroquinone⁶⁴ and NADH.⁶⁴

Figure 2.3 Electrochemical redox signals of (A) hydroquinone, (B) acetaminophen, (C) NADH at the surface of amorphous carbon(AC), BPPG, EPPG, chemically reduced graphene (CrG) and thermally reduced graphene (TrG) in phosphate buffer solution (pH 7.2). Reproduced from reference 64.

2.2.2 Metallic impurities

Before carrying on any further studies on the effects of present metallic impurities in nanocarbons, it is always important to know what kind of metallic impurities are there and the amount of them. Unlike the carbonaceous impurities, which have similar elemental compositions to nanocarbons, metallic impurities are different elements which are able to be detected by many techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray fluorescence analysis (XRF), neutron activation analysis (NAA), energy dispersive X-ray spectroscopy (EDX) and inductively coupled plasma mass spectrometry/optical emission spectrometry (ICP-MS/OES). However, techniques including XPS and EDX are surface analysis techniques and cannot detect the metallic impurities even around several wt% of the material. Therefore, a technique with higher detect limitation would be preferred, such as ICP-MS/OES which can detect the metallic impurities even at ppb level (0.01 wt%).

As metal based chemicals were employed in most of the synthesis methods for aforementioned nanocarbons, it will not be surprised that the prepared carbon nanomaterials contain significant amount of metallic impurities. The common purification method is oxidative treatment which treats the material with strong mineral acid and washed repeatedly at high temperature. Since usually metals are soluble in acidic solution, the metallic impurities would dissolve into the acidic solution and lower the amount of metallic impurities. Sometimes the metallic impurities could be enclosed into the tubular structure or sheathed behind graphene layers which could cause the metallic impurities cannot be removed completely. Such purification method could decrease the amount of metallic impurities to 1-10 wt%.⁶⁶

The electrochemical studies can be then carried on when the compositions of the material were obtained. The electrochemical properties of many metal based catalysts have been studied for long time and well recognized. In addition, even the purified carbon nanomaterial, such as GNRs, which contains low amount of metallic impurities (11.9 ppm of Mn based impurities)⁶⁷, can still enhance the electrocatalytic properties of GNR towards oxygen reduction reaction (ORR). Such result suggest that the minute amount of electrocatalytic metal based impurities can still cause the overlapping of diffusion layers and form a macroelectrode system.⁶⁸⁻⁷⁰ As such, the observed electrochemical performance of the nanocarbons can be strongly influenced by the present electroactive metallic impurities.

Compton and co-workers³⁴ first brought this metallic impurities issue to the scientific community. A study on oxidation of hydrazine was performed and the result indicates that CNTs exhibit a quite different electrochemical response from EPPG electrode. Interestingly, the Fe³⁺ modified electrode also exhibited a similar oxidative wave towards hydrazine. Such result (Figure 2.4) suggests that the electrochemical response of both CNTs and Fe³⁺ were in good agreement with each other and showing that the present Fe based impurities of CNTs were responsible for the enhanced electrochemical properties towards the oxidation of hydrazine. Later in this research area, more and more reports showing the electrocatalyzing of important analytes (i.e., hydrogen peroxide,^{71,72} amino acids,⁷³ glucose⁷⁴ and cumene hydroperoxide⁷⁴) by nanocarbons was actually caused by the present metallic impurities.

Figure 2.4 Cyclic voltammogram of electrochemical oxidation of hydrazine in phosphate buffer solution (pH 7.2). Reproduced from reference 34.

Meanwhile, there are several kinds of metallic impurities present in the prepared nanocarbons,^{75,76} which means the metallic impurities could also contain different metallic components. In order to study the effects of multi-component metallic impurities, the hydrogen peroxide was employed as the analyte and measured on CNTs which contain multicomponent metallic impurities with different ratio of iron. The result indicates that, the even percentage of iron down to 1%, such mixed system can still influence the electrocatalytic properties towards hydrogen peroxide.^{66,72}

Apart from the important analytes, the metallic impurities were able to catalyze important reactions in energy storage area as well, such as oxygen reduction reaction (ORR)^{36,37,38}. Oxygen reduction reaction is one of the most important reactions in fuel cell, the

efficiency for reducing oxygen directly limits the working efficiency of fuel cell.⁷⁷ Currently, the most efficient and widely used catalyst for reducing oxygen is platinum which has limited availability and high cost. Recently, nanocarbons including CNTs, graphenes and GNRs were proposed to be the next generation catalysts for important reactions, such as ORR. There are large amount of reports showing that heteroatom doped graphenes could dramatically enhance the electrocatalytic properties toward ORR.⁷⁸⁻⁸¹

Several studies have been done on the effects of metallic impurities in nanocarbons towards ORR.^{36,37,38} In order to study the effects, the ICP-MS were used to obtain the detailed composition information of nanocarbons. In case of the graphenes,³⁶ electrocatalytic properties towards ORR at the graphenes prepared via different methods (Staudenmaier method and Hummers method) showing quite different electrocatalytic properties toward ORR. In order to carry on the further studies, ICP-MS was performed to obtain the detailed composition of starting material graphite and different graphenes. Results indicated that all of them do contain some amount of metallic impurities, including Fe, Co, Ni and Mn. Thus electrochemical measurements were performed on different graphenes and impurities, the results were recorded and shown in Figure 2.5. Clearly, among all present metallic impurities, only the manganese based impurities (likely MnO_2) showing the best electrocatalytic properties and well agreed with the graphenes prepared via Hummers method contain lots of manganese based impurities. Such result suggests that the present manganese based impurities are responsible for the enhancement in electrocatalytic properties towards ORR and similar results also shown with other types of nanocarbons, such as CNTs³⁷ and GNRs³⁸. Meanwhile, the ICP-MS result also further confirmed that the impurities coming from both

starting material and synthesis method. Moreover, graphenes prepared from Hummers method will be contaminated with thousands ppm of Mn based impurities which can dramatically influence the electrochemistry properties of graphenes.

Figure 2.5 Electrochemical reducing oxygen at the surface of present metallic impurities, graphenes and bare glassy carbon electrode. Reproduced from reference 36.

In summary, the term “inherent” for the enhanced electrochemistry properties from nanocarbons would be preferred to use after carefully purification and characterization. Due

to the similarity in structure of CNTs, graphenes and GNRs, the effects of the carbonaceous and metallic impurities in CNTs could also extend to either graphenes or GNRs.

2.2.3 Doping

In impurities studies, the impurities can be considered as the foreign materials or elements which were accidentally introduced into the materials. On the other hand, the impurities that were introduced into the materials on purposely which can tailor the electronic properties of the material are so called “doping”. Doping of nanocarbons, such as CNTs and graphenes has been studied as a popular method which is able to modify the structures and properties of the aforementioned nanocarbons.

The level of doping, directly relates to the carrier density which is one of the most important factors for the performance of the doped material. Few studies have been done to figure out the factors that can affect the doping level for doped graphenes.^{82,83} Nitrogen doped graphenes which were synthesized via different temperatures were employed. Results suggest that the doping level can be affected by the synthesis temperature, higher doping level (5 at% of N) was obtained by increasing the temperature.⁸² Meanwhile, another doping level study⁸³ was performed by varying the both synthesis temperature and types of precursors (types of graphite oxide). Results (shown in Figure 2.6) indicate that instead of the temperature, the types of precursors do influence the doping level a lot, and the prepared nitrogen doped graphenes contain up to 7 at% of N.⁸³

Figure 2.6 Amount of doped N in graphenes varying with different precursors and temperatures. St represents graphene prepared from Staudenmaier graphite oxide, Ho is graphene from Hofmann graphite oxide and Hu is graphene from Hummers graphite oxide. Reproduced from reference 83.

Several reports showed that the heteroatom (e.g., nitrogen, phosphorus and boron) doped graphenes can dramatically influence the electrochemistry properties of graphenes.⁸⁴⁻⁸⁸ Such dopant can be divided into p-type (electron acceptors) dopant including boron, and n-type (electron donors) dopant including nitrogen and phosphorus. Theoretically, the p-type doped graphenes could inhibit the performance in reduction and enhance the oxidation performance, and similarly the n-type doped graphene would perform oppositely which can enhance the reduction and inhibit the oxidation.^{10,11,12,89} Lots of literatures showed that the n-type doped graphenes, especially for nitrogen doped graphenes can dramatically enhanced the electrocatalytic properties towards ORR by comparing their onset potential for reducing oxygen.¹⁰⁻¹² However, only few reports indicate that the p-type doped graphenes (i.e., boron doped graphene) showing an inhibited reduction reaction (shown in Figure 2.7).^{89,90}

Figure 2.7 Electrochemical behaviors of reducing oxygen at the surface of boron doped graphenes and bare glassy carbon electrode. Reproduced from reference 89.

Herein, clear results have been shown that both impurities and doping can influence the electrochemistry properties of the nanocarbons. The effects of impurities are more specific to one or few analytes and reactions. The doping can tailor the electrochemistry properties of the doped nanocarbons in either an enhanced reduction with inhibited oxidation (n-type) or an inhibited reduction with enhanced oxidation (p-type).

2.3 Electrochemical studies of 3D layered nanomaterials

Layered nanomaterials (i.e., graphenes and layered TMDs) exhibit promising electrocatalytic properties towards energy related reactions, such as oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Such potential nanomaterials have attracted vast amount of attentions in the field of energy storage and energy production. Such energy related reactions do require relative large surface area due to the reactions are occurring on the surface of the catalysts. Thus, a 3D electrode such as Ni foam,⁹¹ carbon foam,⁹² and aerogel⁹³ that deposited with target nanomaterial would be preferred for the studies on energy related reactions.

In the field of energy storage, oxygen reduction reaction is one of the most important reactions which can limit the working efficiency of fuel cell. Since nanocarbons were considered as the next generation catalysts for ORR, several literatures showing that nanocarbons do have dramatically enhancement in electrocatalytic properties towards ORR under 2D conditions (drop cast prepared electrode)¹⁰⁻¹² and only few studies were performed under 3D conditions.^{91,94} Mullen and co-workers prepared a 3D nitrogen doped graphene aerogel decorated with Fe₃O₄ which exhibits promising electrocatalytic properties towards ORR.⁹⁵ Meanwhile, it is well known that nitrogen dopant for graphene is an n-type dopant which can enhance the occurring reduction reaction. Such aerogel with a mixed catalyzing system showing an enhanced onset potential around -190 mV (vs Ag/AgCl) for ORR (Figure 2.8).⁹⁴ Another study has been done by Wang *et al.* with a 3D graphene prepared by depositing graphenes onto the 3D porous Ni foam.⁹¹ The 3D graphenes were then prepared with different deposition time which in this case different number of graphene layers were

coated onto the Ni foam, and the number of layers was further confirmed by the Raman spectra. Results indicate that the 3D support Ni foam does not have electrocatalytic properties towards ORR and the prepared 3D graphenes exhibiting enhanced electrocatalytic properties towards ORR corresponds to increasing number of graphene layers.⁹¹

Figure 2.8. Electrocatalytic properties towards oxygen reduction reaction of the prepared 3D nitrogen doped graphene aerogel. (A) Electrocatalytic properties of 3D nitrogen doped graphene with and without dissolved oxygen, (B) Electrocatalytic properties towards oxygen reduction reaction at 3D N doped graphene with different rotation speed (colored differently). Reproduced from reference 94.

Another important energy related reaction is hydrogen evolution reaction, which basically contains two steps, absorption and reduction of H^+ to $H\cdot$ on catalysts' surface and then recombination of another hydrogen and desorption of formed H_2 .⁹² Recently, layered TMDs, such as MoS_2 ⁹⁶⁻¹⁰⁰ and WS_2 ^{101, 102} showed promising properties towards HER. Unfortunately, number of studies on 3D TMDs is limited.^{92,93,103} A study on 3D MoS_2 and WS_2

were performed by Orme and co-workers who have successfully synthesized the aerogel of both TMDs via freeze dried method.⁹³ However, only 3D MoS₂ was studied by volumetric method and exhibit an enhanced electrocatalytic properties towards HER. Compared with the bare 3D support and the prepared 3D MoS₂ exhibit excellent electrocatalytic properties towards HER and behave close to Pt (shown in Figure 2.9). Another study on 3D MoS₂/rGO hydrogel was done by Liu's group,¹⁰³ the 3D material was prepared by one-pot hydrothermal method and also showing a remarkable electrocatalytic properties towards HER. On the other side, Pumera and co-workers showed another study on 3D M_{1-x}W_xS₂ solid solution, which chemically deposit MoS₂, WS₂ and their mixtures onto the 3D carbon foam. Such study mainly focusing on the electrocatalytic performance of prepared 3D solid solutions towards HER, and interesting results were observed, which indicate an increasing trend in the enhancement of catalyzing HER correlates to increasing amount of W content.⁹²

Figure 2.9 Electrocatalytic properties of prepared 3D support(GMA), first scan of MoS₂, 300th scan of MoS₂ and Pt towards hydrogen evolution reaction. Reproduced from reference 93.

Herein, layered nanomaterials including graphenes and TMDs showed promising properties in energy related field under 3D conditions. Prepared 3D layered nanomaterials not only increase the material's surface area, but also increase the number of active sites (usually defects) which would be one of the most important factors that can influence the efficiency of future applications. Since the number of studies performed under 3D condition is less than 2D condition studies, more 3D studies would be preferred and helpful for such high potential layered nanomaterials.

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Chapter 3

Influence of carbonaceous impurities on electrochemistry of carbon nanotubes and graphenes

3.1	<i>Influence of carbonaceous impurities on electrochemistry of carbon nanotubes</i>
3.1.1	<i>Introduction</i>
3.1.2	<i>Results and discussions for study on acetaminophen</i>
3.1.3	<i>Results and discussions for study on cytochrome c</i>
3.1.4	<i>Experimental</i>
3.2	<i>Influence of carbonaceous impurities on electrochemistry of graphenes</i>
3.2.1	<i>Introduction</i>
3.2.2	<i>Results and discussions</i>
3.2.3	<i>Experimental</i>

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2. Lu Wang, Adriano Ambrosi, Martin Pumera, Carbonaceous Impurities in Carbon Nanotubes are Responsible for Accelerated Electrochemistry of Cytochrome c. *Anal. Chem.*, **2013**, 85, 6195-6197.

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Contributions:

L. Wang conducted most of the experiments. A. Ambrosi and M. Pumera conceptualized and directed the projects. All authors contributed to discussion and writing of the manuscripts.

The influence of carbonaceous impurities, metallic impurities and doping on the electrochemistry of carbon nanotubes (CNTs), graphenes and graphene nanoribbons (GNRs) were well documented for various analytes and reactions, and this will be extended in the **Chapter 3, 4 and 5** to include additional findings.

The applications of these nanocarbons have been extended to several fields, such as elemental chemistry, clinical research and energy related research, which were reported for the remarkable enhancement of signal responses, sensitivity toward the analytes or reactions. All the aforementioned electrocatalytic properties were reported as the inherent electrochemical properties of the carbon nanomaterials.

In **Chapter 3**, the influences of carbonaceous impurities on electrocatalytic performance of CNTs and graphenes towards sensing of various analytes were studied respectively.

In **Chapter 4**, the influences of metallic impurities on electrocatalytic properties of CNTs, graphenes and graphene nanoribbons (GNRs) towards energy related reactions, such as oxygen reduction reaction (ORR), were studied.

In **Chapter 5**, the influence of heteroatom doped graphenes were studied.

Chapter 3, 4 and 5 are the collective work in addressing Objective 1.

Chapter 3.1 Influence of carbonaceous impurities on electrochemistry of carbon nanotubes

3.1.1 Introduction

Carbon nanotubes (CNTs) have attracted vast amount of interest from scientific research community and industry due to their specific properties.^{1,2} CNTs are prepared via metallic catalysts induced growth^{3,4} and during this synthesized process, not only tubular carbon nanostructures are formed, but also carbonaceous impurities are formed, such as nanographite and amorphous carbons.^{5,6,7} Therefore, the as-prepared CNTs contain lots of impurities, ranging from carbonaceous impurities to metallic impurities. For instance, a single wall carbon nanotube sample contains about 30 wt% of carbonaceous impurities and similar amount of metallic impurities^{8,9} and it is really difficult to completely remove the metallic impurities¹⁰ and the carbonaceous impurities from CNTs.⁹

The metallic impurities within CNTs are proved to be responsible for the enhanced electrocatalytic effects towards hydrogen hydrazine¹¹, peroxide¹², halothane¹³, sulphides¹⁴, amino acids¹⁵, glucose¹⁶, organic peroxides¹⁷, L-glutathione¹⁸, even at about 100 ppm amounts¹⁹. Meanwhile, some of catalyzed compounds should not be electrocatalyzed by the metals and thus it would be important to find out that whether CNTs are catalysts or some other impurities. It is important to note that sp^2 hybridized carbon, such as CNTs²⁰, graphenes or graphite have two major structures, sp^2 basal plane and edge plane or defect. In this case, the edges and defect can enhance the heterogeneous electron transfer (HET) rates and the basal plane shows slow HET rates towards lots of compounds^{21,24} and CNTs' surface contains most basal plane and the electroactive edges or defects are negligible on surface.

Nanographite impurities, which consist high ratio of edges compared to the sp^2 basal planes.²⁵ Interestingly, it has been found that the onion-like nanocarbon²⁶ impurities, which also contain large amount of edge sites in CNTs, were responsible for electrocatalytic performance of nicotinamide adenosine dinucleotide (NADH), ferro/ferricyanide, epinephrine, cysteine, glutathione and norepinephrine.²⁶ Furthermore, nanocarbon impurities within CNTs were also responsible for the enhanced HET of ascorbic acid²⁷, ferro/ferricyanide²⁸, azo compounds²⁹, carbamazepine³⁰, enzyme cofactors³³, organic hydrazines³¹, hydroquinone³², signal transducing amino acids³³, phenols³⁴, nitric oxide, insulin, and extracellular thiols³⁵. Moreover, amorphous carbon impurities which contain large amount of defects in sp^2 lattice also showed electrocatalytic properties of CNTs at low concentrations³⁶.

Herein, the enhanced electrocatalytic properties of CNTs toward acetaminophen³⁷ and cytochrome c ³⁸ were studied in order to make sure that the performed electrochemical properties are caused by CNTs or the impurities within CNTs.

3.1.2 Results and discussions for study on acetaminophen

The acetaminophen exhibits an oxidation potential at $\sim +430$ mV on bare glassy carbon (GC) electrode with another broad reduction wave at $\sim +30$ mV. While at CNTs' surfaces, the oxidation occurred at $\sim +350$ mV and reduction occurred at $+250$ mV.³⁷ Then the work in Ref. [37] was repeated by using three different CNTs (CNT-1, 2, and 3) and the results were shown in Figure 3.1.1. According to the recorded voltammetric profile, acetaminophen exhibited similar electrochemical behaviors on all three CNTs to the one showed in Ref [37]. CNT-1 exhibits second oxidation wave at $+475$ mV, which was caused by the underlying GC electrode and electrochemistry behaviors of acetaminophen at bare GC electrode showed an oxidation peak at $+520$ mV and a broad reduction wave at -22 mV which is quite different from the CNTs' surfaces. Then the measured cyclic voltammetry of acetaminophen at pure CNTs (No metallic and carbonaceous impurities, act as reference material) modified electrode, the redox properties of acetaminophen were performed similar to bare GC electrode, which showed an oxidation peak at $+470$ mV with another reduction wave at $+12$ mV.

Figure 3.1.1 Electrochemical behaviors of acetaminophen on bare GC electrode and different CNTs surfaces in phosphate buffer (50 mM, pH 7.2), with 0.1 mM of acetaminophen. Scan rate: 100 mV/s.

Then the impurities present in CNT-1, 2 or 3 were studied for any possible enhancement in electrochemistry toward acetaminophen. The voltammograms of acetaminophen on these present metal oxide nanoparticles, such as Co_3O_4 , Fe_3O_4 , NiO , and MoO_3 modified electrodes are shown in Figure 3.1.2. The electrochemistry behaviors of acetaminophen at these metal based surfaces are similar to bare GC electrode, which exhibited oxidation potential between +475 mV and +510 mV and a reduction peak at approximately -10 mV. In addition, the oxidation and reduction peaks of Co_3O_4 showed around +900 mV were caused by Co_3O_4 itself and not related to acetaminophen. The results shown in Figure 3.1.2 indicating that the enhancement of electrocatalytic properties of CNT-1, 2, and 3 was not caused by the present metallic impurities.

Figure 3.1.2 Electrochemical behaviors of 0.1 mM acetaminophen on the presented metallic impurities surfaces, CNT-1 and pure CNTs for comparison. Other conditions as in Figure 3.1.1.

Subsequently, the carbonaceous impurities within CNTs were studied. The electrochemistry behaviors of acetaminophen at amorphous carbon (AC) and nanographite particles were shown in Figure 3.1.3. Both amorphous carbon and nanographite showed fast electron transfer, with oxidation peak at +365 mV for both and reduction peak at +305 mV and +300 mV, respectively. The redox behaviors of acetaminophen at these impurities are similar to the behaviors at CNT-1, 2 and 3 and different from pure CNTs.

Figure 3.1.3 Electrochemical behaviors of 0.1 mM acetaminophen on the carbonaceous impurities surface, CNT-1 and pure CNTs. Conditions: as in Figure 3.1.1.

In conclusion, the observed “enhanced electron transfer properties towards acetaminophen”³⁷ at non-pure CNTs is actually caused by the carbonaceous impurities presented within CNTs, not the inherent electrochemical properties of CNTs themselves. These findings are important for current graphene research which has been shown many remarkable electrochemical properties of graphene are caused by residual impurities.^{39,40}

3.1.3 Results and discussions for study on cytochrome *c*

The work on electrocatalytic properties of CNTs towards cytochrome *c*³⁸ were re-studied by examining the electrochemical behaviors of cytochrome *c* on pure CNTs, CNT-4 and the presented impurities. The scanning electron micrograph in Figure 1 of Ref. [38] shows highly contrasted bright spots in CNTs which could be either metallic or carbonaceous impurities, and clearly not belong to CNTs’ structure. Therefore, electrochemistry properties toward cytochrome *c* on CNT-4 (contains 0.65 wt. % of Co, 0.014 wt. % of Fe, 0.07 wt. % of

Mo and 0.5 wt. % of Ni, investigated by house ICP-MS analysis), presented metallic impurities based oxides, carbonaceous impurities, and pure CNTs were studied, and the pure CNTs were employed as the reference materials.⁴¹

Figure 3.1.4 Electrochemical behaviors of 0.3 mM cytochrome *c* at bare glassy carbon (GC) electrode, CNT-1, and pure CNT. Conditions: phosphate buffer (50 mM, 7.2 pH) with scan rate of 50 mV/s.

The cyclic voltammogram of cytochrome *c* on CNT-4 was recorded. According to Figure 4.1.4 the first reduction wave appears at ~ -50 mV, and reach the maximum point at -160 mV; the second reduction wave starts at -415 mV. While in the control experiment on pure CNTs modified electrode, cyclic voltammogram showed clear reduction of cytochrome *c* at about -420 mV and similar result was obtained at bare glassy carbon (GC) carbon electrode. Therefore it is obvious that the reduction peak at -160 mV was not caused by pure CNTs.

Figure 3.1.5 Electrochemical behaviors of 0.3 mM cytochrome *c* at bare GC electrode, Fe_3O_4 , Co_3O_4 , MoO_2 , NiO , and amorphous carbon (AC). Conditions as in Figure 3.1.4.

Therefore, the cyclic voltammetry of cytochrome *c* at presented metal oxide nanoparticles modified electrodes were recorded and the resulted cyclic voltammograms of cytochrome *c* did not show any significant difference from bare GC electrode were shown in Figure 3.1.5 In contrast, the electrode modified with amorphous carbon (AC) showed a strong reduction wave for cytochrome *c* with appear at -100 mV, peak at -225 mV, and a poorly defined reduction wave at about -400 mV to -500 mV. Therefore, it is obvious that, the metallic impurities presented in CNT-4 were not responsible for enhanced electrocatalytic performance but AC was. Therefore, comparing with the results³⁸ obtained for cytochrome *c* at CNTs which were claimed to be electrocatalytic, it is clear that the observed electrocatalytic properties were caused by the contained carbonaceous impurities.

In conclusion, the observed remarkable electrocatalytic properties³⁸ toward cytochrome *c* were actually caused by the presented carbonaceous impurities of CNTs, not the inherent electrocatalytic properties of CNTs themselves.

3.1.4 Experimental

3.1.4.1 Apparatus

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and a glassy carbon (GC, 3 mm diameter) electrode was used as the working electrode.

3.1.4.2 Materials

Acetaminophen, Cytochrome *c*, *N,N*-dimethylformamide (DMF), CNT-1, CNT-2 and CNT-3⁴²⁻⁴⁴, CNT-4, pure CNTs^{18, 45}, phosphate buffer (pH 7.2), amorphous carbon (AC) and nanographite were purchased from Sigma Aldrich. All CNTs were characterized previously (CNT-1 consists of 8.9 wt% of carbonaceous impurities, 0.64 wt% of Fe, 0.035 wt% of Mo, 0.096 wt% of Co, and 0.32 wt% of Ni. CNT-2 consists of 8.5 wt% of carbonaceous impurities, 0.22 wt% of Mo, 1.25 wt% of Fe, and 0.013 wt% of Ni. CNT-3 consists of 8.5 wt% of carbonaceous impurities, 0.045 wt% of Fe, 1.18 wt% of Mo and 3.33 wt% of Co. CNT-4 consists of 0.07 wt% of Mo, 0.014 wt% of Fe, 0.65 wt% of Co, and 0.5 wt% of Ni). GC (3 mm diameter) electrodes, Pt electrode, and Ag/AgCl (saturated) electrode were purchased from CHInstruments, TX, USA.

3.1.4.3 Procedures

Carbon samples were used as-received without any modification or purification. For electrode modification, the CNTs and impurities were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 μ L of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 μ m alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode.

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Chapter 3.2 Influence of carbonaceous impurities on electrochemistry of graphenes

3.2.1 Introduction

Graphenes showed promising electrocatalytic properties towards a wide range of analytes. Such properties have a dramatic potential on both the electrochemical sensing research fields¹ and energy storage². It would be important to find out whether some of these reported remarkable electrocatalytic properties of graphenes are caused by their inherent electrochemistry properties or the impurities within the graphenes.^{3,4} It has been found that both chemically and thermally reduced graphenes that prepared from graphite will contain some amount of metallic impurities inherently present in starting material graphite samples. These metallic impurities were found out to be responsible for the electrocatalytic properties of the graphenes toward reduction of cumene hydroperoxide (CHP) and oxidation of L-glutathione, sodium hydrogen sulfide and hydrazine.^{3,4} The presence of impurities within graphene materials and their effects on the electrocatalytic properties attract more and more attentions in scientific community.⁵⁻⁸ The influence of metallic impurities on electrochemical properties was demonstrated for the carbon nanotubes (CNTs), which metallic impurities were the actual causes for the electrocatalytic behaviors for various analytes.⁹⁻¹¹

Recently, there are lots of literatures reported the remarkable electrocatalytic properties of graphene for important compounds, such as nicotinamide adenine dinucleotide (NADH),¹² hydroquinone,^{13,14} and acetaminophen.¹⁵ It has been shown that the metallic impurities were responsible for the electrocatalytic properties of these compounds and these graphenes were not the case.¹⁶ Meanwhile, the carbonaceous impurities present in CNTs can

also be electroactive for many compounds^{17,33,18}, such as azo compounds,^{18a} organic hydrazines,^{18b} some amino acids,^{33a} hydroquinone,^{33b} NADH,^{33a} and acetaminophen.^{33c} Therefore, there would be a possibility that carbonaceous impurities within the graphenes might also be electroactive toward the mentioned compounds.

3.2.2 Results and discussions

Herein, the study of electrochemical properties of carbonaceous impurities (amorphous carbon) within graphenes towards important compounds such as NADH, hydroquinone and acetaminophen will be shown below.

Reduced graphenes with large amount of “amorphous” portion¹⁹ were employed as sample materials in following measurements. In detail, following materials were used: (i) thermally reduced graphene (TrG) and chemically reduced graphene (CrG) as sample graphene materials in electrochemistry measurements; (ii) Two forms of highly oriented pyrolytic graphite (HOPG) electrodes were used, basal plane HOPG (BPPG) and edge plane HOPG (EPPG) of which pristine graphene is the direct single layer derivative.²⁰ In this case, the observed electrochemistry behaviors of TrG and CrG should be similar to such deviations; (iii) amorphous carbon (AC) with a poorly graphitized structure and lots of sp^3 hybridized carbon was employed as the material simulating the carbonaceous impurities.^{18d}

Figure 3.2.1 Raman spectrums of CrG, TrG, AC and graphite.

Raman spectrums of TrG, CrG, AC and graphite were shown in Figure 3.2.1. It is clear that TrG, CrG and AC showed an intense *D*-band signal at 1350 cm^{-1} which is caused by disordered and defects from carbon structures.²¹ The *G* band appears at 1575 cm^{-1} is caused by sp^2 hybridized carbons and is shown in all samples.²² It is clear that the *G* band of TrG and AC is much broader than graphite's which is caused by the overlapping of *D'* band at 1620 cm^{-1} .^{1,20} *D'* band is also available in CrG with a relatively lower intensity which caused by lower degree of structural disorder. The *2D* band at 2700 cm^{-1} is corresponding to crystalline graphitic materials which is generally indication of disordered materials and can also be

caused by a partial amorphization and reduction of sp^2 domains.²²⁻²⁴ Raman spectrums clearly showed that both CrG and TrG are materials with large amount of defects or impurities and similar to AC.

Figure 3.2.2 Electrochemical behaviors of (A) 10 mM hydroquinone, (B) 1 mM acetaminophen and (C) 2 mM NADH on thermally (TrG) and chemically (CrG) reduced graphenes, basal plane

(BPPG) and edge plane (EPPG) pyrolytic graphite and amorphous carbon (AC). Conditions: phosphate buffer (50 mM, pH 7.2) with scan rate of 100 mV/s.

Hydroquinone,^{13,14} NADH¹² and acetaminophen^{14,15} will be studied on different graphene surfaces and AC modified electrode. Figure 3.2.2 shows electrochemistry behaviors of these compounds on TrG, CrG, EPPG, BPPG and AC surfaces. Hydroquinone (Fig 3.2.2, A) shows an oxidation wave starts at -40 mV at both TrG and CrG surfaces, and reach maximum at +290 mV for both reduced graphene surfaces, and a reduction wave appears at +200 mV reach maximum of -76 mV for both graphene surfaces. Electrochemistry behaviors of hydroquinone on both BPPG and EPPG showed very differently. At BPPG, oxidation wave of hydroquinone appears at 165 mV, and reaches maximum at 575 mV, with reduction wave appearing at +54 mV and getting maximum at -279 mV. Similarly, the oxidation wave of hydroquinone at EPPG appears at +60 mV, and reaches maximum at +443 mV, and with reduction wave presenting at +58 mV and reaching maximum at -172 mV. Therefore, it is clear that electrocatalytic behavior of hydroquinone at TrG and CrG surfaces is not similar to either BPPG or EPPG. Meanwhile, electrochemical behavior on AC surfaces exhibit oxidative wave appearing at -30 mV, reach maximum at +319 mV and the reduction appearing at +200 mV and reaching maximum at -91 mV, which exhibit similar electrochemical behaviors of hydroquinone on graphene surfaces.

Figure 3.2.2 B shows the recorded electrochemical behaviors of acetaminophen on different samples. Oxidation of acetaminophen at TrG surface appears at +245 mV and reaches maximum at +403 mV, reduction wave appearing at +445 mV and getting maximum at +284 mV. Then the acetaminophen at both BPPG and EPPG electrodes behave similar. The

oxidation of acetaminophen appears at +334 mV, and reach maximum at +525 mV while reduction appears at +200 mV and reach maximum at -50 mV. Similar to hydroquinone, electrochemical behaviors of acetaminophen at graphene surfaces are very different from BPPG and EPPG electrodes. The electrochemical properties of acetaminophen are studied at AC surface; the cyclic voltammograms behaves closely to the ones recorded at TrG surface. Oxidation of acetaminophen at AC surface appears at +245 mV, and reaches maximum at +396 mV. The reduction wave appears at +445 mV and reaches maximum at +236 mV. It is clear that electrochemistry behaviors of TrG are similar to AC.

Lastly, the redox properties of NADH at CrG, EPPG, BPPG and AC were shown in Figure 3.2.2, C. The oxidation of NADH appears at +100 mV at CrG with maximum at +507 mV. Similarly, electrochemical behaviors of NADH at AC surface showed oxidation wave appearing at +100 mV and reach maximum at +490 mV. However, NADH shows oxidation wave on EPPG and BPPG at +400 and +430 mV, respectively, and reaches maximum at +662 and +775 mV, respectively. Thus, results clearly indicate that the electrocatalytic properties towards acetaminophen were caused by AC impurities within graphenes.

In conclusion, the previously reported remarkable electrocatalytic properties of graphenes towards hydroquinone, acetaminophen and NADH are actually caused by the presence of carbonaceous impurities within graphenes.

3.2.3 Experimental

3.2.3.1 Materials

N,N-dimethyl formamide (DMF), hydroquinone, reduced form of β -nicotinamide adenine dinucleotide (NADH), acetaminophen, potassium chloride, potassium ferrocyanide, potassium phosphate disodium salt, and potassium ferricyanide were purchased from Sigma Aldrich. Amorphous carbon (AC) (particle size 29 nm) was obtained from Asbury Carbons, NJ.

3.2.3.2 Apparatus

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and a glassy carbon (GC, 3 mm diameter) electrode was used as the working electrode.

Raman spectrums were obtained via a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with CCD detector, Ar laser with excitation wavelength of 514.5 nm and a 100 $\times$ objective lens were employed on an Olympus optical microscope.

3.2.3.3 Procedures

Chemically reduced graphene (CrG) was prepared by dispersing 80.5 mg graphite oxide powder into water to form a 1.0 mg/ml colloidal solution. The formed mixture was then ultrasonicated for 3 hours and prior to the addition of 5 wt. % sodium carbonate until pH

reach 9-10. 800 mg of sodium borohydride was added into the dispersion under vigorous stirring over 20 min. Then the mixture was heated up to 80 °C for 1 hour. The mixture was then repeatedly washed with water by using centrifugation (8000 rpm, 10 min) when mixture cooling to room temperature. The formed pallet was dried at 60 °C for 5 days in vacuum oven before use.

Thermally reduced graphene (TrG) was prepared by applying thermal exfoliation to graphite oxide at 1050 °C. Firstly, 0.2 g graphite oxide was placed in a porous quartz glass capsule which in a vacuum tight tube furnace that under controlled atmosphere and connected to a magnetic manipulator. Then the magnetic manipulator allows creating a temperature gradient over 1000 °Cmin⁻¹. Then sample was flushed with nitrogen and repeated evacuation of tube furnace in order to remove the oxygen and inserted by magnetic manipulator to preheated furnace for 3 min.

For the electrochemistry measurements, the samples were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 µL of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 µm alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode. EPPG electrode surface was polished with 0.05 mm alumina on a polishing pad before each measurement. BPPG electrode surface was renewed by cleaving the top graphite layers with a scotch tape followed by a washing step in acetone to remove glue residues and DI water.

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Chapter 4

Influence of metallic impurities on electrochemistry of carbon nanotubes and graphenes

4.1	<i>Influence of metallic impurities on electrochemistry of carbon nanotubes</i>
4.1.1	<i>Introduction</i>
4.1.2	<i>Results and discussions</i>
4.1.3	<i>Experimental</i>
4.2	<i>Influence of metallic impurities on electrochemistry of graphenes</i>
4.2.1	<i>Introduction</i>
4.2.2	<i>Results and discussions for metallic impurities within chemically reduced graphenes</i>
4.2.3	<i>Results and discussions for metallic impurities within electrochemically reduced graphenes</i>
4.2.4	<i>Experimental</i>
4.3	<i>Influence of metallic impurities on electrochemistry of graphene nanoribbons</i>
4.3.1	<i>Introduction</i>
4.3.2	<i>Results and discussions</i>
4.3.3	<i>Experimental</i>

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L. Wang conducted most of the experiments. C. K. Chua and C. H. A. Wong synthesized the materials. B. Kherzi performed impurities characterization. A. Ambrosi, R. D. Webster and M. Pumera conceptualized and directed the projects. All authors contributed to discussion and writing of the manuscripts.

Chapter 4.1 Influence of metallic impurities on electrochemistry of carbon nanotubes

4.1.1 Introduction

It is well known that carbon nanotubes (CNTs) are grown from metallic catalyst precursors which make CNTs contaminated with metallic contents¹ and such impurities are hardly to be removed from the CNTs and will remain several wt% in the CNTs even after purification procedures.¹⁻⁶ Compton and co-workers have pointed out that the metallic impurities remain in the CNTs are responsible for the remarkable electrocatalytic properties of CNTs toward glucose,⁷ hydrogen peroxide,⁸ hydrazine¹¹ and halothane.⁹ It has already been showed that the metallic impurities within CNTs are responsible for the enhancement of electrocatalytic behaviors toward glutathione¹⁰ and organic peroxides¹¹. Furthermore, it has been shown that even 100 ppm of metallic impurities can still enhance the electrocatalytic performance of CNTs.¹² Moreover, the metallic impurities present in CNTs such as Co and Mo can also contain trace levels of Fe impurities within themselves and these metallic impurity nanoparticles can still enhance the electrocatalytic properties of the system.¹³

Oxygen reduction reaction (ORR) is one of the most important reactions for fuel cells and zinc-air batteries. The most efficient and low overpotential for reducing of oxygen is catalyzed by Pt supported on carbon surfaces.¹⁴ However, because of the high cost of Pt, it is important to find an electrocatalytic system to replace Pt and large amount of works have reported on using of metal oxide decorated carbon materials, such as heteroatoms doped carbon nanotubes (CNTs) as an efficient catalyst for ORR. It has already been pointed out that

Co, Mn and Fe based oxides supported CNTs can be used as an efficient catalyst for ORR.¹⁵⁻²⁰

There are also some reports on *metal-free* catalysis for ORR on nitrogen,²¹⁻²⁴ boron,²⁵ or B and N²⁶ doped CNTs and all these claimed metal free catalysts are working remarkable as no metal towards ORR²¹⁻²⁶.

However, most of CNTs were synthesized by using metal containing catalyst, such as iron(II) phthalocyanine,^{21,22} ferrocene,^{25,26} or other metallic catalysts;^{23,24} and during this process large amount of metallic impurities will be added into CNTs.¹ Therefore, synthesis of such "metal free" CNTs leads to the contamination of CNTs with metallic impurities.²⁷ In case of the claimed "metal-free" nitrogen doped CNTs, authors did not perform any extensive characterization on CNTs which can prove that the CNTs are really metal free. Techniques such as neutron activation analysis, ICP-MS/OES, or X-Ray fluorescence are able to provide accurate and detail information about the amount of metallic impurities remain in CNTs and none of these technique are performed to support such metal free claims. It is important to point out that the X-ray photoelectron spectroscopy (XPS) which was used in most cases^{21,23,25} is not sensitive enough and have a detect limitation of 0.1 wt%²⁸ and it is a typical surface sensitive technique which cannot detect even several wt% of metallic impurities within samples.²⁹

4.1.2 Results and discussions

It was reported recently that trace amount of metallic impurities can enhance the activity of metal free nitrogen doped amorphous carbon for ORR,³⁰ and the metallic impurities within graphenes are also electroactive for ORR.³¹ Herein, the case of metal free

CNTs catalyzed ORR was re-studied, since these CNTs were synthesized by using metal containing catalysts.²¹⁻²⁶

Figure 4.1.1 Recorded electrochemical behaviors of oxygen reduction reaction (ORR) at bare glassy carbon (GC) electrode and (A) Co_3O_4 , NiO , Fe_3O_4 , and MnO_2 surfaces; (B) MnO_2 , CNT-pure, CNT-1, and CNT-2 in 0.1 M KOH air-saturated solution. Scan rate: 100 mV/s.

In this work, pure CNTs (CNT-pure), the as received carbon nanotubes (CNT-1) and the “cleaned” carbon nanotubes (CNT-2) were used to study the electrochemical properties towards ORR. The CNT-2 was the “purified” version of CNT-1 which by means after extensive

purified in chlorine gas for 10 min of CNT-1,³² and then sample CNT-2 was obtained. The metallic impurities of CNTs were measured by in-house X-ray fluorescence (XRF) analysis.³² CNT-1 contains 30 ppm of Fe, 150 ppm of Ni, 5960 ppm of Mn, and 6160 ppm of Co and the “cleaned” CNT-2 contains 200 ppm of Co and 140 ppm of Mn and no Ni or Fe detected. These results also agree with the previous reports which pointed out that it is highly challenging to completely remove impurities even by extensive purification.^{6,11} No impurities were found in CNT-pure by XRF or ICP-MS.

Prior to the study of ORR on these three CNTs, the glassy carbon (GC) electrode was modified with metal oxides that present in CNTs, such as Co_3O_4 , MnO_2 , Fe_3O_4 , and NiO , and their potential catalytic effects towards ORR were recorded. The electrochemical behaviors were recorded at the presented metal oxide surfaces and shown in Figure 4.1.1,A. The onset potential towards ORR at Co_3O_4 , Fe_3O_4 , and NiO modified electrode is -310, -312 and -298 mV, which are close to GC's electrochemical behavior. This result clearly indicates that the mentioned Co_3O_4 , Fe_3O_4 , and NiO do not perform electrocatalytic effect towards ORR. Meanwhile, onset potential at MnO_2 for ORR is -200 mV, which showed much lowering result of the overpotential needed for ORR at bare GC electrode by about 100 mV. Then the CNTs' electrochemical behaviors were recorded and shown in Figure 4.1.1,B. The onset potential for ORR is -295 mV from pure CNTs, which perform quite close to bare GC electrode for ORR. It is obvious that pure CNTs do not have any enhancement in electrocatalytic properties towards ORR. The onset potential for ORR at the CNT-2 is -247 mV, while the CNT-1 showed an onset potential at -219 mV, which is quite close to MnO_2 (-200 mV). Therefore, it is clear that the onset potential for ORR shift positively along with the increasing amount of Mn based

impurities. Therefore, from the comparison of resulting onset potential, it is clear that the residual metallic impurities within CNTs are the actual causes for the enhancement of electrocatalytic properties toward ORR.

Figure 4.1.2 Value of onset potentials for all studied materials for oxygen reduction reaction.

In conclusion, the pure CNTs do not have any electrocatalytic properties towards ORR. Even the extensive purified CNTs still contain significant amount of residual metallic impurities and are able to behave strong electrocatalytic properties towards ORR. The electrocatalytic activity for ORR is correlated to the amount of Mn based metallic impurities in the CNTs. Therefore, the claimed enhanced “metal-free” ORR on heteroatom doped CNTs could be caused by the residual metallic impurities within the CNTs.

4.1.3 Experimental

4.1.3.1 Materials

Carbon nanotubes (CNT-1) (98%, -OH terminated, 5-15 nm/ 1-5 μ m) were obtained from Bucky, USA. MnO_2 powder was obtained from Alfa Aesar. N,N-dimethylformamide (DMF), Co_3O_4 , NiO, Fe_3O_4 , nanoparticles and CNT-pure were purchased from Sigma Aldrich. CNTs were extensively characterized previously (CNT-1 contains 0.616 wt% of Co, 0.003 wt% of Fe, 0.015 wt% of Ni and 0.596 wt% of Mn; CNT-2 contains 0.02 wt% of Co, and 0.014 wt% of Mn). Glassy carbon (GC) electrode Pt and Ag/AgCl (saturated) electrodes were purchased from CHI Instruments, TX, USA.

4.1.3.2 Apparatus

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and a glassy carbon (GC, 3 mm diameter) electrode was used as the working electrode.

4.1.3.2 Procedures

CNTs were purified in a quartz glass reactor that connects to a magnetic manipulator at 1000 $^{\circ}\text{C}$. CNT-1 (0.2 g) was placed in a porous quartz glass capsule which was in a vacuum tube furnace under the controlled atmosphere and connected with a magnetic manipulator. The

reactor was repeatedly flushed with nitrogen to remove oxygen. Then the evacuated reactor was filled with CNT-1 and chlorine, and quickly inserted to the preheated furnace. The sample was then treated in a chlorine/nitrogen (1000 mL/min) atmosphere for 10 min. Then the treated CNTs were removed from the hot zone and evacuated three times. Finally, nitrogen was refilled in order to remove the chlorine from the reactor.

For the electrochemistry measurements, the samples were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 μ L of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 μ m alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode.

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Chapter 4.2 Influence of metallic impurities on electrochemistry of graphenes

4.2.1 Introduction

Significant research was done on so called “metal-free” oxygen reduction reaction on surface of heteroatoms doped carbon materials,^{1, 2} and recently on graphene surfaces.³⁻⁹ In these reports, graphenes were doped with heteroatoms, such as boron, nitrogen, sulphur or their combination (i.e. N and S, or N and B) and showing remarkable electrocatalytic properties towards oxygen reduction reaction (ORR).³⁻⁹ It is interesting to note that such studies on ORR with (non-metallic) heteroatoms doped graphenes are claimed as “*Metal-Free*” in the title, and no extensive characterization was done to prove that the materials are indeed metal free. Such extensive characterization of trace metal impurities such as X-ray fluorescence (XRF), ICP-MS/OES, and neutron activation analysis can provide the accurate compositions.³⁻⁹ However, it is well known that similar to CNTs,^{10,11} graphene materials, especially the one prepared from graphite, contains significant amount of metallic impurities which can affect their electrocatalytic properties.¹² Graphenes claimed as “metal-free” electrocatalysts for ORR in the mentioned works are synthesized from graphite with applying the Hummers oxidative method¹³ at the very beginning stage. This oxidation method consists of using permanganate oxidant to prepare the intermediate material graphite oxides (GOs), which can be subsequently reduced/doped to graphenes.³⁻⁹ The graphite contains large amount of metallic impurities (i.e. Mo, Fe, Ni, Co, V, Mn, and Cr) with up to 2 wt% of the material¹⁴⁻¹⁹ and it has been shown that the presented metallic impurities in carbon materials can strongly affect their electrocatalytic properties and even at trace levels.^{10,20-24}

4.2.2 Results and discussions for metallic impurities within chemically reduced graphenes

Herein, the influence of residual manganese (Mn) based impurities in chemically reduced graphene will be studied and the manganese based impurities are introduced during the oxidation process Hummers' method.²⁵

In this work, graphenes were prepared from same starting material, natural graphite via two different oxidation methods to form different graphenes. One is prepared via employing the Hummers method¹³ (permanganate oxidant) prior the chemically reduction with hydrazine to form reduced graphene oxide (Hu-G). Another control graphene material was synthesized by applying the Staudenmaier method,²⁶ which use chlorate oxidant to generate the GOs and then chemically reduced with hydrazine to form reduced graphene oxide (St-G). The amount of metallic impurities in the starting material graphite and the formed reduced graphene oxides (rGOs) was then characterized by ICP-MS analysis and summarized in Table 4.2.1. It can be seen that the amount of metallic impurities are in high ppm range and especially for graphenes prepared via the Hummers method (Hu-G) which contains an approximately 500 times larger amount of Mn than the graphene prepared via the Staudenmaier method (St-G). It is important to note that, even the starting material, graphite, still contains ppm levels of Mn which could be the primary source of introducing Mn impurities to the graphene prepared via the Staudenmaier method.

Table 4.2.1. Metallic impurity compositions (ppm) in graphite (starting material), St-G and Hu-G as determined by ICP-MS analysis.

Carbon materials			
Impurity	Graphite	Hu-G	St-G
Fe	4224	927.57	1685.87
Co	3.3	0.28	7.12
Ni	33.7	18.03	13.77
Mn	24.9	8311.25	17.89

In order to better understand the electrocatalytic properties of graphenes, the electrochemistry properties of metal oxide nanoparticles towards ORR were studied in 0.1 M KOH solution. Linear sweep voltammograms (LSV) of glassy carbon (GC) electrode modified with Fe_3O_4 , Co_3O_4 , NiO , and MnO_2 are recorded in Figure 4.2.1. It can be seen that the onset potential of ORR is practically close to the bare GC (-267 mV) electrode, with the exception of MnO_2 (-94 mV), which indicate a clear catalytic behavior of Mn oxide for the ORR.

Figure 4.2.1 Electrochemical behaviors of bare glassy carbon (GC) electrode and GC electrode modified with NiO, Co_3O_4 , Fe_3O_4 and MnO_2 particles in air-saturated 0.1 M KOH solution. Scan rate: 0.1 V/s.

Subsequently, the electrochemical behaviors of the Hu-G and St-G are studied and shown in Figure 4.2.2. According to recorded voltammetric profile the graphene samples showed quite different onset potentials for the ORR. Hu-G, which contains more than 8000 ppm of Mn impurities, exhibited the onset potential at -134 mV for ORR. The graphenes prepared via the Staudenmaier method (St-G) which contain a low content of Mn (~18 ppm) showed the onset potential at -183 mV. Thus, it is obvious that Mn impurities within graphenes are responsible for the remarkable electrocatalytic properties towards ORR.

Figure 4.2.2 Electrochemical behaviors recorded on bare glassy carbon (GC) electrode and GC electrode modified with Hu-G and St-G graphene materials in air-saturated 0.1 M KOH solution. Scan rate: 0.1 V/s.

Figure 4.2.3 Onset potential for all measured materials.

According to the Figure 4.2.3, it is clear that the Mn impurities in graphene cause an enhancement effect towards ORR. Even at extremely lower content of Mn, a negative shift can be obtained (St-G with 18ppm of Mn). It is a clear that the Mn impurities in graphenes even at extremely low levels (0.0018 wt%) may still have a profound influence in the catalysis towards ORR. This result is also agreed with other reports which manganese oxide nanoparticles are used to decorate with graphene and perform enhancement on the performance of ORR.²⁷⁻²⁹

In conclusion, even trace levels of metallic impurities, in this case manganese oxide, can still influence graphenes' electrochemical properties and have a strong enhancement towards ORR. It is highly recommend to exam an extensive characterization of the materials which would be employed as catalysis for the ORR. The present metallic impurities should be carefully studied on possible effects of graphenes. Trace levels of impurities are inherently present in starting material, graphite and could be increased during the chemical treatments while prepare graphenes. In particular, the widely used Hummers method causes significant contaminations of Mn based impurities while the using of permanganate oxidant.²⁵ The term of "metal-free" in relation to graphene materials should be used only when an extensive characterization is provided and prove there are no metallic impurities present. The reported heteroatom doped "metal-free" graphene reports for the ORR, using the Hummers method to synthesis the graphene³⁻⁹ and therefore introducing a significant amount of Mn impurities to formed graphenes. It is likely that the residual manganese impurities in graphene are responsible for the ORR.

4.2.3 Results and discussions for metallic impurities within electrochemically reduced graphenes

In this work, the natural graphite was employed as starting material, and then the graphite oxide was synthesized by applying Hummers method (Hu-GO) or Staudenmaier method³⁰ (St-GO) to graphite, and the formed graphite oxide was then electrochemically reduced in phosphate buffer and labeled as Hu-ErGO and St-ErGO, respectively.

The morphology of graphene oxides and electrochemical reduced graphene oxides were obtained via SEM and shown in Figure 4.2.4. Fig 4.2.4,A and C show the morphology of St-GO and Hu-GO with a structure of stacked graphite oxide layers. In addition, the image of Hu-GO (Fig 4.2.4,C) shows a clear charging effect which can be caused by the highly oxidized condition, and the Hu-ErGO (Fig 4.2.4,D) shows no charging effect which indicate a significant reduction of Hu-GO.

Figure 4.2.4 SEM images of (A) St-GO, (B) St-ErGO, (C) Hu-GO, (D) Hu-ErGO, at 5000 magnification with scale bar of 1 μm .

The electrochemistry properties towards ORR were studied on bare GC, edge plane pyrolytic graphite (EPPG), basal plane pyrolytic graphite (BPPG), ErGOs and present impurities in air saturated 0.1 M KOH solution as shown in Figure 4.2.5. The oxygen reduction reaction of bare GC electrode, EPPG electrode, BPPG electrode, and ErGOs were shown in Figure 4.2.5,A, and obviously Hu-ErGO behave the best with onset potential (defined as potential at 10% of the wave current³¹) at -173 mV. The St-ErGO showed an onset potential at -263 mV, which is relatively close to bare GC electrode, EPPG electrode, and BPPG electrode. The EPPG electrode was used as a benchmark for the electrochemistry of sp^2 carbon materials, which

can possess high heterogeneous electron transfer rates^{14, 32} due to its high density of the edge and free of impurities, and shows an onset potential at -280 mV. Similarly, BPPG and bare GC were also used in control experiment and showed similar onset potential at -269 mV and -285 mV, respectively. Therefore, all three reference materials performed much more negative than the Hu-ErGO. In order to investigate why this was the case, linear sweep voltammograms were performed at various metal oxide and hydroxide, and shown in Figure 4.2.5,B. The onset potential for ORR at GC electrode modified with Co_3O_4 particles was -263 mV (vs. Ag/AgCl), Fe_2O_3 was -263 mV, $\text{FeO}(\text{OH})$ was -266 mV, Fe_3O_4 was -268 mV, NiO was -258 mV, and finally MnO_2 was -185 mV. Therefore, the results clearly indicate that MnO_2 (-185 mV) perform much less negative onset potential than all the other metal oxides and hydroxide, and shows a similar onset potential to Hu-ErGO (-173 mV). Meanwhile, the EPPG electrode (-280 mV) shows a much more negative onset potential than Hu-ErGO and MnO_2 , which indicate that the remarkable ORR performance of Hu-ErGO could be caused by manganese based impurities of Hu-ErGO (1931 ppm of Mn). According to the ICP-MS result, the Hu-ErGO contains 1931 ppm of Mn, and St-ErGO contains 6 ppm of Mn. For Hu-ErGO the large amount of Mn impurity can be contributed by the Mn from starting material (graphite), and the Hummers' method using permanganate as oxidizing agent which will add lots of Mn impurity into the formed graphene. For St-ErGO the Staudenmaier's method using chlorate as oxidizing agent so no extra Mn impurity will be added during synthesis, the Mn impurity will only be contributed by the starting material (graphite). In this case, the Hu-ErGO behaves much better than St-ErGO for ORR also agreed with amount of Mn impurity within the graphenes.

Figure 4.2.5 Linear sweep voltammetry of (A) bare GC, EPPG, BPPG, St-ErGO, Hu-ErGO and MnO_2 , (B) bare GC, FeO, Fe_2O_3 , Fe_3O_4 , FeOOH, Co_3O_4 , NiO, and MnO_2 in 0.1 M KOH solution at scan rate of 10 mV/s.

In conclusion, the ErGO for both Hu-GO and St-GO were successfully prepared. The electrochemical properties of ErGOs and present metal oxides and hydroxide towards ORR were studied, and the large difference in electrocatalytic properties towards ORR for St-ErGO and Hu-ErGO could be caused by the large amount of Mn impurity which was added in the Hummers' method.

4.2.4 Experimental

4.2.4.1 Materials

Natural graphite was obtained from Asbury Carbons (Asbury, NJ). MnO_2 powder and Hydrazine were purchased from Alfa Aesar. *N,N*-dimethylformamide (DMF), sulfuric acid (95-98%), hydrochloric acid (37%), potassium hydroxide, potassium chlorate (98%), Fe_3O_4 , Co_3O_4 , and NiO nanoparticles were purchased from Sigma Aldrich.

4.2.4.2 Apparatus

For the electrochemistry measurements, the samples were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 μL of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 μm alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode.

4.2.4.3 Procedures

Synthesis of Hummers graphite oxide. Graphite oxide was synthesized by the modified Hummers method, 0.5 g of NaNO_3 , 0.5 g of natural graphite, and 23 mL H_2SO_4 were stirred within an ice bath and 3 g of KMnO_4 was added into the mixture at 0 °C. Then the mixed solution was heated up to 35 °C and stirred for 1 hour to form a paste. Then 40 mL water was added to the formed paste to obtain a solution and subsequently stirred for 30 min while temperature was raised up to 90 °C and keep the temperature for 15 min. 100 mL of water was slowly added with another 3 mL of H_2O_2 (30%) until evolution of gas was stopped and

the dark brown color was changed to yellow. Then the solution was washed and filtered with 100 mL of water, and the filter cake was re-dispersed in water by mechanical agitation. Centrifugation was performed at 6,600× g for 15 min in water to obtain a neutral pH of the supernatant, and graphite oxide powder was then dried in oven at 60 °C for 2 days before use.

Synthesis of Staudenmaier graphite oxide. Graphite oxide was synthesized by the Staudenmaier method, 9 mL of fuming nitric acid and 17.5 mL of sulphuric acid (95-98%) were added to a reaction flask that contains a magnetic stir bar and then the reaction flask was cooled by immersion in an ice bath for 15 min. 1 g of graphite was then added to the mixture while stirring in order to obtain a well dispersed solution. 11 g of potassium chlorate was added to the mixture over 15 min to avoid sudden increment in temperature and formation of explosive gas while the flask in ice bath. When the potassium chlorate was dissolved, the reaction flask was loosely capped to allow gas evolution and the mixture was stirred for 96 hours at room temperature. When reaction was finished, the formed solution was poured into 1 L of deionized (DI) water and then filtered. Then the graphite oxide was re-dispersed and washed in HCl (5%) solutions to remove sulphate ions, and finally washed with DI water until the solution reach neutral pH. The prepared graphite oxide powder was dried in vacuum oven at 60 °C for 48 hours before use.

Synthesis of chemically reduced graphene. 49.8 mg of as-prepared graphite oxide was dispersed in water to form a colloidal solution (1 mg/mL) and sonicated for 3 hours. 2L of 32.1 mmol hydrazine hydrate was then added slowly at 47 °C and the formed suspension was heated up to 100 °C for 24 hours. The mixture was then washed repeatedly with water and methanol by using centrifugation (8,00 rpm, 10 min) while the formed mixture was cooled to

room temperature. The prepared sample pellet was dried at 60 °C in oven for 2 days before use.

Synthesis of electrochemically reduced graphene. The graphite oxide was reduced by using LSV in the range between 0 V and -1.2 V in phosphate buffer solution (pH 7.2). At least 2 scans were applied to double check the graphite oxide is reduced and no more reduction peaks shown in this potential range. The prepared electrode was dipped into DI water before use, to rinse off any adsorbed materials.

For the electrochemistry measurements, the samples were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 μ L of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 μ m alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode. EPPG electrode surface was polished with 0.05 mm alumina on a polishing cloth before each measurement. BPPG electrode surface was renewed by cleaving the top graphite layers with a scotch tape followed by a washing step in acetone to remove glue residues and DI water.

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Chapter 4.3 Influence of metallic impurities on electrochemistry of graphene nanoribbons

4.3.1 Introduction

There are several literatures were reported recently suggesting that the heteroatoms doped graphene nanoribbons (GNRs), which were synthesized by unzipping of carbon nanotubes (CNTs), as a "metal-free" catalyst¹⁻³ for oxygen reduction reaction (ORR). Therefore, the method of synthesizing such "metal-free" GNRs should be discussed. CNTs which are known as a nanomaterial which contains several wt% of residual metallic impurities^{4,5} The GNRs that prepared via "unzipping" by applying permanganate oxidant to CNTs will also contain significant amount of impurities that come from CNTs.⁶ In addition, the method used for unzipping of CNTs to form graphene oxide nanoribbons (GONRs) employed permanganate as an oxidizing agent⁶ which will add more manganese based impurities to prepared GNRs as well.^{7,8} However, these residual manganese impurities in the graphene can dramatically enhanced the ORR performance. Schuhmann *et al.* showed that the metallic impurities in carbon materials can influence the electrochemical performance towards ORR.^{9,10} This is caused by the overlapping diffusion layers of nanoparticle catalyst arrays distributed at less electrocatalytic material.^{11,12}

4.3.2 Results and discussions

Herein, the influences of residual metallic impurities on electrochemistry properties of GNRs were studied. GNRs were synthesized by using the unzipping method via applying permanganate oxidant to unzip CNTs to form GONRs,^{1,2,6} and subsequently the prepared GONRs were reduced by applying lithium aluminium hydride (LAH) to obtain GNRs.¹³ The

prepared GNRs were then characterized by applying scanning transmission electron microscopy (STEM) for morphology, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) for density of defects and C/O/N contents, and more importantly, inductively coupled plasma mass spectrometry (ICP-MS) for trace metallic impurities analysis. Then the electrocatalytic properties of the GNRs and present metal impurities were studied by using voltammetric methods.

Figure 4.3.1 Scanning transmission electron (STEM) images of GNRs (A, B) with scale bars of 1 μm and 100 nm, respectively. (C) Raman spectrum of GNRs. (D) Survey of GNRs and high resolution spectrum of (E) C1s and (F) N1s region.

STEM analysis (Figure 4.3.1, A, B) showed successfully unzipped CNTs by applying the permanganate oxidation method. In order to show these GNRs do contain defects/edge plane which can enhance electron transfer¹⁴, the Raman spectroscopy was performed and shown in Figure 4.3.1, C. The Raman spectrum for synthesized GNRs shows G band at 1560 cm⁻¹ which

was caused by the presence of sp^2 lattice carbon atoms and the D band appears at 1350 cm^{-1} which indicates the sp^3 hybridized carbon atoms. The ratio between the D band and G band intensities (I_D/I_G) was used to calculate the degree of disorder in the structure. The I_D/I_G ratio for GNRs is 1.33. The average crystallite sizes (L_a) of the GNRs can be then calculated according to the intensity of D and G band by using of Eq. 1¹⁵:

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

where λ_{laser} is the wavelength of the excitation laser in nm, and I_G and I_D are the intensities of the G and D bands. The calculated average crystallite size of GNRs was 12.6 nm, which is typical for chemically reduced graphenes (CrG) that synthesized from graphene oxides (GOs).¹⁶

Survey of GNRs (Figure 4.3.1, D) showed that the GNRs mainly consist of carbon and oxygen. The high resolution XPS of the C1s (Figure 4.3.1, E) gives detail bonding information of residual oxygen containing groups at different binding energy levels, such as C=C bonds locate at 284.5 eV, C-C bonds locate at 285.4 eV, C-O bonds locate at 286.3 eV, C=O bonds locate at 287.4 eV, O-C=O bonds locate at 288.5 eV, and $\pi-\pi^*$ interactions locate at 290 eV. According to the high resolution C1s, GNRs contain 46.31 at% of C=C bonds, 14.17 at% of C-C bonds, 26.19 at% of C-O bonds, 5.15 at% of C=O bonds, and 5.91 at% of O-C=O bonds, and 2.27 at% of $\pi-\pi^*$ interactions. Then the high resolution XPS for N1s region was shown to further confirm no nitrogen was accidentally doped in which because LAH was used instead of hydrazine as the reducing agent.¹⁷ No residual metallic impurities were detected from XPS results, which was caused by the poor detection limitation of XPS (about 0.1 at%). Therefore,

the GNRs were also measured by using ICP-MS for the determination of trace metallic impurities. As a result, the GNRs contain 5.0 ppm of Ni, 127.4 ppm of Fe, 4.5 ppm of Co, 16.0 ppm of Mo, 8.7 ppm of W, and 11.9 ppm of Mn.

Figure 4.3.2 Recorded electrochemical behaviors on bare glassy carbon (GC) electrode and (A) GNRs, and Pt/C modified GC electrode, and EPPG electrode; (B) with Co₃O₄, MoO₃, Fe₂O₃, Fe₃O₄, WO₃, FeO(OH), NiO, and MnO₂ in air-saturated 0.1 M KOH solution. Scan rate: 0.01 V/s.

Subsequently, electrochemical behaviors of GNRs, edge plane pyrolytic graphite (EPPG) electrode, basal plane pyrolytic graphite (BPPG) electrode and present impurities'

surfaces were studied by linear sweep voltammetry (LSV) in air saturated 0.1 M KOH solution and shown in Figure 4.3.2. ORR of GNRs showed the onset potential¹⁸ at -176 mV, Pt/C showed the onset potential of ORR at -101 mV and the EPPG electrode showed an onset potential for ORR at -280 mV, which is similar to the bare GC electrode, at -276 mV. Evidently, even GNRs, without any doping, showed more electrocatalytic properties toward ORR than EPPG and BPPG electrodes which indicate that edges planes/defects cannot play dominant role in the system. Then recorded LSV of different metal oxide and hydroxide modified electrodes were studied and shown in Figure 4.3.2,B. The onset potential for Co₃O₄ modified electrode was -247 mV, FeO(OH) was -237 mV, Fe₂O₃ was -240 mV, Fe₃O₄ was -273 mV, WO₃ was -278 mV, MoO₃ was -264 mV, NiO was -259 mV, and finally the MnO₂ was -173 mV. Therefore, it is obvious that MnO₂ performs much more electrocatalytic performance than the rest of metallic impurities. Furthermore, the onset potential observed from MnO₂ modified electrode was close to the onset potential of GNRs. One can conclude that the Mn based impurities within GNRs dominate the material's electrocatalytic performance towards ORR. It is highly likely that the so called "metal-free" ORR electrocatalytic performance of GNRs^{1,2} which were synthesized via applying permanganate to unzip the CNTs, was actually caused by Mn based metallic impurities. It is important to note that CNTs can contain metal carbides and the carbides and oxides are co-existing, and when CNTs were treated at 400°C, the Fe₃C would convert itself to iron oxide.¹⁹ In addition, the MnO₂ based impurities, which are found to be main reason for enhanced ORR performance of GNRs were not introduced from the synthesis of CNTs but introduced as contamination by unzipping the CNTs with

KMnO₄ in sulphuric acid condition and there is no doubts that Mn is in the form of oxide and not carbide.

In conclusion, GNRs prepared by unzipping of CNTs will contain significant amount of metallic impurities and the introduced manganese based impurities have a highly electrocatalytic effects toward ORR.

4.3.2 Experimental

4.3.2.1 Materials

N,N-dimethylformamide (DMF), Fe₂O₃, FeO(OH), MoO₃, WO₃, Fe₃O₄, NiO and Co₃O₄, nanoparticles, CNTs, sulfuric acid (95–98% w/v), tetrahydrofuran, methanol, lithium aluminum hydride, hydrochloric acid (37% w/v), and sodium sulfate were purchased from Sigma Aldrich. Hydrogen peroxide, MnO₂ powder, and hydrazine hydrate were purchased from Alfa Aesar. Potassium permanganate and ultrapure nitric acid were purchased from J. T. Baker. Diethyl ether was purchased from RCI Labscan. Ethanol was purchased from Merck.

4.3.2.2 Apparatus

Scanning transmission electron microscope (STEM) images were obtained by JEOL (Japan) 7600F Field Emission Scanning Electron Microscope. Raman spectrums were obtained by using confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. The 514.5 nm excitation wavelength Ar laser and a 100× objective lens were employed on an Olympus optical microscope. The sample of X-ray photoelectron spectroscopy (XPS) was prepared by placing a layer of sample onto carbon tape

which was attached to the sample holder. Then XPS sample was the investigated by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer was employed to obtain the survey and high resolution spectrums for selected ranges. Trace metal analysis was carried on by using the Agilent 7700x ICP-MS (Japan).

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and a glassy carbon (GC, 3 mm diameter) electrode was used as the working electrode.

4.3.2.3 Procedures

Preparation of graphene oxide nanoribbons (GONRs). The method was presented by Tour and co-workers which is unzipping CNTs.⁶ 300 mg of CNTs were stirred in 120 mL of concentrated H₂SO₄ for 12 hours at room temperature. 1650 mg of KMnO₄ (550% w/w) were then added to the mixture and stirred for 1 hour. The formed mixture was then heated up to 55 °C for 30 min and the reaction progress was monitored by sampling few drops of the mixture in an Eppendorf tube which containing 1 mL of ultrapure water. A red color of the test solution indicated to the formation of Mn (IV) and implied complete reaction. Another Eppendorf tube with 2-3 drops of H₂O₂ and 1 mL of water were also tested with the mixture with sonication, and a dark yellow color and high dispersibility of the solid indicated completion of reaction. Then reaction temperature was raised up to 70 °C, and then cooled to room temperature.

The formed mixture was then poured into 360 mL of water with 10 mL of 27% H_2O_2 solution and filtered with a 0.22 μm RC membrane. The residue was stirred in 120 mL H_2O for 30 min and sonicated for 15 min. Subsequently, 15 mL of HCl (37%) was added to induce flocculation and filtered with a 0.22 μm RC membrane again. The mixture was stirred in 120 mL ethanol for 30 min and sonicated for 15 min and together with 120 mL of diethyl ether the mixture was then filtered through a 0.22 μm PTFE membrane. The filtered GONRs were washed with ether (3 x 40 mL) and dried in an oven at 50 $^\circ\text{C}$ for 4 days.

Reduction of graphene oxide nanoribbons. 100 mg of the formed GONRs was stirred in dry THF (60 mL) and sonicated for 3 hours. 400 mg of LAH were added to the mixture portion-wise in ice bath until no bubble formed. The formed mixture was then transfers slowly to a solution of 1600 mg of LAH in dry THF (60 mL) at 0 $^\circ\text{C}$, and then allowed to stir under reflux for 24 hours. The reaction was quenched with saturated sodium sulfate, together with 1 M of HCl at 0 $^\circ\text{C}$ till a clear solution was obtained. Then the mixture was filtered with a 0.22 μm PTFE membrane, the residue was washed with water, and dried in an oven at 60 $^\circ\text{C}$ for 5 days to obtain GNRs.

For the electrochemistry measurements, the samples were dispersed into DMF to form 5 mg/mL suspensions. The formed suspensions were then sonicated for 5 min before use. 1 μL of the prepared suspension was used to drop onto a GC electrode surface which had been polished with 0.05 μm alumina on a polishing pad. The formed coating was allowed to evaporate at room temperature, and creates a homogeneous film on surface of electrode. EPPG electrode surface was polished with 0.05 mm alumina on a polishing cloth before each

measurement. BPPG electrode surface was renewed by cleaving the top graphite layers with a scotch tape followed by a washing step in acetone to remove glue residues and DI water.

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Chapter 5

Influence of heteroatom doping of graphenes

5.1 *Influence of nitrogen doping of graphenes*

5.1.1 *Introduction*

5.1.2 *Results and discussions*

5.1.3 *Experimental*

5.2 *Influence of boron doping of graphenes*

5.2.1 *Introduction*

5.2.2 *Results and discussions*

5.2.3 *Experimental*

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2. Lu Wang, Zdenek Sofer, Petr Simek, Ivo Tomandl, Martin Pumera, Boron-Doped Graphene: Scalable and Tunable p-Type Carrier Concentration Doping. *J. Phys. Chem. C*, **2013**, 117, 23251-23257.

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Contributions:

L. Wang conducted most of the experiments. Z. Sofer, P. Simek, and I. Tomandl synthesized the heteroatom doped graphenes. M. Pumera conceptualized and directed the projects. All authors contributed to discussion and writing of the manuscripts.

Chapter 5.1 Influence of nitrogen doping of graphenes

5.1.1 Introduction

Graphene is single layer graphite with atomically thickness, which carbon atoms covalently bonded into a hexagonal lattice. Due to this special structure, graphenes have lots of remarkable properties, such as good optical transparency, high electrical conductivity, large surface area and high thermal conductivity. Therefore, graphene has developed rapidly in the various fields, such as chemistry, biology, physics and material, and also explore the applications of graphene based materials in efficient catalysts,^{1,2} electrochemical storage,³ sensors,⁴ electronics and optoelectronics.^{5,6} Doping of heteroatom such as sulphur⁷, boron,⁸ nitrogen,⁹⁻¹² halogens^{13, 14} phosphorus¹⁵ or hydrogen^{16,17} can tailor the electrochemical properties and electronic properties of graphenes, which could enhance the electrochemical performance of doped graphenes. Especially for N-doped graphenes which have attracted vast attention due to its remarkable electrochemical performance in lithium-ion batteries,^{11,12} super capacitors,¹⁸ advanced catalyst support¹⁹ and fuel cells.⁹⁻¹¹ The level of doping is of high importance as carrier density is the key factor for tailoring the performance of the graphenes. However, there are limited numbers of studies focusing on the parameters that can influence the level of doping.

There are several methods on synthesis N-doped graphenes. Some of them simply mix nitrogen containing precursors (i.e. melamine) together with graphene materials, and then carbonize the formed mixture.²⁰ Nitrogen can also be doped by thermal exfoliation of graphite oxides (GiOs) in ammonia atmosphere.^{21,22} Solvent based method were also applied

by using GiOs and shift base precursors, to synthesis N-doped graphenes.²³ Usually, the amount of doped nitrogen was in range of 2-4 at%^{10,11,19} and in order to dope larger amounts of nitrogen, CVD based method can reach 9-11 at%.^{12,18}

5.1.2 Results and discussion

The effects of amount of doping nitrogen by different precursors and conditions for N-doped graphenes were studied. The scalable method was employed which can produce gram level quantities of graphenes via oxidizing of graphite to graphite oxides (GiOs) and subsequent thermal exfoliated under NH_3 atmosphere to obtain N-doped graphenes. Parameters, such as graphite oxide's preparation methods and exfoliation temperature were changed during synthesis process. The control materials were thermally exfoliated in N_2 atmosphere.

The starting materials of N-doped graphenes were GiOs which prepared by applying either chlorate oxidants (Hofmann and Staudenmaier methods)^{24,25} or permanganate oxidant (Hummers method) to oxidize graphite.²⁶ The N-doped graphenes were synthesized by thermally exfoliation of GiOs in NH_3 atmosphere. The influence of the type of graphite oxides and exfoliation temperatures on the amount of doped nitrogen and density of defects were studied. In this work, the N-doped graphenes were labeled by oxidation method of graphite (Staudenmaier for St, Hofmann for Ho, Hummers for Hu), and a term "N" indicates thermal exfoliation in NH_3 atmosphere and followed by exfoliation temperature (e.g. "St-N-600").

The morphologies of all N-doped graphenes were studied by scanning electron microscopy (SEM) and shown in Figure 5.1.1. The SEM images were obtained at magnification

of 3,000 $\times$ and 20,000 $\times$ for different graphenes. All graphenes showed an exfoliated structure and confirmed successful exfoliation state of all exfoliated GOs in NH₃ atmosphere.

Figure 5.1.1 Scanning electron microscopy (SEM) images of N-doped graphenes which were prepared from Staudenmaier (St) graphite oxides at 600 °C, 800 °C and 1000 °C, Hofmann (Ho) graphite oxides at 600 °C, and Hummers (Hu) graphite oxides at 600 °C with magnification of (A) 3,000 $\times$ and (B) 20,000 $\times$. Scale bar of 1 μ m.

The defect densities of N-doped graphenes were investigated by using Raman spectroscopy. Figure 5.1.2 showed the Raman spectrums and I_D/I_G ratio for N-doped

graphenes synthesized by different precursors and temperatures. The G band shown at 1560 cm^{-1} is caused by the presence of sp^2 lattice carbon atoms in the graphene framework and a D band at 1350 cm^{-1} indicates the defects in graphene framework and also relates to the amount of doped nitrogen atoms.

Figure 5.1.2 Left: I_D/I_G ratio and Raman spectrums for doped graphenes that synthesized from (A) Staudenmaier (St) graphite oxides, (C) Hofmann (Ho) graphite oxides, and (E) Hummers

(Hu) graphite oxides at 600 °C. Right: I_D/I_G ratio and Raman spectrums for doped graphenes synthesized from Staudenmaier graphite oxides at (B) 600 °C, (D) 800 °C, and (F) 1000 °C.

The ratio of intensities between D and G band (I_D/I_G) is used to calculate the degree of disorder in a carbon structure. I_D/I_G ratio for St-N-600, Ho-N-600, Hu-N-600 is 0.89, 0.95, and 1.02, respectively, which showed an increasing trend. This result indicates that Hu-N-600 contains the highest density of defects and St-N-600 contains lowest density of defects. Interestingly, increasing exfoliation temperature did not perform a monotonic trend and St-N-600, St-N-800, and St-N-1000 showed I_D/I_G ratio of 0.89, 0.41 and 0.77 as bar chart in Figure 5.1.2.

For those graphenes that exfoliated at 600 °C, only St-N-600 shows a 2D band at 2700 cm^{-1} , which represents a low degree of disorder in carbon structure. On the other side, among all Raman spectrums of N-doped graphenes, only graphenes synthesized by using Staudenmaier GiOs show a 2D band at 2700 cm^{-1} also indicates that the doped Staudenmaier graphenes contain a relatively lower disorder carbon structure.

The average crystallite sizes (L_a) of the graphenes can be calculated based on the intensity of D and G band by the Eq 1.²⁷:

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

where λ_{laser} is the wavelength of the excitation laser, and I_G and I_D are the intensities of the G and D bands. Then the crystallite sizes for N-doped graphenes were calculated and showed that the L_a of Ho-N-600, Hu-N-600, St-N-600, St-N-800 and St-N-1000 are 15.98 nm, 17.15 nm, 14.97 nm, 6.90 nm and 12.95 nm, respectively.

The effect of the precursors of doped graphenes was studied first. The material compositions and bonding information of N-doped graphenes were studied by applying XPS onto graphenes. The survey and high resolution XPS of C1s and N1s were obtained for doped graphenes and shown in Figure 5.1.3, 5.1.4 and 5.1.5. The survey and high resolution XPS of C1s shown in Figure 5.1.3 and 5.1.4 indicate that the graphenes were successfully reduced via thermal exfoliation and the nitrogen was successfully doped into the graphenes.

Figure 5.1.3 Left: Nitrogen content and survey XPS for N-doped graphenes synthesized from (A) Staudenmaier (St) graphite oxides, (C) Hofmann (Ho) graphite oxides, and (E) Hummers

(Hu) graphite oxides at 600 °C. Right: Nitrogen content and Survey for N-doped graphenes synthesized from Staudenmaier (St) graphite oxides at (B) 600 °C, (D) 800 °C, and (F) 1000 °C.

Results clearly indicate that the amount of doped nitrogen for different starting materials increases in a trend of St-N -600, Ho-N -600 and Hu-N -600 from 2.5 at%, 4.3 at% to 7.2 at% and shown in Figure 5.1.3. It is clear that the formed N-doped graphenes which synthesized from the Hummers GOs have the highest amount of doped nitrogen than Hofmann and Staudenmaier GOs have the least amount of doped nitrogen. Furthermore, the amount of doped nitrogen also confirmed with the I_D/I_G ratio of N-doped graphenes that prepared by the Hummers GOs are larger than the graphenes that are prepared from Hofmann GOs and the N-doped graphenes prepared by Staudenmaier GOs have the lowest I_D/I_G ratio. Therefore the results proved that doping of nitrogen atoms into graphene framework will influence the I_D/I_G ratio, the I_D/I_G ratio will increase with the amount of doped nitrogen. In addition, the C/O ratio for St-N-600, Ho-N-600 and Hu-N-600 are 11.6, 12.1 and 11.8, respectively, which showing a similar reduction level.

In the exfoliation temperature study, the N content of St-N-600, St-N-800 and St-N-1000 are 2.5 at%, 0.94 at% and 2.18 at%, respectively. In this case, the results show no trend along the exfoliation temperature, which indicate that the exfoliation temperature cannot influence the amount of doped nitrogen. Similar to the precursors' study, the I_D/I_G ratio of St-N-600, St-N-800 and St-N-1000 are 1.02, 0.41 and 0.77, which also agree with doping of N will produce defects in the graphite framework and increase the I_D/I_G ratio. On the other hand, the C/O ratio of St-N -600, St-N -800 and St-N -1000 are 11.6, 15.1 and 15.5 which indicate an increasing trend along with the increasing exfoliation temperatures. This result also further

confirmed that higher exfoliation temperature can enhance the reduce level of graphenes. The XPS results also confirm with the nitrogen determination by combustible elemental analysis, as shown in Table 5.1.1.

Table 5.1.1. Combustible elemental analysis (at%) of doped graphenes.

Sample	N	C	H	O
St-N-600	2.25	90.03	1.09	6.63
Ho-N-600	4.22	82.51	3.25	10.02
Hu-N-600	6.86	76.46	7.35	9.33
St-N-800	2.30	90.56	1.56	5.58
St-N-1000	1.94	90.03	2.27	5.76

Figure 5.1.4 Left: High resolution XPS of C1s of N-doped graphenes synthesized from (A) Staudenmaier (St) graphite oxides, (C) Hofmann (Ho) graphite oxides, and (E) Hummers (Hu) graphite oxides at 600 °C. Right: High resolution XPS of C1s of N-doped graphenes prepared by Staudenmaier (St) graphite oxides at (B) 600 °C, (D) 800 °C, and (F) 1000 °C.

The high resolution XPS of C1s gives insight into the bonding information of oxygen containing groups at different binding energy levels, C=C bonds appear at 284.5 eV, C-C bonds

appear at 285.4 eV, C-O bonds appear at 286.3 eV, C=O bonds appear at 287.4 eV, O-C=O bonds appear at 288.5 eV and pi-pi interactions appear at 290 eV, and the detailed bonding information for oxygen containing groups are shown in Table 5.1.2.

Table 5.1.2. Bonding information (%) obtained from the high resolution C1s XPS for all N-doped graphenes.

	C=C	C-C	C-O	C=O	O-C=O	π - π^*
Hu-N-600	56.0	18.5	10.2	8.5	2.1	2.1
Ho-N-600	53.0	21.9	10.8	4.3	4.5	5.4
St-N-600	60.3	19.7	10.6	4.3	2.7	2.4
St-N-800	61.7	12.6	15.1	5.5	3.9	1.1
St-N-1000	57.2	17.8	9.1	7.4	3.7	4.8

Figure 5.1.5 Left: high resolution XPS of N1s of doped graphenes synthesized from (A) Staudenmaier (St) graphite oxides, (C) Hofmann (Ho) graphite oxides, (E) Hummers (Hu) graphite oxides at 600 °C, and (G) the bar chart of the doped nitrogen content. Right: high

resolution XPS of N1s of doped graphenes synthesized from Staudenmaier (St) graphite oxides at (B) 600 °C, (D) 800 °C, (F) 1000 °C and (H) the bar chart of the doped nitrogen content.

The high resolution XPS of N1s for N-doped graphenes are shown in Figure 5.1.5. The high resolution XPS of N1s show the bonding information at different energy levels, such as pyridine-like N appear at 397.9 eV, pyrrole-like N appear at 399.1 eV and quaternary (graphitic) N appear at 401.3 eV. Then the St-N-600, Ho-N-600 and Hu-N-600 contain 48.6 %, 38.8 % and 46.1 % of pyridine-like N, 27.6 %, 14.5 % and 40.6 % of pyrrole-like N, and 23.8 %, 46.6 % and 13.3 % of graphitic N, respectively. In temperature study, the St-N-600, St-N-800 and St-N-1000 contain 48.6 %, 41.2 % and 42.3 % of pyridine-like N, 27.6 %, 28.4 % and 10.5 % of pyrrole-like N, 23.8 %, 30.4 % and 47.1 % of graphitic N, respectively.

According to the specific resistivity measurements (4-point method), the specific resistivity of the graphenes are directly relate to the amount of doped nitrogen. It is obvious, Hu-N-600 which contains 7.2 at% of N exhibited the highest resistivity while the lowest amount of nitrogen performed (in St-N-800, with 0.94 at% of N) the lowest resistivity.

Table 5.1.3. Specific resistivity (Ohm.cm) of doped graphenes.

Sample	Specific resistivity
St-N-600	5.6×10^{-5}
Ho-N-600	2.3×10^{-4}
Hu-N-600	1.7×10^{-3}
St-N-800	2.6×10^{-4}
St-N-1000	3.5×10^{-5}

In conclusion, different types of starting materials, such as types of graphite oxides (GiOs) that used for the preparation of the N-doped graphenes, has major influence on doping

level. Among three types of precursors, Staudenmaier GiOs, Hofmann GiOs and Hummers GiOs, the Hummers GiOs can be introduced with the highest amount of nitrogen (7.2 at%) and the Staudenmaier GiOs can be introduced the least amount of nitrogen (0.94 at%) under same condition. Therefore, the types of GO for preparing doped graphenes should be always considered as an important factor.

5.1.3 Experimental

5.1.3.1 Materials

Graphite microparticles (<50 μm) was purchased from KOH-I-NOOR GRAFIT. Sulfuric acid (96%), potassium permanganate (98%), nitric acid (fuming, >98%), nitric acid (65%), potassium chlorate (98%), silver nitrate (99.8%), hydrochloric acid (35%), hydrogen peroxide (30%), and barium nitrate (99 %) were purchased from PENTA. Nitrogen (99.9999%) and Ammonia (99.9995%) was purchased from SIAD. Sodium phosphate monobasic *N,N*-dimethylformamide (DMF), and potassium phosphate dibasic were obtained from Sigma Aldrich.

5.1.3.2 Apparatus

Scanning electron microscopy (SEM) images were obtained by using a JEOL (Japan) 7600F field emission scanning electron microscopy. Raman spectrums were obtained by using confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. The 514.5 nm excitation wavelength Ar laser and a 100 $\times$ objective lens were employed on an Olympus optical microscope. The sample of X-ray photoelectron spectroscopy (XPS) was prepared by placing a layer of sample onto carbon tape which was

attached to the sample holder. Then XPS sample was the investigated by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer was employed to obtain the survey and high resolution spectrums for selected ranges.

The combustible elemental analysis was measured by CHN PE 2400 Series II (Perkin Elmer, USA). In CHN operating mode, the instrument employs a classical combustion principle to convert the sample elements to sample gases, such as CO₂, H₂O and N₂. The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases, separation and detection. The accuracy of CHN determination is better than 0.30% abs. Internal calibration was performed by using N-phenyl urea.

For electrical resistivity measurements of graphenes, 40 mg of the graphenes were compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the prepared capsule was measured by a 4-probe technique using the Van der Pauw method²⁸. The resistivity measurements were then carried on with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit with 10 mA measuring current.

5.1.3.3 Procedures

Synthesis of Staudenmaier graphite oxide. Graphite oxide was synthesized by the Staudenmaier method, 9 mL of fuming nitric acid and 17.5 mL of sulphuric acid (95-98%) were added to a reaction flask that contains a magnetic stir bar and then the reaction flask was cooled by immersion in an ice bath for 15 min. 1 g of graphite was then added to the mixture while stirring in order to obtain a well dispersed solution. 11 g of potassium chlorate was added to the mixture over 15 min to avoid sudden increment in temperature and formation

of explosive gas while the flask in ice bath. When the potassium chlorate was dissolved, the reaction flask was loosely capped to allow gas evolution and the mixture was stirred for 96 hours at room temperature. When reaction was finished, the formed solution was poured into 1 L of deionized (DI) water and then filtered. Then the graphite oxide was re-dispersed and washed in HCl (5%) solutions to remove sulphate ions, and finally washed with DI water until the solution reach neutral pH. The prepared graphite oxide powder was dried in vacuum oven at 60 °C for 48 hours before use.

Graphite oxide preparation with the Hofmann method. 87.5 mL of sulfuric acid (96%) and 27 mL of nitric acid (65%) were added to a reaction flask with a magnetic stir bar and the mixed solution was then cooled by an ice bath for 30 min. 5 g of graphite was added to the mixture while stirring to avoid agglomeration and obtain a homogeneous dispersion. 55 g of potassium chlorate was slowly added into the mixture while in an ice bath which in order to avoid formation of explosive chlorine dioxide gas and a sudden increment in temperature. When potassium chlorate was dissolved, the reaction flask was loosely capped to let the gas to escape and the mixture was stirred for another 96 hours. When reaction was complete, the formed mixture solution was poured to 3 L of water and decanted which was used to remove sulfate ions, and the prepared graphite oxides were then dispersed in HCl (5%) solution and repeatedly centrifuged and dispersed in water until negative reaction were achieved. Then the formed graphite oxide slurry was dried in a vacuum oven at 60 °C for 2 days before use.

Synthesis of Hummers graphite oxide. Graphite oxide was synthesized by the modified Hummers method, 0.5 g of NaNO_3 , 0.5 g of natural graphite, and 23 mL H_2SO_4 were stirred

within an ice bath and 3 g of KMnO_4 was added into the mixture at $0\text{ }^\circ\text{C}$. Then the mixed solution was heated up to $35\text{ }^\circ\text{C}$ and stirred for 1 hour to form a paste. Then 40 mL water was added to the formed paste to obtain a solution and subsequently stirred for 30 min while temperature was raised up to $90\text{ }^\circ\text{C}$ and keep the temperature for 15 min. 100 mL of water was slowly added with another 3 mL of H_2O_2 (30%) until evolution of gas was stopped and the dark brown color was changed to yellow. Then the solution was washed and filtered with 100 mL of water, and the filter cake was re-dispersed in water by mechanical agitation. Centrifugation was performed at $6,600 \times g$ for 15 min in water to obtain a neutral pH of the supernatant, and graphite oxide powder was then dried in oven at $60\text{ }^\circ\text{C}$ for 2 days before use.

Thermally exfoliation. Thermally reduced graphene was prepared by applying thermal exfoliation to graphite oxide at $1050\text{ }^\circ\text{C}$. Firstly, 0.2 g graphite oxide was placed in a porous quartz glass capsule which in a vacuum tight tube furnace that under controlled atmosphere and connected to a magnetic manipulator. Then the magnetic manipulator allows creating a temperature gradient over $1000\text{ }^\circ\text{Cmin}^{-1}$. Then sample was flushed with nitrogen and repeated evacuation of tube furnace in order to remove the oxygen and inserted by magnetic manipulator to preheated furnace for 3 min.

Synthesis of nitrogen doped graphene. The N-doped graphenes were synthesized by applying thermally exfoliation to prepared graphite oxides in NH_3 atmosphere. 100 mg of graphite oxides were placed in a quartz glass capsule which in the horizontal quartz glass reactor and connected to the magnetic manipulator. The reactor was then repeatedly evacuated and flushed with N_2 before shifting the samples to the hot zone. While the sample was in the hot zone the flowing N_2 was then switched to NH_3 . The exfoliation temperature of samples was

kept constantly for 12 min at 600 °C, 800 °C and 1000 °C, respectively. The NH₃ (300 mL/min) was used to remove the exfoliation byproducts.

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Chapter 5.2 Influence of boron doping of graphenes

5.2.1 Introduction

Doping of graphenes with electron withdrawing (p-type doping) or electron donating (n-type doing) groups is important for tailoring the electronic properties of graphenes.¹ In case of doped graphene, electron donating groups (n-type) include nitrogen²⁻⁶ and phosphorus⁷, and electron withdrawing group (p-type) includes boron.⁸ Doping of such elements can change the density of electron in the graphene nanosheets and therefore to tailor their electrochemical properties.⁹ The amount of doping is one of the most important factors for tailoring the electrochemical performance of the materials. However, a scalable synthesis method is required for potentially large amount of doped graphenes.

There are several reports claimed that N-doped graphenes perform remarkable electrocatalytic properties towards reduction of H₂O₂ and oxygen^{2,6,9}, which have important implications for the area of fuel cells. In addition, the N-doped graphenes were considered as materials which have relatively larger capacitance than un-doped graphenes. Recently, B-doped graphenes were claimed to be electrocatalytic towards oxygen reduction reaction (ORR)¹⁰ and have enhanced capacitance in comparison to graphenes.¹¹ It seems that same properties are enhanced no matter what kinds of atoms were doped.^{2,6,10,11,12}

A synthesis method with scalable production and tunable doping levels by thermally exfoliation of graphite oxides (GiOs) under BF₃ atmosphere at different exfoliation temperature was shown. In theory, the electrochemical properties of prepared p-doped (electron withdrawing) graphenes, should perform more electrocatalytic toward the

oxidation of compound, and less electrocatalytic toward the reduction.¹³⁻¹⁵ This is however the opposite of some reports on B-doped graphenes catalyzed ORR.¹⁰⁻¹²

5.2.2 Results and discussions

B-doped graphenes were synthesized by thermal exfoliation of GiOs in atmosphere of boron trifluoride diethyl etherate at 1000 °C in N₂/H₂, at 800 °C in N₂, and 1000 °C in N₂. While graphite oxide underwent exfoliation and deoxygenation¹⁶⁻¹⁹, it was doped with boron as well. The prepared B-doped graphenes were carefully characterized to study its morphology, density of defects, elemental composition and electrocatalytic properties towards oxygen reduction reactions (ORR) and its capacitance. The B-doped graphenes are labeled as G-B in this work.

Figure 5.2.1 Scanning electron microscopy (SEM) images of graphenes that doped with 23 ppm of boron, 140 ppm of boron and 590 ppm of boron with magnifications of (A) 370 $\times$, (B) 6,000 $\times$ and (C) 40,000 $\times$. Scale bars are 10 μm for 370 $\times$, 1 μm for 6,000 $\times$, and 100 nm for 40,000 $\times$, respectively.

The morphology of the prepared B-doped graphenes (G-B), were obtained by SEM. Figure 5.2.1 shows the SEM images of B-doped graphenes synthesized via thermally exfoliating at 1000 $^{\circ}\text{C}$ in N_2/H_2 atmosphere, at 800 $^{\circ}\text{C}$ in N_2 atmosphere, and at 1000 $^{\circ}\text{C}$ in N_2 atmosphere, respectively. All doped graphenes showed exfoliated structures and confirmed graphite oxides were successful thermal exfoliated in BF_3 atmosphere.

Consequently, the effects of exfoliation temperatures on the amount of doped boron were studied by prompt gamma-ray analysis (PGAA) which can be used for determination the amount of doped boron. As shown in Figure 5.2.2, the exfoliation of graphite oxides at 1000 °C in N₂/H₂ atmosphere led to doping of graphene at levels of 23 ppm boron (G-B-23ppm), while with exfoliation in N₂ atmosphere, more boron were introduced to graphenes, 140 ppm boron (G-B-140ppm) at 800 °C and 590 ppm (G-B-590ppm) at 1000 °C. The results obviously showed larger amount of boron can be introduced into the graphenes with higher exfoliation temperature. This result was confirmed the successful doping state of B-doped graphenes.

Figure 5.2.2 PGAA spectrums of graphenes doped with (A) 23 ppm of B, (B) 140 ppm of B and (C) 590 ppm of boron.

Figure 5.2.3 Raman spectrums of graphenes that doped with (A) 23 ppm, (B) 140 ppm and (C) 590 ppm of boron.

Defect densities of B-doped graphenes were investigated by applying Raman spectroscopy to samples. Figure 5.2.3 shows the Raman spectrums of three B-doped graphenes. According to the Raman results, *D* band at 1350 cm⁻¹ represents the presence of defects that caused by the sp³ hybridized carbon atoms, and a *G* band at 1560 cm⁻¹ indicates the pristine sp² lattice carbon atoms in the graphene framework. The ratio of intensity between *D* and *G* band (*I_D*/*I_G*) can be used to calculate the degree of disorder in graphene structures and the *I_D*/*I_G* ratio for G-B-23ppm, G-B-140ppm, and G-B-590ppm are 0.903, 0.632 and 0.732, respectively. The average crystallite sizes (*L_a*) of different graphenes can be calculated based on the intensity of *D* band and *G* band by the Eq 1.²⁰:

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

where λ_{laser} is the wavelength of the excitation laser, and *I_G* and *I_D* are the intensities of the *G* and *D* bands. The average crystallite sizes of graphenes were calculated as 18.6 nm for G-B-23ppm, 26.6 nm for G-B-140ppm and 23.0 nm for G-B-590ppm. All graphene samples exhibit *D'* band and 2*D* band at 1620 cm⁻¹ and 2700 cm⁻¹, which indicate a low degree of disorder in their structure.

The material compositions of B-doped graphenes were studied by using XPS which can not only determine the material compositions but also bonding information for samples. The survey and high resolution C1s of B-doped graphenes were recorded and shown in Figure 5.2.4. The results for graphenes indicate that graphenes were successfully reduced by thermally exfoliation and the oxygen contents were mostly removed. The C/O ratios are 14.2 for G-B-23ppm, 8.9 for G-B-140ppm, and 16.1 for G-B-590ppm. The high resolution C1s give

detailed information of bonding information of residual oxygen containing groups, at different binding energy levels, C=C bonds at 284.5 eV, C-C bonds at 285.6 eV, C-O bonds at 286.6 eV, C=O bonds at 287.6 eV and O-C=O bonds at 289.6 eV. The G-B-23ppm, G-B-140ppm and G-B-590ppm consists of 67.0 at%, 60.8 at%, and 68.5 at% of C=C bonds, 14.8 at%, 18.2 at% and 13.9 at% of C-C bonds, 7.0 at%, 8.4 at% and 6.9 at% of C-O bonds, 2.4 at%, 3.0 at%, and 2.8 at% of C=O bonds, and 8.8 at%, 9.5 at%, and 7.9 at% of O-C=O bonds, respectively. Although XPS cannot detect the boron, it is still useful for investigation of oxygen containing groups.

Figure 5.2.4 Left: Survey of B-doped graphenes. Right: C1s high resolution XPS of B-doped graphenes. Doping level: (A, B) 23 ppm of boron, (C, D) 140 ppm of boron and (E, F) 590 ppm of boron.

Combustible elemental analysis was employed to study the elemental compositions of the prepared graphenes, which is helpful for obtaining the absolute contents of boron in such prepared graphenes. Combined with XPS results, it could provide further insight to the composition and bonding situation of graphenes. According to the measurement, G-B-23ppm contains 82.48 at% of carbon, 10.04 at% of H and 7.48 at% of O. G-B-140ppm contains 82.28 at% of C, 10.03 at% of H, 7.69 at% of O. G-B-590ppm contains 84.83 at% of C, 9.63 at% of H and 5.54 at% of O.

The electrical resistivity of the prepared B-doped graphenes was investigated by four point measurements. The electrical resistivity of G-B-13ppm was $9.5 \times 10^{-5} \Omega \cdot \text{cm}$, G-B-140ppm was $2.1 \times 10^{-5} \Omega \cdot \text{cm}$ and G-B-590ppm was $2.3 \times 10^{-4} \Omega \cdot \text{cm}$. Therefore, the electrical resistivity was increased with the amount of doped boron, which is caused by the electron acceptor properties of boron.

Figure 5.2.5 Electrochemical behaviors of oxygen reduction reaction (ORR) in 0.1M KOH solution on the surfaces of B-doped graphenes and bare glassy carbon (GC) electrode. Conditions: scan rate 100 mV/s.

The electrochemical properties of the prepared B-doped graphenes toward ORR were recorded and shown in Figure 5.2.5. It is clear no reduction peak appeared in N_2 saturated KOH solution, and a significant reduction peak showed -460mV for O_2 in air-saturated KOH solution. In this case, the observed reduction peak at -460 mV is caused by the reduction of oxygen. It is obvious that the oxygen reduction peaks shift negatively along the potentials for the increasing amount of doped boron. Therefore, the higher amount of boron doped, the lower the electrocatalytic activity towards ORR for B-doped graphenes. This result agrees with the general concept of hole-doping electrochemistry,²¹ but disagrees with some of the previous observations.¹² It is important to note that the mentioned articles on catalyzing oxygen reduction on B-doped graphene surfaces did not compared graphenes with different amount of boron dopant.

Figure 5.2.6 Weight specific capacitance measured at scan rates of 25 mV/s, 50 mV/s, 75 mV/s, 100 mV/s, 200 mV/s and 400 mV/s of graphenes that doped with (A) 23 ppm, (B) 140 ppm and (C) 590 ppm of boron. (D) Bar chat of the weight specific capacitance for prepared B-doped graphenes.

The weight specific capacitances of B-doped graphenes were studied by using cyclic voltammetry capacitive charge-discharge current, and the capacitance can be expressed as:

$$C = \frac{I}{\nu} \quad (2)$$

where C is capacitance (F), ν is the scan rate (mV/s, can be expressed as dE/dt) and I is current (A).²²

The capacitances of B-doped graphenes were studied by observing the current at potential of 0.15 V (vs. Ag/AgCl) with scan rates of 25 mV/s, 50 mV/s, 75 mV/s, 100 mV/s, 200mV/s and 400 mV/s and shown in Figure 5.2.6. The weight specific capacitance of G-B-23ppm, G-B-140ppm and G-B-590ppm are 11.6 F/g, 10.7 F/g and 10.3 F/g, respectively, which show a decreasing trend along with an increasing amount of boron content. Again, this is in contrary to previous claims where B-doped graphenes¹¹ (and N-doped graphenes as well²³) showed higher capacitance than undoped materials.

In conclusion, a scalable synthesis method for B-doped graphene with tunable doping level of boron by using thermal exfoliation in an atmosphere with boron trifluoride diethyl etherate at different exfoliation temperatures was reported. The increasing doping level of boron resulting in a more negative potential shifts for ORR. This result agrees with theory that p-doped materials are expected to perform worse electrocatalytic performance in reduction reactions. Similarly, doping with higher level of boron also make graphenes perform a decreased capacitance.

5.2.3 Experimental

5.2.3.1 Materials

Sulphuric acid (98%), hydrochloric acid (37%), nitric acid (fuming, 98%), barium nitrate (99.5%), silver nitrate (99.5%), and potassium chlorate (98%) were obtained from PENTA. Graphite microparticles (<50 μm) were obtained from KOOH-I-NOOR Graphite. Boron trifluoride diethyl etherate, *N,N*-dimethylformamide (DMF), potassium hydroxide, potassium ferrocyanide, potassium phosphate monobasic, potassium chloride, sodium chloride and

sodium phosphate dibasic were obtained from Sigma Aldrich. Hydrogen (99.9999%) and nitrogen (99.9999%) were purchased from SIAD.

5.2.3.2 Apparatus

Scanning electron microscopy (SEM) images were obtained by using a JEOL (Japan) 7600F field emission scanning electron microscopy. Raman spectrums were obtained by using confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. The 514.5 nm excitation wavelength Ar laser and a 100× objective lens were employed on an Olympus optical microscope. The sample of X-ray photoelectron spectroscopy (XPS) was prepared by placing a layer of sample onto carbon tape which was attached to the sample holder. Then XPS sample was the investigated by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer was employed to obtain the survey and high resolution spectrums for selected ranges.

Prompt Gamma-ray Analysis was used to determine amount of boron in the graphenes. The PGAA measurements were carried on the PGAA facility which is installed at LWR-15 nuclear reactor.²⁴ The samples were irradiated in thermal neutron beam with flux $\sim 3 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$. The gamma spectrums were taken with the well-shielded 25 % HPGe detector.

The combustible elemental analysis was measured by CHN PE 2400 Series II (Perkin Elmer, USA). In CHN operating mode, the instrument employs a classical combustion principle to convert the sample elements to sample gases, such as CO₂, H₂O and N₂. The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases,

separation and detection. The accuracy of CHN determination is better than 0.30% abs. Internal calibration was performed by using N-phenyl urea.

For electrical resistivity measurements of graphenes, 40 mg of the graphenes were compressed into a capsule ($\frac{1}{4}$ " diameter) under a pressure of 400 MPa for 30 s. The resistivity of the prepared capsule was measured by a 4-probe technique using the Van der Pauw method²⁵. The resistivity measurements were then performed with Keithley 6220 current source and Agilent 34970A data acquisition/switch unit with 10 mA measuring current.

5.2.3.3 Procedures

Synthesis of Staudenmaier graphite oxide. Graphite oxide was synthesized by the Staudenmaier method, 9 mL of fuming nitric acid and 17.5 mL of sulphuric acid (95-98%) were added to a reaction flask that contains a magnetic stir bar and then the reaction flask was cooled by immersion in an ice bath for 15 min. 1 g of graphite was then added to the mixture while stirring in order to obtain a well dispersed solution. 11 g of potassium chlorate was added to the mixture over 15 min to avoid sudden increment in temperature and formation of explosive gas while the flask in ice bath. When the potassium chlorate was dissolved, the reaction flask was loosely capped to allow gas evolution and the mixture was stirred for 96 hours at room temperature. When reaction was finished, the formed solution was poured into 1 L of deionized (DI) water and then filtered. Then the graphite oxide was re-dispersed and washed in HCl (5%) solutions to remove sulphate ions, and finally washed with DI water until the solution reach neutral pH. The prepared graphite oxide powder was dried in vacuum oven at 60 °C for 48 hours before use.

Synthesis of boron doped graphenes. The prepared Staudenmaier graphite oxides were then used as precursors and the boron trifluoride diethyl etherate ($\text{BF}_3\text{Et}_2\text{O}$) was used as boron precursor. The bubbler filled with liquid boron trifluoride diethyl etherate and was used for exfoliation at 20 °C and 1000 mbar. In two samples' preparation, N_2 was used as carrier gas with flow rate of 100 mL/min. The hydrogen/nitrogen mixture N_2 (0.5 L/min) and H_2 (0.5 L/min) was used for the third sample preparation. The reactor was kept flushed with N_2 . The flow of boron precursor was hold for 5 min before transferring the sample to hot zone, and the thermally exfoliation was performed for 12 minutes at 800 °C and 1000 °C.

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and a glassy carbon (GC, 3 mm diameter) electrode was used as the working electrode.

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Chapter 6

Electrochemical studies of 3D layered nanomaterials

6.1	<i>Electrochemical studies of 3D layered nanomaterials</i>
6.1.1	<i>Introduction</i>
6.1.2	<i>Results and discussions of 3D graphenes</i>
6.1.3	<i>Results and discussions of 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solutions</i>
6.1.4	<i>Experimental</i>

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

1. Lu Wang, Zdenek Sofer, Adriano Ambrosi, Petr Simek, Martin Pumera, 3D-graphene for electrocatalysis of oxygen reduction reaction: Increasing number of layers increases the catalytic effect. *Electrochem. Commun.* **2014**, 46, 148-151.

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2. Lu Wang, Zdenek Sofer, Jan Luxa, Martin Pumera, $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ Solid Solutions as 3D Electrodes for Hydrogen Evolution Reaction. *Adv. Mater. Int.*, **2015**, 2, 1500041.

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Contributions:

L. Wang conducted most of the experiments. Z. Sofer, J. Luxa, P. Simek, synthesized the materials. M. Pumera conceptualized and directed the projects. All authors contributed to discussion and writing of the manuscripts.

Layered nanomaterials have been explored electrochemically for potential applications in energy storage and energy production prior to the discovery of graphenes and some layered transition metal dichalcogenides (TMDs), such as MoS₂ and WS₂. Since then, the use of graphenes and TMDs in energy related field attract vast amount of interest due to their remarkable electrocatalytic properties towards oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER).

However, in such research field, providing an experimental condition that close to real industrial condition would important and necessary. Thus, for these layered nanomaterials with such surface electroactive properties, the large surface area is always required prior to the real industrial purpose for either ORR (fuel cell related reaction) or HER (clean energy production).

Unfortunately, most of the related research reports still focus on their electrochemistry properties under 2D conditions (drop cast prepared electrode surface), not much research has been performed under 3D conditions (3D samples) which the prepared 3D material can provide much larger surface area than 2D material.

Therefore, the electrochemical studies of different 3D layered nanomaterials were well documented for various reactions, and this will be extended in the **Chapter 6** to include additional findings.

Chapter 6 is the collective work in addressing Objective 2.

Chapter 6.1 Electrochemical studies of 3D layered nanomaterials

6.1.1 Introduction

Oxygen reduction reaction (ORR) is one of the most important reactions in fuel cells and Zn-air batteries¹, which currently limits the efficiency of those applications. Graphene materials, such as heteroatom doped graphenes which provide large surface area and remarkable electrocatalytic properties toward ORR, were also suggested as ideal materials for ORR.² However, the use of graphenes in real applications, such as devices, still have problems which in this case, graphenes tend to restack which resulted in decreasing surface area.^{3,4} Three dimensional graphene is typically synthesized by CVD deposition of carbon precursor gas on 3D nickel foam⁵⁻⁷ or graphitization of 3D carbon,^{2,8} and is able to provides mechanical robustness and enhance the electrochemical performance towards ORR²⁻¹⁰, and electrochemical sensing^{6,7}. The electrochemical performance of 3D graphenes for ORR was studied by comparing double, triple and few layers 3D graphenes' electrocatalytic properties toward ORR.

On the other side, hydrogen evolution reaction (HER) is another important part of fuel cell and the layered transition metal dichalcogenides (TMDs) were considered as the potential catalysts for such reaction. The formula of TMDs is MX_2 where M contains a transition metal such as Mo, W and Re; and X contains a chalcogen such as S and Se, and some of these TMDs have layered structures. In this case, single layer or few layers of TMDs can be extracted by various exfoliation methods, such as mechanical and chemical approaches. There are several types of layered TMDs and the band gap of TMDs mainly depends on their chemical

compositions. Therefore, different TMDs can perform different band gaps and fluorescence properties,¹¹ and also be able to exhibit different electrochemical properties¹², which is important to the future energy related applications.¹³

Theoretically, band gap of TMDs can be tailored by preparing their solid solutions, such as making TMDs with mixed transition metals such as $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ ($0 \leq x \leq 1$)¹⁴ or mixed chalcogenides such as $\text{MoS}_y\text{Se}_{2-y}$ ($0 \leq y \leq 2$).^{15,16} It has been shown in previous studies that the band gap¹⁷ and optical properties¹⁸ are able to be changed by preparing $\text{MoS}_y\text{Se}_{2-y}$ solid solutions and $\text{M}_{1-x}\text{W}_x\text{S}_2$ solid solutions¹⁹. There are several literatures on the utility of TMDs²⁰, such as suggesting MoS_2 ²¹⁻²⁵, MoSe_2 ^{26,27}, WS_2 ^{28,29}, and WSe_2 ²⁵ as great catalysts for HER. However, the overall process of HER is mainly performing on the surface of the material, and in order to perform high efficient HER, a large electroactive surface area is required.

Unfortunately, research on the effects study of electrocatalytic performance of such layered nanomaterials were mainly focusing on 2D electrodes, and towards to their possible applications, a higher surface area would be prefer which make the 3D condition more important to such materials.

6.1.2 Results and discussions for 3D graphenes

The 3D graphenes were successfully synthesized by depositing carbon from CH_4/H_2 mixture gas (1000 °C, 0.6 mbar) onto nickel foam with different deposition time. The morphology and elemental mapping were investigated by scanning electron microscopy (SEM), defect density was studied by Raman spectroscopy, elemental compositions and detailed bonding information were obtained by X-ray photoelectron spectroscopy (XPS), and

lastly electrocatalytic properties toward ORR were studied via voltammetric method. The as-prepared 3D graphenes are labeled as 3D-G-DL for double layers, 3D-G-TL for triple layers and 3D-G-FL for few layers. The number of the coated graphene layers was investigated by Raman spectroscopy, and described in the following text.

Figure 6.1.2.1 Scanning electron microscopy (SEM) images (A and B) and elemental mappings (C and D) of Ni foam (row 1), double layer 3D graphenes (second row), triple layer 3D graphenes (third row), and multi layer 3D graphenes (fourth row), at magnification of 130x for C and Ni.

The morphology of nickel foam and 3D graphenes were obtained by SEM and shown in Figure 6.1.2.1 at (A) 10,000 $\times$ and (B) 130 $\times$ magnifications. The SEM images clearly show

successfully deposition of graphenes onto the Ni foam via CVD method. The coverage of graphenes increases along with the increasing number of grown graphene layers. The elemental maps of Ni foam and 3D graphenes were shown in Figure 6.1.2.1 (C) and (D) and found that the amount of carbon element was increased with the increasing number of grown layers.

Figure 6.1.2.2 Raman spectrums of Ni foam (A), double layers 3D graphenes (B), triple layers 3D graphenes (C) and few layers 3D graphenes (D).

In order to study the defect density of 3D graphene, Raman spectroscopy was employed and shown in Figure 6.1.2.2. The G band presents at 1560 cm^{-1} indicates the presence of sp^2 lattice carbon atoms in graphene sheet and a 2D band appears at 2700 cm^{-1} indicates of crystalline graphitic material. The small peak at 800 cm^{-1} represents the Ni from nickel support. The ratio of intensity of D and G band for 3D-G-FL, 3D-G-TL and 3D-G-DL are 2.38, 2.34 and 1.88, respectively. The result indicates a decreasing intensity of 2D peak along with the increasing number of grown layers. Furthermore, the number of the layers of the 3D graphenes can be investigated via Raman spectrums from the ratio of G and 2D band's intensity; the 3D-G-DL on average contains two layers (I_G/I_{2D} ratio of 1.88), 3D-G-TL has approximately three layers (I_G/I_{2D} ratio of 2.34) and 3D-G-FL contains of three layers and more (I_G/I_{2D} ratio of 2.38).³⁰

Figure 6.1.2.3 Survey of Ni foam (A), double layers 3D graphenes (B), triple layers 3D graphenes (C), and few layers 3D graphenes (D).

The bonding information and elemental compositions of nickel support and 3D graphenes were obtained by XPS. The Survey XPS for double layers 3D graphenes, triple layers 3D graphenes, and few layers 3D graphenes were shown in Figure 6.1.2.3, the grown carbon are 85.8 at% for double layers, 93.3 at% for triple layers and 95.0 at% for few layers,

respectively. This result further confirmed with elemental maps (Figure 6.1.2.1) and shows the carbon content keep increasing with increasing layers of graphene.

Figure 6.1.2.4 High resolution C1s of (A) double layers 3D graphenes, (B) triple layers 3D graphenes, and (C) few layers 3D graphenes.

The detailed bonding information for residual oxygen containing groups of graphenes was obtained in the high resolution C1s XPS in Figure 6.1.2.4. The bonding information of residual oxygen containing groups are shown at different binding energy levels, C=C bonds at 284.5 eV, C-C bonds at 285.4 eV, C-O bonds at 286.3 eV, C=O bonds at 287.4 eV, O-C=O bonds at 288.5 eV and π - π interactions at 290 eV. The 3D-G-DL contains 59.057 at % of C=C bonds, 19.699 at % of C-C bonds, 9.330 at % of C-O bonds, 3.398 at % of C=O bonds, 6.205 at % of O-C=O bonds and 2.312 at % of π - π interactions. 3D-G-TL contains 63.844 at % of C=C bonds, 18.591 at % of C-C bonds, 7.768 at % of C-O bonds, 3.547 at % of C=O bonds, 2.806 at % of O-C=O bonds, and 3.444 at % of π - π interactions. 3D-G-FL contains 60.064 at % of C=C bonds, 16.806 at % of C-C bonds, 8.824 at % of C-O bonds, 4.676 at % of C=O bonds, 4.345 at % of O-C=O bonds and 5.285 at % of π - π interactions. The amount of π - π interactions exhibits an increasing trend along with the increasing layers of grown graphenes.³¹

Figure 6.1.2.5 Voltammetric profile of Ni foam, double layers (DL) 3D graphenes, triple layers (TL) 3D graphenes, and few layers (FL) 3D graphenes.

The electrocatalytic properties towards ORR on Ni foam, 3D-G-DL, 3D-G-TL, and 3D-G-FL were studied by linear sweep voltammetry (LSV) in air saturated 0.1 M KOH solution by using the three electrode configuration and the 3D Ni foam/3D graphenes were employed as working electrode and used directly. The electrochemical behaviours were recorded and shown in Figure 6.1.2.5. It is clear that Ni foam does not perform any enhancement in electrocatalytic properties toward ORR, while with increasing number of grown layers, the height of oxygen reduction peak keep increasing. In addition, the onset potential for 3D-G-DL, 3D-G-TL, and 3D-G-FL are -315 mV, -296 mV and -252 mV which also exhibit an increasing trend of electrocatalytic performance toward ORR along with the increasing numbers of layers.

In conclusion, the 3D graphenes were successfully synthesized via CVD with varied number of graphene layers. An increasing electrocatalytic trend of 3D graphenes toward oxygen reduction reaction was observed with increasing numbers of grown graphene layers. This finding shall have profound influence on the applications of 3D graphene in future electrochemical energy devices.

6.1.3 Results and discussions for 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solutions

Herein, the electrocatalytic performance of 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ ($0 \leq x \leq 1$) solid solution system was investigated, which deposits different ratios of W and Mo in the MS_2 solid solution onto 3D freestanding interconnected glassy carbon (GC) foam. (Scheme 6.1.3.1)

Scheme 6.1.3.1 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution coated on glassy carbon foam. Left: Photograph of actual 3D glassy carbon foam (length 2.33 cm); Right: Schematic diagram of 3D glassy carbon foam coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution.

The solid solutions of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ were synthesized by depositing ammonium tetrathiomolybdate, ammonium tetrathiotungstenate and their mixtures onto GC foam by thermal treatment in N_2 atmosphere. Using of tetrathiotungstenate and tetrathiomolybdate mixtures for preparing of $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$ solid solution via decomposition at high temperature has already been reported.^{32, 33} Then the accurate ratios between transition metals, morphology, elemental compositions and bonding information were investigated by several

different techniques. Lastly, the linear sweep voltammetry (LSV) was used for studying the electrocatalytic performance toward HER.

Firstly, the Electro Thermal Vaporization Inductively Coupled Plasma Optical Emission Spectrometry (ETV-ICP/OES) was used to obtain the exact compositions of prepared 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solutions. According to the result, a combination of Mo/W precursors with ratio of 3:1 can form a solid solution with ratio of $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$, the Mo/W precursor with ratio of 1:1 resulting in $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ composition, and the Mo/W precursor with ratio of 1:3 form a composition of $\text{Mo}_{0.14}\text{W}_{0.86}\text{S}_2$. When Mo/W precursors were present as 1:0 or 0:1 ratio, the prepared materials were purely MoS_2 and WS_2 coated 3D samples.

Figure 6.1.3.1 Scanning electron microscopy (SEM) images at different magnifications of (A, B) 3D glassy carbon foam, (C, D) MoS₂ coated 3D foam, (E, F) Mo_{0.51}W_{0.49}S₂ coated 3D foam,

(G, H) $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ coated 3D foam, (I, J) $\text{Mo}_{0.14}\text{W}_{0.84}\text{S}_2$ coated 3D foam, (K, L) WS_2 coated 3D foam. Scale bar at left of 100 μm , right of 10 μm .

The morphologies of prepared 3D $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution materials were obtained by SEM, as well as elemental maps. Figure 6.1.3.1 shows the GC foam contains a freestanding 3D interconnected network structure and the coated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution can be seen as the “contrast coating” on the GC foam. The contrast difference of Mo/W and carbon is due to the different atomic number, the larger atomic numbers and the larger contrast difference (number of scattered electrons). Thickness of the layers is approximately 1-2 μm calculated based of GC foam surface area and loading of grown Mo and W (1 - 2 wt%).

Figure 6.1.3.2 Survey for (A) glassy carbon foam, (B) MoS_2 coated 3D foam, (C) $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$ coated 3D foam, (D) $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ coated 3D foam, (E) $\text{Mo}_{0.14}\text{W}_{0.84}\text{S}_2$ coated 3D foam, (F) WS_2 coated 3D foam.

The elemental compositions and bonding information were investigated by XPS. The survey and high resolution XPS for Mo3d and W4f are recorded and shown in Figure 6.1.3.2. The results indicate that the 3D GC support only contains C and O, and no W and Mo can be

found. In addition, with an increasing ratio of W precursor, the amount of grown W also increased in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution.

Figure 6.1.3.3 High resolution spectrums for Mo3d (row 1) and W4f (row 2), for (A) MoS_2 coated 3D foam, (B), (E) $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$ coated 3D foam, (C), (F) $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ coated carbon foam, (D), (G) $\text{Mo}_{0.14}\text{W}_{0.84}\text{S}_2$ coated 3D foam, and (H) WS_2 coated 3D foam.

The detailed bonding information was investigated via high resolution Mo3d and W4f and shown in Figure 6.1.3.3. Mo3d spectrum contains peaks at 232.4 eV and 229.3 eV represent $\text{Mo}^{4+}3d_{3/2}$ and $\text{Mo}^{4+}3d_{5/2}$, respectively, and peaks at 236.1 eV and 233.1 eV are caused by $\text{Mo}^{6+}3d_{3/2}$ and $\text{Mo}^{6+}3d_{5/2}$, respectively.^{34,35} In W4f spectrum, the peaks shown at 35.1 eV and 33 eV represent $\text{W}^{4+}4f_{5/2}$ and $\text{W}^{4+}4f_{7/2}$, and peaks shown at 38.4 eV and 36.2 eV represent $\text{W}^{6+}4f_{5/2}$ and $\text{W}^{6+}4f_{7/2}$, respectively.³⁶

Table 6.1.3.1 Bonding information for as-prepared 3D TMD solid solution samples.

Bonding information	MoS ₂	Mo _{0.51} W _{0.49} S ₂	Mo _{0.21} W _{0.79} S ₂	Mo _{0.14} W _{0.86} S ₂	WS ₂
Mo ⁴⁺	57.3 %	80.4 %	62.6 %	61.5 %	0 %
Mo ⁶⁺	42.7 %	19.6 %	37.4 %	38.5 %	0 %
W ⁴⁺	0 %	65.1 %	63.7 %	64 %	44 %
W ⁶⁺	0 %	34.9 %	36.3 %	36 %	56 %

The amount of Mo⁴⁺, Mo⁶⁺, W⁴⁺ and W⁶⁺ are shown in Table 6.1.3.1. There is a roughly decreasing trend in W⁶⁺ along with the decreasing ratio of WS₂ content.

Figure 6.1.3.4 Voltammetric profile of 3D glassy carbon foam and prepared 3D MoS₂, 3D Mo_{0.51}W_{0.49}S₂, 3D Mo_{0.21}W_{0.79}S₂, 3D Mo_{0.14}W_{0.86}S₂, and 3D WS₂ electrodes in 0.5 M H₂SO₄ at a scan rate of 2 mV/s.

The electrocatalytic behaviors towards HER of 3D GC foam coated with Mo_xW_{1-x}S₂ alloy materials were investigated by linear sweep voltammetry (LSV) and shown in Figure

6.1.3.4. LSV showed decreasing overpotential with increasing amount of W content in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution. The potential for all 3D electrodes at current of -1.5 mA were -402.4 mV, -380.4 mV, -363.3 mV, -346.2 mV, -326.7 mV, and -238.8 mV for 3D GC foam, 3D MoS_2 , 3D $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$, 3D $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$, 3D $\text{Mo}_{0.14}\text{W}_{0.86}\text{S}_2$, and 3D WS_2 electrode. It is clear that the electrochemical performance of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution can be tailored by changing the ratio of transition metals in the solid solution.

HER is a two step reaction and the first step is adsorption and reduction of $\text{H}^+(\text{aq})$ to $\text{H}(\text{ads})$ on sample's surface. Then the second step is combination of $\text{H}(\text{ads})$ with other hydrogen and form $\text{H}_2(\text{g})$. The second step can proceed by recombining with another $\text{H}(\text{ads})$ at the surface (Tafel step) or recombination with another $\text{H}^+(\text{aq})$ to form $\text{H}_2(\text{g})$. The key factor in kinetics of HER and rate constant is strength of the adsorption of $\text{H}^\cdot$ on surface. Too strong adsorption would inhibit the second step's efficient and too weak interaction of $\text{H}^\cdot$ with surface could lower the first step rate. Due to the pure MoS_2 and WS_2 performed distinct G_{H} for $\text{H}^\cdot$ adsorption³⁷, the monotonic shift for their solid solution with different compositions is not surprising.

In conclusion, the 3D electrodes coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution with different Mo/W ratios were successfully prepared. The morphology, bonding information, elemental compositions and electrochemical properties for hydrogen evolution were studied. Unfortunately, the solid solution system does not exhibit any enhancement towards hydrogen evolution reaction and such result also indicate a better electroactivity from W content rather Mo content.

6.4 Experimental

6.4.1 Materials

Potassium hydroxide was obtained from Sigma Aldrich. Nitrogen (99.9999%), methane (99.9995%) and hydrogen (99.9999%) were purchased from Linde Gas. 1/8" thickness nickel metal foam (99.99% purity, 95% porosity) was purchased from MTI Corporation. Acetone (99.9%) was obtained from Lach-Ner. Reticulated vitreous carbon foam was purchased from ERG Aerospace Corporation. Ammonium tungstenate, ammonium heptamolybdate tetrahydrate, ammonia (25%) and N,N-dimethylformamide (DMF) were purchased from Penta. Nitrogen (99.9999%) and hydrogen sulfide (99.5%) for solid solution were purchased from SIAD.

6.4.2 Apparatus

Scanning electron microscopy (SEM) images were obtained by using a JEOL (Japan) 7600F field emission scanning electron microscopy. Raman spectrums were obtained by using confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector. The 514.5 nm excitation wavelength Ar laser and a 100× objective lens were employed on an Olympus optical microscope. The sample of X-ray photoelectron spectroscopy (XPS) was prepared by placing a layer of sample onto carbon tape which was attached to the sample holder. Then XPS sample was the investigated by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer was employed to obtain the survey and high resolution spectrums for selected ranges.

The Mo/W content ratios were investigated by ETV-ICP OES via Spectro ARCOS spectrometer (SPECTRO Analytical Instruments, Germany). 1 mg of the prepared sample was homogenized and powdered with spectroscopically pure graphite at weight ratio of 1:10 and then directly vaporized in ETV system at 2400 °C, in Ar/CCl₂CF₂ mixture that connected to ICP-OES.

The voltammetric analysis was carried on by using Autolab (PGSTAT 101, Ecochemie, Utrecht, The Netherlands). The electrochemical measurements were carried on at room temperature in a voltammetric cell (5 ml) by applying a three-electrode configuration. An Ag/AgCl (saturated) electrode was used as a reference electrode, a Pt electrode was used as an auxiliary electrode, and the prepared 3D samples were used as the working electrode.

6.4.3 Procedures

The deposition of graphenes was carried on in a hot wall quartz reactor filled with hydrogen/methane. The Ni support was sonicated in acetone for 10 min and dried out at 100 °C and then shifted into the hot wall reactor which was repeatedly flushed with N₂. The temperature was heated up to 1000 °C with 7 °C.min⁻¹ heating rate in 50 mL/min hydrogen atmosphere under reduced pressure (0.7 mbar) and the deposition was carried on in hydrogen/methane mixture (20 mL.min⁻¹ H₂ and 20 mL.min⁻¹ CH₄) under 0.6 mbar pressure. Then the deposition time varies from 0.5 to 2 hours to obtain 3D graphenes with different number of grown layers. Then the prepared sample was allowed to cool on room temperature in hydrogen atmosphere (50 mL/min, 0.7 mbar). The deposition time of 3D-G-DL was 30 min, of 3D-G-TL was 90 min and 3D-G-FL was deposited for 120 min.

Ammonium tetrathiomolybdate was synthesized from ammonium heptamolybdate and hydrogen sulfide. Ammonium heptamolybdate (10 g) was dispersed into 30 ml of deionized (DI) water together with ammonia (100 ml, 25 wt%). Hydrogen sulfide was passed through the solution for 4 hours with about 1-2 bubbles per second. The prepared ammonium tetrathiomolybdate was then separated by suction filtration and dried in vacuum oven at room temperature. Similar to the preparation of Ammonium tetrathiomolybdate, ammonium tetrathiotungstate was prepared in similar method. Hydrogen sulfide was passed through saturated solution of ammonium tungstate (100 ml) in diluted ammonia (1:1 by vol.) for 10 hours. Then the formed ammonium tetrathiotungstate was removed by suction filtration and dried in vacuum oven at room temperature as well.

The precursor solutions consist of ammonium tetrathiomolybdate, ammonium tetrathiotungstate, and the mixtures which dispersed in DMF. The GC foam was then placed in the prepared solution containing 5 wt% of Mo and W with adequate Mo/W molar ratio to the compositions of $\text{Mo}_{0.25}\text{W}_{0.75}\text{S}_2$, $\text{Mo}_{0.50}\text{W}_{0.50}\text{S}_2$ and $\text{Mo}_{0.75}\text{W}_{0.25}\text{S}_2$ and then ultrasonicated for 10 min. The treated GC foam was dried for 24 hours in vacuum oven at 50 °C. Then the GC foam was annealed under N_2 atmosphere for 2 hours at 700 °C. The temperature changing rates were set as 20 °Cmin⁻¹ and the flow rate of N_2 was 500 mlmin⁻¹.

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Chapter 7

Conclusion and Epilogue

7.1 Conclusion

7.1.1 *Influence of impurities on the electrochemistry of carbon nanotubes and graphenes*

7.1.2 *Influence of doping of graphenes*

7.1.3 *Electrochemical studies of 3D layered nanomaterials*

7.2 Epilogue

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7.1 Conclusion

Due to the excellent inherent electrochemistry properties shown by carbon nanotubes and graphenes, the use of aforementioned nanocarbons as electrode substrate was considered as one of the best electrode substrate. However, it has been showed that such carbon nanomaterials exhibit similar electrochemistry properties to graphite and any exceptions are corresponding to the present impurities and doping. Therefore, the PhD project is mainly focusing on the influence of impurities and doping of nanocarbons by performing detailed composition characterizations, control experiments, appropriate purification method as well as the voltammetric technique to explore the real properties of nanocarbons and impurities.

Layered nanomaterials including graphenes and transition metal dichalcogenides exhibit promising electrocatalytic properties in energy related field. Energy related reactions such as oxygen reduction reaction and hydrogen evolution reaction, such reactions are mainly occurring on the surface of the catalyst. In case of real industrial condition requirement, a large active surface is always preferred. Therefore, the second focus for this PhD project is to study the electrochemistry properties of the layered nanomaterials that under a 3D condition.

Therefore, two main focus of research are emphasized in this project. The first focus is to show the electrochemical roles of the enclosed impurities in the nanocarbons as well as the effects of different types of doping for graphenes. The second focus is to study the 3D layered nanomaterial, such as graphenes and TMDs, to explore their performance towards energy related reactions under 3D condition.

7.1.1 Influence of impurities on the electrochemistry of carbon nanotubes and graphenes

Impurities usually coming from two sources, starting material and synthesis process, especially for carbon nanotubes and graphenes, the carbon source, metal based catalysts and metal based chemicals are commonly employed during the synthesis process and introduce large amount of carbonaceous impurities and metallic impurities. Such impurities usually remain ppm level and keep invisible from some commonly used characterization techniques, such as X-ray photoelectron spectroscopy (usually can detect content with higher than 0.1 at%). However, even the material with few ppm impurities, the electrochemistry properties can still be dramatically influenced.

The influence of carbonaceous impurities on electrochemistry of carbon nanotubes and graphenes is presented in **Chapter 3** and showing special redox signals for detecting of important analytes. Then the electrochemical study on the influence of present metallic impurities in carbon nanotubes and graphenes towards oxygen reduction reaction is shown in **Chapter 4**. Results clearly indicate that the manganese based impurities can dramatically enhance the electrocatalytic properties towards oxygen reduction reaction even with extremely low content (11.9 ppm).

7.1.2 Influence of doping of graphenes

Introducing foreign atoms into carbon framework can be considered as doping of graphenes which can tailor the properties of the prepared graphenes. The doping level of dopant is the most important factor that directly relates to the carrier density of the graphenes. The dopants for graphenes can be divided into two groups, n-type dopants (electron donor) and p-type dopants (electron acceptor) which can theoretically enhance the reduction reaction/inhibit oxidation reaction and inhibit reduction reaction/enhance the oxidation reaction.

Therefore, the factor that can affect doping level for nitrogen doped graphenes and the electrochemical study on boron doping of graphenes were shown in **Chapter 5**. Results indicate that the types of graphite oxide (different synthesized methods) can influence the doping level and the Hummers method prepared graphite oxide can be doped the most. Meanwhile, the boron dopants which can be considered as the p-type dopant and inhibit the reduction reaction as well as increase the specific weight capacitance.

7.1.3 Electrochemical studies of 3D layered nanomaterials

Layered nanomaterials including graphenes and layered transition metal dichalcogenides such as MoS_2 and WS_2 exhibited promising electrocatalytic properties towards energy related reactions, for instance, oxygen reduction reaction and hydrogen evolution reaction. Both of the aforementioned energy related reactions were occurring on the surface of the catalyst, which means if the catalyst contains larger surface area; the efficiency of the reaction can also be enhanced. Thus a 3D electrode that covered/made by the catalyst would be preferred for better catalyzing performance.

Chapter 6 explored the electrochemistry performance of graphenes and transition metal dichalcogenides that coated onto 3D support via volumetric method. In case of energy storage, the layered graphene coated 3D Ni foam exhibited an enhanced oxygen reduction reaction along with the increasing number of graphene layers. For clean energy production, 3D coated MoS_2 , WS_2 , and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solutions with different ratios of Mo and W content were prepared and indicating that the 3D coated TMDs can perform the catalyzing effect towards hydrogen evolution and the enhancement increases with the increasing amount of W content.

7.2 Epilogue

Perspective

The current research focus of nanoscience and nanotechnology in the field of nanomaterials has been shifted from fullerene to carbon nanotubes, graphenes as well as layered transition metal dichalcogenides. All of these nanomaterials have attracted vast amount of attentions from both of scientific community and industries due to their unique properties which make them high potential in applications ranging from electronic devices to sensing substrates.

Unfortunately, for carbon nanotubes and graphenes, most of those amazing properties are corresponding to the impurities present, not themselves. Lots of research have been done and indicate that the present impurities can dramatically influence the electrocatalytic properties of carbon nanotubes and graphenes. This finding not only indicates the reasons for the performed remarkable electrocatalytic properties, but also points out the future direction for modifying of carbon nanomaterials.

The energy related reactions, for instance, oxygen reduction reaction and hydrogen evolution reaction which are important to the applications that relate to energy storage and energy generation, such as fuel cells and solar cells. In case of real life applications, such batteries do contain large 3D electrodes which could provide large active surface of the catalysts. However, the number of electrochemical studies that performed on 3D electrode is limited and lots of materials' properties remain unclear under that condition. Thus, it would be important and useful to perform more studies of the nanomaterials under 3D condition.

The research on effects of present impurities provides a direction for future modifying of carbon nanomaterials specific to electrocatalytic properties and applications. For instance, for sensing or ORR, introducing of carbonaceous impurities or Mn based impurities could strongly enhance the electrochemical performance and either n-type material or p-type material could enhance the electrochemical performance towards either reduction based applications or oxidation based applications as well. Meanwhile, the research on 3D coated nanomaterial is still in its early stage. Collective efforts from the scientific community is utmost important towards the understanding of electrochemical performance for 3D electrode in the field of energy related research.

Appendices

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Carbonaceous impurities in carbon nanotubes are responsible for accelerated electrochemistry of acetaminophen

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ABSTRACT

We show here that previous claims in the literature about the enhanced electrochemical properties of carbon nanotubes towards the electrochemistry of acetaminophen are incorrect. The observed electrochemical properties are in fact due to the carbonaceous impurities present within the carbon nanotubes.

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1. Introduction

Carbon nanotubes (CNT) have been deemed as excellent electrocatalysts for a large variety of compounds [1]. Strong promises were given, raising high expectations [2]. However, this excitement lasted only few years, until Compton, followed by others, discovered that residual metallic catalyst impurities in CNT were responsible for their electrocatalytic effect towards hydrogen peroxide [3], hydrazine [4], halothane [5], glucose [6], amino acids [7], organic peroxides [8], sulphides [9], and L-glutathione [10], even at very low (~100 ppm) amounts [11]. Some compounds were not electrocatalyzed by the metals and thus the question on whether CNT had somehow special catalytic properties or not had remained unanswered for more than a couple of years. One should be reminded that materials based on sp^2 hybridised carbon, such as graphite, CNT [12] or graphene are of significantly heterogeneous nature, having two major features, sp^2 basal plane and edge plane/defects; both the edges and the defects of the plane show fast heterogeneous electron transfer (HET) while basal plane exhibits a slow HET rate towards many compounds [13–16]. Most of the surface of CNT consists of the “basal-plane” like walls while the highly electroactive edges are only located at the tips or on negligible portion of CNT surface as defects. Nanographite impurities, on the contrary, exhibit a large number of edge sites compared to the basal plane portion [17]. Perhaps therefore not surprisingly it was shown that onion-like nanocarbon impurities [18] (containing a large number of electroactive edge sites) in CNT samples were responsible for the electrocatalysis of ferro/ferricyanide, nicotinamide adenosine dinucleotide (NADH), epinephrine, norepinephrine, cysteine, and glutathione [18]. Later on, it was shown that nanocarbon impurities in

CNT were the actual cause for enhanced HET of ferro/ferricyanide [19] (even at 5% wt.), carbamazepine [20], azo compounds [21], organic hydrazines [22], signal transducing amino acids [23], enzyme cofactors [23], phenols [24], ascorbic acid [25], hydroquinone [26], insulin, nitric oxide, and extracellular thiols [27]. Similarly, another type of nanocarbon impurities rich in sp^3 defects on an sp^2 lattice, amorphous carbon, was shown to dominate the electrochemical properties of CNT at minute concentrations [28].

Here we demonstrate that the reported enhanced electron transfer properties of carbon nanotube modified electrodes towards the electrochemistry of acetaminophen [29] are unambiguously due to the carbonaceous impurities present and not to the carbon nanotubes themselves.

2. Experimental section

2.1. Apparatus

Voltammetric analysis was performed using an electrochemical analyser Autolab PGSTAT 101 (Eco Chemie, Utrecht, The Netherlands). Electrochemical tests were performed in a 5 mL voltammetric cell at room temperature (25 °C) using a three-electrode configuration. A glassy carbon (GC, 3 mm diameter) electrode was used as working electrode, an Ag/AgCl and a platinum electrode acted as reference and auxiliary electrode, respectively (CH Instruments, TX, USA).

2.2. Materials

Acetaminophen, phosphate buffer (pH 7.2), CNT-A, CNT-B and CNT-C [30–32], pure CNT [10,33], amorphous carbon and nanographite nanofibers were obtained from Sigma-Aldrich. All CNT had been extensively characterised previously (CNT-A contains 0.64% (wt.) of Fe,

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0.096% of Co, 0.035% of Mo and 0.32% of Ni and 8.9% of carbonaceous impurities; CNT-B contains 1.25% of Fe, 0.22% of Mo and 0.013% of Ni and 8.5% of carbonaceous impurities; CNT-C contains 3.33% of Co, 1.18% of Mo and 0.045% of Fe and 8.5% of carbonaceous impurities).

2.3. Procedures

Carbon materials did not require further purification and were used as-received. For modification of the GC electrode, the CNT, the amorphous carbon and the nanographite nanofibers were dispersed in DMF (5 mg/mL). The solutions were then sonicated for 5 min prior the deposition of 1 μ L of the suspension onto the GC electrode surface that had been previously polished with 0.05 μ m alumina on a polishing cloth. The coating was allowed to dry at room temperature, creating a carbon material film over the electrode surface. All experiments were carried out in phosphate buffer at pH 7.2.

3. Results and discussion

In the work illustrated in Ref. [29], the authors show that while acetaminophen exhibits on bare screen printed electrode an oxidation potential at $\sim +430$ mV (vs. Ag pseudoreference electrode) with a broad reduction wave at $\sim +30$ mV, at carbon nanotubes modified electrode, such oxidation occurred at $\sim +350$ mV with the reduction signal occurring at $\sim +250$ mV, with a well-defined response in both the anodic and cathodic regions. We investigated more in detail the electrochemistry of acetaminophen using three different samples of carbon nanotubes (CNT-A, B, and C). As shown in Fig. 1, the electrochemical behaviour of acetaminophen on all three CNT exhibits very similar behaviour to the one described in Ref. [29], showing well defined oxidation and reduction wave at $+380$ and $+300$ mV (vs. Ag/AgCl), respectively. Using the CNT-A, a second oxidation wave occurred at $\sim +475$ mV, which is due to the underlying glassy carbon electrode, as we will discuss below. The redox properties of acetaminophen at a bare GC electrode are very different, exhibiting in fact, an oxidation peak at $+520$ mV and a broad poorly defined reduction wave at ~ -22 mV. Interestingly, using a pure CNT sample (CNT not containing any metallic or carbonaceous impurities) as electrode modifier, the voltammetric profile of acetaminophen resembled that of the bare GC surface, showing an oxidation peak at $+470$ mV and reduction wave at $+12$ mV.

Knowing that CNT-A, B and C contain different types and amount of impurities, we investigated whether such impurities were responsible or not for the observed enhanced electrochemistry. We firstly tested the metallic impurities, namely Fe_3O_4 , NiO , Co_3O_4 and MoO_3 as the CNT-A, B and C contain these residual metallic impurities

Fig. 2. Electrochemical response of 0.1 mM acetaminophen on the metal-oxide modified electrode surfaces. Also shown is the response of impure and pure CNT for comparison. Other conditions as in Fig. 1.

(see Experimental section for details). The voltammograms of acetaminophen at electrode modified with these metal oxide nanoparticles are shown in Fig. 2. The voltammetric profiles are very similar to the one on glassy carbon, showing oxidation potential between $+475$ and $+510$ mV for various metal oxides and reduction peak ~ -10 mV. Note that the oxidation/reduction peak of Co_3O_4 around $+900$ mV originates from inherent electrochemistry of this metal oxide and it is not related to acetaminophen. The results showed in Fig. 2 clearly exclude any electrocatalytic effect of the metallic impurities present in CNT-A, B and C, towards the redox behaviour of acetaminophen.

We next turned to investigate whether the carbonaceous impurities within the CNT could cause the observed electrocatalytic effect. The cyclic voltammetric responses of acetaminophen at amorphous carbon and nanographite modified electrodes are shown in Fig. 3. It can be seen that both surfaces exhibit fast electron transfer, with oxidation potential of $+365$ mV and reduction potential of $+305$ and $+300$ mV for amorphous carbon and nanographite, respectively. The electrochemical behaviour of acetaminophen at these carbonaceous impurities is strikingly similar to the behaviour at CNT-A, B and C and very different from the electrochemistry at pure CNT. It is evident from these results that both the carbonaceous impurities (amorphous carbon and nanographite) are responsible for the electrocatalytic behaviour of the CNT towards the electrochemistry of

Fig. 1. Redox properties of acetaminophen on various carbon nanotube samples as well as on GC electrode. Conditions: 50 mM phosphate buffer, pH 7.2 containing 0.1 mM of acetaminophen. Scan rate 100 mV/s.

Fig. 3. Electrochemical response of 0.1 mM acetaminophen on the various nanocarbon surfaces. Conditions: as in Fig. 1.

acetaminophen. These impurities present in all CNT-A, B and C samples dominate their electrochemical properties.

4. Conclusion

We demonstrated here that the observed “enhanced electron transfer properties” of CNT towards the electrochemistry of acetaminophen [29] is due to the carbonaceous impurities present within them, and clearly not due to the “unique” properties of the CNT themselves. Interestingly, the metallic impurities did not affect in any way the redox behaviour of acetaminophen. These findings are also important in relation to the current graphene research where it has already started to be apparent that many electrochemical properties of graphene materials are altered by the impurities present within them [34,35].

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Carbonaceous Impurities in Carbon Nanotubes are Responsible for Accelerated Electrochemistry of Cytochrome *c*

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S Supporting Information

ABSTRACT: There have been many reports on the excellent electrocatalytic properties of carbon nanotubes toward many substrates. Here, we wish to address and investigate the apparent “good promotion” of the electron transfer to cytochrome *c* as previously shown and attributed to the electrocatalytic properties of carbon nanotubes (Wang et al. *Anal. Chem.* **2002**, *74*, 1993). We will show here that the observed electrocatalytic effect toward this probe could be mainly attributed to the carbonaceous impurities present within the carbon nanotubes samples, instead of the carbon nanotubes themselves.

Carbon nanotubes (CNT) have attracted significant interest from the academic research community as well as from industries due to their varying and unique properties.^{1,2} Carbon nanotubes are typically prepared by metallic catalyst-induced growth.^{3,4} During this growth, not only are tubular carbon structures created but also other forms of carbon, such as nanographitic particles or amorphous carbons, precipitate.^{5–7} As prepared CNT contain large amounts of impurities, ranging from residual metallic nanoparticle impurities to carbonaceous impurities. For example, a typical single-walled CNT sample might contain up to ~30% in weight worth of metallic impurities and similar amounts of carbonaceous impurities.^{8,9} It is very difficult to completely remove all traces of metallic impurities from CNT sample,¹⁰ and it is even more challenging to remove carbonaceous impurities, as their physical properties are close to those of the CNT.⁹

There has been a large amount of publications reporting outstanding electrochemical properties of CNT.¹¹ This was debunked by Compton's group, whose group was the first to show that it was in fact the metallic impurities within CNT that were responsible for the catalytic oxidation or reduction of a variety of compounds, i.e., hydrazine,¹² hydrogen peroxide,¹³ glucose,¹⁴ and halothane.¹⁵ The same group also demonstrated that carbonaceous impurities in CNT, present in the form of nanoions, were responsible for the observed electrocatalytic properties toward many analytes, such as ferro/ferricyanide, ruthenium salts, nicotinamide adenosine dinucleotide (NADH), epinephrine, and norepinephrine.¹⁶ These findings were later extended to other carbonaceous impurities, such as nanographite and amorphous carbon.^{17–19} These reports were confirmed and followed by others, as summarized in recent reviews.^{11,20} Despite several reports demonstrating that electrocatalysis was attributed to CNT erroneously, this issue is often

downplayed by a large part of the electrochemistry community with comments that only few compounds are affected.¹¹ Here, we wish to show that this problem of erroneous attribution of electrocatalysis to CNT is much broader and extends into the electrochemistry of proteins.

Carbon nanotubes have been reported to act as electrocatalysts toward the reduction of cytochrome *c*.²¹ From a careful examination of the effects generated by pure CNT (impurities-free), standard CNT samples (impurities-rich), and individual impurities (metallic or carbonaceous), we have been able to distinguish here the effect coming from each individual constituent. The results clearly show that the major contribution to the catalytic reduction of cytochrome *c* is from the carbonaceous impurities which promoted a faster electrochemistry for this probe compared to the isolated metallic impurities or pure CNT.

■ EXPERIMENTAL SECTION

Apparatus. All voltammetric experiments were measured by using an electrochemical analyzer Autolab PGSTAT 101 (Ecochemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Methrom Autolab B. V.). The electrochemical measurements were performed in a 5 mL voltammetric cell at room temperature (25 °C) by using a three-electrode configuration. The GC electrode functioned as the working electrode, and platinum disk and an Ag/AgCl (saturated) electrodes were used as the auxiliary and reference electrode, respectively.

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Materials. Cytochrome *c*, *N,N*-dimethylformamide (DMF), phosphate buffer (pH 7.2), MWCNT-*i* (0.65% (wt) of Co, 0.014% of Fe, 0.07% of Mo, and 0.5% of Ni), pure MWCNT, NiO, Co₃O₄, Fe₃O₄, and MoO₂ nanoparticles obtained from Sigma-Aldrich. Amorphous carbon black (particle size 29 nm) was received from Asbury Carbons, NJ. Glassy Carbon (GC, 3 mm diameter), Pt, and Ag/AgCl electrodes were purchased from CHInstruments, TX, USA.

Procedures. Carbon materials were used as-received without any further purification. All nanoparticles were dispersed in DMF at a total concentration of 5 mg/mL for modification of the working electrode. A 1 μ L portion of the sonicated suspension was then cast onto a GC electrode surface that had previously been polished with 0.05 μ M alumina particles on a cloth. The deposited nanotube solution was allowed to dry in air at room temperature resulting in a carbon nanotube film on the electrode surface. GC electrodes modified with metal nanoparticles and amorphous carbon were prepared using the same procedure. All measurements were performed in phosphate buffer at pH 7.2.

RESULTS AND DISCUSSION

When revisiting ref 21 reporting on the electrocatalytic properties of CNT toward cytochrome *c*, one can clearly notice the highly contrasted bright spots on the scanning electron micrograph (SEM) presented there (Figure 1, ref 21). It is difficult to assess from the quality of the image whether these spots are metallic or carbonaceous impurities; however, it is clear that they do not structurally resemble nanotubes.²¹ We therefore examined the electrochemistry of commercial carbon nanotube samples (Sigma-Aldrich; labeled as MWCNT-*i*) which contained metallic (0.65% (wt) of Co, 0.014% of Fe, 0.07% of Mo, and 0.5% of Ni, according to in house ICPMS analysis) as well as carbonaceous impurities (~15% of carbonaceous impurities) and compared the results to the electrochemistry of pure MWCNT^{18,22} (impurities-free), amorphous carbon (representing carbonaceous impurities¹⁹), and NiO, Fe₃O₄, Co₃O₄, and MoO₂ nanoparticles (representing metallic impurities).

First, we recorded the cyclic voltammograms to investigate the reduction potential of cytochrome *c* on MWCNT-modified electrode. It can be seen from Figure 1 that the first reduction wave starts at $\sim$ -50 mV (vs Ag/AgCl reference electrode), reaching a maximum at -160 mV; and a second reduction wave appears at -415 mV. It should be mentioned that electrochemistry of cytochrome *c* typically provides quasireversible

Figure 1. Cyclic voltammogram of 0.3 mM cytochrome *c* at MWCNT-*i*, pure MWCNT, and bare GC electrode. Conditions: 50 mM phosphate buffer, pH 7.2; scan rate of 50 mV/s.

one electron transfer reaction. The second reduction wave signal observed at MWCNT-*i* modified electrode originates from the presence of underlying glassy carbon electrode, similarly as in other cases of CNT modified electrodes.²³ When performing control experiments using pure MWCNT, no reduction wave appeared at around -150 mV and the cyclic voltammogram exhibited a single reduction signal of cytochrome *c* only at $\sim$ -420 mV. A similar result originated when the bare glassy carbon electrode was used. Therefore, it is clear that the reduction wave at -160 mV does not originate from the inherent electrochemical properties of MWCNTs. The electrochemical response of the modified electrodes in the blank buffer is shown in Figure S1 (Supporting Information). We then proceeded to investigate the effects of the individual impurities (carbonaceous and metallic).

We performed cyclic voltammetry of cytochrome *c* at glassy carbon electrode modified with metal oxide nanoparticles which were identified as impurities present in MWCNT-*i* by ICPMS. Figure 2 shows the cyclic voltammograms of

Figure 2. Cyclic voltammogram of 0.3 mM cytochrome *c* at amorphous carbon (AC), Co₃O₄, NiO, MoO₂, Fe₃O₄, and bare GC electrode. Conditions as in Figure 1.

cytochrome *c* at the Fe₃O₄, MoO₂, NiO, and Co₃O₄ modified electrode surface, where it can be seen that no catalytic effect was shown with the voltammograms having similar features as the bare glassy carbon electrode. In contrast, the amorphous carbon modified GC electrode exhibited a strong reduction wave for cytochrome *c* starting at $\sim$ -100 mV and reaching a first reduction peak at -225 mV, with a following increase of current into a poorly defined second reduction wave at $\sim$ -500 mV. It is apparently clear from these experiments that, among the impurities present within the MWCNT-*i* sample, those of carbonaceous nature were responsible for the observed electrocatalytic effects toward the reduction of cytochrome *c*, while the metallic impurities have no participation and the CNT material does not play a role in the observed behavior. The electrochemical response of the corresponding modified electrodes in the blank buffer is shown in Figure S2 (Supporting Information).

It would appear, therefore, that the previously claimed electrocatalytic effects of CNT modified electrodes for the reduction of cytochrome *c* were most likely generated by the presence of carbonaceous impurities that are normally found in commercial CNT samples. Thus, no special or particular catalytic properties can be assigned to the CNT material itself.

■ CONCLUSION

We have managed to revisit and challenged the claims on the extraordinary electrocatalytic properties of carbon nanotubes toward the electrochemistry of cytochrome *c* as presented in a 2002 article.²¹ By a careful and systematic investigation on the effect of each of the components present in a commercial CNT sample, which includes the carbonaceous impurities and the metallic impurities, as well as the CNT material itself, we proved that the electrocatalytic properties originate from the carbonaceous impurities, with the carbon nanotubes themselves presenting no contribution to the accelerated electrochemistry observed.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Could Carbonaceous Impurities in Reduced Graphenes be Responsible for Some of Their Extraordinary Electrocatalytic Activities?

Lu Wang, Adriano Ambrosi, and Martin Pumera*^[a]

Abstract: Thermally and chemically reduced graphene materials contain significant amounts of carbonaceous impurities that are similar in structure to amorphous carbon. Herein, we show that the claimed electrocatalytic activities of these materials for the oxidation of NADH, acetaminophen, and hydroquinone are mainly due to the presence of carbonaceous impurities.

Keywords: electrocatalysis • electrochemistry • graphene • impurities • oxidation

Introduction

Graphene materials have been shown to exhibit profound electrocatalytic activity towards a wide variety of compounds. Such properties have had dramatic impacts on both the fields of energy storage^[1] and electrochemical sensing.^[2] We have recently questioned whether some of these reported excellent electrocatalytic properties of graphenes were due to the inherent electrochemistry of graphene itself or to impurities that coexisted within the graphene materials.^[3,4] We have found that both thermally and chemically reduced graphene materials that were prepared from graphite contained metallic impurities that were inherently present not only in natural graphite, but also in synthetic graphite samples. These impurities were found to be responsible for the electrocatalytic behavior of graphene materials for the reduction of cumene hydroperoxide and for the oxidation of L-glutathione, sodium hydrogen sulfide, and hydrazine.^[3,4] The presence of impurities within graphene materials and their effects on the material's properties are important focuses in the growing field of graphene research^[5,6] because they may result in major alterations in the electrochemical, mechanical, and electronic properties of the graphene material.^[7,8] The strong influence of metallic catalyst impurities on electrochemical properties has similarly been demonstrated for carbon nanotubes (CNTs), for which metallic impurities were found (first by Compton and co-workers^[9] and later by others^[10]) to be responsible for the electrocatalysis of a wide range of compounds that was originally deemed to be catalyzed by the CNTs themselves.^[9–11]

Many reports have recently been published that have shown the outstanding electrocatalytic behavior of graphene materials for the oxidation/reduction of important com-

pounds, such as nicotinamide adenine dinucleotide (NADH),^[12] which is a cofactor of over 300 enzymes and is often used in biofuel cells and biosensors,^[13] hydroquinone,^[14,15] which is often used as a mediator in biofuel cells and biosensors,^[16] and acetaminophen.^[15,17] We have previously investigated whether metallic impurities were responsible for the observed profound shifts in the redox potentials of these compounds and found that this was not the case.^[18] However, before assigning with certainty the catalytic properties to the graphene materials, further investigations and characterizations are necessary, keeping in mind the history of electrocatalysis at CNT-based electrodes.^[19] In fact, it has been found (first by Compton and co-workers^[20] and then by others^[18,21]) that, besides metal impurities, carbonaceous impurities are also extremely active in CNT samples for the electrocatalysis of numerous compounds, that is, azo compounds,^[21a] organic hydrazines,^[21b] some amino acids,^[18a] NADH,^[14a,20] hydroquinone,^[18b] and acetaminophen.^[18c] With this result in mind, it could be expected that, similar to the case of CNTs, carbonaceous impurities within graphene materials may also play an active role in the electrocatalysis of these above-mentioned compounds.

Herein, we show that carbonaceous impurities in the form of amorphous carbon within graphene samples are responsible for the observed electrocatalytic effects of the graphene surfaces towards important compounds, such as NADH, hydroquinone, and acetaminophen.

Results and Discussion

Before we embark on a description of the data that support our claim, it is important to provide an insight into the materials that we worked with. Graphene was defined by IUPAC in 1995 as “a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi-infinite size”.^[22] It must be emphasized that most of the “graphenes” that are produced in large-scale syntheses (in gram quantities; note that any practical electrochemical application works with a large amount

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of electrode materials) are obtained from graphite by its oxidation into graphite oxide and subsequent exfoliation/reduction, either by using thermal or chemical routes.^[23] Such as-prepared “reduced graphene” does not really fit the IUPAC definition of graphene, because it consists of a largely heterogeneous material. It contains a large number of defects, such as holes in the structure, ad-atoms, pentagon/heptagon carbon rings, multilayer graphene structures, and dangling bonds.^[24] The crystallite size of such reduced graphenes with a pristine sp^2 lattice is typically around 10 nm.^[25] Structurally, such reduced graphenes resemble amorphous carbon, which is defined by IUPAC as “a carbon material without any long-range crystalline order. Short-range order exists, but with deviations in the interatomic distances and/or interbonding angles with respect to the graphite lattice, as well as to the diamond lattice”.^[22] Thus, reduced graphenes are made up of a large portion of “amorphous” fragments.^[26] Taking this result into account, our experiments were conducted with the following graphene materials: 1) Thermally reduced graphene (TR-G) and chemically reduced graphene (CR-G) as typical graphene materials that are used in electrochemistry. 2) Highly oriented pyrolytic graphite (HOPG) as a reference carbon material, of which pristine graphene is the direct single-layer derivative.^[22] We used two forms of HOPG electrode materials, that is, edge-plane HOPG (EPPG) and basal-plane HOPG (BPPG). The electrochemistry of graphene can be directly related to the electrochemistry of EPPG,^[27] which means that any deviation in the electrochemistry of TR-G and CR-G from the behavior of the EPPG electrode may be attributed to the presence of additional materials (impurities). These impurities actively participate in the electrocatalytic event. 3) Amorphous carbon black (AC), with a poorly graphitized structure and a large amount of sp^3 hybridized carbon, was used to simulate amorphous carbon impurities.^[21d]

Figure 1 shows the Raman spectra of the TR-G, CR-G, and AC materials, together with that of graphite for comparison. The spectra of TR-G and CR-G both show an intense signal at about 1350 cm^{-1} (D band), which is generated by the doubly resonant disorder-induced mode. An intense D band is generally associated with very disordered and defect-rich carbon structures.^[28] As expected, the Raman spectrum of AC also shows an intense D band. The peak at about 1575 cm^{-1} (G band), which originates from the in-plane vibration of sp^2 carbon atoms, is characteristic of graphitic materials with sp^2 -hybridized carbons and is present in all of the examined materials.^[29] However, the G bands in the spectra of TR-G and AC are significantly broadened in comparison to, for example, that of graphite. This broadening is due to the overlapping of another active Raman band, called the D' band, at about 1620 cm^{-1} , which becomes active in the presence of structural defects.^[30] In fact, the D' band is also visible in the Raman spectrum of CR-G at a lower intensity, thus indicating a lower degree of structural disorder as compared to that in TR-G and AC, but still quite significant when compared to graphite. The 2D band at about 2700 cm^{-1} is indicative of crystalline

Figure 1. Raman spectra of CR-G, TR-G, AC, and graphite, normalized to the intensity of the G band.

graphitic materials.^[29] A broad, irregular 2D band (or its absence) is a general indication of highly disordered materials and it can also be attributed to the partial amorphization and reduction of sp^2 domains.^[31,32] The Raman spectra of AC and TR-G did not show any bands in this region, thus reaffirming their highly disordered structure with small sp^2 domains. It is also important to note the high degree of similarity between the structural conformations of TR-G and AC. The CR-G material shows a more intense 2D band in its Raman spectrum. This result also indicates the presence of larger crystalline domains in CR-G than in TR-G and AC, but still smaller when compared to graphite, which showed a sharper 2D band. Thus, these Raman spectra clearly show that the CR-G and TR-G materials contain large defective domains, either in their structures or coexistent as impurities, and therefore they possess similar characteristics as AC.

The electrochemical behavior of the vast majority of these compounds is different on the basal plane of graphene to on its end/edges/defects. Therefore, we compared the electrochemistry of edge-plane pyrolytic graphite, basal-plane pyrolytic graphite surfaces with reduced graphene, and amorphous carbon surfaces. We studied the electrochemical profiles of three compounds that were previously deemed to be electrocatalytically oxidized on graphene surfaces, that is, hydroquinone,^[14,15] NADH,^[12] and acetaminophen.^[15,17] Knowing that these compounds are not electroca-

talyzed by metal/metal-oxide impurities,^[18] we focused our attention on investigating the effect of amorphous carbon impurities. Figure 2 shows cyclic voltammograms of these compounds on reduced graphene, EPPG, BPPG, and amor-

Figure 2. Redox properties of A) 10 mM hydroquinone, B) 1 mM acetaminophen, and C) 2 mM NADH on thermally (TR-G) and chemically reduced graphene (CR-G), edge-plane (EPPG) and basal-plane pyrolytic graphite (BPPG), and amorphous carbon (AC). Conditions: 50 mM phosphate buffer, pH 7.2. Scan rate: 100 mV s⁻¹.

phous carbon (AC) surfaces. Upon cycling the potential from -0.5 mV to +1.0 V and back, hydroquinone (Figure 2A) shows oxidation waves that start at -40 mV on both the TR-G and CR-G surfaces and reach a maximum at +290 mV for both reduced graphenes. The corresponding reduction waves start at +200 mV, with a peak maximum at -76 mV for both of the reduced graphenes. On the other hand, the voltammetric behavior of hydroquinone on both BPPG and EPPG show dramatically different profiles. The oxidation wave of hydroquinone on BPPG starts at +165 mV and reaches a maximum at +575 mV, whereas the

reduction wave starts at +54 mV and reaches a maximum at -279 mV. However, on EPPG, the oxidation of hydroquinone starts at +60 mV, with a peak maximum at +443 mV, and the subsequent reduction wave starts at +58 mV, with a peak maximum at -172 mV. Thus, it is clear that the electrochemical behavior of hydroquinone on TR-G and CR-G surfaces is not related to either BPPG or EPPG. Interestingly, the electrochemical behavior on amorphous carbon surfaces shows an oxidative wave that starts at -30 mV, with a peak maximum at +319 mV, whereas the reduction wave starts at +200 mV, with a peak maximum at -91 mV. Thus, there is a clear similarity between the electrochemical behavior of hydroquinone on the reduced graphene surfaces and that of amorphous carbon.

Figure 2B shows the voltammetric behavior of acetaminophen on various surfaces. The oxidation of acetaminophen on thermally reduced graphene surfaces starts at +245 mV and the oxidation wave reaches a maximum at +403 mV, whereas the reduction wave starts at +445 mV and reaches a maximum at +284 mV. The redox properties of acetaminophen on the BPPG and EPPG electrodes are very similar to each other: The oxidation starts at +334 mV and reaches a maximum at +525 mV, whilst the reduction wave starts at +200 mV with a peak maximum at -50 mV. Once again, it is clear that the electrochemical behavior of acetaminophen on a thermally reduced graphene surface is dramatically different from that on BPPG or EPPG electrodes. When the redox properties of acetaminophen are studied at amorphous carbon modified electrode, one can see that the cyclic voltammogram profile closely resembles the profile at the thermally reduced graphene electrode. In fact, the oxidation of acetaminophen on an amorphous carbon surface starts at +245 mV and reaches a maximum at +396 mV. The reduction wave starts at +445 mV, with a peak maximum at +236 mV. It is clear that the electrochemistry of thermally reduced graphene much more closely resembles that of amorphous carbon than that of highly oriented pyrolytic graphite.

We have also highlighted the redox behavior of important co-enzyme NADH on chemically reduced graphene, EPPG, BPPG, and amorphous carbon surfaces (Figure 2C). The oxidation of NADH starts at about +100 mV at the chemically reduced graphene electrode and reaches a maximum at +507 mV. Similarly, the cyclic voltammogram of NADH on an amorphous carbon surface shows an oxidation wave starting at about +100 mV, with a peak maximum at +490 mV. On the contrary, NADH oxidation at EPPG and BPPG electrodes start at +400 and +430 mV and then reaches a maximum at +662 and +775 mV, respectively. Once again, it is clear that there is no similarity between the electrochemical responses of reduced graphene and HOPG (which is, in principle, multilayer-stacked graphene).^[22,33] Rather the response of reduced graphene is similar to that of amorphous carbon.

Conclusions

In conclusion, we have demonstrated that the previously reported extraordinary properties of reduced graphenes towards the redox chemistry of hydroquinone, acetaminophen, and NADH are not due to the properties of the graphene materials themselves but rather to the presence of carbonaceous impurities that catalyze their oxidation.

Experimental Section

Materials

DMF, potassium chloride, potassium phosphate disodium salt, potassium ferrocyanide, potassium ferricyanide, hydroquinone, acetaminophen, and the reduced form of β -nicotinamide adenine dinucleotide (NADH) were purchased from Sigma–Aldrich (Singapore). Amorphous carbon black (AC) (particle size: 29 nm) was obtained from Asbury Carbons, NJ. Glassy carbon electrodes (diameter: 3 mm) were obtained from CH Instruments, TX, USA.

Apparatus

All voltammetric experiments were performed on an Autolab PGSTAT101 electrochemical analyzer (Methrom Autolab B.V., The Netherlands) that was connected to a personal computer and controlled by NOVA software Version 1.8 (Methrom Autolab B.V.). Electrochemical experiments were performed in a voltammetric cell (5 mL) at RT by using a three-electrode configuration with a Pt electrode (Autolab) as an auxiliary electrode and a Ag/AgCl electrode (CH instruments) as a reference electrode. All electrochemical potentials are reported versus the Ag/AgCl reference electrode. Raman spectra were obtained on a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific, Japan) at an excitation wavelength of 514.5 nm by using an argon-ion laser beam with a backscattering geometry and a CCD detector.

Procedures

Chemically reduced graphene (CR-G) was obtained by dispersing graphite oxide powder (80.5 mg) in ultrapure water to give a colloidal solution (1.0 mg mL^{-1}). The mixture was ultrasonicated (150 W) for 3 h prior to the addition of sodium carbonate (5 wt.%) until pH 9–10 was reached. Sodium borohydride (800 mg, 21.1 mmol) was added over 20 min into the dispersion under vigorous stirring. Then, the reaction mixture was heated at 80 °C for 1 h. After cooling the mixture to RT, it was washed repeatedly with ultrapure water by using centrifugation (8000 rpm, 10 min). The sample pallet was dried at 60 °C for 5 days in a vacuum oven before use.

Thermally reduced graphene (TR-G) was obtained by the thermal exfoliation/reduction of graphite oxide at high temperatures (1050 °C). Graphite oxide (0.2 g) was placed in a porous quartz-glass capsule that was connected to a magnetic manipulator inside a vacuum-tight tube furnace under a controlled atmosphere. The application of a magnetic manipulator allowed the creation of a temperature gradient of over $1000^\circ\text{C min}^{-1}$. The sample was flushed with nitrogen gas by the repeated evacuation of the tube furnace to remove any trace amounts of oxygen and then quickly inserted into a preheated furnace by using a magnetic manipulator and held in the furnace for 3 min. The flow of nitrogen gas during the exfoliation procedure was 1000 mL min^{-1} to remove the byproducts of the exfoliation procedure.

For the electrochemistry measurements, solutions of the graphene materials (TR-G and CR-G) and amorphous carbon were prepared by dispersion in DMF at a concentration of 5 mg mL^{-1} . Then, the suspension was placed into an ultrasonic bath for 30 min, after which the suspension ($1 \mu\text{L}$) was pipetted onto the surface of a glassy carbon (GC) electrode that had previously been polished with 0.05 mm alumina on a polishing cloth. The EPPG electrode surface was polished with 0.05 mm alumina on a polishing cloth before each measurement. The BPPG electrode surface was renewed by cleaving off the top graphite layers with Scotch

tape, followed by a washing step in acetone to remove any glue residues and deionized (DI) water.

The suspension was allowed to evaporate at RT, thus creating a randomly distributed film on the surface of the GC electrode. Cyclic voltammetry experiments were performed at a scan rate of 100 mV s^{-1} by using phosphate buffer (pH 7.2) as the supporting electrolyte.

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Residual metallic impurities within carbon nanotubes play a dominant role in supposedly “metal-free” oxygen reduction reactions†

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Oxygen reduction reactions (ORRs) are of key importance in the area of electrochemical energy production. The replacement of the Pt industrial standard with heteroatom doped metal-free carbon nanotubes was previously suggested for ORRs. Here we will show that the ORR electrocatalysis on these supposedly metal-free materials is likely in fact due to the presence of residual metallic impurities within the carbon nanotubes and that these impurities play a dominant role.

Oxygen reduction reactions (ORRs) are of key importance for fuel cells as well as for zinc-air batteries. Efficient, low potential cathodic reduction of oxygen is typically catalyzed by Pt supported on carbon surfaces.¹ However, due to the high cost of Pt there is a huge interest in replacing Pt with other electrocatalytic systems.¹ A number of studies have been published on the utilization of non-noble metal oxide decorated carbon surfaces, including carbon nanotubes for ORRs. It has been shown that Fe, Co and Mn-based oxides supported on CNTs act as efficient catalysts for ORRs.^{2–7} There have also been reports on *metal-free* catalysis of ORRs on nitrogen,^{8–11} boron,¹² or B/N¹³ doped carbon nanotubes. These claims of metal-free electrocatalysis of ORRs on CNTs are remarkable as no metal is supposedly involved in the electrocatalysis of ORRs;^{8–13} if these claims were correct they would indeed have very significant impact on the practical industrial applications of such metal-free materials in energy production and storage devices.

There are two main shortcomings of the claims of “metal-free” catalytic ORRs on doped carbon nanotubes in the above mentioned research studies.^{8–13} Firstly, the vast majority of carbon nanotubes used have been prepared using metal containing catalysts, *i.e.* ferrocenes,^{12,13} iron(II) phthalocyanines,^{8,9} or other metallic catalysts;^{10,11} and this is known to introduce a significant amount of residual metallic impurities within the carbon nanotubes.¹⁴ Supposedly “metal-free” synthesis of CNTs leads

to the contamination of the CNTs during the processing by metals.¹⁵ Secondly, when claiming the “metal-free” electrocatalysis of ORRs on nitrogen-doped CNTs, the authors did not in fact perform any *sensitive* characterization of the CNT materials which could prove that the samples were indeed *metal-free*. Techniques such as ICP-MS/OES, neutron activation analysis or X-ray fluorescence would have been able to provide an accurate insight into the amount of metal impurities in carbon nanotubes; however, these analyses were not typically performed to prove such metal-free claims. Note that X-ray photoelectron spectroscopy (XPS) which was used in some cases^{8,10,12} is not sensitive enough, having a general limit of detection of 0.1% wt (1000 ppm).¹⁶ In addition, XPS being a surface sensitive technique, is unable to detect even several wt% of residual catalyst metallic impurities within CNTs.¹⁷

It is well-known from the literature that carbon nanotubes which are grown from metallic catalyst precursors contain a residual metallic content.¹⁴ Such residual metallic impurities are practically impossible to remove from the produced carbon nanotubes and remain within them even after several attempted acid washing procedures, at levels as high as several wt%.^{14,18–22} It should also be noted that methods capable of detecting ppm amounts of metallic impurities include X-ray fluorescence analysis (XRF), electron microscopy/energy dispersive X-ray spectroscopy, ICP-MS/OES (down to ppb levels) or neutron activation analysis (NAA); whereas, as mentioned above, surface analysis methods such as XPS are unable to detect even several wt% of metallic impurities within the CNTs.¹⁷ It has been demonstrated by Compton and co-workers that residual catalyst metallic impurities within the carbon nanotubes are actually responsible for the supposed unique electrocatalytic properties of CNTs towards hydrazine,¹⁹ hydrogen peroxide,²³ glucose,²⁴ and halothane.²⁵ We have demonstrated that the residual metallic catalysts within CNTs are responsible for the electrocatalytic oxidation of glutathione²⁶ and the reduction of a whole group of organic peroxides.²⁷ Moreover, it has been shown that even 100 ppm (that is 0.01 wt%) of metallic impurities can dominate the electrochemistry of carbon nanotubes.²⁸ Additionally, it has been demonstrated that residual metallic impurities present in CNTs (*i.e.* Co/Mo) contain trace levels of impurities (*i.e.* Fe) within

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themselves and these “impurities within impurities”, present at the levels of tens of atoms per metallic impurity nanoparticle, can dominate the electrochemistry of the system as well.²⁹

Recently there have been reports showing that trace metal residues promote the activity of a supposedly metal-free nitrogen-doped amorphous carbon catalyst for the ORR,³⁰ and that metallic impurities within graphene are the catalytic sites for ORRs in supposedly metal-free graphenes.³¹ Here we wish to re-visit the case of carbon nanotubes and ORR, since there were many strong claims that were made of metal-free ORRs at nitrogen and/or boron doped carbon nanotubes where these carbon nanotubes were prepared using metal containing catalysts.^{8–13} We will show that metallic impurities within carbon nanotubes are in fact responsible for the ORR on the surface of carbon nanotubes.

We chose to investigate the ORR at three different carbon nanotubes – pure CNTs, as received carbon nanotubes and “cleaned” carbon nanotubes. We labeled them CNT-pure, CNT-as and CNT-cleaned, respectively, in the following text. The cleaned carbon nanotubes were prepared from CNT-as by means of extensive purification using chlorine gas at 1000 °C for 10 min.³² The metal content in the carbon nanotubes was determined by in-house X-ray fluorescence analysis.³² CNT-as contained 5960 ppm of Mn, 150 ppm of Ni, 30 ppm of Fe and 6160 ppm of Co. CNT-cleaned contained residual catalyst metallic impurities even after an extensive cleaning procedure at levels of 140 ppm of Mn and 200 ppm of Co with no traces of Ni or Fe detected by XRF. This is consistent with previous reports showing that it is highly challenging to decrease the amount of impurities even by extensive purification.^{19–22} CNT-pure were not found to contain detectable amounts of metallic impurities by XRF or ICP-MS. Note that the conductivity of different carbon nanotube samples used here may differ. However, all of them exhibit metallic conductivity, as they have a multilayer structure. Electrocatalytic properties of CNTs are not related to conductivity (provided they are of metallic conductivity) but to the catalytic sites (either N-doped sites as suggested by many reports or metals) which are “just” wired by CNTs to the current collector.³³ Therefore, the difference in the conductivities of CNTs does not play a role in the present study of the electrocatalytic effect. Prior to the investigation of ORRs on these three CNTs samples, we modified a glassy carbon (GC) electrode with oxides of metals found in CNTs, such as MnO₂, Fe₃O₄, Co₃O₄ and NiO in an attempt to better understand the potential catalytic effect that metallic impurities found in CNTs can have on the system. The linear sweep voltammograms were recorded at these metal oxide surfaces in air saturated 0.1 M KOH solution. For a clearer comparison, typical and representative voltammograms have been baseline-corrected and are summarized in Fig. 1A (original recordings can be found in Fig. S1A, ESI†). The onset potentials for ORRs at Fe₃O₄, Co₃O₄ and NiO are –312, –310 and –298 mV, which are close to –298 mV (vs. AgCl) of the underlying GC (see Fig. 2 for graphical representation of onset potentials obtained). This clearly shows that above-mentioned iron, cobalt and nickel oxides do not exhibit an electrocatalytic effect on the ORR under these conditions. The onset potential for the ORR at MnO₂ is –200 mV, exhibiting catalytic lowering of the overpotential needed for ORR by ~100 mV. Consequently, we turned our attention to the investigation of the ORR on the carbon nanotubes

Fig. 1 Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and (A) a GC electrode modified with Co₃O₄ (green line), NiO (magenta line), Fe₃O₄ (blue line), and MnO₂ (red line) materials. (B) a GC electrode modified with MnO₂ (red line), CNT-as (magenta line), CNT-cleaned (blue line), CNT-pure (green line). Scan rate: 100 mV s⁻¹.

samples in question. Fig. 1B shows the baseline corrected linear sweep voltammograms in air saturated KOH (0.1 M) at the as-received, cleaned and pure CNTs (original recordings can be found in Fig. S1B, ESI†). The onset potential for O₂ reduction is –295 mV for pure CNTs, which is practically similar to the onset potential for the ORR at the GC electrode. This clearly demonstrates that pure CNTs do not exhibit any electrocatalytic effect on the ORR. The onset potential for O₂ reduction at the

Fig. 2 Onset potentials for ORRs measured for all studied materials.

cleaned CNT is lower at -247 mV, while the as-received carbon nanotubes exhibit an onset potential of -219 mV for ORR, which is rather close to the onset potential value of MnO_2 (-200 mV). In addition, we performed the control experiments using Fe, FeO , Fe_2O_3 , Co and FeOOH and no electrocatalytic effect was observed. We show these results in Fig. S2 and S3 in the ESI.† It is thus obvious that with the increasing amount of manganese-based impurities within the CNTs, the onset potential of ORR shifts towards a more positive potential resulting in such CNTs to exhibit an electrocatalytic reduction towards O_2 . Therefore, from the comparison of the metal content in the CNTs, it is clear from the metal content and the supposed catalytic properties of CNTs towards ORRs that the metallic impurities are the ones truly responsible for the electrocatalytic reduction of O_2 , and not inherent CNT materials themselves.

In summary, we have demonstrated that pure carbon nanotubes do not exhibit any electrocatalytic effect towards the ORR. We also showed carbon nanotubes that contain residual catalyst metallic impurities, either before or after extensive purification procedures are very much capable of exhibiting strong electrocatalytic properties towards ORRs. The catalytic activity is directly correlated to the amount of impurities in the CNTs. In light of these conclusions, it is very likely that the claimed “metal-free” ORRs on heteroatom doped carbon nanotubes are in fact a result of residual metallic impurities present within the CNTs. This is supported by the fact that in most of these supposedly “metal-free” catalytic ORRs on doped CNTs, the characterization of the metal content in the CNT materials was not attempted at all^{12,13} or even if it was, insensitive techniques such as XPS were used.^{8–10} We strongly urge the scientists in the community of “metal-free” catalysis on CNTs to use highly sensitive techniques, such as XRF, ICP-MS or nuclear activation analysis to support their metal-free claims.

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Highlight by K. P. Loh and J. Lu

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“Metal-Free” Catalytic Oxygen Reduction Reaction on Heteroatom-Doped Graphene is Caused by Trace Metal Impurities**

Lu Wang, Adriano Ambrosi, and Martin Pumera*

Abstract: The oxygen reduction reaction (ORR) is of high industrial importance. There is a large body of literature showing that metal-based catalytic nanoparticles (e.g. Co, Mn, Fe or hybrid Mn/Co-based nanoparticles) supported on graphene act as efficient catalysts for the ORR. A significant research effort is also directed to the so-called “metal-free” oxygen reduction reaction on heteroatom-doped graphene surfaces. While such studies of the ORR on nonmetallic heteroatom-doped graphene are advertised as “metal-free” there is typically no sufficient effort to characterize the doped materials to verify that they are indeed free of any trace metal. Here we argue that the claimed “metal-free” electrocatalysis of the oxygen reduction reaction on heteroatom-doped graphene is caused by metallic impurities present within the graphene materials.

The oxygen reduction reaction (ORR) is of utmost technological importance as it is a key reaction in fuel cells and next-generation Zn batteries.^[1] The most efficient and widely used catalyst for the ORR is platinum. However, its limited accessibility at large scale encouraged an intensive search for alternative non-Pt catalysts that are more easily available at low costs and demonstrate comparable catalytic properties for the ORR. There is a large body of literature showing, for example, that metal-based catalytic nanoparticles (e.g. Co, Mn, Fe or hybrid Mn/Co-based nanoparticles) supported on graphene or carbon nanotubes act as efficient catalysts for the ORR.^[2–9] A significant research effort is also directed to the so-called “metal-free” oxygen reduction reaction on heteroatom-doped carbon surfaces,^[10,11] and more recently on graphene surfaces.^[12–18] In these instances, graphene doped with nitrogen, boron, sulfur or in combinations (i.e. nitrogen/sulfur or nitrogen/boron) provided significant electrocatalytic effects for the ORR.^[12–18] While such studies on the ORR with heteroatom-doped (nonmetallic) graphene are advertised as “metal-free”, there is typically no sufficient effort to characterize the doped materials to verify that they are indeed free of any trace metal. Characterization techniques for trace metals such as ICP-MS/OES, X-ray fluorescence or neutron

activation analysis would easily provide the actual material composition with the types and levels of impurities present, but are never employed.^[12–18] This is striking since it is already well-known that similar to carbon nanotubes,^[19,20] graphene materials, especially those prepared using graphite as a starting material, contain a significant amount of metallic impurities which influence their electrochemical properties.^[21]

Graphene used as “metal-free” electrocatalyst for the ORR in the aforementioned studies are prepared from graphite and it is important to note that the Hummers oxidation method is usually applied.^[22] This involves the use of permanganate oxidant to obtain an intermediate material, graphite oxide, prior to a reduction/doping step to give graphene.^[12–18] It is known for decades that graphite contains large varieties of metallic impurities with a contribution up to 2 wt % of the material.^[23–31] These impurities consist of Fe, Ni, Co, Mo, Mn, V, and Cr.^[24] It has been previously shown by Compton and others that these metallic impurities within sp² carbon nanomaterials dramatically influence the electrocatalytic properties of the nanomaterials and that they can, in some cases, dominate the electrochemistry of the materials even when present at only trace levels.^[19,32–36] It was shown that even impurities within known impurities, such as clusters of tens of iron atoms in large Co/Mo-based nanoparticle impurities, are able to catalyze important reduction reactions.^[37] From a broader perspective, one should also mention that traces of Cu impurities at low parts per million levels in FeCl₃ were found to be responsible for cross-coupling synthetic reactions;^[38,39] and 50 ppb of Pd impurities were the source of catalysis in supposedly transition-metal-free Suzuki-type cross-coupling reaction.^[40,41] Recently there was an important report showing that trace metal residues were responsible for the electrocatalytic effect in the ORR at amorphous carbon surfaces.^[42]

Here we wish to highlight that residual manganese-based metallic impurities in graphene play an extremely active role in the electrocatalysis of the oxygen reduction reaction on supposedly metal-free graphene electrodes. Manganese-based impurities are present abundantly in graphene prepared by the Hummers oxidation method which applies a large amount of permanganate oxidant.^[43,44]

In this work, we employed natural graphite (from a single source) as a starting material to prepare two different graphene materials. One of the graphene materials was prepared employing the Hummers oxidation method^[22] (permanganate oxidant) prior to a chemical reduction treatment with hydrazine to obtain graphene (G-HU). At the same time, a control graphene material was prepared using the Staudenmaier oxidation method,^[45] which uses a chlorate oxidant, to produce hydrazine-reduced graphene (G-ST). The

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Table 1: Content of metallic impurities (ppm) in the starting natural graphite and the graphene materials prepared by Hummers method (G-HU) and Staudenmaier method (G-ST) as determined by ICP-MS analysis.

Impurity	Graphite	G-HU	G-ST
Fe	4224	927.6	1685.9
Co	3.3	0.3	7.1
Ni	33.7	18.0	13.8
Mn	24.9	8311.3	17.9

amount of metallic impurities present in the graphite starting material as well as in the graphene products were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis and summarized in Table 1. All impurities are in the high ppm range with the graphene prepared by the Hummers method, G-HU (using permanganate oxidant), containing a much higher amount of manganese than the graphene prepared by the Staudenmaier method, G-ST (using chlorate oxidant). The higher Mn content in the graphene obtained using the permanganate oxidation method as compared to that obtained from the chlorate oxidation method is consistent with previous findings.^[43,44,46]

Even the graphite starting material contains Mn at ppm level, which is likely to be the primary source of contamination in the graphene prepared by the Staudenmaier method (see Table 1). We wish to highlight again here that the previously reported studies on “metal-free” electrocatalysis of the ORR typically applied the Hummers method to prepare the graphene materials,^[12–18] and therefore one may expect a similar concentration of manganese in such materials. To better understand the electrocatalytic behavior of the graphene materials, initial investigations on the electrochemistry of metal oxide nanoparticles towards oxygen reduction in KOH electrolyte solution were carried out. We recorded linear sweep voltammograms of glassy carbon electrodes (GCs) modified with Fe_3O_4 , NiO , Co_3O_4 , and MnO_2 as well as of the bare GC electrode. For a clearer comparison, typical and representative voltammograms have been baseline-corrected and are summarized in Figure 1 (original recordings can be found in Figure S1 of the Supporting Information). The oxygen reduction onset potentials using these metal oxides were practically indistinguishable from that obtained with the bare GC (−267 mV vs. Ag/AgCl; all potentials in this work are stated vs. Ag/AgCl electrode), with the striking exception of MnO_2 (−94 mV). Manganese(IV) oxide-modified GC electrodes showed, in fact, a significant onset potential shift of 173 mV, which indicated a clear catalytic behavior of MnO_2 for the oxygen reduction reaction. Consequently, we investigated the behavior of the graphene materials, G-HU and G-ST.

The graphene materials showed significantly different onset potentials for the reduction of oxygen (Figure 2). G-HU rich in Mn-based impurities (> 8000 ppm) showed an onset potential at −134 mV, which has the largest potential shift of about 133 mV as compared to bare GC. The graphene prepared by the Staudenmaier method, consisting of a very low content of Mn-based impurities (about 18 ppm), gave an onset potential at −183 mV, which was about 50 mV more

Figure 1. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and a GC electrode modified with Co_3O_4 (blue line), NiO (pink line), Fe_3O_4 (green line), and MnO_2 (red line) nanoparticles. Scan rate: 0.1 V s^{-1} .

Figure 2. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and a GC electrode modified with G-HU (red line), and G-ST (blue line) graphene materials. Scan rate: 0.1 V s^{-1} .

negative than that recorded for G-HU. It is clear that the Mn-based impurities exhibit a strong influence on the oxygen reduction reaction.

A graphical comparison of the onset potentials recorded for all the materials is summarized in Figure 3. It is indicative that the presence of Mn-based impurities in graphene causes a catalytic effect towards the ORR. According to these results a catalytic effect is evident even for the G-ST which despite a Mn content as low as 18 ppm (0.0018 wt %) showed a potential shift of about 80 mV in comparison to the bare GC electrode. This is a clear indication that even a slight trace of Mn metallic impurities in graphene materials is sufficient to alter or dominate their electrocatalytic properties towards oxygen reduction reaction. This result is also consistent with other reports where manganese oxide nanoparticles are used

Figure 3. Onset potentials for ORR measured for all materials.

in conjunction with graphene-supported materials to promote the catalytic oxygen reduction at more positive potentials, functioning as electrocatalyst of the ORR.^[4-6]

In conclusion, we have demonstrated that trace (ppm) levels of metallic impurities, in our case manganese oxide, found in graphene have profound influences on the observed oxygen reduction reaction potentials. In light of these findings, it is highly recommended to perform precise and complete characterizations of all materials employed for the catalysis of oxygen reduction reactions.

We also wish to draw a more general conclusion from our findings in view of previous reports on electrocatalysis of ORR on graphene surfaces. Impurities in the order of parts per million are inherently present in graphite and very likely increase during subsequent chemical treatments applied to fabricate graphene.^[43,44,46] Moreover, reported “metal-free” studies on the catalytic effects of heteroatom-doped graphene materials for the ORR typically employed Hummers (permanganate) method to prepare graphene^[12-18] and should therefore likely suffer from a significant contamination of Mn besides other impurities.^[43,44,46] It is very probable that trace levels of manganese oxide in these graphene materials were responsible for the reported “metal-free” electrocatalysis.^[12-18] As such, we strongly advocate that for all “metal-free” graphene catalytic reactions, elemental analysis of metal contents in graphene should be provided to support the “metal-free” claims.

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Short communication

Remarkable electrochemical properties of electrochemically reduced graphene oxide towards oxygen reduction reaction are caused by residual metal-based impurities

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ABSTRACT

Oxygen reduction reaction (ORR) is one of the most important electrochemical reactions in the field of energy storage. Remarkable catalytic properties towards ORR at “metal-free” electrochemically reduced graphene oxide (ErGO) were previously reported. We demonstrate here that the remarkable enhancement towards ORR of a “metal-free” ErGO is caused by residual metallic impurities instead of ErGO itself.

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1. Introduction

Oxygen reduction reaction (ORR) is of key importance for fuel cells as well as vanadium-air battery and zinc-air batteries [1,2]. Currently, the most efficient and widely used catalyst for ORR is platinum which has high cost and limited resources [3]. Therefore, an intensive search for non-Pt catalysts with low cost and comparable catalytic properties is encouraged. A large number of literature reports have been published on the utilization of carbon nanomaterials, such as carbon nanotubes [4–9] carbon nanoribbons [10,11] and graphene materials [12–16] as catalytic surfaces for ORR. Meanwhile, metal-based catalytic particles embedded onto graphene or carbon nanotubes are also efficient catalysts for ORR [17–21]. It is well-known that, similar to carbon nanotubes, graphene materials, especially those prepared from graphite, contain significant amount of metallic impurities, and several reports also pointed out that the remarkable ORR catalytic properties were caused by residual metallic impurities within the carbon materials [22–26].

We wish to address the reported “metal-free” electrocatalysis at electrochemically reduced graphene oxide (ErGO) [21]. Even through a similar work on chemically reduced graphene oxide has been reported previously by us [22], the influence of impurities on the electrochemistry of the electrochemically reduced graphene oxide is still necessary to study. This is due to the fact that electrochemical reduction does not use reagents which also contain traces of impurities [27]. In addition, there

is large number of article claiming metal-free ORR on graphene (including electrochemically reduced graphene oxide) and these claims should be verified [21]. The graphene oxide (which was later reduced by electrochemical means) was synthesized from graphite using Hummers method [28]. It is important to note that, the Hummers method involves using permanganate as an oxidant to oxidize graphite into graphite oxide (GiO), followed by ultrasonication treatment to form graphene oxide (GO) and thereafter electrochemical reduction was performed to obtain ErGO. It is known for decades that graphite contains large varieties of metallic impurities with a contribution of up to 2 wt.% [29–34]. These impurities include Fe, Ni, Co, Mo, Mn, V, and Cr [30]. Previous reports have indicated that even a trace amount of impurities can dramatically influence the electrocatalytic properties or dominate the electrochemistry of the carbon materials [22–26,35–39]. The treatment of graphite with Hummers method (utilizing KMnO_4) leads to the incorporation of Mn-based impurities at high ppm levels in the resulting graphite oxide and further propagates to subsequent graphene derivatives [24,40]. Here we show that this is also the case for electrochemically reduced graphene oxide, which in actual fact, is not metal-free and where the metallic impurities could be responsible for the catalysis towards ORR.

2. Material and methods

2.1. Materials

Sulfuric acid (95–98%), sodium nitrate, hydrochloric acid (37%), phosphoric acid (85%), potassium chlorate (98%), *N,N*-dimethylformamide

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(DMF), potassium phosphate dibasic, sodium phosphate monobasic, potassium ferricyanide, potassium ferrocyanide, potassium hydroxide, Co_3O_4 , FeO , Fe_2O_3 , Fe_3O_4 , FeOOH and NiO particles were purchased from Sigma-Aldrich. Graphite (natural, powder, flake size of $45\text{ }\mu\text{m}$) was obtained from Asbury Carbons (Asbury, New Jersey). MnO_2 powder was purchased from Alfa Aesar. Potassium permanganate and fuming nitric acid ($>90\%$) were obtained from J. T. Baker.

2.2. Apparatus

The scanning electron microscopy (SEM) images were obtained by a JEOL 7600 F field emission scanning electron microscopy (JEOL, Japan). All voltammetric experiments were measured by using an electrochemical analyzer Autolab PGSTAT 101 (Ecochemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Metrohm Autolab B. V.). The electrochemical measurements were performed by using a three-electrode configuration at room temperature. A glassy carbon (GC) electrode was used as the working electrode, a platinum disk and a Ag/AgCl (saturated) electrode were used as the auxiliary and reference electrodes, respectively. Trace metal analysis was performed using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS, Japan). Prior to analysis, samples were digested by using a Milestone Ethos one microwave digestion system (Italy) using ultrapure nitric and hydrochloric acids (J. T. Baker).

2.3. Procedure

2.3.1. Synthesis of graphite oxide by Staudenmaier oxidation method

17.5 mL of sulfuric acid (95–98%) and 9 mL of nitric acid ($>90\%$) were added to a reaction flask containing a magnetic stir bar. The mixture was cooled at $0\text{ }^\circ\text{C}$ for 15 min. 1 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and obtain a homogeneous dispersion. 11 g of potassium chlorate was slowly added to the mixture (over 15 min) at $0\text{ }^\circ\text{C}$ in order to avoid sudden increases in temperature and the formation of chlorine dioxide gas, which is explosive at high concentrations. After the complete dissolution of potassium chlorate, the reaction flask was loosely capped to allow evolution of gas and the mixture was stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 1 L of ultrapure water and filtered. GiO was then redispersed and washed by centrifugation (10000 rpm) repeatedly in 5% HCl solutions to remove sulfate ions. GiO was finally washed with ultrapure water until a neutral pH of supernatant was obtained. The GiO slurry was then dried in a vacuum oven at $30\text{ }^\circ\text{C}$ for 5 days prior to usage.

2.3.2. Synthesis of graphite oxide by Hummers oxidation method

Graphite (0.5 g) was stirred with 23.0 mL of H_2SO_4 (95–98%) for 20 min at $0\text{ }^\circ\text{C}$ prior to the addition of NaNO_3 (0.5 g) in portions. The mixture was left to stir for 1 h. KMnO_4 (3 g) was then added in portions at $0\text{ }^\circ\text{C}$. The mixture was subsequently heated to $35\text{ }^\circ\text{C}$ for 1 h. Water (40 mL) was then added into the mixture and resulted in the temperature of the mixture to rise up to $90\text{ }^\circ\text{C}$. The temperature was maintained at $90\text{ }^\circ\text{C}$ for 30 min. Additional water (100 mL) was added into the mixture. This was followed by a slow addition of 30% H_2O_2 ($\sim 10\text{ mL}$). The warm yellow solution was centrifuged (10000 rpm) and washed with warm water (100 mL) followed by a copious amount of ultrapure water until a neutral pH of supernatant was obtained. The GiO slurry was then dried in a vacuum oven at $30\text{ }^\circ\text{C}$ for 5 days prior to usage.

2.3.3. Electrochemical reduction of graphene oxide

The prepared graphite oxides were first dispersed in DMF to obtain a 5 mg/mL suspension with 30 min ultrasonication treatment to obtain exfoliated graphene oxide (Hu-GO and St-GO). The graphene oxide was reduced on the GC electrode by using LSV in the range between 0 V and -1.2 V in 50 mM phosphate buffer solution (pH 7.2). 2 scans were applied to ensure that the graphite oxide was reduced with no

more reduction peaks shown in this potential range. The prepared electrode was dipped into ultrapure water before use, to rinse off any adsorbed materials.

2.3.4. Electrochemical experiments

Metal oxide and hydroxide particles were dispersed in DMF to prepare 5 mg/mL suspensions for modification of the glassy carbon electrode. The GC electrode was cleaned with ultrapure water, and polished with a $0.05\text{ }\mu\text{m}$ alumina polishing cloth, and then cleaned with ultrapure water again. For linear sweep voltammetry (LSV) measurements, the prepared suspensions were sonicated for 5 min and subsequently a $1\text{ }\mu\text{L}$ of suspension was drop-casted onto the GC electrode and was allowed to dry at room temperature. All ORR measurements were performed in 0.1 M KOH solution at a scan rate of 10 mV/s .

3. Results and discussions

In this work, natural graphite was employed as starting material to produce graphite oxide by applying Hummers (Hu-GiO) [28] and Staudenmaier (St-GiO) [41] oxidation methods. Consequently, Hu-GiO and St-GiO were exfoliated via ultrasonication treatment and subsequently electrochemically reduced and hereafter labeled as Hu-ErGO and St-ErGO, respectively. The oxidation methods based on Hummers and Staudenmaier approaches were investigated since the Hummers method uses KMnO_4 as oxidant while the Staudenmaier utilizes KClO_3 as oxidant.

Prior to electrochemical reductive treatment, the Hu-GiO and St-GiO were extensively characterized by ICP-MS for trace metal analysis. St-GiO contains 6.00 ppm of Mn, 574.04 ppm of Fe, 0.38 ppm of Co and 4.11 ppm of Ni while Hu-GiO contains 1931.99 ppm of Mn, 298.01 ppm of Fe, 0.21 ppm of Co, and 1.31 ppm of Ni. The presence of approximately 300 times more Mn-based impurities in Hu-GiO than St-GiO further confirmed the fact that the employment of Hummers oxidation method will embed a large amount of Mn-based impurities into the prepared graphene materials which could remain difficult to remove.

The morphology of the graphene oxide and electrochemically reduced graphene oxide materials were obtained via SEM as shown in Fig. 1. Fig. 1A and C show the morphologies of St-GO and Hu-GO, which resemble stacked structure of graphene oxide layers. Fig. 1B and D show the corresponding ErGO materials.

The oxygen reduction reaction performances of St-ErGO and Hu-ErGO were examined in an air-saturated 0.1 M KOH solution as shown in Fig. 2A. These were compared against bare GC, edge plane pyrolytic graphite (EPPG), basal plane pyrolytic graphite (BPPG) as well as metal oxide and hydroxide particles that are likely to be present as impurities in the ErGO materials. Hu-ErGO exhibited the lowest onset potential (defined as potential at 10% of the wave current [42]) for ORR at -173 mV (vs. Ag/AgCl ; this corresponds to 829 mV vs. RHE). On the hand, St-ErGO showed an onset potential at -263 mV , which was relatively close to the onset potentials of bare GC, EPPG and BPPG electrodes. It should be noted that St-ErGO contains a lower amount of Mn-based impurities as the Staudenmaier oxidation method applied for the preparation of its St-GiO precursor uses KClO_3 as oxidant. The EPPG electrode which is typically used as a non-catalytic control case and benchmark for the electrochemistry of sp^2 carbon materials due to its large proportion of edge sites per area compared to other forms of ordered carbon materials [43], exhibited an onset potential of -280 mV . Similarly, BPPG and bare GC electrodes which were also used as control cases showed similar onset potentials at -269 mV and -285 mV , respectively. All the three electrodes applied as control cases (EPPG, BPPG and bare GC electrodes) showed more negative onset potentials than Hu-ErGO. In order to investigate why Hu-ErGO showed a lower onset potential, we performed linear sweep voltammograms on various metal oxide and hydroxide particles which are likely to be present as impurities in Hu-ErGO and St-ErGO (Fig. 2B). The

Fig. 1. SEM images of (A) St-GO, (B) St-ErGO, (C) Hu-GO, (D) Hu-ErGO, at 5000 $\times$ magnification with scale bar of 1 μ m.

onset potential for ORR at a bare GC electrode modified with Co_3O_4 particles was observed at -263 mV (vs. Ag/AgCl), Fe_2O_3 at -263 mV, FeOOH at -266 mV, Fe_3O_4 at -268 mV, NiO at -258 mV, and finally

MnO_2 at -185 mV (817 mV vs. RHE). In this case, the onset potential for MnO_2 is close to the work done by Schuhmann *et al.* (approximately 730 mV vs. RHE) [24]. The results clearly indicated that ORR at MnO_2 occurred at a less negative onset potential than all the other types of metal oxide and hydroxide particles, and which also perform quite similar to Hu-ErGO (-173 mV). Moreover, the fact that the EPPG electrode (-280 mV) showed a more negative onset potential than Hu-ErGO and MnO_2 indicated that the remarkable ORR performance of Hu-ErGO could be caused by the presence of Mn-based impurities in Hu-ErGO (1931 ppm of Mn). According to the ICP-MS result as aforementioned, Hu-ErGO contains 1931 ppm of Mn while St-ErGO contains 6 ppm of Mn. In the case of Hu-ErGO, the large amount of Mn-based impurities was introduced predominantly by KMnO_4 treatment in the Hummers oxidation method while a small percentage was attributed to the inherent impurity of the graphite starting material [44]. In the case of St-ErGO, the Staudenmaier oxidation method applied chlorate as oxidizing agent and therefore the presence of Mn-based impurities was solely due to the inherent impurity of the graphite starting material. The clear correlation between the amount of Mn-based impurities and position of onset potentials for ORR thus indicated that electrochemically reduced graphene oxide materials are not entirely “metal-free” and ORR catalysis on their surfaces is primarily metal-driven.

4. Conclusions

Electrochemically reduced graphene oxide materials have been successfully prepared using either chlorate- (Staudenmaier method) or permanganate-based (Hummers method) oxidation methods. This differs from the previous works where reduced graphene is reduced with thermal exfoliation or chemical reduction. We have showed that the graphite oxide prepared using permanganate-based oxidant contains significantly more Mn-based impurities. The study on the ORR performances of the ErGO materials against possible metal oxide and hydroxide particles suggested that the large differences in electrocatalytic properties towards ORR between St-ErGO and Hu-ErGO could be

Fig. 2. Linear sweep voltammetry of (A) bare GC, EPPG, BPPG, St-ErGO, Hu-ErGO and MnO_2 , (B) bare GC, FeO , Fe_2O_3 , Fe_3O_4 , FeOOH , Co_3O_4 , NiO , and MnO_2 in air-saturated 0.1 M KOH solution at a scan rate of 10 mV/s.

caused by the large amount of Mn-based impurities, which was predominantly introduced in the Hummers method. Therefore, we have demonstrated that previously reported “metal-free” electrocatalysis at electrochemically reduced graphene oxide materials were likely not entirely “metal-free”. Therefore, we wish to underline the fact that before any claims of “metal-free” electrocatalytic effect on electrochemically reduced graphene oxide materials are made, a sensitive determination (e.g., by ICP-MS) of metallic impurities should be performed.

Conflict of interest

Authors do not have conflict of interests.

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So-Called “Metal-Free” Oxygen Reduction at Graphene Nanoribbons is in fact Metal Driven

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The oxygen reduction reaction (ORR) is of key importance in the field of electrochemical energy production. Remarkable catalytic properties of “metal-free” graphene nanoribbons towards the ORR were suggested in previous reports. Herein, we show that the electrocatalytic properties of an undoped supposedly “metal-free” graphene nanoribbon towards the ORR is actually caused by metallic impurities within the graphene nanoribbons.

The search for an abundant, stable, and low-cost catalyst for the oxygen reduction reaction (ORR) is undisputedly one of the key challenges of materials science for a sustainable future. Electrocatalysis of oxygen reduction is highly important, as it is part of the fuel-cell cycle and occurs in zinc-air batteries.^[1] Platinum (typically deposited onto a carbon substrate) is a well-established catalyst for oxygen reduction. In recent years, many catalysts based on transition metals that are more abundant have been employed. Recently, there has been an emerging trend of so-called “metal-free” electrocatalysis by using nanocarbons, such as graphene or graphene nanoribbons doped with p-block elements (usually nitrogen or boron). These materials have been suggested as rivals to or as replacements for platinum.^[2,3] Herein, we wish to challenge the claims that nitrogen-doped graphene nanoribbons, prepared by unzipping carbon nanotubes (CNTs), act as a “metal-free” catalyst,^[4–6] and we wish to show that residual metallic impurities actually dominate the ORR.

Before moving forward, we should first discuss the method of preparation of such doped “metal-free” graphene nanoribbons (GNRs). CNTs, which are well known to contain several weight percent of residual catalyst metallic impurities,^[7,8] are “unzipped” by using permanganate oxidation.^[9] The use of CNTs for the preparation of GNRs combines the two worst facets of both worlds in terms of impurities: carbon nanotubes and graphene. First, residual metallic impurities in CNTs were shown to be responsible for their electrocatalytic effect towards the oxidation/reduction of hydrazine,^[10] hydrogen peroxide,^[11] halothane,^[12] glucose,^[13] amino acids,^[14] and oxygen.^[15] Even after unzipping CNTs, many metallic impurities persist, and they are responsible for the electrocatalytic oxida-

tion of HS[−] and hydrazine molecules on the nanoribbon surface.^[16] Second, the method used to unzip CNTs to graphene oxide nanoribbons uses permanganate as an oxidizing agent.^[9] It was previously shown that the permanganate method, if employed for oxidation and exfoliation of graphite to graphite/graphene oxide flakes, inadvertently introduces parts per million levels of manganese.^[17,18] This residual amount of manganese in the graphene flakes electrocatalyzes the ORR, which is mistakenly assigned to p-element (nonmetallic) doping in the graphene sheets.^[17] Schuhmann and co-workers showed that residual metal impurities within the carbon material will influence the performance of the material towards the ORR.^[19,20] This is due to the fact that small amounts of randomly distributed nanoparticle catalysts can dominate the electrochemistry of the electrode. This is caused by overlapping diffusion layers of such nanoparticle catalyst arrays distributed through the less electroactive material (i.e., carbon).^[21,22] As such, the electrode behavior provides a response that would correspond to a macroelectrode made of the catalytic materials, whereas the real amount of the catalyst can be < 1%.^[23,24] Herein, we wish to revisit recent work outlining the unzipping of CNTs, pyrolyzing the polyaniline or pyrrole groups on them,^[4,5] or heating them in the presence of ammonia and H₃BO₃,^[6] and claiming a “metal-free” catalyzed ORR.

We synthesized GNRs by using the standard method involving oxidative permanganate opening of CNTs to yield graphene oxide nanoribbons in the same manner as that previously published.^[4,5,9] The graphene oxide nanoribbons were subsequently reduced by using lithium aluminum hydride to yield GNRs.^[25] The resulting GNRs were characterized by scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy for morphology, C/O/N content, and density of defects, respectively, and, more importantly, by inductively coupled plasma mass spectrometry (ICP-MS) for trace metal analysis. Finally, we investigated the electrocatalytic effect of the GNRs and the metal impurities by using linear sweep voltammetry (LSV).

STEM analysis (Figure 1 A,B) showed that CNTs were successfully unzipped by the permanganate oxidation method. To show that these GNRs contain defects that facilitate electron transfer,^[26] we performed Raman spectroscopy. Figure 1 C shows the Raman spectrum of the prepared GNRs. The G band at approximately $\tilde{\nu} = 1560\text{ cm}^{-1}$ indicates the presence of sp² lattice carbon atoms in the GNR, and the D band at approximately $\tilde{\nu} = 1350\text{ cm}^{-1}$ represents defects caused by the sp³-hybridized carbon atoms. The ratio of the intensities of the D and G bands (I_D/I_G) is used to indicate the degree of disorder in the carbon structure. The I_D/I_G ratio for the GNRs is 1.33. The average crystallite sizes (L_a) of the various materials can be cal-

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Figure 1. A, B) Scanning transmission electron micrographs of prepared graphene nanoribbons; scale bars 1 μm and 100 nm, respectively. C) Raman spectrum of graphene nanoribbons. D) Wide spectra XPS of graphene nanoribbons and high-resolution detail of the E) C 1s and F) N 1s areas.

culated on the basis of the intensities of the D and G bands by using Equation (1):^[27]

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

in which λ_{laser} is the wavelength of the excitation laser in nm (514.5 nm), and I_G and I_D are the intensities of the Raman G and D bands, respectively. The resulting value of L_a was 12.6 nm, which is typical for chemically reduced graphene samples prepared from graphene oxide.^[28]

Wide-scan XPS (Figure 1D) shows that the major components of the GNRs are carbon and oxygen (note that the detection limit of XPS is ≈ 0.1 at%; metallic impurities within CNTs at levels of several wt% were shown to be undetectable by XPS^[29]). The high-resolution XPS of the C 1s signal (Figure 1E) gives insight into the chemical composition of residual

oxygen-containing groups, as they show different energy levels, such as C=C bonds at 284.5 eV, C–C bonds at 285.4 eV, C–O bonds at 286.3 eV, C=O bonds at 287.4 eV, O–C=O bonds at 288.5 eV, and π – π^* shake-ups at 290 eV. Careful fitting and quantification of the high-resolution XPS spectra showed that the GNRs contain 46.31 at% of C=C, 14.17 at% of C–C, 26.19 at% of C–O, 5.15 at% of C=O, and 5.91 at% of O–C=O bonds, whereas 2.27 at% corresponds to π – π^* interactions. We intentionally acquired a detailed area corresponding to the N 1s position to ascertain the absence/presence of nitrogen. As expected, no signal was detected because hydrazine was not used as the reducing agent.^[30] We intentionally omitted the use of hydrazine as a reducing agent, because we did not want to introduce nitrogen into the nanoribbon structure inadvertently (which is the case if hydrazine is used as the reducing agent, and this results in incorporation of several at% of N in the matrix^[31]) to see whether the GNRs possessed “electrocatalytic” properties towards ORR in the absence of nitrogen. No metal impurities were detected by XPS, which is not surprising

given the poor detection limits of XPS (≈ 0.1 at%) and the fact that it is a highly surface-sensitive method.^[29] As such, we also analyzed the GNRs by using ICP-MS to determine the presence of trace amount of metals. The ICP-MS data show the presence of Ni at a level of 5.0 ppm, Fe at 127.4 ppm, Co at 4.5 ppm, Mo at 16.0 ppm, W at 8.7 ppm, and Mn at 11.9 ppm.

We subsequently investigated the apparent electrocatalysis of oxygen reduction by linear sweep voltammetry in air-saturated 0.1 M KOH solution on the GNRs and related surfaces, such as an edge plane pyrolytic graphite (EPPG) electrode, metal oxides related to found metallic impurities at the modified glassy carbon electrode (GC), as well as a bare GC electrode, as shown in Figure 2 oxygen reduction at the GNRs (undoped with N; containing only metallic impurities) showed an onset potential (defined as the potential at 10% of the wave current^[32]) at -176 mV (vs. Ag/AgCl); the onset potential of the ORR at a Pt/C electrode is -101 mV (vs. Ag/AgCl). An EPPG electrode (which is often used as a benchmark for the electro-

Figure 2. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution by using a bare glassy electrode and A) GC electrode modified with graphene nanoribbons, Pt/C, and EPPG electrodes; B) with Co_3O_4 , Fe_2O_3 , Fe_3O_4 , $\text{FeO}(\text{OH})$, MoO_3 , WO_3 , NiO , and MnO_2 . Scan rate 0.01 V s^{-1} .

chemistry of sp^2 carbon materials because it possesses high heterogeneous electron-transfer rates^[26] due to a very high density of edges, the highest possible from any carbon material, and is free of impurities) shows an onset potential of -280 mV , whereas control experiments on a GC electrode, which was used as the underlying surface, show an onset potential at a similar value of -276 mV . Evidently, even undoped GNRs show a lower overpotential for the ORR than the EPPG electrode. The edges/defects cannot play a dominant role in this case, as EPPG possesses a maximal edge density and still performs in a way similar to that of the basal plane of graphite (BPPG). To investigate why this was the case, we obtained the linear scan voltammograms of various metal oxide and hydroxide-modified electrodes (Figure 2B). The onset potential for the ORR at the GC electrode modified with Co_3O_4 particles was -247 mV (vs. Ag/AgCl), Fe_2O_3 was -240 mV , $\text{FeO}(\text{OH})$ was -237 mV , Fe_3O_4 was -273 mV , MoO_3 was -264 mV , WO_3 was -278 mV , NiO was -259 mV , and finally MnO_2 was -173 mV . It is clear that MnO_2 has a much lower negative onset potential than the rest of the metal oxides/hydroxides. Furthermore, the onset potential of the ORR at the MnO_2 surface closely coincides with the onset potential of an electrode modified with GNRs (which contain metallic impurities; onset potential -176 mV) and with that of a Pt/C-modified electrode (onset potential -101 mV). Given the fact that pure edge plane pyro-

lytic graphite shows an onset potential for the ORR at -280 mV , one can conclude that manganese-based impurities of the GNRs dominate the material's properties towards the ORR. This is because these materials were prepared by permanganate unzipping of the CNTs. It is highly likely that the previously reported^[4,5] so-called "metal-free" oxygen reduction reaction of GNRs first prepared by permanganate unzipping of CNTs were dominated by manganese-based metallic impurities. We note that these nanoribbons were deemed metal-free on the basis of XPS data, but as noted above, XPS is a highly insensitive method for determining metals at the parts per million level. Note that CNTs can contain metal carbides. However, the oxides and carbides coexist, and if CNTs are treated at 400°C , Fe_3C is converted into iron oxides.^[33] We wish to highlight that MnO_2 , which is found to be the main culprit here for the enhanced activity of nanoribbons in the ORR, does not originate from the synthesis of the CNTs (which contain Fe, Ni, W, Mo, Co), but it is introduced as a contaminant by postprocessing oxidative treatment with KMnO_4 in the presence of sulfuric acid (standard procedure to open CNTs to ribbons^[9]), and there is no doubt that Mn is in the form of an oxide and not a carbide. To exclude mass-transfer limitations we performed linear-sweep voltammetry of the GNR modified electrode under rotation (rotating disc electrode, RDE). The onset potential was found to be the same as that in the stationary electrode case (Figure S1, Supporting Information). In addition, we attempted to investigate if electrocatalysis at metal oxides and GNRs is inhibited by strongly complexing ions, such as SCN^- . We found that the onset potential of oxygen reduction in 0.1 M KOH at GNRs is unaffected by the presence of 10 mM KSCN (Figure S2). Some variations in onset potentials at metal oxides (both positive and negative) were observed (Figures S3 and S4).

In conclusion, we demonstrated that graphene nanoribbons prepared by permanganate unzipping of carbon nanotubes contain metallic impurities and that manganese-based impurities have a highly catalytic effect on the oxygen reduction reaction. We wish to recommend that before any claims of a "metal-free" electrocatalytic effect of graphene nanoribbon materials are made, sensitive determination (e.g., by ICP-MS) of metallic impurities is first performed.

Experimental Section

Materials

N,N-Dimethylformamide (DMF), MoO_3 , WO_3 , Fe_2O_3 , $\text{FeO}(\text{OH})$, Co_3O_4 , Fe_3O_4 , NiO nanoparticles, multiwalled carbon nanotubes (MWCNTs), sulfuric acid (95–98% w/v), hydrochloric acid (37% w/v), THF, methanol, lithium aluminum hydride, and sodium sulfate were obtained from Sigma–Aldrich. MnO_2 powder and hydrogen peroxide were obtained from Alfa Aesar. Potassium permanganate was obtained from J. T. Baker. Diethyl ether was obtained from RCI Labscan. Ethanol was obtained from Merck. Ultrapure nitric acid was purchased from J. T. Baker.

Apparatus

Scanning transmission electron microscope (STEM) images were obtained by using a JEOL 7600F field emission scanning electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) samples were prepared by compacting a uniform layer of the materials on a carbon tape. The XPS samples were measured by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer to obtain survey and high-resolution C1s, O1s, and N1s spectra. All voltammetric experiments were measured by using an Autolab PGSTAT 101 electrochemical analyzer (Ecochemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Metrohm Autolab B. V.). Trace metal analysis was performed by using an Agilent 7700x ICP-MS (Japan). Prior to analysis, samples were digested by using Milestone Ethos one microwave digestion system (Italy).

Synthesis methods

Preparation of graphene nanoribbons

The method outlined by Tour and co-workers was adapted slightly to unzip MWCNTs.^[9] MWCNTs (300 mg) were stirred in concentrated H₂SO₄ (120 mL) for 12 h at room temperature. KMnO₄ (1650 mg, 550% w/w) was then added to the mixture, which was stirred for 1 h at room temperature. The mixture was then heated to 55 °C for 30 min in an oil bath. The reaction progress was monitored by sampling 2–3 drops of the mixture in an Eppendorf tube containing ultrapure water (1 mL). A red hue of the test solution corresponding to the formation of Mn^{IV} implied complete consumption of KMnO₄ (and thus, reaction completion). A separate Eppendorf tube with water (1 mL) and H₂O₂ (2–3 drops) was also tested with the mixture with ultrasonication; a dark yellow color as well as high dispersibility of the solid indicated reaction completion. The temperature was then raised to 70 °C, it was allowed to stabilize, and it was then cooled to room temperature. The mixture was poured into water (360 mL, in an ice bath) with 27% H₂O₂ solution (10 mL) and then filtered through a RC membrane (0.22 µm). The residue was stirred in H₂O (120 mL) for 30 min and ultrasonicated for 15 min. HCl (37%, 15 mL) was added to induce flocculation, and the mixture was filtered again (RC, 0.22 µm). The residue was stirred in ethanol (120 mL) for 30 min and ultrasonicated for 15 min. Diethyl ether (120 mL) was added, and the mixture was filtered through a polytetrafluoroethylene (PTFE) membrane (0.22 µm). The filtered graphene oxide nanoribbons (GONRs) were washed with ether (3×40 mL) and dried in an oven at 50 °C for 4 days. The GONRs obtained (100 mg) were then stirred in dry THF (60 mL) and ultrasonicated for 3 h. Lithium aluminum hydride (LAH, 400 mg) was then added to the mixture portionwise in a 0 °C ice bath until bubbling was no longer observed. The mixture was then transferred dropwise into a solution of LAH (1600 mg) in dry THF (60 mL) at 0 °C and then allowed to stir under reflux for 24 h. The reaction was quenched with saturated sodium sulfate, and this was followed by the addition of 1 M HCl at 0 °C until a clear solution was obtained. The mixture was filtered over a PTFE membrane (0.22 µm), and the residue was washed with copious amounts of ultrapure water and then dried in an oven at 60 °C for 5 days to afford graphene nanoribbons.

Electrochemistry

All powders, including graphene nanoribbons, were dispersed in DMF to prepare a 5 mg mL⁻¹ suspension for modification of the glassy carbon electrode. The GC electrode was cleaned with deionized water, polished with a 0.05 µm alumina polishing cloth, and then cleaned with deionized water again. Metal oxide suspensions was placed directly onto the GC electrode (no mixing with carbon materials or Nafion in the case of linear sweep voltammetry (LSV) without a RDE system employed, which is in all cases with exception of Figure S1 and related data). For rotating disk electrode measurement (Figure S1 and related data), the sample suspension was prepared with 10 wt% of Nafion for 5 mg mL⁻¹, and the measurements were performed by using an AUTOLAB rotator RDE80352. For LSV, the prepared suspensions were sonicated for 5 min and 1 µL of suspension was dropped by pipette onto the GC electrode. The dropped suspension was allowed to dry at room temperature. Both of the RDE and GC electrodes had a diameter of 3 mm.

Keywords: carbon • electrochemistry • graphene nanoribbons • metallic impurities • oxygen reduction reaction

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Nitrogen doped graphene: influence of precursors and conditions of the synthesis†

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Heteroatoms doped graphenes, especially nitrogen doped graphenes, have attracted much attention due to their remarkable performance as parts of lithium-ion batteries, advanced catalyst supports, super capacitors and fuel cells. The performance of doped materials strongly depends on the level of doping. While the nitrogen doped graphenes are synthesized by various methods, the parameters influencing the level of doping are seldom studied. Here we prepare nitrogen doped graphenes by exfoliation of different graphite oxides (*i.e.* Staudenmaier, Hofmann and Hummers) in an ammonia atmosphere at various exfoliation temperatures (*i.e.* 600 °C, 800 °C and 1000 °C). We study the efficiency of nitrogen doping using characterization methods such as scanning electron microscopy, Raman spectroscopy, combustible elemental analysis and X-ray photoelectron spectroscopy. We show that the level of doping strongly depends on the type of the starting graphite oxide. This has very important implication on the fabrication of doped graphenes and we suggest that the graphite oxide preparation route must be always considered when one performs heteroatom doping of graphenes *via* a thermal exfoliation route. In addition, we present an optimized, scalable technique for fabrication of large quantities of highly nitrogen doped (>7 at.%) graphenes.

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Introduction

Graphene is a single layer of graphite, with carbon atoms covalently bonded in a hexagonal lattice. Due to this unique structure, graphene exhibits various interesting properties, such as high electrical conductivity, high thermal conductivity, good optical transparency, and large surface area.¹ Doping of heteroatoms such as boron,² nitrogen,^{3–6} phosphorus,⁷ sulphur,⁸ halogens^{9,10} or hydrogen^{11,12} can tailor the electronic and electrochemical properties of graphene, which can dramatically enhance the performance of doped graphene. Nitrogen doped graphene has attracted much attention due to its remarkable performance as parts of lithium-ion batteries,^{5,6} advanced catalyst supports,¹³ super capacitors¹⁴ and fuel cells.^{3–5} The level of doping is of high importance as carrier density is crucial for tuning the performance of the material. Even though properties of N doped graphene strongly depend on the concentration of the dopant, a limited number of studies actually investigate the variables influencing the level of doping.

There are different approaches of doping of graphene with heteroatoms. Some approaches are based on simply mixing

graphene materials with a nitrogen containing precursor (*i.e.* melamine) and a carbonized mixture.¹⁵ Nitrogen doping can be also achieved by thermal exfoliation of graphite oxide in an ammonia atmosphere.^{16,17} Solvent-based precursors were tested by using graphene oxide and Schiff base precursors, leading to N doped graphene.¹⁸ The amount of nitrogen introduced into the graphene lattice has been reported typically in the range of 2–4 at.%.^{4,5,13} The only methods capable of introduction of larger amounts of 9–11 at.% are CVD based methods.^{6,14}

Here we present a study of the effects of nitrogen level doping by using different precursors and conditions. We employ the scalable method capable of production of gram quantities of the doped material *via* oxidative treatment of graphite to graphite oxide and consequent thermal exfoliation in the NH₃ atmosphere. We vary parameters such as the starting material preparation method (permanganate *vs.* chlorate based oxidation of graphite to graphite oxide; such materials exhibit very different structural characteristics,¹⁹ even though they have similar C/O ratios) and temperature of exfoliation in the NH₃ atmosphere. We will show that the starting material preparation method has a profound influence on doping levels of N doped graphene. The influence of the condition used will be investigated by detailed characterization by scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy, as well as combustible elemental analysis. We show that by optimization of the synthetic conditions, it is possible to achieve doping over 7 at.% nitrogen in the graphene lattice.

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Results and discussion

The precursors of N doped graphenes were graphite oxides (GO) which were synthesized using chlorate oxidants (Staudenmaier and Hofmann methods)^{20,21} and permanganate oxidants (Hummers method).²² The nitrogen doped graphenes were prepared by thermal exfoliation of graphite oxides in the ammonia atmosphere. The influence of the starting graphite oxide type as well as of exfoliation temperature on the nitrogen doping and density of defects was studied. The control experiments were carried out by exfoliation of GO in the N₂ atmosphere. The N doped graphenes are labelled in the following text by the method of precursor synthesis (Staudenmaier (ST), Hofmann (HO), Hummers (HU)), by exfoliation temperature and by suffix "N" in the case of exfoliation in the NH₃ atmosphere (e.g. "ST-600-N"). For control materials exfoliated in the N₂ atmosphere, suffix "N" is not used.

Morphology

The morphology of all reduced graphene samples was investigated by SEM. Fig. 1 shows the SEM images of different types of nitrogen doped graphenes which were obtained at magnification of 3000× and 20 000×. SEM images for control (N₂ atmosphere exfoliated) graphene are shown in the ESI, Fig. S1.† All materials showed a typical exfoliated structure in agreement with previous studies and confirmed successful thermal exfoliation of all types of graphite oxide samples in the NH₃ atmosphere. We have also recorded XRD to provide full characterization of resulting N doped materials (Fig. S2, ESI†).

Raman spectroscopy was used in order to determine the defect density of nitrogen doped graphene that was prepared by different methods and at different temperatures. Fig. 2 shows the Raman spectra and the I_D/I_G ratio for the nitrogen doped graphene prepared by different methods and under different conditions. The G band at approximately 1560 cm⁻¹ indicates the presence of sp² lattice carbon atoms in the graphene sheet and a D band at approximately 1350 cm⁻¹ represents the defects caused by the sp³ hybridized carbon atoms, which is, as we will show later, related to doping of nitrogen atoms.

The ratio between D and G band intensities (I_D/I_G) is used to indicate the degree of disorder in a carbon structure. The I_D/I_G ratio for ST-600-N, HO-600-N, HU-600-N increases from 0.89 to 0.95 and to 1.02, respectively. This indicates that the highest density of defects can be found in HU-600-N while the lowest density of defects in ST-600-N. This reflects the fact that the graphite oxides are very different materials which undergo exfoliation *via* different routes, as shown previously.^{23,24} Interestingly, the increasing temperature of exfoliation from 600 °C to 1000 °C did not lead to a monotonic trend; ST-600-N, ST-800-N, and ST-1000-N displayed I_D/I_G of 0.89, 0.41 and 0.77 respectively as shown in the bar chart in Fig. 2.

Among the graphenes prepared at 600 °C, only the ST-600-N exhibits a 2D band at approximately 2700 cm⁻¹, which indicates a lower degree of disorder in its carbon structure than HU-600-N and HO-600-N. In fact, all Raman spectra of nitrogen doped graphenes prepared from ST graphite oxide at different temperatures

Fig. 1 Scanning electron micrographs of nitrogen doped graphenes prepared from Staudenmaier (ST) graphite oxide at 600 °C, 800 °C and 1000 °C, Hofmann (HO) graphite oxide at 600 °C, and Hummers (HU) graphite oxide at 600 °C. Magnification of (A) 3000× and (B) 20 000×. Scale bar of 1 μm.

show a 2D band at approximately 2700 cm⁻¹ indicating that all three nitrogen doped ST graphenes have a lower disorder structure when compared to other two graphite oxides.

The average crystallite sizes (L_a) of the various materials can be calculated based on the D and G band intensities by application of eqn (1):²⁵

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

where λ_{laser} is the wavelength of the excitation laser in nanometres, and I_G and I_D are the intensities of the Raman G and D

Fig. 2 Left: the I_D/I_G ratio and Raman spectra for nitrogen doped graphenes prepared from (A) Staudenmaier (ST) graphite oxide, (B) Hofmann (HO) graphite oxide, and (C) Hummers (HU) graphite oxide at 600 °C. Right: the I_D/I_G ratio and Raman spectra for nitrogen doped graphenes prepared from Staudenmaier (ST) graphite oxide at (D) 600 °C, (E) 800 °C, and (F) 1000 °C.

bands, respectively. Then we calculated the crystallite sizes in nitrogen doped graphene samples. We found the L_a of ST-600-N, HO-600-N, HU-600-N, ST-800-N and ST-1000-N to be 14.97 nm, 15.98 nm, 17.15 nm, 6.90 nm and 12.95 nm, respectively. Raman spectra of control graphene materials (exfoliated in N_2 atmosphere) are shown in Fig. S3 (ESI[†]).

X-ray photoelectron spectroscopy

The elemental compositions of nitrogen doped graphene samples were investigated by using XPS. The XPS can obtain not only the elemental composition, but also bonding information for selected elements. The wide scan, and C 1s and N 1s high resolution XPS were obtained for all doped graphene samples and shown in Fig. 3–5 (corresponding XPS spectra of undoped graphene materials exfoliated in inert gas atmosphere are shown in Fig. S4 and S5 (ESI[†])). The wide scan and high resolution XPS of C 1s shown in Fig. 3 and 4 for all nitrogen doped graphenes indicate that the oxygen containing groups were mostly removed, the thermally reduced graphenes were prepared successfully, and the nitrogen was successfully introduced into the graphene lattice. No nitrogen was observed in control (undoped) graphene samples prepared by exfoliation in the N_2 atmosphere.

The C/O ratio for ST-600-N, HO-600-N and HU-600-N are 11.6, 12.1 and 11.8 respectively, indicating that thermal reduction of graphite oxides was successfully achieved. The nitrogen content for different precursors increases in the row ST-600-N,

Fig. 3 Left: N content and wide scan XPS for nitrogen doped graphenes prepared from (A) Staudenmaier (ST) graphite oxide, (B) Hofmann (HO) graphite oxide, and (C) Hummers (HU) graphite oxide at 600 °C. Right: N content and wide scan XPS for nitrogen doped graphenes prepared from Staudenmaier (ST) graphite oxide at (D) 600 °C, (E) 800 °C, and (F) 1000 °C.

Fig. 4 Left: high resolution XPS of C 1s of nitrogen doped graphenes prepared from (A) Staudenmaier (ST) graphite oxide, (B) Hofmann (HO) graphite oxide, and (C) Hummers (HU) graphite oxide at 600 °C. Right: high resolution XPS of C 1s of nitrogen doped graphenes prepared from Staudenmaier (ST) graphite oxide at (D) 600 °C, (E) 800 °C, and (F) 1000 °C.

HO-600-N and HU-600-N from 2.5 at.%, 4.3 at.% to 7.2 at.%, respectively (Fig. 3). It is apparent that the nitrogen doped graphene prepared from Hummers graphite oxide contains the largest amount of nitrogen; in contrast, the Staudenmaier graphite oxide as the precursor leads to the lowest amount of nitrogen doping. It is noteworthy that density of defects (I_D/I_G ratio) exhibits the same trend as nitrogen content and appears to be closely related.

Consequently, we have studied the influence of exfoliation temperature on the N content and the reduction of GO. The C/O ratios of ST-600-N, ST-800-N and ST-1000-N are 11.6, 15.1 and 15.5 which show an increasing trend towards increasing exfoliation temperature. ST-600-N, ST-800-N and ST-1000-N contained 2.5 at.%, 0.94 at.% and 2.18 at.% of nitrogen, respectively. There is no clear monotonic trend for the amount of doped nitrogen along the exfoliation temperature. However, similar to the influence of the precursors study, the I_D/I_G ratio was closely related to nitrogen doping levels. The XPS data are generally consistent with nitrogen determination by combustible elemental analysis, as shown in Table 1.

The high resolution XPS of the C 1s signal provides the insight into the chemical composition of residual oxygen containing groups, as they show different energy levels, C=C bond of 284.5 eV, C-C bond of 285.4 eV, C-O bond of 286.3 eV, C=O bond of 287.4 eV, O-C=O bond of 288.5 eV and π - π interactions of 290 eV. The detailed bonding information for all nitrogen doped graphenes is shown in Table 2. The high resolution XPS of N 1s for nitrogen doped graphenes are shown in Fig. 5. Similar to high resolution C 1s, high resolution XPS of the N 1s signal shows the chemical compositions at different energy levels; pyridine-like N bond at 397.9 eV, pyrrole-like N bond at 399.1 eV and quaternary N at 401.3 eV. In the precursors study, ST-600-N, HO-600-N and HU-600-N contain 48.6 at.%, 38.8 at.% and 46.1 at.% of pyridine-like N bond, 27.6%, 14.5% and 40.6% of pyrrole-like N bond, and 23.8 at.%, 46.6 at.% and 13.3 at.% of quaternary N bond respectively. In the temperature study, ST-600-N, ST-800-N and ST-1000-N contain 48.6 at.%, 41.2 at.%

Table 1 Combustible elemental analysis of N doped graphene

Sample	at.% N	at.% C	at.% H	at.% O
ST-600-N	2.25	90.03	1.09	6.63
HO-600-N	4.22	82.51	3.25	10.02
HU-600-N	6.86	76.46	7.35	9.33
ST-800-N	2.3	90.56	1.56	5.58
ST-1000-N	1.94	90.03	2.27	5.76

Table 2 Bonding arrangement in doped graphenes (%) from high resolution C 1s XPS for all nitrogen doped graphene samples

	C=C	C-C	C-O	C=O	O-C=O	π - π
HU-600-N	56.0	18.5	10.2	8.5	2.1	2.1
HO-600-N	53.0	21.9	10.8	4.2	4.5	5.4
ST-600-N	60.3	19.7	10.6	4.2	2.7	2.4
ST-800-N	61.7	12.6	15.1	5.5	3.9	1.1
ST-1000-N	57.2	17.8	9.1	7.4	3.7	4.8

Fig. 5 Left: high resolution XPS of N 1s of nitrogen doped graphenes prepared from (A) Staudenmaier (ST) graphite oxide, (B) Hofmann (HO) graphite oxide, (C) Hummers (HU) graphite oxide at 600 °C, and (D) the bar chart of the nitrogen bonding information for nitrogen doped graphenes. Right: high resolution XPS of N 1s of nitrogen doped graphenes prepared from Staudenmaier (ST) graphite oxide at (E) 600 °C, (F) 800 °C, (G) 1000 °C and (H) the bar chart of the nitrogen bonding information for nitrogen doped graphenes.

and 42.3 at.% of pyridine-like N bond, 27.6 at.%, 28.4 at.% and 10.5 at.% of pyrrole-like N bond, 23.8 at.%, 30.4 at.% and 47.1 at.% of quaternary N bond respectively.

From specific resistivity measurements (4-point method), it can be seen that specific resistivity of the material is directly related to the nitrogen doping levels; as it can be seen in Table 3, when we compare three graphenes prepared by different methods at the same temperature, HU-600-N with 7.2 at.% of N shows the highest resistivity while the lowest amount of nitrogen doping in ST-600-N the lowest resistivity. As it can be observed, there is higher resistivity at high nitrogen concentrations due to the fact that increase of pyrrole-like N and quaternary nitrogen moieties increase the defect concentrations which act as a scattering centres of free carriers. In addition, quaternary nitrogen creates p-doping site, effectively withdrawing electrons. When we look at the relation of conductivities based on graphene prepared by the Staudenmaier method at different temperatures, there is not a clear dependency as varied densities of defects may influence the conductivity as well. Resistivity of

Table 3 Specific resistivity of N doped graphenes

Sample	Specific resistivity (ohm cm ⁻¹)
ST-600-N	5.6×10^{-5}
HO-600-N	2.3×10^{-4}
HU-600-N	1.7×10^{-3}
ST-800-N	2.6×10^{-4}
ST-1000-N	3.5×10^{-5}

graphenes exfoliated in the inert atmosphere (undoped) are stated in Table S1 (ESI[†]).

Conclusions

It was found that the type of the precursor, such as the type of graphite oxide used for preparation of the nitrogen doped graphene, has a major influence on the level of doping. This is a major contribution to the field since graphite oxides prepared by chlorate or permanganate routes are typically treated as interchangeable. Our findings on nitrogen doped graphenes confirm previous observations on sulphur doped graphenes, where a similar trend related to the preparation route of graphite oxide was observed.⁸ This is due to the differences in the structures of graphite oxides prepared by different methods. Among three types of precursors, Staudenmaier graphite oxide, Hofmann graphite oxide and Hummers graphite oxide, under same conditions, the Hummers graphite oxide can be doped with the highest amount of nitrogen (7.2 at.%) and the Staudenmaier graphite oxide can be doped the least amount of nitrogen (0.94 at.%). Therefore, we strongly suggest that the type of used graphite oxide for preparation of doped graphenes shall be always considered as an important variable.

Experimental

Materials

Graphite microparticles (<50 μm) were obtained from KOH-I-NOOR GRAFIT, Czech Republic. Sulfuric acid (96%), nitric acid (65%), nitric acid (fuming, >98%), potassium chlorate (98%), potassium permanganate (98%), hydrogen peroxide (30%), hydrochloric acid (35%), silver nitrate (99.8%) and barium nitrate (99%) were obtained from PENTA, Czech Republic. Nitrogen gas (99.9999%) and ammonia (99.9995%) were obtained from SIAD. *N,N*-Dimethylformamide (DMF), potassium phosphate dibasic, and sodium phosphate monobasic were purchased from Sigma-Aldrich.

Apparatus

The scanning electron microscopy (SEM) images were obtained by using a JEOL 7600F field emission scanning electron microscope (JEOL, Japan). The Raman spectra were obtained by a confocal micro-Raman LabRam HR instrument from Horiba Scientific in a backscattering geometry with a CCD detector. A 514.5 nm Ar laser and a 100× objective lens were mounted on an Olympus optical. The calibration is made by using a silicon reference with a peak position at 520 cm⁻¹ and a resolution less

than 1 cm⁻¹. X-ray photoelectron spectroscopy (XPS) samples were prepared by compacting a uniform layer of the materials on a carbon tape. The XPS samples were measured by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer in order to obtain survey and high resolution C 1s, O 1s and N 1s spectra.

The combustible elemental analysis was performed with CHN PE 2400 Series II from Perkin Elmer (USA). In CHN operating mode (the most robust and interference free mode), the instrument employs a classical combustion principle to convert the sample elements to simple gases (CO₂, H₂O and N₂). The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases, separation and detection. A microbalance MX5 (Mettler Toledo) is used for precise weighing of samples (1.5–2.5 mg per single sample analysis). The accuracy of CHN determination is better than 0.30% abs. Internal calibration was performed using *N*-phenyl urea.

Specific resistivities of MVGs were measured by first compressing 40 mg each of the materials into a capsule (diameter 63.5 mm) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was then measured according to the van der Pauw method²⁶ with a 4-probe technique, using a home-made system with a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit.

X-ray powder diffraction data were collected at room temperature with an X'Pert PRO θ - θ powder diffractometer with a parafocusing Bragg–Brentano geometry using Cu K α radiation ($\lambda = 1.5418$ Å, $U = 40$ kV, and $I = 30$ mA). Data were scanned with an ultrafast detector X'Celerator over the angular range 5–80° (2θ) with a step size of 0.0167° (2θ) and a counting time of 20.32 s per step. Data evaluation was performed in the software package HighScore Plus.

Graphite oxide preparation with the Staudenmaier method

87.5 mL of sulfuric acid (96% concentration) and 27 mL of fuming nitric acid were added to a reaction flask which contains a magnetic stir bar. The mixture was subsequently cooled by immersion in an ice bath for 30 min. Then 5 g of graphite was added into the mixture with vigorous stirring motion to avoid agglomeration and obtain a homogeneous dispersion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period) while the reaction flask was kept in an ice bath to avoid a sudden increment in temperature and formation of explosive chlorine dioxide gas. When potassium chlorate was completely dissolved, the reaction flask was loosely capped to allow the evolved gas to escape and the mixture was continuously stirred vigorously for 96 h at room temperature. When reaction was finished, the mixture was poured into 3 L of deionized water and decanted. In order to remove sulfate ions, graphite oxide was then redispersed in HCl (5%) solution and repeatedly centrifuged and redispersed in deionized (DI) water until a negative reaction on chloride and sulfate ions (with AgNO₃ and Ba(NO₃)₂ respectively) was achieved. Then the graphite oxide slurry was dried in a vacuum oven at 60 °C for 48 h before use.

Graphite oxide preparation with the Hofmann method

27 mL of nitric acid (65%) and 87.5 mL of sulfuric acid (96%) were added to a reaction flask (Pyrex beaker with thermometer) which contains a magnetic stir bar and the mixture was then cooled by immersion in an ice bath for 30 min. In order to avoid agglomeration and obtain a homogeneous dispersion, 5 g of graphite was added to the mixture with vigorous stirring motion. 55 g of potassium chlorate was slowly added to the mixture (over a 30 min period) while the reaction flask was kept in an ice bath to avoid a sudden increment in temperature and formation of explosive chlorine dioxide gas. When potassium chlorate was completely dissolved, the reaction flask was loosely capped to allow the evolved gas to escape and the mixture was continuously stirred vigorously for 96 h at room temperature. When reaction was finished, the mixture was poured into 3 L of deionized water and decanted. In order to remove sulfate ions, graphite oxide was then redispersed in HCl (5%) solution and repeatedly centrifuged and redispersed in deionized (DI) water until a negative reaction on chloride and sulfate ions (with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ respectively) was achieved. Then the graphite oxide slurry was dried in a vacuum oven at 60 °C for 48 h before use.

Graphite oxide preparation with the Hummers method

2.5 g of sodium nitrate and 5 g of graphite were stirred with 115 mL of sulfuric acid (98%) and the mixture was cooled in an ice bath. 15 g of potassium permanganate was added with vigorous stirring over two hours. In following 4 hours, the mixture was allowed to reach room temperature before being heated to 35 °C for 30 min. Then the mixture was poured into a flask which contains 250 mL of DI water and further heated to 70 °C. The temperature of mixture was held constantly for 15 min and poured into 1 L of DI water. Hydrogen peroxide (3%) was added to remove unreacted manganese dioxide and potassium permanganate. Then the mixture was allowed to settle and decanted. The formed graphite oxide was purified by repeated centrifugation and redispersion in DI water until a negative reaction on sulfate ion (with $\text{Ba}(\text{NO}_3)_2$) was achieved. Then the graphite oxide slurry was dried in a vacuum oven at 60 °C for 48 h before use.

Thermally reduced graphenes

Thermally reduced graphenes (TR-G) were formed by thermal exfoliation/reduction of graphite oxides at 600 °C and 1000 °C. 0.1 g of graphite oxide was placed into a porous quartz glass capsule which connects to a magnetic manipulator and placed inside a vacuum tight tube furnace with a controlled atmosphere. The magnetic manipulator is able to create a temperature gradient over 1000 °C min^{-1} . In order to remove oxygen, the sample was flushed with nitrogen gas by repeated evacuation of the tube furnace. Then the sample was inserted by the magnetic manipulator to a preheated furnace and held in the furnace for 12 min. The flow of nitrogen (99.9999%) during the exfoliation procedure was 1000 mL min^{-1} to remove any byproducts from the procedure.

Synthesis of N doped graphene

The nitrogen doped graphene was prepared by exfoliation of produced graphite oxide in the ammonia atmosphere. 100 mg of graphite oxide were placed inside the quartz glass capsule connected to the magnetic manipulator and placed in the horizontal quartz glass reactor. The reactor was repeatedly evacuated and flushed with nitrogen before the insertion of the sample within the hot zone. Subsequently the sample was inserted in the hot zone of the reactor and the nitrogen flow was switched to ammonia. The temperature of samples was held constantly for 12 min at 600 °C, 800 °C and 1000 °C. The ammonia with a flow rate of 300 mL min^{-1} was used in order to remove the exfoliation byproducts.

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Boron-Doped Graphene: Scalable and Tunable p-Type Carrier Concentration Doping

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ABSTRACT: Precisely engineered changes in Fermi levels of graphene-based materials are of high importance for their applications in electronic and electrochemical devices. Such applications include photoelectrochemical reactions or enhanced electrochemical performance toward reduction of oxygen. Here we describe a method for scalable and tunable boron doping of graphene via thermal exfoliation of graphite oxide in BF_3 atmosphere at different temperatures. The temperature and atmospheric composition during exfoliation influences the kinetics of decomposition of the reactants and levels of doping, which range from 23 to 590 ppm. The resulting materials were characterized by prompt γ -ray analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, and scanning electron microscopy. Recent claims on enhanced catalytic properties of boron-doped graphenes toward the reduction of oxygen were addressed, as well as similar claims on enhanced capacitance.

INTRODUCTION

Doping of graphene with electron-donating or electron-withdrawing groups is important for changing the electronic properties of graphene.¹ Such electron-donating groups include nitrogen^{2–6} or phosphorus,⁷ while electron-withdrawing group include boron.⁸ Doping by electron-donating (n-type, electron donors) or -withdrawing groups (p-type, electron acceptors) changes the electron density of the graphene sheets and as such influences its electrochemical property.⁹ The level of doping is of high importance as carrier density is crucial for tuning the performance of the material. Another important issue with production of doped materials is to produce scalable methods for potentially large quantities of doped materials manufactured. Here we present a technique for scalable production and tunable doping levels by exfoliation of graphite oxide in BF_3 atmosphere at different temperatures. As secondary objective, we investigate the electrochemical properties of such p-doped materials and compare them to the ones found in literature.

It has been claimed that nitrogen-doped graphenes exhibit unusual (as compared to pure graphene) electrocatalytic effects toward reduction of H_2O_2 and oxygen,^{2,6,9} which have very important implications for biosensing and fuel cells applications, respectively. Nitrogen-doped graphenes were also claimed to have large capacitance when compared to graphene. Interestingly, boron-doped graphene was claimed to exhibit similar effects, being electrocatalytic toward oxygen reduction¹⁰ and having increased capacitance in comparison to pure graphene.¹¹ It seems that regardless of the atoms doped in graphene the very

same properties are enhanced.^{2,6,10–12} As such, we wish to further address this issue. In theory, with increased doping of materials with electron-deficient components, the easier would be the oxidation of the compound, while the reduction becomes more difficult.^{13–15} This is contrary to some previous reports on boron-doped graphene catalyzing the electrochemical reduction of oxygen.^{10–12} Here we prepared boron-doped graphene with different concentrations of boron as mentioned above. With detailed characterization using scanning electron microscope, Raman spectroscopy, X-ray photoelectron spectroscopy, and prompt γ -ray analysis, and cyclic voltammetry, we studied how increasing the concentration of boron in graphene influences its electrochemical properties, such as its electrocatalysis toward reduction of oxygen and its capacitance.

RESULTS AND DISCUSSION

Boron-doped graphenes were prepared by thermal exfoliation of graphite oxide in an atmosphere with boron trifluoride diethyl etherate at 1000 °C in N_2/H_2 , 800 °C in N_2 and 1000 °C in N_2 . The graphite oxide underwent exfoliation, deoxygenation (producing H_2O , CO, CO_2 , and more complex organic molecules^{16–19}) and simultaneous doping with boron. The resulting boron-doped graphenes were characterized by prompt γ -ray analysis (PGAA), scanning electron microscopy (SEM), X-

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Figure 1. Scanning electron micrographs of boron-doped graphenes containing 23 ppm of B, 140 ppm of B, and 590 ppm of B. Images were obtained at (A) 370X, (B) 6000X, and (C) 40 000X magnifications and scale bars are 10 μm , 1 μm , and 100 nm, respectively.

ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry (CV) to study their electrocatalytic properties toward oxygen reduction as well as its capacitance. We abbreviate all boron-doped graphenes as B-G in this paper.

First, we investigated whether the thermal shock treatment of graphite oxide in BF_3 atmosphere led into exfoliation of graphite oxide (GO). The morphology of the product, boron-doped graphene (B-G), was studied by SEM. Figure 1 shows the SEM images of boron-doped graphenes that were prepared by exfoliation at 1000 $^\circ\text{C}$ in N_2/H_2 atmosphere (containing 23 ppm of B), 800 $^\circ\text{C}$ in N_2 atmosphere (containing 140 ppm of B), and 1000 $^\circ\text{C}$ in N_2 atmosphere (containing 590 ppm of B). All materials showed a typical exfoliated structure in agreement with previous studies and confirmed successful thermal exfoliation of graphite oxide in BF_3 atmosphere.

Consequently, we study the effect of exfoliation temperature upon level of graphene doping with boron by prompt γ -ray analysis (PGAA). PGAA is an absolute method of determination of trace levels of an element. The absolute content of boron in samples was determined relatively to H_3BO_3 liquid standard with known boron concentration. As shown in Figure 2, it was found that exfoliation of graphite oxide at 1000 $^\circ\text{C}$ in N_2/H_2 atmosphere led to doping of graphene at levels of 23 ppm boron, while with exfoliation in nitrogen atmosphere a larger amount of boron was introduced, 140 ppm boron at 800 $^\circ\text{C}$ and 590 ppm at 1000 $^\circ\text{C}$. This result clearly shows that, with higher exfoliation temperature, higher amount of boron atoms can be doped into the graphene. Also, we observed the significant decrease of boron concentration for GO exfoliated in atmosphere with hydrogen. Therefore, this result has confirmed successful doping of boron into the graphene sheets.

Having determined the level of doping of graphene with boron, we consequently characterize the defect density in boron-doped graphene using Raman spectroscopy. Figure 3 shows the Raman spectra of three boron-doped graphenes. The D band at approximately 1350 cm^{-1} indicates the presence of defects caused by the sp^3 -hybridized carbon atoms, while the pristine sp^2 lattice carbon atoms in the graphene sheet shows a G band at approximately 1560 cm^{-1} . The ratio between D and G band intensities (I_D/I_G) can be used as an indication of the degree of disorder in a carbon structure and the I_D/I_G ratio for 23 ppm B-G, 140 ppm B-G, and 590 ppm B-G are 0.903, 0.632, and 0.732, respectively. The average crystallite sizes (L_a) of the various materials can be estimated based on the D- and G-band intensities by application of the eq 1.²⁰

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

where λ_{laser} is the wavelength of the excitation laser in nanometers and I_G and I_D are the intensities of the Raman G and D bands, respectively.

We calculated the crystallite sizes in boron-doped graphenes. We found that the L_a of 23 ppm B-G is 18.6 nm, 140 ppm B-G is 26.6 nm, and 590 ppm B-G of is 23.0 nm. All three boron-doped graphenes exhibit both D' band and 2D band at approximately 1620 and 2700 cm^{-1} , respectively, which indicate a low degree of disorder in their carbon structure.

Consequently, we determined the elemental compositions of boron-doped graphenes using XPS. XPS is a chemical analysis method and it is useful to determine not only the elemental composition but also bonding arrangement. The wide scan and C 1s high-resolution XPS of boron-doped graphenes were obtained. The wide scan and high-resolution XPS of C 1s

Figure 2. PGAA spectra of boron-doped graphenes containing (A) 23 ppm of B, (B) 140 ppm of B, and (C) 590 ppm of B.

shown in Figure 4 for three graphenes indicate that the oxygen-containing groups were mostly removed and the thermally reduced graphenes were prepared successfully. The C/O ratios obtained from wide scan XPS are 14.2 for 23 ppm B-G, 8.9 for 140 ppm B-G, and 16.1 for 590 ppm B-G. The high-resolution XPS of C 1s signal give insight into the chemical composition of residual oxygen-containing groups, as they show different energy levels, C=C bond of 284.5 eV, C–C bond of 285.6 eV, C–O bond of 286.6 eV, C=O bond of 287.6 eV and O–C=O bond of 289.6 eV. The boron-doped graphenes prepared at 1000 °C in N₂/H₂, 800 °C in N₂, and 1000 °C in N₂ contain 67.0%, 60.8%, and 68.5% of C=C bonds, 14.8%, 18.2%, and 13.9% of C–C bonds, 7.0%, 8.4%, and 6.9% of C–O bonds, 2.4%, 3.0%, and 2.8% C=O bonds, and 8.8%, 9.5%, and 7.9% O–C=O bonds, respectively. Although XPS is not sensitive enough to measure trace amounts of boron, it is highly useful for determination of residual oxygen-containing groups in reduced graphene.

Combustible elemental analysis was also used to determine the elemental composition of the boron-doped graphenes. This method is useful to measure the absolute content of the combustible elements in the bulk material. In combination with

Figure 3. Raman spectra of boron-doped graphenes: doping level (A) 23 ppm, (B) 140 ppm, and (C) 590 ppm of B.

XPS, it provides further insight to the composition and bonding character of graphene sheets. 23 ppm B-G contained 82.48 atom % of C, 10.04 atom % of H, and 7.48 atom % of O; 140 ppm B-G contained 82.28 atom % of C, 10.03 atom % of H, and 7.69 atom % of O; 590 ppm B-G contained 84.83 atom % of C, 9.63 atom % of H, and 5.54 atom % of O. In addition, no nitrogen was found in any sample.

The electrical resistivity of the resulting boron-doped materials was studied by four point measurements of compressed tablets manufactured from the materials. The electrical resistivity of 13 ppm B-G was of $9.5 \times 10^{-5} \Omega \cdot \text{cm}$, of 140 ppm B-G $2.1 \times 10^{-5} \Omega \cdot \text{cm}$, and of 590 ppm B-G $2.3 \times 10^{-4} \Omega \cdot \text{cm}$. As can be observed from these results, higher content of boron in graphenes increases the electrical resistivity which is in accordance with the electron acceptor properties of boron.

The electrocatalytic activity of the prepared boron-doped graphenes toward oxygen reduction reaction (ORR) was investigated. We recorded cyclic voltammograms in both air and N₂ saturated 0.1 M KOH aqueous solution at three boron-doped surfaces. It is possible to observe significant reduction peak ~ -460 mV for air saturated KOH solution; no observable electrochemical reduction took place in N₂-saturated KOH solution. This signifies that the reduction peak ~ -460 mV is indeed originating from the reduction of oxygen. Cyclic voltammograms recording reduction of oxygen on boron-

Figure 4. (Left) Wide-scan X-ray photoelectron spectra of boron-doped graphenes. (Right) C 1s high-resolution X-ray photoelectron spectra of boron-doped graphenes. Doping level (A,B) 23 ppm, (C,D) 140 ppm, and (E,F) 590 ppm of B.

doped graphenes with different doping levels, bare GC in 0.1 M KOH solution are shown in Figure 5. It is clear that the reduction peak shifts to increasingly negative potentials for the graphenes that contain increasing concentrations of boron dopant. Therefore, the more boron atoms doped, the lower the

Figure 5. Oxygen reduction reaction performed 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.

electrocatalytic activity toward oxygen reduction for boron-doped graphene. This is in agreement with the general concept of hole-doping electrochemistry,²¹ but in contrast to some of the previous observations.¹² It should also be noted that the above-mentioned articles on oxygen reduction on boron-doped graphenes did not compare graphenes with different boron content.

We determined the weight-specific capacitance of boron-doped graphenes using cyclic voltammetry capacitive charge–discharge current, and the capacitance can be expressed as

$$C = \frac{I}{\nu} \quad (2)$$

where C is capacitance (F), I is current (A), and ν is the scan rate (mV/s, can be expressed as dE/dt).²²

The capacitances of boron-doped graphenes were investigated by measuring the current at an applied potential of 0.15 V with scan rates of 25, 50, 75, 100, 200, and 400 mV/s. As shown in Figure 6, the weight-specific capacitances of boron-doped graphene prepared at 1000 °C in N_2/H_2 , 800 °C in N_2 , and 1000 °C in N_2 are 11.6, 10.7, and 10.3 F/g, respectively, which

Figure 6. Weight-specific capacitance measured at scan rates of 25, 50, 75, 100, 200, and 400 mV/s of boron-doped graphenes with doping level of (A) 23 ppm, (B) 140 ppm, and (C) 590 ppm of B. (D) Comparison of the weight-specific capacitance on the above-mentioned B-doped graphenes.

indicate a decreasing trend of weight-specific capacitance with an increasing amount of doped boron atoms. Again, this is contrary to previous claims where B-doped graphenes¹¹ (and N-doped graphenes as well²³) demonstrated higher capacitance than nondoped counterparts. It should be noted that there is no theoretical background explanation, while in both cases, hole and electron doping, one should expect enhanced capacitance. The method used in mentioned paper by Han et al.¹¹ is based on hydroboration reaction well-known from organic chemistry. From the mechanism of such reaction, we can suppose formation of sp^3 -hybridized carbon with covalently bonded BH_2 group to the graphene backbone. It is not possible to obtain direct substitution of carbon with boron by the methods presented in Han et al.¹¹

CONCLUSIONS

We report a scalable method for tunable doping of boron atoms into the graphene framework via thermal exfoliation in an atmosphere with boron trifluoride diethyl etherate at various temperatures. The increasing amount of boron in doped graphenes leads to increasingly larger negative potentials needed for oxygen reduction reaction. This is in agreement with theory, where p-doped materials are expected to demonstrate lower electrocatalytic abilities in reduction reactions. In similar fashion, doping with higher concentrations of boron leads to a decrease in capacitance of the resulting materials.

EXPERIMENTAL SECTION

Materials. Sulfuric acid (98%), nitric acid (fuming, 98%), hydrochloric acid (37%), barium nitrate (99.5%), silver nitrate (99.5%), and potassium chlorate (98%) were purchased from PENTA, Czech Republic. Graphite microparticles (<50 μm) were purchased from KOOH-I-NOOR Graphite, Czech Republic. Boron trifluoride diethyl etherate, potassium ferrocyanide, potassium hydroxide, *N,N*-dimethylformamide (DMF), sodium phosphate dibasic, potassium phosphate monobasic,

sodium chloride, and potassium chloride were purchased from Sigma-Aldrich. Nitrogen of 99.9999% purity and hydrogen of 99.9999% purity were obtained from SIAD, Czech Republic. Glassy carbon electrodes of 3 mm diameter were purchased from CH Instruments, TX.

Apparatus. A JEOL 7600F field emission scanning electron microscopy (JEOL, Japan) was used to obtain SEM images. 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× objective lens that was mounted on an Olympus optical microscope were used to measure the Raman spectra of the samples. The calibration is made by using a silicon reference with a peak position at 520 cm^{-1} and a resolution less than 1 cm^{-1} . X-ray photoelectron spectroscopy (XPS) samples were prepared by compacting a uniform layer of the materials on a carbon tape. A monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer are implemented to measure the survey and high-resolution C 1s, O 1s, and B 1s spectra. All voltammetric experiments were carried out by an Autolab PGSTAT101 electrochemical analyzer (Eco Chemie, The Netherlands). Electrochemical experiments were performed in a voltammetric cell (5 mL) at room temperature by using a three-electrode configuration. A glassy carbon electrode was used as working electrode, a platinum electrode as auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. All electrochemical potentials are reported versus the Ag/AgCl electrode.

The combustible elemental analysis was performed with CHN PE 2400 Series II from Perkin-Elmer (USA). In CHN operating mode (the most robust and interference free mode), the instrument employs a classical combustion principle to convert the sample elements to simple gases (CO_2 , H_2O , and N_2). The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases, separation, and detection. A microbalance MX5 (Mettler Toledo) is used for precise weighing of samples (1.5–2.5 mg per single sample).

analysis). The accuracy of CHN determination is better than 0.30% abs. Internal calibration was performed using N-phenylurea.

Prompt γ -ray analysis (PGAA) was used to determine boron content in the graphene samples. These PGAA measurements were performed the PGAA facility which is installed at LWR-15 nuclear reactor.²⁴ The samples were irradiated in thermal neutron beam with flux $\sim 3 \times 10^6$ n cm⁻² s⁻¹. The gamma spectra were taken with the well-shielded 25% HPGe detector.

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 4-probe technique using the Van der Pauw method.²⁵ 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.

Procedures. Graphite Oxide Synthesis. The graphite oxide was prepared by Staudenmaier method²⁶ by adding 27 mL of nitric acid (fuming, 98%) and 87.5 mL of sulfuric acid (98% concentration) to a reaction flask which containing a magnetic stir bar. Then 5 g of graphite was added when the mixture was cooled to 0 °C. In order to get the homogeneous dispersion and avoid agglomeration, the mixture was vigorously stirred. 55 g of potassium chlorate was slowly added to the mixture while the flask was at 0 °C. When the added potassium chlorate was completely dissolved, the reaction flask was loosely capped to allow the gas that evolved during the reaction to escape. The mixture was kept stirring for 72 h at room temperature and when the reaction was finished, the mixture was poured into 3 L of distilled water and decanted. The formed graphite oxide was dispersed in HCl (5%) solutions in order to remove sulfate ions. Then the graphite oxide was repeatedly centrifuged and redispersed into distilled water until a negative reaction on chloride and sulfate ions (with AgNO₃ and Ba(NO₃)₂, respectively) was achieved. Finally, the graphite oxide was dried at 50 °C for 48 h in a vacuum oven before use.

Synthesis of Boron-Doped Graphene. The prepared graphite oxide was used as starting material and boron trifluoride diethyl etherate (BF₃Et₂O) as a boron precursor. The bubbler filled with liquid precursor was used for exfoliation at 20 °C and 1000 mbar. Nitrogen with flow rate of 100 mL/min was used as a carrier gas and was diluted with 1 L/min of nitrogen and a hydrogen/nitrogen mixture (0.5 L/min N₂ and 0.5 L/min H₂). The reactor was kept flushed with nitrogen. The flow of boron precursor was stabilized for 5 min before transferring of sample to the hot zone of the reactor, and then the exfoliation was carried out for 12 min at 800 and 1000 °C.

Cyclic Voltammetry. Cyclic voltammetry experiments were carried out in a 5 mL voltammetric cell at room temperature. Graphene materials were prepared in DMF in a concentration of 1 mg/mL and sonicated for 5 min and 1 μ L of the suspension was dropped onto the GC electrode, which was renewed by polishing with 0.05 μ m alumina particles on a polishing pad and washed with deionized water. The suspension on GC electrode was allowed to dry at room temperature. The weight-specific capacitance (C_w) was devised from the amount of graphene-related material deposited on the GC electrode.

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Notes

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Short communication

3D-graphene for electrocatalysis of oxygen reduction reaction: Increasing number of layers increases the catalytic effect

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ABSTRACT

Oxygen reaction reaction (ORR) is of enormous importance for energy storage and generation devices. Graphene offers catalytic properties towards ORR; however, its performance is often hindered by restacking of the graphene sheets. Here we show that mechanically rigid 3D graphene deposited on nickel template can act as efficient catalyst for ORR. We compare electrocatalytic activity of double, triple and few-layer 3D graphene. We show that the multilayer 3D graphene exhibits higher electrocatalytic activity than the other two samples towards ORR. These findings shall have a dramatic impact on the construction of graphene based fuel cells and batteries.

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1. Introduction

Oxygen reduction reaction (ORR) is of utmost technological importance due its key role in fuel cells and Zn–air batteries [1]. ORR is typically catalyzed by Pt on carbon support. Graphene materials emerged as ideal materials for oxygen reduction reaction [2]. Graphene offers high surface area and electrocatalytic activity towards ORR [3,4]. However, the problem with the use of graphene in real devices is that it tends to restack and thus the surface area is substantially reduced [5,6].

Three dimensional graphene is structurally a well-defined material which offers mechanical robustness in all three directions. It is typically fabricated by CVD deposition of carbon containing gas on 3D nickel foam [7–10] or graphitization of 3D carbon [2,11]. 3D graphene has been used for ORR [2–13], electrochemical sensing of dopamine [8] and glucose [9]. Here we wish to study in depth the performance of 3D graphene for ORR. We will compare double, triple and few-layer 3D graphene performance towards ORR and we will show that with increased number of graphene layers the ORR electrocatalytic activity increases.

2. Experimental section

2.1. Materials

Potassium hydroxide was purchased from Sigma-Aldrich. Hydrogen of 99.9999% purity, nitrogen of 99.9999% purity and methane of 99.9995% purity were obtained from Linde Gas, Czech Republic. Nickel

metal foam (99.99% purity, 95% porosity, 1/8" thickness) was obtained from MTI Corporation, USA. Acetone (99.9%) was obtained from Lach-Ner, Czech Republic.

2.2. Apparatus

The scanning electron microscopy (SEM) images and EDX were obtained by a JEOL 7600F field emission scanning electron microscopy (JEOL, Japan). The Raman spectra were obtained by 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× objective lens were mounted on an Olympus optical. The calibration is made by using a silicon reference with a peak position at 520 cm^{−1} and a resolution less than 1 cm^{−1}. X-ray photoelectron spectroscopy (XPS) samples were prepared by compacting a uniform layer of the materials on a carbon tape. The XPS samples were measured by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer in order to obtain survey and high resolution C1s spectra.

2.3. BET

Equilibrium adsorption isotherms of nitrogen were measured at 77 K using static volumetric adsorption systems (ASAP 2020 analyzer, Micromeritics). Before adsorption measurements the sample was kept at 350 °C for 5 h under vacuum. The adsorption isotherms were fitted in the BET surface area, the micropore volume by the t-plot method and the pore size distribution by the BJH method. BET surface area of Ni foam is 776 cm² per nickel foam cm². Langmuir surface area is 946 cm² per nickel foam cm².

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2.4. Synthesis of 3D graphene

The deposition of graphene was performed in horizontal hot-wall quartz reactor in hydrogen/methane atmosphere. Prior the deposition Ni foam substrate was ultrasonicated in acetone for 10 min and dried at 100 °C. The substrate was placed in the hot wall reactor and reactor was repeatedly flushed with nitrogen. The heating on the deposition temperature (1000 °C with 7 °C·min⁻¹ heating rate) was performed in hydrogen atmosphere (50 mL·min⁻¹) under reduced pressure (0.7 mbar). For the graphene deposition was used hydrogen/methane mixture (20 mL·min⁻¹ H₂ and 20 mL·min⁻¹ CH₄) under 0.6 mbar pressure. The deposition time varieties from 0.5 up to 2 h in order to obtained graphene with different numbers of layers. The cooling on room temperature was performed in hydrogen atmosphere (50 mL·min⁻¹, 0.7 mbar). The sample named as DL-3D-G was deposited for 30 min, sample named as TL-3D-G was deposited for 90 min and sample named as FL-3D-G was deposited for 120 min.

2.5. Cyclic voltammetry

Cyclic voltammetry experiments were carried out in a 5 mL voltammetric cell at room temperature. The 3D graphenes were directly cleaned by DI water and then connected to Autolab PGSTAT 101 to be used as working electrode. A platinum electrode was used as an auxiliary electrode and an Ag/AgCl (saturated) electrode worked as a reference electrode. The measurement at scan rate of 100 mV/s. Onset potential was determined as potential at 10% of the wave current [14].

3. Results and discussion

3D graphenes were successfully prepared by deposition from CH₄/H₂ mixture at 1000 °C and 0.6 mbar by different deposition time. Then the Ni foam substrate and 3D graphenes with different layers were characterized by scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrocatalytic property towards ORR. The graphene is labeled as double-layer (DL-3D-G), triple-layer (TL-3D-G) and few-layer (FL-3D-G). The number of the layers was determined by Raman spectroscopy, as described in the following text.

3.1. Scanning electron microscopy

The morphology of Ni foam and all 3D graphenes was studied by SEM and shown in Fig. 1 at magnification of (A) 10,000× and (B) 130×. The SEM images clearly show graphene deposited via CVD on the Ni foam. The graphene coverage increases with increasing number of layers of graphene deposited. The elemental mapping of Ni foam and 3D graphene is depicted in Fig. 1(C) and (D) and shows an increasing trend of amount of carbon with the increasing layers of graphene.

3.2. Raman spectroscopy

The information of the defect density of graphene was obtained by Raman spectra (Fig. 2). The G band at approximately 1560 cm⁻¹ indicates the presence of sp² lattice carbon atoms in the graphene sheet and a 2D band at approximately 2700 cm⁻¹ is indicative of crystalline graphitic material. In addition, peak located approximately 800 cm⁻¹ indicates the presence of Ni foam. The I_G/I_{2D} of double-layered 3D

Fig. 1. SEM images of Ni foam, DL-3D graphene, TL-3D graphene and FL-3D graphene at magnification of (A) 10,000× and (B) 130× with scale bar of 1 μm and 100 μm, respectively. Elemental mapping of (C) carbon and (D) Ni of (B) SEM images at 130× magnification.

Fig. 2. Raman spectra of (A) Ni foam, (B) DL-3D graphene, (C) TL-3D graphene, and (D) FL-3D graphene.

graphene, triple-layered 3D graphene and few-layered 3D graphene is 1.88, 2.34 and 2.38, respectively. Therefore a decreasing trend of 2D peak was shown according to the graphene with increasing layers. More importantly, Raman spectroscopy can bring insight on the number of the layers of the graphene. From the ratio of peaks G band and 2D band, we can say that DL-3D graphene on average consists of two layers (I_G/I_{2D} ratio of 1.88), TL-3D graphene contains 3 layers (I_G/I_{2D} ratio of 2.34) and FL-3D graphene consists of 3 layers and more (I_G/I_{2D} ratio of 2.38) [15].

3.3. X-ray photoelectron spectroscopy

The elemental composition and bonding information of Ni foam and 3D graphenes were investigated by X-ray photoelectron spectroscopy (XPS). According to the wide scan XPS for DL-3D graphene, TL-3D graphene and FL-3D graphene shown in Fig. 3, the amount of carbon is 85.8 At%, 93.3 at.% and 95.0 at.% respectively. The amount of carbon obtained from XPS agrees with the elemental mapping showing increasing carbon content for increasing layers of graphene.

The detail bonding information of graphene was shown in the high resolution C1s XPS in Fig. 4. The chemical composition of residual oxygen containing groups, as they show different energy levels, C=C bond of 284.5 eV, C–C bond of 285.4 eV, C–O bond of 286.3 eV, C=O bond of 287.4 eV, O–C=O bond of 288.5 eV and pi–pi bond of 290 eV. The DL-3D graphene contains 59.057 at.% of C=C bond, 19.699 at.% of

Fig. 3. Wide scan XPS of (A) Ni foam, (B) DL-3D graphene, (C) TL-3D graphene, and (D) FL-3D graphene.

C–C bond, 9.330 at.% of C–O bond, 3.398 at.% of C=O bond, 6.205 at.% of O–C=O bond and 2.312 at.% of pi–pi bond. TL-layered 3D graphene contains 63.844 at.% of C=C bond, 18.591 at.% of C–C bond, 7.768 at.% of C–O bond, 3.547 at.% of C=O bond, 2.806 at.% of O–C=O bond, and 3.444 at.% of pi–pi bond. FL-layered 3D graphene contains 60.064 at.% of C=C bond, 16.806 at.% of C–C bond, 8.824 at.% of C–O bond, 4.676 at.% of C=O bond, 4.345 at.% of O–C=O bond and 5.285 at.% of pi–pi bond. In addition, the increasing trend of pi–pi bond also indicates the graphene layer interaction which will increase with increasing layers of graphene [16].

3.4. Electrochemistry

The electrocatalytic properties towards oxygen reduction reaction (ORR) of Ni foam, DL-3D graphene, TL-3D graphene, and FL-3D graphene were studied by linear sweep voltammetry (LSV) in 0.1 M KOH solution by using the three electrode configuration and use Ni foam/3D graphene instead of working electrode. The electrocatalytic behaviors were recorded and shown in Fig. 5. According to the results shown in Fig. 5, Ni foam does not have any electrocatalytic properties towards ORR and with increasing layers of graphene, the height of reduction peak also keeps increasing. The onset potential for DL-3D graphene, TL-3D graphene, and FL-3D graphene are –315 mV, –296 mV and –252 mV, respectively, which also show an increasing trend of electrocatalytic properties towards ORR with increasing layers of graphene. One should note that onset potentials ~–260 mV (vs.

Fig. 4. High resolution C1s spectra of (A) DL-3D graphene, (B) TL-3D graphene, and (C) FL-3D graphene.

Ag/AgCl) were previously reported for ORR on glassy carbon macroscopic electrode [17]. It should be highlighted that some catalytic systems, i.e. MnO_2 shows much higher shift to anodic direction for ORR than ~ 260 mV [17] but this effect was not observed here. While potential shift in general can also originate from varying electrode geometry [18,19]; however, in our case the electrode is well defined by Ni foam skeleton and the differences in reduction potentials are related only to the number of graphene layers.

Fig. 5. Cyclic voltammetry of Ni foam, DL-3D graphene (DL-3D-G), TL-3D graphene (TL-3D-G), and FL-3D graphene (FL-3D-G).

4. Conclusions

We have fabricated 3D graphene with varied numbers of graphene layers. We show that with increasing number of graphene layers, the catalytic activity of 3D graphene towards oxygen reduction reaction increases. This finding shall have a profound influence on application of 3D graphene in electrochemical energy devices.

Conflict of interest

Authors declare no conflict of interest.

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Mo_xW_{1-x}S₂ Solid Solutions as 3D Electrodes for Hydrogen Evolution Reaction

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Layered transition metal dichalcogenides (TMDs) recently attracted the renewed attention of researchers. The generalized formula of TMDs is MX₂ where M consists of a transition metal (i.e., Mo and W) and X of a chalcogen (i.e., S, Se, and Te), many of them forming layered (graphite-like) anisotropic structures. Similar to graphite, individual layers can be extracted by various methods, including mechanical (Scotch-tape) or chemical approaches. Unlike graphene, there is wide variety of layered TMDs and one can choose the band gap MX₂ depending on chemical composition. Different TMDs show different band gaps and, thus, fluorescence properties.^[1] TMDs with different compositions also exhibit different electrocatalytic effects,^[2] which is paramount to the energy-related applications of TMDs.^[3]

Theoreticians suggested that the band gap of TMDs can be tuned by creating their solid solutions either by having metal dichalcogenides with mixed metal elements (i.e., Mo_xW_{1-x}S₂ (0 ≤ x ≤ 1)^[4] or mixed chalcogenides (i.e., MoS_ySe_{2-y} (0 ≤ y ≤ 2)).^[5,6] Indeed, it has been proven experimentally that the band gap^[7,8] and, consequently, optical properties^[9] can be tuned by creating MoS_ySe_{2-y} solid solutions as well as by M_{1-x}W_xS₂ solid solutions.^[10] However, despite extensive literature on the utility of TMDs,^[11] especially of MoS₂,^[12–16] MoSe₂,^[17,18] WS₂,^[19,20] and WSe₂^[16] for efficient catalysts for hydrogen evolution reaction (HER), no research has been done on investigating the effect of layered TMD solid solutions on electrocatalytic performance. The Mo_xW_{1-x}S₂ nanosheet triangles were successfully synthesized previously by chemical vapor deposition (CVD) method but their utility for HER was not investigated.^[4] In addition, most of the published systems deal only with 2D electrodes whereas efficient hydrogen evolution requires large surface areas and preferably 3D electrodes.

Herein, we investigate the electrocatalytic performance of Mo_xW_{1-x}S₂ (0 ≤ x ≤ 1) systems grown from 3D freestanding interconnected glassy carbon foam to form a platform with different ratios of Mo and W in the Mo_xW_{1-x}S₂ solid solution (Scheme 1). The morphology, elemental composition, bonding

information, and electrocatalytic properties toward HER of 3D mixed MoS₂ and WS₂ samples are studied.

The solid solutions of Mo_xW_{1-x}S₂ were prepared by deposition of ammonium tetrathiomolybdate, ammonium tetrathiotungstenate, and their mixtures onto the 3D carbon foam followed by thermal treatment in nitrogen atmosphere. Use of tetrathiotungstenate and tetrathiomolybdate mixtures for synthesis of Mo_xW_(1-x)S₂ solid solution by high temperature decomposition was reported by several authors.^[21,22] The as-prepared 3D Mo_xW_{1-x}S₂ samples were then characterized by scanning electron microscopy (SEM) for morphology, energy-dispersive X-ray spectroscopy (EDS) for elemental mapping, electro thermal vaporization inductively coupled plasma-optical emission spectroscopy (ETV-ICP OES) for ratio of metals in the solid solution, X-ray photoelectron spectroscopy (XPS) for elemental composition and bonding information, and linear sweep voltammetry (LSV) for electrocatalytic properties toward hydrogen evolution reaction.

ETV-ICP OES was used to determine the exact composition of solid solutions Mo_xW_{1-x}S₂. It was found that for a combination of Mo/W precursors 3:1, the final composition of solid solution on 3D support was Mo_{0.51}W_{0.49}S₂, the Mo/W precursor ratio of 1:1 led to Mo_{0.21}W_{0.79}S₂ composition, and the precursor ratio Mo/W of 1:3 led to Mo_{0.14}W_{0.86}S₂. When Mo/W precursors were present in a 1:0 or 0:1 ratio, the resulting materials were pure MoS₂- and WS₂-coated 3D glassy carbon materials, respectively. The thermodynamic calculations were performed in order to proof the stability of MoS₂ and WS₂ toward carbide formation in order to confirm the suitability of carbon support for synthesis of 3D MoS₂ and WS₂ structures. The phase diagram of MoS₂ and WS₂ thermal stability and carbide formation are shown in Figure S1 (Supporting Information). The MoS₂ is stable up to about 1570 °C while WS₂ is stable up to about 1450 °C and only over these temperatures carbides start to form. These results show high potential of carbon based supports for high temperature synthesis of MoS₂ and WS₂ structures due to its high thermal stability and low tendency toward carbide formation. In addition we performed X-ray diffraction (XRD) on bulk amount of material (MoS₂, WS₂, and Mo_xW_{1-x}S₂) that were prepared under similar experimental conditions by thermal decomposition of (NH₄)₂MoS₄, (NH₄)₂WS₄, and (NH₄)₂Mo_xW_{1-x}S₄ precursors. The XRD showed successful synthesis of single phase compounds. The results are shown in Figure S2 (Supporting Information).

The morphologies of prepared 3D Mo_xW_{1-x}S₂ alloys were investigated by SEM and elemental maps were obtained by SEM/EDX. Figure 1 shows the structure of carbon foam with a freestanding 3D interconnected network as recorded by SEM. The coated Mo_xW_{1-x}S₂ is visible as the “contrast coating” on

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Scheme 1. Transition metal chalcogenide solid solution $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ coated 3D glassy carbon foam. Left: Photograph of actual 3D glassy carbon foam (length 2.33 cm). Right: Schematic diagram of 3D glassy carbon coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ solid solution.

the carbon foam. The higher contrast of Mo/W compared to the underlying carbon originates from their larger atomic numbers and larger number of scattered electrons. The elemental map shown in Figure S3 (Supporting Information) further confirmed the compositions of the coatings. Thickness of the layers is $\approx 1\text{--}2\ \mu\text{m}$ calculated on the base of carbon support surface area and total loading of Mo and W in the range of 1–2 wt. %.

The composition information and bonding information was obtained from XPS via wide scan and high-resolution spectroscopy for Mo3d and W4f. The wide scans for all samples are shown in Figure 2 and indicate that the substrate 3D carbon foam contains C and O, and that no Mo and W is involved. XPS analysis demonstrates that with an increasing amount of W precursor there is a larger amount of W in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy.

In addition, the detail bonding information was studied by high-resolution XPS for Mo3d and W4f in Figure 3. For high-resolution Mo3d spectra, the peaks at 229.3 and 232.4 eV indicate $\text{Mo}^{4+}3d_{5/2}$ and $\text{Mo}^{4+}3d_{3/2}$, respectively, and the peaks at 233.1 and 236.1 eV are caused by $\text{Mo}^{6+}3d_{5/2}$ and $\text{Mo}^{6+}3d_{3/2}$, respectively.^[23,24] For the W4f spectra, the peaks shown at 33 and 35.1 eV indicate $\text{W}^{4+}4f_{7/2}$ and $\text{W}^{4+}4f_{5/2}$, respectively, and the peaks around 36.2 and 38.4 eV indicate $\text{W}^{6+}4f_{7/2}$ and $\text{W}^{6+}4f_{5/2}$, respectively.^[25]

The amount of Mo^{4+} and Mo^{6+} in the samples containing MoS_2 and the amount of W^{4+} and W^{6+} in the samples containing WS_2 are summarized in Table 1. There is a broadly increasing trend in the amount of W^{6+} along with the increasing ratio of WS_2 content. The high-resolution XPS of S2p is shown in Figure S4 (Supporting Information).

The electrocatalytic properties toward HER of 3D electrodes coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy materials were studied by LSV.

Figure 4 shows linear sweep voltammograms that show a monotonic decrease of overpotential with an increasing amount of W (decreasing x) in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy. The potential for all samples at $-1.5\ \text{mA}$ were -402.4 , -380.4 , -363.3 , -346.2 , -326.7 , and $-238.8\ \text{mV}$ for bare 3D carbon foam, pure MoS_2 , $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$, $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$, $\text{Mo}_{0.14}\text{W}_{0.86}\text{S}_2$, and WS_2 coated 3D carbon foam, respectively. It is obvious that the electrocatalytic activity of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloys can be tuned by varying the ratio of transition metals in the compounds.

We observed a monotonic lowering of overpotential of HER with an increased proportion of W in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloys. HER is two step reaction which involves adsorption and reduction of H^+ (aq) to $\text{H}^{\cdot}$ (ads) on the surface. The second step is recombination with another hydrogen and desorption as H_2 (g). The second step can proceed via recombination with another $\text{H}^{\cdot}$ (ads) at the surface of the material (Tafel step) or H^+ (aq) which is reduced by electron but not adsorbed, resulting to H_2 (g) evolution. The key factor for kinetics of this reaction and apparent rate constant is strength of adsorption of the $\text{H}^{\cdot}$ on the metal surface. Too strong adsorption would make the second step rate limiting while too weak interaction of $\text{H}^{\cdot}$ with surface would make first step rate limiting. Since MoS_2 and WS_2 exhibit distinct ΔG_{H} for $\text{H}^{\cdot}$ adsorption,^[26] the monotonic shift for their solid solution with different compositions is somehow not surprising. The MoS_2 and WS_2 are very stable materials in acidic environment which does not have strong oxidation ability.

In conclusion, we have successfully synthesized 3D electrodes coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloys with different Mo/W ratios. The morphology, elemental composition, bonding information, and electrocatalytic properties toward HER were studied.

Figure 1. SEM images at different magnifications (scale bar at left of 100 μm and right of 10 μm) of A,B) pure 3D carbon foam, C,D) pure MoS_2 -coated 3D carbon foam, E,F) $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$ -coated 3D carbon foam, G,H) $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ -coated 3D carbon foam, I,J) $\text{Mo}_{0.14}\text{W}_{0.86}\text{S}_2$ -coated 3D carbon foam, and K,L) pure WS_2 -coated 3D carbon foam.

Experimental Section

Materials: Reticulated vitreous carbon foam used as a support for TMDs was obtained from ERG Aerospace Corporation (USA).

Figure 2. Wide scan XPS for A) carbon foam, B) pure MoS_2 -coated carbon foam, C) $\text{Mo}_{0.51}\text{W}_{0.49}\text{S}_2$ -coated carbon foam, D) $\text{Mo}_{0.21}\text{W}_{0.79}\text{S}_2$ -coated carbon foam, E) $\text{Mo}_{0.14}\text{W}_{0.86}\text{S}_2$ -coated carbon foam, and F) pure WS_2 -coated carbon foam.

Ammonium heptamolybdate tetrahydrate and ammonium tungstenate, *N,N*-dimethylformamide (DMF) and ammonia (25%) were obtained from Penta, Czech Republic. Hydrogen sulfide (99.5%) and nitrogen (99.9999%) were obtained from SIAD, Czech Republic.

Apparatus: A JEOL 7600F field emission scanning electron microscope (JEOL, Japan) was used to obtain SEM images for 3D TMDs. EDX was obtained via Oxford instruments x-stream2 and mics+. XPS samples were prepared by compacting a piece of 3D TMD onto a carbon tape. The XPS samples were measured by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer in order to obtain survey and high-resolution W4f, Mo3d, and S2p spectra. The Mo/W ratio was measured by Electro Thermal Vaporization Inductively Coupled Plasma Optical Emission Spectrometry (ETV-ICP OES) using Spectro ARCOS spectrometer (SPECTRO Analytical Instruments, Germany). One milligram of the sample was powdered and homogenized with spectroscopically pure graphite in weight ratio 1:10 and directly vaporized in ETV system (2400 $^{\circ}\text{C}$, Ar/ CCl_2CF_2 mixture) connected to ICP-OES.

All voltammetry experiments were performed using an Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie, The Netherlands). Electrochemical experiments were performed in a voltammetric cell (5 mL) at room temperature by using a three-electrode configuration. The 3D samples were connected by a copper tape to the Autolab and were used as working electrodes directly, a platinum electrode as an auxiliary electrode, and an Ag/AgCl electrode as a reference electrode.

The XRD was performed using PANalytical X'Pert PRO diffractometer in Bragg-Brentano parafocusing geometry. A $\text{CuK}\alpha$ radiation was used. Diffraction pattern were collected between 5° and 80° of 2θ . The obtained data were evaluated using PANalytical HighScore software.

Synthesis Methods: Ammonium tetrathiomolybdate was prepared by reaction of ammonium heptamolybdate with hydrogen sulfide. 10 g of ammonium heptamolybdate was dissolved in 30 mL of

Figure 3. High-resolution XPS for Mo3d (higher row) and W4f (lower row) for A) pure MoS₂-coated carbon foam, B,E) Mo_{0.51}W_{0.49}S₂-coated carbon foam, C,F) Mo_{0.21}W_{0.79}S₂-coated carbon foam, D,G) Mo_{0.14}W_{0.86}S₂-coated carbon foam, and H) pure WS₂-coated carbon foam.

Table 1. Bonding information for as-prepared 3D TMDs.

Bonding information	MoS ₂ [%]	Mo _{0.51} W _{0.49} S ₂ [%]	Mo _{0.21} W _{0.79} S ₂ [%]	Mo _{0.14} W _{0.86} S ₂ [%]	WS ₂ [%]
Mo ⁴⁺	57.3	80.4	62.6	61.5	0
Mo ⁶⁺	42.7	19.6	37.4	38.5	0
W ⁴⁺	0	65.1	63.7	64	44
W ⁶⁺	0	34.9	36.3	36	56

water and 100 mL of ammonia (25 wt%). Hydrogen sulfide was passed through the solution for 4 h (about 1–2 bubbles s^{−1}). Formed ammonium tetrathiomolybdate was separated by suction filtration and dried in a vacuum oven at room temperature. Ammonium tetrathiotungstate was prepared in a similar way. Hydrogen sulfide was passed through 100 mL of saturated solution of ammonium tungstate in diluted ammonia (1:1 by vol.) for 10 h. Formed ammonium

tetrathiotungstate was removed by suction filtration and dried in a vacuum oven at room temperature.

The coatings of carbon foam consisted of solutions of ammonium tetrathiotungstate, ammonium tetrathiomolybdate, and their mixtures in DMF. The carbon foam was placed in a solution containing 5 wt% of Mo, W, and their mixtures in adequate Mo/W molar ratio corresponding to the composition of Mo_{0.25}W_{0.75}S₂, Mo_{0.50}W_{0.50}S₂, and Mo_{0.75}W_{0.25}S₂ and ultrasonicated for 10 min. Subsequently, the carbon foam was dried in a vacuum oven at 50 °C for 24 h. The precursor-coated carbon foam was annealed in a nitrogen atmosphere at 700 °C for 2 h. The heating and cooling rates were 20 °C min^{−1} and the flow rate of nitrogen was 500 mL min^{−1}. The TMD coverage of 3D glassy carbon was 2% wt.

Calculations: Equilibrium calculations were carried out using FactSage 6.4 software. We have utilized the equilibrium module with input composition corresponding to the formula (NH₄)₂MoS₄, (NH₄)₂WS₄, and 50-fold excess of carbon to imitate conditions used in experimental part of this work. The equilibrium module uses Gibbs energy minimization to identify the most probable reaction. The calculations were done for constant composition and 1 bar nitrogen pressure, while changing the temperature from 800 to 2000 °C with step of 10 °C.

Figure 4. LSV of glassy carbon foam and prepared pure MoS₂, Mo_{0.51}W_{0.49}S₂, Mo_{0.21}W_{0.79}S₂, Mo_{0.14}W_{0.86}S₂, and pure WS₂ coated carbon foam in 0.5 M H₂SO₄ at a scan rate of 2 mV s^{−1}.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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