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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF rGO-SnO₂-Fe₂O₃-TiO₂ AND rGO-Fe₂O₃-SnO₂-TiO₂ TERNARY NANO-COMPOSITE AS ELECTRODES IN SODIUM-ION BATTERIES

by

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Dissertation in fulfilment of the requirement for the degree
MASTER IN TECHNOLOGY

in

CHEMISTRY

in the

FACULTY OF SCIENCE

of the

UNIVERSITY OF JOHANNESBURG

Supervisor : PROF. P. G. NDUNGU
Co-supervisor : DR. N. W. MAXAKATO
DECLARATION

I hereby declare that this dissertation, which I herewith submit for the research qualification

MASTER IN TECHNOLOGY IN CHEMISTRY

to the University of Johannesburg, Department of Applied Chemistry, is, apart from the recognised assistance of my supervisors, my own work and has not previously been submitted by me to another institution to obtain a research diploma or degree.

__________________________________ on this ____ day of _______________
(Candidate)

__________________________________ on this ____ day of _______________
(Supervisor)
I dedicate this work to Jehovah God, without WHOM it would not be.
ACKNOWLEDGEMENTS

My deepest gratitude goes to but is not limited to the following:

❖ **My supervisors**
  ❖ Prof. P. G. Ndungu
  ❖ Dr. N. W. Maxakato

❖ **Funding**
  ❖ National Research Foundation (NRF)
  ❖ University of Johannesburg’s Faculty of Science
  ❖ Eskom

❖ **Support, assistance, guidance...**
  ❖ Family, friends, University of Johannesburg and fellow researchers
PRESENTATIONS AND PUBLICATIONS

A manuscript titled “Graphene ternary oxide system for sodium energy storage system” has been completed and ready for submission to a peer-reviewed journal.
ABSTRACT

Rechargeable batteries are an integral part of modern life and technology development as energy sources and energy storage systems. Currently, lithium batteries’ (both rechargeable and non-rechargeable) features and consequently its performance surpasses those of its counterparts by far. For that reason, lithium batteries are leading the battery market. However, their rapid growth and demand is projected to exceed the limited recoverable resources of lithium. Therefore, sourcing equivalent battery types and/or technologies is crucial.

Sodium-ion rechargeable batteries are the most credible alternative mainly due to the abundance, even distribution and feasible recovery of this resource. In addition, sodium and lithium have similar physical and chemical properties and thus similar energy storing / supplying mechanisms. However, the larger and heavier sodium-ion has inherently slower diffusion rates and thus experiences a few challenges with the lithium cell configuration such as compatible active electrode material. Therefore, the development of sodium-ion electrode material is the key to the success and commercialization of sodium-ion batteries.

The SnO$_2$ and Fe$_2$O$_3$ metal oxides have been reported to exhibit high capacities when used as anode material in sodium-ion batteries although at short life cycles due to the extreme volume expansion they experience during cycling. On the other hand, graphene oxide and TiO$_2$ have been reported to exhibit moderate reversible capacity but for long life cycles due to their insignificant volume change during cycling. Hybrids of the four materials in different combinations have been reported to exhibit high reversible capacities and long-life cycles. For that reason, in this study the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites were synthesized, characterized and evaluated as anode material in sodium-ion battery half cells.

Graphene oxide was synthesized by chemical exfoliation of graphite and coated with layers of SnO$_2$, Fe$_2$O$_3$, and TiO$_2$ metal oxides in different combinations by means of the solvothermal and/or hydrothermal and/or co-precipitation methods. When the synthesized nanomaterial were analyzed with the FTIR, Raman spectroscopy, SEM, TEM, TGA, BET, UV-Vis spectroscopy, and XRD analytical techniques; their physical, chemical and optical properties were positively matched to their pure compounds.

The electrochemical performance of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites was evaluated using sodium-ion battery half cells. The half cells consisted of a counter and reference electrode made from sodium metal, 1 M NaClO$_4$/PC electrolyte solution in addition to the ternary nanocomposites as the active material in the working electrodes. The cells were assembled in a nitrogen filled glove box with oxygen and moisture concentration of ≤0.5 ppm and 62 ppm — 69 ppm respectively. The ternary nanocomposites exhibited uncharacteristically low
capacity, that faded drastically during cycling in addition to short life cycles (<20 cycles) when compared to the reported electrochemical performance of individual components or their hybrids. The investigation of the physical properties of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposites after electrochemical characterization with the XRD and TEM analytical techniques, revealed insignificant volume change. Whilst the Raman spectroscopy technique demonstrated insignificant structural changes. Thus, attesting to the efficiency of graphene and TiO$_2$ in controlling volume change of SnO$_2$ and Fe$_2$O$_3$ metal oxides. The insignificant volume and structural changes also meant that the poor electrochemical performance of the sodium-ion battery half cells could not be attributed to the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposites. The uncharacteristically low and fading capacity that resulted in the short life cycles for the half-cells was rather attributed to the numerous side reactions of the sodium metal electrode with H$_2$O and O$_2$. Due to the high oxygen and moisture concentration (>0.1 ppm) during cell assembly and electrolyte solution preparation. Unfortunately, due to the reactive nature of the sodium metal with moisture, the full capability of the ternary nanocomposites was not determined.
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<tr>
<td>%</td>
<td>Percent</td>
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<tr>
<td>-(C₂H₂F₂)n⁻</td>
<td>Polyvinylidene fluoride</td>
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<td>Aluminum chloride</td>
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<td>aq.</td>
<td>Aqueous</td>
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<td>Analytical reagent</td>
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<tr>
<td>DMAC</td>
<td>N, N-dimethylacetamide</td>
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mAhg⁻¹
mg
min.
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MoS₃
MoSe₂
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MWh
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Na₂Sₓ
Na₂Ti₃O₇
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NaCoO₂
NaFeSO₄F

Kilowatt
Kilowatt hour
Lithium
Lithium-ion
Lithium-ion battery
Lithium cobalt oxide
Lithium iron phosphate
Lithium iron fluorosulphate
Lithium nickel manganate
Lithium hexafluorophosphate
Molar
Square meter per gram
Milliampere hour per gram
Milligram
Minimum
Milliliter
Metal Oxide
Molybdenum (VI) ion
Molybdenum trisulfide
Molybdenum diselenide
Megawatt
Megawatt hour
Not Applicable
Sodium
Bis(trifluoromethane)sulfonimide sodium
Sodium ion
Sodium lithium nickel manganese oxide
Sodium vanadium fluorophosphate
Sodium iron fluorophosphate
Sodium polysulfide
Sodium titanium oxide
Sodium vanadium three-fluorophosphate
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</tr>
<tr>
<td>P⁵⁺</td>
<td>Phosphorus (V) ion</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Lead (IV) oxide</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>S</td>
<td>Sulfur</td>
</tr>
<tr>
<td>S²⁻</td>
<td>Sulfide ion</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>Silicon ion</td>
</tr>
<tr>
<td>SIB</td>
<td>Sodium ion battery</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin</td>
</tr>
<tr>
<td>SnCl₂·2H₂O</td>
<td>Stannous chloride dihydrate</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Tin dioxide</td>
</tr>
<tr>
<td>TaS₂</td>
<td>Tantalum(IV) sulfdide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TiS₂</td>
<td>Titanium disulphide</td>
</tr>
<tr>
<td>Triglyme</td>
<td>Triethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet visible spectroscopy</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume per volume</td>
</tr>
<tr>
<td>VS₂</td>
<td>Vanadium (IV) sulphide</td>
</tr>
<tr>
<td>Whdm⁻³</td>
<td>Watt-hour per cubic decimeter</td>
</tr>
<tr>
<td>Whkg⁻¹</td>
<td>Watt-hour per kilogram</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>Wm$^{-1}$K$^{-1}$</td>
<td>Watts per meter-kelvin</td>
</tr>
<tr>
<td>wt.</td>
<td>Weight</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray powder diffraction</td>
</tr>
<tr>
<td>ZEBRA</td>
<td>Zero-Emission Batteries Research Activity cell</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Beta</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>Maghemite</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Theta</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>Maximum wavelength</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>Micrometer</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

1 Overview

This chapter outlines the power of lithium-ion batteries on the world-wide rechargeable battery market in addition to exploring the need to replace or provide alternatives to lithium-ion batteries due to diminishing lithium resources. This chapter also discusses sodium as the possible replacement for lithium along with a brief overview of research thus far on the challenges and breakthroughs surrounding sodium-ion batteries.

1.1 Background and Motivation

Lithium-ion batteries have dominated the market of rechargeable batteries since the first commercial one was made available in 1991 by Sony Corporation [1, 2]. There is great potential for increased and continual growth in the lithium battery market as the world moves from the use of fossil fuels to more environmentally friendly alternatives of electric, hybrid, and plug-in vehicles [3]. This is due to their superior performance when compared to other rechargeable batteries in their class. Some of the key advantages, with lithium-ion batteries, include their modest size and weight [4, 5], high energy density [5-9], good performance [10], low self-discharge [11] and long cycle life (>1000 cycles at 80% depth of discharge) [12, 13]. Lithium-ion batteries, as a result of their excellent attributes, are rapidly replacing the classic lead-acid batteries for use in golf carts and utility vehicles. They are also the leading power storage system for portable devices, power tools, electric vehicles and hybrid vehicles. They are however not without flaws, the most critical one being the accessibility of its main component: lithium. The 20 ppm lithium reserve on earth [3] is not enough to accommodate the growing consumer and industrial demands for the group 1 metal. As a result, researchers are looking into sodium, as a possible replacement for use in batteries.

Sodium and lithium are both alkali metals, that is, they have similar ns¹ valence electron configuration as a result they have similar physical and chemical properties. Sodium is also a 1000 times more abundant than lithium [3] and unlike lithium, its natural resources are evenly distributed world-wide [14], making it an economical alternative. When used in batteries, both the sodium-ion batteries (SIBs) and the lithium-ion batteries (LIBs) have the same main components, (i.e. cathode-anode electrode pair, organic electrolyte, and porous separator) and the same electrochemical process (i.e. intercalation/de-intercalation) to produce electric current [3].

However, due to the fact that the sodium ion radius (Na⁺) is larger [15, 16] and the ion is heavier than that of the lithium cation (Li⁺) [3], the insertion/extraction mechanism in SIBs experiences challenges. This results in batteries that have lower voltage, larger volume change during charge/discharge, poor
cycle and discharge performance among other things, especially when equivalent LIBs electrode materials are used.

In the search for suitable anode and cathode materials for SIBs, transition-metal oxides have come into the spotlight as they have high theoretical capacity (500 — 1000 mAhg\(^{-1}\)), are naturally abundant and highly corrosion resistant [17, 18]. Previous research has been done on individual, binary or tertiary combinations of metal oxides, and in some cases mixed with an electronically conductive agent, such as a carbon material to adjust for their poor electron conductivity [3, 17]. Tang et al. [3] reported that mixtures of layered oxide materials (binary, tertiary or more) have shown excellent performance, with certain combinations producing SIBs cathodes with suitable voltages and excellent capacity. Cai et al. [19] also reported on mixed metal oxides for LIBs anode and attributed the enhanced performance to synergistic effects between the various metal oxides used. Other progressive research on the development of SIBs anode material has been done on sodium alloying metals combined with carbon [3].

However, more research is required to combat the large volume expansion, inferior rate capability and electrode cracking that leads to poor cycling stability and low power densities during the charge/discharge process [17, 18, 20]. In this regard, the synthesis and characterization of nanocomposites that can be used in SIBs. The alternative materials may overcome problems such as volume expansion, charge/discharge capability and conductivity of the sodium-ion battery. The alternative material that will be investigated, exploits the synergistic effects between the excellent conductivity of graphene materials, lack of memory effect and the high capacity of SnO\(_2\), the high theoretical capacity of Fe\(_2\)O\(_3\) and finally the insignificant volume change of TiO\(_2\).

Graphene oxide, SnO\(_2\), γ-Fe\(_2\)O\(_3\) and TiO\(_2\) are being considered in this research as part of the active material in the negative electrode of an SIB due to the abundance of their raw materials [21, 22], low costs [15, 23, 24] and relatively environmentally benign nature [15].

In addition, graphene oxide (GO) has a high specific surface area [16, 23, 25-28] experimentally demonstrated to range between 270 —1550 m\(^2\)g\(^{-1}\) [28], as a result can provide more active sites during the de/intercalation process when used as an electrode material. GO also has superior thermal conductivity [25, 26, 29] (5000Wm\(^{-1}\)K\(^{-1}\)) that is a thousand times larger than that of copper [27], good thermal stability [27], thus broadening the operating temperature range of the battery and strong mechanical strength [25] with a Young’s modulus of 1.0TPa and a stiffness of 130GPa [27]. Due to these attributes, graphene oxide will be used as the base on which the SnO\(_2\), γ-Fe\(_2\)O\(_3\) and TiO\(_2\) metal oxides are coated on when fabricating the negative electrode of an SIB in this research.

Unfortunately, GO also has a low theoretical (149 mAhg\(^{-1}\)) and low experimental reversible capacity (~100 mAhg\(^{-1}\)) but for long cycle life (>1000 cycles) when used as an anode material in sodium-ion batteries [30]. In literature, the low capacity of graphene oxide has been circumvented by
incorporating sodium alloying metals and/or transition metals such as SnO$_2$ and Fe$_2$O$_3$ into the graphitic lattice of graphene oxide due to their high theoretical capacity, 1378 mAhg$^{-1}$ [31] and Fe$_2$O$_3$ 1007 mAhg$^{-1}$ [23] respectively. The resultant hybrids have been experimentally demonstrated to deliver higher capacity than that of the pristine graphene oxide, e.g. rGO-SnO$_2$ [32], Fe$_2$O$_3$@graphene nanosheets [23] or individual metal oxides (SnO$_2$-TiO$_2$ [33], Fe$_2$O$_3$-TiO$_2$ [34] and SnO$_2$-Fe$_2$O$_3$ [35]). The hybrids with graphene oxide or TiO$_2$ also exhibited lesser volume expansion after cycling. The large volume expansion experienced by sodium-alloying metals and transition metals during charge-discharge cycles causes cracking, pulverization, loss of electrical contact, and unstable solid electrolyte interphase which inevitably leads to fading of capacity and thus short cycle life [3, 36, 37]. This excessive volume expansion has been successfully controlled by integration, coating or confinement of sodium-alloying metals and/or transition metals or their oxides with materials that do not undergo volume change such as GO or with insignificant volume change during cycling such as TiO$_2$. For example, the graphene-SnO$_2$-TiO$_2$ nanocomposite delivered high reversible capacity (499.3 mAhg$^{-1}$ at 0.2C) for 50 cycles when tested in a LIB. The TEM and SEM images of the graphene-SnO$_2$-TiO$_2$ showed well dispersed nanoparticles on expanded sheets. Consequently, the team attributed the good performance on the reduction of agglomeration of SnO$_2$ due to the presence of TiO$_2$ [38].

Therefore, the graphene sheets in this research will form the base on which the SnO$_2$ and Fe$_2$O$_3$ metals oxides will be coated on, then confined with a layer of TiO$_2$, i.e. rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites. Thus the graphene and TiO$_2$ will confine the SnO$_2$ and Fe$_2$O$_3$ metal oxides during cycling as a result may overcome problems such as large volume expansion, inferior rate capability and electrode cracking of the sodium-ion battery.

### 1.2 Problem statement

Lower voltage, large volume expansion and inferior rate capability are the main challenges hindering the replacement of lithium with sodium in the rechargeable battery market. Especially when equivalent LIBs electrode materials are used regardless the fact that both types of batteries have the same operating technique and components. For example, lithium cobalt oxide (LiCoO$_2$), the first commercial LIBs positive electrode material introduced by Sony in 1991 is still widely used, due to its high energy density. When used in SIBs however, sodium cobalt oxide (NaCoO$_2$) exhibits both lower voltage and inferior rate capability [3]. Mainly because the cation radius of sodium is larger (1.02 Å vs. 0.76 Å) and weighs more (23.00 u vs. 6.94 u) than the lithium cation, thus diffuses slower with equivalent LIBs electrode materials.

Therefore, the key to enhancing the critical features of SIBs is finding anode and cathode material/s that work well with the size & weight of Na$^+$ ions during insertion/extraction process of storing/supplying energy.
Research thus far, has discovered that transition metals, sodium alloying metals and carbon as anode and/or cathode materials when used individually or in combinations have enhanced the performance of SIBs [3, 19]. For example Wang et al. [32], used a combination of a sodium alloying metal oxide and carbon. The team anchored ~5 nm SnO$_2$ nanoparticles on reduced graphene oxide to yield an “anode that delivered a reversible Na-storage capacity of 330 mAh$^{-1}$ with an outstanding capacity retention of 81.3% over 150 cycles”. Whereas, Zhao et al. [39] combined two transition metals, Nb-doped anatase TiO$_2$ particles, and produced an anode material with “high capacity, excellent cycling performance, and excellent rate capability”. These few examples substantiate the idea that improved performance of SIBs can be achieved by combining transition metals, sodium alloying metals and carbon. In this regard, this research aims at developing an alternative SIBs anode material by using a novel combination of metal oxides of Sn, Fe, and Ti with carbon nanomaterial (graphene oxide or reduced graphene oxide).

1.3 Hypothesis

The development of nanocomposites from GO, SnO$_2$, γ-Fe$_2$O$_3$ and TiO$_2$ will provide a suitable anode material that can be used in SIBs.

1.4 Aims and Objectives

This section outlines the aims of this research as well as the specific objectives used to attain them.

1.4.1 Main aim

This research aims at synthesizing a nanocomposite containing graphene oxide, SnO$_2$, γ-Fe$_2$O$_3$ and TiO$_2$. Graphene oxide (GO) will be synthesized and then modified by layering TiO$_2$, SnO$_2$, γ-Fe$_2$O$_3$ in a few different potential combinations. The synthesized graphene-based nanocomposites as well as the intermediary materials will be fully characterized, and the ternary system will be evaluated as anode material for sodium ion batteries.

1.4.2 Specific objectives

The aims will be achieved through the following specific objectives:

- Synthesis and characterization of rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites.
Investigation of the physical-chemical properties of the various nanomaterials using several techniques such as, but not limited to; FTIR, Raman spectroscopy, SEM, TEM, TGA, BET, UV-Vis spectroscopy and XRD.

Investigate the electrochemical properties of the various nanomaterials using cyclic voltammetry, charge-discharge cycle and other suitable techniques.

Single cell battery assembly and testing of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites and the intermediary nanocomposites as anode material for metal ion batteries.

1.5 Dissertation setup

This dissertation is made up of six chapters, the summary of the content of each chapter is outlined below.

Chapter 1: Introduction

This chapter discusses the background of the research topic, the problem statement in addition to the aim and objectives of the investigation.

Chapter 2: Literature review

This chapter covers literature review on lithium rechargeable batteries — how they work, their advantages and disadvantages, benefits and weaknesses of modification thus far. It also goes into detail on the motives, pros, cons, etc. on the research for their projected replacement.

Chapter 3: Materials and methods

In this chapter, the research methodology, characterization techniques in addition to the application methods are discussed.

Chapter 4: Results and discussion

This chapter gives a detailed discussion of the results obtained from characterization of the nanomaterials and nanocomposites synthesized.

Chapter 5: Application

This chapter contains results and discussions of the application of synthesized nanoparticles as anode material in sodium-ion batteries.
Chapter 6: Conclusions and Recommendations

The conclusions and recommendations from this investigation's findings are presented in this chapter.
1.6 References


CHAPTER 2: LITERATURE REVIEW

2 Overview

This chapter covers literature review on rechargeable batteries with emphasis on lithium-ion and sodium-ion rechargeable batteries — how they work, their advantages and disadvantages.

2.1 Introduction

Rechargeable or secondary batteries are essentially reusable batteries. The electrochemical process by which they store, and supply energy is reversible and can be repeated hundreds and in some cases thousands of times before the rechargeable batteries are completely spent. They serve as the primary source of energy and energy storage system for modern-machines [1] ranging from portable electronic devices [2, 3], electric vehicles [4, 5] to even medical devices [6].

All batteries have three basic parts, two electrodes and an electrolyte [7], material that conduct electrical current and ions respectively. When the battery is connected to a device and is supplying energy, i.e. discharging, there is spontaneous movement of both the electrons and ions as illustrated in Figure 2.1.

![Schematic diagram of the operation of a rechargeable battery](image)

**Figure 2.1:** Schematic diagram of the operation of a rechargeable battery [8]

The electrons move from the electrode with the more negative potential (anode) to the more positive potential electrode (cathode) [7, 9] through an external circuit while the negatively charged ions...
(anions) move to the anode and the positively charged ions (cations) move to the cathode through the electrolyte [10]. During the process of energy storage or charging, an external larger voltage is applied to the battery in the opposite direction thus causing a reverse in the movement of both the electrons and ions [7].

2.2 Brief history of rechargeable batteries

Rechargeable batteries were first developed more than a century and a half ago with the invention of the lead-acid battery in 1859 [5], which is still widely used in the automotive industry, e.g. golf carts, lawn mowers, tractors, aircraft, marine, micro-hybrid vehicles, motorized chairs, and various types of motorized vehicles. [11]. The endurance of the lead-acid battery in the rechargeable battery market is due to their low-cost [7], good performance and long-life cycle [11].

The early 1900s saw the introduction of the nickel-based secondary batteries, first with the nickel-iron system which was durable and had relatively long-life cycles. It was commercialized by Thomas Edison as a source of energy for electric vehicles but was eventually mainly used for stationary applications and railroad vehicles [12]. Unfortunately, due to high costs, maintenance requirements and lower specific energy, they were quickly replaced by the nickel-cadmium rechargeable battery.

The nickel-cadmium rechargeable battery underwent several changes in its design and consequently its application from the pocket-plate in 1909, sintered-plate design in the 1950’s to finally pioneering the sealed design technology widely used in portable electronic devices’ batteries to date [5, 12]. The pocket-plate nickel-cadmium batteries were very rugged, had long life cycles and required very little maintenance, and as a result were used for materials-handling trucks, mining vehicles, start-up of diesel engines, among other applications. The sintered-plate design was preferred for applications that required lighter materials and superior performance such as aircrafts, communications and electronics equipment [12]. The sealed design nickel-cadmium rechargeable battery still finds widespread use in consumer portable electrical devices such as power tools and emergency lighting. The nickel-cadmium battery was superseded by the nickel-metal hydride battery in 1990, the last of the notable nickel-based rechargeable batteries, as it offered higher specific energy and energy density, at lower cost in addition to being less toxic [12].

Soon after in 1991 lithium-ion batteries (LIBs) were introduced to the consumer market and have had a great impact on the rechargeable battery market to date [13, 14]. LiBs are the consumers preferred choice because of their modest size and low weight [1], high energy density [3, 15, 16], good performance [17], low self-discharge [18] and long cycle life (>1000 cycles at 80% depth of discharge) [7, 12]. The properties and performance of the common rechargeable batteries in the current battery market (i.e. lead acid, nickel-cadmium, nickel metal hydride and lithium-ion rechargeable battery) are compared in Table 2.1.
Table 2.1: Components, characteristics and performance of the common rechargeable batteries in the current battery market [9, 10, 19]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lead acid</th>
<th>Nickel-cadmium</th>
<th>Nickel-metal hydride</th>
<th>LIBs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Lead</td>
<td>Cadmium</td>
<td>Metal hydride</td>
<td>Li(C)</td>
</tr>
<tr>
<td>Cathode</td>
<td>PbO₂</td>
<td>NiOOH</td>
<td>NiOOH</td>
<td>LiCoO₂</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>aq. H₂SO₄</td>
<td>aq. KOH</td>
<td>aq. KOH</td>
<td>LiPF₆</td>
</tr>
<tr>
<td>Voltage</td>
<td>2.1</td>
<td>1.3</td>
<td>1.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Practical Energy Density (W h dm⁻³)</td>
<td>70</td>
<td>100</td>
<td>240</td>
<td>400</td>
</tr>
<tr>
<td>Cycle life (times)</td>
<td>300</td>
<td>500</td>
<td>500</td>
<td>1000</td>
</tr>
<tr>
<td>Memory effect</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Insignificant</td>
</tr>
<tr>
<td>Self-discharge (%/month)</td>
<td>0</td>
<td>25 – 30</td>
<td>30 – 35</td>
<td>2 – 5</td>
</tr>
<tr>
<td>Toxicity</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Weight (grams)</td>
<td>13 000</td>
<td>21</td>
<td>27</td>
<td>14</td>
</tr>
<tr>
<td>Advantages</td>
<td>Low cost</td>
<td>Moderate costs,</td>
<td>Higher capacity,</td>
<td></td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Too heavy</td>
<td>Not environmentally friendly</td>
<td>Higher self-discharge</td>
<td>Limited cobalt resources</td>
</tr>
<tr>
<td>Application</td>
<td>Car, Lighting</td>
<td>Emergency lighting</td>
<td>Toys,</td>
<td>Cellular phone,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Power tools, etc.</td>
<td>Digital camera, etc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Laptop computer, etc.</td>
</tr>
</tbody>
</table>
The lead acid battery has the highest nominal voltage bar from LIBs, and low production costs however due to its weight, it is usually used for starting, lighting and ignition (SLI) automotive applications. Conversely, the nickel-cadmium and nickel-metal hydride rechargeable batteries provide lower operational voltage yet due to the longer life cycle, higher energy density and most importantly their lighter weight (as compared to the lead acid battery), they are typically used for portable electronic devices such as power tools, toys, and digital cameras. Lithium-ion rechargeable batteries’ characteristics and consequently its performance far exceeds those of its counterparts which has extended its scope of application from everyday portable consumer electronic devices such as cellphones to emergency and medical devices and even in the transport sector for electric vehicles.

2.3 Lithium-ion battery (LIB)

The success of the lithium-ion battery is owed to two discoveries before which, LIBs had short life cycles and frequently resulted in operational faults most commonly fire incidents. The first is the discovery of intercalation electrodes in 1978 [5], i.e. compounds that can reversibly incorporate and release the lithium cation into their layered structure during the charge-discharge process. The second, is the use of an organic electrolyte in the early 1980’s that extended the operational life of LIBs by several hundred cycles [20].

Subsequent research focused on the improvement of its cathode. Cathode materials have different chemistries which lends different properties to batteries [21]. Some of the cathode material used for LIBs since their discovery include lithium cobalt oxide (LiCoO$_2$), lithium iron phosphate (LiFePO$_4$) and lithium nickel manganese oxide (LiNi$_{0.5}$Mn$_{0.5}$O$_2$) are still in use as cathode material in 37.2%, 5.2% and 29% respectively, of lithium-ion batteries in the market as stated in the 2014 published research work of Gratz and co-workers [4]. The investigation into LIBs cathode material continues with focus on lowering production costs and increasing battery capacity and performance [21].

2.4 Operating principle of the Lithium-Ion Battery (LIB)

Similar to a typical battery, the LIB consists of an anode, cathode and electrolyte [10]. In LIBs, the energy is stored and supplied through movement of lithium cations in and out of the structure layers of electrode materials, from the cathode to the anode during charging and vise-versa during discharging [17, 22] as visually represented in Figure 2.2.
During charging, the chemical reaction in the LiCoO$_2$ cathodic material of a LIB is:

\[
\text{LiCoO}_2 \rightarrow \text{Li}_{(1-x)}\text{CoO}_2 + x\text{Li}^+ + xe^- \tag{1}
\]

While that in the anodic material can be expressed as:

\[
6\text{C} + x\text{Li}^+ + xe^- \rightarrow \text{C}_6\text{Li}_x \tag{2}
\]

The electrochemical mechanism of the LiCoO$_2$ LIB can be represented by the reversible equation:

\[
\text{LiCoO}_2 + 6\text{C} \leftrightarrow \text{Li}_{(1-x)}\text{CoO}_2 + \text{C}_6\text{Li}_x \tag{3}
\]

When the battery is supplying energy or discharging, the reverse equations holds true [8].

2.5 Application, Demand and Growth of Lithium-Ion Battery (LIB)

Lithium-ion rechargeable batteries are used in four sectors, namely the consumer, automotive, industrial and energy storage sectors [24]. In 2013, the consumer sector was the leading global consumer of lithium-ion rechargeable batteries accounting for 60.3% revenue of the global LiBs market, whilst the automotive, industrial and energy storage sectors contributed 18.3%, 14.5% and 6.9% respectively [24].

Since 2010 — 2015, there has been an increase in the global lithium-ion battery consumption by 23% per year on average [25] largely attributed to the advancement of technology in the mobile
information and communications sector [26]. The majority of cellphone users replace their mobile phones well before they reach the end of their lifespan, estimated between 2 ─ 3 years [18, 27] due to advances in technology and “fashion obsolescence” [27]. As a result, there are billions of mobile phones in use worldwide, while millions are in disuse, in users’ possession waiting to be discarded [27]. Making the global market for both the rechargeable and non-rechargeable lithium-ion batteries to reach $10.7 billion value in 2015 [25] and it is projected to continually increase. Primarily, due to the rapid growth of grid and renewable energy storage in addition to the automotive sector as the world moves from finite non-renewable fossil fuels especially oil in the transport sector, to environmentally friendly alternatives such as solar and wind [5, 21, 28, 29].

2.6 Sustainability of Lithium-Ion Battery Demand and Growth

Unfortunately, although the battery market is the main consumer of global lithium produced, it is not its sole consumer [30] and in most of the applications, lithium cannot be substituted [31]. Lithium is also in demand in the ceramics and glass, lubricating greases, polymer production, continuous casting mold flux powders and air treatment sectors [30]. In its 2018 report, United States Geological Survey (USGS) stated that in 2017 the battery market consumed nearly half of the global lithium produced (46%) followed by the ceramics and glass sector at 27% [30].

Lithium in nature is found in minerals, brines, sedimentary rocks and sea water [32]. To date minerals and brines are the sources of lithium worldwide [30, 32], the latter currently the major and economical source of lithium [33]. Lithium is not commercially recovered from either sedimentary rock [32] or sea water even though sea water is estimated to contain more than 2,000,000 million tons of lithium [28, 32, 33]. The feasibility and practicality of the various processes available are not plausible on a large scale, and thus to date has not been achieved [28, 32]. Currently, lithium recovered from recycling carries higher costs than that recovered from natural sources as a result, recycled lithium accounts for less than 1% of the total lithium world supply [31]. However, this is projected to change with the increase in demand for LIBs by 25% by 2050 [31].

There is significant variation in the reported quantity of global lithium resources [28] and consequently the projected time for exhaustion of this finite resource. For example, Martin et al. [31] reported lithium resources to be approximately 34 million tons with a theoretical static range of 435 years. In contrast, USGS projects availability of lithium resources for the next 135 years at 1 ─ 3 times the current consumption, as quoted by Narins et al. [34] from their 2015 published report. Vikström et al. [28] attributed this difference to the fact that different studies use different deposits and different number of deposits to collect data. Nevertheless, most studies agree that the resources of lithium are limited therefore, other battery types as well as technologies should be explored for energy storage [28, 35].
2.7 Sodium-Ion Battery (SIB)

Research into sodium-ion batteries (SIBs) was initiated in the 1960’s alongside LIBs [5, 10, 35], however due to the rapid development and commercial success of LIB technology, it declined [3, 35, 36]. In light of the projected depletion of lithium resources due to the rapid growth and demand of LIBs, sodium-ion technology research is expanding as SIBs are considered as a probable replacement of LIBs.

Sodium-ion batteries are the credible alternative to LIBs mainly because sodium’s natural resources are abundant and evenly distributed worldwide [30, 35-38], making SIBs the economical choice. As reported by USGS in Mineral Commodity Summaries 2018 report, salt (NaCl) deposits are in nearly every country on earth and the oceans contain a virtually inexhaustible supply of this mineral [30]. In addition, the more than 7 500 desalination plants in operation worldwide supplying fresh water discharge high concentration of dissolved salts (mainly NaCl) reject water back into the oceans which is harmful to marine life and environments [39]. This discharge could be used as raw material for SIBs.

Another appealing attribute of SIBs is the fact that lithium and sodium have similar chemical properties [40] and consequently similar chemical storage mechanism when used in a battery [35-37]. Lithium and sodium are both alkali metals, i.e. they have ns\(^1\) valence electron configuration as a result during chemical reactions they both easily loose the electron in their outermost s-orbital to form the +1-oxidation state.

2.7.1 History of Sodium-Ion Battery (SIB)

Sodium rechargeable batteries can be classified into three categories based on operational temperature, namely: 1) high temperature (~300\(^\circ\)C); 2) moderately high temperature (100 ─ 200 \(^\circ\)C and the 3) ambient temperature [5] sodium rechargeable battery.

2.7.1.1 High temperature sodium rechargeable battery

The high temperature sodium rechargeable battery, similar to all batteries consist of three basic components — cathode, anode and electrolyte. The anode is melted sodium metal separated from the molten sulfur cathode by a solid sodium beta alumina (Na-\(\beta''\)-\(\text{Al}_2\text{O}_3\)) which also acts as the electrolyte [41], i.e.

\[
\text{Liquid Na} \big| \text{Na-}\beta''\text{-Al}_2\text{O}_3 \big| \text{Molten S, Current Collector} \quad (4)
\]

16
Heating the battery activates it and maintains the reactants and products in a liquid state during the charge-discharge process [5]. When the sodium-sulfur (Na-S) battery is discharging, sodium is oxidized and while sodium ions move through the electrolyte to the molten sulfur where they react to form sodium polysulfides, the electrons move via the external circuit [3, 5]. The first product of discharge is Na$_2$S$_5$;

$$2Na + 5S \rightarrow Na_2S_5 \quad (5)$$

which gets reduced further to lower polysulfides, i.e. Na$_2$S$_4$, Na$_2$S$_3$, Na$_2$S$_2$ as discharge continues [3, 5]. During charging the process is reversed.

The Na–S batteries have several advantages including a relatively high voltage of 2.1 V [5, 10], quick reversibility between charging and discharging [42], long life cycles (>2500 cycles at 100% depth of discharge) [41], low maintenance [42] and a low self-discharge rate [5]. However, due to the high operational temperature ~300°C [3, 5, 10, 41, 42], the Na–S battery has inherent disadvantages such as indirect discharging [42], corrosion — its reactants and products are highly corrosive at this temperature [3] causing cell failure from accumulation of corrosion at the cathode as well as deterioration of seals, solid electrolyte or cell container [5]. The high operational temperature has also disqualified it as a probable power source for the consumer and automotive sectors [5]. On the other hand, due to their power ratings (several MW power loads and MWh order capacities) [41], they are tailor-made for stationary applications — emergency back-up, grid and renewable energy storage [5, 41]. According to Ellis et al. [3], the Na–S batteries have been used as a power source in industrial and energy storage applications since 2003 in “174 locations in six countries around the world, storing 305,000 kW of electricity”.

2.7.1.2 Moderately high temperature sodium rechargeable battery

Moderately high temperature sodium rechargeable batteries were pioneered by Abraham et al. in the late 1970s [5], to circumvent the many inherent disadvantages of the melted sodium-molten sulfur battery due to its high operational temperature (~300°C) [43]. It has the same components as the Na-S high temperature battery bar from the cathode [43], i.e.

Liquid Na | Na-β''-Al$_2$O$_3$ | Na$_2$Sn, organic solvent, conducting Na salt \quad (6)

Instead of molten sulfur, the battery uses a soluble sulfur cathode consisting of sodium polysulfides (Na$_2$S$_n$) dissolved in an organic solvent, N,N-dimethylacetamide (DMAC) and 0.4 M sodium tetrafluoroborate (NaBF$_4$), as the supporting electrolyte [43]. This feature enabled the operational temperature to decrease significantly to slightly above the melting temperature of sodium (100°C — 150°C).
As in a high temperature Na-S battery, during discharge of the moderate temperature Na-S battery, sodium ions migrate to the soluble sulfur cathode through the Na-$\beta''$-Al$_2$O$_3$ electrolyte where they react with reduced sulfur to form polysulfides [5]. As discharge progresses, the sulfur is reduced further from $\text{S}_{42}^-$ to $\text{S}_{2.032}^-$ in the first discharge until $\text{S}_{22}^-$ level, where discharge becomes difficult [43]. The cell exhibited an open-circuit voltage of 1.83 V and was chemically stable for charge-discharge cycles for up to 30 days at moderate current densities, $1 - 4\text{C}$ [43]. It became clear that the weakness of this cell was its solvent, DMAC [5]. For the moderate temperature Na-S battery to be on par with its high temperature counterpart, complete reduction of sulfur is essential, and this would require a solvent that can achieve a solubility of $\sim 1.3 \text{ M Na}_2\text{S}_{10}$ [43]. However, very little research was done to identify such a solvent as a result this battery was never commercialized.

Instead, subsequent research focused on transition metal-sulfide or -chloride as cathode materials incorporated into a eutectic mixture of NaCl and AlCl$_3$ [5]. The breakthrough in this research was in the 1980s by South African researchers who utilized liquid sodium as the negative electrode separated by a solid sodium $\beta''$-alumina electrolyte from a mixture of NiCl$_2$ cathode active material in molten NaAlCl$_4$ which acts as the secondary electrolyte [44, 45], i.e.

$$\text{Liquid Na} \mid \text{Na-$\beta''$-Al}_2\text{O}_3 \mid \text{Molten NaAlCl}_4, \text{NiCl}_2$$  \hspace{1cm} (7)

They named this Na-NiCl$_2$ battery, the ZEBRA (Zero-Emission Batteries Research Activity) cell [3]. It operates in the 175°C to 300°C range, preferably at 250°C [5]. When the ZEBRA cell is discharged, sodium ions generated from oxidation of sodium move through the solid electrolyte assisted by the secondary electrolyte to the NiCl$_2$ cathode material. The electrochemical reaction for the cell is:

$$\text{NiCl}_2 + 2\text{Na} \leftrightarrow 2\text{NaCl} + \text{Ni}$$  \hspace{1cm} (8)

The forward reaction represents the discharging process, while the reverse occurs when the cell is charging.

The ZEBRA battery has a nominal operational voltage of 2.58 V [3, 5, 10], its specific energy (115 Wkg$^{-1}$) approaches that of LIBs (150 Whkg$^{-1}$) [10, 46] and has a long cell life (>2000 cycles) [44]. Its most appealing attribute is that it consists of low cost, abundant materials [5] that can be assembled in the discharged state, removing the hazard of handling molten sodium [3, 10, 47]. In addition, its cathode material consists of mostly solid materials which reduces the corrosive environment experienced by the Na-S high temperature battery thus making it safer [3].

Most of the challenges that ZEBRA batteries have are intrinsic, such as; 1) Self-discharge from the high operational temperature [42], 2) potential safety hazard from the use molten sodium as an electrode [46], and 3) high internal resistance during discharge which decreases its specific power [47]. Moreover, at present ZEBRA batteries can only be used for applications that require large
capacity batteries (> 20 kWh), which excludes them from powering small battery (3 kWh) hybrid vehicles [48]. Despite these challenges, ZEBRA batteries have been in use since the mid-1990s for automotive applications. According to Sudworth [47], in an article titled, Zebra batteries, published in 1994: All the Mercedes-Benz 190 cars on the island of Rugen, in Germany were powered by ZEBRA batteries. Ten years later, Dustmann [48] reported that ZEBRA batteries had been incorporated in several more car makes such as Renault Twingo and Clio, Opel Astra and BMW 3 Series as well as several pure electric battery buses in Italy and Mercedes-Benz vans (Vito and Sprinter). They are also being used for stationary applications as a back-up energy source for telecommunications [47, 48].

Research into the ZEBRA battery is still ongoing, most of which has been focused on improving its energy density (190 Wh dm\(^{-3}\)) which is half that of LiBs (400 Wh dm\(^{-3}\)) [10]. For example, Böhm and Beyermann [49] discovered that by modifying the geometry of the ceramic electrolyte from round to a clover-leaf shape, the energy density of the cell improved. The same team also discovered that doping the cell with iron has the same positive effect on the energy density [49]. Whilst Prakash et al. [50] managed to stabilize the ZEBRA cell capacity by adding sulfur to the cell thus preventing grain growth of Ni.

2.7.1.3 Ambient temperature sodium rechargeable battery

Ambient temperature sodium rechargeable batteries can only store and supply energy through the insertion-extraction of sodium-ions in between the structure layers of the positive and negative electrodes, unlike its higher temperature counterparts which can use either the displacement-type electrode process or insertion-extraction process [5]. The cell configuration of these batteries is similar to that of LiBs, i.e. a positive and negative electrode separated electronically by a porous polymer membrane while connected ionically by a non-aqueous sodium-ion conducting electrolyte [5, 51, 52]. This configuration has a couple of challenges: 1) Compatible electrolyte material, if metallic sodium is used as the negative electrode as they are in direct contact. 2) Alternatively, compatible active materials, if both the anode and cathode serve as insertion materials [5]. This section discusses research thus far on these challenges.

The first logical step when searching for compatible battery material for SIBs is to study compatible battery material for LiBs [35]. These are materials whose structures and chemistries have been proven successful in LiBs [53]. This is because the two battery types have similar intercalation chemistry [38] and normally the open crystal structure that permits the intercalation of lithium-ions also allows sodium-ion intercalation [53]. This strategy has exceptions though derived from the physical attributes of the two ions [35, 38], i.e. sodium-ion is heavier (23.00 u) and larger (1.02 Å) than the lithium-ion (6.94 u and 0.76 Å) [38, 52], thus has slower diffusion rates [52] and is more polarizing [35, 38]. A few examples of these exceptions are: 1) the use of graphite as an anode
material for SIBs. Although it is the most common anode LIBs material [3], it has insignificant capacity when used in SIBs [52] as only small amounts of sodium-ions are inserted reversibly between graphite layers [5] 2) when aluminum is used as a current collector for the anode in LIBs, aluminum–lithium alloy is formed [35, 51]. This is not the case in SIBs as sodium does not alloy with aluminum [52], therefore current collectors for both electrodes can be made from the economical aluminum [35] and thus avoid the risk of corrosion [52]. 3) LiCrO$_2$ and NaCrO$_2$ as electrode material in LIBs and SIBs respectively. Although both compounds have quite similar crystal structures [35], LiCrO$_2$ is inactive (<10 mAh$^{-1}$) in LIBs [53] while NaCrO$_2$ exhibited a high capacity of 120 mAh$^{-1}$ in SIBs [54].

2.7.2 Ambient temperature sodium rechargeable battery: Positive electrode materials

The investigation for compatible material that can intercalate sodium-ions in SIBs began in 1980 with TiS$_2$ [51]. Newman and Klemann [55] used solid sodium as the anode and sodium-triethyl (N-pyrrolyl) borate in dioxolane as the electrolyte. Sadly, the cell had short life cycle (<20 cycles) and unstable capacity that decreased with cycling [55]. Several other transition metal-sulfide compounds were also studied such as TaS$_2$, MoS$_2$, VS$_2$, TiS$_3$, MoS$_3$, and NiPS$_3$ [5, 53]. These studies revealed that transition metal-sulfide compounds as cathode materials for SIBs have poor electrochemical properties thus further investigation of their compatibility has not been pursued very much over the years [53].

Eventually research focus turned to transition metal-oxides [5]. These layered oxides with a general formula AMO$_2$, where A is Na or Li and M represents transition metals individually or in combination, most commonly Co, Mn and Ni, proved very successful in LIBs providing high intercalation potentials and energy densities [3]. The most noted of these compounds was Na$_x$CoO$_2$. This cathode material is the counterpart of the most renowned and still widely used cathode material for LIBs, LiCoO$_2$. Its study for SIBs was inevitable and has been extensively investigated. Ding et al. [56] studied P2-phase Na$_{0.74}$CoO$_2$ as the active material in the positive electrode of a half cell. The team used sodium metal as the negative electrode while a non-aqueous solution of 1 M NaPF$_6$ or 1 M NaClO$_4$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate at a 1:1 (v/v) ratio served as the electrolyte. Celgard 2400 polyethylene was used as a separator. The cell had a reversible capacity of 107 mAh$^{-1}$ within the 2.0–3.8 V potential range. However, potential faded by 0.1% per cycle for the first 40 cycles when NaPF$_6$ was used as the electrolyte [56].

Another well studied metal oxide was NaCrO$_2$. The Na-NaCrO$_2$ cell studied by Komaba et al. [54] consisted of a solid sodium metal as the negative electrode, a 1 M solution of NaClO$_4$ in propylene carbonate as the electrolyte and NaCrO$_2$ compound as the active positive electrode material. It
exhibited a high reversible capacity of 100 mAhg\(^{-1}\) — 120 mAhg\(^{-1}\) when cycled between 2 V and 3.5 V \[5, 54\].

### 2.7.2.1 Sodium manganese oxides

Use of NaMnO\(_2\) has been investigated and shown to be capable of high reversible capacities of 132 mAhg\(^{-1}\) and insignificant structural change even after 20 cycles \[57\]. The cells were tested by Ma et al. \[57\] using 1 M NaPF\(_6\) in EC : DMC as the electrolyte, monoclinic NaMnO\(_2\) as the active material of the positive electrode and sodium metal as the negative electrode \[57\].

Use of NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) has been reported. The Na-NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) battery provided a high reversible capacity of 185 mAhg\(^{-1}\) between 2.5 V and 4.5 V vs. Na/Na\(^+\), with almost all the sodium-ion being extracted at a voltage of 4.5 V \[5\]. This capacity is the highest reported of all the layered oxide SIB cathode materials to date \[5\]. When the potential is limited to 3.8 V, the irreversible capacity was suppressed \[5\] resulting in insignificant sodium-Ni disordering unfortunately at a cost to capacity which decreased to 130 mAhg\(^{-1}\) \[53\].

Another metal oxide that has been investigated is Na\(_{0.85}\)Li\(_{0.17}\)Ni\(_{0.21}\)Mn\(_{0.64}\)O\(_2\). This innovative active cathode material was developed by a team at Argonne National Laboratories \[5\]. The cell operates with a sodium metal as the anode, propylene carbonate with 1 M NaClO\(_4\) salt as the electrolyte and Na\(_{0.85}\)Li\(_{0.17}\)Ni\(_{0.21}\)Mn\(_{0.64}\)O\(_2\) as the active anode material \[58\]. The Na-Na\(_{0.85}\)Li\(_{0.17}\)Ni\(_{0.21}\)Mn\(_{0.64}\)O\(_2\) cell has an operational voltage of \(~\)3.4 V and a capacity between 95 mAhg\(^{-1}\) — 100 mAhg\(^{-1}\) while maintaining structural integrity during cycling \[58\]. The team also used the Na\(_{0.85}\)Li\(_{0.17}\)Ni\(_{0.21}\)Mn\(_{0.64}\)O\(_2\) cathode material with TiO\(_2\) nanotube as the anode. This cell has an operation voltage of 1.8 V and a discharge capacity of 80 mAhg\(^{-1}\) \[5\].

Other materials explored in the quest for compatible cathode materials for SIBs were NASICON-type compounds, olivines, sodium fluorophosphates, andavorite sodium iron fluorosulfate compound.

### 2.7.2.2 NASICON type compounds

Delmas et al. were the first to demonstrate that NASICON (NAtrium Super Ion CONductor) type compounds, can be used as cathode material in both LIBs and SIBs \[59\]. These compounds were pioneered by Goodenough and co-workers as solid electrolytes due to their structural stability and fast ion conduction \[3, 60\]. They have an A\(_2\)M\(_2\)(XO\(_4\))\(_3\) general formula where A is either a lithium-ion or sodium-ion, M is a transition metal and X represents Si\(^{4+}\), P\(^{5+}\), S\(^{6+}\), Mo\(^{6+}\), etc. \[53\]. NASICON-type compounds have demonstrated good discharge capacities and high lithium-ion mobility in LIBs \[38\], however their performance in SIBs was poor \[53\]. Recently, the compounds were revisited and showed promising performance in SIBs when coated with carbon, e.g. when Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) was
studied in a half cell, it exhibited reversible capacity of 93 mAhg\(^{-1}\) in the 2.7 V — 3.8 V voltage range [53].

2.7.2.3 Olivine LiFePO\(_4\)

Compounds that contain iron and phosphate are renowned for their structural and chemical stability, environmentally benign character and low cost [3, 61]. It is due to these reasons that LiFePO\(_4\) phase compound with an olivine structure has been considered as a possible cathode material for LIBs [62]. The structure, synthesis, electrochemical behavior, mechanism, and other key properties of olivine LiFePO\(_4\) has been studied extensively [62]. When used as a cathode material in LIBs, the olivine exhibited long cycle life, high thermal stability, high specific capacity between 100 mAhg\(^{-1}\) — 150 mAhg\(^{-1}\) depending on synthesis method, particle size, etc. [61]. The success of olivine C/LiFePO\(_4\) as a cathode in LIBs [61] led to several studies of olivine NaFePO\(_4\) as a probable cathode in SIBs. One of the latest investigations is by Oh et al. [63] using olivine NaFePO\(_4\) synthesized by electrochemical delithiation of LiFePO\(_4\) to FePO\(_4\) followed by sodiation. This cathode material when tested in a sodium cell showed outstanding results, i.e. long cycle life (>50 cycles), high and stable rate capability (125 mAhg\(^{-1}\)) which is 80% of the theoretical value, operational voltage of 2.7 V and structural stability even after 50 cycles [63].

2.7.2.4 Sodium fluorophosphates

SIB cathode material from sodium fluorophosphates compounds such as NaVPO\(_4\)F, Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\), Na\(_{1.5}\)VOPO\(_4\)F\(_{0.5}\) and Na\(_2\)FePO\(_4\)F have thus far exhibited the same electrochemical behavior as their lithium analogs [38].

The substantial research of sodium vanadium fluorophosphates compounds is due to their appealing attributes such as economical starting materials, safe applications and high operational potentials [38]. The research into electrochemical properties of sodium vanadium fluorophosphates was pioneered by Barker et al. [3] initially using NaVPO\(_4\)F [64] then Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\) compounds [65]. The team used a unique hybrid Na/Li-ion cell that consisted of a graphite anode and a lithium salt electrolyte. Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\) compound demonstrated highly reversible and stable capacity of 120 mAhg\(^{-1}\) at 2C and long cycle life (>400 cycles) [3]. The electrochemical properties of NaVPO\(_4\)F compound were tested against metallic lithium and hard carbon anodes [38]. The cell was tested between a 3 — 4 V range at C/4 and demonstrated charge-discharge specific capacity of 117 mAhg\(^{-1}\) and 107 mAhg\(^{-1}\) respectively. However, this capacity was not stable and faded after 100 cycles [38].

Another type of sodium fluorophosphates compounds are the layered sodium iron fluorophosphate compounds. When NaFePO\(_4\)F was tested in a sodium-ion cell in the 2.90 V — 3.04 V range, it demonstrated a stable high reversible capacity of 96 mAhg\(^{-1}\) [3, 53].
2.7.2.5 Tavorite sodium iron fluorosulfate

Similarly, NaFeSO$_4$F was studied due to an appealing feature in its lithium counterpart, i.e. LiFeSO$_4$F has a multi-channel Li ion conduction, however the same does not hold true for NaFeSO$_4$F [53]. Tavorite sodium iron fluorosulfate compound exhibits insignificant electrochemical activity (~0.08 Sodium-ion transfer) in a sodium cell up to 4.2 V but was electrochemically active in a hybrid lithium-ion cell [53].

As it has been evidenced, probable cathode active material for SIBs are layered oxides with tertiary or greater transition metals [52] in addition to phosphate-based materials [38].

2.7.3 Ambient temperature sodium rechargeable battery: Negative electrode materials

The dominating anode material in LIBs to date is graphite. Graphite is abundant [30] therefore economical, it readily accommodates lithium-ion into its graphitic structure up to 1:6, Li:C ratio and due to the fast Li intercalation kinetics, it exhibits a high reversible capacity (>360 mAhg$^{-1}$) that is virtually equivalent to its theoretical capacity (372 mAhg$^{-1}$) [53]. It was therefore, the natural first choice when compatible anode materials for SIBs were sought. However, when used as an anode material in SIBs, its electrochemical performance is poor [52]. Under normal pressures only an extremely small number of sodium-ions are intercalated into the graphitic sheets (~NaC$_{186}$) [66] due to its inadequate interlayer spacing of 0.34 nm [52] rather than 0.37 nm theoretically calculated to be crucial for significant sodium intercalation [67].

Despite the disappointing performance of graphite as anode material in SIBs, further studies were conducted on this graphitic material as well as other carbonaceous material. Thomas et al. [68] discovered that mechanical grinding enhanced the electrochemical performance of graphite. The ground graphite (<20 μm) exhibited a reversible capacity of 187 mAhg$^{-1}$, a massive improvement to the 16 mAhg$^{-1}$ reversible capacity delivered by the unground graphite [69]. Deoff et al. [70] investigated the electrochemical properties of petroleum-coke carbon before grinding (70 μm particle size) and after grinding to an average of 1 μm. The unground petroleum-coke carbon intercalated an insignificant amount of sodium-ion compared to the ground (~NaC$_{30}$) which gave a reversible capacity of 85 mAhg$^{-1}$ [70]. In 2000, Stevens and Dahn, pioneered the use of hard carbons as anode material for SIBs with an impressive reversible capacity of 300 mAhg$^{-1}$ [52, 66]. One of the recent published investigation on hard carbon as an anode is by Komaba et al. [71] in a full cell with NaNi$_{0.5}$Mn$_{0.5}$O$_2$ as the active material in the cathode. This battery has an operational voltage of 3 V with a reversible capacity of 150 mAhg$^{-1}$ even after 50 cycles. Wang et al. [72] studied reduced graphene oxide in a sodium-ion cell which showed a stable high reversible capacity of 141 mAhg$^{-1}$ at 0.2C in addition to long life cycle (>1000 cycles). The excellent performance was attributed to the
higher electrical conductivity, larger interlayer spacing and disordered structure of reduced graphene oxide [75]. Several more carbon materials were studied such as pitch-based carbon fibers [68], hydrogen-containing carbon [66], and carbon fibers [69].

Further studies in the quest for negative electrode material that can intercalate sodium-ions in SIBs were conducted on sodium-alloying metals. The product of sodium and its alloying metals are the storing mechanism for sodium-ions during the intercalation process in SIBs [53], i.e.

\[
M + nNa^+ + ne^- = Na_nM
\]  

(6)

Amongst these metals, tin and antimony have received the greatest attention due to their high theoretical capacity of 846 mAhg\(^{-1}\) and 660 mAhg\(^{-1}\) respectively [52]. However, sodium-alloying metals have two weaknesses observed in both SIBs and LIBs, namely: 1) volume expansion, e.g. the final discharge product of tin-sodium alloy in a SIBs (Na\(_{15}\)Sn\(_4\)) is 420% of its original size [73]. The effect of volume expansion is twice more severe in SIBs than LIBs [52] 2) aggregation of metal nanoparticles from repeated cycling, i.e. sodiation and de-sodiation that results in the fading of capacity [52]. Excessive volumetric expansion has been successfully suppressed by mixing sodium-alloying materials with fixed volume materials such as carbon [52, 74]. For example, Qian et al. used a Sb/C nanocomposite as an anode in SIBs which showed a stable high reversible capacity of 610 mAhg\(^{-1}\) at 100 mAg\(^{-1}\) over 100 cycles [75]. Lu et al. [76] compared the electrochemical performance of pure Sn\(_2\)O\(_2\) and Sn\(_2\)O\(_2\)/C. Sn\(_2\)O\(_2\)/C delivered a high reversible capacity of 411 mAhg\(^{-1}\) at 50 mAhg\(^{-1}\) whilst that of Sn\(_2\)O\(_2\) is close to zero at 500 mAhg\(^{-1}\) [76].

Titanium-based material have also been put in the spot light as possible anode material because titanium is abundant [30], economical [52] and titanium-based anode materials studied thus far have exhibited good cycling stability and capacity retention. For example, NaTi\(_{2}\)(PO\(_4\))\(_3\) showed capacities that were ~90% of the theoretical capacity when studied in both aqueous and non-aqueous cells, at 123 mAhg\(^{-1}\) and 120 mAhg\(^{-1}\) respectively as reported by Park et al. [77]. While Na\(_2\)TiO\(_2\) delivered a specific capacity of 200 mAhg\(^{-1}\) as reported by Senguttuvan et al. [78]. Chen et al. [79] investigated the electrochemical performance of TiO\(_2\)/graphene nanocomposites in a sodium battery. This hybrid electrode delivered a stable specific capacity 90 mAhg\(^{-1}\) at ~36C for a long cycle life (>4000 cycles) [79]. Therefore, in general titanium-based materials, however, deliver lower capacities (<200 mAhg\(^{-1}\)) as anode material in SIBs [52].

It can then be concluded that from the research thus far, the plausible anode materials for SIB technology are hybrids of sodium-alloying materials and carbon.
2.7.4 Ambient temperature sodium rechargeable battery: Electrolytes

Electrolytes are an integral part of any battery and the main contributor to its safety and performance, e.g. life-time, capacity, rate capability, and other properties [52, 80]. An ideal electrolyte has the following features, 1) Ionic conductivity, i.e. provides effective transportation of lithium-ions or sodium-ions between the anode and cathode during charge-discharge process. 2) Chemically stable, i.e. should not disintegrate or chemically react with any components of the cell. 3) Electrochemically stable, i.e. must not be affected by the oxidation and reduction reactions during cycling. In addition to forming a stable solid electrolyte interphase (SEI) that decreases irreversible electrolyte consumption and thus enables the battery to maintain first cycle capacity. 4) Thermal stability, i.e. have low melting and high boiling points, to enable the battery to operate in a wide temperature range. Needless to say, like all battery components, an electrolyte should also be environmentally friendly and economical.

Currently, SIB electrolytes are made up of sodium salts dissolved in organic solvents [52]. However, sodium salts are less soluble in organic solvents than their lithium analogs, thus limiting the compatible organic solvents available [38]. Fortunately, research thus far on sodium analogs of lithium salts, e.g. ClO$_4^-$, BF$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$, and [N(CF$_3$SO$_2$)$_2$]$_-$ [80], dissolved in similar organic solvents, e.g. propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), dimethyl ether (DME), and triethylene glycol dimethyl ether (triglyme) [52] has produced promising results [56, 63, 72, 76]. Several studies have been done on the effect of different sodium salts in various organic solvents: Bhide et al. [81] studied NaPF$_6$, NaClO$_4$ and NaCF$_3$SO$_3$ salts in a 30:70 (wt%) solvent mixture of ethylene carbonate and dimethyl carbonate in a half cell with Na$_0.7$CoO$_2$ as a positive electrode and demonstrated NaPF$_6$–EC:DMC as the best electrolyte. Similarly, Ponrouch et al. [82] studied NaClO$_4$, NaPF$_6$ and Na[N(CF$_3$SO$_2$)$_2$] sodium salts dissolved in different combinations of several organic solvent, i.e. EC:DMC, EC:DME, EC:PC and EC:Triglyme. The team investigated the electrolyte mixtures in Na/hard carbon cells, and found NaPF$_6$–EC:PC to be the optimum electrolyte. Again in 2013, Ponrouch et al. [83] in a similar study with a different cell, hard carbon|Na$_3$V$_2$(PO$_4$)$_3$F$_3$, established that either NaClO$_4$ or NaPF$_6$ dissolved in EC$_{0.45}$: PC$_{0.45}$: DMC$_{0.10}$ delivered good performance for SIB cells. Therefore, the most utilized electrolyte in SIB studies currently is 1 M NaClO$_4$ or 1 M NaPF$_6$ sodium salt dissolved in pristine ethylene carbonate or propylene carbonate, or a mixture of the two solvents [84-86].

2.8 Advances, challenges and prospects of the Sodium-Ion Battery, SIB

Great strides have been made in the study of ambient temperature sodium rechargeable batteries also known as sodium-ion rechargeable batteries, SIBs since their inception nearly forty years ago yet to date these batteries have not been commercialized [51]. The two major challenges of SIBs are their energy density and cycle life when compared to LIBs.
The energy density of SIBs is inherently lower than that of LIBs due to the weight and radius difference of the sodium and lithium ions [38, 40], however recent developments of SIBs cathode and anode materials are gradually bridging the gap. The best candidates of anode and cathode materials discovered so far are listed in Table 2.2 with their values for the two challenging features for SIBs; specific capacity and charge-discharge cycles.

Table 2.2: The best anode and cathode material candidates for Sodium-Ion Battery (SIB) [40]

<table>
<thead>
<tr>
<th>Active Material</th>
<th>Anode / Cathode</th>
<th>Specific Capacity / mAhg(^{-1})</th>
<th>Charge-Discharge cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_{0.44})MnO(_2)</td>
<td>Cathode</td>
<td>120</td>
<td>1000</td>
</tr>
<tr>
<td>(\alpha)-Fe(_{2})O(_3)/C nanotubes</td>
<td>Cathode</td>
<td>99</td>
<td>500</td>
</tr>
<tr>
<td>Na(_3)V(_2)(PO(_4))(_3)/C</td>
<td>Cathode</td>
<td>30</td>
<td>30 000</td>
</tr>
<tr>
<td>Na(_3)V(_2)(PO(_4))(_3)/graphene</td>
<td>Cathode</td>
<td>90</td>
<td>300</td>
</tr>
<tr>
<td>Na(<em>{1.5})VPO(</em>{4.6})F(_{0.7})</td>
<td>Cathode</td>
<td>130</td>
<td>500</td>
</tr>
<tr>
<td>Na(<em>{0.45})Ni(</em>{0.22})Co(<em>{0.11})Mn(</em>{0.66})O(_2)</td>
<td>Cathode</td>
<td>135</td>
<td>250</td>
</tr>
<tr>
<td>Na(_3)MnFe(CN)(_6)</td>
<td>Cathode</td>
<td>145</td>
<td>1200</td>
</tr>
<tr>
<td>Na(<em>2)Fe(</em>{0.17})O(_2)</td>
<td>Cathode</td>
<td>170</td>
<td>30 ─ 40</td>
</tr>
<tr>
<td>Hard carbon</td>
<td>Anode</td>
<td>300</td>
<td>120</td>
</tr>
<tr>
<td>Carbon nanostructure</td>
<td>Anode</td>
<td>298</td>
<td>210</td>
</tr>
<tr>
<td>Sn</td>
<td>Anode</td>
<td>400</td>
<td>150</td>
</tr>
<tr>
<td>CuO nanowires</td>
<td>Anode</td>
<td>300</td>
<td>450</td>
</tr>
<tr>
<td>Na(_2)TiO(_7)</td>
<td>Anode</td>
<td>107</td>
<td>500</td>
</tr>
<tr>
<td>Na(<em>{2/3})Co(</em>{1/3})Ti(_{2/3})O(_2)</td>
<td>Anode</td>
<td>90</td>
<td>3 000</td>
</tr>
<tr>
<td>Na(_2)TiO(_3)</td>
<td>Anode</td>
<td>40</td>
<td>5 000</td>
</tr>
</tbody>
</table>

Tin anode material gave the highest specific capacity (400 mAhg\(^{-1}\)), however this was achieved at the lowest charge-discharge cycles of 150 (Table 2.2). Tin behaves similar to other sodium-alloying metals such as antimony and silicon deliver high capacity, however the large volume expansion during charge-discharge cycles causes cracking, pulverization, loss of electrical contact, and unstable solid electrolyte interphase which inevitably leads to fading of capacity and thus short life cycle [40, 52, 87]. Excessive volume expansion has been successfully controlled by integration, coating or confinement of sodium-alloying metals or their oxides with materials that do not underdo volume change or with insignificant volume change during cycling. Wu et al. [87] successfully controlled volume change of silicon nanotube anode material by confining them inside ion-permeable silicon oxide shells. The team delivered high reversible capacity of 1780 mAhg\(^{-1}\) at C/5 for 6000 cycles while retaining more than 85% of their initial capacity when tested in lithium half cells [87]. Liang et al. [88] incorporated TiO\(_2\), which has insignificant volume change of 3 ─ 4% when intercalating Li\(^+\), by anchoring it alongside SnO\(_2\) on graphene sheets. The graphene-SnO\(_2\)-TiO\(_2\)
nanocomposite delivered high reversible capacity (499.3 mAhg\(^{-1}\) at 0.2C) for 50 cycles when tested in a LIBs. The TEM and SEM images of the graphene-SnO\(_2\)-TiO\(_2\) showed well dispersed nanoparticles on expanded sheets. Consequently, the team attributed the good performance on the reduction of agglomeration of SnO\(_2\) due to the presence of TiO\(_2\) [88]. Whilst Lu et al. [76] reduced volume expansion of SnO\(_2\) particles by coating with carbon, which has a fixed volume [52]. This Na-SnO\(_2\)/C cell delivered high reversible capacities of 411 mAhg\(^{-1}\) at 50 mAhg\(^{-1}\) with 58% capacity retention over 50 cycles [76].

On the other hand, titanium-based anode material and Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C as cathode active material retain their capacity for the highest number of charge-discharge cycles (Table 2.2), several thousand for titanium material and up to 30 000 for Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C [40]. Unfortunately, these features are attained at low capacities (<150 mAhg\(^{-1}\)).

For sodium-ion batteries to be able to compete with and eventually replace LIBs, they will need to provide 2 — 4 Wh of energy required for mobile phones and 30 — 100 Wh for laptops [10] with a minimum of 200–300 cycles and an 80% capacity retention [40]. The consumer market, largely driven by mobile phones and laptop sales, is currently predominantly powered by the LiCoO\(_2\) battery. The LiCoO\(_2\) battery consists of a LiCoO\(_2\) cathode (155 mAhg\(^{-1}\)) with graphite anode (350 mAhg\(^{-1}\)), providing an operational voltage of 3.8 V and specific energy of 408 Whkg\(^{-1}\) (based on the electrode materials only) [40]. SIBs are gradually approaching these specifications as Sawicki and Shaw [40] observed that a battery constructed from Na\(_{1.5}\)VPO\(_{4.8}\)F\(_{0.7}\) and carbon nanostructure as the active cathode and anode material, respectively could provide an operational voltage of 3.3 V and a specific capacity of 299 Whkg\(^{-1}\) with a 95% capacity retention during its 210 cycle life (Table 2.2). However further research is required to enhance the specific energy and life cycle of SIBs, through the optimization of the individual components of this battery if they are to replace LIBs.

In this regard, this research aims at improving the specific energy and reducing volume expansion thus increasing life cycle of SIBs with rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) ternary nanocomposites as active anode material.

### 2.8.1 Incorporating nano-carbons

Graphene refers to 1 — 10 layers of carbon atoms in a hexagonal honeycomb lattice that are bound together by sp\(^2\) covalent bonds [89, 90]. The first physical study of the properties of graphene was by Novoselov et al. [91], after successful mechanical exfoliation of the graphitic layers from graphite, before then the study of this graphitic material was theoretical as it was reputed not to exist [90]. These properties include: 1) high specific surface area [92-97], theoretically predicted to be ~2600 m\(^2\)g\(^{-1}\) [96] and experimentally demonstrated to range between 270 m\(^2\)g\(^{-1}\) — 1550 m\(^2\)g\(^{-1}\) using the Brunauer, Emmett and Teller (BET) method, depending on synthesis method used [96]. The high
surface area is an appealing feature in an electrode material as it can provide more active sites during the de/intercalation process [94]. 2) good thermal stability [94], thus broadening the operating temperature range of the battery. 3) superior thermal conductivity [89, 92, 93] at 5000 Wm\(^{-1}\)K\(^{-1}\) is a thousand times larger than that of copper [94]. 4) strong mechanical strength [92]. Graphene is reported as the “strongest material ever tested” [98] with a Young’s modulus of 1.0 TPa and a stiffness of 130 GPa [94]. In addition, graphene is an appealing electrode material because of the abundance and low cost of its raw material. Carbon is the fourth most common element in the universe often recovered in its elemental forms (i.e., coal, graphite, and diamond) [99]. The recoverable resources of graphite, the most commonly used graphene precursor, are reported to be 800 million tons worldwide as reported by USGS in their Mineral Commodity Summaries 2018 report [30].

There are many methods available to synthesize graphene [94, 96, 99]. However, at present, chemical exfoliation of graphitic material is the accepted method for high yield of graphene at low costs [94]. Chemical synthesis of graphene involves the formation of graphite oxide, by reacting graphite with strong oxidizing agents thus intercalating oxygen-containing functional groups within the graphitic layers which increases the interlayer spacings [89]. The increased space between the layers weakens their interaction and leads to their separation in aqueous solution [94]. The exfoliated graphite oxide sheets are then chemically reduced to yield graphene [89]. Chemically synthesized graphene is not completely de-oxygenated and contains some defects, therefore to distinguish it from pristine graphene it is denoted as reduced graphene oxide.

When used as an anode material in sodium-ion batteries, it delivered high reversible capacity (141 mAh\(^{-1}\)) at low current densities (40 mAh\(^{-1}\)) for long cycle life (>1000 cycles) or moderate reversible capacity (93.3 mAh\(^{-1}\)) for high currents densities (200 mAh\(^{-1}\)) at a short cycle life (250 cycles) [72].

2.8.2 Design of the Ternary oxide nanocomposites

Tin Oxide (SnO\(_2\)) is being considered in this research as part of the active material in the negative electrode of a SIB due to its high theoretical capacity (667 mAh\(^{-1}\) for SIBs) [100], low costs [101], large reserves [30] and good safety [101]. Su at al. [86] used hydrothermally synthesized ~60 nm SnO\(_2\) nanoparticles as anode material for SIB. These nanocrystals exhibited high reversible capacity of 432 mAh\(^{-1}\) even after 100 cycles [86]. When Su at al. [102] embedded SnO\(_2\) nanoparticles in graphene to restrain the excessive volume expansion characteristic of SnO\(_2\) nanoparticles during charge–discharge, the SnO\(_2\)@graphene nanocomposite anode exhibited higher reversible capacity of 638 mAh\(^{-1}\) with virtually no loss in capacity within 100 cycles compared to the 432 mAh\(^{-1}\) of the pristine SnO\(_2\) nanoparticles.
Iron (III) oxide ($\text{Fe}_2\text{O}_3$) has appealing features that make it a desirable active anode material such as environmental safety, low costs [97], abundant raw material [30], high capacity and good cycling performance [97]. Unfortunately, similar to SnO$_2$ it has severe volume change during cycling. However, when graphene is integrated with Fe$_2$O$_3$ nanoparticles, excessive volume expansion is limited [97], as graphene prevents aggregation of iron oxide nanoparticles [103]. For example, when Jian et al. [97] anchored Fe$_2$O$_3$ nanocrystals on graphene nanosheets, the Fe$_2$O$_3$@graphene nanosheets as anode material delivered a high reversible capacity of 400 mAhg$^{-1}$ which was retained for over 200 cycles at a current density of 100 mAhg$^{-1}$ [97].

Titanium dioxide (TiO$_2$) is exceptionally stable, non-toxic, economical [85], abundant [30], has insignificant volume change (3 ─ 4%) during cycling [104], long life cycle and cycle stability as anode material [88]. Xu et al. used anatase TiO$_2$ nanocrystals as anode material in a sodium-ion battery, which delivered 150 mAhg$^{-1}$ reversible capacity for over 100 cycles [104]. When the TiO$_2$ nanospheres were supported on graphene, the rGO-TiO$_2$ nanocomposite yielded a higher reversible capacity (208 mA hg$^{-1}$) compared to the pristine TiO$_2$ nanoparticles (150 mAhg$^{-1}$) for a longer cycle life of over 300 cycles [84].

Composites containing titanium dioxide and/or iron (III) oxide and/or tin oxide and/or graphene such as SnO$_2$-Fe$_2$O$_3$ [105], SnO$_2$-TiO$_2$ [106], Fe$_2$O$_3$-TiO$_2$ [107], graphene-Fe$_2$O$_3$-SnO$_2$ [16, 108], graphene-SnO$_2$-TiO$_2$ [13, 14, 88, 109] have exhibited enhanced electrochemical performance compared to the individual components when used as electrode material. This has been attributed to the combined effect of the unique properties contributed by the individual components in the composites. There is however, limited information in literature of composites of all three metal oxides of interest and graphene as electrode material for either SIBs or LIBs. Hence this research, to study the properties and effects of such a composite as an electrode material in SIBs.

The design of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites as active anode material for sodium-ion battery is based on the synergistic effects of the following principles as observed in the hybrids and rGO-binary metal oxides as reported in literature:

- High specific capacities of SnO$_2$ and Fe$_2$O$_3$
- Fixed volume of graphene oxide and insignificant volume change of TiO$_2$ to mitigate extreme volume change and agglomeration of transition metal oxides during cycling thus maintaining capacity and increasing life cycle of the SIB. As a result, the metal oxides are confined between the graphene sheets and the TiO$_2$ coating to moderate reduce the extreme volume change and agglomeration experienced by these metal oxides during cycling.
- Exceptional electron transport capabilities of reduced graphene oxide.
2.9 Key Findings and Conclusions

Lithium-ion batteries have become a crucial part of modern life as an energy source / storage device in the consumer, automotive, industrial and energy storage sectors. Since 2010, the global lithium-ion battery consumption has increased by 23% annually. This growing demand of LIBs is projected to surpass mineral and brine deposits, which are currently the economical and practical sources of lithium. Despite the fact that sea water is estimated to contain an “unlimited” supply of lithium (>2,000,000 million tons), the processes presently available are not feasible or practical to recover lithium on a large scale from this source. Therefore, an alternative is needed.

Sodium-ion technology research has been renewed as the plausible replacement of LIBs. The main reasons that make sodium a credible alternative are the abundance, even distribution and feasible recovery of its resources thus making it an economical choice. In addition, sodium and lithium have similar chemistries thus similar chemical storage mechanism when used in a battery. Therefore, the technology and expertise gathered over the years for LIBs can most often be utilized for SIBs successfully. Lastly, the energy density of the SIBs are virtually comparable to those of the LIBs, despite the slight inherent difference due to the weight and radius difference of their ions, when suitable candidates of anode and cathode materials are used.

To date, the best anode material for SIBs has been demonstrated to be the hybrids of sodium-alloying materials and carbon. Whilst the best cathode material is reported to be phosphate-based materials.
2.10 References


CHAPTER 3: MATERIAL AND METHODS

3 Overview

This chapter describes the research design, chemicals, materials, synthesis methods and the characterization techniques used in this investigation.

3.1 Research design and scope

The research design and scope of this work is indicated in the flow diagram below.

Figure 3.1: Detailed schematic illustration of the research design and scope.
3.2 Reagents and materials

All the chemicals used in this investigation were used as received without further purification. The chemicals and materials used for the synthesis of nanomaterial and the fabrication of working electrodes are listed in Table 3.1.

Table 3.1: List of chemicals and materials for the synthesis of nanomaterial and fabrication of working electrodes.

<table>
<thead>
<tr>
<th>Chemical / Material</th>
<th>Chemical Formula</th>
<th>Notes</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite powder</td>
<td>C</td>
<td>&lt;20μm, synthetic</td>
<td>Sigma-Aldrich, Switzerland</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>KMnO₄</td>
<td>AR, min. 99.0%</td>
<td>Merck, South Africa</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>AR, (95 – 99)%</td>
<td>Merck, South Africa</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>AR, min. 85.0%</td>
<td>Merck, South Africa</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>30 wt. %</td>
<td>Sigma-Aldrich, Germany</td>
</tr>
<tr>
<td>Absolute alcohol</td>
<td>C₂H₅OH</td>
<td>AR, min. 99.5%</td>
<td>Merck, South Africa</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>CP, (30 – 33)%</td>
<td>Crest Chemicals</td>
</tr>
<tr>
<td>pH indicator strips</td>
<td>N/A</td>
<td>Non-bleeding, pH 0 -14</td>
<td>Merck, Germany</td>
</tr>
<tr>
<td>Titanium isopropoxide</td>
<td>C₁₂H₂₈O₄Ti</td>
<td>27.8% - 28.6%</td>
<td>SRLChem, India</td>
</tr>
<tr>
<td>Stannous chloride</td>
<td>SnCl₂·2H₂O</td>
<td>ACS, (98.0 – 103.0)%</td>
<td>Merck, Germany</td>
</tr>
<tr>
<td>Ferric chloride hexahydrate</td>
<td>FeCl₃·6H₂O</td>
<td>AR, (99 – 102)%</td>
<td>Sigma-Aldrich, Germany</td>
</tr>
<tr>
<td>Iron (II) chloride tetrahydrate</td>
<td>FeCl₂·4H₂O</td>
<td>ReagentPlus, 98%</td>
<td>Sigma-Aldrich, Germany</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>NH₄OH</td>
<td>AR, min. 25%</td>
<td>Merck, South Africa</td>
</tr>
<tr>
<td>Polyvinylidene fluoride</td>
<td>-(C₂H₅F₂)ₓ</td>
<td>Melt viscosity 27.18 K Poise</td>
<td>Alfa Aesar, Germany</td>
</tr>
<tr>
<td>1-methyl-2-pyrrolidene</td>
<td>C₅H₉NO</td>
<td>99+%</td>
<td>Alfa Aesar, Germany</td>
</tr>
<tr>
<td>Copper foil</td>
<td>Cu</td>
<td>0.025mm, 99.8%</td>
<td>Alfa Aesar, Germany</td>
</tr>
<tr>
<td>Sodium perchlorate monohydrate</td>
<td>NaClO₄·H₂O</td>
<td>ACS, (85.0-90.0%)</td>
<td>Merck, Germany</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>C₄H₆O₃</td>
<td>Anhydrous, 99.7%</td>
<td>Merck, Germany</td>
</tr>
<tr>
<td>Molecular sieve, 4Å</td>
<td>Na₂O·Al₂O₃·2SiO₂·9/2H₂O</td>
<td>Density = 0.00g/mL</td>
<td>VWR BDH Chemicals, Belgium</td>
</tr>
</tbody>
</table>
3.3 Methodology

This section focuses on the method used for the synthesis of graphene oxide and the methods used for its modification with layers of 1:1:1 TiO\textsubscript{2} : SnO\textsubscript{2} : Fe\textsubscript{2}O\textsubscript{3} nanomaterial in different possible combinations.

3.3.1 Synthesis of graphene oxide: Improved method

The improved synthesis of graphene oxide method [1] with adaptation was used to synthesize graphene oxide (GO). 3.0027 grams of synthetic graphite powder was weighed out into a 1000-mL round bottom flask. The round bottom flask was placed into an ice-water bath on a magnetic stirrer plate, then 360-mL of H\textsubscript{2}SO\textsubscript{4} was added slowly while moderately stirring. This mixture was left to stir for 30 minutes, then 40-mL of H\textsubscript{3}PO\textsubscript{4} was slowly added while moderate stirring of the mixture was maintained. Subsequently, 18.0266 grams of KMnO\textsubscript{4} was added slowly to the mixture, a spatula full every minute, while stirring. After each addition, the mixture was left to stir until all the KMnO\textsubscript{4} had visibly reacted before addition of another amount. The mixture was left to stir in ice-water for 30 minutes after all the KMnO\textsubscript{4} was added. Then continued to stir without ice-water until the mixture reached room temperature. The round bottom flask was then inserted into silicon oil on a hot plate, whose temperature had been controlled overnight to approximately 50˚C. The mixture was stirred slowly for 24 hours at 50˚C. The resultant pale purple mixture was decanted slowly into 400-mL ice, then 5-mL of 30% H\textsubscript{2}O\textsubscript{2} was added slowly while stirring turning the mixture a light brown color. The mixture was separated by centrifugation at 4000 rpm for 4 hours and the supernatant liquid discarded. The solid material was washed by centrifugation in succession twice each, with 200-mL deionized water, 200-mL 30% HCl and 200-mL absolute ethanol at 4000 rpm for 10 minutes each whilst the supernatant liquid was decanted away. The separated GO was dried in an oven at 50˚C for 72 hours, left to cool naturally to room temperature and then weighed. The final yield of the synthesized graphene oxide was 3.5459 grams. The synthesized graphene oxide was then pulverized with a pestle in mortar and stored in a glass polytop vial.

3.3.2 Synthesis of TiO\textsubscript{2}: Solvothermal method

The TiO\textsubscript{2} nanocomposites were prepared using the solvothermal method as previously reported [2]. 225-mL of absolute ethanol was measured with a measuring cylinder and transferred into a dry 400-mL beaker on a magnetic stirrer plate. The absolute ethanol was stirred vigorously while 6.2707 grams of titanium isopropoxide was added drop-wise. The mixture was left to stir vigorously for 30 minutes after adding all the titanium isopropoxide. Then 9-mL of deionized water was added drop-wise while vigorously stirring, turning the clear, transparent mixture cloudy. Vigorous stirring was
maintained for 30 minutes after all the deionized water had been added. The cloudy mixture was then divided into four parts with a measuring cylinder (100-mL, 52-mL, 52-mL and 30-mL) and then transferred into 200-mL, 100-mL, 100-mL and 50-mL Teflon lined stainless steel autoclaves respectively. The autoclaves were placed in the oven set at 180˚C for 8 hours. Subsequently, the autoclaves were left to reach room temperature naturally. The cloudy mixture from the autoclaves was recombined in a dry 400-mL beaker, then separated using a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid was discarded whilst the white solid was washed using a centrifuge at 7000 rpm for 10 minutes with absolute ethanol and then deionized water, three times each. The separated white solid was then dried at 50˚C in an oven overnight and left to reach room temperature naturally before weighing. The final yield of the TiO$_2$ nanoparticles was 1.9890 grams. The synthesized TiO$_2$ nanoparticles were then powdered with a pestle in mortar and stored in a glass polytop vial.

### 3.3.3 Synthesis of SnO$_2$: Hydrothermal method

The SnO$_2$ nanoparticles were prepared using the hydrothermal method according to literature [2]. 225-mL of deionized water was measured with a measuring cylinder and transferred into a dry 400-mL beaker. The deionized water was stirred vigorously with a magnetic stirrer. Subsequently, 2.7164 grams of SnCl$_2$·2H$_2$O was weighed into a 100-mL beaker then added slowly into the deionized water while vigorous stirring was maintained. The mixture was left to stir vigorously for 30 minutes after all the SnCl$_2$·2H$_2$O was added. The resultant transparent mixture was divided with a measuring cylinder into 100-mL, 50-mL, 50-mL and 25-mL, which were decanted into 200-mL, 100-mL, 100-mL and 50-mL Teflon lined stainless steel autoclaves respectively. The autoclaves were heated at 180˚C in an oven for 12 hours then left to reach room temperature naturally. Subsequently, the mixture from all four autoclaves were decanted into a dry 400-mL beaker. The combined mixture was separated with a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid was decanted away. Whilst the solid was washed three times with deionized water using a centrifuge at 7000 rpm for 10 minutes. The separated pale-yellow solid was dried at 50˚C in an oven overnight and left to reach room temperature naturally before weighing. The final yield of the SnO$_2$ nanoparticles was 0.3616 grams. The synthesized SnO$_2$ nanoparticles were ground with a pestle in mortar then stored in a glass polytop vial.

### 3.3.4 Synthesis of γ-Fe$_2$O$_3$: Gravimetric method

The γ-Fe$_2$O$_3$ nanoparticles were prepared using the co-precipitation method as previously reported [3]. 1.4051 grams FeCl$_3$·6H$_2$O and 0.9612 grams FeCl$_2$·4H$_2$O were weighed out into a 600-mL beaker. Then 350-mL of deionized water was measured with a measuring cylinder and transferred into the 600-mL beaker with the weighed iron salts. The weighed FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O salts
were dissolved in deionized water by moderate stirring for 30 minutes with a magnetic stirrer. Subsequently, 2.5-mL of ammonia solution was added drop-wise into the honey colored mixture while stirring to precipitate the $\gamma$-Fe$_2$O$_3$ nanoparticles. The resultant dark brown mixture was stirred moderately for 5 minutes. An additional 2.5-mL of ammonia solution was added drop-wise into the dark brown colored mixture turning the mixture black. Moderate stirring was then maintained for 30 minutes. The synthesized $\gamma$-Fe$_2$O$_3$ nanoparticles were separated by a magnet and washed using a centrifuge at 7000 rpm for 10 minutes, three times with absolute ethanol. Whilst the supernatant liquid was decanted away. The separated black solid was dried at 50°C in an oven overnight then left to reach room temperature naturally before weighing. The final yield of the $\gamma$-Fe$_2$O$_3$ nanoparticles was 0.7370 grams. The synthesized $\gamma$-Fe$_2$O$_3$ nanoparticles were pulverized with a pestle in mortar then stored in a glass polytop vial.

### 3.3.5 Synthesis of rGO-SnO$_2$: Hydrothermal method

The rGO-SnO$_2$ nanocomposite was prepared using the hydrothermal method according to literature [2]. 0.2677 grams of the synthesized powdered graphene oxide was weighed out into a 400-mL beaker. Then 225-mL of deionized water measured with a measuring cylinder was decanted into the 400-mL beaker with GO. The beaker was immersed into an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the graphene oxide. Subsequently, the brown mixture was stirred vigorously using a magnetic stirrer. Then 2.6969 grams of SnCl$_2$·2H$_2$O was weighed into a 100-mL beaker then added slowly into the GO dispersion while vigorous stirring was maintained. Vigorous stirring was maintained for 30 minutes after adding all the SnCl$_2$·2H$_2$O. The mixture was then divided with a measuring cylinder into 100-mL, 50-mL, 50-mL and 25-mL, which were decanted into 200-mL, 100-mL, 100-mL and 50-mL Teflon lined stainless steel autoclaves respectively. The autoclaves were heated at 180°C for 12 hours in an oven. After thermal treatment, the autoclaves were left to reach room temperature naturally. The brown mixture was recombined in a 400-mL beaker then separated using a centrifuge at 7000 rpm for 10 minutes while the supernatant liquid was decanted away. The separated brown solid was washed three times with deionized water using a centrifuge at 7000 rpm for 10 minutes each time. The separated solid was then dried at 50°C in an oven overnight and left to cool to room temperature naturally before weighing. The final yield of the rGO-SnO$_2$ nanocomposite was 1.1868 grams. The synthesized rGO-SnO$_2$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

### 3.3.6 Synthesis of rGO-Fe$_2$O$_3$: Gravimetric method

The rGO-Fe$_2$O$_3$ nanocomposite was prepared using the co-precipitation method as previously reported [3]. 0.1214 grams of the powdered as-synthesized graphene oxide nanosheets were weighed out into a 250-mL beaker. Then 150-mL of deionized water measured with a measuring
cylinder was decanted into the 250-mL beaker with graphene oxide. The 250-mL beaker was immersed in an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the graphene oxide. Separately, 1.8709 grams FeCl$_3$·6H$_2$O and 0.6912 grams FeCl$_2$·4H$_2$O were weighed out into a 1000-mL beaker. Then 350-mL of deionized water was measured with a measuring cylinder and decanted into the 1000-mL beaker with the iron salts. The FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O salts were dissolved with deionized water by moderate stirring using a magnetic stirrer. The brown GO dispersion was added into the honey colored aqueous solution of Fe$^{2+}$ and Fe$^{3+}$ ions and moderately stirred for 2 hours at room temperature. After two hours, while continuously stirring, 1-mL of ammonia solution was added drop-wise into the mixture turning it dark brown. The mixture was left to stir for 5 minutes. Then an additional 1-mL of ammonia solution was added drop-wise into the mixture turning it black. Moderate stirring was maintained for 30 minutes. The precipitated rGO-Fe$_2$O$_3$ nanocomposite was separated using a magnet and the supernatant liquid discarded. The rGO-Fe$_2$O$_3$ nanocomposite was then washed using a centrifuge at 7000 rpm for 10 minutes, three times with absolute ethanol. The rGO-Fe$_2$O$_3$ nanocomposite was dried at 50˚C in an oven overnight then left to reach room temperature naturally before weighing. The final yield of the rGO-Fe$_2$O$_3$ nanocomposite was 0.9187 grams. The synthesized rGO-Fe$_2$O$_3$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

3.3.7 Synthesis of rGO-SnO$_2$-TiO$_2$

The rGO-SnO$_2$-TiO$_2$ nanocomposite was prepared using a combination of the solvothermal and hydrothermal methods as previously reported [2]. 0.1274 grams of the powdered graphene oxide was weighed out into a 250-mL beaker. Then 100-mL of deionized water measured with a measuring cylinder was decanted into the 250-mL beaker with GO. The beaker was then placed in an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the graphene oxide nanosheets. The graphene oxide dispersion was then moderately stirred using a magnetic stirrer. 1.2039 grams of SnCl$_2$·2H$_2$O was weighed into a weighing boat then added slowly into the brown mixture while moderate stirring was maintained, no color change was observed. Moderate stirring was maintained for 30 minutes. The mixture was separated into two 50-mL with a measuring cylinder then transferred into two 100-mL Teflon lined stainless steel autoclaves. The two autoclaves were heated in an oven at 180˚C for 12 hours. The brown mixture was recombined in a 250-mL beaker then separated with a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid decanted away. The separated brown solid (i.e. rGO-SnO$_2$ nanocomposite) was washed using a centrifuge at 7000 rpm for 10 minutes, with deionized water three times.

The as-prepared rGO-SnO$_2$ nanocomposite was decanted into a 250-mL beaker using 100-mL of absolute ethanol. The beaker was then immersed in the ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the rGO-SnO$_2$ nanocomposite. The brown mixture was then moderately stirred using a magnetic stirrer. 2.7177
grams of titanium isopropoxide was weighed into a 100-mL beaker then added drop-wise into the rGO-SnO$_2$ nanocomposite dispersion while moderate stirring was maintained. Moderate stirring was maintained for 30 minutes. Subsequently, 4-mL of deionized water was added drop-wise while moderately stirring the mixture. The resultant milky-brown mixture was left to stir for another 30 minutes. Then decanted into a 200-mL Teflon lined stainless steel autoclave and placed in an oven at 180˚C for 8 hours. Subsequently, the mixture was left to reach room temperature before separation by centrifugation at 7000 rpm for 10 minutes. The supernatant liquid was decanted away whilst the solid material, i.e. rGO-SnO$_2$-TiO$_2$ nanomaterial was washed using a centrifuge at 7000 rpm for 10 minutes, with absolute ethanol and then deionized water, three times each. The separated brown solid was dried at 50˚C in an oven overnight, then left to cool to room temperature before weighing. The final yield of the rGO-SnO$_2$-TiO$_2$ nanocomposite was 0.8864 grams. The synthesized rGO-SnO$_2$-TiO$_2$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

### 3.3.8 Synthesis of rGO-SnO$_2$-Fe$_2$O$_3$

The rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was prepared using a combination of the hydrothermal and co-precipitation method as previously reported [2, 3]. 0.1229 grams of the powdered as-synthesized graphene oxide was weighed into a 250-mL beaker. Then 100-mL of deionized water measured with a measuring cylinder was transferred into the beaker with the weighed graphene oxide. The beaker was then placed into an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the graphene oxide nanosheets. The brown graphene oxide dispersion mixture was then moderately stirred using a magnetic stirrer. 1.2040 grams of SnCl$_2$·2H$_2$O was weighed into a weighing boat then added slowly into the brown mixture while moderate stirring was maintained (no color change was observed). Moderate stirring was maintained for 30 minutes after adding all the SnCl$_2$·2H$_2$O. The brown dispersion was decanted into a 200-mL Teflon lined stainless steel autoclave and placed in an oven at 180˚C for 8 hours. Subsequently, the mixture was left to reach room temperature and then separated by centrifugation at 7000 rpm for 10 minutes. The supernatant liquid was decanted away whilst the solid material, i.e. rGO-SnO$_2$ nanomaterial was washed using a centrifuge at 7000 rpm for 10 minutes, with deionized water three times.

Subsequently, the separated rGO-SnO$_2$ nanocomposite was decanted into a 250-mL beaker with 150-mL of deionized water. The beaker was placed in an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the rGO-SnO$_2$ nanomaterial. Separately, 1.8746 grams FeCl$_3$·6H$_2$O and 0.6917 grams FeCl$_2$·4H$_2$O were weighed out into a 1000-mL beaker. Then 350-mL of deionized water measured with a measuring cylinder was added before moderately stirring the mixture for 30 minutes to dissolve the iron salts. The brown rGO-SnO$_2$ dispersion was slowly added to the amber colored, aqueous solution of Fe$^{2+}$ and Fe$^{3+}$ ions whilst moderately stirring. Moderate stirring was maintained for 2 hours at room temperature. After two hours, while continuously stirring, 1-mL of ammonia solution was added drop-wise into the
mixture, turning it dark brown. The dark brown mixture was moderately stirred for five minutes. Then, 1-mL of ammonia solution was added drop-wise into the mixture, turning it black. The mixture was moderately stirred for 30 minutes. The rGO-SnO$_2$-Fe$_2$O$_3$ precipitate was left to settle then separated with a magnet. The supernatant liquid was discarded. The separated rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was washed using a centrifuge at 7000 rpm for 10 minutes, three times with absolute ethanol. Then dried at 50°C in an oven overnight. The rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was cooled to room temperature naturally before weighing. The final yield of the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was 1.2062 grams. The synthesized rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

3.3.9 Synthesis of rGO-Fe$_2$O$_3$-SnO$_2$

The rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite was prepared using a combination of the hydrothermal and co-precipitation method as previously reported [2, 3]. 0.1254 grams of the powdered as-synthesized graphene oxide was weighed out into a 250-mL beaker. Then 150-mL of deionized water measured with a measuring cylinder was added in the 250-mL beaker with graphene oxide. The beaker was then placed inside an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the GO. Separately, 1.8799 grams of FeCl$_3$·6H$_2$O and 0.6932 grams of FeCl$_2$·4H$_2$O were weighed out into a 1000-mL beaker. Then 350-mL of deionized water measured with a measuring cylinder was added before moderately stirring the mixture for 30 minutes to dissolve the iron salts. The brown GO dispersion was slowly added to the yellowish-brown colored iron salt mixture whilst moderately stirring. Moderate stirring was maintained for 2 hours at room temperature. After two hours, while continuously stirring, 1-mL of ammonia solution was added drop-wise into the mixture. The resultant dark brown mixture was moderately stirred for five minutes. Then, 1-mL of ammonia solution was added drop-wise into the mixture. The subsequent black mixture was left to settle then separated with a magnet. The supernatant liquid was discarded. The separated rGO-Fe$_2$O$_3$ nanocomposite was washed using a centrifuge at 7000 rpm for 10 minutes, three times with absolute ethanol. Then the rGO-Fe$_2$O$_3$ nanocomposite was decanted into a 250-mL beaker with 150-mL of deionized water. The beaker was immersed in the ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the synthesized rGO-Fe$_2$O$_3$ nanocomposite. The rGO-Fe$_2$O$_3$ dispersion was then stirred moderately using a magnetic stirrer. Subsequently, 1.2034 grams of SnCl$_2$·2H$_2$O was weighed into a 100-mL beaker then slowly added into the rGO-Fe$_2$O$_3$ dispersion while moderately stirring. Moderate stirring was maintained for 30 minutes. The mixture was separated into 100-mL and 50-mL with a measuring cylinder, which were then decanted into a 200-mL and 100-mL Teflon lined stainless steel autoclaves respectively. The autoclaves were heated in an oven at 180°C for 12 hours, then left to reach room temperature naturally. The mixture from the two autoclaves was combined in a 250-mL beaker then separated
using a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid was discarded and the solid washed using a centrifuge at 7000 rpm for 10 minutes, three times with deionized water. The separated rGO-Fe₂O₃-SnO₂ solid was dried at 60°C in an oven overnight, then cooled to room temperature naturally before weighing. The mass of the dried rGO-Fe₂O₃-SnO₂ nanocomposite was 1.2198 grams. The synthesized rGO-Fe₂O₃-SnO₂ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

3.3.10 Synthesis of rGO-Fe₂O₃-TiO₂

The rGO-Fe₂O₃-TiO₂ nanocomposite was prepared using a combination of the co-precipitation and solvothermal method as previously reported [2, 3]. 0.1227 grams of graphene oxide were weighed out into a 250-mL beaker. Then 120-mL of deionized water was measured with measuring cylinder then transferred into the 250-mL beaker with graphene oxide. The beaker was then placed in the ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the graphene oxide. Separately, 1.8925 grams of FeCl₃·6H₂O and 0.6906 grams of FeCl₂·4H₂O were weighed out into an 800-mL beaker. Then dissolved with 300-mL of deionized water by moderate stirring on a magnetic stirrer plate at room temperature. The amber colored iron salts mixture was continuously stirred while the brown graphene oxide dispersion was added slowly. The resultant mixture was moderately stirred for 2 hours. After two hours, 1-mL of ammonium solution was added drop-wise, turning the brown mixture dark brown. The dark brown solution was left to stir for five minutes. Then, 1-mL of ammonium solution was added drop-wise, turning the dark brown mixture black. The mixture was separated with a centrifuge at 7000 rpm for 5 minutes. The supernatant liquid was discarded and the black solid (i.e. rGO-Fe₂O₃ nanocomposite) was washed using a centrifuge at 7000 rpm for 10 minutes, with absolute ethanol three times.

The synthesized rGO-Fe₂O₃ nanocomposite was decanted into a 250-mL beaker using 100-mL absolute ethanol. The beaker was placed inside an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the rGO-Fe₂O₃ nanocomposite. Then vigorously stirred on a magnetic stirrer plate at room temperature. Subsequently, 2.8286 grams of titanium isopropoxide were weighed into a 100-mL beaker and added drop-wise the brown rGO-Fe₂O₃ dispersion while stirring vigorously (no color change was observed). Vigorous stirring was maintained for 30 minutes. Then 4-mL of deionized water was added drop-wise turning the mixture a milky-brown color. The milky-brown mixture was stirred vigorously for 30 minutes. Then separated into two 52-mL with a measuring cylinder which were decanted into two 100-mL Teflon lined stainless steel autoclaves for thermal treatment in an oven at 180°C for 8 hours. The autoclaves were left to reach room temperature before the mixture was recombined in a 250-mL beaker. The combined mixture was transferred into centrifuge tubes to be separated at 7000 rpm for 10 minutes with a centrifuge. The supernatant liquid was discarded. The separated solid was washed using a centrifuge at 7000 rpm for 10 minutes, with absolute ethanol and then deionized water, three times each. The
separated solid, i.e. rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite was dried at 50°C in an oven overnight, then left to reach room temperature before weighing. The final yield of the rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite was 1.6647 grams. The synthesized rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

3.3.11 Synthesis of rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$

The rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite was prepared using a combination of the solvothermal, hydrothermal and co-precipitation methods as previously reported [2, 3]. 0.1193 grams of the pulverized, as-synthesized graphene oxide was weighed out into a 250-mL beaker. Then 100-mL of deionized water measured with a measuring cylinder was added into the GO beaker. The beaker was immersed in an ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for 30 minutes to disperse the graphene oxide nanosheets. In the intervening time, 1.1944 grams of SnCl$_2$·2H$_2$O were weighed into a weighing boat. The beaker with the graphene oxide dispersion was removed from the ultrasonic bath and placed on a magnetic stirrer plate, then moderately stirred at room temperature. Whilst stirring, the weighed SnCl$_2$·2H$_2$O was added slowly into the brown dispersion without any apparent color change. Moderate stirring of the brown dispersion was maintained for 30 minutes. The mixture was then divided into two 50-mL’s with a measuring cylinder, then transferred into two 100-mL Teflon lined stainless steel autoclaves. The autoclaves were heated in an oven at 180°C for 12 hours, then left to cool to room temperature. The mixture was combined in a 250-mL beaker then separated with a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid was discarded. The black and white solid was washed three times with deionized water using a centrifuge at 7000 rpm for 10 minutes each.

The as-synthesized rGO-SnO$_2$ nanocomposite was transferred into a 250-mL beaker using 150-mL of deionized water. Then dispersed by placing the rGO-SnO$_2$ nanocomposite/water mixture in the ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour. Separately, 1.9030 grams of FeCl$_3$·6H$_2$O and 0.6921 grams of FeCl$_2$·4H$_2$O were weighed out into a 1000-mL beaker. Then 400-mL of deionized water was measured with a measuring cylinder then added into the weighed iron salts beaker. The beaker was then placed on a magnetic stirrer plate and the iron salts dissolved in deionized water at room temperature by moderate stirring. The honey colored aqueous solution of Fe$^{2+}$ and Fe$^{3+}$ ions was continuously stirred while the brown rGO-SnO$_2$ / water dispersion was added slowly. The resultant grey mixture was moderately stirred for 2 hours. After two hours, while continuously stirring, 2-mL of ammonia solution was added drop-wise into the mixture turning it a muddy-brown color. The mixture was left to stir for 5 minutes. Then, an additional 2-mL of ammonia solution was added drop-wise into the muddy-brown color mixture turning it a black color. The mixture was left to settle then separated with a magnet. The supernatant liquid was discarded and the black solid washed three times with absolute ethanol using a centrifuge at 7000 rpm for 10 minutes each time.
The synthesized rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite was transferred into a 250-mL beaker with 100-mL of absolute ethanol. The beaker was then placed in the ultrasonic bath (SciTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite. The resultant black mixture was vigorously stirred with a magnetic stirrer at room temperature. Then 2.8217 grams of titanium isopropoxide were added drop-wise into the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite dispersion. The mixture was left to stir moderately for 30 minutes. Subsequently, 4-mL of deionized water was added drop-wise while vigorously stirring, turning the mixture brown-black. The mixture was stirred moderately for 30 minutes, then decanted into a 200-mL Teflon lined stainless steel autoclave. The autoclave was heated at 180˚C for 8 hours in an oven. Then left to cool to room temperature naturally. The mixture was separated using a centrifuge at 7830 rpm for 4 hours and 30 minutes. The supernatant liquid was discarded. The brown-black solid was washed three times with absolute ethanol and then deionized water using a centrifuge at 7000 rpm for 10 minutes each. The separated solid, i.e. rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite was dried at 50˚C in an oven overnight, then left to reach room temperature before weighing. The final yield of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite was 2.0242 grams. The synthesized rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

### 3.3.12 Synthesis of rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$

The rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite was prepared using a combination of the solvothermal, hydrothermal and co-precipitation methods as previously reported [2, 3]. 0.1201 grams of the pulverized, as synthesized graphene oxide was weighed out into a 250-mL beaker. Then 150-mL of deionized water measured with a measuring cylinder was added into the GO beaker. The beaker was placed inside the ultrasonic bath (SciTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the graphene oxide nanosheets. In the meantime, 1.9280 grams of FeCl$_3$·6H$_2$O and 0.6906 grams of FeCl$_2$·4H$_2$O were weighed out into a 1000-mL beaker. Then mixed with 400-mL of deionized water measured with a measuring cylinder. The aqueous solution of Fe$^{2+}$ and Fe$^{3+}$ ions was stirred moderately using a magnetic stirrer at room temperature for 30 minutes. Then the GO dispersion was added slowly whilst moderately stirring was maintained. The resultant brown mixture was continuously stirred for two hours. After two hours, 2-mL of ammonium solution was added drop-wise turning the mixture a dark brown color. The dark brown mixture was left to stir for 5 minutes. Then, 2-mL of ammonium solution was added drop-wise turning the dark brown color to black. The mixture was separated with a centrifuge at 7000 rpm for 10 minutes. The supernatant liquid was discarded and the black solid (i.e. rGO-Fe$_2$O$_3$) was washed three times with absolute ethanol using a centrifuge at 7000 rpm.

The as-prepared GO-Fe$_2$O$_3$ nanocomposite was transferred from the centrifuge tubes using 100-mL of deionized water into a 250-mL beaker. The beaker was immersed in an ultrasonic bath (SciTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the rGO-Fe$_2$O$_3$.
nanocomposite. Then placed on a magnetic stirrer plate and the rGO-Fe$_2$O$_3$ dispersion moderately stirred at room temperature. Subsequently, 0.1955 grams of SnCl$_2$·2H$_2$O were weighed into a weighing boat then added slowly into the rGO-Fe$_2$O$_3$ dispersion while moderate stirring was maintained. The resultant mixture was stirred moderately for 30 minutes. Then decanted into a 200-mL Teflon lined stainless steel autoclave, which was then placed in an oven set at 180˚C for 12 hours. Afterwards, the autoclave was allowed to reach room temperature naturally. The cooled mixture was then separated with a centrifuge at 7830 rpm for 1 hour and 30 minutes. The supernatant liquid was discarded. Whilst the black solid (i.e. rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite) was washed three times with absolute ethanol using a centrifuge at 7000 rpm for 10 minutes.

The as-prepared rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite was transferred from the centrifuge tubes into a 250-mL beaker using 100-mL of absolute ethanol. The beaker was then placed in the ultrasonic bath (ScienTech ultrasonic cleaner 703, at Frequency: Hi and Power: 005) for one hour to disperse the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite. The beaker was then placed on a magnetic stirrer plate and the rGO-Fe$_2$O$_3$-SnO$_2$ dispersion moderately stirred. Subsequently, 2.8454 grams of titanium isopropoxide were weighed into a 100-mL beaker and then added drop-wise into the rGO-Fe$_2$O$_3$-SnO$_2$ dispersion whilst moderate stirring was maintained. The resultant black-brown mixture was continuously stirred for 30 minutes. Then 4-mL of deionized water was added drop-wise into the dispersion. Moderate stirring was continued for 30 minutes. The resultant mixture was the decanted into a 200-mL Teflon line stainless steel autoclave. The autoclave was heated at 180˚C for 8 hours in an oven. The autoclave was allowed to cool to room temperature naturally before the mixture was transferred into centrifuge tubes. Then separated at 7830 rpm for 1 hour 30 minutes using a centrifuge. The supernatant liquid was discarded. The brown-black solid was washed using a centrifuge at 7000 rpm for 10 minutes, with absolute ethanol and then deionized water, three times each. The separated solid, i.e. rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite was dried at 50˚C in an oven overnight, then left to reach room temperature before weighing. The final yield of the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite was 1.9404 grams. The synthesized rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite was pulverized with a pestle in mortar then stored in a glass polytop vial.

### 3.4 Physical and chemical characterization techniques

The physical-chemical properties of the synthesized graphene-based nanocomposites as well as the intermediary products were studied with the aim of conclusive identification using the following analytical techniques: FTIR, Raman spectroscopy, SEM, TEM, TGA, BET, UV-Vis spectroscopy, and XRD. This section discusses the information each technique can provide and its relevance to this investigation.
3.4.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is an absorption spectroscopy technique used for both qualitative and quantitative analysis of asymmetrical molecular species [4] in gas, liquid and solid samples [5, 6]. This is because asymmetrical molecules have a change in dipole moment and are therefore able to absorb infrared radiation [6]. The frequency of the infrared radiation absorbed by the molecule is identical and distinctive to the natural vibration frequency of the molecule. By comparison of the unknown sample spectra with that of pure compounds, the molecular species can be identified. In this research, all samples were solid materials ground to a powder. Approximately, 10 mg of each nanomaterial synthesized was mixed thoroughly with ~1000 mg of potassium bromide using a pestle & mortar. This mixture was pressed into pellets in a die at 40 psi, then analyzed using the PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

3.4.2 Raman spectroscopy

Raman spectroscopy is a non-destructive molecular spectroscopy technique that provides information on the identity, chemical composition and structure of molecules in a wide variety of sample types (e.g. aqueous solutions, powder, gas and liquid) across multiple fields of study [6]. It is however, restricted to molecules that have a change in polarizability during vibration when irradiated with light in the visible, near-infrared, or near ultraviolet range of the electromagnetic spectrum [4]. Raman spectra provide a “fingerprint” of the molecule under study and by evaluation of the spectra of the unknown sample with that of pure compounds, conclusive identification can be assumed. For this research, the powdered synthesized nanomaterial were analyzed without further treatment using the Alpha300 R Raman microscope by WITec.

3.4.3 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) is a molecular absorption spectroscopy technique used mostly for quantitative analysis of inorganic and organic species in any of the three phases of matter [7]. It is limited to molecules that contain pi bonds or atoms with lone pair electrons as energy of light in the ultraviolet/visible region (i.e. 190 nm – 800 nm wavelength) is insufficient to cause electron transitions in single bonds and is therefore not absorbed by such molecules [7]. By comparing the wavelength/s at peak of absorption/s, $\lambda_{\text{max}}$, on spectra of unknown compounds with those of pure compounds, the molecule can be identified. Unfortunately, ultraviolet-visible spectra do not have enough detail to allow conclusive identification of analyte species and are therefore used in combination with other analytical techniques for qualitative analysis [6]. In this research, approximately 1.5 mg of the synthesized nanomaterial were dispersed in 8-mL of deionized water by
sonication for 15 minutes. Then analyzed using the Shimadzu, UV-2450 ultraviolet-visible spectrophotometer, in the 190 nm – 800 nm wavelength range.

### 3.4.4 X-Ray powder diffraction

X-Ray powder diffraction (XRD) is an invaluable analytical technique used mostly for determining the identity, purity and crystallinity [4] of solid samples across a wide variety of disciplines, such as geology, engineering, and biology. It exploits the fact that each crystalline material has a unique powder diffraction pattern [6]. Positive match between the diffraction pattern of the unknown powder with that of the pure crystalline material typically yields unambiguous identification of the unknown compound [6]. For this research, the samples were powdered and homogenized using a pestle in mortar. Then analyzed with the X’Pert Pro core, Phillips X-ray diffractometer from PANalytical, at a scanning range of 4˚—90˚ 2θ and a radiation source of Cu Kα (0.154 nm).

### 3.4.5 Thermogravimetric Analysis – Differential Thermal Analysis

Thermogravimetric Analysis (TGA) is a thermal technique in which the mass of a sample is measured continually against increasing temperature or at constant temperature over time [6]. This information is used to determine the physical properties of material such as purity, solvent / water content, thermal stability and melting point. Whereas, Differential Thermal Analysis, DTA is a thermal technique in which the difference in temperature between the sample and an inert reference is measured and plotted while both are subjected to similar thermal conditions. It provides invaluable data of endothermic and exothermic processes of polymers, clays, minerals, metals, and alloys among others [6]. A TGA-DTA is a thermogravimetric analyzer coupled to a DTA analyzer, therefore simultaneously analyses the mass and temperature difference of a sample as a function of temperature. In this research, the powdered synthesized nanomaterial were analyzed without further treatment using the Hitachi Star7200RV Thermal Analysis system.

### 3.4.6 Scanning Electron Microscopy – Energy Dispersive X-ray spectroscopy

Scanning Electron Microscopy (SEM) is an electron optical microscope technique that provides information about the structure, texture and complexity of surfaces of solids [4, 6]. It scans the surfaces of thick or thin solid samples in a “rectangular pattern of parallel lines” [4, 6] using a beam of focused electrons to attain “magnification of x10 – x100 000 of images” [8]. It is however limited to samples that conduct electricity, therefore non-conducting samples are coated with a thin layer of metallic film before analysis [6]. Scanning Electron Microscopy with Energy Dispersive X-ray
spectroscopy, SEM/EDX is essentially the power of sample imaging at nanoscale coupled with X-ray analysis to provide identification and quantification of elements in a solid material. In this research, the aluminum stand / sample holder was covered with a carbon tape, then sprinkled with a thin layer of powdered as-synthesized nanomaterial. The metal oxides nanomaterial synthesized were further coated with a thin film of carbon using the Quorum_Q300T ES before analysis with the Vega 3 Tescan SEM/EDX microscope.

3.4.7 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) similar to Scanning Electron Microscopy, is an electron optical microscope technique. However, in TEM the beam of electrons are transmitted through a thin layer of sample to form an image [8]. This difference enables the TEM to provide further information of material such as particle size and shape at a superior resolution of 0.1 nm – 0.2 nm [8]. For this research, the samples were dispersed in absolute ethanol and sonicated for 10 minutes. A drop of this mixture was “drop-casted” on a carbon coated copper grid. The ethanol was left to dry before analysis using the JEM-2100 Electron microscope.

3.4.8 Brunauer-Emmett-Teller method

Brunauer-Emmett-Teller method (BET) is a thermodynamic technique used for the determination of surface area, pore size and pore size distribution on solids surfaces. It is based on the adsorption of a gas, usually nitrogen on the surface of a solid for the measurement of its specific surface area [4]. For this research, 200 mg – 300 mg of the powdered synthesized nanomaterial were analyzed without further treatment using the Micromeritics ASAP 2460 surface area and porosity analyzer.

3.5 Fabrication of the sodium-ion battery half-cells

The electrochemical performance of the synthesized ternary nanocomposites was evaluated in a PAT-Cell™, using a three-electrode cell half-cell. The half-cell consisted of an rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ or rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ working electrode in addition to a counter and a reference electrode made from sodium metal. The electrodes were physically separated by a glass fibre, however connected by an ion conductive 1 M NaClO$_4$ electrolyte solution. The cell was assembled in a nitrogen filled glove box with oxygen and moisture concentration of ≤0.5 ppm and 62 ppm – 69 ppm respectively.
3.5.1 Fabrication of the working electrodes

The working electrodes were assembled according to the modified method of Li et al. [9]. Explicitly, active material (rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ or rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite), binder (PVDF) and conductor (graphite) at a weight ratio of 80 : 10 : 10, were mixed into a slurry with an N-methyl-2-pyrrolidene solvent using a pestle in mortar. The slurry was subsequently cast on 18 mm diameter, 0.025 mm thick copper foil disk current collector using a doctor blade before drying overnight at 80°C in an oven. Please note that the active material was dried overnight at 80°C in an oven then left in a desiccator to cool before weighing.

3.5.2 Fabrication of the counter electrode

The counter electrode was made from a cube of sodium metal cut into 18 mm diameter, paper thin disk. The sodium metal was manipulated in paraffin inside a glove box. The paraffin was removed from the sodium disk with cyclohexane just before inserting into the PAT-Cell™.

3.5.3 Fabrication of the reference electrode

The reference electrode was an 18 mm diameter ring made from sodium metal supplied by EL-CELL Electrochemical test Equipment Company. It was used as received, without further treatment.

3.5.4 Fabrication of the electrolyte

Sodium perchlorate monohydrate salt (NaClO$_4$·H$_2$O) was dried overnight in the oven at 100°C then allowed to reach room temperature in a desiccator. Then 3.5115 grams of this salt was weighed out into a 25-mL volumetric flask. Then, dissolved and topped to the mark with propylene carbonate. The water content of the electrolyte solution was removed using molecular sieve. The molecular sieve was activated by drying at 300°C in an oven overnight. Then cooled to room temperature in a round bottom flask with an argon gas atmosphere. Subsequently, the cooled activated molecular sieve and NaClO$_4$/PC solution were decanted into a glass polytop vial. Then sealed with PTFE tape and transferred inside the glove box.
3.6 Electrochemical characterization techniques

The electrochemical properties of the synthesized nanomaterial were studied with the following electro-analytical techniques: cyclic voltammetry and charge/discharge cycle, in order to evaluate their performance as anode material in a sodium battery.

3.6.1 Cyclic Voltammetry

Cyclic Voltammetry (CV) is an electro-analytical method that can be used for quantitative measurements but is mostly used for qualitative analysis of organic, inorganic, biological and metal-organic systems [6]. In cyclic voltammetry, an analyte is exposed to a triangular potential wave excitation signal while its current response is measured [7]. The study of the resultant current versus applied potential plot, provides fundamental information on the redox processes, stability, electron transfer kinetics, and intercalation mechanisms of the analyte [10]. For this research, the Interface 1000 Potentiostat/Galvanostat/ZRA by Gamry instruments was used for the measurement of cyclic voltammetry of the synthesized nanomaterial.

3.6.2 Charge/discharge cycle

Charge/Discharge cycle is the process of supplying and draining electrical current to and from a rechargeable battery. The subsequent potential versus capacity and capacity versus cycle numbers plots provide information on the stability, capacity and longevity of the rechargeable battery. For this research, the charge/discharge cycle of the nanomaterial was measured with the aid of the Interface 1000 Potentiostat/Galvanostat/ZRA by Gamry instruments.
3.7 References


CHAPTER 4: RESULTS AND DISCUSSIONS

4 Overview

This chapter discusses in detail the physical and chemical properties of the synthesized nanomaterial and nanocomposites (Chapter 3, sub-sections 3.3.1 — 3.3.12) discovered during their characterization with the analytical techniques discussed in Chapter 3, section 3.4.1 — 3.4.8.

4.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis of nanomaterial and nanocomposites

Each powdered nanomaterial and nanocomposite synthesized was diluted x100 with potassium bromide salt, mixed thoroughly with a pestle in mortar then pelletized at 40 psi using a die. The pellets were analyzed using the PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer, in the 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) spectral range.

4.1.1 FTIR analysis of Graphite and Graphene Oxide (GO)

Graphene oxide in this research was prepared by oxidation of purchased synthetic graphite powder, through its treatment with strong aqueous oxidizing agents [1, 2]. This method forms graphene, 1 - 10 graphitic layers [3], by expanding and separating the graphite layers through addition of oxygen-containing functional groups [4] such as hydroxides and epoxides between the graphitic layers and carboxyl, carbonyl and phenols at the edges [5-7]. This was observed through the study and comparison of the FTIR spectra of synthesized graphene oxide and its synthetic graphite powder precursor (Figure 4.1).
Figure 4.1: FTIR spectra of purchased synthetic graphite powder and synthesized graphene oxide, GO. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

The intense, broad peak observed at 3427 cm\(^{-1}\) was assigned to the O-H stretching vibrations [2, 8-10] expected in the 3000 cm\(^{-1}\) — 3700 cm\(^{-1}\) range [8, 9] for adsorbed or surface water. Whereas the 1731 cm\(^{-1}\) peak (1720 cm\(^{-1}\) — 1740 cm\(^{-1}\)) [2] was assigned to the C=O stretching vibrations from carbonyl and carboxyl groups [2, 8-11], the peak at 1633 cm\(^{-1}\) has been attributed to the C=O stretching vibrations of the COOH group [12]. Lastly, the 1054 cm\(^{-1}\), 1221 cm\(^{-1}\) and 1398 cm\(^{-1}\) peaks were accredited to the C-O stretching vibrations for the alkoxy, epoxy and carboxyl groups respectively [8-10, 12, 13]. In comparison, the FTIR spectrum of graphite had less oxygen-containing functional groups [14]. The 1740 cm\(^{-1}\) and 1230 cm\(^{-1}\) peaks for the carbonyl and epoxy groups' vibrations respectively, were notably absent on the FTIR spectrum for graphite. Whilst the two distinct carboxyl group peaks at 1630 cm\(^{-1}\) and 1396 cm\(^{-1}\) in addition to the alkoxy group peak at 1057 cm\(^{-1}\) were present at lower intensities. The hydroxyl group peak at 3440 cm\(^{-1}\) peak for graphite was not present at such low intensities as compared to the GO spectrum. The shoulder on this peak was a lot more pronounce for the GO.

4.1.2 FTIR analysis of TiO\(_2\)

An investigation of the identity and purity of the synthesized TiO\(_2\) nanoparticles by exploring its functional groups through FTIR yielded the spectrum in Figure 4.2, with three prominent peaks.
The broad absorption band peaking at 3418 cm\(^{-1}\) and the 1633 cm\(^{-1}\) peak were attributed to the stretching vibrations of the hydroxyl group [15-19]. Whilst the 684 cm\(^{-1}\) absorption peak was due to the Ti–O–Ti stretching vibration mode distinctive of TiO\(_2\), typically observed in the 400 cm\(^{-1}\) – 800 cm\(^{-1}\) range [20-22]. The low intensity absorption peak at 1396 cm\(^{-1}\) was ascribed to the Ti-O modes [16].

### 4.1.3 FTIR analysis of SnO\(_2\) and rGO-SnO\(_2\)

The SnO\(_2\) and rGO-SnO\(_2\) nanoparticles were synthesized using the hydrothermal method with stannous chloride (SnCl\(_2\)-2H\(_2\)O) as the precursor and SnO\(_2\) nanoparticles synthesized in the absence of GO. The FTIR spectrum of the synthesized rGO-SnO\(_2\) nanocomposite (Figure 4.3) had the 3437 cm\(^{-1}\), 1645 cm\(^{-1}\), 1392 cm\(^{-1}\), 1165 cm\(^{-1}\) and 1053 cm\(^{-1}\) absorption peaks ascribed to the stretching vibrations of O-H of surface water, C=O and C-O of the carboxyl group and the C-O in the epoxy and alkoxy groups respectively [8, 10, 12].
Figure 4.3: FTIR spectra of the synthesized graphene oxide, rGO-SnO$_2$ and SnO$_2$ nanoparticles respectively. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

These oxygen-containing functional groups characteristic of GO were at a notably lower intensity in the rGO-SnO$_2$ spectrum compared to that of GO of the same concentration, denoting partial reduction of graphene oxide [20]. However, since the FTIR measurements were conducted on mass-mass ratio of material to KBr, the lower intensity of the oxygen-containing functional groups peaks characteristic of GO in the rGO-SnO$_2$ spectrum could also be due to the higher molar mass of Sn, i.e. the amount of GO in the rGO-SnO$_2$ nanocomposite might be lower compared to GO hence the lower intensities. Lastly, the rGO-SnO$_2$ spectrum had a mutual prominent peak at 624 cm$^{-1}$ with the SnO$_2$ spectrum that was attributed to the anti-symmetric O–Sn–O stretching characteristic of SnO$_2$ in the 600 cm$^{-1}$ – 660 cm$^{-1}$ range [23-27]. SnO$_2$ nanoparticles’ spectrum exhibited two more prominent peaks at 3439 cm$^{-1}$ and 1627 cm$^{-1}$ ascribed in literature as the stretching and bending vibrations of the –OH group and water absorbed on the surface of SnO$_2$ particles respectively [25-28].

4.1.4 FTIR analysis of γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$

The GO in rGO-Fe$_2$O$_3$ was partially reduced, symbolized by the reduction in the number of oxygen-containing functional groups with those present at a lower intensity compared to unmodified GO (Figure 4.4) [20].
Figure 4.4: FTIR spectra of the synthesized graphene oxide, rGO-Fe₂O₃ and γ-Fe₂O₃ nanoparticles respectively. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

Explicitly, the absence of the 1731 cm⁻¹ absorption peak for the C=O stretching vibrations from carbonyl and carboxyl groups [10, 11] and the 1221 cm⁻¹ characteristic peak of the C-O stretching vibrations for the epoxy groups [9, 13]. Whilst the O-H stretching vibrations peak at 3406 cm⁻¹, the 1633 cm⁻¹ peak of the C=O stretching vibration for the carboxyl group and the C-O stretching vibrations for the alkoxy at 1034 cm⁻¹ [2, 8] appeared at lower intensity. The synthesized γ-Fe₂O₃ nanoparticles had the same ─OH bands for surface water at 3417 cm⁻¹ and 1633 cm⁻¹ as the other synthesized metal oxides ─ TiO₂ and SnO₂ ─ in this investigation (Figure 4.2 and Figure 4.3). The distinguishing peak/s for gamma iron (III) oxide by FTIR analysis depend on its particle size. Gamma-Fe₂O₃ with particle size less than 8 nm exhibit only a single strong absorption band at ~580 cm⁻¹ [29]. As the particle size increases, the number of absorption bands increases, i.e. 9 nm — 12 nm particle size, has three characteristic absorption bands at 640 cm⁻¹, 696 cm⁻¹ and 729 cm⁻¹ whilst for γ-Fe₂O₃ nanoparticles in the 13 nm — 18 nm range, Li et al. [30] reported seven absorption bands. The crystal sizes of the γ-Fe₂O₃ nanoparticles synthesized in this investigation averaged 7.5 nm from the Scherrer formula (Section 4.2.4), consequently only one strong absorption band was expected. The strong distinctive absorption peak at ~582 cm⁻¹ on the FTIR spectra of both the synthesized γ-Fe₂O₃ and rGO-Fe₂O₃ nanoparticles characteristic of the Fe-O stretching bond in gamma iron (III) oxide was consistent with previous reported work [29-32]. The method used was optimized to produce the gamma iron oxide, and the FTIR results support the notion that the gamma form was synthesized successfully. Further comments on the confirmation of gamma phase are provided in the XRD section (Section 4.2.4).
4.1.5 FTIR analysis of rGO-SnO$_2$-Metal oxide

The FTIR spectra of the synthesized rGO-SnO$_2$-metal oxide nanocomposite, i.e. rGO-SnO$_2$-Fe$_2$O$_3$ and rGO-SnO$_2$-TiO$_2$ exhibited the same oxygen-containing functional groups characteristic of graphene oxide as the FTIR spectrum of their precursor (rGO-SnO$_2$) with virtually the same intensity (Figure 4.5).

![FTIR spectra of synthesized nanocomposites](image)

*Figure 4.5:* FTIR spectra of the synthesized rGO-SnO$_2$-Fe$_2$O$_3$, rGO-SnO$_2$-TiO$_2$, and rGO-SnO$_2$ nanocomposites respectively. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

Specifically the absorption peaks at ~3400 cm$^{-1}$, ~1630 cm$^{-1}$, ~1390 cm$^{-1}$ and ~1200 cm$^{-1}$ for the O-H stretching vibration, C=O stretching vibrations of the COOH group, C-O stretching vibration for the carboxyl group and C-O stretching vibration for the epoxy group respectively [10, 12, 13]. Thus, suggesting that the second metal oxide were most likely not intercalated into the graphitic structure (i.e. there are no C-O-M bonds) but rather the metal oxides probably sit on the surface of the nanomaterial. Both rGO-SnO$_2$-TiO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$ spectra contained an additional peak, a broad absorption band at 500 cm$^{-1} – 700$ cm$^{-1}$, which symbolized the presence of the bi-metals oxides in the nanocomposites. For the rGO-SnO$_2$-TiO$_2$ nanocomposite this peak, incorporated both the anti-symmetric O–Sn–O stretching vibration characteristic of SnO$_2$ [23, 26] and the Ti–O–Ti stretching vibration mode used to characterize the presence of TiO$_2$ [21, 22], as graphically represented in the comparison plot in Figure 4.6a.
Figure 4.6: FTIR spectra of synthesized (a) rGO-SnO$_2$-TiO$_2$, SnO$_2$ and TiO$_2$, nanoparticles respectively; and (b) rGO-SnO$_2$-Fe$_2$O$_3$, SnO$_2$ and Fe$_2$O$_3$ nanoparticles respectively. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

Similarly, the broad peak on the rGO-SnO$_2$-Fe$_2$O$_3$ spectrum ranging at 550 cm$^{-1}$ – 700 cm$^{-1}$ represented both the distinguishing peaks for SnO$_2$ [24] and γ-Fe$_2$O$_3$ nanoparticles [31], clearly evident in the comparison plot in Figure 4.6b.

4.1.6 FTIR analysis of rGO-Fe$_2$O$_3$-Metal oxide

Similar to the FTIR spectra of synthesized rGO-SnO$_2$-metal oxide nanocomposites, the FTIR spectra of the synthesized rGO-Fe$_2$O$_3$-metal oxides, i.e., rGO-Fe$_2$O$_3$-SnO$_2$ and rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposites exhibited the four distinguishing GO peaks observed on the FTIR spectrum of their precursor (Figure 4.7).
Figure 4.7: FTIR spectra of synthesized rGO-Fe$_2$O$_3$, rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanoparticles respectively. The spectra were acquired using KBr pellets (1:100 mass ratio) and a PerkinElmer TL 8000 Balanced flow FT-IR EGA system spectrometer.

These oxygen-containing functional groups characteristic of graphene oxide were observed at ~3430 cm$^{-1}$, ~1640 cm$^{-1}$, ~1390 cm$^{-1}$ and ~1050 cm$^{-1}$ with virtually the same intensity as that of their precursor, rGO-Fe$_2$O$_3$. They were ascribed to the O-H surface water stretching vibrations, C=O carboxyl stretching vibrations, C-O carboxyl group stretching vibrations and the C-O alkoxy group stretching vibrations respectively [2, 11, 12]. The same principle as the rGO-SnO$_2$-metal oxide nanocomposites was thus applied to the synthesized rGO-Fe$_2$O$_3$-metal oxides FTIR spectra, that is, the second metal oxide were most likely not intercalated into the graphitic structure. The presence of both the Fe$_2$O$_3$ and TiO$_2$ metal oxides in the rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite was indicated by the occurrence of the broad distinct peak ranging between 450 cm$^{-1}$ – 700 cm$^{-1}$ with a peak maximum at 577 cm$^{-1}$ (Figure 4.8a). This absorption peak included both the ~580 cm$^{-1}$ Fe-O stretching vibrations distinct for γ-Fe$_2$O$_3$ nanoparticles in the 6 nm – 8 nm range [30] as well as the Ti–O–Ti stretching vibration peak expected in the 400 cm$^{-1}$ – 800 cm$^{-1}$ range [20-22], both easily identifiable in the comparison spectra in Figure 4.8a.
The FTIR spectrum of the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite had a broad split peak in the 530 cm$^{-1}$ – 700 cm$^{-1}$ range (Figure 4.8b), that covered the Fe-O stretching vibrations peak at ~580 cm$^{-1}$ typical in γ-Fe$_2$O$_3$ nanoparticles [29-32] in addition to the anti-symmetric O–Sn–O stretching at ~620 cm$^{-1}$ for distinguishing SnO$_2$ nanoparticles [23-27]. This peak was testament to the presence of γ-Fe$_2$O$_3$ and SnO$_2$ metals oxides nanoparticles in the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite.

4.1.7 FTIR analysis of ternary systems

The FTIR spectra of the two ternary nanocomposites, rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ at equivalent concentrations are almost replicas of each other (Figure 4.9a).
Both the ternary systems’ FTIR spectra exhibited the oxygen containing functional groups’ peaks distinctive of graphene oxide, i.e. surface water, carboxyl and alkoxy group peaks at 3420 cm\(^{-1}\), 1638 cm\(^{-1}\), 1400 cm\(^{-1}\) and 1046 cm\(^{-1}\). The intensity and positions of these characteristic peaks were virtually similar to those of their precursors, rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) and rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) indicating that the third incorporated metal oxides were merely supported on the nanocomposite rather than bonded to the graphitic lattice. The three metal oxides were deposited separately, thus three peaks were expected. However, due to the similarity in the characteristic peak positions of the metal oxides, i.e. 623 cm\(^{-1}\) for SnO\(_2\), 582 cm\(^{-1}\) for γ-Fe\(_2\)O\(_3\) and 684 cm\(^{-1}\) for TiO\(_2\) \([23, 25, 29]\), these peaks overlapped and formed a broad 462 cm\(^{-1}\) — 794 cm\(^{-1}\) peak, as graphically represented in the comparison plot in Figure 4.9b. Signifying the successful incorporation of the metals oxides onto graphene sheets that is, the synthesis of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) ternary nanocomposites.

### 4.2 X-Ray powder diffraction (XRD) analysis of nanomaterial and nanocomposites

The synthesized nanomaterial and nanocomposites were pulverized and homogenized individually using a pestle in mortar. Each nanomaterial sample was packed into a silicon sample holder, and then levelled before analysis using the X’Pert Pro core, Phillips X-ray diffractometer from PANalytical, at a scanning range of 4° — 90° 2θ with a radiation source of Cu Kα (0.154 nm).
4.2.1 XRD analysis of Graphite and Graphene oxide (GO)

The identity and purity of the purchased synthetic graphite powder and as-synthesized graphene oxide (GO) were further investigated by X-Ray powder diffraction analysis, Figure 4.10a and Figure 4.10b respectively, show the X-ray diffractograms from the analysis.

Graphite exhibited a distinctive sharp peak at 2θ = 26.56° corresponding to (0 0 2) crystal planes associated with the diffraction of the repeated plane of graphite [14, 33-35]. In addition to the relatively low intensity (0 0 4) reflection peak at 2θ = 54.69° with an interplanar spacing of 0.18 nm. In graphene oxide, the (0 0 4) reflection peak disappeared whereas the (0 0 2) reflection peak shifted to a lower angle of 2θ = 10.05° with a wider interplanar spacing of 0.88 nm in contrast to that of graphite at 0.34 nm at angle of 2θ = 26.56° [14, 33-37]. The difference in the interplanar spacing of the (0 0 2) reflection peak was ascribed to the intercalation of water molecules and oxygen-containing functional groups between the graphite layers during oxidation [36, 37]. The interplanar spacing between the crystal planes of the synthesized nanomaterial and nanocomposites were measured using the X’Pert Pro MRD (Materials Research Diffractometer).

4.2.2 XRD analysis of TiO₂

The XRD spectrum of the as-synthesized powdered TiO₂ nanoparticles (Figure 4.11) had distinct diffraction peaks at 2θ = 25.32°, 36.99°, 37.85°, 38.59°, 58.05°, 53.96°, 55.08°, 62.74°, 68.85°, 70.31° and 75.12° which corresponded to the (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0) and (2 1 5) crystal planes.
Figure 4.11: XRD spectrum of the as-synthesized TiO$_2$ nanoparticles. The sample was packed into a silicon sample holder, and then levelled before analysis with the X Pert Pro core, Phillips X-ray diffractometer to obtain the spectrum.

All the diffraction peaks were indexed to that of pure anatase standard, JCPDS 21-1272 as noted in literature [20, 38, 39]. The average crystal sizes of the as-prepared anatase nanoparticles were calculated using the Scherrer formula from the line broadening of the (1 0 1) peak:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Equation 4.1

where $D$ is the crystallite size (nm), $\lambda$ is the wavelength of the x-rays, i.e. Cu K\textalpha{} (0.154 nm), $\beta$ is the full width at half maximum height of the diffraction peak (radians) which was calculated using Origin software from the XRD spectra of synthesized nanomaterial, and $\theta$ is the Bragg diffraction angle of corresponding peak in degrees [40-42]. The crystallite size of the as-prepared anatase TiO$_2$ nanoparticles was 13 nm.

4.2.3 XRD analysis of SnO$_2$ and rGO-SnO$_2$

The synthesized SnO$_2$ and rGO-SnO$_2$ nanoparticles’ XRD spectra (Figure 4.12) had the same distinct diffraction peaks at $2\theta = 26.66^\circ$, 33.93$^\circ$, 38.02$^\circ$, 51.86$^\circ$, 54.85$^\circ$ and 66.08$^\circ$ for the similar crystal planes; (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0) and (3 0 1) respectively, as the SnO$_2$ cassiterite standard, JCPDS file number 41-1445 as stated in literature [43-45].
Figure 4.12: XRD spectra of the as-synthesized SnO$_2$ and rGO-SnO$_2$ nanomaterial respectively. The samples were packed individually into silicon sample holders, and then levelled before analysis with the X’Pert Pro core, Phillips X-ray diffractometer to obtain the spectra.

The graphene oxide in the rGO-SnO$_2$ nanocomposite was reduced during the hydrothermal process of anchoring SnO$_2$ particles on the graphene sheets, resulting in the disappearance of the (0 0 2) reflection peak of graphite oxide at 2θ = 10.05° [46-48]. Instead a (0 0 2) reflection peak at 2θ ~ 26° emerged which overlapped with the (1 1 0) reflection peak of SnO$_2$ at 2θ = 26.63° [47, 49]. The crystallite size of the anchored SnO$_2$ nanoparticles in rGO-SnO$_2$ nanocomposite was 5 nm and 7 nm for the pristine SnO$_2$ nanomaterial when calculated using the (1 1 0) reflections peaks at 2θ = 26.73° and 26.68° from each spectrum respectively.

4.2.4 XRD analysis of γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$

Gamma iron (III) oxide, γ-Fe$_2$O$_3$ has the same diffraction peaks as iron (II,III) oxide, Fe$_3$O$_4$ at (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystal planes [50, 51]. The distinguishing reflection peaks are the low intensity (1 1 0), (2 1 0) and (2 1 1) peaks at approximately 2θ = 14°, 24° and 27° [50]. The XRD spectra of the as-synthesized powdered γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$ nanoparticles (Figure 4.13) had the (1 1 0) and (2 1 1) characteristic peaks at 14.34° and 27.21° 2θ, which substantiated that the synthesized material is the gamma phase of iron (III) oxide nanoparticles, with a cubic structure.
Figure 4.13: XRD spectra of the synthesized γ-Fe₂O₃ and rGO-Fe₂O₃ nanoparticles respectively. The samples were packed individually into silicon sample holders, and then levelled before analysis with the XPert Pro core, Phillips X-ray diffractometer to obtain the spectra.

It was also noted that there were no (0 0 2) reflection peaks for either graphene oxide or reduced graphene oxide at the characteristic ~ 10° or ~ 26° 2θ positions on the rGO-Fe₂O₃ spectrum. This was ascribed to the disordered stacking of the rGO-Fe₂O₃ layers [52-55]. The crystallite size of the synthesized pristine γ-Fe₂O₃ nanoparticles calculated from the (3 1 1) peak at 2θ = 35.61° reflection peak was 7 nm. However, on the XRD spectrum of the rGO-Fe₂O₃ nanoparticles in the 2θ = 35° region there were overlapped broad peaks. As a result the 2θ = 57.26° (5 1 1) reflection peak was used to calculate the crystallite size of the rGO-Fe₂O₃ nanoparticles, which was determined to be 7 nm as well. Both the XRD spectra of the γ-Fe₂O₃ and rGO-Fe₂O₃ nanoparticles exhibited higher background or lower signal intensity compared to the XRD spectra of the other synthesized nanomaterial as iron samples fluoresce.

4.2.5 XRD analysis of rGO-SnO₂-Metal oxide

The XRD spectra of the rGO-SnO₂-TiO₂ and rGO-SnO₂-Fe₂O₃ nanocomposites had the characteristic diffraction peaks of the anchored metals oxides, especially for the rGO-SnO₂-TiO₂ nanocomposite, as graphically presented in the comparison diffractograms plots in Figure 4.14a and Figure 4.14b respectively.
Figure 4.14: XRD spectra of the as-synthesized (a) TiO$_2$, SnO$_2$ and rGO-SnO$_2$-TiO$_2$ nanoparticles respectively; and (b) γ-Fe$_2$O$_3$, SnO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$ nanoparticles respectively. The samples were packed individually into silicon sample holders, and then levelled before analysis with the X’Pert Pro core, Phillips X-ray diffractometer to obtain the spectra.

The spectra of both nanocomposites were devoid of the distinct (0 0 2) reflection peak for graphene oxide at $2\theta = 10.05^\circ$, this has been attributed to the reduction of GO during the intercalation of the metals oxides in literature [56]. The distinguishing (0 0 2) reflection peak at $2\theta = 26.6^\circ$ for reduced graphene oxide was also absent, which Jiang et al. [20] attributed to its close proximity to or overlapping with the (1 1 0) SnO$_2$ and (1 0 1) TiO$_2$ reflection peaks corresponding to $2\theta = 26.66^\circ$ and $25.32^\circ$ respectively in rGO-SnO$_2$-TiO$_2$ nanocomposites. Whereas Ding et al. [49] proposed the absence to be due to the homogeneous coating of the metal oxide on well dispersed graphene oxide sheets. The crystallite size of the SnO$_2$ and TiO$_2$ metal oxides coated on graphene oxide was 5 nm, when calculated using the $2\theta = 33.96^\circ$ diffraction peak. Consistent with the 5 nm particle size reported by Liang et al. [56] when SnO$_2$ and TiO$_2$ were coated on GO by the hydro- and solvo-thermal methods. The crystallite size of the Fe$_2$O$_3$ and SnO$_2$ nanoparticles coated on rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposites was calculated to be an average of 6 nm using the $2\theta = 26.49^\circ$ diffraction peak.

### 4.2.6 XRD analysis of rGO-Fe$_2$O$_3$-Metal oxide

The XRD spectra of rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites were compared to the XRD spectra of Fe$_2$O$_3$ & TiO$_2$ and Fe$_2$O$_3$ & SnO$_2$ nanoparticles respectively (Figure 4.15a and Figure 4.15b).
Figure 4.15: XRD spectra of the as-synthesized (a) TiO$_2$, γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$-TiO$_2$ nanoparticles respectively; and (b) SnO$_2$, γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanoparticles respectively. The samples were packed individually into silicon sample holders, and then levelled before analysis with the X’Pert Pro core, Phillips X-ray diffractometer to obtain the spectra.

The diffraction peaks in each nanocomposite spectrum were indexed to the two metal oxides anchored without any impurities. The crystallite size of the TiO$_2$ and Fe$_2$O$_3$ nanoparticles anchored in the rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite when calculated using the Scherrer formula from the $2\theta = 25.30^\circ$ and $57.34^\circ$ peaks was 15 nm. While the crystallite size of Fe$_2$O$_3$ and SnO$_2$ coated on the graphitic layers of the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite was calculated to be an average of 3 nm using the $2\theta = 26.73^\circ$ diffraction peak assuming composite crystallites.

4.2.7 XRD analysis of ternary systems

All the diffraction peaks in the XRD spectra of rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ were indexed to cassiterite SnO$_2$, gamma Fe$_2$O$_3$ and anatase TiO$_2$ metal oxides as represented in Figure 4.16a and Figure 4.16b of the comparison plots.
Figure 4.16: XRD spectra of the as-synthesized (a) TiO$_2$, SnO$_2$, γ-Fe$_2$O$_3$ and rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanoparticles respectively; and (b) TiO$_2$, SnO$_2$, γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanoparticles respectively. The samples were packed individually into silicon sample holders, and then levelled before analysis with the X’Pert Pro core, Phillips X-ray diffractometer to obtain the spectra.

The crystallite size of the metal oxides in the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite, calculated with the $2\theta = 47.94^\circ$ diffraction peak was 10 nm. The crystallite size of the layered metal oxide nanoparticles in the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary composite was 4 nm when calculated using the Scherrer equation for the $2\theta = 48.18^\circ$ diffraction peak.

4.3 Scanning Electron Microscopy — Energy Dispersive X-ray spectroscopy (SEM-EDX) analysis of nanomaterial and nanocomposites

The powdered nanomaterial and nanocomposites were analyzed without further treatment after coating on the carbon tape layered alumina sample holder using the Vega 3 Tescan SEM-EDX microscope.

4.3.1 SEM-EDX analysis of Graphite and Graphene oxide (GO)

The structural composition of purchased graphite powder and synthesized graphene oxide were studied with the scanning electron microscope, Figure 4.17a and Figure 4.17c represents the images.
Both graphite and graphene oxide were made up of layers; while those of graphite were flaky and thin, graphene oxide layers were fluffy and sponge-like [35]. The SEM-EDX spectrum of graphite powder used (Figure 4.17b) validated it as pristine with only the carbon peak. The EDX used could conceivably not be sensitive enough to detect the minor O₂ and C peaks from adsorbed water and oxidized surface of graphite as exhibited in the FTIR data. The graphene oxide SEM-EDX spectrum (Figure 4.17d) had the expected carbon and oxygen peaks for the graphitic layers and oxygen containing functional groups. In addition, it contained sulfur and phosphorus peaks, conceivably from remnants of the oxidizing agents used, i.e. sulfuric acid and phosphoric acid due to inadequate washing of the synthesized graphene oxide. Whilst the chloride contamination could possibly be from the HCl wash due to the inadequate subsequent absolute ethanol wash.
4.3.2 SEM-EDX analysis of TiO$_2$

The synthesized anatase TiO$_2$ nanoparticles appeared to be coarse, clusters of irregular shapes that had a wide size distribution when studied with a scanning electron microscope (Figure 4.18a), which corresponded to similar work by Bellardita et al. [57].

![Figure 4.18: Powdered as-synthesized TiO$_2$ nanoparticles' (a) SEM image and (b) SEM-EDX spectrum. The image and spectrum were acquired with a Vega 3 Tescan SEM-EDX microscope.](image)

The SEM-EDX spectrum (Figure 4.18b) demonstrated practically pure anatase TiO$_2$ nanoparticles with a slight (0.2%) vanadium contamination.

4.3.3 SEM-EDX analysis of SnO$_2$ and rGO-SnO$_2$

The synthesized SnO$_2$ nanoparticles had the spherical shape characteristic of pure SnO$_2$ nanoparticles [58-60] when analyzed using the scanning electron microscope, as shown in Figure 4.19a.
Figure 4.19: Powdered as-synthesized SnO$_2$ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum; and powdered as-synthesized rGO-SnO$_2$ nanoparticles’ (c) SEM image and (d) SEM-EDX spectrum. The images and spectra were acquired with a Vega 3 Tescan SEM-EDX microscope.

The synthesized SnO$_2$ nanoparticles were also agglomerated, a phenomenon that Selvi et al. [59] attributed to high surface area of nanoparticles whereas Santhanalkshmi and Rajesh [58] ascribed it to the large number of oxygen vacancies. The rGO-SnO$_2$ nanoparticles had the same morphology as graphene oxide, i.e. layers of fluffy sponge (Figure 4.19c). However, on the rGO-SnO$_2$ nanoparticles’ spectrum there were smooth spherical nanoparticles distributed homogeneously on the layers which denoted the successful intercalation of the SnO$_2$ nanoparticles onto the graphene oxide sheets. The SEM-EDX spectrum confirmed the purity of the synthesized SnO$_2$ nanoparticles (Figure 4.19b), with only 1.1% chloride contamination undoubtedly from the precursor, SnCl$_2$·2H$_2$O used due to insufficient washing. While the 9.2% carbon was from the thin film of carbon coated on the nanoparticles’ sample for analysis. The elemental composition analysis of the rGO-SnO$_2$ nanocomposite by SEM-EDX (Figure 4.19d) revealed that the composite contained the expected elements, i.e. carbon, tin, oxygen and chlorine from the confirmed chlorine contamination from the precursor, SnCl$_2$·2H$_2$O caused by inadequate washing.
4.3.4 SEM-EDX analysis of γ-Fe₂O₃ and rGO-Fe₂O₃

A study of the morphology of the synthesized γ-Fe₂O₃ nanoparticles by SEM revealed that the nanoparticles were rough, aggregated with asymmetrical shapes and wide size distribution (Figure 4.20a) [61].

![SEM images and EDX spectra of γ-Fe₂O₃ and rGO-Fe₂O₃ nanoparticles](image)

Figure 4.20: Powdered as-synthesized γ-Fe₂O₃ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum; and powdered as-synthesized rGO-Fe₂O₃ nanoparticles’ (c) SEM image and (d) SEM-EDX spectrum. The images and spectra were acquired with a Vega 3 Tescan SEM-EDX microscope.

The SEM-EDX spectrum (Figure 4.20b) proved that the co-precipitation method used for synthesis of γ-Fe₂O₃ provides pure nanoparticles, as it contained only the constituents of γ-Fe₂O₃ bar from the slight chloride contamination from the FeCl₃·6H₂O and FeCl₂·4H₂O precursors due to insufficient washing of the γ-Fe₂O₃ yield. The rGO-Fe₂O₃ nanoparticles’ SEM image in Figure 4.20c had sponge-like layers with a rough texture symbolizing the incorporation of the γ-Fe₂O₃ nanoparticles on the graphene oxide layers. There were also clusters of irregular shaped nanoparticles of varying sizes that could be attributed to surplus and/or agglomeration of γ-Fe₂O₃ nanoparticles. The rGO-Fe₂O₃
nanocomposite similar to the γ-Fe₂O₃ nanoparticles, had ~1% chloride, which was the only contaminant in the rGO-Fe₂O₃ nanoparticles synthesized as observed on the SEM-EDS spectrum in Figure 4.20d.

4.3.5 SEM-EDX analysis of rGO-SnO₂-Metal oxide

The SEM images of rGO-SnO₂-TiO₂ and rGO-SnO₂-Fe₂O₃ nanocomposites are represented by the images in Figure 4.21a and Figure 4.21c respectively.

![Figure 4.21: Powdered as-synthesized rGO-SnO₂-TiO₂ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum; and powdered as-synthesized rGO-SnO₂-Fe₂O₃ nanoparticles’ (c) SEM image and (d) SEM-EDX spectrum. The images and spectra were acquired with a Vega 3 Tescan SEM-EDX microscope.](image)

The images showed abundant nanoparticles attached to sponge-like layers, to such an extent that the texture of the layers was coarse, signifying the uniform layering of the metal oxides on the graphene oxide layers. There appeared to also be some separate clusters of nanoparticles in both images that could be due to the agglomeration and/or excess of the metal oxides. The identity of the
uniformly anchored nanoparticles was disclosed by the SEM-EDX spectra of both nanocomposites. The rGO-SnO$_2$-TiO$_2$ nanocomposites SEM-EDX spectrum (Figure 4.21b) exhibited Ti, Sn, O and C only, i.e. its constituent elements only without contamination. Similarly, the elemental analysis of rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposites by SEM-EDX revealed that the nanomaterial was composed of Fe, Sn, O and C with a 1% chloride contamination from the FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O precursors, due to inadequate washing of the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite yield.

### 4.3.6 SEM-EDX analysis of GO-Fe$_2$O$_3$-Metal oxide

SEM images of rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites in Figure 4.22a and Figure 4.22c respectively, portrayed them as coarse puffy flakes with nanoparticles of different sizes and shapes clustered on top and separate from the flakes.

![Figure 4.22](image)

Figure 4.22: Powdered as-synthesized rGO-Fe$_2$O$_3$-TiO$_2$ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum; and powdered as-synthesized rGO-Fe$_2$O$_3$-SnO$_2$ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum. The images and spectra were acquired with a Vega 3 Tescan SEM-EDX microscope.
Symbolizing incorporation of the nanoparticles onto graphene layers with a slight excess and agglomeration of the metal oxides. SEM-EDX elemental analysis of the rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite (Figure 4.22b) revealed that the composite consisted of iron, tin, oxygen and carbon as expected with a low contaminant concentration of vanadium. In the same way, the SEM-EDX spectrum of the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites reflected the expected elements, i.e. Sn, O, C and Fe with a slight contamination from chloride that has been established to be from the precursors.

### 4.3.7 SEM-EDX analysis of ternary systems

One of the objectives of this research was to synthesize rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites, i.e. layer SnO$_2$, Fe$_2$O$_3$ and TiO$_2$ metal oxides within the graphitic lattice of graphene oxide. The SEM image of both ternary systems (Figure 4.23) showed sponge-like flakes with coarse surface due to uniform coating of nanoparticles thus attesting to the successful layering of the metals oxides.

Figure 4.23: Powdered as-synthesized rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum; and powdered as-synthesized rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanoparticles’ (a) SEM image and (b) SEM-EDX spectrum. The images and spectra were acquired with a Vega 3 Tescan SEM-EDX microscope.
Whilst the SEM-EDX elemental analysis of both ternary systems provided evidence of the identity of the metals as tin, titanium and iron thus indicating successful attainment of the set-out objective, i.e. synthesis of the rGO-SnO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> and rGO-Fe<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>-TiO<sub>2</sub> ternary nanocomposites.

4.4 Transmission Electron Microscopy (TEM) analysis of nanomaterial and nanocomposites

Approximately 1 mg of each powdered synthesized nanomaterial was dispersed in 8-mL absolute ethanol by sonication for 10 minutes. This mixture was then "drop cast" on a carbon coated copper grid for analysis with a JEM-2100 Electron microscope after drying.

4.4.1 TEM analysis of Graphite and Graphene oxide (GO)

Structural analysis of the purchased synthetic graphite powder and synthesized graphene oxide using a transmission electron microscope revealed that the two graphitic materials were made up of thin, transparent paper-like layers (Figure 4.24).

**Figure 4.24**: TEM images of (a) purchased synthetic graphite powder and (c) as-synthesized graphene oxide, GO. SAED pattern of (b) purchased synthetic graphite powder and (d) as-synthesized graphene oxide, GO. The images and diffractograms were acquired with a JEM-2100 Electron microscope.
However, while graphite sheets were flat (Figure 4.24a), graphene oxide sheets were wrinkled (Figure 4.24c) [35] due to the incorporation of oxygen-containing functional groups onto its layers [62]. The extent of wrinkles denoted the extent of defects from the inclusion of oxygen into the structure [63]. Further investigation of the crystalline structure of the two graphitic material by Selected Area Electron Diffraction (SAED) revealed that graphite had both the (0 0 4) and (0 0 2) crystal planes, with interplanar spacing d(Å) calculated at 2.0 and 3.4 respectively (Figure 4.24b). However, in graphene oxide the (0 0 4) crystal plane was absent, only the (0 0 2) crystal plane at increased interplanar spacing was present (0.89 nm vs. 0.88 nm from XRD) [64] corroborating the crystalline structure information from XRD (Section 4.2.1). The interplanar spacing was calculated with the equation below:

\[
\text{Interplanar spacing (d)} = \frac{2}{\text{Diameter of the circle or Distance between two bright spots}}
\]

Equation 4.2

The diameter of the circle or distance between two bright spots was measured using a ruler and the scale bar at the bottom of the diffractogram was then used to convert the measured diameter or distance from centimeters to nanometers. Subsequently, the calculated interplanar spacing was compared to that of the standard nanomaterial studied as reported in literature. Please note that the quality of the SAED diffractograms when the document was converted to PDF was altered and increased the number of rings observed. For clarity, the original rings were marked with blue circles whilst the GO SAED diffractogram contains only one clear white light ring.

4.4.2 TEM analysis of TiO$_2$

Further study of the structure and crystallinity of the TiO$_2$ nanoparticles by TEM produced the image and SAED pattern in Figure 4.25a and Figure 4.25b respectively.
Figure 4.25: Powdered as-synthesized TiO$_2$ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The TiO$_2$ nanoparticles synthesized were of varying shapes and sizes, mainly spherical (Figure 4.25a) with an average size of 14 nm ± 3 nm (Figure 4.25c) consistent to the 13 nm from the XRD measurements (Section 4.2.2). Particle size of the nanomaterial synthesized in this research was a measure of their diameter using ImageJ software. The calculated interplanar spacing d(Å) from the five diffraction rings corresponded to (2 0 4), (1 0 5), (1 1 2), (1 0 3) and (1 0 1) crystal planes were within reasonable limits to those of pure anatase standard (JCPDS 21-1272) (Figure 4.25b).

4.4.3 TEM analysis of SnO$_2$ and rGO-SnO$_2$

The TEM image of the SnO$_2$ nanoparticles (Figure 4.26a) positively matched that of its SEM image (Figure 4.19a), in that, it had round nanoparticles connected by an irregular network [27, 58, 59].
The average particle size of the synthesized SnO\textsubscript{2} was 157nm ± 34 nm (Figure 4.26c), when calculated using ImageJ software from a further magnified image. The SAED pattern (Figure 4.26b) had five of the six characteristic crystal planes of the cassiterite standard (JCPDS file number 41-1445) thus affirming that the synthesized nanoparticles were SnO\textsubscript{2} with a tetragonal structure.

The SnO\textsubscript{2} nanoparticles were homogeneously distributed on the graphitic layers of the synthesized rGO-SnO\textsubscript{2} nanocomposite [46, 47, 65] as clearly represented on the TEM image of the rGO-SnO\textsubscript{2} nanocomposite in Figure 4.27a.
Figure 4.27: Powdered as-synthesized rGO-SnO$_2$ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The image depicts a thin translucent layer coated with mostly circular nanoparticles. The average size of the SnO$_2$ nanoparticles on the rGO-SnO$_2$ nanocomposite calculated from the 50 nm magnification TEM image using ImageJ was 5 nm ± 1 nm which is within reasonable limits of the 4.25 nm calculated from the XRD spectrum (Section 4.2.3). The size of the SnO$_2$ nanoparticles was significantly reduced after coating on graphene oxide (157 nm to 5 nm) as previously reported in literature [66]. In solution, there are fewer nucleation sites, resulting in bigger particle sizes. Whereas, on the graphene oxide, the number of nucleation sites are numerous resulting in smaller particle sizes of the metal oxide coated on the graphitic material. The crystalline structure when studied from the SAED pattern (Figure 4.27b), revealed four diffraction rings. The calculated interplanar spacing d(Å) of these diffraction rings positively matched that of (2 1 1), (1 1 1), (1 0 1) and (1 1 0) crystal planes for cassiterite SnO$_2$ nanoparticles. Thus, indicating successful incorporation of the SnO$_2$ nanoparticles in the graphitic layers of GO, i.e. successful synthesis of rGO-SnO$_2$. 

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4.4.4 TEM analysis of γ-Fe₂O₃ and rGO-Fe₂O₃

TEM image of γ-Fe₂O₃ (Figure 4.28a) showed aggregates and separate nanoparticles of different shapes with sizes ranging from 5 nm – 10 nm (Figure 4.28c).

![TEM image of γ-Fe₂O₃](image)

![SAED pattern](image)

![Particle size histogram](image)

Figure 4.28: Powdered as-synthesized γ-Fe₂O₃ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The average size of the synthesized γ-Fe₂O₃ nanoparticles was 7 nm ± 2 nm (Figure 4.28c), when calculated using ImageJ software which positively matched the 7 nm from the XRD spectrum using the Scherrer equation and the number & position of the γ-Fe₂O₃ distinguishing peaks on the FTIR spectrum. The SAED pattern (Figure 4.28b) consisted of four diffraction rings, that had calculated interplanar spacing d(Å) similar to (4 2 2), (2 2 2), (3 1 1) and (1 1 1) crystal planes for gamma phase of iron (III) oxide nanoparticles, with a cubic structure.
The TEM image of the rGO-Fe$_2$O$_3$ nanocomposite (Figure 4.29a) exhibited 7 nm ± 1 nm sized (Figure 4.29c) \(\lambda\)-Fe$_2$O$_3$ particles of various shapes uniformly coated on flat, exfoliated graphene oxide sheets [54, 67].

![Figure 4.29](image)

**Figure 4.29:** Powdered as-synthesized rGO-Fe$_2$O$_3$ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The crystalline structure of the synthesized rGO-Fe$_2$O$_3$ nanocomposite from the TEM SAED pattern (Figure 4.29b) had the (4 2 2), (2 2 2), (3 1 1) and (1 1 1) crystal planes represented by the four diffraction rings that had the same interplanar spacing \(d(\text{Å})\) as those for the gamma Fe$_2$O$_3$ nanoparticles. Indicating that \(\gamma\)-Fe$_2$O$_3$ were successfully intercalated into the graphitic lattice of GO to form rGO-Fe$_2$O$_3$ nanocomposite.
4.4.5 TEM analysis of rGO-SnO$_2$-Metal oxide

The TEM image of the rGO-SnO$_2$-TiO$_2$ nanocomposite (Figure 4.30a) demonstrated well expanded graphene oxide sheets that were covered with a dense layer of 7 nm ± 1 nm metal oxide nanoparticles (Figure 4.30c) and on some fragments, agglomerates of these nanoparticles.

![TEM Image](image1)

**Figure 4.30:** Powdered as-synthesized rGO-SnO$_2$-TiO$_2$ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The SAED pattern for the rGO-SnO$_2$-TiO$_2$ nanocomposite (Figure 4.30b) had four diffraction rings which were indexed to the (2 1 0) and (1 1 0) crystal planes of SnO$_2$ in addition to the (1 0 3) and (1 0 1) planes of TiO$_2$. Therefore, substantiating the XRD, FTIR and SEM results that cassiterite and anatase were incorporated on the graphitic structure of the rGO-SnO$_2$-TiO$_2$ nanocomposite.

Although the SnO$_2$ and Fe$_3$O$_4$ metals oxides were visibly incorporated onto the graphene oxide layers, the thick coating that seem overlapped and/or as agglomerates in some parts of the rGO-
SnO$_2$-Fe$_2$O$_3$ TEM image (Figure 4.31a) hinted at an excessive quantity of metals oxides ratio to the GO.

The use of ImageJ on a further magnified TEM image to calculate the particle size of the SnO$_2$ and Fe$_2$O$_3$ metal oxides anchored on GO in the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite revealed that these nanoparticles were an average of 9 nm ± 2 nm in size (Figure 4.31c). Further study of the crystalline structure of the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite by SAED (Figure 4.31c), revealed four diffraction rings that were indexed to SnO$_2$ and γ-Fe$_2$O$_3$ metals oxides. Therefore, attesting to the successful synthesis of rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite.
4.4.6 TEM analysis of rGO-Fe$_2$O$_3$-Metal oxide

The TEM image of rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite (Figure 4.32a), revealed a smooth sheet of graphene oxide layered with connected, overlapping and clustered γ-Fe$_2$O$_3$ and SnO$_2$ nanoparticles of an average 4 nm ± 0.8 nm size (Figure 4.32c).

![TEM image of rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite](image)

**Figure 4.32:** Powdered as-synthesized rGO-Fe$_2$O$_3$-SnO$_2$ nanoparticles’ (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.

The SAED pattern in Figure 4.32b had clear five diffraction rings that were indexed to the (3 0 1), (2 1 1) and (2 0 0) crystal planes for cassiterite along with the (2 2 0) and (1 1 1) crystal planes for gamma iron (III) oxide. Affirming that the nanoparticles layered on the graphene oxide of the GO-Fe$_2$O$_3$-SnO$_2$ nanocomposite sheets are γ-Fe$_2$O$_3$ and SnO$_2$. 
The TEM image of the rGO-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanocomposite (Figure 4.33a) consisted of a flat transparent sheet representing graphene oxide covered by 10 nm ± 2 nm (Figure 4.33c) varying shaped nanoparticles, denoting γ-Fe\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} metal oxides (Figure 4.33b).

![Figure 4.33: Powdered as-synthesized rGO-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanoparticles' (a) TEM image; (b) SAED pattern and the (c) Particle size histogram. The image and diffractogram were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.](image)

The SAED pattern (Figure 4.33c) confirmed the nanoparticles coated on graphene oxide sheets as γ-Fe\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} metal oxides from a comparison of the interplanar spacing of the diffraction rings to that of the crystal planes of the metals oxides standards. Namely, the (4 2 2), (4 0 0), (3 1 1) and (1 1 1) crystal planes of γ-Fe\textsubscript{2}O\textsubscript{3} in addition to the (1 0 1) crystal plane for TiO\textsubscript{2}. 

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4.4.7 TEM analysis of ternary systems

Consistent with SEM results, the TEM image of rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite (Figure 4.34a) showed thin, translucent sheets densely layered with nanoparticles thus demonstrating the incorporation of the metal oxides onto the graphitic lamellar structure.

The average size of the anchored metals oxides’ nanoparticles was 9 nm ± 2 nm when calculated from a further magnified TEM image using ImageJ which is consistent with the 10 nm calculated using the Scherrer equation (Section 4.2.7). The SAED pattern (Figure 4.34b) confirms the identity of the nanoparticles layered on graphene oxide as SnO$_2$, Fe$_2$O$_3$ and TiO$_2$.

The TEM image of the synthesized rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite (Figure 4.35a) is further evidence of the accomplishment of the objective of layering Fe$_2$O$_3$, SnO$_2$ and TiO$_2$ metal oxides on the graphitic layers.
The image showed a flat, transparent layer of graphene oxide covered with 4 nm ± 0.8 nm nanoparticles (Figure 4.35c) of different shapes. The identity of the nanoparticles through study of their crystal structure using TEM SAED (Figure 4.35b) revealed five diffraction rings, the interplanar spacing of which, positively matched that of the crystal planes for the Fe$_2$O$_3$, SnO$_2$ and TiO$_2$ metal oxides.

### 4.5 Ultraviolet-visible spectroscopy (UV-Vis) analysis of nanomaterials and nanocomposites

In this research, ~0.18 mg/L aqueous dispersions of the synthesized nanomaterial and nanocomposites were analyzed with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer, in the 190 nm – 800 nm wavelength range.
4.5.1 UV-Vis analysis of Graphite and Graphene oxide (GO)

When solid or aqueous dispersions of graphene oxide is irradiated with light in the 190 nm – 800 nm wavelength range, i.e. with ultraviolet and visible light, the resultant absorbance spectrum exhibits two characteristic peaks. Namely the main peak in the 227 nm — 231 nm range and a weak shoulder peak at approximately 300 nm [2, 8, 34, 35, 68, 69]. As expected, the UV-Vis absorbance spectrum of the as-synthesized graphene oxide nanoparticles (Figure 4.36a) exhibited a main peak at 230.4 nm which was attributed to the $\pi - \pi^*$ transitions of the aromatic C – C ring. In addition to a shoulder peak at 305.9 nm from the $n - \pi^*$ transitions of C=O of carbonyl groups, as previously reported [2, 8, 34, 35, 68, 69].

![Figure 4.36: UV-Vis absorption spectra of ~0.2 mg/L aqueous dispersions of the; (a) as-synthesized graphene oxide, GO; and (b) purchased synthetic graphite powder respectively. The spectra were acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.](image)

Whereas for the UV-Vis absorbance spectrum of graphite, only one absorption peak at 250 nm was expected due to the $\pi - \pi^*$ transitions of the C=C bonds as graphite does not have C=O bonds in its structure therefore the $n - \pi^*$ transitions peak should be absent [35]. The aqueous dispersions of purchased synthetic graphite in this research conformed to previous UV-Vis analysis of solid graphite reported in literature, i.e. exhibited a single low intensity peak at 265 nm in its absorbance spectrum thus affirming that aqueous dispersions were stable for the analysis. The optical band gap of the as-synthesized nanomaterial in this research were calculated using the absorption edge wavelength from their UV-Vis absorption spectra and the following equation:

\[
\text{Band Gap Energy (E)} = \frac{hc}{\lambda}
\]

Equation 4.3
where $h$ is Plank's constant ($6.626 \times 10^{-34}$ Joules sec), $c$ is the speed of light ($3.0 \times 10^8$ meter per second) and $\lambda$ is the cut off wavelength / absorption edge in $10^{-9}$ meters. The band gap of the as-synthesized powdered graphene oxide was 2.76 eV, consistent with 2.7 eV [70] and 2.8 eV [71] GO band gap values reported. The band gap of graphite has been reported to range between 0.03 eV − 0.04 eV when measured using Galvanomagnetic, de Haas-van Alphen, and other experiments [72]. It was not calculated in this research due to the indistinct absorption peak of its spectrum.

### 4.5.2 UV-Vis analysis of TiO$_2$

The exciton absorption band maximum, $\lambda_{\text{max}} = 256.96$ nm for the aqueous dispersion of the synthesized TiO$_2$ nanoparticles (Figure 4.37) was consistent to that of 250 nm ─ 265 nm previously reported [73, 74].

![Figure 4.37](image)

**Figure 4.37**: UV-Vis absorption spectrum of ~0.2 mg/L aqueous dispersion of the synthesized TiO$_2$ nanoparticles. The spectrum was acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.

The absorption of optical light by anatase nanoparticles was attributed to the indirect transitions between the valleys as TiO$_2$ is an indirect band gap semiconductor [73, 74]. The calculated band gap of the synthesized TiO$_2$ nanoparticles was 3.29 eV, which was within reasonable limits of the 3.2 eV characteristic value widely reported in literature [75, 76].
4.5.3 UV-Vis analysis of SnO$_2$ and rGO-SnO$_2$

The UV-Vis spectrum of aqueous dispersion of synthesized SnO$_2$ nanoparticles (Figure 4.38) exhibited a strong absorption peak at 282 nm, similar to previously reported studies [77-79].

![UV-Vis absorption spectrum of ~0.2 mg/L aqueous dispersion of the synthesized SnO$_2$ nanoparticles. The spectrum was acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.](image)

Santhanalkshmi and Rajesh [58] attributed the absorption of UV-Vis by SnO$_2$ nanoparticles to the $n - \pi^*$ inter electronic transition of d electrons whereas Das et al. [77] ascribed it to the “hexacoordinated polymeric Sn–O–Sn-type species”. The UV-Vis spectra of aqueous dispersions for graphene oxide, SnO$_2$ and rGO-SnO$_2$ nanoparticles for the same concentration were compared in Figure 4.39b.
The UV-Vis spectrum for rGO-SnO$_2$ nanoparticles was devoid of the renowned GO absorption bands at 227 nm — 231 nm and ~300 nm, but rather had a wide peak with an absorption maximum at 265.21 nm as reported in similar studies [46, 80]. This 255 — 266 nm peak on the UV/Vis spectrum of rGO-SnO$_2$ nanoparticles has been documented as the red shift of the ~230 nm graphene oxide peak after reduction [46, 80, 81]. The calculated band gap of the synthesized rGO-SnO$_2$ nanocomposite (3.36 eV) was higher than that of GO (2.76 eV). The band gap of nonstoichiometric and hygroscopic compounds like graphene oxide is proportional to the molar oxygen concentration, i.e. increasing the concentration of oxygen-containing functional groups intercalated into the graphitic lattice of GO, increases the band gap and vice-versa [6, 82]. Therefore, intercalation of the SnO$_2$ metal oxide into the graphitic structure of GO resulted in an increase in band gap of the rGO-SnO$_2$ nanocomposite.

### 4.5.4 UV-Vis analysis of γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$

The analysis of aqueous dispersions of the synthesized γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$ nanoparticles with a UV-Vis spectrometer yielded the spectra in Figure 4.40a and Figure 4.40b respectively.
Figure 4.40: UV-Vis absorption spectrum of ~0.2 mg/L aqueous dispersion of the synthesized; (a) $\gamma$-Fe$_2$O$_3$ nanoparticles; (b) rGO-Fe$_2$O$_3$ and; (c) $\gamma$-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$ nanomaterial respectively. The spectra were acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.

The spectra equally had the two $\gamma$-Fe$_2$O$_3$ distinguishing absorption bands, at 248 nm and $\lambda_{\text{max}} = 350.33$ nm, from the excitation of surface plasmon vibrations [83, 84], indicative of the successful synthesis of iron oxide nanoparticles. The UV-Vis absorption of rGO-Fe$_2$O$_3$ nanoparticles compared to that of pristine $\gamma$-Fe$_2$O$_3$ (Figure 4.40c) had no clear shifts, i.e. the bandgap of rGO-Fe$_2$O$_3$ nanoparticles is 2.07 eV whereas synthesized pristine $\gamma$-Fe$_2$O$_3$ is 2.14 eV, both within the 1.8 eV -- 2.2 eV range noted for $\gamma$-Fe$_2$O$_3$ [85]. Denoting that graphene oxide merely provides a platform on which the $\gamma$-Fe$_2$O$_3$ were anchored rather than the C-O-M bonds as projected (Section 4.5.3). Substantiated further by the lower band gap of the rGO-Fe$_2$O$_3$ nanocomposite (2.07 eV) compared to that of GO (2.76 eV).
4.5.5 UV-Vis analysis of rGO-SnO$_2$-Metal oxide

The UV-Vis spectra of aqueous dispersions of rGO-SnO$_2$ and rGO-SnO$_2$-TiO$_2$ as well as rGO-SnO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$ nanomaterial at the same concentration were compared, Figure 4.41a and Figure 4.41b respectively, represent the comparison plots.

![Figure 4.41: UV-Vis absorption spectra of ~0.2 mg/L aqueous dispersions of the synthesized; (a) rGO-SnO$_2$-TiO$_2$ and rGO-SnO$_2$ nanomaterial respectively and; (b) synthesized rGO-SnO$_2$-Fe$_2$O$_3$ and rGO-SnO$_2$ respectively. The spectra were acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.](image)

The absorption band of both rGO-SnO$_2$-Metal Oxide nanocomposites had a substantial increase in both the light absorbed in the UV region as well as a red shift of the absorption edge compared to that of the rGO-SnO$_2$ nanoparticles. This visual observation was substantiated by the narrowed band gap of rGO-SnO$_2$-TiO$_2$ nanocomposite at 3.08 eV (402 nm) and 2.59 eV (478 nm) for the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite compared to 3.36 eV of the GO-SnO$_2$ nanocomposite.

4.5.6 UV-Vis analysis of GO-Fe$_2$O$_3$-Metal oxide

Equivalent to rGO-SnO$_2$-metal oxide composites discussed above (Section 4.5.5), the rGO-Fe$_2$O$_3$-metal oxide composites displayed an increase in the light absorbed in the UV region, the rGO-Fe$_2$O$_3$-TiO$_2$ composite (Figure 4.42a) more so than the rGO-Fe$_2$O$_3$-SnO$_2$ (Figure 4.42b).
Figure 4.42: UV-Vis absorption spectra of ~0.2 mg/L aqueous dispersions of the synthesized; (a) rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$ respectively and; (b) rGO-Fe$_2$O$_3$-SnO$_2$ and rGO-Fe$_2$O$_3$ respectively. The spectra were acquired with a Shimadzu, UV-2450 ultraviolet-visible spectrophotometer.

However, unlike the other nanomaterial and nanocomposites where addition of a metal oxide resulted in a red shift — significant or not, the rGO-Fe$_2$O$_3$-Metal oxide composites exhibited a substantial blue shift. The band gap of the rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites were (422 nm) 2.93 eV and (415 nm) 2.98 eV respectively compared to 2.07 eV of rGO-Fe$_2$O$_3$ nanoparticles at an absorption edge of the 599 nm.

4.5.7 UV-Vis analysis of ternary systems

The UV-Vis spectra of the aqueous dispersions of the synthesized ternary nanocomposites, i.e. rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ (Figure 4.43a) and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ (Figure 4.43b), had a similar significant increase in absorbance in the UV region compared to their binary system counterparts.
However, that is where the similarities ended. The absorption edge of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite shifted to a longer wavelength (526 nm), resulting in a narrower band gap of 2.35 eV compared to (478 nm) 2.59 eV of rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite. Whereas, the shift in absorption edge between the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ (399 nm) and rGO-Fe$_2$O$_3$-SnO$_2$ (415 nm) was in the opposite direction but insignificant as confirmed by the band gap calculation of 3.10 eV vs. 2.98 eV respectively.

The absorption edge and band gap values of the synthesized nanomaterial are summarized in Table 4.1
Table 4.1: The absorption edge and calculated band gap values of the synthesized nanomaterial and composites.

<table>
<thead>
<tr>
<th>Synthesized Nanomaterial</th>
<th>Absorption edge / nm</th>
<th>Band gap / eV</th>
</tr>
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<tr>
<td>GO</td>
<td>449</td>
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<td>TiO$_2$</td>
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<td>2.59</td>
</tr>
<tr>
<td>rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$</td>
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<td>2.98</td>
</tr>
<tr>
<td>GO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$</td>
<td>399</td>
<td>3.10</td>
</tr>
</tbody>
</table>

4.6 Thermogravimetric Analysis — Differential Scanning Calorimetry (TGA-DTA) analysis of nanomaterial and nanocomposites

The nanomaterial and nanocomposites were pulverized and homogenized with a pestle in mortar. Then analyzed without further treatment using the Hitachi Star7200RV Thermal Analysis system, at a heating rate of 10°C per minute from room temperature to 900°C in a nitrogen gas atmosphere.

4.6.1 TGA-DTA analysis of Graphite and Graphene oxide (GO)

Thermal analysis of purchased synthetic graphite powder and synthesized graphene oxide yielded the TGA-DTA plots in Figure 4.44a and Figure 4.44b respectively.
Figure 4.44: TGA-DTA scans of: (a) purchased synthetic graphite powder and; (b) powdered as-synthesized graphene oxide. The scans were acquired with a Hitachi Star7200RV Thermal Analysis system, at a heating rate of 10°C.min⁻¹ from ~25°C – 900°C in a nitrogen gas atmosphere.

The purchased synthetic graphite powder exhibited little weight loss, less than 1.5% below 900°C [86]. Indicating that the graphite used in this research was pristine, without adsorbed water and thermally stable at temperatures below 900°C [35]. The 1.5% weight loss could conceivably be from the loss of oxidative by-products on the surface of the graphite as observed with the FTIR data. In contrast, graphene oxide was thermally unstable due to the reduced van der Waals interaction [86]. Graphene oxide experienced a three-step decomposition process from approximately 100°C with the removal of adsorbed water molecules as steam as widely documented in literature [2, 35, 86, 87]. The second step was marked by a sharp exothermic peak on the DTA curve at 193°C [4] corresponding to the main weight loss from the decomposition of the labile oxygen-containing functional groups [86, 88] or “degradation of graphene oxide” [89]. The third and final step with an endothermic DTA slope peaking at ~700°C was attributed to the removal of more stable oxygen-containing functional groups [86].

4.6.2 TGA-DTA analysis of TiO₂

The synthesized TiO₂ nanomaterial underwent three transitions when thermally treated at 10°C per minute from room temperature to 900°C in a nitrogen gas atmosphere as visually represented by TGA-DTA curves in Figure 4.45.
Figure 4.45: TGA-DTA scans of the powdered as-synthesized TiO$_2$ nanoparticles. The scans were acquired with a Hitachi Star7200RV Thermal Analysis system, at a heating rate of 10°C.min$^{-1}$ from ~25°C ─ 900°C in a nitrogen gas atmosphere.

The first step at 106°C on the TGA curve corresponding to a 3.62% weight loss was due to the evaporation of adsorbed solvents, i.e. water and ethanol [18, 38, 90]. The second step at 387°C corresponding to a large endothermic dip on the DTA curve was attributed to the change of remnant amorphous anatase to crystalline form [91]. The final transition was an exothermic process symbolized by the pronounced peak on the DTA curve, for the phase transition of the synthesized anatase nanomaterial to rutile [18, 91].

4.6.3 TGA-DTA analysis of SnO$_2$ and rGO-SnO$_2$

The TGA-DTA curves from thermal analysis of SnO$_2$ nanoparticles (Figure 4.46a) and rGO-SnO$_2$ (Figure 4.46b) nanocomposite, under the same temperature range (~25°C ─ 900°C) and inert environment, had a similar first transition step from the evaporation of adsorbed water molecules between 80°C ─ 100°C [20, 27].
There was a broad endothermic peak on the DTA curve of SnO$_2$ nanoparticles from 236$^\circ$C – 684$^\circ$C, which was attributed to the decomposition of Sn(OH)$_4$ at 150$^\circ$C – 450$^\circ$C temperature range and loss of “chemically adsorbed water” from 450$^\circ$C – 650$^\circ$C [27]. The last part of the TGA-DTA curve for rGO-SnO$_2$ resembled that of GO, i.e. decomposition of the labile oxygen-containing functional groups at 100$^\circ$C – 300$^\circ$C followed by the complete breakdown of the graphene oxide from 300$^\circ$C – 600$^\circ$C [20]. From 600$^\circ$C – 900$^\circ$C, there was more than a 20% mass loss in this region on the rGO-SnO$_2$ nanocomposites’ TGA curve which was ascribed to the degradation of GO observed at much lower temperatures without metal oxide layers.

4.6.4 TGA-DTA analysis of γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$

The synthesized γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$ nanomaterial both had adsorbed residue water that was dehydrated at 100$^\circ$C – 200$^\circ$C [92] when heated at room temperature to 900$^\circ$C in a nitrogen gas atmosphere, as represented by the step in their TGA curves in Figure 4.47a and Figure 4.47b respectively.
Figure 4.47: TGA-DTA scans of the powdered as-synthesized; (a) γ-Fe₂O₃ nanomaterial and; (b) rGO-Fe₂O₃ nanocomposite. The scans were acquired with a Hitachi Star7200RV Thermal Analysis system, at a heating rate of 10°C.min⁻¹ from ~25°C – 900°C in a nitrogen gas atmosphere.

The graphene oxide in the rGO-Fe₂O₃ nanocomposite began to decompose at 300°C – 600°C indicated by the step in the TGA curve and matching endothermic dip on the DTA curve. The two nanomaterial also shared a broad exothermic DTA peak that had no counterpart on the TGA curve as it was from the phase transition of Fe₂O₃ nanoparticles from gamma to alpha [93-95] which involves no change in mass [92].

4.6.5 TGA-DTA analysis of rGO-SnO₂-Metal oxide

The results from Thermal Gravimetric and Differential Thermal analysis of rGO-SnO₂-TiO₂ and rGO-SnO₂-Fe₂O₃ nanocomposites in a nitrogen atmosphere from room temperature to 900°C at a heating rate of 10°C per minute are represented by TGA-DTA curves in Figure 4.48a and Figure 4.48b respectively.
As expected, both nanocomposites had three transitions. The first was from dehydration of water adsorbed on the surface at <150°C signified by the first step on the TGA curves. The second transition was indicated by the endothermic broad peak on both DTA curves from the decomposition of graphene oxide in the 300°C – 600°C temperature range. The third and final transition was an exothermic process peaking at ~660°C on the DTA curves, also observed on the pristine Fe₂O₃ and TiO₂ DTA curves, attributed to the phase transition of Fe₂O₃ from gamma to alpha and TiO₂ anatase to rutile. It was also noted that the rGO-binary-metal oxide composites exhibited lower mass loss compared to the rGO-single metal oxide composites.

4.6.6 TGA-DTA analysis of rGO-Fe₂O₃-Metal oxide

The rGO-Fe₂O₃-TiO₂ and rGO-Fe₂O₃-SnO₂ were further characterized by thermal analysis to determine their purity and thermal stability among other properties, Figure 4.49a and Figure 4.49b represent the TGA-DTA curves from the study.
Figure 4.49: TGA-DTA scans of the powdered as-synthesized; (a) rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite and; (b) rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite. The scans were acquired with a Hitachi Star720RV Thermal Analysis system, at a heating rate of 10°C.min$^{-1}$ from ~25°C ─ 900°C in a nitrogen gas atmosphere.

The TGA curves of rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites had the first step at ~100°C, symbolizing the loss of surface water. The second transition for both nanomaterial corresponded to the initial decomposition of graphene oxide signified by a broad peak from 130°C ─ 750°C on the DTA curve due to the loss of labile oxygen-containing functional groups. The last step on both TGA curves had a decline denoting the complete breakdown of graphene oxide. The last segment of the DTA curve for rGO-Fe$_2$O$_3$-TiO$_2$ had the now familiar exothermic peak attributed to the phase transition of the metal oxides, γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$ and anatase-TiO$_2$ to rutile-TiO$_2$. Whereas the final segment of the DTA curve for the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite had a similar yet more pronounced endothermic slope than that observed on the DTA curve for the SnO$_2$ nanoparticles (Figure 4.46a), attributed to loss of "chemically adsorbed water" by Zhu at al. [27].

4.6.7 TGA-DTA analysis of ternary systems

The TGA-DTA curves for the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposites represented in Figure 4.50a and Figure 4.50b, are identical.
Figure 4.50: TGA-DTA scans of the powdered as-synthesized; (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite and; (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite. The scans were acquired with a Hitachi Star7200RV Thermal Analysis system, at a heating rate of 10°C.min$^{-1}$ from ~25°C – 900°C in a nitrogen gas atmosphere.

The study of the curves revealed that the nanocomposites experienced a three-step decomposition process and phase transition of the metals oxides when heated at 10°C.min$^{-1}$ from room temperature to 900°C in a nitrogen environment, similar to their precursors. The decomposition steps were attributed to the loss of surface water at <150°C as well as the initial and final decomposition of graphene oxide through the loss of oxygen-containing functional groups from >150°C – 750°C. The phase transition of the metals occurred between 630°C – 900°C as denoted by the exothermic DTA broad peaks. The ternary nanocomposites exhibited a lower total mass loss compared to their rGO-binary-metal oxide precursors.

4.7 Raman analysis of nanomaterials and nanocomposites

The synthesized solid nanomaterial and nanocomposites were powdered and homogenized before analysis with an Alpha300 R Raman microscope by WITec without further treatment. The Raman analysis was conducted at the Geology department of the University of Johannesburg’s Auckland Park campus.

4.7.1 Raman analysis of Graphite and Graphene oxide (GO)

The Raman spectrum of the purchased synthetic graphite powder had a similar pattern to that of the synthesized graphene oxide (Figure 4.51). The samples exhibited two characteristic bands in the 200 cm$^{-1}$ – 2000 cm$^{-1}$ spectral range, i.e. the G band at ∼1580 cm$^{-1}$ and D band at ∼1350 cm$^{-1}$, as widely documented in literature [2, 8, 35, 62, 88].
The G band was accredited to the first-order scattering of the $E_{2g}$ mode [96-99] whilst the D band was attributed to defects in the graphitic material that resulted in the disruptions of the symmetrical hexagonal graphene framework such as edge and internal structure defects as well as dangling bonds [21, 63]. The G band of the purchased synthetic graphite was prominent and sharp, observed at 1581 cm$^{-1}$ [88] on the other hand the G band of graphene oxide was broader and shifted to higher wavenumber (1592 cm$^{-1}$) [2, 8, 35, 88] due to the oxygenation of graphite [98]. The purchased synthetic graphite used in this research had low defect concentration symbolized by the low intensity D band at 1355 cm$^{-1}$ [8]. In contrast, the D band of graphene oxide (1350 cm$^{-1}$) was prominent and broader than that of graphite due to oxidation which created defects, vacancies and distortions of the $sp^2$ domains [98]. The ratio of the relative intensity of the D and G band ($I_D/I_G$) which is proportional to the disorder in graphitic material, i.e. the $I_D/I_G$ value increases with increased functionalization of the graphitic structure. As a result, the $I_D/I_G$ value is used to evaluate the presence and extent of disorder [8, 35, 62, 98] or the extent of functionalization [99] in graphitic material. As clearly observed with the $I_D/I_G$ value of purchased synthetic graphite and graphene oxide at 0.48 and 0.98 respectively in this research. Graphene oxide had a higher value due to the incorporation of the oxygen containing functional groups into its graphitic layers.
4.7.2 Raman analysis of TiO$_2$

The structural composition and identity of synthesized TiO$_2$ nanoparticles was further analyzed using a Raman microscope in the 200 cm$^{-1}$ - 2000 cm$^{-1}$ spectral range with a 20X magnification lens and 5 mW power. Figure 4.52 is a representation of the Raman spectrum from the analysis.

![Raman spectrum of TiO$_2$](image)

**Figure 4.52:** Raman spectrum of the synthesized TiO$_2$ nanoparticles. The spectrum was acquired using an Alpha300 R Raman microscope by WITec with a 20X magnification lens and 5 mW power.

The spectrum had the characteristic modes of the crystalline anatase phase without any impurities, i.e. the E$_{g(1)}$ band (147 cm$^{-1}$), B$_{1g(1)}$ band (399 cm$^{-1}$), E$_{g(2)}$ band (643 cm$^{-1}$), and the A$_{1g}$ + B$_{1g(2)}$ modes centered at 520 cm$^{-1}$, respectively [18, 19, 21, 90]. Thus, demonstrated that the solvothermal method used to synthesize the TiO$_2$ nanoparticles yields pristine crystalline anatase phase TiO$_2$ nanoparticles.

4.7.3 Raman analysis of SnO$_2$ and rGO-SnO$_2$

The Raman spectrum of rGO-SnO$_2$ nanocomposite was a combination of the spectra of its constituents, i.e. graphene oxide and SnO$_2$ (Figure 4.53), demonstrating the successful synthesis of rGO-SnO$_2$ nanocomposite.
The Raman spectrum of rGO-SnO$_2$ nanocomposite exhibited the D and G bands at the same wavenumber as GO, specifically at 1350 cm$^{-1}$ and 1596 cm$^{-1}$ respectively. However, at a higher value for the $I_D/I_G$ ratio (1.12) compared to the bare graphene oxide (0.98). Signifying that the process introduced more defects, since the ratio increased, accordingly the G-band character decreased, and D-band increased. In addition, similar to the Raman spectrum of SnO$_2$, it contained the three inter electronic vibration modes characteristic of SnO$_2$, namely; the $E_g$ for the Sn-O, the $A_{1g}$ for Sn=O and the $B_{2g}$ for the Sn-O-Sn [58, 100].

4.7.4 Raman analysis of γ-Fe$_2$O$_3$ and rGO-Fe$_2$O$_3$

The Raman spectrum of rGO-Fe$_2$O$_3$ nanocomposite exhibited the D and G band at ~1350 cm$^{-1}$ and ~1590 cm$^{-1}$ as projected (Figure 4.54a) due to the hybridization and disorder in the sp$^2$ carbon atoms of GO respectively [101].
Figure 4.54: Raman spectra of the as-synthesized: (a) rGO-Fe$_2$O$_3$, and (b) rGO-Fe$_2$O$_3$, γ-Fe$_2$O$_3$ and graphene oxide nanoparticles respectively. The spectra were acquired using an Alpha300 R Raman microscope by WITec with a 20X magnification lens and 2.5 mW power.

The $I_D/I_G$ ratio for the rGO-Fe$_2$O$_3$ nanocomposite could not be reliably calculated as the D band overlapped with one of the characteristic peaks for the γ-Fe$_2$O$_3$ nanoparticles. The added functional group on the graphene oxide layers was due to the four distinct bands in both the spectra of γ-Fe$_2$O$_3$ nanoparticles and rGO-Fe$_2$O$_3$ nanocomposite (Figure 4.54b), at 212 cm$^{-1}$, 275 cm$^{-1}$, 393 cm$^{-1}$ and 583 cm$^{-1}$ wavenumbers that were within reasonable limits to those characteristic of γ-Fe$_2$O$_3$ as reported in literature [102, 103].

4.7.5 Raman analysis of rGO-SnO$_2$-Metal oxide

Further structural analysis of the rGO-SnO$_2$-Fe$_2$O$_3$ and rGO-SnO$_2$-TiO$_2$ nanocomposites using a Raman microscope revealed that the respective metals oxides were incorporated onto the graphitic framework. Firstly, the Raman spectra (Figure 4.55) of both rGO-SnO$_2$-metal oxides exhibited the two distinct bands of graphene oxide at 1351 cm$^{-1}$ and 1598 cm$^{-1}$, for the D band due to disordered carbon and the G band attributed to sp$^2$ hybridized carbon respectively [20] thus confirming the presence of graphene oxide in the bi-metal oxide composites.
Secondly, the ratio of the area under the D and G bands ($I_D/I_G$) used to measure the degree of disorder in graphitic material was 1.19 for the rGO-SnO$_2$-TiO$_2$ nanocomposite, higher than that of their precursor, rGO-SnO$_2$ (1.12) thus indicating some further functionalization of the graphitic layers of graphene oxide. However, due to the γ-Fe$_2$O$_3$ nanoparticles peak overlapping with the D peak of the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite, the $I_D/I_G$ ratio for this composite could not be reliably determined. Third and lastly, standard spectra of the metal oxides were positively matched to the respective composites as visually illustrated in Figure 4.55. Namely, the bands at 214 cm$^{-1}$, 281 cm$^{-1}$, 391 cm$^{-1}$ and 583 cm$^{-1}$ wavenumbers characteristic of γ-Fe$_2$O$_3$ nanoparticles [103] and the 644 cm$^{-1}$ band due to the $A_{1g}$ vibration mode of SnO$_2$ [20, 104] in the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposites’ Raman spectrum. Similarly, the Raman spectrum of rGO-SnO$_2$-TiO$_2$ nanocomposite exhibited the 622 cm$^{-1}$ band due to the inter electronic $A_{1g}$ vibration mode of Sn=O [58, 105], in addition to the distinct 147 cm$^{-1}$ main $E_g$ vibration mode of anatase [20]. The rGO-SnO$_2$-TiO$_2$ nanocomposites’ Raman spectrum contained two pronounced bands at 251 cm$^{-1}$ and 422 cm$^{-1}$ wavenumbers as well, instead of the 399 cm$^{-1}$ ($B_{1g}$) and 520 cm$^{-1}$ ($A_{1g}$) as projected.

4.7.6 Raman analysis of rGO-Fe$_2$O$_3$-Metal oxide

The characterization of rGO-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposites by Raman spectroscopy produced the spectra in Figure 4.56a and Figure 4.56b.
As expected, both spectra exhibited the two typical bands for graphene oxide, the D band at 1344 cm\(^{-1}\) and G band at 1598 cm\(^{-1}\) for the presence of the graphitic layers in their structure. The defect concentration of the nanocomposites expressed by the intensity ratio of the D and G peaks (I\(_D\)/I\(_G\)) was not determined as both nanocomposites (rGO-Fe\(_2\)O\(_3\)-SnO\(_2\) and rGO-Fe\(_2\)O\(_3\)-TiO\(_2\)) contain the characteristic \(\gamma\)-Fe\(_2\)O\(_3\) nanoparticles peak that overlap with their D peak. Nevertheless, the individual metal oxide bands were observed on the spectra of the respective nanocomposites thus confirming their successful integration into the composites. Specifically, the 618 cm\(^{-1}\) band for SnO\(_2\) [20] and the characteristic \(\gamma\)-Fe\(_2\)O\(_3\) bands at 217 cm\(^{-1}\), 273 cm\(^{-1}\), and 390 cm\(^{-1}\) for the rGO-Fe\(_2\)O\(_3\)-SnO\(_2\) nanocomposite [103]. The rGO-Fe\(_2\)O\(_3\)-TiO\(_2\) nanocomposites’ Raman spectrum similarly, had the characteristic bands of its metals oxides, i.e. the two \(E_g\) modes for TiO\(_2\) at 148 cm\(^{-1}\) and 643 cm\(^{-1}\) [90] in addition to the 222 cm\(^{-1}\) band at a slightly lower wavenumber of 193 cm\(^{-1}\) and the broad band peaking at 356 cm\(^{-1}\) encompassing the 289 cm\(^{-1}\) and 408 cm\(^{-1}\) distinguishing bands for the gamma Fe\(_2\)O\(_3\) [103] as visually represented in Figure 4.56b.

### 4.7.7 Raman analysis of ternary systems

The Raman spectra of the rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) and rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) nanocomposites were identical (Figure 4.57a) both exhibiting the two main features used to distinguish graphene oxide when analyzed using Raman spectroscopy, i.e. the D band (1346 cm\(^{-1}\)) attributed to the breathing mode of K-point photons with \(A_{1g}\) symmetry and the graphitic (G) band (1596 cm\(^{-1}\)) due to the first order scattering of the \(E_{2g}\) phonon of the \(sp^2\) carbon-carbon atoms [106].
Figure 4.57: Raman spectra of the powdered as-synthesized: (a) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ ternary nanocomposites respectively and the: (b) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$, rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$, Fe$_2$O$_3$, TiO$_2$ and SnO$_2$ nanomaterial respectively. The spectra were acquired using an Alpha300 R Raman microscope by WITec with a 20X magnification lens and 2.5 mW power.

A comparison plot of both ternary systems with the standard Raman spectra of GO, SnO$_2$, Fe$_2$O$_3$ and TiO$_2$ revealed the presence of all metals oxides in both structures (Figure 4.57b). Namely; the $A_{1g}$ band (626 cm$^{-1}$) for SnO$_2$ [105]; the TiO$_2$ bands $E_{g(1)}$ at 154 cm$^{-1}$, $B_{1g(1)}$ (396 cm$^{-1}$) and $A_{1g} + B_{1g(2)}$ at 508 cm$^{-1}$ [21] in addition to the three $\gamma$-Fe$_2$O$_3$ bands at 221 cm$^{-1}$, 255 cm$^{-1}$ and 390 cm$^{-1}$ [103].

4.8 Brunauer-Emmett-Teller method for the analysis of nanomaterial and nanocomposites

The surface area and porosity of the synthesized nanomaterial were analyzed using nitrogen physical adsorption method. The powdered as-synthesized nanomaterial were degassed at 90°C for 10 hours prior to characterization with the Micromeritics ASAP 2460 surface area and porosity analyzer at 77K (~196.15°C) using nitrogen gas. The BET analysis was conducted at the Chemistry department of the University of Johannesburg’s Auckland Park campus.

4.8.1 BET analysis of Graphite and Graphene oxide (GO)

Textural analysis of purchased synthetic graphite powder and powdered as-synthesized graphene oxide using the Brunauer-Emmett-Teller method (BET) exhibited type IV adsorption-desorption isotherms for both nanomaterial with H3 and H2 respectively (Figure 4.58a and Figure 4.58b). Indicative of mesoporous structures with slit shaped pores of non-uniform size and/or shape [107], which is expected since the GO consists of loosely aggregated sheets of material.
Mesoporous structures are appealing in electrode material as they allow effective movement of the electrolyte in addition to providing the space allowance for the de/intercalation-induced strain [108, 109]. The Barrett-Joyner-Haleda (BJH) desorption average pore diameter for graphite and graphene oxide were 16.20 nm and 6.01 nm, both within the accepted range for mesoporous structures, i.e. 2 nm – 50 nm [107]. The BET surface area of the as-synthesized graphene oxide (30.94 m²/g) was more than that of purchased graphite (6.39 m²/g) this has been attributed to oxidation of graphite in literature [62]. The reaction of graphite with strong oxidizing agents increases the interlayer spacing of the graphitic layers [3, 110] and therefore the overall space contribution of its oxidation product [62], i.e. graphite oxide and graphene oxide after exfoliation, which in this investigation increased to \( d = 0.88 \) nm from 0.34 nm of the pristine graphite (Section 4.2.1). The surface area and porosity of the synthesized nanomaterial were calculated with the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Haleda (BJH) method, respectively from the desorption branch of the isotherms using the MicroActive software.

4.8.2 BET analysis of TiO₂

The BET surface area of the synthesized TiO₂ nanoparticles was 109.15 m²/g which was comparable to similar work in literature (89 – 122) m²/g [111, 112]. The BJH desorption average pore diameter was 8.00 nm denoting mesopores (i.e. 2 nm – 50 nm), most likely due to porosity between TiO₂ nanoparticles’ [107]. The mesoporous structure of the synthesized TiO₂ nanoparticles was further attested by its adsorption-desorption curve which was a type IV isotherm with an H2 hysteresis (Figure 4.59), characteristic of mesoporous solids with cylindrical pores or pores caused by aggregation of spheroidal particles of non-uniform size or shape [107].
4.8.3 BET analysis of SnO$_2$ and rGO-SnO$_2$

The powdered as-synthesized SnO$_2$ and rGO-SnO$_2$ nanomaterial were both mesoporous solids with inhomogeneous pore size distribution ranging between 2 nm — 50 nm. Denoted by type IV adsorption-desorption isotherms (Figure 4.60a and Figure 4.60b) with distinct H3 hysteresis loops in the 0.4 — 1 P/P$_0$ range when analyzed using the BET method [107].
The BET surface area of the rGO-SnO\(_2\) nanocomposite was 178.81 m\(^2\)/g with a BJH desorption average pore diameter of 3.84 nm whilst SnO\(_2\) nanoparticles’ surface area was calculated to be 96.09 m\(^2\)/g using the BET method and its BJH desorption average pore diameter was 7.45 nm. Seema et al. [25] ascribed the difference in surface area to bilateral anchored SnO\(_2\) particles on graphene layers which reduces restacking of the graphitic layers. Thus, increasing the space between the layers of graphene oxide and inevitably the overall space of the nanocomposite.

### 4.8.4 BET analysis of γ-Fe\(_2\)O\(_3\) and rGO-Fe\(_2\)O\(_3\)

The BET adsorption-desorption curves for surface and porosity analysis of γ-Fe\(_2\)O\(_3\) and rGO-Fe\(_2\)O\(_3\) nanomaterial are represented in Figure 4.61a and Figure 4.61b respectively.

![Figure 4.61a](image)

*Figure 4.61a:* Nitrogen adsorption-desorption isotherms of the powdered as-synthesized; (a) γ-Fe\(_2\)O\(_3\) nanoparticles and; (b) rGO-Fe\(_2\)O\(_3\) nanocomposite. The isotherms were acquired using the Micromeritics ASAP 2460 surface area and porosity analyzer.

The adsorption-desorption curves were similar, they exhibited type IV isotherms with an H2 hysteresis loop, distinct of mesoporous solids with pores of non-uniform shape or size [107]. The BET surface area of rGO-Fe\(_2\)O\(_3\) (256.89 m\(^2\)/g), similar to the surface area of rGO-SnO\(_2\) versus pristine SnO\(_2\), was larger than that of pristine γ-Fe\(_2\)O\(_3\) (168.90 m\(^2\)/g). Therefore, the same principle can be ascribed to the surface area variance of γ-Fe\(_2\)O\(_3\) and rGO-Fe\(_2\)O\(_3\), that is, the γ-Fe\(_2\)O\(_3\) nanoparticles anchored on both sides of the graphitic layers of GO reduce restacking as well as increase the interlayer spacing of the graphene layers thus causing an increase in space contribution in rGO-Fe\(_2\)O\(_3\) nanocomposite [113]. The BJH desorption average pore diameter for the rGO-Fe\(_2\)O\(_3\) nanocomposite was 4.50 nm and that for γ-Fe\(_2\)O\(_3\) nanoparticles was 9.63 nm, both within the characteristic mesopores range (i.e. 2 nm — 50 nm) [107].
4.8.5 BET analysis of rGO-SnO$_2$-Metal oxide

Surface area measurements of rGO-SnO$_2$-TiO$_2$ (156.51 m$^2$/g) indicated a significant reduction in the calculated BET surface area after hydrothermal anchoring of TiO$_2$ nanoparticles on rGO-SnO$_2$ nanocomposite (178.81 m$^2$/g). In contrast, the anchored γ-Fe$_2$O$_3$ nanoparticles on rGO-SnO$_2$, significantly enhanced the BET surface area of the resultant GO-SnO$_2$-Fe$_2$O$_3$ nanocomposite (191.42 m$^2$/g). However, both nanomaterial were mesoporous with relatively similar BJH desorption average pore diameter of 5.08 nm and 5.77 nm for rGO-SnO$_2$-TiO$_2$ and rGO-SnO$_2$-Fe$_2$O$_3$ respectively. Predictably from the BJH pore distribution calculations, both curves have a typical type IV mesoporous structure adsorption-desorption isotherm (Figure 4.62a and Figure 4.62b) \[107\].

![Figure 4.62: Nitrogen adsorption-desorption isotherms of the powdered as-synthesized; (a) rGO-SnO$_2$-TiO$_2$ nanocomposite and; (b) rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposite. The isotherms were acquired using the Micromeritics ASAP 2460 surface area and porosity analyzer.](image)

The isotherms differ in the type of hysteresis loop, the rGO-SnO$_2$-TiO$_2$ nanocomposite had an H3 type signifying slit shaped pores of different shape and size whilst the rGO-SnO$_2$-Fe$_2$O$_3$ nanocomposites had an H2 loop, representing spherical or cylindrical pores.

4.8.6 BET analysis of GO-Fe$_2$O$_3$-Metal oxide

In contrast to the rGO-SnO$_2$-metal oxide nanocomposites, both the BET surface area of the rGO-Fe$_2$O$_3$-metal oxide nanocomposites, i.e. rGO-Fe$_2$O$_3$-TiO$_2$ (137.92 m$^2$/g) and rGO-Fe$_2$O$_3$-SnO$_2$ (217.19 m$^2$/g) were lower compared to their precursor, rGO-Fe$_2$O$_3$ (256.89 m$^2$/g). The adsorption-desorption curves were distinctly those of mesoporous solids with plate-like pores of non-uniform size or shape as denoted by the type IV isotherms with H2 hysteresis loops for both nanocomposites (Figure 4.63).
Figure 4.63: Nitrogen adsorption-desorption isotherms of the powdered as-synthesized; (a) rGO-Fe$_2$O$_3$-TiO$_2$ nanocomposite and; (b) rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite. The isotherms were acquired using the Micromeritics ASAP 2460 surface area and porosity analyzer.

The BJH desorption average pore diameter for the rGO-Fe$_2$O$_3$-SnO$_2$ nanocomposite was 4.49 nm and that for the GO-Fe$_2$O$_3$-TiO$_2$ nanocomposite was 8.09 nm, equally distinctive of mesopores, i.e. 2 nm < size < 50 nm [107].

4.8.7 BET analysis of ternary systems

The ternary systems’ — rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ — adsorption-desorption isotherms were identical, both type IV with H3 hysteresis loops (Figure 4.64a and Figure 4.64b), indicative of solids with mesopores of varying sizes and shapes.
Figure 4.64: Nitrogen adsorption-desorption isotherms of the powdered as-synthesized; (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite and; (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite. The isotherms were acquired using the Micromeritics ASAP 2460 surface area and porosity analyzer.

The BJH desorption average pore diameter for the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ ternary nanocomposite was 11.65 nm whilst that for rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ was 7.94 nm thus further confirming the mesoporous structure of the solids, i.e. within the characteristic mesopores size range, 2 nm — 50 nm [107]. The BET surface areas were 128.28 m$^2$/g for rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and 166.14 m$^2$/g rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ both lower than their precursors, i.e. rGO-SnO$_2$-Fe$_2$O$_3$ (191.42 m$^2$/g) and rGO-Fe$_2$O$_3$-SnO$_2$ (217.19 m$^2$/g) after anchoring TiO$_2$ as observed with rGO-SnO$_2$-TiO$_2$ and its corresponding precursor (Section 4.8.5).

A summary of the key factors discovered by analysis of the synthesized nanomaterial by BET method are summarized in Table 4.2.
Table 4.2: Summary of the BET method key factors for the synthesized nanomaterial and nanocomposites.

<table>
<thead>
<tr>
<th>Synthesized Nanomaterial</th>
<th>Surface Area (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume(cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>6.39</td>
<td>16.20</td>
<td>0.040</td>
</tr>
<tr>
<td>GO</td>
<td>30.94</td>
<td>6.01</td>
<td>0.030</td>
</tr>
<tr>
<td>TiO₂</td>
<td>109.15</td>
<td>8.00</td>
<td>0.27</td>
</tr>
<tr>
<td>SnO₂</td>
<td>96.09</td>
<td>7.45</td>
<td>0.12</td>
</tr>
<tr>
<td>rGO-SnO₂</td>
<td>178.81</td>
<td>3.84</td>
<td>0.078</td>
</tr>
<tr>
<td>rGO-SnO₂-TiO₂</td>
<td>156.51</td>
<td>5.08</td>
<td>0.15</td>
</tr>
<tr>
<td>rGO-SnO₂-Fe₂O₃</td>
<td>191.42</td>
<td>5.77</td>
<td>0.27</td>
</tr>
<tr>
<td>rGO-SnO₂-Fe₂O₃-TiO₂</td>
<td>128.28</td>
<td>11.65</td>
<td>0.34</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>168.90</td>
<td>9.63</td>
<td>0.42</td>
</tr>
<tr>
<td>rGO-Fe₂O₃</td>
<td>256.89</td>
<td>4.50</td>
<td>0.27</td>
</tr>
<tr>
<td>rGO-Fe₂O₃-TiO₂</td>
<td>137.92</td>
<td>8.09</td>
<td>0.30</td>
</tr>
<tr>
<td>rGO-Fe₂O₃-SnO₂</td>
<td>217.19</td>
<td>4.49</td>
<td>0.24</td>
</tr>
<tr>
<td>rGO-Fe₂O₃-SnO₂-TiO₂</td>
<td>166.14</td>
<td>7.94</td>
<td>0.34</td>
</tr>
</tbody>
</table>

4.9 Key Findings and Conclusions

The oxygen containing functional groups on the FTIR spectra of the rGO-metal oxide nanocomposites were fewer, with those present at lower intensities compared to the unmodified GO. Indicating the reduction of GO. However, the oxygen containing functional groups on the FTIR spectra of the rGO based bi- and tri-metals oxides nanocomposites were similar in number and intensity to their rGO-metal oxide precursor. Indicating that the second and third metal oxides were not bonded on the graphitic lattice but rather coated on the surface of the nanocomposites. Probably due to the high metal oxide to GO ratio.

The XRD analysis revealed the phases of the metal oxides as anatase (TiO₂), cassiterite (SnO₂) and gamma (Fe₂O₃). No new phases of the metal oxides were observed in either the rGO-bi-metals oxides or rGO-tri-metals oxides nanocomposites indicating that the metals did not alloy.

The SEM and TEM analysis agreed with FTIR analysis on the excessive quantity of metals oxides ratio to the GO for the rGO-bi-metals oxides and rGO-tri-metals oxides nanocomposites. Explicitly, the SEM and TEM images of the rGO-bi-metals oxides and rGO-tri-metals oxides exhibited translucent sheets (graphene oxide layers) with overlapped and/or agglomerates of nanoparticles (metal oxides). The agglomeration of active particles results in increased Na⁺ diffusion rate and thus irreversible capacity loss. Therefore, for future work it is recommended that the metal oxide to graphene oxide ratio be reduced. The interlayer spacing of the diffraction rings on the SAED pattern of the metal oxides and their rGO based nanocomposites, positively matched those of the anatase.
(TiO$_2$), cassiterite (SnO$_2$) and gamma (Fe$_2$O$_3$) standards. No new phases of the metal oxides were observed thus agreeing with the XRD findings.

The band gap of the metal oxides and rGO-metal oxides calculated from their UV-Vis spectra were similar to previously reported values in literature. The band gap of the metal oxides and rGO-metal oxides calculated from their UV-Vis spectra were similar to previously reported values in literature. There is limited information in literature of the binary or ternary composite nanomaterials synthesized as electrode material for either SIBs or LIBs and thus band gap information of these nanomaterial were not compared to previous research.

The synthesized nanomaterial had adsorbed water which were exhibited in both their FTIR spectra and TGA curves. Therefore, the ternary nanocomposites were dried before weighing for the fabrication of the half cells for electrochemical characterization due to highly reactivity nature of sodium with moisture. The TGA curves of the rGO based nanocomposites also demonstrated the three stage decomposition of graphene oxide as expected at $>150^\circ C - 750^\circ C$, in addition to the phase transformation of the metal oxides in the $630^\circ C - 900^\circ C$ range. The rGO-binary-metal oxide composites exhibited lower mass loss compared to the rGO-single metal oxide composites. It was also noted that the ternary nanocomposites exhibited a lower total mass loss compared to their rGO-binary-metal oxide precursors.

The synthesized nanomaterials exhibited the projected characteristic bands as reported in literature when analysed with the Raman technique, i.e. the D and G bands for the graphitic material (graphite, graphene oxide and reduced graphene oxide) in addition to the TiO$_2$, SnO$_2$ and Fe$_2$O$_3$ metal oxides without impurities. Thus, corroborating the XRD, FTIR and TEM-SAED results that new phases of the metal oxides were formed in the bi and tri-metal oxides nanocomposites. The I$_D$/I$_G$ value, used to evaluate the degree of functionalization increased with the incorporation of the metal oxides for the rGO-SnO$_2$ nanocomposite compared to that of GO. Signifying that the process introduced more defects, since the ratio increased, accordingly the G-band character decreased, and D-band increased. However, due to the $\gamma$-Fe$_2$O$_3$ nanoparticles peak overlapping with the D peak of the nanocomposites incorporated with the $\gamma$-Fe$_2$O$_3$ nanocomposites, the I$_D$/I$_G$ ratio for these composites could not be reliably determined.

The BET surface area of graphene oxide increased with the incorporation of the metal oxides due to the increase in interlayer spacing and thus overall space contribution of the resultant nanocomposites. However, it was observed that when the TiO$_2$ nanoparticles were incorporated into the graphitic lattice, the BET surface area decreased.
4.10 References


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CHAPTER 5: APPLICATION

5 Overview

This chapter discusses in detail the electrochemical properties of the synthesized ternary systems (rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$) discovered during their characterization with cyclic voltammetry and galvanostatic charge/discharge electro-analytical techniques. This chapter also details the physical properties exhibited by the ternary systems after their performance as anode material in a sodium battery using the Raman, XRD and TEM analytical techniques.

5.1 Electrochemical characterization of the ternary systems

The electrochemical performance of the synthesized ternary nanocomposites was evaluated in a PAT-Cell™ (Figure 5.1a), using a half-cell. The half-cell consisted of an rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ or rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ working electrode in addition to a counter and a reference electrode made from sodium metal. The electrodes were physically separated by a glass fibre, however connected by an ion conductive 1 M NaClO$_4$/PC electrolyte solution as illustrated in Figure 5.1b. The cells were assembled in a nitrogen filled glove box with oxygen and moisture concentrations of $\leq$0.5 ppm and 62 ppm — 69 ppm respectively.

![Figure 5.1: The half-cells’ (a) shell i.e. PAT-Cell™; and (b) arrangement inside the PAT-Cell™](image)

The cyclic charge-discharge and cyclic voltammetry measurements were conducted with the Interface 1000 Potentiostat using the Framework software both by Gamry instruments (Figure 5.2a), in the 0.01 V — 2.4 V voltage range versus Na/Na$^+$. The section below discusses the findings in detail.
5.1.1 Charge-discharge analysis of the ternary systems

The open circuit voltage of the two ternary nanocomposites’ half cells was evaluated prior to cyclic voltammetry and cyclic charge-discharge measurements. The PAT-Cell\textsuperscript{TM} was inserted into the Patstand\textsuperscript{TM} then connected to the Interface 1000 Potentiostat (Figure 5.2a). Subsequently, the Framework software was started (Figure 5.2b) and the open circuit voltage value read. The rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} and rGO-Fe\textsubscript{2}O\textsubscript{3}-SnO\textsubscript{2}-TiO\textsubscript{2} half cells exhibited relatively similar high open circuit voltage of 2.60 V and 2.66 V respectively (Figure 5.2).

![Figure 5.2: Open circuit voltage of the rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} and rGO-Fe\textsubscript{2}O\textsubscript{3}-SnO\textsubscript{2}-TiO\textsubscript{2} half cells before electrochemical characterisation.](image)

After the open voltage measurements, the cyclic charge-discharge program on the Framework software was selected. The cyclic charge-discharge measurements were conducted at a constant current density of ±45 mAg\textsuperscript{-1} (0.5 mA at C/20) between the 0.01 V — 2.4 V voltage range versus Na/Na\textsuperscript{+}. The charge-discharge voltage profiles of the rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} and rGO-Fe\textsubscript{2}O\textsubscript{3}-SnO\textsubscript{2}-TiO\textsubscript{2} electrodes in the 1 — 5\textsuperscript{th}, 10\textsuperscript{th}, 15\textsuperscript{th}, and 20\textsuperscript{th} cycles are represented in Figure 5.3.
Figure 5.3: Initial charge-discharge voltage profiles; (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ ternary nanocomposites; and (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites. Subsequent charge-discharge voltage profiles (2 — 5th, 10th, 15th, and 20th cycles) of the (c) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ ternary nanocomposites; and (d) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites. Rate capacity profiles with coulombic efficiency of the; (e) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ ternary nanocomposites; and (f) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites. The profiles were acquired at a constant current density of ±45 mAg$^{-1}$ (0.5 mA at C/20) within the 0.01 V — 2.4 V voltage range versus Na/Na$^+$. with the Interface 1000 Potentiostat using the Framework software both by Gamry instruments.
The charge-discharge voltage profiles indicated that the prepared rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) anodes exhibited unstable low capacities that decreased with cycling. The initial discharge (Na\(^+\) insertion) and charge (Na\(^+\) extraction) capacities for the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) anode were 87.29 mAh\(^{-1}\) and 1.79 mAh\(^{-1}\) respectively, demonstrating a very low columbic efficiency of 2.1% (Figure 5.3a). Similarly, rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) anode exhibited a large irreversible capacity loss during the first charge-discharge cycle, with initial discharge and charge capacities of 172.69 mAh\(^{-1}\) and 6.76 mAh\(^{-1}\) respectively (Figure 5.3b). However, the initial discharge capacity of the rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) anode was nearly twice that of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) anode. The initial large irreversible loss in capacity has been observed widely in Sn-, Fe- and Ti-based electrodes in both lithium- and sodium-ion cells though not as extreme as in this study and it is attributed to the irreversible formation of the solid electrolyte interphase (SEI) on the surface of the working electrodes from the reaction of metallic sodium and organic electrolytes. [1-7].

The discharge capacity faded drastically during subsequent cycles from 19.30 mAh\(^{-1}\) — 0.88 mAh\(^{-1}\) for the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) anode (Figure 5.3c) and 21.03 mAh\(^{-1}\) — 1.08 mAh\(^{-1}\) for the rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) anode (Figure 5.3d) within 20 cycles, with an average columbic efficiency of 30% and 22% respectively. In literature SnO\(_2\), TiO\(_2\), Fe\(_2\)O\(_3\) and carbon anode material used as hybrids or individually in sodium-ion battery half cells, using sodium metal as the counter electrode have exhibited high reversible capacities, high cycling stability and capacity retention [8, 9]. For example, C-TiO\(_2\) electrode investigated by Tahir et al. exhibited a high reversible capacity of 227 mAh\(^{-1}\) that was fully retained from the second cycle up to 300 cycles with an impressive 98% columbic efficiency [9]. The significant difference between these studies and the current investigation is the moisture and oxygen content of the glove box used for sodium cell assembly and solvent preparation. Typically, the moisture and oxygen content of the glove box are maintained below 0.1 ppm [8, 9] due to the highly reactivity nature of sodium with moisture. Whereas in this current investigation the concentrations of moisture and oxygen were 62 ppm — 69 ppm and ≤0.5 ppm respectively in the glove box during assembly of the cells. Therefore, the plausible cause for the low and fading capacity may well be accredited to the several side reactions observed in literature when sodium ions are de/intercalated in aqueous media [10]. These include but are not limited to reactions of electrode material with H\(_2\)O or O\(_2\), intercalation of protons into electrode material, reactions resulting in the release of H\(_2\) or O\(_2\) gases, and the dissolution of electrode materials in water [10]. These side reactions consume the electrolyte and sodium and consequently decreased cell performance [11].

In addition, the most probable source of moisture is the NaClO\(_4\)/PC electrolyte solution used. The NaClO\(_4\)/PC electrolyte solution was prepared from sodium perchlorate monohydrate salt (NaClO\(_4\)∙H\(_2\)O). The salt was dried overnight at 100°C in an oven. Then left to reach room temperature naturally in a desiccator before weighing (3.5115 grams), dissolving and diluting to the mark in 25-mL volumetric flask with propylene carbonate. Cyclic charge-discharge measurements of the ternary systems with the above electrolyte resulted in system error (Figure 5.4). As a result, moisture from the electrolyte solution was removed using the Schlenk line with nitrogen as the inert gas.
Unfortunately, the cyclic charge-discharge measurements still resulted in a system error. Most probably due to the long gas line and the use of nitrogen instead of argon as the inert gas. Finally, molecular sieve was used to dry the NaClO₄/PC electrolyte solution. The molecular sieve was dried for 15 hours in the oven at 300°C before cooling in an argon gas atmosphere. Then both the NaClO₄/PC electrolyte solution and molecular sieve were decanted into a glass polytop vial and left for 2 hours prior to electrochemical measurement. However, even though dried with molecular sieve, moisture content of the NaClO₄/PC electrolyte solution most probably still exceeded 0.1 ppm. Please note that the ternary nanocomposites were dried before assembling the anodes and subsequently the cells as the FTIR and TGA data revealed adsorbed moisture on the surface of these nanomaterials. Therefore, the prepared rGO-SnO₂-Fe₂O₃-TiO₂ and rGO-Fe₂O₃-SnO₂-TiO₂ anodes could not be the contributing factor to the moisture content.

Figure 5.4: Print screen picture of the system error or cell malfunction of the ternary systems’ (a) discharge voltage profile; and (b) charge voltage profiles.

On the other hand, the theoretical capacities of the metal oxides under study are; SnO₂ (1378 mAhg⁻¹) [5], TiO₂ (671 mAhg⁻¹)[12], and Fe₂O₃ (1007 mAhg⁻¹) [6] based on equation 1 — 3 respectively.

\[
4SnO_2 + 31Na^+ + 31e^- \rightarrow Na_{15}Sn_4 + 8Na_2O \tag{1}
\]

\[
2Na + TiO_2 \leftrightarrow 2NaO + Ti \tag{2}
\]

\[
Fe_2O_3 + 6Na^+ + 6e^- \leftrightarrow 2Fe^0 + 3Na_2O \tag{3}
\]

When calculated using the formula:
\[ Q = \frac{nF}{M_w} \quad \text{Equation 5.1} \]

where \( n \) is the number of electrons in the reaction, \( F \) is Faraday’s constant (96 500C), and \( M_w \) is the molecular weight / mass. There is consensus that only an extremely small number of sodium-ions can be intercalated into the graphitic sheets, however, literature reports are divided on the amount that can be reversibly inserted into carbonaceous material, e.g. NaC\(_{15}\) [13], NaC\(_{70}\) [13], NaC\(_{186}\) [14]. In this study, the theoretical specific capacity of graphene oxide was calculated to be 149 mAhg\(^{-1}\) based on equation 4.

\[ 15C + Na^+ + e^- \rightarrow NaC_{15} \quad (4) \]

Therefore, the theoretical specific capacity of both the ternary nanocomposites was determined to be 976 mAhg\(^{-1}\) by

\[ Q_{rGO/SnO_2/TiO_2/Fe_2O_3} = (Q_{rGO} \times 4.9\%) + (Q_{SnO_2} \times 31.7\%) + (Q_{TiO_2} \times 31.7\%) + (Q_{Fe_2O_3} \times 31.7\%) \quad (5) \]

where \( Q_{rGO/SnO_2/TiO_2/Fe_2O_3} \), \( Q_{rGO} \), \( Q_{SnO_2} \), \( Q_{TiO_2} \), and \( Q_{Fe_2O_3} \), correspond to the theoretical capacities of the ternary nanocomposites, graphene oxide, SnO\(_2\), TiO\(_2\), and Fe\(_2\)O\(_3\) respectively. The mass percentages of the individual components were calculated from the mass weighed during synthesis.

To further investigate the electrochemical performance of the ternary nanocomposites, the charge-discharge cycles were studied at varied current densities, starting at the low current rate of C/20 up to C/1 (1C = 976 mAg\(^{-1}\)). The ternary nanocomposites’ half cells short circuited at current rates higher than C/20, thus no charge-discharge cycles were observed. Increasing the current higher than 0.5 mA whilst maintaining the discharge rate at 20 hours had the same effect on cells, i.e. cell malfunction without any charge-discharge cycles was observed (Figure 5.4). Conceivably from increased resistance at the interface of the electrolyte and active material in addition to inadequate diffusion of sodium-ions caused by the high rates [4]. However, in the current study most likely the several side reactions from the presence of moisture aggravated the effect from faded capacity usually observed with increased current rates [4] to cell malfunction. Please note that the charge-discharge cycles measurements at varied current densities were studied on new half-cells.

### 5.1.2 Cyclic Voltammetry analysis of the ternary systems

Initially the Na-ion insertion–extraction behavior of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) anode material was to be investigated by cyclic voltammetry between the 0.01 V — 2.4 V voltage range versus Na/Na\(^+\), at a scan rate of 50 mV s\(^{-1}\). However, due to the noise only measurements up
to 1.5 V could be made (Figure 5.5). Conceivably, as a result of these measurements being preceded by the charge-discharge investigations that proved/resulted in the cells’ fading electrochemical performance (Section 5.1.1). The open circuit voltage after the charge-discharge measurements prior to CV measurements was ±1.5 V (Figure 5.5c).

Figure 5.5: Cyclic voltammograms of the (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ anode material between 0.01 V and 1.5 V at a scan rate of 50 mV s$^{-1}$ for the first six cycles. (c) Open circuit voltage of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ half cells after charge-discharge measurements electrochemical characterisation.

Figure 5.5a and Figure 5.5b represent the first six CV curves of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites respectively. The curves demonstrate the different sodium insertion/extraction potentials of TiO$_2$, Fe$_2$O$_3$, and SnO$_2$. The first discharge process of both ternary nanocomposites exhibited an irreversible peak at 0.36 V that was related to the possible reduction of Fe$_2$O$_3$ to Fe corresponding to equation 3. The redox peaks for the reduction of Fe$_2$O$_3$ were projected at potentials of 0.3 V/1.3 V (cathodic/anodic) as reported in literature [15]. These redox peaks are typically not observed in subsequent scans due to the low redox kinetics in sodium-
ion batteries [15]. The irreversible cathodic peak at 0.36 V has also been linked in literature to the consumption of sodium-ions during the formation of the solid electrolyte interphase (SEI) [16]. The subsequent scans exhibited overlapping, highly reproducible cathodic and anodic peaks, at 0.97 V and 0.65 V potentials respectively. These redox peaks were attributed to the possible reduction of TiO$_2$ to metallic titanium [9] corresponding to equation 2 and reduction of SnO$_2$ to metallic Sn [17], most likely according to equation 4.

$$SnO_2 + 4Na^+ + 4e^- \rightarrow Sn + 2Na_2O \quad (4)$$

In addition, the first cathodic scan exhibited higher current from 0.94 V — 1.54 V vs. Na$^+$/Na than the subsequent scans which was attributed to the irreversible formation of a solid electrolyte interphase (SEI) [6] due to reductive electrolyte decomposition. The current in the 0.94 V — 1.54 V voltage range decreased with each subsequent scan denoting unstable cycling of the ternary nanocomposites, which was in good agreement with the charge-discharge measurements. As these cells had already been cycled, the SEI should have already been formed [18] and thus no SEI peaks should have been observed. However, the numerous side reactions of the sodium metal electrode with H$_2$O and O$_2$ most probably resulted in the formation of an unstable SEI. These side reactions re-exposes the fresh sodium surface to the electrolyte and the SEI forms again, thus consuming the electrolyte and sodium and consequently decreasing cell performance [11].

5.2 Physical properties: defects and morphology of the ternary nanocomposites after application

After electrochemical characterization, the working electrodes (rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ or rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite, PVDF and graphite in N-methyl-2-pyrrolidene solvent) were homogenized using a pestle in mortar then analyzed with XRD, TEM and Raman analytical techniques.

5.2.1 XRD analysis of the ternary systems after application

Each used working electrode sample was packed into a silicon sample holder, and then levelled before analysis using the X’Pert Pro core, Phillips X-ray diffractometer from PANalytical, at a scanning range of 4˚ – 90˚ 2θ with a radiation source of Cu Kα (0.154 nm).

The XRD spectra of the ternary electrodes after the charge-discharge and cyclic voltammetry measurements exhibited the same diffraction peaks, at relatively similar 2θ positions as the pristine ternary nanocomposites (Figure 5.6), which were indexed to cassiterite SnO$_2$, gamma Fe$_2$O$_3$ and anatase TiO$_2$ metal oxides without impurities (Section 4.2.7).
The crystallite size of the layered metals oxides on the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode was calculated from virtually similar 29 diffraction peak as its pristine counterpart (48.05° vs. 47.94°). The crystallite size of the layered metal oxides on the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode exhibited a 28.85% increase compared to its pristine counterpart, i.e. from 9.6 nm to 12.27 nm. On the other hand, the crystallite size of the SnO$_2$, Fe$_2$O$_3$ and TiO$_2$ metal oxides on the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode was 5.37 nm vs. 4.15 nm of its pristine counterpart using relatively similar 29 diffraction peaks (35.39° vs. 35.56°). The metal oxides nanoparticles layers on rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode experienced a 29.40% increase in size during electrochemical characterization. When SnO$_2$ and Fe$_2$O$_3$ metal oxides are used as active material electrode in either sodium- or lithium-ion batteries, they experience severe volume expansion during cycling (up to 420%) that results in fading capacity of the batteries [19]. However, by incorporating fixed volume materials such as carbon or materials with insignificant volume change such as TiO$_2$ in the electrode, volume expansion has been effectively restrained [20, 21]. Therefore, the insignificant increase in crystalline size (29% vs. 420%) of the layered metals oxides on the ternary electrodes during cycling was attributed to the presence of the TiO$_2$ and graphene oxide. The insignificant increase thus indicated that the fading capacity of the sodium-ion battery half cells in this study cannot be due to the ternary electrodes but rather the result of side reactions of sodium due to the aqueous environment.

It also denoted insignificant structural change of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary electrodes when used as anode material in a sodium-ion battery within 20 cycles. However, the latter can only be conclusively proved when the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary electrodes are electrochemically tested at moisture and oxygen levels below 0.1
ppm, i.e. at their full capacity. Especially, when considering the change in the relative intensities and additional peaks/shoulders evident on the rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} electrode (after electrochemical characterization) XRD spectrum that may possibly be from crystallite changes and the breaking of the nanomaterial. However, due to the short cycle life of the sodium battery half cells in this research was not clearly observed.

5.2.2 TEM analysis of the ternary systems after application

Approximately 1 mg of each powdered used working electrode (rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} or rGO-Fe\textsubscript{2}O\textsubscript{3}-SnO\textsubscript{2}-TiO\textsubscript{2} nanocomposite, PVDF and graphite in N-methyl-2-pyrrolidene solvent) was dispersed in 8-mL absolute ethanol by sonication for 10 minutes. This mixture was then “drop cast” on a carbon coated copper grid for analysis with a JEM-2100 Electron microscope.

The TEM image of the pristine rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanocomposite is similar to that of the rGO-SnO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} electrode after electrochemical characterization as represented in Figure 5.7a and Figure 5.7b respectively.
Figure 5.7: TEM images of the; (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite before application; and (b) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode after application. SAED pattern of the; (c) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite before application; and (d) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode after application. Particle size histogram of the; (e) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite before application; and (f) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode after application. The images and diffractograms were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.
Both images consisted of a transparent film coated with nanoparticles of different shapes with an average size of \( \approx 9 \text{ nm} \pm 2 \text{ nm} \) (Figure 5.7e and Figure 5.7f). Further illustrating the insignificant volume change of the \( \text{SnO}_2 \) and \( \text{Fe}_2\text{O}_3 \) metal oxides due to the presence of the graphene oxide layers and TiO\(_2\) nanoparticles in the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) electrode. Structural analysis of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) electrode by Selected Area Electron Diffraction (SAED) revealed that the SAED pattern of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) electrode (Figure 5.6d) is similar to its pristine counterpart (Figure 5.6c). The two nanomaterials exhibited five diffraction rings, which were indexed to the (2 0 0) crystal plane of TiO\(_2\), the (1 1 1), (1 0 1) and (1 1 0) crystal planes of SnO\(_2\) in addition to the (1 1 1) crystal plane of \( \gamma \)-Fe\(_2\)O\(_3\). However, the diffraction rings of the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) electrode exhibited a slight increase in interplanar spacing \( d(\text{Å}) \) of 0.37 Å on average compared to the pristine rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) nanocomposite. Therefore, the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) nanocomposite can be used as active material in a sodium-battery with insignificant volume and structural changes within 20 cycles.

Analogous to the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) electrode/pristine pair, the TEM images of the rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) nanocomposite before and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) electrode after electrochemical characterization are similar. The two nanocomposites consisted of layers of transparent, paper thin sheets coated with nanoparticles of different shapes (Figure 5.8a and Figure 5.8b).
Figure 5.8: TEM images of the; (a) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite before application; and (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode after application. SAED pattern of the; (c) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite before application; and (d) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode after application. Particle size histogram of the; (e) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite before application; and (f) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode after application. The images and diffractions were acquired with a JEM-2100 Electron microscope whilst the particle size is a measure of the diameter of the nanoparticles using ImageJ software.
The average particle size of the nanoparticles coated on the layers on both images was ~4 nm ±1nm (Figure 5.8e and Figure 5.8f), indicating insignificant volume change of the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanomaterial during cycling, accredited to the presence of TiO$_2$ and GO. The crystal morphology of the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite before and after cycling was virtually the same. The before and after SAED patterns exhibited the (2 2 0), (1 0 1) and (1 1 0) crystal planes of SnO$_2$, the (2 0 0) crystal plane of TiO$_2$ as well as the (1 1 1) crystal plane of γ-Fe$_2$O$_3$; with a minor increase in interplanar spacing d(Å) of 0.063Å on average. Thus indicating the stability of the rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposites when used as anode material in sodium-ion battery within 20 cycles.

### 5.2.3 Raman analysis of ternary systems after application

The homogenized ternary systems’ working electrodes (rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ or rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite, PVDF and graphite in N-methyl-2-pyrrolidene solvent) used in half cell sodium battery tests were further analysed with an Alpha300 R Raman microscope by WITec without further treatment.

The Raman spectra of the ternary electrodes were virtually identical (Figure 5.9), analogous to their pristine counter parts (Section 4.7.7). Similar to the Raman spectra of the pristine ternary nanocomposites (Before), the Raman spectra of the electrodes after electrochemical characterisation (After) had both the D and G bands (Figure 5.9a) characteristic of carbon allotropes, typically observed at ~1350 cm$^{-1}$ and ~1580 cm$^{-1}$ respectively [22].

![Figure 5.9: Raman spectra of the powdered; (a) rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite before electrochemical characterization and rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode after electrochemical characterization, and (b) rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ nanocomposite before electrochemical characterization and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ electrode after electrochemical characterization. The spectra were acquired using an Alpha300 R Raman microscope by WITec with a 20X magnification lens and 2.5mW power.](image-url)
However, the D and G bands on the used ternary electrodes spectra exhibited a change in band position and shape. In particular the G band, it increased in intensity, narrowed and shifted to lower wavenumbers (from 1596 cm\(^{-1}\) to 1585 cm\(^{-1}\)) resembling that of graphite (Figure 4.51). This has been attributed to the restoration of the sp\(^2\) network during the reduction of graphene oxide [23]. Substantiating, that the carbon atoms in the rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) electrode nanomaterial were sp\(^2\) bonded with fewer defects was the low I\(_D\)/I\(_G\) ratio value of 0.50 compared to that of their pristine counterparts (1.18) and synthesized graphene oxide (0.98). As noted in section 4.7.1, the ratio of the relative intensity of the D and G band (I\(_D\)/I\(_G\)) is an indicator of the extent of disorder in graphene, increasing with functionalization of the graphitic structure or in this case, decreasing with removal of functional groups. There was a peak on the spectra of both ternary electrodes at 1076 cm\(^{-1}\) that could not be accounted for. The characteristic bands for the metals oxides in the 26 3 cm\(^{-1}\) — 1006 cm\(^{-1}\) range were not observed, i.e. the A\(_{1g}\) band (626 cm\(^{-1}\)) for SnO\(_2\) [24]; the B\(_{1g(1)}\) (396 cm\(^{-1}\)) and A\(_{1g}\) B\(_{1g(2)}\) (508 cm\(^{-1}\)) TiO\(_2\) bands [25] in addition to the γ-Fe\(_2\)O\(_3\) band at 390 cm\(^{-1}\) [26]. However, the broad band ranging from 51 cm\(^{-1}\) —231 cm\(^{-1}\) was most likely due to the E\(_{g(1)}\) (154 cm\(^{-1}\)) TiO\(_2\) band and the two γ-Fe\(_2\)O\(_3\) bands at 221 cm\(^{-1}\) and 255 cm\(^{-1}\). Please note that the last step of the CV measurements was the reduction step.

### 5.3 Key Findings and Conclusions

The rGO-SnO\(_2\)-Fe\(_2\)O\(_3\)-TiO\(_2\) and rGO-Fe\(_2\)O\(_3\)-SnO\(_2\)-TiO\(_2\) half cells exhibited low initial capacities of 87 mAhg\(^{-1}\) and 173 mAhg\(^{-1}\) respectively when cycled at constant current density of ±45 mAg\(^{-1}\) (0.5 mA at C/20). When compared to the calculated theoretical capacity of the ternary nanocomposites (976 mAhg\(^{-1}\)) and previously reported work on individual or different combinations of graphene, SnO\(_2\), Fe\(_2\)O\(_3\), and TiO\(_2\). The capacity of both ternary nanocomposites faded drastically within 20 cycles which again was in contrast with the electrochemical performance of the individual components or different combinations thereof as reported in literature.

Therefore, the physical properties of the ternary nanocomposites were further studied as fading capacity and short life cycle is usually observed with excessive volume expansion of the SnO\(_2\) and Fe\(_2\)O\(_3\) metal oxides during cycling that results in cracking and reduction in size. Analysis of the ternary nanocomposites after electro-analytical measurements with the XRD, TEM and Raman spectrometry techniques, revealed insignificant structural change of the crystallites. Thereby, excluding volume change as the reason for low and fading capacity but rather demonstrating the effectiveness of graphene oxide and TiO\(_2\) in limiting volume change of SnO\(_2\) and Fe\(_2\)O\(_3\) metal oxides. The reason for the low and fading capacity as well as short life cycle of the half-cells was accredited to the numerous side reactions of sodium metal electrode with H\(_2\)O and O\(_2\). Due to the high oxygen and moisture concentration (>0.1 ppm) during cell assembly and electrolyte solution preparation.
The CV curves demonstrate the different sodium insertion/extraction potentials of TiO$_2$, Fe$_2$O$_3$, and SnO$_2$. The current in the 0.94 V — 1.54 V voltage range decreased with each subsequent CV scan denoting unstable cycling of the ternary nanocomposites, which was in good agreement with the charge-discharge measurements.

For future work, it is recommended that the assembly and preparation of the cells and electrolyte solution be conducted inside in a nitrogen filled glove box with oxygen and moisture concentrations below 0.1 ppm due to the highly reactivity nature of sodium with moisture.
5.4 References

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Na-ion batteries, recent advances and present challenges to become low cost energy


CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6 Overview

This chapter gives a brief summary of the achievements and challenges of the study in addition to the recommendations.

6.1 Conclusions

The main aim of this study was to synthesize and evaluate rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites as suitable anode material for sodium ion batteries. In this regard, the study was moderately successful, i.e. the ternary nanocomposites were successfully synthesized however, not fully evaluated.

Graphene oxide (GO) was used as the base on which the metal oxides (SnO$_2$, TiO$_2$ and Fe$_2$O$_3$) were coated in a different order using the solvothermal and/or hydrothermal and/or co-precipitation methods. When the synthesized nanomaterial were analyzed with the FTIR, Raman spectroscopy, SEM, TEM, TGA, BET, UV-Vis spectroscopy, and XRD analytical techniques; their physical, chemical and optical properties were positively matched to their pure compounds.

When the ternary nanocomposites were evaluated as active anode material in sodium-ion battery half cells, they both exhibited low initial capacities that faded drastically within 20 cycles which was in contrast with the electrochemical performance of the individual components or different combinations thereof as reported in literature. This was attributed to the high oxygen and moisture concentration (>0.1 ppm) during cell assembly and electrolyte solution preparation that resulted in numerous side reactions of the sodium metal electrode with H$_2$O and O$_2$. Further study of the physical properties of the ternary nanocomposites after electrochemical analysis with the XRD, TEM and Raman spectrometry techniques, revealed insignificant structural change of the crystallites.

6.2 Recommendations

- The SEM and TEM images of the rGO based bi- and tri-metal oxide nanocomposites exhibited agglomeration of the coated metals oxides on the graphene sheets indicating excessive quantity of metals oxides ratio to the graphene oxide. The agglomeration of active particles results in increased Na$^+$ diffusion rate and thus irreversible capacity loss. Therefore, for future work it is recommended that the metal oxide to graphene oxide ratio be reduced.
The full capability of the ternary nanocomposites as anode material for a sodium-ion battery were not really evaluated due to the aqueous environment. Therefore, it is recommended that the electrochemical properties of the rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ and rGO-Fe$_2$O$_3$-SnO$_2$-TiO$_2$ ternary nanocomposites be re-evaluated at oxygen and moisture content below 0.1 ppm. This would also shed light on the apparent difference in capacity of the two ternary nanocomposites as observed from the initial charge-discharge voltage profiles.

Environmental conditions of oxygen and moisture content less than 0.1 ppm are expensive and impractical. Therefore, for commercialization and mass production of sodium-ion batteries, it is recommended that SIB anode and cathode material insensitive to aqueous environment be explored.

The rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ electrode (rGO-SnO$_2$-Fe$_2$O$_3$-TiO$_2$ nanocomposite, PVDF and graphite in N-methyl-2-pyrrolidene solvent after electrochemical characterization) XRD spectrum exhibited changes in the relative intensities and additional peaks/shoulders were evident. Therefore, in-depth analysis of the ternary nanocomposites after re-evaluation as anode material in a sodium-ion battery in an environment with oxygen and moisture content below 0.1 ppm is recommended. To identify the phases present and/or any sodium containing species.