Metal oxide and sulfide nanomaterials and nanocomposites for high-performance energy storage

Ayman Amin Abdelhamid Amin

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**METAL OXIDE AND SULFIDE NANOMATERIALS AND
NANOCOMPOSITES FOR HIGH-PERFORMANCE
ENERGY STORAGE**

AYMAN AMIN ABDELHAMID AMIN

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Ayman Amin AbdelHamid Amin

Abstract

There is an alarming energy problem that needs urgent intervention. It is mainly caused by oil supply instability, rising urban pollution and accelerated global warming. This has resulted in a worldwide policy shift towards sustainable energy and green transport, which need reliable energy storage systems. Li-ion batteries and supercapacitors are among the most promising energy storage solutions; however, they are still not able to meet our needs. This is mainly due to the limited energy storage capabilities of the currently used materials.

Novel high-performance energy storage materials are required. Several approaches have been investigated for producing materials with high energy storage capabilities. It was found that size reduction, morphology and structure control, and incorporation of carbonaceous materials are critical factors for a high-performance electrode. However, the current synthesis methods and energy storage performance are still far from optimal.

The main objective of this thesis is to develop facile approaches for synthesizing nanomaterials and nanocomposites with excellent energy storage performance. Two different synthesis strategies were developed. The first involved the synthesis of nickel sulfide and graphene-wrapped nickel sulfide nanopyramids, while the second involved metal oxide and graphene-incorporated metal oxide nanosheets. The synthesized materials were applied as Li-ion battery anodes and supercapacitor electrodes, demonstrating very promising energy storage performance.

Current nickel sulfide synthesis methods are limited by the relatively large and non-uniform nanomaterials obtained. A one-pot colloidal thermal decomposition approach was developed in this thesis to synthesize uniformly sized nickel sulfide nanopyramids, and to evenly anchor them to the surface of graphene sheets. The nickel sulfide nanopyramids showed very promising supercapacitor performance, but suffered from capacity decay as Li-ion battery anode. Graphene wrapping increased the rate capability

of the nanopyramids as supercapacitor, and significantly improved their energy storage performance as Li-ion battery anode.

A novel, facile, versatile and generalized strategy was established for the synthesis of metal oxide nanosheets. Graphene oxide was used as sacrificial template to synthesize metal oxide nanosheets, without the need for hydro/solvothermal reactions or laborious template-removal processes, which limit the currently available methods. The graphene oxide planar-confined growth strategy demonstrated interesting versatility, where the nanosheets' attributes such as crystallinity, crystal structure, crystallite size, surface area, porosity and reduced graphene oxide content could be tuned, simply by adjusting the calcination conditions. The synthesis approach also displayed broad applicability, allowing various binary and doped binary oxide nanosheets, as well as ternary oxide nanosheets to be obtained. The synthesized nanosheets were applied as Li-ion battery anodes and supercapacitor electrodes with very promising energy storage performance.

The facile synthesis methods developed throughout this work produced nanomaterials and nanocomposites with controlled structure and composition, achieving high-performance energy storage. The colloidal approach managed to control the size and uniformity of nickel sulfide nanocrystals, and allowed high dispersion on the surface of graphene sheets, while the graphene oxide planar-confined growth strategy produced a wide variety of metal oxides nanosheets with controlled characteristics. These nanomaterials and nanocomposites showed very promising energy storage performance, which was amongst the best reported in the literature. The excellent energy storage performance could be attributed to the critical roles played by size reduction, morphology control and incorporation of graphene, which were attained by the novel synthesis strategies developed in this thesis.

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Abbreviations

EV	Electric vehicle
LIB	Lithium-ion battery
SC	Supercapacitor
SEI	Solid electrolyte interphase
EDLS	Electrical double layer supercapacitor
FS	Faradaic supercapacitor
CNT	Carbon nanotube
2D	Two dimensional
3D	Three dimensional
1D	One dimensional
rGO	Reduced graphene oxide
NS	Nickel sulfide nanopyrramids
NS/G	Graphene-wrapped nickel sulfide nanopyrramids
G-silica	Graphene-silica
PDDA	Poly(diallyldimethylammonium chloride)
TEM	Transmission electron microscopy
HRTEM	High-resolution transmission electron microscopy
STEM	Scanning transmission electron microscopy
SAED	Selected area electron diffraction
EDX	Energy dispersive X-ray spectroscopy
XRD	X-ray diffractometry
ICDD	International Centre for Diffraction Data
BET	Brunauer, Emmett and Teller
BJH	Barett-Joyner-Halenda
TGA	Thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier-transform infrared spectroscopy
ATR	Attenuated total reflectance
AFM	Atomic force microscopy

SPM	Scanning probe microscopy
PVDF	Polyvinylidene difluoride
VGCF	Vapor-grown carbon fiber
NMP	N-methyl-2-pyrrolidone
CV	Cyclic voltammetry
GCD	Galvanostatic charge/discharge
EIS	Electrochemical impedance spectroscopy
FFT	Fast Fourier transform
OCM	Opposite-charge method

Chapter 1

Introduction

This chapter presents a background and an overview of the dissertation. The world is facing a growing energy problem that is manifested in unstable oil supply, soaring pollution levels and accelerated global warming. This created an urgency to increase the utilization of renewable energy, which needs efficient, reliable and high-capacity energy storage. Li-ion batteries and supercapacitors are very promising energy storage systems; however, electrode materials need further research to improve their current performance. Nanomaterials and carbon-incorporated nanocomposites are very promising energy storage materials. Nevertheless, their synthesis strategies and energy storage performance still need further development. In this thesis, the aim is to develop facile methods for the synthesis of nanomaterials and nanocomposites with controlled morphology, structure and composition that are suitable for high-performance energy storage applications. The specific objectives include the facile synthesis of nickel sulfide/graphene nanocomposite, and the generalized synthesis of binary and ternary oxide nanosheets, for application as Li-ion battery anodes and supercapacitors. The thesis contents are briefly introduced in this chapter, and the major outcomes are summarized.

1.1 Problem Statement

The ever-growing energy demand worldwide is depleting our non-renewable energy resources, and pushing climate change to unprecedented limits. Oil production is already beyond its peak level, which means that future shortages and production instability are foreseeable challenges. Moreover, fossil fuel consumption leads to a constant rise in CO₂ level in the atmosphere. It has been reported that CO₂ level has increased by about 2 folds in the last three decades. This dramatic increase is expected to have severe consequences on the earth's climate due to accelerated global warming [1-3].

To solve this problem, energy supply has to shift to renewable and clean resources. Among the available renewable energy technologies, solar and wind energy are the most mature to date. Increasing their share in total energy consumption can help to slow down fossil fuel consumption and reduce CO₂ emission. Reducing vehicle emissions is also crucial to decrease the surging air pollution, especially in urban areas. This can be done by further developing and adopting electric vehicle technology and infrastructure. Energy storage systems are needed to store the intermittent energy produced by the solar and wind energy plants. They are also critical for the advancement of electric vehicles (EVs) such as battery electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles [4, 5].

Based on the discussion above, high-performance energy storage systems are urgently needed. Batteries are efficient electrochemical energy storage systems that are suitable for this role. Among the various types of batteries, Li-based batteries are the most promising, mainly due to their high energy density. Currently, Li-ion batteries (LIBs) dominate the portable battery market [6], and their development is crucial for the progress of EV technology and renewable energy storage [5]. Supercapacitors (SCs) provide an energy storage technology with higher power density and more stability, but lower energy density. It may be employed to complement batteries, such as in acceleration and regenerative braking in EVs. It can also be used as a backup for batteries to prevent power disruptions [7].

Electrode materials are the most important components in LIBs and SCs. They are the main determinants of the energy density, power density and cycle life. Graphite is the traditional LIB anode material, and was first introduced by Sony Corporation in 1991 [6]. However, graphite suffers from several problems, including a low theoretical capacity of 372 mAh/g [8], poor rate capability, and poor safety profile [9]. On the other hand, SC electrode materials suffer from low energy density, which limits their practical application [7].

In order to improve LIB and SC electrode materials, several approaches were investigated. Among the various strategies studied, size reduction to the nano scale, morphological control, and composite formation with carbonaceous materials have yielded very promising results. However, facile synthesis of high-performance energy storage nanocomposites with controlled morphology and properties remains a major challenge.

1.2 Motivation

Size reduction, morphology control, and composite formation are amongst the most promising approaches for the synthesis of high-performance energy storage materials.

Nanotechnology is regarded as an important enabler in the energy storage field. Conventional bulk materials are inherently limited by ion diffusivity in the solid state. Reducing particle size to the nano scale significantly reduces the effect of this limitation. Moreover, nanoparticles enable a richer variety of electrode reactions and material compositions. They have high surface area that improves contact with electrolyte. In addition, they facilitate electron transport, and better accommodate the strain accompanied by redox reactions [10, 11].

Particle morphology and structure are critical factors for material performance in energy storage. Although nanotechnology can significantly improve LIB and SC electrode performance, there are still several drawbacks that need to be addressed. Complex synthesis, severe electrode/electrolyte side reactions, loose inter-particle contact, and lower material density are some of the main drawbacks of nanomaterials [3, 10, 11].

These challenges can be addressed by controlling the morphology and structure of the nanomaterials. Anisotropic structures, such as one- and two-dimensional nanomaterials have better ion/electron transport capability and enhanced stability, as compared to zero-dimensional nanoparticles [3, 12]. In addition, “secondary nanomaterials” [10], which are microstructures composed of nanodomains, can overcome many of the drawbacks of primary nanoparticles. They may be regarded as a hybrid material. The nanodomains offer the advantages of the nanoparticles for energy storage, while the microstructures provide more stability, higher density, better inter-particle contact, and less complex synthesis [10, 13]. Therefore, controlling the morphology and structure of the nanomaterials can have a significant impact on the material performance.

Synthesis of a nanocomposite comprised of the active material and a carbonaceous material can boost electrode performance. Aside from being an active electrode material at the appropriate voltage range, carbon can improve electrode performance in different ways. The incorporation of a carbon matrix in which the active material is embedded improves overall conductivity and buffers volume change during cycling. This enhances electrode performance and stability. Carbon can also be coated on the surface of the active material to improve conductivity. This leads to enhanced capacity and rate capability [1, 11, 13]. Carbon incorporation complements size and shape control to fabricate a high-performance material for energy storage.

Although many nanocomposites have been reported as energy storage materials, their synthesis strategies and performance are still far from optimal. Further research is required to develop facile synthesis methods, and enhance the energy storage performance. This thesis will focus on the synthesis of nanomaterials and nanocomposites for high-performance energy storage. The research work is guided by the three principles discussed above: size reduction, morphology control and carbon incorporation.

1.3 Scope and Objectives

The broad objective of this thesis is to develop facile methods for the synthesis of nanomaterials and nanocomposites with controlled morphology, structure, composition and properties. These nanomaterials and nanocomposites are applied as high-performance LIB anodes and as SC electrodes. The specific objectives are discussed below.

1.3.1 Facile Synthesis of Nickel Sulfide/Graphene Nanocomposite for High-Performance LIB Anodes and SCs

Metal sulfides can store Li ions by conversion reaction, achieving high theoretical capacities [11]. They are also very promising pseudocapacitive materials [14-16]. However, they suffer from poor kinetics and stability [11, 17, 18].

Nickel sulfide has been used as LIB anode and SC electrode. It has shown very promising performance, however, rapid capacity loss remains a problem [18, 19]. Nanostructures and carbon incorporation have been used to improve nickel sulfide performance [20-28]. However, the hydrothermal/solvothermal approach, which is commonly used in these studies, produces relatively large and non-uniform nanoparticles, which is not optimal for energy storage. Moreover, some of the reported methods use special equipment [28, 29] or multi-step procedures [22, 23, 27] for the nanocomposite synthesis. This renders the synthesis process complicated and/or laborious.

The first objective of this thesis was to synthesize nickel sulfide/graphene nanocomposite using a facile one-pot colloidal method for high-performance energy storage. Graphene-wrapped monodisperse nanocrystals were synthesized using this method. The one-pot synthesis made the procedure less laborious and more practical. Graphene was the chosen carbon allotrope due to its unique two-dimensional morphology and electronic properties [30]. The performance of the nanocomposite was studied as LIB anode and SC electrode, with special emphasis on the role of graphene in the electrode performance.

1.3.2 Generalized Synthesis of Binary Oxide Nanosheets for High-Performance LIB Anodes and SCs

Metal oxide nanosheets have a unique two-dimensional morphology that is very promising for various applications [31-33], including energy storage [34-36]. The nanothickness facilitates ionic and electronic transport, thus improving rate capability [36, 37]. The micrometric lateral dimensions help to buffer volume change during cycling, leading to higher stability [37, 38]. In addition, the high surface area allows more contact with the electrolyte, enhancing access to the electroactive sites [36, 37].

There is a lack of facile, scalable and generalized methods for the synthesis of metal oxide nanosheets. Several approaches have been adopted for the synthesis of metal oxide nanosheets, such as exfoliation [39], thin film deposition [40], hydrothermal/solvothermal synthesis [41, 42] and template-assisted methods [43-46]. However, these approaches are impractical and/or laborious.

The second objective of this thesis was to develop a facile, scalable and generalized strategy for the synthesis of binary oxide nanosheets for high-performance energy storage. The nanosheets were tested as LIB anodes and as SCs, and their performance was optimized via tuning the nanosheets' attributes.

1.3.3 Synthesis of Ternary Oxide Nanosheets for High-Performance LIB Anodes

Ternary oxides are very promising candidates for LIB anodes. TiNb_2O_7 has been recently introduced as a high-potential ($> 1 \text{ V vs. Li}^+/\text{Li}$), insertion-type LIB anode material. The multiple redox reactions provide a high theoretical capacity of over 385 mAh/g [47, 48]. Conversion-type ternary oxides such as NiCo_2O_4 [49], MnCo_2O_4 [50] and FeCo_2O_4 [51] have also attracted much attention as LIB anodes because the mixed metal species synergistically enhance conductivity, electrochemical activity, capacity and stability [49, 50, 52, 53]. In addition, mixed oxides may help to reduce the overall material cost [52, 53].

Although ternary oxides have interesting electrochemical properties, generalized synthesis of ternary oxide nanosheets is quite limited. As discussed in Section 1.3.2, several approaches have been adopted for the synthesis of metal oxide nanosheets. However, these approaches are usually restricted to binary oxides, with limited extension to ternary oxides. There is a need to develop a facile and scalable method that can be used to synthesize various ternary oxide nanosheets.

The third objective of this thesis was to adopt the generalized nanosheet synthesis strategy discussed in Section 1.3.2 to synthesize ternary oxide nanosheets for high-performance LIB anodes. The energy storage capability of the ternary oxide nanosheets was examined, and the nanosheets' attributes were optimized to enhance performance.

1.4 Dissertation Overview

This thesis consists of 7 chapters, which are briefly introduced below:

Chapter 1 presents the problem statement, and the motivation for the research approach adopted. It defines the overall scope, and the specific objectives of the dissertation. It also provides the thesis layout, and the main research outcomes.

Chapter 2 introduces the basic principles of LIBs and SCs. It maps the materials used as LIB anodes and Faradaic SCs, with an in-depth review of relevant materials. The knowledge gaps addressed by the thesis are also presented.

Chapter 3 describes the methods and techniques used for material synthesis, characterization and electrochemical testing. It discusses their underlying principles, and explains the rationale for their use.

Chapter 4 presents graphene-wrapped nickel sulfide nanopyramids as LIB anode and SC electrode. It emphasizes the effect of graphene wrapping on the energy storage performance of nickel sulfide.

Chapter 5 shows a facile, scalable and generalized strategy for the synthesis of binary oxide nanosheets. It investigates the electrochemical performance of the nanosheets as LIB anodes, and demonstrates several strategies to improve performance. It also examines the binary oxide nanosheets for SC applications.

Chapter 6 adopts the strategy used in *Chapter 5* for the synthesis of ternary oxide nanosheets. It presents the performance of the ternary oxide nanosheets as LIB anodes, and discusses the approaches used for optimizing performance.

Chapter 7 interlinks the concepts and strategies used throughout the dissertation. It analyzes the research findings, and reflects on the concepts that motivated the research work. It also suggests approaches for future research.

1.5 Findings and Outcomes

The outcomes of this dissertation are summarized below:

1. Development of a novel one-pot method for the synthesis of graphene-wrapped nickel sulfide nanopyramids with enhanced energy storage performance.
2. Establishment of a generalized and scalable method for the synthesis of binary oxide nanosheets with optimized performance as LIB anodes and SCs.
3. Extension of the nanosheet synthesis strategy to produce ternary oxide nanosheets, which were optimized for LIB anodes.

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Chapter 2

Literature Review

This chapter presents an overview of the literature, and puts the research work within its context. The historical backgrounds of Li-ion batteries and supercapacitors are first discussed, followed by their working principles. The electrode materials of Li-ion battery anodes and Faradaic supercapacitors are then reviewed in detail, with particular emphasis on nanomaterials and carbon-incorporated nanocomposites. The literature review has demonstrated the crucial roles played by nanostructuring, morphology control and carbon incorporation in enhancing the materials' energy storage performance. However, the current synthesis strategies need improvement to render them more facile, generalized, scalable and capable of producing nanomaterials with the desired properties for energy storage applications. The research motivation based on the literature review is thoroughly discussed in the final section of this chapter.

2.1 Historical Background

2.1.1 Li-Ion Batteries

Advances in electrochemical energy storage have started since the nineteenth century. Lead-acid battery and zinc-manganese oxide cell were invented in 1859 and 1866, respectively. Nickel-cadmium battery was introduced later in 1901. Over time, these systems have been further developed for various applications, such as vehicle engine ignition and electronic devices.

The 1960's witnessed increased demand for portable energy, such as for implantable medical devices and portable electronics. It was soon realized that the above-mentioned systems cannot satisfy the increasing energy demand, mainly due to their low energy density. This created an urgent need for new types of batteries that can store more energy [1].

In the 1970's, a new type of rechargeable battery based on Li metal was invented. Li was used as the anode material for two main reasons. Firstly, Li is the most electropositive metal, with an electrochemical potential of -3.04 V vs. standard hydrogen electrode. Secondly, it is the lightest metal, with a molar weight of 6.94 g/mol [2]. These attributes make Li an ideal anode, with a very high theoretical capacity of 3860 mAh/g. TiS_2 was used as the cathode material, since it was able to intercalate the guest Li ions donated by the Li anode. TiS_2 also demonstrated its capability of reversible evolution of its electronic and crystal structures during Li-ion insertion and extraction according to the following equation,

where x is the degree of Li-ion insertion, which varies from 0 to 1 [1].

Unfortunately, Li-metal batteries suffered from serious safety issues. It was found that the highly reactive Li anode reacts with the electrolyte, forming a solid electrolyte interphase (SEI). SEI non-uniformity can cause uneven Li plating during charging, which results in

Li dendrite formation. These Li dendrites are able to short-circuit the cell, and may lead to fire and explosion hazards. This problem hindered the progress of Li batteries.

The breakthrough for practical Li batteries occurred in the late 1970's, and was termed *lithium rocking chair battery*. This concept relies on two intercalation electrodes that donate and accept Li ions alternatively during cycling, and in a reversible manner. This concept was further developed and introduced commercially by Sony in 1991. The battery commercialized by Sony, termed “lithium-ion battery” (LIB), used graphite and LiCoO_2 as anode and cathode materials, respectively [1, 2]. The operating principles of both Li-metal battery and Li-ion battery are illustrated in Figure 2.1.

Figure 2.1. Schematic illustration of (a) a Li-metal battery showing Li dendrite growth at the negative electrode upon cycling, and (b) a Li-ion battery. Reprinted with permission from [2]. © 2001 Nature Publishing Group.

LIB technology is currently the market leader for portable energy. LIBs have enjoyed a great success upon their introduction, mainly due to their high energy density as compared to other conventional rechargeable batteries (Figure 2.2). They are currently the major power source for portable electronics, such as mobile phones, computers and cameras.

Figure 2.2. Gravimetric vs. volumetric energy density of various rechargeable battery systems. Reprinted with permission from [2]. © 2001 Nature Publishing Group.

2.1.2 Supercapacitors

Capacitive charge storage predates the earliest battery systems invented. In the mid-eighteenth century, a simple capacitive device, named Leyden jar, was invented for charge storage. Leyden jar, which consists of a jar coated internally and externally with silver foil, demonstrated its capability to be charged and discharged reversibly [3].

Supercapacitors (SCs) are a special type of capacitors characterized by high energy density. Conventional electrostatic capacitors have high power density, but suffer from limited energy density. SCs filled a gap in energy storage technologies since they have higher power density than batteries, and an enhanced energy density as compared to

conventional capacitors [4]. A comparison of several energy storage technologies regarding specific energy and power is presented in Figure 2.3.

Figure 2.3. Ragone plot comparing energy and power densities of various energy storage technologies. Reprinted with permission from [4]. © 2010 Elsevier. “Electro-chemical capacitors” is a synonym for SCs.

The significance of SCs was not realized until recently. Although the double-layer capacitance was explained by Hermann von Helmholtz as early as 1853, it was only in 1957 that the first SC was patented. The patent was based on charge storage on the surface of porous carbon electrodes. This was followed by a series of patents and commercial products by several companies, such as The Standard Oil Company (USA) and Nippon Electric Company (Japan) [4]. In the 1990’s, special attention was paid to SCs due to their potential application in hybrid electric vehicles [5]. A list of commercial SCs is presented in Table 2.1.

Table 2.1. A list of current commercial SCs. Reprinted with permission from [4]. © 2010 Elsevier.

Company name	Device name	Country	Voltage range (V)	Capacitance (F)
AVX	Bestcap	USA	3.5–12	0.022–0.56
Cap XX	Super Capacitor	Australia	2.25–4.5	0.09–2.8
Copper	Power stor	USA	2.5–5.0	0.47–50
ELNA	Dyna cap	USA	2.5–6.8	0.033–100
ESMA	Capacitor modules	Russia	12–52	100–8000
EPCOS	Ultra-capacitor	USA	2.3–2.5	5–5000
Evans	Capattery	USA	5.5, 11	0.01–1.5
Kold Ban	Kapower	USA	12	1000
Maxwell	Boostcap	USA	2.5	1.6–2600
NEC	Super capacitor	Japan	3.5–12	0.01–6.5
Nesscap	EDLC	South Korea	2.7	10–5000
Panasonic	Gold capacitor	Japan	2.3–5.5	0.1–2000

2.2 Operating Principles

2.2.1 Li-Ion Batteries

LIBs consist of three main components; anode, cathode, and electrolyte-embedded separator. Conventionally, the anode material is graphite, while lithium metal oxide (e.g. LiCoO_2) is used as the cathode. The electrolyte is typically a Li salt (e.g. LiPF_6) dissolved in a mixed carbonate organic medium. The separator isolates the electrodes from each other to prevent cell short circuit, while allowing free Li-ion transport.

LIBs operate based on the Li rocking chair approach (Figure 2.4). During cell charge, Li ions move from the cathode and are intercalated into the anode, while electrons move externally in the same direction. During discharge, Li ions are extracted from the anode and re-inserted into the cathode, and electrons move back externally in the same direction. This process allows energy storage during charging, and release during discharging. The reactions taking place in LIBs can be described by the following equations [6, 7].

Figure 2.4. Schematic illustration of LIB, demonstrating the charge and discharge processes. Reprinted with permission from [8]. © 2006 Elsevier.

LIB with the current configuration is not free from undesired side reactions. The anode reaction that occurs at ~ 0.05 V vs. Li^+/Li is well below the electrolyte reductive decomposition voltage (~ 0.8 V vs. Li^+/Li) (Figure 2.5). Although this may imply that LIBs are not stable due to electrolyte decomposition, they are considered kinetically stable. This is due to the formation of SEI on the anode surface, which prevents further electrolyte decomposition, while allowing continued charging and discharging. On the cathode side, the Li-ion insertion/extraction takes place at ~ 4 V vs. Li^+/Li , which is slightly lower than the electrolyte oxidative decomposition voltage (~ 4.5 V vs. Li^+/Li) (Figure 2.5). Although this is acceptable under normal conditions, LIB is prone to failure due to overcharging. The decomposition processes at both electrodes result in active mass loss and gas evolution, which lead to capacity loss and safety concerns [7].

Figure 2.5. Cyclic voltammetry profiles of anode (MCMB: mesocarbon microbeads), cathode (LiCoO_2) and electrolyte (EC:DMC LiPF_6). EC: ethylene carbonate, DMC: dimethyl carbonate. Reprinted with permission from [7]. © 2010 Elsevier.

2.2.2 Supercapacitors

The basic components of SCs are similar to batteries; however their charge storage mechanism is different. A SC consists of an anode, a cathode and an electrolyte. The electrodes are electrically isolated from each other using a separator. The charge is stored at the interface between the active material particles and the electrolyte. The electrical double-layer interface acts as a capacitor, whose capacitance (C) can be determined according to the following equation,

$$C = A\epsilon / 4\pi d \quad \text{Eq. 2.5}$$

where A is active electrode surface area, ϵ is the electrolyte dielectric constant, and d is the double-layer thickness. The high capacitance of SCs is mainly due to the large electrode surface area and the extremely small thickness of the double layer [4, 5].

There are two main types of SCs (Figure 2.6), which differ in their operating principles. The first is the electrical double-layer SCs (EDLSs). EDLSs operate by physical charge storage on the active material surface, while the electrolyte provides the counter ions to maintain charge neutrality. This leads to the formation of an electrical double layer, albeit with no charge transfer. EDLSs have high power density and good stability; however,

they have low energy density due to the limited physical charge storage. The second type of SCs is Faradaic SCs (FSs) or pseudocapacitors, which involve redox reactions during charge and discharge. FSs operate similarly as batteries, and thus have much higher energy density as compared to EDLS. However, the improved energy storage is achieved at the expense of power density and stability because Faradaic reactions are slower and less stable than physical charge storage [3, 5].

Figure 2.6. Schematic diagram for (a) EDLS and (b) FS. MnO_2 is used as an example of pseudocapacitive materials. Reprinted with permission from [9]. © 2014 The Royal Society of Chemistry.

2.3 Electrode Materials

Electrode materials are the most important components of LIBs and SCs. Materials perform the basic functions of these devices, which is energy conversion and storage. Electrode materials are also the main determinants of the device's energy density, power density and cycle life. Therefore, special attention has been given to develop new materials with enhanced energy storage performance.

There are various materials under research for energy storage. They can be classified according to the electrode type. For LIBs, materials used for anodes and cathodes are examined. For SCs, materials for EDLSs and FSs are studied. The focus of this work is on LIB anode and FS (pseudocapacitive) materials, with particular emphasis on nanomaterials and nanocomposites.

2.3.1 Lithium-Ion Battery Anode Materials

Graphite is not suitable as an anode material for high-performance LIBs. Although graphite has been the conventional LIB anode material, it has several limitations. The fully lithiated state of graphite is limited to LiC_6 . This leads to a theoretical specific capacity of only 372 mAh/g, which results in low energy density. In addition, the limited Li^+ diffusion coefficient in graphite ($< 10^{-6} \text{ cm}^2/\text{s}$) results in low rate capability [6]. Moreover, graphite anode raises safety concerns due to its very low working potential, which may induce potential hazards [10].

Several categories of anode materials are investigated as alternatives to graphite, including insertion-based, alloying-based and conversion reaction-based materials (Figure 2.7). Insertion-based materials are usually transition metal oxides that have very good safety profile, long cycle life and high rate capability, but limited capacity. Alloying-based materials are metals or semi-metals that provide very high capacities, but poor cycle life. Conversion reaction-based materials are transition metal compounds, such as oxides and sulfides. They have high capacities, but low energy efficiency, and suffer from capacity fading issues [11, 12].

Figure 2.7. Diagram illustrating the insertion, alloying and conversion reactions. Reprinted with permission from [13]. © 2009 The Royal Society of Chemistry.

Size reduction is regarded as critical for enhanced energy storage performance. This is a general concept that applies to all types of LIB anode materials. Nanomaterials offer large surface area that exposes more electrochemically active sites, leading to enhanced capacity. They also reduce the lithium ion diffusion length within the materials, which boosts rate performance. In addition, they buffer volume change during cycling, which improves LIB cycle life [6, 14].

Nanostructure is an important factor for optimized LIB anode performance. Optimizing the nanostructure can enhance surface area, which leads to higher contact with the electrolyte and more access to the electrochemically active sites. It can also improve its ability to buffer volume change during cycling, which imparts more stability on the electrode. In addition, it can improve charge transport, which leads to higher rate capability [15-17].

Synthesizing carbon-incorporated nanocomposites is a very promising approach for enhanced LIB anode performance [6, 11]. Nanocomposites of anode materials with carbonaceous materials (such as carbon nanofibers, carbon nanotubes (CNTs), carbon nanoparticles and graphene) have been reported. The carbon components enhanced conductivity, mechanically supported the active materials and prevented active material aggregation/detachment. This resulted in enhanced capacity, stability and rate capability [18].

In the next sections, insertion-based, alloying-based and conversion reaction-based materials will be reviewed in detail. Particular emphasis will be given to nanomaterials and carbon-incorporated nanocomposites.

2.3.1.1 Insertion-Based Metal Oxide Anodes

Insertion-based metal oxides undergo topotactic reaction to store lithium. They are crystalline materials that are able to intercalate Li ions without significant change in their crystal structures [12]. Li ions are inserted into the vacancies in the crystal structure, resulting in high rate capability and very good stability. They also operate within the

electrolyte stability window, which leads to safe battery operation [11]. In addition, they are usually of low cost and non-toxic, which make them very promising anode candidates. However, they have some drawbacks, such as their limited Li storage capacity [6], and their relatively high voltage operation, which lowers energy density.

Insertion-based metal oxides need to accommodate electrons as well. The metal species in insertion-based metal oxides is usually a transition metal that is able to exist in more than one stable valence state. This is because Li^+ intercalation/de-intercalation is accompanied by electron transfer, which alters the valence state of the metal species.

Several insertion-based metal oxides have been reported. Niobium- and titanium-based oxides are very promising candidates. They include niobium pentoxide, titanium dioxide, lithium titanate, and titanium niobate [12].

2.3.1.1.1 Niobium Pentoxide (Nb_2O_5)

Nb_2O_5 is a transition metal oxide that exists in several polymorphs. Nb_2O_5 is a semiconductor with a band gap of 3.4 eV, and a low electric conductivity of $\sim 3 \times 10^{-6}$ S/cm. Many of the properties of Nb_2O_5 depend on its crystal structure, which may be pseudohexagonal (H), orthorhombic (O), tetragonal (T) or monoclinic (M). The crystal structure of Nb_2O_5 can be controlled by heat treatment (Figure 2.8) [19].

Nb_2O_5 has been used as an insertion-based LIB anode [15]. It operates at a potential of > 1 V vs. Li^+/Li , which results in lower energy density. However, the high operating potential ensures much safer battery operation by avoiding electrolyte decomposition at potentials < 1 V vs. Li^+/Li [20]. Nb_2O_5 stores Li ions by intercalation reaction according to the following equation,

where x is the degree of Li^+ intercalation, which is a maximum of 2. This results in a theoretical specific capacity of 200 mAh/g [15].

Figure 2.8. Top: crystal structures of H-Nb₂O₅, O-Nb₂O₅ and M-Nb₂O₅; bottom: evolution of Nb₂O₅ crystal structure with heat treatment. Reprinted with permission from [19]. © 2016 The Royal Society of Chemistry.

All crystalline phases of Nb₂O₅ are electrochemically active. Kumagai et al. [21] tested Li storage in H-Nb₂O₅, O-Nb₂O₅ and M-Nb₂O₅. The three polymorphs achieved a high capacity of 160–180 mAh/g. However, there was an important variation; H-Nb₂O₅ and O-Nb₂O₅ underwent single-phase Li⁺ intercalation, whereas M-Nb₂O₅ showed binary-phase Li⁺ intercalation. The binary phase in monoclinic Li_xNb₂O₅ was explained by increasing ionic repulsion during intercalation. In a later study [22], electrochemical properties of the three polymorphs in addition to T-Nb₂O₅ were compared in terms of capacity and cycling stability. It was found that T-Nb₂O₅ has the best performance. M-Nb₂O₅ showed fast capacity fading, while O-Nb₂O₅ showed a stable performance. The crystal structure stability of T-Nb₂O₅ and O-Nb₂O₅ during Li⁺ intercalation was also demonstrated. A rather important feature of O-Nb₂O₅ was reported by Augustyn et al. who argued that the vacant octahedral sites between the (001) planes allowed for fast Li-ion transport, which led to high rate capability [23].

Designing Nb₂O₅ nanostructures is an important approach to tackle Nb₂O₅'s poor conductivity and pulverization during cycling [15]. Le Viet et al. [24] synthesized H/O/M-Nb₂O₅ nanofibers by electrospinning. They found that all phases displayed good electrochemical activity and cycling stability. M-Nb₂O₅ showed the highest specific capacity of 242 mAh/g at 0.05 A/g, in spite of its larger crystallite size and lower surface area due to the high annealing temperature of 1100 °C. There is no agreement over the

best Nb₂O₅ phase for Li storage, but it is clear from several studies [21, 22, 24] that O-Nb₂O₅, T-Nb₂O₅ and M-Nb₂O₅ are very promising for Li storage.

Many other Nb₂O₅ nanostructures have been reported, with very promising LIB performance. Hydrothermally derived O-Nb₂O₅ nanobelts achieved 180 mAh/g after 50 cycles at 0.1 A/g [25]. Vein-like nanoporous O-Nb₂O₅ prepared by anodization followed by annealing showed a capacity of 201 mAh/g after 300 cycles at 0.4 A/g [20]. O-Nb₂O₅ nanosheets with 50-nm thickness achieved 184 mAh/g at 1C, as compared to 135 mAh/g shown by Nb₂O₅ nanoparticles. The nanosheets showed good rate capability with 90 mAh/g at 5C. They also demonstrated stable cycling with 117 mAh/g retained after 100 cycles at 0.2 A/g. The enhanced nanosheet performance was attributed to its two-dimensional (2D) morphology, which allowed for charge transfer along the lateral dimensions. In addition, its nanothickness improved contact with the electrolyte and facilitated its diffusion within the material [15]. Three-dimensional (3D) O-Nb₂O₅ nanowire array maintained 177 mAh/g after 150 cycles at 0.1 A/g [26]. Other morphologies include nanowires [27], nanospheres [28], flower-like microspheres [29] and urchin-like microspheres [30].

Carbon-incorporated Nb₂O₅ nanocomposites have shown enhanced rate performance. One of the main problems of Nb₂O₅ is its poor conductivity, which mitigates LIB performance especially at high rates. This challenge can be tackled by introducing conductive carbon to improve electron transport [31]. Several Nb₂O₅ nanocomposites with high capacities and enhanced rate capabilities have been reported [31-38]. Mesoporous Nb₂O₅/C was synthesized via evaporation-induced self-assembly, using poly(ethyleneoxide-b-poly(styrene)) block co-polymer as structure-directing agent and carbon source [32]. It showed an enhanced rate capability, achieving 115.1 mAh/g at 5 A/g, as compared to 84.4 mAh/g attained by bare mesoporous Nb₂O₅. Lim et al. [31] synthesized O-Nb₂O₅@C nanocrystals using a water-in-oil microemulsion method; this material achieved 90 mAh/g at 5 A/g. Nb₂O₅/CMK-3 synthesized by nanocasting retained 75.5 mAh/g at 4 A/g, as compared to 43.7 mAh/g obtained by bulk Nb₂O₅ [33].

2.3.1.1.2 Titanium Dioxide (TiO₂)

TiO₂ is a polymorphic transition metal oxide with high Li storage capability. A number of polymorphs with different crystalline structures has been reported for TiO₂, including rutile, anatase, brookite, bronze, ramsdellite, hollandite, columbite and baddeleyite (Table 2.2). The first four polymorphs are very promising candidates as LIB anodes. TiO₂ stores Li ions by intercalation according to the following equation,

where x is the degree of intercalation, which varies from 0 to 1, resulting in a theoretical specific capacity of 335 mAh/g. Li-ion intercalation into the crystal lattice of TiO₂ takes place at > 1 V vs. Li⁺/Li, which leads to safe battery operation. However, it suffers from poor electronic and ionic transport, which limits battery performance [39].

Table 2.2. Properties of various TiO₂ polymorphs. Reprinted with permission from [39]. © 2009 Elsevier.

Structure	Space group	Density (g cm ⁻³)	Unit cell (Å)
Rutile	<i>P4₂/mnm</i>	4.13	$a = 4.59, c = 2.96$
Anatase	<i>I4₁/amd</i>	3.79	$a = 3.79, c = 9.51$
Brookite	<i>Pbca</i>	3.99	$a = 9.17, b = 5.46, c = 5.14$
TiO ₂ (B)	<i>C2/m</i>	3.64	$a = 12.17, b = 3.74, c = 6.51,$ $\beta = 107.29^\circ$
TiO ₂ -II	<i>Pbcn</i>	4.33	$a = 4.52, b = 5.5, c = 4.94$
TiO ₂ (H)	<i>I4/m</i>	3.46	$a = 10.18, c = 2.97$
TiO ₂ -III	<i>P2₁/c</i>	C	$a = 4.64, b = 4.76, c = 4.81,$ $\beta = 99.2^\circ$
TiO ₂ (R)	<i>Pbnm</i>	3.87	$a = 4.9, b = 9.46, c = 2.96$

Anatase is a very promising TiO₂ polymorph for Li storage. It has a body-centered tetragonal crystal lattice constituted of TiO₆ octahedra, whereby Li ions move along the octahedral interstitial sites. In the bulk state, Li⁺ intercalation is usually limited to Li_{0.5}TiO₂, where symmetry is transformed from *I4₁/amd* to orthorhombic *Pmn2₁* space group. This is accompanied by a 4% increase in unit cell volume, which causes capacity fading. It was also found that Li⁺ intercalation into bulk anatase TiO₂ results in phase separation into Li_{0.01}TiO₂ and Li_{0.6}TiO₂, which explains the bi-phasic flat potential curves [39].

Size reduction into the nanoscale is especially critical for anatase TiO_2 . Firstly, nanostructures improve the electronic and ionic transport, resulting in enhanced LIB performance. Secondly, Li^+ insertion mechanism changes, occurring as a solid solution instead of the bi-phasic intercalation observed in the bulk state. Moreover, surface charge storage is more significant in nanomaterials. These properties imparted by the nanosize increase the degree of Li^+ intercalation beyond the 0.5 Li per unit formula [39, 40].

Several TiO_2 nanostructures have been reported as LIB anodes, including nanobelts [41], nanotubes [42, 43], nanorods [42], nanorod-based microspheres [44, 45], nanocrystal-based hollow spheres [46], nanosheet-based hollow spheres [47] and nanoporous hierarchical structure [48]. TiO_2 nanobelts, synthesized by calcination of hydrogen titanate precursors, achieved specific capacities of 204 and 126 mAh/g at 1C and 20C, as compared to 112 and 33 mAh/g in the case of Degussa P25 TiO_2 nanoparticles. The excellent electrochemical properties were ascribed to the nanothickness that improved Li^+ transport, the one-dimensional (1D) structure that facilitated charge transport along the nanobelts, the porous nature of the material that improved contact with the electrolyte, and the flexibility of the nanostructure that accommodated volume change during cycling [41]. Hierarchical hollow spheres composed of ultrathin nanosheets were synthesized by hydrothermal processing of titania-silicone precursor. The hollow spheres demonstrated an impressive rate capability of ~105 mAh/g at 5 A/g (~30C). It has also shown a stable performance, retaining ~123 mAh/g after 200 cycles at 10C. The enhanced performance was explained by the unique hierarchical nanostructure, which allowed good contact with the electrolyte and short Li^+ diffusion paths [47].

Incorporating carbon into TiO_2 nanostructures can help to further improve their electrochemical performance. Various carbon-incorporated TiO_2 nanocomposites have been investigated, including TiO_2/CNTs [49, 50], $\text{TiO}_2/\text{graphene}$ [51-57] and $\text{TiO}_2/\text{carbon}$ [58-61]. Mesoporous $\text{TiO}_2/\text{graphene}$ nanocomposite demonstrated very good stability and excellent rate capability [56]. The nanocomposite retained > 125 mAh/g at 20C. It also achieved 97 mAh/g at 50C, which was 6 folds higher than bare sub-micrometer TiO_2 spheres. The high capacity was explained by quantum-size confinement

effect due to TiO_2 nanosize, while the high rate capability was ascribed to the improved charge transfer in the nanocomposite. Li et al. [55] synthesized sandwich-like nanosheets, whereby graphene sheets were coated with titania on both sides. The nanocomposite showed good cycling stability and high rate capability, achieving 225 and 175 mAh/g at 0.5C and 5C, respectively. The good performance of the nanocomposite was attributed to the nanosize, high porosity, nanothickness and high surface area, which facilitated Li^+ diffusion and enhanced contact with the electrolyte. The role of graphene was especially emphasized; graphene improved conductivity and protected the electrode against pulverization upon prolonged cycling. In addition, the graphene/ TiO_2 junctions were assumed to facilitate electron transfer and enhance interfacial Li storage.

2.3.1.1.3 Titanium Niobate (TiNb_2O_7)

TiNb_2O_7 has been introduced as insertion-based anode by Goodenough's group [62]. TiNb_2O_7 adopts a monoclinic crystalline structure, with a space group of $C2/m$. It has disordered Ti and Nb atoms, and provides 2D interstitial space for Li^+ intercalation (Figure 2.9). It is able to intercalate 5 Li^+ per unit formula, due to the $\text{Ti}^{4+}/\text{Ti}^{3+}$, $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox reactions. Its main advantages include safe battery operation (operating at > 1 V vs. Li^+/Li), and high theoretical specific capacity (387.6 mAh/g), which is higher than that of other insertion-based oxides such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Nb_2O_5 and TiO_2 (which have theoretical specific capacities of 175, 200 and 335 mAh/g, respectively) [15, 39, 62].

Figure 2.9. Schematic diagram illustrating the crystal structure of TiNb_2O_7 . Reprinted with permission from [62]. © 2011 American Chemical Society.

However, TiNb_2O_7 is limited by electronic and ionic conductivity. Similar to the other insertion-based metal oxides, slow kinetics limit the electrochemical performance of TiNb_2O_7 . This is due to the slow electron and ion transfer [63]. The approaches that have been used for tackling this challenge are similar to those used for Nb_2O_5 and TiO_2 . Nanostructures were used in order to reduce Li^+ diffusion paths and improve contact with the electrolyte, thus enhancing Li^+ transport and electrode capacity. Incorporation of carbon was also employed to improve electrode conductivity and rate capability [63, 64].

Upon successful demonstration of the electrochemical activity of TiNb_2O_7 in 2011, several TiNb_2O_7 nanostructures were reported in an effort to improve electrode performance. These include nanoparticles [65], 1D nanostructures [63, 66-68], porous frameworks [64, 69] and hierarchical microspheres [70, 71]. Tang et al. [63] synthesized 1D TiNb_2O_7 nanostructures by electrospinning, followed by calcination. The resulting “nano-pearl-string” TiNb_2O_7 showed a stable performance, maintaining 250 mAh/g after 50 cycles at 1C. They also demonstrated very good rate performance, achieving ~63 mAh/g at 20C (7.74 A/g). Their good performance was explained by the rapid Li-ion diffusion within the bulk of the sample due to the short Li-ion paths mediated by the nanosize. Li et al. [70] argued that the electrochemical performance of TiNb_2O_7 nanostructures could be further improved by designing a hierarchical porous 3D nanostructure. The 3D nanostructure could provide a continuous charge transport pathway, in contrast to the constrained pathways in anisotropic nanostructures. In light of this hypothesis, Li et al. synthesized porous hierarchical TiNb_2O_7 microspheres, which consisted of primary nanocrystallites. These hierarchical nanostructures achieved 258 and ~100 mAh/g at 1C and 20C, respectively, as compared to 138.1 and 36.6 mAh/g shown by bulk TiNb_2O_7 at 1C and 10C, respectively. Moreover, the microspheres could retain 115.2 mAh/g after 500 cycles at 10C.

TiNb_2O_7 /carbon nanocomposites were also reported for enhancing electrochemical performance. Wang et al. [72] investigated carbon-coated TiNb_2O_7 microwires that were composed of primary nanoparticles. It was found that carbon-coated microwires have improved cycling stability, achieving 195 mAh/g after 100 cycles at 0.5 A/g (~1.3C), as

compared to 112.4 mAh/g for the pure microwires. Carbon-coated microwires have also shown significant improvement of rate capability over various rates. They could retain ~75 mAh/g at 6 A/g (~15.5C). Noh and Choi [73] synthesized hierarchical TiNb_2O_7 microspheres, and coated them with reduced graphene oxide (rGO) to improve their electrochemical properties. The rGO-coated microspheres displayed enhanced cycling stability and rate capability. They exhibited 117 mAh/g at 50C, as compared to 35 mAh/g shown by pristine microspheres.

2.3.1.2 Alloying-Based Anodes

Alloying-based materials are metals (M) or semi-metals (SM) capable of forming Li-rich alloys. Li alloying/de-alloying reactions take place at ≤ 1 V vs. Li^+/Li according to the following equation,

Si, Ge and Sn are among the most promising alloying-based anode materials, where $x = 4.4$, resulting in theoretical specific capacities of 4200, 1600 and 999 mAh/g, respectively. Alloying-based materials have attracted much attention, especially due to their high theoretical capacities and low cost. However, they have shown a serious limitation. They tend to experience severe volume change of 300–400% due to the incorporation of a large amount of Li within the alloy. This results in material pulverization, which leads to contact loss from the current collector and capacity fading. Nanostructuring, morphology control and carbon incorporation are promising approaches to mitigate pulverization-induced capacity fading [11, 12, 74].

2.3.1.2.1 Tin Dioxide (SnO_2)

SnO_2 is widely investigated as alloying-based LIB anode, in spite of being a metal oxide that cannot directly form an alloy with Li. SnO_2 acts as an active material precursor, which decomposes to metallic Sn and Li_2O during Li^+ incorporation in the first cycle (Eq. 2.9). The metallic Sn is the actual active material that undergoes alloying/de-alloying reactions with Li^+ during cycling (Eq. 2.10). Although SnO_2 precursor leads to large irreversible capacity and a relatively low theoretical capacity (782 mAh/g), it offers some

advantages. Firstly, it is much easier to handle than metallic Sn, facilitating electrode preparation. Secondly, the Li₂O matrix formed during initial decomposition buffers the volume change caused by the alloying reaction, facilitates Li-ion transport and prevents aggregation of the Sn nanoparticles. This can help to improve the battery performance and mitigate capacity fading.

Size reduction to the nanoscale may lead to additional capacity. It has been shown that for SnO₂ nanomaterials, initial decomposition reaction may be reversible or partially reversible. This results in two reactions taking place during cycling. During initial lithiation, SnO₂ nanomaterial decomposes to form Sn and Li₂O (Eq. 2.9), followed by Li-Sn alloy (Eq. 2.10). During de-lithiation, Li-Sn de-alloying takes place (Eq. 2.10), followed by Sn oxidation to SnO_x (conversion reaction) (Eq. 2.11). Both alloying/de-alloying and conversions reaction take place in subsequent cycles. Although the conversion reaction leads to additional capacity (theoretical capacity increases to 1494 mAh/g), it also contributes to capacity fading [12, 75].

Several strategies have been proposed for stabilizing SnO₂ LIB performance, including synthesizing nanostructures, porous nanomaterials and SnO₂/carbon nanocomposites. Nanostructures such as 1D and 2D materials can help to buffer the severe volume change during cycling. They also improve ionic and electronic diffusion. Introduction of carbonaceous materials help to tolerate the structural strain accompanied by volume change. In addition, they boost the electrode conductivity [75, 76].

Many SnO₂ nanostructures and SnO₂/carbon nanocomposites have been reported as LIB anodes, including SnO₂ nanosheets [77-80], nanoboxes [81], nanowires [82], hollow spheres [83, 84], SnO₂/graphene [85-88] and SnO₂@C [74, 89, 90]. SnO₂ mesoporous nanosheets were synthesized by galvanic replacement method using MnO₂ template. The

nanosheets delivered 620 mAh/g at 1 A/g, and could retain ~400 mAh/g at 4 A/g. Cycling stability was tested for 100 cycles at 1 A/g, where a capacity of 430 mAh/g was retained (vs. 85 mAh/g retained by SnO₂ nanoparticles). The enhanced performance was attributed to the 2D nanosheet structure, which improved kinetics and mitigated the effect of volume change on the electrode integrity [78]. SnO₂ nanoparticles supported on graphene foam have also shown a stable performance, with the capacity reaching 533.7 mAh/g after 150 cycles at 1 A/g, as compared to 44.1 mAh/g achieved by SnO₂ nanoparticles alone. A high rate capability was also demonstrated by the SnO₂/graphene foam, with a capacity of 480.3 mAh/g at 3 A/g. The improved performance of SnO₂ nanoparticles was ascribed to the porous 3D graphene foam that facilitated ionic and electronic transport and buffered SnO₂ volume change during cycling [88].

2.3.1.3 Conversion Reaction-Based Anodes

Conversion reaction-based anodes have attracted great attention since the early 2000's. It was previously believed that the electrochemical conversion of transition metal oxides is irreversible due to the stable nature of Li₂O. However, this was proven incorrect by Poizot et al. who demonstrated reversible conversion reaction of metal oxide nanoparticles [91]. The decomposition of Li₂O was explained by a catalytic effect exerted by the metal nanoparticles that resulted from the initial decomposition of the metal oxides (Figure 2.10). This concept applies to other binary, ternary and complex transition metal-containing compounds such as metal oxides, sulfides, phosphides, fluorides, nitrides, etc. Conversion reaction takes place according to the following equation,

where M is transition metal, and X is O, S, P, F, N, etc. The main advantage of conversion reaction is the high theoretical capacity, which results from the multi-electron transfer. In addition, the wide variety of potential MX chemistries allows tuning of the output voltage, which depends on the bond ionicity [11, 12, 92, 93].

Figure 2.10. Diagram demonstrating reversible conversion reaction of CoO. Reprinted with permission from [94]. © 2005 Elsevier.

Conversion reaction-based anodes face serious challenges. One of their main problems is the voltage hysteresis between charge and discharge, which leads to poor energy efficiency. Other problems include poor kinetics and large volume change during cycling, which reduce rate capability and cause capacity fading. Nanomaterials can help alleviate volume change-induced strain, enhance kinetics and improve contact with the electrolyte. Carbon incorporation can also buffer volume change, increase electronic conductivity, and mitigate excessive SEI formation. Therefore, synthesizing carbon-incorporated nanocomposites is an effective approach to enhance conversion reaction-based anode capacity, stability and rate capability [11, 92, 93].

2.3.1.3.1 Metal Oxides

Metal oxides of various chemistries and compositions have been investigated as conversion reaction-based anode materials. For example, iron oxide nanostructures and nanocomposites with various designs have been reported, including nanosheets [78, 95], iron oxide/graphene [96-100], iron oxide@C [101-103], iron oxide/carbon nanofibers [104], and iron oxide/CNTs [105]. Similarly, many cobalt oxide and nickel oxide nanomaterials and nanocomposites have been studied including, nanosheets [106-108], 1D nanostructures [109, 110], and nanocomposites containing graphene/carbon [111-117].

Nanocomposites have demonstrated enhanced performance as conversion reaction-based anodes. Graphene-supported Fe_2O_3 nanosheets with high surface area were synthesized using a solvothermal approach. They demonstrated good performance as LIB anode, showing a capacity of 662.4 mAh/g after 100 cycles at 1 A/g. The cycling performance of Fe_2O_3 nanosheets/graphene was better than that of Fe_2O_3 nanoparticles/graphene. This was attributed to the better structural affinity between the nanosheets and graphene, which improved surface area and mitigated graphene agglomeration during cycling. The intimate sheet-on-sheet structure also helped to better tolerate the strain during cycling [96]. Co_3O_4 /N-doped graphene showed good cycling stability, achieving 1236 mAh/g after 200 cycles at 0.1C, as compared to 485 mAh/g for pure Co_3O_4 microspheres. An enhanced rate performance was also shown by the nanocomposite; 536 mAh/g was achieved at 2C, as compared to 41 mAh/g achieved by Co_3O_4 microspheres [114]. Similarly, NiO/graphene nanocomposite showed improved stability and rate capability. The nanocomposite achieved 646.1 mAh/g after 35 cycles at 0.1 A/g, as compared to 289.3 mAh/g for pure NiO. The nanocomposite retained 368.5 mAh/g at 0.8 A/g (vs. 56.2 mAh/g in the case of pure NiO) [117]. The performance enhancement demonstrated by the nanocomposites was explained by volume change accommodation, better contact with electrolyte, and better ionic and electronic transfer [96, 114, 117].

Ternary oxides are better electrode materials than binary oxides. Spinel ternary oxides with AB_2O_4 structure (e.g. NiCo_2O_4 , MnCo_2O_4) have been reported to possess higher electronic conductivity and enhanced electrochemical activity, due to the lower activation energy for transfer of electrons between metal species [118, 119]. Such synergistic effect of the complex chemical composition is evident in NiCo_2O_4 ; electrical conductivity of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is 0.1–0.3 S/cm, as compared to 3.1×10^{-5} S/cm for Co_3O_4 [120]. Moreover, using mixed metal species may help to reduce the electrode cost and toxicity, such as in the case of NiCo_2O_4 and MnCo_2O_4 , where the dependence on toxic and expensive cobalt is reduced [121].

Although ternary oxides are superior electrochemically, they still suffer from capacity fading. Ternary oxides undergo conversion reaction, and thus suffer from severe volume

change that affects the electrode performance. Similar to binary oxides, nanostructuring and carbon-incorporated nanocomposites are the most effective strategies for stabilizing the electrode performance. Several NiCo_2O_4 nanostructures and nanocomposites have been reported as LIB anodes, including hollow spheres [118], nanorods [120], NiCo_2O_4 /graphene [122, 123], and NiCo_2O_4 /CNTs [124]. Similarly, MnCo_2O_4 hollow spheres [125, 126], nanofibers [119], flakes [127], and nanocomposites with graphene [128] have been investigated as LIB anodes. Graphene-supported NiCo_2O_4 nanosheets showed a stable performance of 656.5 mAh/g at 0.5 A/g after 50 cycles, and could retain 437 mAh/g at 1 A/g [123]. MnCo_2O_4 nanoparticles embedded in graphene also showed a stable performance, achieving 841.1 mAh/g after 100 cycles at 0.1 A/g. It could still retain 462.1 mAh/g at 4 A/g [128]. The good performances of NiCo_2O_4 /graphene and MnCo_2O_4 /graphene were attributed to the nanostructures and graphene support, which buffer volume change, facilitate charge transport and improve contact with the electrolyte.

2.3.1.3.2 Metal Sulfides

Metal sulfides are another type of conversion reaction-based anode materials. They have higher conductivity than their corresponding oxides, thus, they are expected to have superior electrochemical properties [129]. Metal sulfides are lithiated and de-lithiated in the same manner as metal oxides, except that upon lithiation, the resulting metal nanoparticles are embedded within Li_2S matrix [130]. Several metal sulfides have been used as LIB anodes including cobalt sulfide [16, 131-135], nickel sulfide [129, 136-140], iron sulfide [17, 141-143], copper sulfide [130], zinc sulfide [144], tin sulfide [145], molybdenum sulfide [146], and manganese sulfide [147]. Although they are expected to show better performance than oxides, they also suffer from the large volume change during cycling that leads to capacity fading. In addition, they face another challenge, which is polysulfide dissolution in the electrolyte. Polysulfides reduce electrolyte conductivity, and can reach the cathode side, which affects the battery cycling stability [16, 17]. These challenges can be tackled using carbon-incorporated nanocomposites, as discussed below.

2.3.1.3.2.1 Nickel Sulfide

Nickel sulfide is a promising LIB anode due to its low cost and high capacity. However, it suffers from volume change during cycling and polysulfide dissolution. Stabilizing nickel sulfide electrode can be achieved using carbon-containing nanocomposites [136, 139, 148]. The nanocomposites can help to tolerate volume change, improve conductivity and reduce particle aggregation during cycling. This should improve the electrode performance. Moreover, carbon can help to trap the polysulfides, and thus mitigate their negative effect on the battery performance [16, 129, 149]. Mahmood et al. [139] synthesized Ni_3S_4 nanoparticles coupled to N-doped graphene in a two-step process. The nanocomposite has shown better capacity than the individual nickel sulfide and graphene, indicating a synergistic effect. It achieved a remarkable capacity of 1323.2 mAh/g after 100 cycles at 0.14 A/g, as compared to 494 mAh/g for bare Ni_3S_4 . It also managed to achieve 558.2 mAh/g at 2.8 A/g. Son et al. [138] synthesized nickel sulfide-carbon nanocomposite using ultrasonic spray pyrolysis. In contrast to bare nickel sulfide, which showed fast capacity fading, the nanocomposite demonstrated a stable performance. It managed to achieve 472 mAh/g after 500 cycles at 1 A/g. Moreover, it retained 327 mAh/g at 2.5 A/g. Graphene/carbon improved the electrochemical performance of nickel sulfide by buffering volume change, improving electrode conductivity and trapping polysulfide anions. This resulted in stabilized nickel sulfide performance, and improved rate capability [138, 139].

2.3.2 Faradaic Supercapacitors

FSs (pseudocapacitors) are a type of SCs that is characterized by high energy density. Pseudocapacitors are able to store charge in the double layer, in addition to undergoing Faradaic reactions at the material surface. This results in much larger charge storage than conventional EDLSs, and thus higher energy density. Metal oxides and conducting polymers are the two major material types used for Faradaic SCs [5].

2.3.2.1 Metal Oxides

Metal oxides are very promising materials for pseudocapacitors. Metal oxides have shown better electrochemical stability than conducting polymers. They are able to deliver

very high specific capacitance, about one order of magnitude higher than that for EDLSs [5, 150]. Pseudocapacitive metal oxides need to have good electronic conductivity and to be able to exist in multiple oxidation states in a stable manner [5, 151]. Due to their promising performance, several pseudocapacitive metal oxides are currently investigated (Table 2.3), including manganese oxide [152, 153], cobalt oxide [154], nickel oxide [155], iron oxide [156], and vanadium oxide [157].

Table 2.3. Examples of pseudocapacitive metal oxides. Reprinted with permission from [150]. © 2013 The Royal Society of Chemistry.

Oxide	Electrolyte	Charge storage reaction	Theoretical capacitance (F g ⁻¹)
MnO ₂	Na ₂ SO ₄	MnO ₂ + M ⁺ + e ⁻ = MMnO ₂ (M could be H ⁺ , Li ⁺ , Na ⁺ , K ⁺)	1380 (0.9 V)
NiO	KOH, NaOH	NiO + OH ⁻ = NiOOH + e ⁻	2584 (0.5 V)
Co ₃ O ₄	KOH, NaOH	Co ₃ O ₄ + OH ⁻ + H ₂ O = 3CoOOH + e ⁻ CoOOH + OH ⁻ = CoO ₂ + H ₂ O + e ⁻	3560 (0.45 V)
V ₂ O ₅	NaCl, Na ₂ SO ₄	V ₂ O ₅ + 4M ⁺ + 4e ⁻ = M ₂ V ₂ O ₅ (M could be H ⁺ , Li ⁺ , Na ⁺ , K ⁺)	2120 (1 V)
RuO ₂ , xH ₂ O	H ₂ SO ₄ , Na ₂ SO ₄	RuO ₂ + xH ⁺ + xe ⁻ = RuO _{2-x} , (OH) _x (0 < x < 2)	1200–2200 (1.23 V)

Metal oxide pseudocapacitive materials suffer from some limitations. Metal oxides usually have low conductivity, which affects rate capability. They are also prone to pulverization during cycling, which affects their stability. In addition, it is difficult to control surface area and porosity of bulk metal oxides. These problems can be tackled by synthesizing carbon-incorporated nanocomposites. Nanomaterials have high surface area and enhanced ionic/electronic diffusion. In addition, carbonaceous materials act as a support, which facilitates charge transport and enhances electrode conductivity. This synergistic effect could improve electrode energy density, stability and rate capability [150, 151].

2.3.2.1.1 Mn₃O₄

Mn₃O₄ is an interesting pseudocapacitive material. It is a mixed-valent manganese oxide that has high specific capacitance [158]. It is also non-toxic and of low cost [159]. However, Mn₃O₄ suffers from poor electric conductivity (10⁻⁷–10⁻⁸ S/cm) [160], which affects its capacitance and rate capability [159]. Nanostructuring and carbon

incorporation can improve the electrochemical activity of Mn_3O_4 by exposing more electroactive sites and improving the electrode conductivity [159, 160]. Many studies have been conducted in an effort to improve the pseudocapacitive performance of Mn_3O_4 , such as using Mn_3O_4 nanosheets [161], nanocrystals [158], nano-octahedrons [162], porous nanostructures [163], Mn_3O_4 /carbon [164, 165], and Mn_3O_4 /graphene [159, 160, 166]. Mn_3O_4 nanosheets were synthesized using hexamethylenetetramine as a structure-directing agent. They achieved 398 F/g at a scan rate of 0.005 V/s. The excellent performance was attributed to the high porosity and large internal surface that increase contact with the electrolyte and facilitate ionic diffusion [161]. Dong et al. have shown that Mn_3O_4 nanocrystals have good pseudocapacitive performance, where 55 and 46 F/g were achieved at 10 and 20 A/g, respectively. They also managed to further improve the performance and stability by Cr doping [158]. Lee et al. hydrothermally synthesized Mn_3O_4 nanorods on graphene sheets. The nanocomposite displayed good rate capability, achieving 88 and 83 F/g at current densities of 10 and 20 A/g, respectively, as compared to 12 F/g achieved by bare Mn_3O_4 at 10 A/g. The nanocomposite has also shown a very stable performance over 10,000 cycles [159].

2.3.2.2 Metal Sulfides

Metal sulfides are regarded as an emerging category of pseudocapacitors [167]. They have good electrochemical activity, and are able to undergo surface redox reactions in a stable manner [168, 169]. Various metal sulfides have attracted attention as pseudocapacitive materials including copper sulfide [170], molybdenum sulfide [171], cobalt sulfide [172, 173] and nickel sulfide [167, 169].

2.3.2.2.1 Nickel Sulfide

Nickel sulfide is a promising pseudocapacitive material, due to its good electrochemical properties and low cost [174]. It exists in various phases, many of which have been studied as Faradaic SCs [169]. However, like other pseudocapacitive metal oxides and sulfides, nickel sulfide suffers from cycling-induced pulverization that leads to poor stability [174, 175]. Many reports have studied nickel sulfide nanostructures and nanocomposites to improve and stabilize its pseudocapacitive performance, including

nanocubes, nanospheres, nanoparticles [176], nanoflakes [167], hollow spheres [177], nickel sulfide/carbon nanorods [174], nickel sulfide/CNTs [178, 179], and nickel sulfide/graphene [169, 175, 180, 181]. Pang et al. synthesized NiS₂ nanocubes using a microwave-assisted method. The nanocubes showed good pseudocapacitive performance, achieving 695 F/g at a current density of 1.25 A/g, and 158 F/g at 12.5 A/g. They have also shown a stable performance over 3000 cycles. The good performance of the nanocubes was attributed to their single crystalline nature that facilitated electron diffusion [176]. Yang et al. have investigated the pseudocapacitive performance of NiS/rGO nanocomposite. A very good rate capability was achieved; the nanocomposite showed a specific capacitance of 579 A/g at a current density of 5 A/g. Moreover, a stable performance was demonstrated over 2000 cycles. Yang et al. also demonstrated that bare NiS nanorods failed to achieve similar performance. The enhanced electrochemical performance of the nanocomposite was attributed to the shortened ionic paths, high surface area, improved conductivity and mechanical stability [175].

2.4 Research Motivation

The literature review has clearly shown the important role of nanocomposites in energy storage. Substituting bulk materials with nanomaterials has improved the performance of LIB anodes and FS electrodes by improving charge transport, increasing contact with the electrolyte and buffering volume change. The nanostructure also affected energy storage performance, due to its influence on the material contact with the electrolyte, ionic and electronic transport, and interaction with carbonaceous materials. Carbon incorporation has demonstrated significant performance enhancement, mainly due to increased conductivity and lowered mechanical strain during cycling.

In this thesis, novel methods are reported for the facile synthesis of nanomaterials and nanocomposites for energy storage. Nickel sulfide and graphene-wrapped nickel sulfide nanopyramids were synthesized using a one-pot colloidal method. In addition, a wide variety of binary and ternary oxide nanosheets were synthesized using a facile template-assisted method. The synthesized nanomaterials and nanocomposites were evaluated as Li-ion battery anodes and SC electrodes.

2.4.1 Graphene-Wrapped Nickel Sulfide Nanopyramids for Energy Storage

The literature review has shown nickel sulfide as a promising energy storage material. However, most of the reported synthesis methods involved the hydrothermal/solvothermal approach, which produced non-uniform and relatively large nanoparticles [136, 148, 175, 180, 181]. In addition, many of them used multi-step procedures [129, 139] or required special equipment [138, 149]. Developing a simple one-pot method for synthesizing nickel sulfide/carbon nanocomposites would facilitate the advancement of nickel sulfide as an energy storage material. Ideally, the nanocomposite should be in the form of uniform, small nanoparticles that are well-dispersed on the surface of a carbon support.

In Chapter 4, a novel method is reported for the synthesis of nickel sulfide/graphene nanocomposite as LIB anode and pseudocapacitive electrode. A facile, one-pot colloidal approach is adopted for the synthesis of uniform single-crystalline 25-nm nanopyramids, which are wrapped with graphene sheets. The one-pot method is practical, and offers very good contact between the nickel sulfide nanopyramids and the graphene sheets. The highly dispersed small particles ensure good contact with the electrolyte and facilitate charge transfer. The graphene wrapping enhances the conductivity and buffers volume change during cycling. The single-crystalline nature of the nickel sulfide nanopyramids is helpful for pseudocapacitive activity, as reported in the study by Pang et al. [176].

2.4.2 Metal Oxide Nanosheets for Energy Storage

Metal oxide nanosheets are interesting materials with various potential applications. Nanosheets typically have a thickness less than 5 nm [182, 183], and a lateral dimension of 100 nm up to the micrometer range [183]. Many metal oxides have been designed as nanosheets, and used for applications such as energy storage [116, 184-186], catalysis [187, 188] and sensors [189, 190].

Metal oxide nanosheets are very promising materials for energy storage. Their unique mechanical properties allow for flexibility and tolerance to distortion and wrinkling, which are useful for buffering the volume change and material strain during cycling [95,

191-193]. Their high surface area allows better contact between active material and electrolyte [186, 191, 193-195], which enhances access to electroactive sites. The very small nanosheet thickness facilitates ionic and electronic transport across the material, leading to higher rate capability [186, 191-193]. In addition, their surface electronic structure [95, 191, 194] provides for transport pathways in between the sheets, which may give rise to pseudocapacitive behavior [95].

Many metal oxides nanosheets have been reported for energy storage. Nb_2O_5 [15, 196], TiO_2 [58, 197], Fe_2O_3 [78, 95], SnO_2 [78, 79], Co_3O_4 [106, 107] and NiO nanosheets [108, 116, 198] have been studied as LIB anodes with promising performance. Mn_3O_4 nanosheets have shown very good pseudocapacitive performance [161]. The literature review has elaborated on some of these reports, such as Nb_2O_5 nanosheets [15], nanosheet-based TiO_2 hollow spheres [47], TiO_2 /graphene sandwich-like nanosheets [55], SnO_2 nanosheets [78], and Fe_2O_3 /graphene sheet-on-sheet [96] for LIB anodes. In addition, the pseudocapacitive activity of Mn_3O_4 nanosheets [161] has been discussed.

Various methods are used for the synthesis of metal oxide nanosheets. Mechanical exfoliation [199] and liquid exfoliation [200] are examples of top-down methods. However, they are not scalable, and are limited to intrinsically layered materials [201, 202]. Bottom-up wet-chemical approaches are considered more practical. They include hydrothermal/solvothermal [79, 106, 116, 196], template-assisted [78, 95, 203-205] and template-assisted solvothermal methods [206-208]. However, the hydrothermal/solvothermal methods require autoclaves and are not easily scalable. Many template-assisted methods require an additional step to remove the template, such as using NaOH for etching silica and alumina templates, which renders the synthesis methods laborious [95, 203, 204]. In addition, the current methods mostly report the synthesis of binary oxide nanosheets, and do not extend their methodology to synthesize more complex oxides, such as ternary oxide nanosheets. A facile, generalized and scalable method for the synthesis of a wide range of binary and ternary oxide nanosheets would help to advance the applications of these 2D materials.

In Chapter 5, a novel template-assisted approach is demonstrated for the generalized synthesis of metal oxide nanosheets. The facile synthesis protocol involves neither hydrothermal/solvothermal conditions nor laborious template-removal steps. In addition, the method was manipulated for the synthesis of metal oxide/rGO nanocomposites. The novel method has been developed for the synthesis of a wide range of binary oxide nanosheets and nanocomposites for high-performance LIB insertion-based, alloying-based and conversion reaction-based anodes. The nanosheets have also displayed very promising and stable pseudocapacitive performance.

The novel nanosheet synthesis method has been further developed to synthesize more complex ternary oxides. In Chapter 6, the synthesis of ternary oxide nanosheets and their rGO-incorporated counterparts are presented. The ternary oxide nanosheets and nanocomposites have been evaluated as LIB anode materials.

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Chapter 3

Experimental Methodology

This chapter presents the methodology used for synthesis, characterization and testing of the nanomaterials and nanocomposites. In the first section, the principles of the synthesis methods are discussed, and the rationale for their selection is explained. The methods developed in this thesis aimed at producing nanomaterials and nanocomposites with controlled properties for energy storage applications. The novel synthesis strategies tackled the limitations of the current methods, in terms of the synthesis procedures and the properties of the materials synthesized. The colloidal thermal decomposition approach employed produced uniform nickel sulfide nanopyrramids, and anchored them uniformly to the surface of graphene sheets in a one-pot process. The graphene oxide planar-confined growth strategy provided a platform for the generalized synthesis of binary and ternary oxide nanosheets using a facile method. The techniques employed for materials characterization and their role in the research work are discussed in the second section. Finally, the processes and techniques used for electrochemical assessment of the synthesized materials as Li-ion battery and supercapacitor electrodes are described.

3.1 Nanomaterial/Nanocomposite Synthesis Strategies

The objective of this thesis is the controlled synthesis of nanomaterials and nanocomposites for high-performance energy storage. As discussed in the previous chapters, nanomaterials have demonstrated much better energy storage capabilities than their bulk counterparts. Morphological and structural control was also found to affect a material's energy storage performance. Nanocomposites containing carbonaceous materials could further enhance and stabilize energy storage. Therefore, the adopted synthesis strategies were selected so as to allow for synthesizing nanomaterials, controlling their morphology and phase, and incorporating carbonaceous species within them.

Two synthesis strategies were used throughout this thesis. The first of which is a colloidal approach, which was used for the synthesis of nickel sulfide and graphene-wrapped nickel sulfide nanopyramids. The second strategy is a template-assisted approach, which was used for the synthesis of a wide variety of binary and ternary oxide nanosheets. The following section will discuss both strategies, with particular emphasis on the rationale for their adoption.

3.1.1 Colloidal Synthesis of Nickel Sulfide and Graphene-Wrapped Nickel Sulfide Nanopyramids

Colloidal synthesis strategy is used for the production of ultra-small, uniform, shape-controlled, and well-dispersed nanocrystals. This strategy comprises several methods such as reduction, thermal decomposition and non-hydrolytic sol-gel methods. Many classes of materials have been synthesized using the colloidal approach, including metal, metal oxide and metal chalcogenide nanocrystals [1].

Thermal decomposition is a classical colloidal nanocrystal synthesis method. It involves organometallic precursors, surfactants and organic solvents. At high temperatures, activated precursors act as monomers in a supersaturated condition that undergo burst nucleation. As monomer concentration decreases, nucleation is terminated and monomers are incorporated in the nucleated seeds, resulting in nanocrystal growth. The nanocrystals

are stabilized by the organic surfactants that adhere to the nanocrystal surface (Figure 3.1) [1-3].

Figure 3.1. Diagram depicting colloidal nanocrystal synthesis. $C_{\text{equi.}}$ = equilibrium concentration, $C_{\text{sat.}}$ = saturation concentration. Reprinted with permission from [3]. © 2006 WILEY-VCH.

Organic phase is especially important for size- and shape-controlled nanocrystal synthesis. The organic-medium nanocrystal synthesis produces nanoparticles with desirable properties, such as monodispersity, high crystallinity and excellent dispersion. In addition, organic-phase synthesis facilitates separation of nanocrystal nucleation and growth processes [1, 3].

Nanocrystal size control is critical for monodispersity. One of the most effective approaches for synthesizing monodisperse nanocrystals is separating the nucleation and growth processes. This has been pioneered by Murray et al. [4] who reported the hot-injection method. The organometallic precursors were rapidly injected into hot coordinating solvent resulting in transient monomer supersaturation, and thus burst nucleation. Rapid nucleation leads to sudden decrease in monomer concentration below supersaturation level, which converts the system into growth phase. Another approach for nanocrystal size control is size focusing. The main concept underlying size focusing is that the growth rate is a factor of nanocrystal size. There is a critical size above which growth takes place, while the nanocrystals of smaller size are dissolved. The critical size

decreases with increasing monomer concentration (Figure 3.2). This means that low concentration systems are more amenable to Ostwald ripening because the critical size is large. Size focusing narrows the size distribution by maintaining the monomer concentration high enough such that the average nanocrystal size is larger than the critical size. This can be done by optimizing the monomer concentration and reaction duration [2].

Figure 3.2. Diagram illustrating the concept of size focusing. Reprinted with permission from [2]. © 2005 Nature Publishing Group.

Organic-phase colloidal synthesis allows carbon incorporation within the nanocrystals. The organic surfactants that adhere to the nanocrystals are carbonized upon annealing. Carbon incorporation would enhance the electrochemical properties of the active nanocrystals. This has been demonstrated by Xu et al. who synthesized carbon-coated FeS nanostructures by thermal decomposition of iron(III) acetyl acetonate in oleylamine. 1-dodecanethiol was used as sulfur source and surfactant. The amorphous carbon coating was formed as a result of annealing-induced carbonization of the 1-dodecanethiol C₁₂ tails that adhered to the nanocrystals [5]. Similarly, carbon-coated Co₉S₈ nanodandelions were synthesized using 1-dodecanethiol and oleic acid. The amorphous carbon coating was attributed to the carbonization of the adherent organic surfactants upon annealing [6].

Thermal decomposition-based colloidal synthesis is widely used for producing metal oxide and chalcogenide nanocrystals. Park et al. thermally decomposed metal-oleate complexes for the large-scale synthesis of monodisperse metal oxide nanocrystals

including iron oxide, MnO and CoO [7]. Similarly, magnetite nanocrystals of narrow size distribution were synthesized by thermolysis of iron carboxylate salts [8]. A wide variety of uniform metal chalcogenide nanocrystals, including ZnS, PbS, MnS and CdS were synthesized by heating metal-oleylamine complexes together with sulfur [9]. Choi et al. thermally decomposed metal-oleate complexes in 1-dodecanethiol to synthesize Cu₂S, ZnS, CdS, PbS and MnS nanocrystals [10].

Nanocrystals synthesized by colloidal thermal decomposition method have shown enhanced energy storage capabilities. Carbon-coated FeS nanosheets demonstrated a stable performance as lithium-ion battery (LIB) anode, with a capacity of 615 mAh/g after 100 cycles at 0.1 A/g. It also achieved 349 mAh/g at 3 A/g, which indicated high rate capability [5]. Carbon-coated Co₉S₈ nanodandelions have also demonstrated very good LIB anode performance, with capacities of 520 mAh/g after 50 cycles at 1 A/g, and 373 mAh/g at 6 A/g [6]. Ultra-small CoS nanocrystals have shown high capacitance, achieving 790 F/g at 5 mA/cm². The high capacitance was explained by the small size and high surface area of the nanocrystals [11].

Nickel sulfide nanoparticles are promising as LIB and pseudocapacitive electrode materials. Although nickel sulfide nanoparticles with desirable properties for energy storage could be synthesized via colloidal thermal decomposition method, it was rarely demonstrated in literature. Most of the reported methods adopted the hydrothermal/solvothermal approach [12-19], which was not able to produce ultra-small, uniform nanocrystals. The synthesized nanoparticles were relatively large and non-uniform. Moreover, some of these methods included an additional step to synthesize the precursor [14], or for sulfurization [15, 19]. Other reported methods for the synthesis of nickel sulfide/carbon nanocomposites for energy storage included spray pyrolysis [20] and electrospinning [21]. However, these methods required special equipment that complicated the synthesis process.

In this work, colloidal thermal decomposition method was used for the synthesis of nickel sulfide nanocomposites for LIB and supercapacitor electrodes. Ultra-small monodisperse

nickel sulfide nanopyramids were synthesized using a facile one-step method. The nanopyramids were coated with a carbon layer upon annealing. In addition, reduced graphene oxide (rGO) could be incorporated within the nanopyramids in a one-pot synthesis method. The small uniform size of the nanopyramids and the incorporation of carbonaceous materials were critical for the production of high-performance energy storage electrode.

3.1.1.1 Synthesis of Nickel Sulfide Nanopyramids (NS)

Nickel sulfide nanopyramids were synthesized in an organic-phase system. Oleylamine was used as solvent and surfactant. Oleic acid was used as co-surfactant, and 1-dodecanethiol was used as a sulfur source and co-surfactant. The hot-injection method was employed by rapid injection of 1-dodecanethiol into hot oleylamine/oleic acid solution containing nickel-surfactant complex. The nanopyramids were then allowed to grow by aging. Precursor concentration, relative amounts of surfactants and co-surfactants, growth temperature, and reaction duration were all optimized in order to synthesize ultra-small, monodisperse and single-phase nickel sulfide nanopyramids. The optimized synthesis conditions are described below.

51.4 mg (0.2 mmol) of nickel(II) acetylacetonate was mixed with 5 mL of oleylamine (15.2 mmol) and 1 mL of oleic acid (3.15 mmol) in a 50-mL 3-necked flask, and stirred for 30 min in argon. The solution was heated to 100 °C, and degassed for 15 min. 1 mL of 1-dodecanethiol (4.2 mmol) was injected at 100 °C, and then the temperature was increased to 250 °C, where the solution was aged for 20 min. After cooling, the solution was washed with hexane and ethanol several times. The product was finally calcined at 350 °C for 1 h in argon.

3.1.1.2 Synthesis of Graphene-Wrapped Nickel Sulfide Nanopyramids (NS/G)

GO-oleylamine was prepared by mixing GO (single layer GO, 0.7–1.2 nm thick, Cheap Tubes Inc., Vermont, USA) with 5 mL oleylamine, followed by sonication for 2 h until full dispersion. Synthesis of graphene-wrapped nickel sulfide nanopyramids was the same as that of bare nickel sulfide nanopyramids, except that GO-oleylamine was used

instead of oleylamine. NS/G materials synthesized using 5 mg, 10 mg and 20 mg of GO were specified as NS/G-5, NS/G-10 and NS/G-20, respectively.

3.1.2 Template-Assisted Synthesis of Metal Oxide Nanosheets

Several strategies are employed for the synthesis of metal oxide nanosheets. Conventionally, top-down liquid exfoliation has been used for oxide nanosheet production [22]; however, this method suffers from limitations such as low yield of single sheets, long exfoliation time, difficulty in scaling up [23], and most importantly, non-compatibility with non-layered oxides [24]. In contrast, bottom-up approaches would provide more versatility in metal oxide nanosheet synthesis. Thin film deposition has been used as a bottom-up approach for oxide nanosheet synthesis, for example, electron-beam deposition was used to epitaxially grow titania nanosheets on Pt substrate [25]. However, such complex methods would be very costly and difficult to scale up. Wet-chemical synthesis is another bottom-up approach that has attracted a lot of interest due to its ability to mass produce metal oxide nanosheets at a low cost [24]. Hydrothermal/solvothermal and template-assisted methods are the main wet-chemical approaches for metal oxide nanosheet synthesis.

Hydrothermal/solvothermal approach has been widely used to synthesize metal oxide nanosheets. Nb_2O_5 nanosheets were synthesized by hydrothermal reaction between Nb powder and HF resulting in $\text{Nb}_3\text{O}_7\text{F}$ intermediate nanosheets, which were converted to Nb_2O_5 nanosheets by calcination [26]. Nb-doped TiO_2 nanosheets were synthesized by a hydrothermal reaction, in which nanosheet formation was driven by oriented attachment [27]. NiO nanosheets were synthesized using a solvothermal method, where the solvent mixture was critical for directing the nanosheet synthesis [28]. SnO_2 nanosheets were synthesized by solvothermal reaction in a basic hydroethanolic mixture. However, the mechanism of nanosheet formation was not elucidated [29]. Although hydrothermal/solvothermal synthesis is successful in producing different metal oxide nanosheets, it has some drawbacks. Firstly, the mechanism of nanosheet synthesis is variable, depending to a large extent on the type of oxide synthesized. Therefore, it is not easy to use as standard synthesis process for a wide variety of oxide nanosheets.

Secondly, the hydrothermal/solvothermal approach requires using autoclaves that limit its potential for industrial scale up.

The template-assisted approach is more promising for generalized synthesis of metal oxide nanosheets. Template utilization allows using a single method for the synthesis of different types of metal oxide nanosheets. This is because the nanosheet synthesis depends mainly on the structure of the template, rather than the metal oxide composition. Graphene-silica (G-silica) nanosheets were used as template for the synthesis of several metal oxide nanosheets. Silica was deposited on GO, followed by calcination to form G-silica. G-silica was used as a substrate for the deposition of titania, followed by calcination in Ar. Lastly, silica was removed by etching using NaOH, leaving behind G-TiO₂. Pure TiO₂ nanosheets were also synthesized by calcination in air instead of Ar (Figure 3.3) [30]. This process was successfully used for the synthesis of Co₃O₄ [31] and Nb₂O₅ nanosheets [32]. The synthesized nanosheets had small thickness, porous nature and high surface area [30-32].

Figure 3.3. Scheme illustrating the synthesis of G-TiO₂ and TiO₂ nanosheets using G-silica as a template. Reprinted with permission from [30]. © 2011 WILEY-VCH.

Template-assisted solvothermal synthesis is a hybrid approach for oxide nanosheet synthesis. This approach uses solvothermal reaction for the oxide synthesis, and a two-dimensional (2D) template to direct the oxide growth into the nanosheet morphology.

As an example, soft-template-assisted solvothermal synthesis was used for a generalized synthesis of metal oxide nanosheets [33]. Inverse lamellar micelles were used as soft templates for layered confinement of the inorganic species. A solvothermal reaction was subsequently used to synthesize and crystallize the metal oxide nanosheets (Figure 3.4). This template-directed solvothermal process resulted in the production of very thin oxide nanosheets of various compositions, including TiO_2 , Co_3O_4 , Fe_3O_4 , MnO_2 , ZnO and WO_3 nanosheets.

Figure 3.4. Diagram showing metal oxide nanosheet synthesis using soft lamellar templates. Reprinted with permission from [33]. © 2014 Nature Publishing Group.

GO template, accompanied by solvothermal reaction, was also used for the synthesis of a variety of metal oxide nanosheets. GO is an ideal template for metal oxide nanosheet synthesis because it is a 2D material that can be mass produced. Its surface is covered with various functional groups such as hydroxyl and carboxyl moieties that facilitate its reaction with metal oxide precursors. Moreover, GO is a carbonaceous material that can be easily removed by calcination in air.

Zhu et al. [34] synthesized SnO_2 and Fe_2O_3 nanosheets by solvothermally reacting their chloride precursors with GO, followed by calcination in air. The solvothermal reaction resulted in hybrid nanostructures, where metal oxide nanoparticles were anchored to rGO sheets. Upon calcination in air, rGO was removed, leaving behind metal oxide nanosheets. Similarly, Takenaka et al. [35] synthesized various metal oxide nanosheets

solvothermally using GO template and metal alkoxide precursors. Air calcination was also used to remove rGO.

Although the template-assisted approach is applicable for the synthesis of various metal oxide nanosheets, it still faces some challenges. G-silica-based oxide nanosheet synthesis requires pre-synthesis of the G-silica template, and post-synthesis etching to remove silica [30-32]. This adds two more steps to the process, rendering it more laborious. The methods utilizing soft lamellar template [33] and GO template [34, 35] adopt a solvothermal approach using autoclaves, which limits their potential industrial scale up. In addition, the synthesis of some types of oxide nanosheets using the soft lamellar template requires aging for a long duration, up to 7 days, which makes it very time-consuming. Moreover, the reported template-assisted methods were used to synthesize binary oxides. They have not been extended to obtain more complicated oxides, such as doped binary oxides and ternary oxides.

Based on the discussion above, a generalized metal oxide nanosheet synthesis approach that is free from limiting processes such as hydrothermal/solvothermal reactions, laborious template removal and long synthesis duration is desired. Such an approach should be able to synthesize a wide variety of binary oxides, as well as doped binary oxides and ternary oxides.

3.1.2.1 Novel, Facile and Generalized Template-Assisted Synthesis of Metal Oxide Nanosheets

A GO template-assisted method has been developed in this thesis so as to overcome the above-mentioned limitations. No autoclaves or laborious time-consuming processes were involved. Briefly, GO was dispersed in a solution of metal oxide precursors, where the precursors were bound to the oxygenated groups on the GO surface. The precursor-bound GO was subjected to calcination in air, resulting in the formation of metal oxide nanosheets and removal of the template simultaneously. A wide range of metal oxide nanosheets were synthesized using this method, including binary oxides (Nb_2O_5 , TiO_2 , Fe_2O_3 , SnO_2 , NiO , Co_3O_4 , Mn_3O_4 and ZrO_2), doped binary oxides ($\text{Ti-Nb}_2\text{O}_5$ and Nb-

TiO₂) and ternary oxides (TiNb₂O₇, Ti_{0.61}Nb_{1.29}O₄, Ni_xCo_{3-x}O₄ and Mn_xCo_{3-x}O₄). This approach bypassed the limiting solvothermal and laborious template-removal processes that were used by previous reports [30-35]. Moreover, it demonstrated excellent capability to control nanosheet composition; complex oxides, such as doped binary oxides and ternary oxides were successfully synthesized through this approach.

The novel GO template-assisted method could also control the attributes of the synthesized nanosheets. The calcination conditions (including the calcination atmosphere, temperature and duration) were used to manipulate the properties of the nanosheets, such as crystallinity, crystalline phase, crystallite size, surface area, porosity and retained rGO content.

Controlling the rGO content is especially important for energy storage applications. The main approach used for synthesizing metal oxide/rGO nanosheets involved mild calcination conditions so as to avoid the complete removal of rGO template. Two alternative methods were also used for the synthesis of metal oxide/rGO nanosheets. The first involved calcination of the precursor-bound GO in Ar instead of air, thus retaining the entire rGO template. The second consisted of a post-synthesis step, whereby rGO was introduced within the nanosheets using the “opposite-charge” method as described below. Figure 3.5 illustrates the novel GO template-assisted method for the synthesis of metal oxide nanosheets, as well as the three approaches used for metal oxide/rGO nanosheet synthesis.

Figure 3.5. Scheme illustrating the novel GO template-assisted method for metal oxide nanosheet synthesis. The three approaches used for metal oxide/rGO nanosheet synthesis are also illustrated.

3.1.2.1.1 Synthesis of Metal Oxide Nanosheets Using GO Template

Metal oxide precursors were dissolved in 0.5 mg/mL GO dispersion in absolute ethanol. The dispersion was stirred overnight to allow binding of metal oxide precursors to GO. This was followed by centrifugation, and washing several times with ethanol to remove excess precursors. Precursor-bound GO was dried at 60 °C overnight, and finally calcined in air at different temperatures and durations. When metal acetyl acetonate was used as the metal oxide precursor, the synthesis process (including stirring, centrifugation and washing) was conducted at ≥ 40 °C to avoid precursor precipitation. The optimized metal oxide precursors, their concentrations, stirring temperature and calcination temperature/duration are summarized in Table 3.1. Synthesis parameters could be varied to adjust the nanosheet properties.

3.1.2.1.2 Synthesis of Metal Oxide/rGO Nanosheets

Metal oxide/rGO nanosheets were synthesized by three different approaches.

3.1.2.1.2.1 Mild Calcination

Precursor-bound GO was calcined in air at mild conditions (lower temperature/duration), to avoid complete removal of the reduced GO template. Metal oxide/rGO nanosheets synthesized using mild calcination are listed in Table 3.2.

3.1.2.1.2.2 Calcination in Argon

Precursor-bound GO was calcined in Ar instead of air, consequently, the entire content of rGO template was retained. Metal oxide/rGO nanosheets synthesized using Ar calcination are listed in Table 3.2.

3.1.2.1.2.3 Opposite-Charge Method

In the opposite-charge method, metal oxide/rGO nanosheets were synthesized via interaction between the negatively charged metal oxide nanosheets and the positively charged functionalized GO, followed by calcination in Ar (Figure 3.6).

Positively charged GO was prepared by non-covalent functionalization using poly(diallyldimethylammonium chloride) (PDDA), according to Qiu et al. [36] with some modifications. Briefly, 60 mg of GO was dispersed in 150 mL of deionized water by ultrasonication. This was followed by the dissolution of 3.9 g of NaCl in the GO dispersion. Subsequently, 7.8 mL of PDDA (20 wt% in H₂O, MW = 100,000–200,000) was added to the dispersion, followed by ultrasonication for 1.5 h and stirring overnight. The dispersion was centrifuged, washed three times with deionized water, freeze dried, and finally dried at 60 °C overnight. Positively charged GO-PDDA was dispersed in deionized water at a concentration of 0.5 mg/mL (dispersion A). Negatively charged metal oxide nanosheets were dispersed in a separate tube at a concentration of 0.4 mg/mL (dispersion B). Dispersions A and B were mixed rapidly, ultrasonicated briefly and vortexed. The aggregated nanocomposite was collected by centrifugation, dried at 60 °C overnight, and calcined at 400 °C in Ar for 1 h. Metal oxide/rGO nanosheets synthesized using opposite-charge method are listed in Table 3.2.

Figure 3.6. Scheme demonstrating synthesis of metal oxide/rGO nanosheets using the opposite-charge method.

Table 3.1. Optimized conditions for the synthesis of metal oxide nanosheets.

Metal oxide nanosheets	Metal oxide precursor	Precursor conc. ^a	Stirring temperature (°C)	Calcination temperature (°C) ^b	Calcination duration (h)
Nb ₂ O ₅	Nb(V) chloride	2.96	RT	500–600 ^c	1–3
Nb ₂ O ₅	Nb(V) ethoxide	2.96	RT ^d	500	1
TiO ₂	Ti(IV) butoxide	2.96	RT	500	1
TiNb ₂ O ₇	Ti(IV) butoxide	0.89	RT	700	1
	Nb(V) ethoxide	2.07			
Ti _{0.61} Nb _{1.29} O ₄	Ti(IV) butoxide	0.90	RT	500 ^e	1
	Nb(V) ethoxide	2.10			
ZrO ₂	Zr(IV) propoxide	2.96	RT	400	1
SnO ₂	Dibutyltin dilaurate	2.96	RT	400	1
Fe ₂ O ₃	Fe(III) acetylacetonate	2.96	45	400	1
Co ₃ O ₄	Co(II) acetylacetonate	2.96	45	350	1
NiO	Ni(II) acetylacetonate	2.96	45	350	1
Mn ₃ O ₄	Mn(II) acetylacetonate	2.96	45	350	1
Ni _{1.29} Co _{1.71} O ₄	Ni(II) acetylacetonate	2.37	45	350	1
	Co(II) acetylacetonate	0.59			
Mn _{1.08} Co _{1.92} O ₄	Mn(II) acetylacetonate	0.14	45	500	1
	Co(II) acetylacetonate	2.82			
Co _{0.9} Mn _{2.1} O ₄	Co(II) acetylacetonate	2.46	45	500	1
	Mn(II) acetylacetonate	0.50			

^ammol per 240 mL of absolute ethanol. ^bCalcined in air. ^cGO/NbCl₅ was pre-calcined at 550 °C/2 h/Ar.^dRoom temperature. ^ePre-calcined at 700 °C/2 h/Ar.

Table 3.2. Optimized conditions for the synthesis of metal oxide/rGO nanosheets.

Nanosheet	Metal oxide/rGO synthesis approach	Calcination conditions	rGO content (wt%) ^a
Nb ₂ O ₅ /rGO ^b	Mild calcination	500 °C/1 h/Air	44.7
Nb ₂ O ₅ /rGO ^b	Mild calcination	550 °C/3 h/Air	29.0
Nb ₂ O ₅ /rGO ^b	Mild calcination	600 °C/1 h/Air	17.0
Iron oxide/rGO	Mild calcination	300 °C/1 h/Air	38.3
SnO ₂ /rGO	Mild calcination	375 °C/1 h/Air	40.3
NiO/rGO	Mild calcination	325 °C/1 h/Air	42.9
Co ₃ O ₄ /rGO	Mild calcination	325 °C/0.7 h/Air	21.9
Ni _{1.29} Co _{1.71} O ₄ /rGO	Mild calcination	325 °C/0.8 h/Air	31.3
Mn _{1.08} Co _{1.92} O ₄ /rGO	Mild calcination	325 °C/0.3 h/Air	38.4
Nb ₂ O ₅ /rGO	Ar calcination	700 °C/2 h/Ar	40.5
TiO ₂ /rGO	Ar calcination	700 °C/2 h/Ar	41.4
Ti _{0.61} Nb _{1.29} O ₄ /rGO	Ar calcination	700 °C/2 h/Ar	36.1
Nb ₂ O ₅ /rGO	Opposite charge	400 °C/1 h/Ar	22.9
TiO ₂ /rGO	Opposite charge	400 °C/1 h/Ar	23.6
TiNb ₂ O ₇ /rGO	Opposite charge	400 °C/1 h/Ar	23.8
Ti _{0.61} Nb _{1.29} O ₄ /rGO	Opposite charge	400 °C/1 h/Ar	27.0

^aCalculated using thermogravimetric analysis. ^bNbCl₅ was used as precursor, GO/NbCl₅ was pre-calcined at 550 °C/2 h/Ar.

3.2 Materials Characterization

The properties of the synthesized materials were studied using various techniques, as described in the next sections. Special emphasis was given to morphology and phase analyses to confirm successful synthesis of the nanomaterials with the desired shape, composition and crystal structure. Elemental and chemical analyses were conducted to obtain a better understanding of the material composition. Surface area and porosity were studied due to their importance in electrode-electrolyte interaction. The carbonaceous content was analyzed to optimize the nanocomposite synthesis process. The following sections discuss the characterization techniques employed in detail.

3.2.1 Transmission Electron Microscopy (TEM)

TEM is an invaluable microscopy technique that allows high-magnification and high-resolution imaging. The working principle of TEM is similar to light microscopy, except that the light beam is replaced by an electron beam, and electromagnetic lenses are used instead of glass lenses. Utilization of an accelerated electron beam results in a dramatically enhanced resolution that can reach 0.1 nm. This is due to the very small wavelength of electrons that is 10,000 folds less than that of visible light. Moreover, the electron beam wavelength can be further minimized by increasing the acceleration voltage. An acceleration voltage of 200 kV, allowing a resolution of 0.24 nm, is considered practical for most applications.

TEM can be operated at different imaging modes. Bright-field imaging is done by allowing the transmitted electron beam to pass through the objective aperture. The image contrast is created by electron deflection and diffraction. The first depends on sample thickness and density, while the latter is observed in crystalline materials. Dark-field imaging is done by allowing a single diffraction beam to pass through the objective aperture. Multiple dark-field images can be obtained for a single bright-field image because different diffraction spots can be selected. Another interesting feature of TEM is phase contrast, which is known as high-resolution TEM (HRTEM). In HRTEM, the recombination of phase-different transmitted and diffracted beams results in an interference pattern that shows the periodicity of crystalline materials [37].

Scanning transmission electron microscopy (STEM) is an operation mode in which the images are formed by scanning a demagnified electron probe across the sample in a raster. A high-angle annular dark field detector is used to collect the scattered electrons, whose intensity is dependent on the atomic number (Z), thus known as Z-contrast imaging. STEM also allows elemental microanalysis in nm-size range, such as using energy dispersive X-ray spectroscopy and electron energy-loss spectrometry [38, 39].

Selected area electron diffraction (SAED) is a useful TEM technique for studying a material's crystal structure. Crystalline materials diffract the electron beam, leading to the formation of a diffraction pattern on the objective lens's back-focal plane. Diffraction spots in the pattern correspond to lattice planes. The diffraction pattern can be indexed to determine the structure and orientation of the crystal. Diffraction patterns of polycrystalline samples appear as concentric rings that correspond to lattice planes. This is due to the presence of many single crystals with random orientations.

Energy dispersive X-ray spectroscopy (EDX) is a TEM microanalytical technique that is used for composition analysis. Chemical elements can be identified by analyzing the X-rays emitted from the sample upon its interaction with the incident electron beam. EDX can be used to analyze the chemical composition of a selected sample area and also to provide elemental distribution by line scanning and mapping [37].

TEM analysis was conducted using FEI Tecnai F20 TEM fitted with OXFORD X-Max^N EDX microanalyzer. The microscope was operated at an accelerating voltage of 200 kV. Samples were prepared by dispersion of the solid materials in small amounts of ethanol, followed by deposition on carbon-coated Cu grids, and drying.

3.2.2 X-Ray Diffractometry (XRD)

Diffraction techniques are the main methods used for crystal structure analysis. They are especially useful to determine the exact phase of polymorphic compounds. X-rays, electrons and neutrons can be used for diffraction studies. However, X-ray diffraction is the most commonly used diffraction technique.

X-rays are beams of electromagnetic radiation with short wavelength and high energy. They are generated under vacuum in an X-ray tube, where electrons are accelerated in a high-voltage field towards a metal target. The collision between electrons and metal results in the emission of continuous X-rays, with high-intensity superimposed characteristic X-rays. The emitted radiation is filtered, so that only characteristic X-rays are allowed to be emitted. The wavelengths of the emitted radiation depend on the metal target used, with values in the order of 0.1 nm.

X-ray diffraction is based on the wave interference phenomenon, and is governed by Bragg's law. X-rays generated in the X-ray tube are guided towards the material to be analyzed. The incident in-phase X-rays are deflected by the crystal planes. Constructive interference only occurs when Bragg's law is satisfied as follows.

$$n\lambda = 2d\sin\theta \quad \text{Eq. 3.1}$$

where n is an integer, λ is the wavelength of incident radiation, d is the interplanar spacing and θ is the incident angle. Bragg's law allows calculation of the interplanar spacings of the crystalline sample, and thus determining its crystal structure.

XRD is a spectroscopic technique commonly used for powder X-ray diffraction analysis. In an X-ray diffractometer, a monochromatic X-ray beam hits the sample at variable incident angle (θ). A diffraction pattern is recorded, whereby the diffraction intensity is plotted against 2θ . The material's crystal structure can be identified by matching the diffraction pattern to that of known crystalline materials. Other material properties can also be inferred from the diffraction pattern, such as preferred crystal orientation, crystallite size and residual stress.

XRD is especially useful for crystallite size determination. Peak broadening occurs as crystallite size decreases. This is due to the incomplete destructive interference, which is observed with incident radiation that varies slightly from the Bragg angle. As the crystallite size decreases, the chance of this radiation being cancelled out is reduced, resulting in an increase in peak width [37].

XRD was conducted using PANalytical X'pert PRO and Bruker D8 ADVANCE diffractometers using Cu-K α radiation. Experiments were conducted using a step size of 0.02°, with a dwell time of 1.5 s/step. The 2 θ range was varied according to the material analyzed. The material's crystal structure was identified by matching its diffraction pattern to the powder diffraction files published by the International Centre for Diffraction Data (ICDD). Crystallite size was calculated using Scherrer's equation as follows [40, 41],

$$L = k\lambda / \beta \cos\theta \quad \text{Eq. 3.2}$$

where L is the crystallite size, k is a constant (0.9), λ is the X-ray wavelength, β is the peak full width at half maximum and θ is the Bragg angle at peak maximum.

3.2.3 Nitrogen Adsorption-Desorption Isotherm

Characterization of surface area and porosity is especially important for nanomaterials. As the particle size decreases, more specific surface areas are exposed. In addition, many nanomaterials have a porous nature, which increases the surface area as well. The high surface area and porosity affect the electrochemical performance of the nanomaterials. Therefore, determining specific surface area, porosity and pore size distribution help to explain the material's electrochemical performance.

Various approaches are used for surface area and pore size determination. Surface area can be calculated based on particle size by various methods, such as electrical sensing zone method, sedimentation techniques and optical methods. However, these approaches are limited by the assumption of regular particle geometry, which may underestimate surface area. Pore size can be characterized using small angle X-ray scattering and electron microscopy; however, the applicable pore size range is rather limited. Gas adsorption is the preferred method for surface area and pore size analyses because of its ability to determine the surface area of different geometries and to cover a wide range of pore sizes, and due to its low cost.

Gas adsorption/desorption isotherm is used for surface area determination. Nitrogen is the current standard adsorptive gas. The quantity of N_2 adsorbed on the analyzed material is determined within a pressure range less than the saturation pressure. N_2 adsorption increases with increasing pressure, resulting in multi-layer gas adsorption. Brunauer, Emmett and Teller (BET) method is able to calculate the number of gas molecules required to form a single adsorbed layer. Knowing the effective cross-sectional area of N_2 molecule, surface area can be easily calculated.

Pore size and pore volume can also be determined using N_2 adsorption-desorption isotherm. Kelvin equation correlates pore size with condensation pressure, where condensation pressure increases with increasing pore size. The Barrett-Joyner-Halenda (BJH) method is based on a modified Kelvin equation, and is used for pore size analysis. The pore volume can be calculated from the amount of adsorbed N_2 , by converting it to liquid volume [42].

N_2 adsorption-desorption isotherm was determined using Micromeritics ASAP 2020 at $-196\text{ }^{\circ}\text{C}$. The specific surface area was calculated using the BET method, and pore size analysis was conducted using the BJH method. Samples were degassed at $120\text{ }^{\circ}\text{C}$ overnight before measurement.

3.2.4 Thermogravimetric Analysis (TGA)

TGA is useful for studying material stability, optimizing calcination conditions and determining carbon content. TGA is a thermal analysis technique that probes the mass change of a material with increasing temperature. The atmosphere in which analysis is done can be controlled; an inert atmosphere (e.g. N_2 gas) or an oxidizing atmosphere (e.g. air) can be used. TGA can be used to study the material's thermal stability and determine its decomposition temperature. It can be used to mimic calcination experiments, whereby the precursor decomposition and product formation can be monitored. It can also be used to analyze the carbon content within a thermally stable material, whereby carbon oxidation in air results in mass loss [37].

In this work, TGA was mainly used to determine rGO content within the nanocomposites. It was also used to optimize the calcination conditions for material synthesis. TGA was conducted using the PerkinElmer Pyris 1 thermogravimetric analyzer. Heating rates of 2 °C/min and 5 °C/min under air or N₂ flow were used.

3.2.5 X-Ray Photoelectron Spectroscopy (XPS)

Electron spectroscopy analyzes materials using their characteristic electron emissions. The material is irradiated with photons or electrons, resulting in the emission of electrons from its surface by photoelectric or Auger processes. The emitted electrons are characteristic for specific energy levels, allowing identification of the material's elements and their chemical states. Electron spectroscopy is limited to the surface of the material (≤ 10 nm) due to the low energy of the emitted electrons. However, depth profiling can be done by surface etching.

XPS uses the photoelectric effect to identify chemical elements. An incident X-ray radiation has enough energy to knock out electrons from different shells. These electrons acquire enough energy to escape from the surface of the material, where their kinetic energies can be detected by an electron energy analyzer. The binding energy of a photoelectron is related to its kinetic energy as follows,

$$E_B = h\nu - E_K - \phi \quad \text{Eq. 3.3}$$

where E_B is the photoelectron binding energy, h is Planck's constant, ν is the incident photon frequency, E_K is the photoelectron kinetic energy and ϕ is a parameter indicating the energy required by the photoelectron to leave the surface of the material. The binding energies of the photoelectrons are characteristic to the electronic shells and subshells of the chemical elements from which they are ejected.

XPS spectra allow determination of the chemical state and concentration of chemical elements. Chemical shift of peak binding energy may reveal the oxidation state of the element. Chemical state can also be determined by analyzing peak shape and appearance of extra peaks. Multiplet splitting of core-level peaks takes place if valence electrons are

unpaired. Shake-up satellite peaks are additional peaks that result from the interaction of the photoelectrons with valence electrons, resulting in energy loss. Both phenomena may be specific for certain compounds of the same element, which helps to differentiate between them. Quantitative analysis can be also done, where the concentration of an element is related to its electron signal intensity [37].

In this work, XPS was used to analyze the chemical states of the material's surface. It was conducted with VG ESCALAB 220i-XL using Al K α X-rays. Survey spectra collected at a wide binding energy range were used to detect elements, whose core levels were analyzed using narrow-scan spectra. Calibration was done by referring to C 1s peak at 285 eV.

3.2.6 Fourier-Transform Infrared (FTIR) and Raman Spectroscopies

IR and Raman analyses are two types of vibrational spectroscopies. Both techniques analyze the interaction of radiation with the molecular vibrations, however, with distinct differences. IR spectroscopy measures the resonant photon-mediated transition between the vibrational energy levels. Raman spectroscopy is an off-resonance process, whereby inelastic light scattering takes place as a result of photon-mediated transition to a virtual state. The inelastic photon scattering results in a transition to a vibrational state that is different from original state of the molecule. The energy of the scattered photon may be lower than (Stokes) or higher than (anti-Stokes) that of the incident radiation. IR and Raman spectra allow functional group identification, as well as provide molecular fingerprints.

IR spectroscopy technology has been improved over years. FT has been introduced to speed up analysis, whereby the sample can be irradiated with various frequencies simultaneously. In addition, new technologies have facilitated measurement, such as attenuated total reflectance (ATR). ATR uses an IR-transmitting high refractive index crystal, in which the incident radiation undergoes total internal reflection. This results in evanescent waves that probe the sample, which is in direct contact with the crystal. ATR is a fast and non-destructive technique, with almost no sample preparation requirements.

In addition to its ability to analyze organic and inorganic materials, Raman spectroscopy is very useful for probing carbonaceous materials. Raman spectra of carbon materials have characteristic G and D bands, which are used to identify the presence of carbon and also to examine its state [43, 44].

ATR FTIR was used to confirm GO functionalization with PDDA. It was performed using the PerkinElmer Spectrum 100 with no sample preparation. Raman spectroscopy was used to analyze the nanomaterials and the rGO within the nanocomposites. It was conducted with RENISHAW in Via Raman microscope using 785-nm laser, and the Witec Alpha 300S Raman system using 532-nm laser. Samples were prepared by dispersing the solid materials in ethanol, and then depositing them on clean silicon substrates.

3.2.7 Zeta Potential

Zeta potential measurement is used to determine the net electric charge surrounding dispersed nanoparticles. When charged nanoparticles are dispersed in a medium, they are surrounded by an electric double layer due to electrostatic effects. Zeta potential is the potential difference between the electric double layer and the surrounding dispersant layer.

Zeta potential is measured by probing the mobility of charged particles under an electric field. When an electric field is applied, the charged particles move to the opposite electrode by electrophoresis. An incident laser probes the electrophoretic particles, where the frequency shift of the scattered light is used to determine their velocity. The speed of the particles is used to calculate the zeta potential [45].

In this work, zeta potential was measured to probe the surface charge of GO before and after functionalization with PDDA. It was also used to determine the surface charge of metal oxide nanosheets. Experiments were conducted using Zetasizer Nano-SZ (Malvern Instruments). Samples were prepared by dispersion in deionized water. GO and GO-

PDDA were dispersed at a concentration of 0.5 mg/mL, while metal oxide nanosheets were dispersed at a concentration of 0.4 mg/mL.

3.2.8 Atomic Force Microscopy (AFM)

Scanning probe microscopy (SPM) is used to study material topography and surface features using a solid probe (tip) that scans the surface, while being in very close proximity. SPM examines the surface using near-field interactions, thus, it avoids the resolution limit associated with techniques that use far-field interactions, such as light and electron microscopy. SPM can provide a true topographical image with a resolution higher than 0.1 nm.

AFM is a type of SPM that studies material surface using near-field forces. A variety of near-field forces are used to characterize surface topography, including short-range, van der Waals, electrostatic and capillary forces. The tip is connected to a cantilever whose bending is precisely detected by a laser system. The force exerted on the tip results in cantilever bending and laser beam deflection, which are detected by position-sensitive photodiodes.

AFM operates in two main working modes, static and dynamic. In the static mode, the tip is in contact with the material surface. The cantilever bends to a certain degree, which is kept constant by a feedback loop during scanning. However, this mode has lower image resolution and damages the sample surface. In the dynamic mode, the tip oscillates at a certain frequency. The amplitude of oscillation is maintained at a certain value by a feedback loop during scanning. The tip may be in or out of contact with the sample. Intermittent contact (tapping) mode is a widely used dynamic mode, in which the oscillating tip approaches the sample till light contact, then pulls off to avoid damaging the surface. Tapping mode provides high-resolution imaging and allows for analysis of material's chemical and physical properties [37].

In this work, AFM was used to measure the thickness of metal oxide nanosheets. Samples were dispersed in ethanol, and deposited on clean glass cover slips. AFM analysis was conducted using Bruker Dimension ICON AFM in the tapping mode.

3.3 Electrochemical Measurements

The synthesized materials were assessed for their energy storage performance. In the following section, the processes and techniques used for electrode preparation and electrochemical testing are discussed.

3.3.1 Electrode Preparation and Cell Assembly

3.3.1.1 Li-Ion Batteries (LIBs)

LIB electrode consists of active and inactive materials. The active material is responsible for energy storage, while the inactive materials are required to prepare an electrochemically active and stable electrode. Inactive materials include carbon additives (e.g. acetylene black), which are used to increase the electrode conductivity. They form a conductive network within which the active material is embedded, thus ensuring maximum contact with the current collector. A binder such as polyvinylidene difluoride (PVDF) is used to glue the electrode materials together, thus maintaining mechanical stability.

The active and inactive materials need to be intimately mixed. The active material has to be uniformly dispersed and in good contact with the carbon additives. The binder also needs to be well dispersed throughout the slurry. This can be done by using various techniques such as hydrodynamic shear mixing, ball milling and ultrasonic homogenization.

The slurry requires further processing to prepare the electrode. After adequate mixing of the slurry, it is deposited on a current collector. The current collector is a metal foil; Cu foil is used for anodes, and Al foil is employed for cathodes. It acts as a highly conductive substrate that conducts electrons to and from the electrode materials. The

material-deposited current collector is dried well, and then punched into discs to be used in cell assembly [46].

LIBs are usually assembled as coin cells with a two-electrode configuration. The active material electrode is tested against Li metal, which serves as the counter and reference electrodes. The two electrodes are separated by a membrane that prevents direct electrode contact, but allows Li-ion transport [47]. An organic electrolyte containing Li salt is used as a medium for conducting Li ions. The coin cells are assembled in a glove box with extremely low levels of O₂ and H₂O to prevent their interaction with Li metal, and to avoid H₂O incorporation within the cells, which can be detrimental to their performance [48].

In this work, electrode preparation involved grinding, mixing, ultrasonication and shaking. Mortar and pestle were used to grind the active material, and mix it with acetylene black (Denka) and vapor-grown carbon fibers (VGCFs). After adequate mixing, the active material and carbon additives were dispersed in N-methyl-2-pyrrolidone (NMP) using ultrasonication. This was followed by the addition of PVDF to form a slurry, and shaking for at least two hours. The active material, acetylene black, VGCFs and PVDF were used at a weight ratio of 8:0.5:0.5:1 in the case of nickel sulfide nanopyramids, and 7:1:1:1 in the case of metal oxide nanosheets.

The slurry was further processed to prepare coin cell electrodes. The slurry was coated on Cu or Al foil at a thickness of 80–90 μm using a doctor blade, and then dried at 80–90 °C overnight. The dried electrode was pressed at 4–5 bar and 30 °C in order to improve contact with the current collector, and then punched into 12.7-mm circular discs. The electrodes' masses were measured using a semi-micro balance (Sartorius CP225D, d = 0.01 mg). They were kept in the oven at 80–90 °C till assembly.

Coin cells were assembled in a controlled-environment. Assembly was carried out in Ar-filled glove box with O₂ and H₂O levels of < 1 ppm. CR2032 coin cells were employed for assembly, using 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 by

volume) as electrolyte, and a 25 μm -thick membrane (Celgard) as separator. The assembled cells were crimped using a hydraulic crimping machine (MSK 110, MTI), and left overnight to allow adequate soaking in the electrolyte. Disassembly of coin cells for *ex situ* electrode analysis was done using a hydraulic disassembling machine (MSK 110D, MTI), followed by electrode washing using acetonitrile to remove residual electrolyte.

3.3.1.2 Supercapacitors (SCs)

SC electrode preparation is similar to that of LIBs. The active material is mixed with inactive materials including carbon additives and binder to prepare an electrochemically active and stable electrode. The slurry is prepared similar as for LIB electrodes, and then deposited on a current collector such as Ni foam.

SCs are commonly tested in a three-electrode configuration. The electrode containing the active material is the working electrode, and the potential is determined against a reference electrode. No current passes to the reference electrode to maintain a stable potential throughout the electrochemical process. Current passes only between the working electrode and an auxiliary (counter) electrode [49].

In this work, the SC electrode was prepared using Ni foam as the current collector. Prior to electrode preparation, 1 cm $\times$ 1 cm pieces of Ni foam were soaked in 6 M HCl for 15 min to remove any oxides. After soaking in HCl, they were washed with deionized water and ethanol, dried at 80 $^{\circ}\text{C}$ and then weighed. The slurry was prepared as described in Section 3.3.1.1, deposited on the Ni foam pieces, and then dried at 90 $^{\circ}\text{C}$ overnight. After drying, the electrodes were pressed at 4–5 bar and 30 $^{\circ}\text{C}$, and weighed. The electrode material mass was calculated by subtracting the Ni foam mass.

SC electrodes were tested in a three-electrode system. The material-deposited Ni foam was used as working electrode, Ag/AgCl was employed as reference electrode and Pt wire was used as counter electrode. The electrodes were immersed in 2 M KOH aqueous

electrolyte in the case of nickel sulfide nanopyramids or 1 M Na₂SO₄ aqueous electrolyte in the case of manganese oxide nanosheets.

3.3.2 Cyclic Voltammetry (CV)

CV is an electrochemical technique widely used for studying redox behavior. CV studies the effect of potential change, at a fixed rate, on the current intensity. The potential is varied in both cathodic and anodic directions, such that both reduction and oxidation processes can be studied, respectively. A CV plot shows the potential on X axis and current intensity on Y axis.

CV is one of the main techniques used to study LIB and SC reactions. CV can be conducted over a wide range of potentials so as to determine the potentials at which reactions take place during cell discharge and charge. This helps to elucidate the mechanism of electrode reactions, and to show any side reactions that may occur. The area under the peak corresponds to the amount of charge stored, which can determine the major reactions responsible for charge storage [50, 51].

CV can be used to analyze the mechanism of charge storage. The mechanism of charge storage is either capacitive or diffusion limited. CV analysis of a certain material at various scan rates can determine its charge storage mechanism according to the following equation,

$$I = av^b \quad \text{Eq. 3.4}$$

where I is the current intensity in A, v is the potential scan rate in V/s, while a and b are adjustable parameters. The value of b indicates the charge storage mechanism; $b = 1$ in the case of capacitive storage, and $b = 0.5$ in the case of diffusion-limited storage. [52].

In this work, CV analysis was used to study the redox behavior of active materials, and to analyze their charge storage mechanisms. Experiments were conducted using the AUTOLAB potentiostat/galvanostat. Scan rates for studying LIB electrode reactions were 0.05, 0.1 and 0.5 mV/s, while higher scan rates were used to analyze charge storage

mechanism. For SC electrodes, CV analysis was conducted using various scan rates for potential ranges of 0–0.5 V vs. Ag/AgCl in the case of nickel sulfide, and 0–1 V vs. Ag/AgCl in the case of manganese oxide.

3.3.3 Galvanostatic Charge/Discharge (GCD)

GCD is the main testing technique for LIBs and SCs. A constant current is applied during cell discharge and charge. The variation of potential with time allows determination of charge stored over the potential range studied. GCD curves are also used to study the redox reactions, where the shape of the curve reveals the reaction mechanism. Differential capacity curves, which are plots of dQ/dV against potential, are also used to analyze the redox reactions [51].

GCD is also used to study Coulombic efficiency and cycling stability. Coulombic efficiency is a measure of the charge extracted from the electrode, relative to that inserted. It indicates any charge loss due to side reactions or entrapment within the material. Cycling stability is an assessment of the prolonged use of the electrode material, where the capacity is monitored over a large number of cycles.

LIB GCD measurements were conducted using the LAND-8-MA and LAND-8-SH battery testing systems, while SC GCD experiments were performed using the AUTOLAB potentiostat/galvanostat. All potentials were reported in reference to Li^+/Li in the case of LIB, and Ag/AgCl in the case of SC. Charge storage capacity was calculated according to the following equations,

$$\text{LIBs: } Q_{\text{sp}} = I\Delta t / m \quad \text{Eq. 3.5}$$

$$\text{SCs: } C = I\Delta t / m\Delta V \quad \text{Eq. 3.6}$$

where Q_{sp} is the specific capacity in mAh/g, I is current intensity in mA, Δt is the discharge/charge time in h and m is the mass of active material in g for Eq. 3.5; C is the specific capacitance in F/g, I is current intensity in A, Δt is the discharge time in s, m is the mass of active material in g and ΔV is the potential window in V for Eq. 3.6.

3.3.4 Electrochemical Impedance Spectroscopy (EIS)

EIS is an electrochemical technique that is used to study electrode kinetics. It involves applying an AC potential at different frequencies, and detecting the current response. The output signal helps to reveal various processes, such as charge transfer, double-layer capacitance and diffusion. Impedance is a complex quantity, which comprises real (Z') and imaginary (Z'') parts. The real part is the resistance, while the imaginary part is the reactance (capacitance and inductance) [51, 53].

Nyquist plot helps to analyze the electrochemical behavior of the electrode. Nyquist plot shows the imaginary part of the impedance at each frequency against the real part. In the high frequency region, the system's bulk resistance can be determined from the curve intersection with the real part. The semi-circle in the middle-frequency region represents the charge transfer resistance and double-layer capacitance. The slope of the curve in the low frequency region indicates Warburg impedance, which corresponds to the electrolyte and ionic diffusion. The data can be fitted using an equivalent circuit model to determine the values of the parameters discussed [51, 54].

In this work, EIS was conducted on LIB coin cells using the AUTOLAB potentiostat/galvanostat, coupled with frequency response analyzer. Experiments were done within a frequency range of 100 kHz–10 mHz, at an AC signal amplitude of 10 mV. Data fitting was done using NOVA 2.0 software.

3.4 Conclusion

To sum up, the methodology used in this work is for nanomaterial synthesis, characterization and electrochemical analysis. The synthesis methodology was designed so as to produce carbon-incorporated nanomaterials with controlled morphology and phase. Colloidal thermal decomposition was employed to synthesize nickel sulfide and graphene-wrapped nickel sulfide nanopyramids, where small uniform nanopyramids could be produced, and also anchored to the surface of graphene sheets. A GO template-assisted approach was developed for facile and generalized synthesis of metal oxide and metal oxide/rGO nanosheets, where the properties of the nanosheets and their rGO

content could be controlled by the synthesis conditions. The synthesized nanomaterials' morphology, phase, chemical composition, surface area, porosity and rGO content were analyzed by different characterization techniques. After the nanomaterials' synthesis and characterization, their electrochemical properties and energy storage performance as LIB anodes and SC electrodes were examined.

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Chapter 4

Graphene-Wrapped Nickel Sulfide Nanopyramids with Improved Performance for Li-Ion Battery Anodes and Supercapacitors

This chapter presents the synthesis of nickel sulfide nanopyramids and graphene-wrapped nickel sulfide nanopyramids using a facile one-pot colloidal method. Morphological and structural characterization of the materials are provided. This is followed by an electrochemical analysis and energy storage performance studies, both as Li-ion battery anode and supercapacitor electrode. The results demonstrated the promising energy storage performance of the nickel sulfide nanopyramids, and the ability of graphene wrapping to enhance their capacity and stability as Li-ion battery anode, and improve their rate performance as supercapacitor electrode. The graphene-wrapped nickel sulfide nanopyramids achieved ~1265 mAh/g after 100 cycles at 70 mA/g as Li-ion battery anode, and 670 F/g after 1000 cycles at 20 A/g as supercapacitor, which are excellent results as compared to similar compositions in the literature.

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4.1 Introduction

Metal sulfides are promising conversion reaction-based lithium-ion battery (LIB) anode candidates [1-4], which store Li ions according to Eq. 2.12. However, they suffer from some drawbacks, such as poor kinetics (which is manifested in electrode polarization [5]), dissolution of polysulfides (which reduces electrolyte conductivity), and electrode pulverization during cycling (which causes capacity loss [3]).

In order to overcome these challenges, metal sulfide nanostructures with controlled size and morphology were studied. Carbon incorporation was also employed to improve their electrochemical properties. FeS [2] and Co₉S₈ [3] nanoparticles with various structures were investigated as LIB anodes. It was found that the material structure and the presence of carbon had significant effect on metal sulfide's electrochemical performance. Higher performance was achieved by nanomaterials that have open structure with high surface area, ultra-small dimensions and carbon coating. These properties allowed for good contact with the electrolyte, accommodated volume change during cycling, and provided for short Li-ion and electron diffusion paths and polysulfide entrapment.

Nickel sulfide is a promising anode material for Li-ion batteries [4, 6, 7]. It also suffers from rapid capacity fading due to cycling-induced pulverization and formation of polysulfides [8]. Nanocomposites of nickel sulfide with carbonaceous materials have been used to tackle this problem, with promising results achieved. Son et al. [4] observed a rapid decay of the specific capacity of nickel sulfide upon cycling. The introduction of carbon could stabilize nickel sulfide's electrochemical properties, thus eliminating capacity fading. A specific capacity of ~470 mAh/g was achieved after 500 cycles at a current density of 1 A/g. Mahmood et al. [6] have improved the electrochemical properties of nickel sulfide by synthesizing Ni₃S₄/N-doped graphene nanocomposite in a two-step hydrothermal process. A remarkable specific capacity of ~1300 mAh/g was achieved after 100 cycles, as compared to ~500 mAh/g for bare nickel sulfide nanoparticles.

Metal sulfides are also very promising pseudocapacitive materials [9-11]. Different phases and shapes of nickel sulfide have been reported to have good pseudocapacitive properties. NiS hollow spheres [12], NiS₂ nanocubes [13] and Ni₃S₂ nanoflakes [14] have shown specific capacitances of 927, ~350 and 664 F/g at current densities of 4.08, 5 and 4 A/g, respectively. However, electrode pulverization occurred over prolonged cycling, which led to capacity loss. One of the promising approaches for tackling this problem is to use composites of nickel sulfide nanoparticles with carbonaceous materials in order to stabilize the nickel sulfide performance during cycling. Wang et al. [15] reported higher capacitance and cycling stability for NiS/GO nanocomposite than for NiS and GO alone. Yang et al. [16] showed that the synthesis of NiS nanorods anchored to carbon nanotubes or reduced graphene oxide (rGO) resulted in improved electrode cycling stability.

Facile one-pot synthesis is needed to synthesize nickel sulfide/carbon nanocomposite with controlled size and shape, for high-performance energy storage. Most of the reported methods for nickel sulfide nanocomposite synthesis adopt the hydrothermal/solvothermal approach [6, 7, 15-20], which is not able to produce ultra-small uniform nanocrystals. The synthesized nanoparticles are relatively large and non-uniform. Moreover, some of these methods include an additional step to synthesize the precursor [6], or for sulfurization [16, 18]. Other reported methods for the synthesis of nickel sulfide/carbon nanocomposites for energy storage include spray pyrolysis [4] and electrospinning [21]. However, these methods require special equipment that complicates the synthesis process.

Colloidal synthesis is suitable to synthesize nickel sulfide/carbon nanocomposites with desirable properties for energy storage. Colloidal synthesis using thermal decomposition of organometallic precursors in organic medium is able to produce small, uniform and well-dispersed nanocrystals [22, 23]. In addition, the synthesized nanocrystals can be coated with carbon by annealing in an inert atmosphere [2, 3]. Moreover, the good dispersion of the nanocrystals in the organic medium would enable their uniform deposition on a carbon support. The small monodisperse size, carbon coating and uniform

dispersion on carbon support are important for high-performance energy storage electrodes.

Herein, a facile one-pot method was reported for the synthesis of nickel sulfide nanopyramids and graphene-wrapped nickel sulfide nanopyramids using colloidal thermal decomposition approach. The synthesized nanomaterials were used as Li-ion battery anodes and supercapacitor (SC) electrodes. The uniform nickel sulfide nanopyramids allowed for good interaction with the electrolyte, short ion and electron paths, and enhanced kinetics [2]. Graphene wrapping provided a support for the dispersion of nickel sulfide nanopyramids, thus enhancing surface area and contact with the electrolyte. It also helped to buffer the volume change of nickel sulfide during cycling, mitigating contact loss with the current collector [24, 25]. Moreover, it improved conductivity and prevented dissolution of polysulfides [26].

4.2 Results and discussion

4.2.1 Materials Characterization

4.2.1.1 Nickel Sulfide (NS) and Nickel Sulfide/Graphene Nanopyramids (NS/G)

Figure 4.1a shows a transmission electron microscopy (TEM) image of nickel sulfide nanoparticles. The nanoparticles have a nanopyramidal shape, with the bases and apices clearly observed in Figure 4.1b. The average size of the nanopyramids is ~25 nm (Figure 4.1a: inset). High-resolution TEM (HRTEM) showed that the nanopyramids are single crystals (Figure 4.1c). A d-spacing of 0.33 nm was measured, which could be indexed to the (220) plane of Ni_3S_4 (JCPDS card # 00-047-1739). The single crystalline nature of the nanopyramids was confirmed by fast Fourier-transform (FFT) pattern (Figure 4.1c: inset), which showed a typical pattern for single crystals [27]. Zone axis was determined to be [100]. Selected area electron diffraction (SAED) of the nanopyramids showed a polycrystalline pattern (Figure 4.1d). The d-spacings detected were 0.32, 0.28, 0.23, 0.21, 0.18 and 0.16 nm, which matched the (220), (311), (400), (422), (511) and (440) planes of Ni_3S_4 (JCPDS card #00-047-1739), respectively.

Figure 4.1. (a, b) TEM images (inset in (a): particle size distribution), (c) HRTEM image (inset: corresponding FFT pattern), and (d) SAED pattern of as-prepared nickel sulfide nanopyramids.

Figure 4.2 shows the X-ray diffractometry (XRD) pattern of nickel sulfide nanopyramids. The XRD peaks could be assigned to the cubic polydymite phase (Ni_3S_4) of space group Fd-3m (JCPDS card #00-047-1739). The peaks at $2\theta = 16.2^\circ, 26.7^\circ, 31.4^\circ, 38.01^\circ, 47.0^\circ, 50.1^\circ, 54.8^\circ, 64.4^\circ$ and 68.5° could be indexed to (111), (220), (311), (400), (422), (511), (440), (533) and (444) reflections, respectively. No other peaks were observed, illustrating the phase purity of the material.

Figure 4.2. XRD pattern of as-prepared nickel sulfide nanopyramids.

Nickel sulfide with triangular shape was previously reported using other methods, either mixed with other shapes [28] or alone [29]. Although the latter method could produce pure nickel sulfide tetrahedral nanostructures, it required pre-synthesis of an organic precursor, which added another step to the synthesis process. In both studies, the triangular shape was thought to be related to differential adsorption of 1-dodecanethiol on the nanocrystal facets. In a study published after my experiments were conducted [30], it was found that Ni_3S_4 nanopyramids were formed only when nickel(II) acetylacetonate and 1-dodecanethiol were used as precursors, in the presence of oleylamine and oleic acid as surfactants. The nanoparticle morphology was very sensitive to any deviation in the experimental conditions. These findings agreed with my results.

Figure 4.3a and b show scanning transmission electron microscopy (STEM) images of NS/G-10. When nickel sulfide nanopyramids grew on the surface of GO sheets, they retained their size and nanopyramidal morphology. Their XRD peaks (Figure 4.3c) were indexed to Ni_3S_4 (JCPDS card #00-047-1739), indicating that the incorporation of GO in the synthesis of nickel sulfide did not affect the morphology or phase of the nanoparticles. This was an advantage since it provided for the facile one-pot synthesis of NS/G nanocomposite. Two extra peaks were noted at $2\theta = 11.3^\circ$ and 22.5° , which corresponded to non-reduced and reduced GO, respectively [31].

Figure 4.3. (a) STEM image, (b) magnified STEM image of the boxed area in (a), and (c) XRD pattern of as-prepared NS/G-10 nanocomposite. • and ■ in (c) indicate GO and rGO XRD peaks, respectively.

4.2.1.2 Calcined Nickel Sulfide and Graphene-Wrapped Nickel Sulfide Nanopyramids

Calcination was performed to remove and/or carbonize the organic compounds in the samples to enhance conductivity, and to further reduce GO. The calcination temperature was chosen according to the thermogravimetric analysis (TGA) results of the synthesis

mixture (oleylamine:oleic acid:dodecanethiol, volume ratio = 5:1:1) (Figure 4.4a), which demonstrated that calcination at 350 °C for 1 h in an inert atmosphere was sufficient to remove the organic compounds. This was confirmed by TGA (in air) of as-prepared and calcined (350 °C/1 h/Ar) nickel sulfide nanopyramids (Figure 4.4b); the weight loss shown by as-prepared nickel sulfide at ~ 220–350 °C, which could be attributed to the loss of organic residues, disappeared after calcination, indicating the removal of most of the organic species during calcination. These conditions were used to calcine the as-prepared nickel sulfide and NS/G samples.

Figure 4.4. TGA of (a) synthesis mixture (oleylamine:oleic acid:dodecanethiol, volume ratio = 5:1:1) in nitrogen (heated from 40 °C to 350 °C at a rate of 2 °C/min, followed by soaking at 350 °C for 60 min, and heating to 800 °C at a rate of 2 °C/min), and (b) as-prepared and calcined (350 °C/1 h/Ar) nickel sulfide nanopyramids in air at a ramp of 5 °C/min.

After calcination at 350 °C/1 h/Ar, the nickel sulfide nanopyramids were aggregated, but the nanopyramidal shape remained intact (Figure 4.5a). The particles were surrounded by ~4 nm-thick carbon layers due to decomposition of the capping agents (Figure 4.5b), however, its content was probably very low due to the absence of significant weight loss in the TGA pattern of calcined nickel sulfide nanopyramids until their decomposition at ~ 670 °C (Figure 4.4b). The nickel sulfide phase changed to Ni_7S_6 after calcination, as indicated by the XRD pattern in Figure 4.5d. This agreed with the lattice d-spacing of 0.58 nm, shown in Figure 4.5c, which corresponded to the Ni_7S_6 XRD peak at $2\theta = 15.5^\circ$.

Minor Ni_3S_2 XRD peaks were observed as well (Figure 4.5d). This transformation to phases with lower sulfur content could be attributed to the loss of some sulfur during calcination [32, 33].

Figure 4.5. (a) TEM image, (b, c) HRTEM images, and (d) XRD pattern of the nickel sulfide nanopyramids after calcination at 350 °C/1 h/Ar. Red arrow in (b) points to the carbon layer, and * in (d) indicates peaks of a minor Ni_3S_2 phase (JCPDS card # 00-030-0863).

In the case of calcined NS/G-10, nickel sulfide nanopyramids were found to be well-dispersed on the surface of the graphene sheets, with no significant change in morphology (Figure 4.6a and b). The nanopyramids were wrapped by graphene sheets upon calcination, which could help to improve their electrochemical properties. XRD pattern of calcined NS/G-10 showed that phase change to Ni_7S_6 had occurred (Figure

4.6c). Minor Ni_3S_2 peaks were observed as well. The diffraction peak of non-reduced GO at $2\theta = 11.3^\circ$ disappeared, showing further reduction of graphene oxide. The (002) peak of rGO shifted from $2\theta = 22.5^\circ$ in NS/G-10 to $2\theta = 24.7^\circ$ in calcined NS/G-10. This corresponded to a decrease of interlayer spacing from 0.395 to 0.360 nm, which could be due to further removal of the remaining oxygenated groups [31].

Raman spectrum of the calcined NS/G-10 nanocomposite (Figure 4.6d) showed a G band at $\sim 1595\text{ cm}^{-1}$, assigned to the vibration of sp^2 carbon atoms in two-dimensional lattice, and a D band at $\sim 1317\text{ cm}^{-1}$, assigned to the defects in graphene layers [34]. The intensity of D band to G band (I_D/I_G) is a measure of disorder and defects, and also graphitization of the sample [34]. It was found that the I_D/I_G ratio increased from 1.41 in GO to 1.73 in calcined NS/G-10, which could be due to the reduction of GO that generated defects. Although new sp^2 domains were restored upon GO reduction, they became smaller in size, causing an increase in the I_D/I_G ratio [35]. The relatively more intense D band could also be attributed to the growth of nickel sulfide nanopyramids on the surface of graphene sheets [33, 34].

rGO (GO calcined at 350°C for 1 h in Ar atmosphere) was analyzed by TGA in air. It was found that the weight loss started at $\sim 420^\circ\text{C}$, and over 90% of the weight was lost by $\sim 650^\circ\text{C}$. Calcined NS showed a weight loss starting at $\sim 670^\circ\text{C}$ (Figure 4.7a). Calcined NS/G-10 exhibited 3 distinct weight loss regions (Figure 4.7b). The first of which ended at $\sim 420^\circ\text{C}$ and was mainly due to loss of moisture and some sulfur [33]. The second region encompassed $\sim 420^\circ\text{C}$ to $\sim 650^\circ\text{C}$, and the third region was from $\sim 650^\circ\text{C}$ to $\sim 750^\circ\text{C}$. Based on the TGA profiles of the rGO and calcined NS, the second and third weight loss regions for calcined NS/G-10 could be associated with graphene and NS, respectively. Thus, the percentage of graphene in calcined NS/G-10 was calculated to be $\sim 17\%$ (from the second weight loss).

Figure 4.6. (a) TEM image, (b) magnified TEM image of the boxed area in (a), and (c) XRD pattern of calcined NS/G-10. * and ■ in (c) indicate Ni_3S_2 (JCPDS card # 00-030-0863) and rGO peaks, respectively. (d) Raman spectra of GO and calcined NS/G-10.

Figure 4.7. TGA profiles of (a) rGO and calcined NS, and (b) calcined NS/G-10. Nitrogen adsorption-desorption isotherms of (c) calcined NS and (d) calcined NS/G-10 (insets: pore size distributions).

Calcined NS and NS/G-10 showed Type IV nitrogen adsorption-desorption isotherms (Figure 4.7c and d), which are characteristic of mesoporous nanocomposites [36]. Brunauer, Emmett and Teller (BET) specific surface area of calcined NS/G-10 ($\sim 66.6 \text{ m}^2/\text{g}$) was almost 3 times that of calcined NS ($\sim 22.5 \text{ m}^2/\text{g}$). Pore size distribution was determined by BJH method. Both calcined NS and NS/G-10 were mesoporous in nature, with most of the pores being $\sim 3\text{--}6 \text{ nm}$ in size. However, smaller pores ($< 3 \text{ nm}$) were also observed in calcined NS/G-10. The total pore volume of calcined NS/G-10 ($\sim 0.15 \text{ cm}^3/\text{g}$) was ~ 3 times that of calcined NS ($\sim 0.05 \text{ cm}^3/\text{g}$). The higher BET surface area and porosity of calcined NS/G-10 would facilitate electrolyte access to electrochemically active sites, and buffer volume change of nickel sulfide during cycling. Such

characteristics could enhance the nanocomposite's energy storage capacity, rate performance and stability during cycling [24].

X-ray photoelectron spectroscopy (XPS) spectra (0–1300 eV) of calcined NS and NS/G-10 showed peaks at ~162, 285, 532 and 856 eV, which corresponded to S 2p, C 1s, O 1s and Ni 2p, respectively (Figure 4.8a and d). The C 1s peak dramatically increased from ~25% in calcined NS to ~74% in calcined NS/G-10, due to graphene wrapping. Ni 2p_{3/2} spectrum of calcined NS was fitted to a spin-orbit doublet and a satellite peak at 853.6, 856.2 and 861.6 eV, respectively (Figure 4.8b). Ni 2p_{3/2} spectrum of calcined NS/G-10 was deconvoluted to 2 peaks and a satellite peak at 853.5, 855.8 and 861.7 eV, respectively (Figure 4.8e). The doublet and satellite peaks could be assigned to Ni²⁺, Ni³⁺ and Ni²⁺, respectively [37-39]. The presence of mixed valences for nickel ions could enhance the conductivity of nickel sulfide by allowing hopping of electrons between cations with low activation energy [40]. S 2p spectrum of calcined NS was deconvoluted into a spin-orbit doublet at 162.1 and 163.0 eV, and a satellite peak at 168.4 eV (Figure 4.8c). A spin-orbit doublet and a satellite peak were observed at 161.9, 163.2 and 168.5 eV in the S 2p spectrum of calcined NS/G-10 (Figure 4.8f). S 2p spin-orbit doublet corresponded to S 2p_{3/2} and S 2p_{1/2}, respectively, which were attributed to metal-sulfur bonds and S²⁻ [38].

The C 1s spectra of GO and calcined NS/G-10 were compared. C 1s spectrum of GO could be deconvoluted to 3 peaks at 285.0, 286.9 and 289.3 eV (Figure 4.9a), which could be assigned to C-C or C=C, C-O or C=O and -COOH, respectively [41]. C 1s spectrum of calcined NS/G-10 was deconvoluted into 3 peaks at 285.0, 286.0 and 289.1 eV (Figure 4.9b). The first peak corresponded to C-C or C=C bonds, while the latter two peaks were attributed to oxygenated species. The intensities of the peaks corresponding to the oxygenated species were decreased in calcined NS/G-10, confirming the reduction of GO.

Figure 4.8. XPS spectra of (a–c) calcined NS and (d–f) calcined NS/G-10: (a, d) survey, (b, e) Ni 2p_{3/2} and (c, f) S 2p spectra.

Figure 4.9. XPS C 1s spectra of (a) GO and (b) calcined NS/G-10.

4.2.2 Electrochemical Measurements

4.2.2.1 Testing as Li-ion Battery Anode

Cyclic voltammetry (CV) was performed to study the electrochemical behavior of calcined NS and NS/G-10. The first cathodic scan of calcined NS (Figure 4.10a) showed a small peak at ~1.6 V and a strong reduction peak at ~1.2 V, which were attributed to the lithium incorporation in Ni_7S_6 (Eq. 4.1) [33], and the conversion reaction of Ni_7S_6 to Ni and Li_2S (Eq. 4.2), respectively.

Another reduction peak appeared at ~0.65 V, which could be attributed to the formation of solid electrolyte interphase (SEI) due to electrolyte decomposition [2]. In the second cycle, the cathodic peak shifted to ~0.86 V, and was significantly diminished in the third cycle. On the anodic side, the broad peak at ~1.5 V might be due to SEI oxidation [42], while the weak broad peak at ~2.5 V was assigned to the Ni oxidation to nickel sulfide (Eq. 4.2). It is important to note the very low intensity of the Ni oxidation peak, and its disappearance in the subsequent CV cycles of calcined NS.

In contrast, calcined NS/G-10 showed reproducible CV curves with defined reduction and oxidation peaks (Figure 4.10b). On the cathodic side, a small broad pre-lithiation peak (Eq. 4.1) appeared at ~1.5 V, which shifted to ~1.6 V in subsequent cycles. The main reduction peak of Ni_7S_6 to Ni and Li_2S (Eq. 4.2) appeared at ~1.1 V, with no significant shift in subsequent cycles. The peak below 0.7 V could be assigned to the formation of SEI, which was confirmed by its disappearance in the subsequent cycles. On the anodic side, SEI was oxidized at ~1.4 V. Ni oxidation reaction to Ni_7S_6 (Eq. 4.2) could be observed at ~2.1 V. In subsequent cycles, the SEI oxidation peak disappeared, and only lithium extraction peak was observed at ~2.2 V.

Figure 4.10. (a, b) CV curves and (c, d) GCD profiles of calcined (a, c) NS and (b, d) NS/G-10.

In the case of calcined NS, the high voltage of Ni oxidation peak compared to calcined NS/G-10 (~2.5 V vs. ~2.1 V) and the significant cathodic peak shift after the first cycle showed electrode polarization. The significant decrease in the anodic peak intensity and fading of the cathodic peak after the first cycle indicated loss of contact of the active materials due to severe pulverization during reduction and oxidation. On the other hand, the reversible redox peaks of calcined NS/G-10 showed that graphene wrapping helped to maintain the redox reactions of NS nanopyramids, leading to high capacity and cycling stability. This could be attributed to the ability of the graphene wrapping to maintain the active materials in good contact with the current collector.

Galvanostatic charge/discharge (GCD) profiles for calcined NS and NS/G-10 were determined at a current density of 70 mA/g, and a voltage range of 0.01–3 V (Figure

4.10c and d). The first specific discharge capacity of calcined NS was ~ 1340 mAh/g, while the first specific charge capacity was ~ 839 mAh/g, with a Coulombic efficiency of $\sim 63\%$. The very high first discharge capacity and irreversible capacity loss could be due to the decomposition of the electrolyte forming SEI, and the irreversible reactions between NS and Li^+ [2, 42]. A small voltage plateau appeared at ~ 1.7 V corresponding to NS pre-lithiation (Eq. 4.1), the main plateau was at ~ 1.3 V corresponding to NS reduction (Eq. 4.2), and a third plateau at ~ 0.7 V was attributed to SEI formation. The first charge showed smaller plateaus at ~ 1.2 V and ~ 2 V, corresponding to SEI and Ni oxidation, respectively. These discharge and charge plateaus were significantly diminished in the second cycle, which showed a Coulombic efficiency of $\sim 65\%$, and almost disappeared in the 10th cycle. The disappearance of the discharge and charge voltage plateaus over the first 10 cycles illustrated the poor redox capability and very low capacity retention of calcined NS. The low Coulombic efficiencies in the 2nd and 3rd cycles ($\sim 65\%$ and $\sim 88\%$) indicated that a major part of the lithiated active materials could not be de-lithiated. This suggested that reduction caused NS pulverization and contact loss. Coulombic efficiency increased in subsequent cycles reaching $\sim 99\%$ in the 9th cycle; however, the discharge capacity had already dropped to ~ 365 mAh/g.

Calcined NS/G-10's initial discharge and charge capacities were ~ 1433 mAh/g and ~ 916 mAh/g, respectively, with a Coulombic efficiency of 63.9%. The main voltage plateaus of the first discharge were at ~ 1.6 V, ~ 1.3 V and ~ 0.7 V, corresponding to pre-lithiation, reduction and SEI formation, respectively. The first charge plateau corresponding to Ni oxidation was at ~ 1.9 V. Discharge capacities in the 2nd and 10th cycles were ~ 923 mAh/g and ~ 852 mAh/g, respectively, and the charge capacities were ~ 859 mAh/g and ~ 834 mAh/g, respectively, with Coulombic efficiencies of $\sim 93\%$ and $\sim 98\%$, respectively. The irreversible capacity loss in the first cycle could be attributed to SEI formation. The high Coulombic efficiencies after the first cycle demonstrated the positive effect of graphene on the maintenance of NS redox reactions. The stability of the voltage profiles in the first 10 cycles further confirmed that the nanocomposite underwent stable lithium insertion and extraction, and that graphene wrapping of NS nanopyramids stabilized the redox

processes by providing a conductive support that could maintain the engagement of the active materials in the redox reactions.

Cyclic performance of calcined NS/G-10 was assessed at 70 mA/g between 0.01 V and 3 V (Figure 4.11a). NS/G-10 suffered an irreversible capacity loss in the first cycle due to SEI formation, and capacity fading continued for 6 cycles. However, this trend was reversed, and the capacity increased until the 100th cycle, reaching ~1265 mAh/g. A high Coulombic efficiency of $\geq 96\%$ was maintained during cycling. On the other hand, the capacity of calcined NS decreased dramatically during the first 20 cycles, reaching ~227 mAh/g after 100 cycles (Figure 4.11a).

Cycling stability results showed the crucial role played by graphene wrapping for stabilizing nickel sulfide redox processes. In the absence of graphene wrapping, calcined NS was subjected to severe pulverization leading to contact loss with the current collector, which isolated the active material and caused capacity decline. In the case of NS/G-10, graphene wrapping helped to maintain contact between the active material and current collector, as demonstrated in Figure 4.11c. Although nickel sulfide nanopyramids suffered from pulverization after prolonged cycling, the disintegrated nanoparticles remained attached to the graphene surface, which maintained contact with the current collector and prevented capacity decay. Graphene also increased electronic and ionic transport, prevented nanoparticle agglomeration, improved surface area and porosity, and mitigated polysulfide dissolution, thus further enhancing electrode performance.

Capacity increase over cycling was observed for calcined NS/G-10. This phenomenon was previously investigated. It was concluded that the main mechanism responsible for capacity increase was the catalytically enhanced electrolyte decomposition at low potential, leading to the formation of a gel-like polymer, which would dissolve during charging [43-45]. It was also postulated that the capacity increase might be caused by the slow reaction of irreversible Li_2O formed during the first discharge [46]. The Li_2O gradually decomposed over cycling, leading to capacity increase, a process referred to as an activation period. Another possible explanation for capacity increase was the

disintegration of the NS nanoparticles over cycling, which increased the surface area of the exposed active material, resulting in enhanced capacity. This could be inferred from the TEM images of calcined NS/G-10 after 3 and 30 cycles (Figure 4.11b and c). After 3 cycles, some nanopyramids were still observed on the surface of graphene sheets, while after 30 cycles, only irregular and very small particles could be seen.

Figure 4.11. (a) Cycling performance of calcined NS and NS/G-10. TEM images of calcined NS/G-10 after (b) 3 cycles and (c) 30 cycles.

The contribution of rGO in the capacity of calcined NS/G-10 was investigated (Figure 4.12a). Cycling performance of rGO prepared by calcination of GO at 350 °C for 1 h in

Ar showed an initial capacity of ~1311 mAh/g at a current density of 70 mA/g. The capacity of rGO significantly decreased to ~921 mAh/g in the second cycle, due to SEI formation during the first discharge. After the second cycle, capacity declined gradually until it stabilized after 40 cycles at ~474 mAh/g. This means that the contribution of rGO in the capacity of calcined NS/G-10 after 40 cycles is only ~81 mAh/g. Moreover, the capacity decline during the first 40 cycles is in stark contrast to the capacity increase shown by calcined NS/G-10. The low capacity contribution of rGO, and the different performance trends between rGO and calcined NS/G-10 clearly showed that the enhanced performance of calcined NS/G-10 was not due to the energy storage capacity of rGO. Instead, it was due to the ability of graphene to stabilize the electrochemical performance of nickel sulfide nanopyramids.

GO content was varied during the synthesis of NS/G, in order to determine the effect of graphene loading on the nanocomposite's electrochemical performance. Calcined NS/G-5 and NS/G-20 were analyzed using TGA to determine their graphene contents. The loading of graphene in calcined NS/G-5 and NS/G-20 was ~8.5 wt% and ~30 wt%, respectively (Figure 4.12b). Cycling stability of calcined NS/G-5 was very poor as compared to NS/G-10; NS/G-5's capacity decreased to ~382 mAh/g after 50 cycles (Figure 4.12c). Although it exceeded calcined NS in specific capacity by ~144 mAh/g, the rapid decrease in capacity showed that the amount of graphene in the nanocomposite was not sufficient to stabilize nickel sulfide and maintain its redox processes. NS/G-20's specific capacity reached ~851 mAh/g after 50 cycles (Figure 4.12c), which was superior to the performance of calcined NS and NS/G-5. However, it was still lower than that of NS/G-10, which reached ~1066 mAh/g after 50 cycles (Figure 4.11a). Although the loading of graphene in NS/G-20 was almost double that in NS/G-10, its specific capacity was lower. These results indicated that the optimum amount of graphene for stabilizing the electrochemical performance in the nanocomposite was ~10–20%. Nanocomposites containing higher loadings of graphene still have good performance, but they have lower specific capacities due to the lower loadings of nickel sulfide.

Figure 4.12. (a) Cycling performance of rGO. (b) TGA profiles and (c) cycling performance of calcined NS/G-5 and NS/G-20.

Calcined NS and NS/G-10 were cycled at higher current densities in order to assess their rate performance (Figure 4.13a). Calcined NS/G-10 showed specific capacities of ~852, 669, 553, 287 and 133 mAh/g at the 10th cycle at current densities of 0.07, 0.5, 1, 3 and 5 A/g, respectively. It also displayed excellent ability to recover when it was cycled again at 0.07 A/g, whereby it achieved a specific capacity of ~1036 mAh/g at the 10th cycle. In contrast, calcined NS showed specific capacities of ~292, 78, 55, 26 and 17 mAh/g at 0.07, 0.5, 1, 3 and 5 A/g, respectively, at the 10th cycle. After returning to 0.07 A/g current density, ~272 mAh/g was achieved at the 10th cycle. The superior rate performance of NS/G-10 was attributed to the ability of graphene to maintain good dispersion of the NS nanopyramids, which shortened electron and Li⁺ diffusion paths, and enhanced the electrode kinetics. In addition, the larger specific surface area and pore volume of the nanocomposite allowed for greater electrolyte access to the

electrochemically active sites, which further improved electrode kinetics. Moreover, graphene wrapping formed a conductive network that boosted the electrode conductivity and prevented contact loss of the active material.

Nyquist plots (Figure 4.13b) showed that the diameter of the semicircle in the medium-frequency region was reduced upon incorporation of graphene (Figure 4.13b inset), indicating a lower contact and charge transfer impedance compared to calcined NS [33, 47]. This was attributed to the conductive network formed by graphene, which wrapped around the NS nanopyramids. Fitting the impedance spectra revealed that R_e and $R_{(sf+ct)}$ decreased from 2.8 Ω and 209 Ω to 2.1 Ω and 150 Ω , respectively, upon graphene wrapping. The higher slope of the inclined line in the low frequency region of calcined NS/G-10's plot showed lower Warburg impedance. This indicated that the Li^+ diffusion was facilitated in the nanocomposite [33, 48]. It could be due to less aggregation of NS nanopyramids, and the higher specific surface area and pore volume of the nanocomposite.

Figure 4.13. (a) Rate performance and (b) EIS of calcined NS and NS/G-10. Insets in (b): (bottom) magnified high-middle frequency region of the Nyquist plots and (top) the equivalent circuit model used for fitting. R_e is the ohmic resistance due to electrolyte and cell components, $R_{(sf+ct)}$ is the surface film and charge transfer resistance, CPE is constant phase element and Z_w is Warburg impedance.

The performance of NS/G-10 is superior to that reported in previous studies investigating nickel sulfide as LIB anode. The results were compared to reports investigating the same nickel sulfide phase (Ni_7S_6), and also to those studying NiS phase, which has a comparable theoretical specific capacity to Ni_7S_6 phase. The theoretical specific capacities of Ni_7S_6 and NiS phases are ~ 534 and ~ 591 mAh/g, respectively. Ni_7S_6 /carbon nanocomposite (carbon content = 17 wt%) achieved 571 and 479 mAh/g at 0.5 and 1 A/g, respectively [4]. NiS/N-doped graphene (graphene content = 13.3 wt%) has a capacity of ~ 425 mAh/g after 50 cycles at 50 mA/g, and retained ~ 245 mAh/g when cycled at 1 A/g [7]. NiS anchored on rGO (rGO content = 25 wt%) achieved 521 mAh/g after 100 cycles at 100 mA/g, and retained 447 mAh/g at 1 A/g [18]. NiS nanosheets containing 31.8 wt% graphene showed a capacity of 481 mAh/g after 100 cycles at 50 mA/g, and retained 386 mAh/g at 0.8 A/g [49]. NiS@carbon nanofiber network with 63.6 wt% carbon achieved ~ 250 mAh/g at 1 A/g [21]. This comparison demonstrated the optimized performance of the graphene-wrapped nickel sulfide nanopyramids, which achieved ~ 1265 mAh/g after 100 cycles at 70 mA/g, and retained ~ 669 and ~ 553 mAh/g at 0.5 and 1 A/g, respectively. The high performance could be attributed to the small uniform size of the nanopyramids that enhanced access to the electrolyte and improved Li^+ and electron transport. The entrapment of the nanopyramids within rGO sheets formed a conductive network that facilitated electron transport to and from the active material. The good contact of nickel sulfide to the surface of rGO also prevented contact loss during cycling, thus maintaining the engagement of the active material.

4.2.2.2 Testing as Supercapacitor Electrode

CV curves of calcined NS and NS/G-10 showed redox peaks characteristic of pseudocapacitors (Figure 4.14a, b). This was different from the rectangular CV curves that were shown by electric double layer supercapacitors [16]. The symmetrical redox peaks indicated good reversibility of the redox reactions [13]. At high scan rates, the anodic and cathodic peaks shifted to higher and lower voltages, respectively, due to electrode polarization at high current densities [12]. It was observed that the linear relationship between the cathodic peak current (I_p) and the scan rate (ν) could be best

fitted as I_p vs. $v^{1/2}$ (Figure 4.14c, d). This showed that the redox reaction of nickel sulfide was diffusion limited [14].

Based on previous reports [12, 14], the redox peaks observed in the CV curves could be assigned to the following reaction,

According to the previous equation, the theoretical specific capacitance was calculated to be ~2130 F/g using the following equation [38],

$$C_s = Q / \Delta V = nF / m\Delta V \quad \text{Eq. 4.4}$$

where C_s is the theoretical specific capacitance, Q is the amount of charge stored per gram of active material, ΔV is the potential window, n is the number of charge transferred during the redox reactions, F is Faraday constant and m is the molar mass of the active material.

GCD was conducted at current densities of 3–20 A/g in a potential window of 0–0.45 V vs. Ag/AgCl (Figure 4.15a, b). The potential plateaus during charge and discharge corresponded to the CV oxidation and reduction peaks, respectively. The symmetrical charge and discharge curves indicated good pseudocapacitive properties and reversible redox reactions [14]. Calcined NS achieved specific capacitances of ~1495, 1171, 878 and 449 F/g at 3, 5, 10 and 20 A/g, respectively (Figure 4.15c). Calcined NS/G-10 achieved specific capacitances of ~1337, 1156, 956 and 778 F/g at 3, 5, 10 and 20 A/g, respectively (Figure 4.15c). It was observed that calcined NS/G-10 showed better performance at high current densities (10 and 20 A/g). At 20 A/g, calcined NS retained only 30% of the specific capacitance achieved at 3 A/g, while calcined NS/G-10 could retain ~58%. This showed that the nanocomposite improved the redox behavior of nickel sulfide at high current densities.

Figure 4.14. CV curves of calcined (a) NS and (b) NS/G-10. Plots of I_p vs. (c) $v^{1/2}$ and (d) v .

Cyclic performance was evaluated by continuous charge and discharge for 2000 cycles at 5 A/g in the potential range of 0–0.45 V vs. Ag/AgCl (Figure 4.16a). The specific capacitance of calcined NS increased over the first 500 cycles until ~1210 F/g. It was relatively stable at 1000–1100 F/g over the next 1500 cycles. The specific capacitance after 2000 cycles was ~1010 F/g, which was ~83% of the maximum specific capacitance. Similarly, the specific capacitance of calcined NS/G-10 increased over the first 300 cycles to ~1170 F/g. It slightly decreased to ~1110 F/g after 1000 cycles, and then gradually declined to ~830 F/g after 2000 cycles. It could retain ~71% of its maximum specific capacitance after 2000 cycles.

Figure 4.15. Chronopotentiometry curves of calcined (a) NS and (b) NS/G-10 at various current densities. (c) Plot of specific capacitances of calcined NS and NS/G-10 vs. current density.

The presence of graphene did not improve the cycling performance of nickel sulfide. The NS/G-10 nanocomposite actually showed a lower specific capacitance after 2000 cycles. However, the cycling performance at 20 A/g was different. Calcined NS and NS/G-10 achieved maximum specific capacitances of ~400 and 890 F/g, respectively, after 100 cycles (Figure 4.16b). The specific capacitances then decreased gradually to ~220 and 670 F/g, respectively, after 1000 cycles. The 3-fold higher specific capacitance of calcined NS/G-10 compared to calcined NS after 1000 cycles showed that graphene had a critical role in improving the pseudocapacitive performance of nickel sulfide at high current densities.

Figure 4.16. Cycling performance of calcined NS and NS/G-10 at a current density of (a) 5 A/g and (b) 20 A/g.

The specific capacitance of calcined NS at a current density of 5 A/g was compared to previous reports of nickel sulfide at the same or lower current densities. Calcined NS had higher specific capacitance than Ni_3S_2 [14], NiS [12, 15, 50, 51], NiS_2 [13] and mixed-phase nickel sulfides [10, 19, 52]. The excellent performance of the nickel sulfide nanopyramids could be attributed to their small size, which shortened the ionic and electronic diffusion paths [53], exposed more electroactive sites, and improved contact with the electrolyte [54]. Carbon coating upon calcination might have contributed to the high pseudocapacitive performance by improving electronic transport [55] and stabilizing the nanoparticles. The single-crystalline nanopyramidal structure could have facilitated diffusion of electrons and improved the electrochemical activity, as previously reported for NiS_2 nanocubes [13].

Graphene wrapping of the nickel sulfide nanopyramids did not improve their pseudocapacitive properties at low current densities. However, graphene's presence was important at high current densities. This could be explained by the enhanced electronic transport due to the high conductivity of graphene, which improved the electrode kinetics [19]. This was augmented by the direct anchoring of the nanopyramids to the surface of the rGO sheets in one-pot synthesis, which further facilitated electronic transport [34]. In addition, the higher surface area and porosity of the nanocomposite facilitated electrolyte transport and ionic diffusion, which improved the rate capability of the electrode [16, 19].

4.3 Conclusion

Nickel sulfide nanopyramids were prepared by a facile colloidal synthesis method. They have high initial specific capacity when used as Li-ion battery anode, but suffered from rapid capacity fading. As supercapacitor electrode, they demonstrated remarkable specific capacitances of ~1495 and 1171 F/g at current densities of 3 and 5 A/g, respectively. Graphene wrapping was used to improve the electrochemical properties of nickel sulfide nanopyramids. It dramatically improved the performance of the Li-ion battery anode, achieving a specific capacity of ~1265 mAh/g after 100 cycles. Graphene also helped to improve the pseudocapacitive rate performance, enabling the nanocomposite to achieve a 3-fold higher specific capacitance at 20 A/g after 1000 cycles.

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Chapter 5

Generalized Synthesis of Binary Oxide Nanosheets for High-Performance Li-Ion Battery Anodes and Supercapacitors

This chapter presents a novel strategy for the synthesis of binary oxide nanosheets using graphene oxide template. It demonstrates the synthesis of a wide variety of binary and doped binary oxide nanosheets, while emphasizing the ability of the synthesis strategy to control the nanosheets' attributes, such as crystallinity, crystallite size, surface area and rGO content. Electrochemical properties and energy storage capabilities of the synthesized nanosheets as Li-ion battery anodes and supercapacitor electrodes are discussed in detail. The broad applicability of the synthesis method allowed for producing metal oxide nanosheets for various types of Li-ion battery anodes, including insertion-based, alloying-based and conversion-based oxides, as well as for supercapacitors, with very good energy storage performance demonstrated. The synthesis strategy also showed interesting versatility, which allowed optimizing the nanosheets' attributes to improve their performance.

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5.1 Introduction

Metal oxide nanosheets, with thickness of less than 5 nm and lateral dimensions of 100 nm up to micrometer range [1], have shown promise for applications in areas such as energy storage [2-5], catalysis [6, 7] and sensors [8, 9]. In particular, the unique structure of the nanosheet is expected to improve energy storage performance. The enhanced structural integrity that results from the micrometric lateral dimensions can buffer volume change during cycling [10-13], thus enhancing stability. The ultrathin nanosheet thickness promotes ion and electron transport across the material, yielding higher rate capability [5, 10, 12, 13]. In addition, the high surface area of the nanosheets allows for good contact between the active material and the electrolyte [5, 10, 13-15], facilitating access to the electrochemically active sites. The special surface electronic structure of the nanosheets [10, 11, 14] may also give rise to unique properties such as pseudocapacitive behavior [11].

High-performance energy storage has been previously demonstrated by metal oxide nanosheets [13, 16-22]. Nb_2O_5 nanosheets synthesized using a two-step hydrothermal method displayed higher performance, as compared to Nb_2O_5 nanoparticles. The nanosheets have an initial capacity of 184 mAh/g at 0.2 A/g, as compared to 135 mAh/g shown by Nb_2O_5 nanoparticles. The nanosheets could still retain ~90 mAh/g at 1 A/g [17]. The high performance of the nanosheets was ascribed to the unique two-dimensional (2D) morphology that facilitated charge transport and enhanced contact with the electrolyte. The beneficial effects of the 2D morphology were also demonstrated by the highly stable performance shown by TiO_2 nanosheets, which have higher capacity than TiO_2 nanoparticles, achieving ~112 mAh/g at 20C [23]. The nanosheet morphology also enabled materials to possess enhanced pseudocapacitive activity; Mn_3O_4 nanosheets could achieve 398 F/g at a scan rate of 0.005 V/s [22], and MnO_2 nanosheets attained ~1183 and ~559 F/g at current densities of 5 and 25 A/g, respectively [21].

Carbon incorporation has a significant effect on metal oxide nanosheet energy storage performance [2, 15, 20, 24-27]. Fe_2O_3 /graphene sheet-on-sheet nanocomposite demonstrated the stabilizing role played by carbonaceous materials in electrode

performance. Bare Fe_2O_3 nanosheets have a capacity of ~ 466 mAh/g after 50 cycles at 0.1C, which increased to ~ 801 mAh/g upon introduction of graphene sheets. The enhanced performance was attributed to the intimate contact between Fe_2O_3 and graphene sheets, which prevented agglomeration, buffered volume change of iron oxide during cycling, and enhanced electrode conductivity [28]. Similarly, the performance of NiO nanosheets improved substantially when anchored to graphene sheets, achieving ~ 492 mAh/g at 3.6 A/g [2]. Fe_3O_4 nanosheets/carbon nanofibers nanocomposite was also reported to have enhanced pseudocapacitive activity. It achieved 135 F/g at 420 mA/g, as compared to 83 F/g for pure Fe_3O_4 . The enhanced pseudocapacitive activity was ascribed to the high conductivity of the carbon nanofibers that boosted electron transfer, and the good dispersion of Fe_3O_4 nanosheets on the surface of carbon nanofibers, which resulted in high surface area and increased exposure to the electrolyte [15].

Generalized synthesis strategies of metal oxide nanosheets are quite limited. Metal oxide nanosheets were conventionally synthesized using exfoliation methods [29]. However, the exfoliation technique is time-consuming, difficult to scale up, and limited to intrinsically layered oxides [1, 30]. Bottom-up approaches, such as thin film deposition were investigated; however, such complex methods would not be practical on the industrial scale [31]. Wet-chemical bottom-up approach has been considered the favored methodology for large-scale synthesis of metal oxide nanosheets [1].

The wet-chemical approach commonly employs hydro/solvothermal reactions [17, 19, 32, 33] and/or templates for metal oxide nanosheet synthesis. Although the hydro/solvothermal approach has been successful in the preparation of various metal oxide nanosheets, the experimental conditions varied and the results depended to a great extent on the synthesized metal oxide. Therefore, it is difficult to establish a generalized hydro/solvothermal reaction that is able to synthesize various metal oxide nanosheets. Template-assisted approach is more suitable for such generalized metal oxide nanosheet synthesis. This is because the material structure is directed by the 2D template utilized. G-Silica was used as a 2D template to synthesize TiO_2 [25], Nb_2O_5 [24] and Co_3O_4 nanosheets [34]. Inverse lamellar micelles were used as soft templates for the synthesis of

various metal oxide nanosheets [35]. Moreover, graphene oxide (GO), being a well-known 2D material, was used as a template for the synthesis of a wide variety of metal oxide nanosheets [36, 37].

Currently used template-assisted methods suffer from some limitations. Methods using inorganic templates such as SiO_2 and alumina need a post-synthesis step to remove the templates. They usually use corrosive solutions such as NaOH [11, 24, 25, 34], which renders the methods laborious. The soft-template- and GO-template-assisted methods described above employed a solvothermal reaction to synthesize the metal oxides, while using the template to direct their 2D growth [35-37]. Although the authors managed to work around the lack of generalization of the hydro/solvothermal reaction for metal oxide nanosheet production, they still need autoclaves for the synthesis. The utilization of autoclaves limits the process scalability on the industrial scale.

Based on the discussion above, there is a need to develop a generalized method for the synthesis of metal oxide nanosheets, which is facile and free from using autoclaves or harsh template-removal processes. In this chapter, a novel method for the generalized synthesis of binary oxide nanosheets using a template-assisted approach, without hydro/solvothermal reactions or special template-removal processes, is described. The synthesis process is versatile, allowing the tuning of nanosheets' attributes. For example, the synthesis conditions were manipulated to allow the synthesis of metal oxide/reduced GO (rGO) nanosheets. The nanosheets were assessed for their energy storage performance as lithium-ion battery (LIB) anodes and pseudocapacitive materials.

GO sheets were used as 2D templates to promote the binary oxide growth in nanosheet structure. GO was selected because of its 2D nature, and the presence of oxygenated functional groups on its surface, which allowed for binding to precursor molecules. The oxide precursor molecules were first mixed with GO for binding of the precursors to the GO functional groups, followed by collection and drying of the GO/precursor sheets. The GO/precursor sheets were then subjected to calcination in air to allow the oxide synthesis and growth in 2D nanostructure. Meanwhile, air calcination oxidized the carbonaceous

template, leading to its simultaneous removal. The synthesis process could be manipulated to control the nanosheets' properties. This was done by varying the calcination conditions, such as calcination atmosphere, temperature and duration, whereby the nanosheets' crystallinity, crystallite size, surface area, porosity and rGO content were controlled.

Optimizing the rGO content within the nanosheets is critical for energy storage applications. Three different approaches were adopted for metal oxide/rGO nanosheet synthesis. The main approach was mild air calcination, where the GO/precursor sheets were calcined at relatively low temperature and duration to control the rGO content retained after calcination. The second approach was calcination of GO/precursor sheets in Ar, which resulted in the reduction and retention of the entire GO template content. The third approach was a post-synthesis method, where rGO was incorporated within the metal oxide nanosheets after their synthesis using the opposite-charge method. The advantages and disadvantages of each approach will be discussed in detail.

5.2 Results and Discussion

5.2.1 Materials Characterization

5.2.1.1 Nb₂O₅ and Nb₂O₅/rGO Nanosheets

Nb₂O₅ nanosheets with controlled properties were synthesized using the GO planar-confined growth strategy. With NbCl₅ as the precursor, Nb₂O₅ nanosheets were synthesized by pre-calcination at 550 °C/2 h/Ar, followed by calcination in air at 500–600 °C. Figure 5.1a–c illustrates their transmission electron microscopy (TEM) images. The nanosheet structure was clearly observed, with the wrinkling and folding inherited from the GO template; folding occurred as a result of surface tension [35]. The lateral dimensions of the nanosheets extended well into the micrometer range, which would improve the material's structural stability [16]. The nanosheets were mesoporous, and composed of interconnected primary nanoparticles, as revealed by high-resolution TEM (HRTEM) images (Figure 5.1d–f). The nanosheet crystal structures were determined to be orthorhombic Nb₂O₅ (JCPDS # 00-030-0873) from X-ray diffractometry (XRD)

(Figure 5.2a) and selected area electron diffraction (SAED) patterns (Figure 5.1a–c: insets).

Figure 5.1. (a–c) TEM (insets: SAED patterns) and (d–f) the corresponding HRTEM images of Nb_2O_5 nanosheets synthesized using NbCl_5 as precursor, and calcined in air at the conditions specified (pre-calcined at 550 °C/2 h/Ar).

The nanosheet crystallinity, crystallite size, surface area, porosity and rGO content were modified by changing the calcination conditions (temperature/duration).

Crystallinity increased by increasing calcination temperature and duration. At a lower calcination temperature and a shorter calcination duration (500 °C/1 h), weakly crystalline nanosheets were obtained, as revealed by HRTEM (Figure 5.1d), SAED (Figure 5.1a: inset) and XRD (Figure 5.2a). As calcination temperature and duration increased, crystallinity increased, and the crystallites grew in size, as observed in the HRTEM images (Figure 5.1d–f). The crystallite size was calculated from the (001) XRD peak using Scherrer's equation (Eq. 3.2). It increased from 14.3 nm upon calcination at 500 °C/1 h to 22.3 nm at 550 °C/3 h and 600 °C/1 h. It was noticed that crystallite growth occurred along the [001] direction, as indicated by the HRTEM images (Figure 5.1d–f).

This was confirmed by the increase in (001)/(180) XRD peak intensity ratio from 0.74 to 0.77 and 0.93, as calcination temperature/duration increased from 500 °C/1 h to 550 °C/3 h and 600 °C/1 h, respectively (Figure 5.2a). This could enhance Nb₂O₅ nanosheet LIB performance since Li⁺ ions were expected to move freely along the natural tunnels between the (001) planes [38].

The GO template was not completely removed by calcination. Residual rGO loadings of 44.7 wt%, 29.0 wt% and 17.0 wt% were detected for samples calcined at 500 °C/1 h, 550 °C/3 h and 600 °C/1 h, respectively (Figure 5.2b). The residual rGO was also detected as a characteristic XRD peak at $2\theta = 26.6^\circ$, the intensity of which decreased as calcination temperature/duration increased.

Figure 5.2. (a) XRD patterns and (b) TGA profiles (conducted in air at a ramp of 2 °C/min) of Nb₂O₅ nanosheets synthesized using NbCl₅ as precursor, pre-calcined at 550 °C/2 h/Ar, and calcined in air at the conditions specified.

Surface area and porosity were also amenable to control using calcination conditions. The BET specific surface areas of Nb₂O₅ nanosheets were 74.7 and 64.5 m²/g when calcined at 500 °C/1 h and 550 °C/3 h, respectively (Figure 5.3c). This decrease in surface area could be attributed to grain growth. The nanosheet mesoporosity was shown by the Type IV adsorption-desorption isotherms (Figure 5.3a). As calcination conditions increased from 500 °C/1 h to 550 °C/3 h, the average pore size (Figure 5.3b) and pore volume (Figure 5.3d) increased from 4 to 23 nm, and from 0.13 to 0.37 cm³/g, respectively. The

increase in pore size and porosity could be explained by coarsening (Ostwald ripening), which is a process involving the growth of larger particles at the expense of smaller ones, accompanied by enhanced porosity [39].

Figure 5.3. (a) Nitrogen adsorption-desorption isotherms, (b) pore size distributions, (c) BET surface areas, and (d) pore volumes of Nb_2O_5 nanosheets synthesized using NbCl_5 as precursor, and calcined in air at the conditions specified (pre-calcined at 550 °C/2 h/Ar).

Nb_2O_5 nanosheets could be synthesized using other precursors to yield varied nanosheet properties. With niobium(V) ethoxide (Nb-eth) as precursor, Nb_2O_5 nanosheets were obtained by direct calcination in air at 350–600 °C/1 h. The nanosheet structure was clearly shown by TEM (Figure 5.4a–d). However, the nanosheets appeared thicker and more compact when calcined at 600 °C/1 h. The nanosheets' crystallinity could be controlled by calcination temperature. Nb_2O_5 nanosheets were amorphous when calcination temperatures of < 500 °C were used, and crystalline when calcined at ≥ 500 °C (Figure 5.4e). Nb_2O_5 nanosheet synthesis using Nb-eth as precursor resulted in almost

a 4-fold increase in yield, as compared to synthesis using NbCl_5 as precursor (Figure 5.4f). The higher yield was probably due to the better interaction between the alkoxide precursor and GO. The thickness of Nb_2O_5 nanosheets synthesized at 500 °C/1 h was determined to be ~2 nm by atomic force microscopy (AFM) (Figure 5.4g), demonstrating the effectiveness of this strategy in deriving ultrathin metal oxide nanosheets.

Surface area and porosity of Nb_2O_5 nanosheets could also be controlled by calcination conditions. BET surface area decreased from 112.7 m^2/g to 26.2 m^2/g as calcination temperature increased from 350 °C/1 h to 600 °C/1 h, respectively (Figure 5.5a, c). This might have occurred due to crystal growth, where the nanosheets were amorphous at 350 °C, and crystalline at ≥ 500 °C, with crystallite sizes of 28.9 and 35.4 nm at 500 °C and 600 °C, respectively. Pore volume increased from 0.22 to 0.27 cm^3/g as calcination temperature increased from 350 °C to 500 °C (Figure 5.5d), due to coarsening, which also resulted in larger average pore size (Figure 5.5b). However, at 600 °C, pore volume dramatically decreased to 0.04 cm^3/g . This was probably due to the dominance of macropores, which agreed with the TEM images that showed large pores and more compact and thicker sheets (Figure 5.4d).

Nb_2O_5 nanosheets synthesized using Nb-eth as precursor were almost free of rGO (Figure 5.6a). Only the nanosheets synthesized at 350 °C/1 h retained ~3 wt% of rGO, while those calcined at higher temperatures were completely free of rGO. The absence of rGO, in contrast to Nb_2O_5 nanosheets synthesized using NbCl_5 as precursor, might be due to the higher yield of Nb_2O_5 nanosheets synthesized using Nb-eth as precursor. The lower content of GO in GO/Nb-eth might have resulted in faster template removal. In addition, Nb_2O_5 has catalytic activity [40], thus, the larger amount of Nb_2O_5 might have exerted a catalytic effect, promoting GO removal at a faster rate. This could be clearly observed in Figure 5.4f, where GO was completely removed from GO/Nb-eth and GO/ NbCl_5 at 530 °C and 650 °C, respectively. In addition, pre-calcination of GO- NbCl_5 at 550 °C/2 h/Ar further retarded complete rGO removal, as seen from the continued decrease in weight beyond 650 °C in Figure 5.6b. This might be due to an enhanced contact between the oxide and rGO, resulting from the pre-calcination. Henceforth, Nb_2O_5 nanosheets

synthesized using Nb-eth and NbCl_5 as precursors are designated as Nb_2O_5 and $\text{Nb}_2\text{O}_5/\text{rGO}$ nanosheets, respectively.

Nb_2O_5 and $\text{Nb}_2\text{O}_5/\text{rGO}$ nanosheets synthesized with Nb-eth and NbCl_5 , respectively, showed different behaviors. Nb-eth has a higher affinity to GO sheets, resulting in more deposition on their surfaces, leading to a 4-fold increase in the Nb_2O_5 nanosheet yield. It was observed that at the same calcination conditions of 500 °C/1 h/air, Nb_2O_5 nanosheets have a higher crystallinity and larger crystallite size, as compared to $\text{Nb}_2\text{O}_5/\text{rGO}$ nanosheets (Figures 5.4e and 5.2a, and Table 5.1). In addition, Nb_2O_5 nanosheets have a lower surface area, especially after harsher calcination conditions (Table 5.1), which indicated more pronounced coarsening. This behavior could be explained by the lower rGO content in the Nb_2O_5 nanosheets. rGO could have slowed down crystallization and crystal growth in $\text{Nb}_2\text{O}_5/\text{rGO}$, resulting in less crystallinity and more tolerance to harsh calcination conditions. The higher rGO content retained within the $\text{Nb}_2\text{O}_5/\text{rGO}$ nanosheets could be ascribed to the relatively low affinity of NbCl_5 to GO and pre-calcination at 550 °C/2 h/Ar. The low affinity of NbCl_5 to GO resulted in relatively high content of GO in the nanocomposite, which needed harsher calcination conditions for its complete removal, as compared to GO/Nb-eth (Figure 5.4f). In addition, the lower Nb_2O_5 yield in $\text{Nb}_2\text{O}_5/\text{rGO}$ would reduce the Nb_2O_5 -catalyzed removal of rGO. Pre-calcination at 550 °C/2 h/Ar resulted in strongly bound rGO that resisted removal even beyond 650 °C, as demonstrated by TGA (Figure 5.6b). These two factors resulted in rGO retention within the $\text{Nb}_2\text{O}_5/\text{rGO}$ nanocomposites after calcination in air. The very close contact between rGO and Nb_2O_5 could be demonstrated by the high temperature (~900 °C) required for the complete rGO removal from the nanocomposites (Figure 5.2b).

Figure 5.4. (a–d) TEM images, (e) XRD patterns, and (g) AFM profile of Nb₂O₅ nanosheets synthesized using Nb-eth as precursor, and calcined in air at the conditions specified. (f) TGA profiles (conducted in air at a ramp of 2 °C/min) of as-synthesized GO/NbCl₅ and GO/Nb-eth.

Figure 5.5. (a) Nitrogen adsorption-desorption isotherms, (b) pore size distributions, (c) BET surface areas, and (d) pore volumes of Nb_2O_5 nanosheets synthesized using Nb-eth as precursor, and calcined in air at the conditions specified.

Figure 5.6. TGA profiles (conducted in air at a ramp of 2 °C/min) of (a) Nb_2O_5 nanosheets synthesized using Nb-eth as precursor, and calcined in air at the conditions specified, and (b) as-synthesized GO/NbCl₅, pre-calcined at 550 °C/2 h/Ar.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of elements in Nb₂O₅ nanosheets. Nb core level spectrum (Figure 5.7a) showed a peak doublet at binding energies of 207.5 and 210.3 eV, which agreed with the reported binding energies for Nb 3d_{5/2} and Nb 3d_{3/2} of Nb⁵⁺, respectively. Both peaks had similar full width at half-maximum, and were separated by 2.75 eV. The intensity ratio of Nb 3d_{5/2} peak to Nb 3d_{3/2} peak was 1.5. These criteria further confirmed the peak doublet assignment to Nb₂O₅ [41]. O1s spectrum (Figure 5.7b) showed two peaks at 530.6 eV and 531.8 eV, which were attributed to the oxygen species in Nb₂O₅ and hydroxyl groups, respectively [41]. Raman spectrum (Figure 5.7c) further confirmed the orthorhombic Nb₂O₅ phase; the peaks at 231 cm⁻¹ and 687 cm⁻¹ were attributed to the vibrations of octahedral cations and Nb-O bond stretching, respectively [42].

Figure 5.7. XPS (a) Nb 3d and (b) O 1s, and (c) Raman spectra of Nb₂O₅ nanosheets synthesized using Nb-eth as precursor at 500 °C/1 h/air.

5.2.1.2 TiO₂ Nanosheets

TiO₂ nanosheets were synthesized using GO template and Ti(IV) butoxide as precursor, followed by calcination in air. The nanosheet structure was shown by TEM images (Figure 5.8a–c). TiO₂ nanosheets adopted an anatase crystal structure (JCPDS # 00-021-1272), as shown by XRD (Figure 5.8d). SAED pattern (Figure 5.8e: inset) confirmed the anatase phase, whose (101) and (200) planes were identified by HRTEM (Figure 5.8e). Crystallite size calculated from the (101) XRD peak increased from 8.6 nm at calcination conditions of 350 °C/1 h to 12.6 nm at 500 °C/1 h and 550 °C/1 h. TGA analysis (Figure 5.8f) showed that TiO₂ synthesized at 350 °C retained ~3 wt% of rGO, while those calcined at 500 °C and 550 °C were free of rGO. The thickness of TiO₂ nanosheets obtained by calcination at 500 °C/1 h was found to be ~1.3 nm by AFM analysis (Figure 5.8g).

TiO₂ nanosheets were mesoporous as demonstrated by the Type IV adsorption-desorption isotherms (Figure 5.9a). Similar to Nb₂O₅ nanosheets, BET surface area (Figure 5.9c) of TiO₂ nanosheets decreased, while pore size and volume increased (Figure 5.9b, d) with increasing calcination temperature. TiO₂ nanosheets calcined at 350 °C and 500 °C have BET surface areas of 98.7 m²/g and 43.4 m²/g, and pore volumes of 0.12 and 0.16 cm³/g, respectively.

TiO₂ nanosheets were analyzed using XPS. Ti core level spectrum (Figure 5.9e) showed a peak doublet at 459.0 eV and 464.7 eV, with a splitting of 5.7 eV, which could be assigned to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺ [43, 44]. O 1s spectrum's (Figure 5.9f) main peak at 530.2 eV was due to the oxygen species in TiO₂ [43], while the peaks at 532.0 eV and 534.1 eV could be assigned to hydroxyl groups and adsorbed H₂O, respectively [41]. The synthesis conditions and properties of Nb₂O₅ and TiO₂ nanosheets are summarized in Table 5.1.

Figure 5.8. (a–c) TEM images, (d) XRD patterns, (e) HRTEM image (inset: SAED pattern), (f) TGA profiles (conducted in air at a ramp of 5 °C/min), and (g) AFM profile of TiO₂ nanosheets, calcined in air for 1 h at the temperatures specified.

Figure 5.9. (a) Nitrogen adsorption-desorption isotherms, (b) pore size distributions, (c) BET surface areas, (d) pore volumes, and XPS (e) Ti 2p and (f) O 1s spectra of TiO₂ nanosheets, calcined in air at the conditions specified.

Table 5.1. Synthesis conditions and properties of Nb₂O₅ and TiO₂ nanosheets.

Nanosheet	Calcination conditions	Precursor	Phase	Crystallite size (nm) ^a	rGO content (wt%)	BET surface area (m ² /g)
Nb ₂ O ₅ /rGO ^b	500 °C/ 1 h/air	NbCl ₅	Orthorhombic	14.3	45	74.7
Nb ₂ O ₅ /rGO ^b	550 °C/ 3 h/air	NbCl ₅	Orthorhombic	22.3	29	64.5
Nb ₂ O ₅	350 °C/ 1 h/air	Nb(V) ethoxide	Amorphous	-	3.0	112.7
Nb ₂ O ₅	500 °C/ 1 h/air	Nb(V) ethoxide	Orthorhombic	28.9	0	69.4
Nb ₂ O ₅	600 °C/ 1 h/air	Nb(V) ethoxide	Orthorhombic	35.4	0	26.2
TiO ₂	350 °C/ 1 h/air	Ti(IV) butoxide	Tetragonal (anatase)	8.6	3.0	98.7
TiO ₂	500 °C/ 1 h/air	Ti(IV) butoxide	Tetragonal (anatase)	12.6	0	42.8

^aBased on (001) peak of Nb₂O₅ and (101) peak of TiO₂. ^bPre-calcined at 550 °C/2 h/Ar.

5.2.1.3 Iron Oxide and Iron Oxide/rGO Nanosheets

Iron oxide nanosheets were synthesized at different calcination temperatures to control their rGO content and crystallinity. At 300 °C/1 h, the nanosheets were amorphous as shown by TEM and XRD results (Figure 5.10a, d, g). They retained a high rGO content of 38.3 wt% (Figure 5.10h), thus they were designated as iron oxide/rGO nanosheets. Increasing the calcination temperature to 325 °C reduced rGO content to 7.4 wt% (Figure 5.10h), however, the nanosheets were still amorphous (Figure 5.10b, e, g). The nanosheets were crystallized at 400 °C/1 h (Figure 5.10c, f, g), with their XRD pattern assigned to α -Fe₂O₃ phase. Crystalline Fe₂O₃ still maintained the nanosheet morphology, as observed using TEM and AFM. The nanosheet thickness was determined to be only ~1 nm using AFM analysis (Figure 5.11).

Figure 5.10. (a–c) TEM images, (d–f) HRTEM images, (g) XRD patterns, and (h) TGA profiles (conducted in air at a ramp of 5 °C/min) of iron oxide nanosheets, calcined in air at the conditions specified.

Figure 5.11. AFM profile of iron oxide nanosheets calcined in air at 400 °C/1 h: (a) topology and (b) thickness plot. The blue arrow in (a) points to the nanosheet whose thickness is plotted in (b).

5.2.1.4 SnO₂ and SnO₂/rGO Nanosheets

Tin oxide nanosheets were synthesized at 375 °C/1 h (Figure 5.12a) and 400 °C/1 h (Figure 5.12d). They displayed weak crystallinity at 375 °C/1 h (Figure 5.12c, g), with their XRD pattern assigned to the orthorhombic SnO₂ phase, which was confirmed with HRTEM (Figure 5.12b). Its crystallite size could not be accurately determined using the XRD peaks due to the very low peak intensity. The nanosheets had a high rGO content of 40.3 wt% (Figure 5.12h), were thus designated as SnO₂/rGO nanosheets. At 400 °C/1 h, crystallinity improved as indicated by the sharper XRD peaks (Figure 5.12g), with the SnO₂ phase further confirmed by SAED pattern (Figure 5.12f) and HRTEM (Figure

5.12e). Interestingly, the crystallite size was still very small, ~ 4.9 nm, as calculated from the (110) XRD peak. The rGO content decreased to only 3.3 wt% (Figure 5.12h).

Figure 5.12. (a, d) TEM images, (b, e) HRTEM images, (c, f) SAED patterns, (g) XRD patterns, and (h) TGA profiles (conducted in air at a ramp of 5 °C/min) of SnO₂ nanosheets, calcined in air at the conditions specified.

5.2.1.5 Broad Applicability of the Synthetic Strategy

The GO planar-confined growth strategy was used to synthesize a wide variety of binary oxide nanosheets to demonstrate its broad applicability. The binary oxide nanosheets synthesized include ZrO₂, NiO, Co₃O₄ and Mn₃O₄.

Zirconia nanosheets were synthesized using GO template at 400 °C/1 h (Figure 5.13a). They have a tetragonal ZrO₂ phase as determined by XRD (Figure 5.13c) and HRTEM

(Figure 5.13b), and a crystallite size of 9.2 nm. ZrO_2 is not commonly used for energy storage applications, thus, they were not examined for such applications. However, ZrO_2 is commonly used in the catalysis field [45, 46], where the unique nanosheet morphology may be of special importance; for example, Ni catalytic activity for dry reforming of methane was enhanced when supported on ZrO_2 nanosheets, as compared to other ZrO_2 structures [47].

Figure 5.13. (a) TEM image, (b) HRTEM image, and (c) XRD pattern of ZrO_2 nanosheets.

NiO , Co_3O_4 and Mn_3O_4 nanosheets were synthesized at 325 °C (Figure 5.14a–c) and 350 °C (Figure 5.14d–f). XRD patterns (Figure 5.14j–l), supported by HRTEM images (Figure 5.14g–i) and SAED patterns (Figure 5.14g–i: insets), showed that the nanosheets calcined at 350 °C crystallized into the rhombohedral NiO , cubic Co_3O_4 and tetragonal Mn_3O_4 phases, respectively. The rGO content decreased with increasing calcination temperature, where the nanosheets retained 42.9, 21.9 and 25.0 wt%, and 2.7, 4.9 and 3.6 wt% of rGO at 325 °C and 350 °C, respectively (Figure 5.14m–o). Therefore, the nanosheets synthesized at 325 °C were designated as NiO/rGO , $\text{Co}_3\text{O}_4/\text{rGO}$ and manganese oxide/rGO nanosheets. Crystallites were still small even for the nanosheets calcined at 350 °C, which were 8.4 nm, 11.8 nm and 17.5 nm, respectively. Synthesis conditions and properties of the iron oxide, SnO_2 , NiO , Co_3O_4 and Mn_3O_4 nanosheets are summarized in Table 5.2.

Figure 5.14. (a–f) TEM images, (g–i) HRTEM images (insets: SAED patterns), (j–l) XRD patterns, and (m–o) TGA profiles (conducted in air at a ramp of 5 °C/min) of (a, d, g, j, m) NiO, (b, e, h, k, n) Co₃O₄, and (c, f, i, l, o) Mn₃O₄ nanosheets, calcined in air at the conditions specified.

Table 5.2. Synthesis conditions and properties of various binary oxide nanosheets.

Nanosheet	Calcination conditions ^a	Precursor	Phase	Crystallite size (nm) ^b	rGO content (wt%)	BET surface area (m ² /g)
Iron Oxide/rGO	300 °C/1 h	Fe(III) acetylacetonate	Amorphous	-	38.3	44.2
Iron Oxide	325 °C/1 h	Fe(III) acetylacetonate	Amorphous	-	7.40	118.4
SnO ₂ /rGO	375 °C/1 h	Dibutyltin dilaurate	Orthorhombic	N/A ^c	40.3	78.0
SnO ₂	400 °C/1 h	Dibutyltin dilaurate	Orthorhombic	4.9	3.30	93.6
NiO/rGO	325 °C/1 h	Ni(II) acetylacetonate	Rhombohedral	N/A ^c	42.9	87.4
NiO	350 °C/1 h	Ni(II) acetylacetonate	Rhombohedral	8.4	2.70	70.1
Co ₃ O ₄ /rGO	325 °C/0.7 h	Co(II) acetylacetonate	Cubic	10.5	21.9	31.9
Co ₃ O ₄	350 °C/1 h	Co(II) acetylacetonate	Cubic	11.8	4.90	28.1
Manganese oxide/rGO	325 °C/1 h	Mn(II) acetylacetonate	Amorphous	-	25.0	74.4
Mn ₃ O ₄	350 °C/1 h	Mn(II) acetylacetonate	Tetragonal	17.5	3.60	34.7

^ain air. ^bBased on strongest peak. ^cCrystallite size could not be calculated due to low XRD peak intensity.

5.2.1.6 Doped Binary Oxide Nanosheets

Doping has been reported to be a successful strategy to improve material electrochemical properties. Nb doping of TiO₂ has been shown to improve conductivity and enhance Li⁺ diffusion, resulting in improved energy storage performance, especially the rate capability [48, 49].

The GO planar-confined growth strategy is able to introduce dopants to binary oxide nanosheets at the desired doping ratios. This has been demonstrated by doping of Nb₂O₅ and TiO₂ nanosheets with Ti and Nb ions, respectively.

5.2.1.6.1 Ti-Doped Nb₂O₅ Nanosheets

Ti-doped Nb₂O₅ nanosheets were synthesized at various Ti doping at% (Figure 5.15a–c), which were calculated using EDX analysis to be 2, 7.5 and 25 at%. TEM images showed that the nanosheet morphology was obtained for all three doping levels. EDX elemental maps clearly showed the uniform distribution of the Ti dopant within the Nb₂O₅ nanosheets (Figure 5.15d–l), suggesting the absence of phase separation.

XRD was conducted to confirm phase purity and to investigate the effect of doping on Nb₂O₅ crystal structure. Ti-doped Nb₂O₅ nanosheets adopted the orthorhombic crystal structure of Nb₂O₅, and no TiO₂ phase was observed (Figure 5.16a). This indicated that doping has occurred, rather than separate TiO₂ growth, which agreed with the homogeneous Ti distribution observed by EDX mapping. It was noted that more drastic calcination was needed for crystallization as the Ti dopant ratio increased. Contrary to pure Nb₂O₅ nanosheets that crystallized at 500 °C/1 h, Ti-doped Nb₂O₅ nanosheets (7.5 at%) crystallized at 600 °C/1 h, while Ti-doped Nb₂O₅ nanosheets (25 at%) needed 700 °C for crystallization. Ti-doped Nb₂O₅ nanosheets (7.5 and 25 at%) have lower (001)/(180) peak intensity ratios and smaller crystallite sizes than Ti-doped Nb₂O₅ (2 at%) and pure Nb₂O₅ nanosheets calcined at 600 °C/1 h (Table 5.3). This could be due to an inhibitory effect of Ti doping on Nb₂O₅ crystallization. The inhibitory effect of doping on crystallite growth and phase transformation has been previously reported [48, 50, 51]. The successful doping of Nb₂O₅ by Ti ions could be confirmed by XRD peak shift, where diffraction peaks shifted to higher 2θ angles as Ti doping increased (Figure 5.16b), due to the incorporation of Ti⁴⁺ (which has a smaller ionic radius than Nb⁵⁺ by 0.03 Å) into the Nb₂O₅ crystal lattice [48, 52]. Similar peak shifts were previously observed when a dopant of different ionic radius was introduced to the host lattice [48, 50].

Figure 5.15. (a–c) TEM images, (d, g, j) STEM images, and (e, f, h, i, k, l) EDX elemental maps of Ti-doped Nb_2O_5 nanosheets, with (a, d–f) 2, (b, g–i) 7.5 and (c, j–l) 25 at% Ti.

XPS analysis was used to confirm Ti doping and to study the chemical states of Ti and Nb ions. Ti was detected by XPS (Figure 5.16c), confirming successful doping. Ti $2p_{3/2}$ peak at 458.8 eV showed that Ti ions existed in the Ti^{4+} state. The low intensity of Ti

$2p_{3/2}$ peak and the absence of $Ti\ 2p_{1/2}$ peak could be explained by the low Ti doping level (2 at%) in the sample analyzed by XPS. Nb core level spectrum (Figure 5.16d) showed a peak doublet at 207.2 eV and 210.0 eV, which could be assigned to $Nb\ 3d_{5/2}$ and $Nb\ 3d_{3/2}$ of Nb^{5+} , respectively. Synthesis conditions and properties of Ti-doped Nb_2O_5 nanosheets are summarized in Table 5.3.

Figure 5.16. (a) XRD patterns with the (001) peaks magnified in (b), and XPS (c) Ti 2p and (d) Nb 3d spectra of Ti-doped Nb_2O_5 nanosheets, with different at% Ti.

5.2.1.6.2 Nb-Doped TiO_2 Nanosheets

Similarly, Nb-doped TiO_2 nanosheets were synthesized, in an effort to improve the electrochemical properties of TiO_2 nanosheets. Nb was doped into the TiO_2 crystal structure at 4, 8, 10 and 20 at%, as calculated using EDX analysis.

Nb-doped TiO_2 adopted the nanosheet structure at all doping levels (Figure 5.17a–d), with no obvious morphological variation from pure TiO_2 nanosheets. EDX mapping showed the homogeneous distribution of Nb dopant and the absence of phase separation (Figure 5.17e–p).

XRD was used to analyze the crystal structure of the Nb-doped TiO_2 nanosheets. Only the anatase phase could be observed in the diffraction patterns at all doping levels (Figure 5.18a), which indicated successful doping without introduction of a separate phase. The doped nanosheets were crystallized at 500 °C/1 h, similar to pure TiO_2 nanosheets. However, it was noticed that the crystallite size decreased from 12.6 nm for pure TiO_2 to ~10 nm for the doped nanosheets, which agreed with the crystal growth inhibition phenomenon explained earlier. However, at the high doping ratio of 20 at%, crystallite size increased substantially to ~22 nm. Similar phenomenon has been reported by Arbiol *et al.*, who studied Nb-doped TiO_2 . They have noticed that grain growth was suppressed as Nb doping level increased. However, this was reversed at high Nb doping ratios, where rapid grain growth was observed. They argued that at a certain doping ratio, solubility level of Nb into TiO_2 lattice was reached, due to excessive stress, leading to segregation and grain growth [53]. However, XRD did not reveal the appearance of any new phase in Nb-doped TiO_2 nanosheets (20 at%). In contrast to Ti-doped Nb_2O_5 nanosheets, the larger ionic radius of Nb^{5+} dopant resulted in a peak shift to lower 2θ angles for Nb-doped TiO_2 (Figure 5.18b).

XPS analysis was performed to detect Nb dopant and to study the chemical states of Ti and Nb ions. Nb 3d core level spectrum (Figure 5.18c) showed a peak doublet at 207.4 eV and 210.1 eV, which could be assigned to Nb 3d_{5/2} and Nb 3d_{3/2} of Nb^{5+} , respectively. Ti 2p spectrum (Figure 5.18d) showed the 2 main peaks at 459.0 eV and 464.7 eV, corresponding to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti^{4+} , respectively. However, another small peak was observed at 457.2 eV, which could be due to Ti 2p_{3/2} Ti^{3+} [54, 55]. The presence of a minor Ti^{3+} content might be due to Ti^{4+} reduction as a charge compensation mechanism to counter the excess positive charge introduced by Nb^{5+} [51]. Synthesis conditions and properties of Nb-doped TiO_2 nanosheets are summarized in Table 5.3.

Figure 5.17. (a–d) TEM images, (e–h) STEM images, and (i–p) EDX elemental maps of Nb-doped TiO_2 nanosheets, with (a, e, i, m) 4, (b, f, j, n) 8, (c, g, k, o) 10 and (d, h, l, p) 20 at% Nb.

Figure 5.18. (a) XRD patterns with the (101) peaks magnified in (b), and XPS (c) Nb 3d and (d) Ti 2p spectra of Nb-doped TiO₂ nanosheets, with different at% Nb.

Table 5.3. Synthesis conditions and properties of doped binary oxide nanosheets.

Nanosheet	Dopant	Doping at%	Calcination conditions	Crystallite size (nm) ^a	(001)/(180) peak intensity ratio
Nb ₂ O ₅	-	-	600 °C/1 h	35.4	1.1
Nb ₂ O ₅	Ti	2	600 °C/1 h	35.2	1.1
Nb ₂ O ₅	Ti	7.5	600 °C/1 h	29.3	0.72
Nb ₂ O ₅	Ti	25	700 °C/1 h	23.6	0.65
TiO ₂	-	-	500 °C/1 h	12.8	-
TiO ₂	Nb	4	500 °C/1 h	10.0	-
TiO ₂	Nb	8	500 °C/1 h	10.1	-
TiO ₂	Nb	10	500 °C/1 h	10.3	-
TiO ₂	Nb	20	500 °C/1 h	22.1	-

^aBased on (001) peak of Nb₂O₅ and (101) peak of TiO₂.

5.2.1.7 Metal Oxide/rGO Nanosheets

Incorporation of rGO within metal oxides is beneficial for energy storage applications, because it helps to improve electrode conductivity, mitigate pulverization during cycling and reduce material detachment and contact loss. The main strategy used to incorporate rGO within the nanosheets was mild calcination during metal oxide nanosheet synthesis. This allowed the retention of some of the rGO content, as the calcination conditions were not sufficient for its complete oxidation. Metal oxide/rGO nanosheets synthesized using the mild-calcination approach include Nb₂O₅/rGO, iron oxide/rGO, SnO₂/rGO, NiO/rGO, Co₃O₄/rGO and Mn₃O₄/rGO.

However, it was not always possible to retain an appropriate rGO content using mild calcination, such as in the case of Nb₂O₅ nanosheets (synthesized using Nb-eth as precursor) and TiO₂ nanosheets. In these cases, mild calcination could not be used because it would compromise crystallinity, which is critical for the insertion-based oxides that store Li⁺ by the intercalation mechanism. Two other strategies were used to synthesize Nb₂O₅/rGO (using Nb-eth as precursor) and TiO₂/rGO nanosheets, while maintaining crystallinity, namely Ar-calcination and opposite-charge methods.

5.2.1.7.1 Calcination in Argon

Metal oxide/rGO nanosheets could be synthesized by calcining GO/precursor in an inert atmosphere. Instead of air calcination that was used for oxide nanosheet synthesis and template removal, Ar calcination resulted in oxide synthesis, while retaining all the rGO template content.

Nb₂O₅/rGO and TiO₂/rGO nanosheets were synthesized by Ar calcination at 700 °C/2 h/Ar. TEM showed that the nanosheets synthesized by Ar calcination consisted of Nb₂O₅ and TiO₂ nanoparticles, anchored to the surface of rGO sheets (Figure 5.19a, b, d, e). HRTEM revealed the (001) and (101) planes of orthorhombic Nb₂O₅ and anatase TiO₂, respectively (Figure 5.19c, f). The oxide crystal structures were confirmed by XRD (Figure 5.19g, h). However, a minor rutile phase was observed in the case of TiO₂/rGO nanosheets. The rutile phase appeared due to the harsh calcination conditions (700 °C/2

h) that were needed for the oxide crystallization, because of the oxygen-limited conditions. Although drastic calcination conditions were used, the Nb_2O_5 and TiO_2 nanoparticles had small crystallite sizes of 11.9 and 6.7 nm, respectively. They also displayed very high surface areas of 166.4 and 214.7 m^2/g , respectively. Their rGO contents were calculated using TGA to be 40.5 and 41.4 wt%, respectively (Figure 5.19i).

Figure 5.19. (a, b, d, e) TEM images, (c, f) HRTEM images, (g, h) XRD patterns, and (i) TGA profiles (conducted in air at a ramp of 5 °C/min) of (a–c, g, i) $\text{Nb}_2\text{O}_5/\text{rGO}$ and (d–f, h–i) TiO_2/rGO nanosheets, synthesized using Ar-calcination method. * in (h) indicates rutile TiO_2 XRD peaks.

5.2.1.7.2 Opposite-Charge Method

The opposite-charge method (OCM) is a post-synthesis process, whereby metal oxide nanosheets are grafted with rGO nanosheets. First, GO was functionalized with poly(diallyldimethylammonium chloride) (PDPA) to reverse its surface charge to be

positive. The positively charged GO-PDDA interacted electrostatically with the intrinsically negatively charged metal oxide nanosheets, leading to precipitation. The metal oxide nanosheets/GO nanocomposite was then calcined in Ar to reduce the GO, forming metal oxide/rGO nanosheets.

Figure 5.20. (a) FTIR spectra of GO, PDDA and GO-PDDA. (b) Zeta potential of GO, GO-PDDA, Nb₂O₅ and TiO₂ nanosheets. (c) XRD patterns of GO and rGO (calcined at 400 °C/1 h/Ar).

GO functionalization was probed using Fourier-transform infrared spectroscopy (FTIR) (Figure 5.20a). GO showed IR absorption bands for C=O, C=C and C-O groups at 1733 cm⁻¹, 1620 cm⁻¹, 1192/1043 cm⁻¹, respectively [56]. The C=C, CH₂ and C-N functional groups of PDDA could be detected at 1641 cm⁻¹, 1472 cm⁻¹ and 1215 cm⁻¹, respectively [56-58]. GO-PDDA has shown peaks at 1726 cm⁻¹, 1628 cm⁻¹, 1471 cm⁻¹, 1218 cm⁻¹ and 1070 cm⁻¹, which could be assigned to C=O, C=C, CH₂, C-O/C-N and C-O groups,

respectively. The peak shifts for some of the functional groups in GO-PDDA might be due to the interaction between GO and PDDA.

Zeta potential analysis was used to determine the surface charge of GO, GO-PDDA and metal oxide nanosheets (Figure 5.20b). It was observed that GO sheets had a negative surface charge of ~ -40 mV, which was reversed to a positive charge of ~ 44 mV upon functionalization with PDDA. Nb_2O_5 and TiO_2 nanosheets had intrinsic negative surface charges of ~ -46 and ~ -24 mV, respectively.

XRD was used to optimize the calcination conditions required for GO reduction (Figure 5.20c). It was observed that the GO (002) peak shifted from $10.3^\circ(2\theta)$ to $24.0^\circ(2\theta)$ after calcination at 400°C in Ar for 1 h, which showed that such calcination conditions were enough for GO reduction [59].

The opposite-charge method resulted in intimate contact between the metal oxide and rGO nanosheets. This close contact was observed in the TEM images (Figure 5.21a, b), and could be explained by the electrostatic interaction between the metal oxide nanosheets and GO-PDDA, which resulted in an intimate sheet-on-sheet structure. This was further confirmed by EDX elemental maps (Figure 5.21c–h), which showed the rGO sheets intermixed with the metal oxide nanosheets. This close contact would be beneficial in energy storage applications because it would maintain the electrical contact between the oxides and the current collector.

XRD analysis was conducted to assess phase stability after calcination. The $\text{Nb}_2\text{O}_5/\text{rGO}$ and TiO_2/rGO nanosheet patterns were assigned to orthorhombic Nb_2O_5 and anatase TiO_2 , respectively, with no phase change or impurity detected (Figure 5.21i, j). TGA analysis was used to determine rGO content, which was found to be 22.9 and 23.6 wt% in $\text{Nb}_2\text{O}_5/\text{rGO}$ and TiO_2/rGO nanosheets, respectively (Figure 5.21k).

In energy storage applications, mild calcination was the main strategy for rGO incorporation within the metal oxide nanosheets, and such nanocomposites were

designated as metal oxide/rGO. The opposite-charge method was used for Nb₂O₅/rGO and TiO₂/rGO nanosheet synthesis when mild calcination could not be used, and they were designated as Nb₂O₅/rGO-OCM and TiO₂/rGO-OCM, respectively. Metal oxide/rGO nanosheets synthesized using Ar calcination were not used for energy storage applications, mainly due to the inability of the Ar-calcination method to control the rGO content during synthesis, and also due to the drastic calcination conditions that were energy demanding and caused the appearance of new phases.

5.2.2 Electrochemical Measurements

The metal oxide nanosheets were evaluated for energy storage applications, including LIB anodes and supercapacitors. Nb₂O₅, TiO₂, iron oxide, SnO₂, NiO and Co₃O₄ nanosheets were investigated as LIB anodes, whereas Mn₃O₄ nanosheets were studied as supercapacitor electrode.

5.2.2.1 Li-Ion Battery Anodes

5.2.2.1.1 Cyclic Voltammetry and Galvanostatic Charge/Discharge Profiles

5.2.2.1.1.1 Nb₂O₅/rGO Nanosheets

Cyclic voltammetry (CV) was conducted to study the reduction and oxidation reactions of Nb₂O₅/rGO nanosheets (29 wt% rGO) during lithiation and de-lithiation, respectively. The broad cathodic and anodic CV peaks indicated pseudocapacitive behavior (Figure 5.22a) [42], which agreed with previous reports on pseudocapacitive Li⁺ storage of Nb₂O₅ [38]. Cathodic peaks appeared at 1.84 V and 1.45 V vs. Li⁺/Li, whereas overlapping anodic peaks were observed at 1.85 V and 1.60 V. These values were in line with previous reports of orthorhombic Nb₂O₅, and they were assigned to Nb^{5+/4+} and Nb^{4+/3+} redox couples, respectively [60-63]. Redox reaction kinetics of Nb₂O₅ nanosheets were studied by analyzing the relation between current intensity and sweep rate during CV (Figure 5.22c). Based on Eq. 3.4, b-value was calculated to be 0.9 (Figure 5.22d), indicating a dominant capacitive charge storage mechanism [64].

Figure 5.21. (a–b) TEM images, (c, f) STEM images, (d, e, g, h) EDX elemental maps, (i, j) XRD patterns, and (k) TGA profiles (conducted in air at a ramp of 5 °C/min) of (a, c–e, i, k) $\text{Nb}_2\text{O}_5/\text{rGO}$ and (b, f–h, j–k) TiO_2/rGO nanosheets, synthesized using the opposite-charge method. Red arrows in (a, b) point to rGO sheets.

Figure 5.22. CV curves conducted at (a) 0.05 mV/s and (c) increasing sweep rates, (b) GCD profile at 1C (inset: differential capacity plot), and (d) log anodic peak current vs. log scan rate plot of Nb₂O₅/rGO nanosheets.

Galvanostatic charge/discharge (GCD) profile revealed monophasic lithiation/delithiation reactions (Figure 5.22b). This was indicated by the sloped line profiles with no observed plateaus, which agreed with the broad peaks observed in the CV profile. The differential capacity plot (Figure 5.22b: inset) showed broad cathodic and anodic peaks at 1.59 and 1.83 V, respectively, which agreed with the CV profile. A high specific capacity of ~212 mAh/g was achieved by Nb₂O₅/rGO during the first discharge, followed by ~195 and ~189 mAh/g in the second and third cycles, respectively. The small capacity loss indicated electrode stability.

5.2.2.1.1.2 TiO₂ Nanosheets

TiO₂ nanosheets (500 °C/1 h/air) were studied with CV (Figure 5.23a) and GCD (Figure 5.23b). The main cathodic and anodic peaks were detected at 1.7 V and 2.1 V, respectively. A small broad cathodic peak was observed at ~1.45 V. The broad anodic

peak at ~2.5 V during the first charge might be attributed to electrolyte side reactions during the first cycle, since it disappeared in subsequent cycles. GCD profile also showed that the main cathodic reaction occurred at 1.75 V, together with a barely observable plateau at 1.45 V. A sloped line was detected below 1.45 V. The main charge plateau was observed at 1.96 V. The differential capacity plot (Figure 5.23b: inset) clearly showed the major cathodic and anodic peaks at 1.75 V and 1.96 V, respectively.

Li^+ storage processes in TiO_2 nanosheets could be explained based on the CV and GCD results. Single-phase Li^+ insertion took place till 1.75 V, where a Li_xTiO_2 solid solution was formed until the Li miscibility limit in the anatase crystal lattice was reached. At 1.7–1.75 V, the main biphasic Li^+ insertion reaction occurred, whereby Li_xTiO_2 and $\text{Li}_{0.55}\text{TiO}_2$ phases coexisted. This was followed by a second two-phase Li^+ insertion at 1.45 V, which was attributed to a secondary sluggish biphasic process involving $\text{Li}_{0.55}\text{TiO}_2$ and LiTiO_2 phases, and was characteristic of small TiO_2 crystals. The discharge sloped line below 1.45 V in the GCD profile corresponded to interfacial Li^+ storage. The initial charge process up to 1.96 V might be attributed to Li^+ extraction from nanosheet interfaces, as well as the reverse of the secondary biphasic Li^+ insertion process. The main Li^+ extraction reaction took place at 1.96 V, and corresponded to the reverse of the main biphasic Li^+ insertion reaction [65-67]. Specific discharge capacities of ~243, ~241 and ~237 mAh/g were achieved during the first 3 cycles, respectively. The high capacity that exceeded the theoretical capacity of ~168 mAh/g was attributed to the nanosize, which allowed extra Li^+ intercalation, in addition to interfacial storage. The stability of the redox reactions was apparent from the CV and GCD profiles, whereby there were no peak shifts, and almost no capacity loss during the first 3 cycles. The main charge storage mechanism was determined by conducting CV at increasing sweep rates (Figure 5.23c). The b-value was calculated to be 0.5 (Figure 5.23d), which indicated that diffusion-controlled Li^+ storage was the main charge storage mechanism.

Figure 5.23. CV curves conducted at (a) 0.1 mV/s and (c) increasing sweep rates, (b) GCD profile at 1C (inset: differential capacity plot), and (d) log anodic peak current vs. log scan rate plot of TiO_2 nanosheets synthesized at $500^\circ\text{C}/1\text{ h}/\text{air}$.

5.2.2.1.1.3 Iron Oxide Nanosheets

Iron oxide nanosheets ($325^\circ\text{C}/1\text{ h}/\text{air}$) as LIB anode were studied using CV (Figure 5.24a) and GCD (Figure 5.24b). During the first discharge, a minor peak appeared at 1.6 V , which corresponded to the initial lithiation of iron oxide [68]. The major sharp peak at 0.7 V was attributed to the decomposition of iron oxide, forming Li_2O matrix and metallic Fe, and electrolyte decomposition forming solid electrolyte interphase (SEI) [69]. The extended overlapped anodic peak was attributed to the oxidation of metallic Fe to Fe^{3+} [69, 70]. The significant peak intensity reduction in the second and third cycles indicated electrode instability causing capacity fading. The GCD profile showed similar results, where the bump at 1.65 V during the first discharge indicated initial lithiation of iron oxide, and the main plateau at 0.87 V was attributed to iron oxide decomposition and

SEI formation. The sloped charge plateau represented the extended anodic peaks observed in the CV profile, and corresponded to the oxidation of metallic iron to iron oxide. A very high initial discharge capacity of ~ 1800 mAh/g was observed, followed by a charge capacity of ~ 1305 mAh/g, with a Coulombic efficiency of $\sim 73\%$. The large capacity loss in the first cycle was attributed to the SEI formation. This was followed by second and third cycle discharge capacities of ~ 1398 and ~ 1235 mAh/g, indicating gradual capacity fading, which agreed with the CV profile.

Figure 5.24. (a) CV curves conducted at 0.1 mV/s, and (b) GCD profile at 0.1 A/g of iron oxide nanosheets synthesized at $325^\circ\text{C}/1$ h/air.

5.2.2.1.1.4 SnO_2 Nanosheets

The CV (Figure 5.25a) profile of SnO_2 nanosheets ($400^\circ\text{C}/1$ h/air) showed two main redox couples, corresponding to conversion and alloying/de-alloying reactions. The first cathodic scan showed a pronounced peak at ~ 0.8 V, which could be attributed to the partially reversible SnO_2 reduction to metallic Sn nanoparticles within Li_2O matrix, and SEI formation. The second cathodic peak appeared at ~ 0.1 V, and was ascribed to Li-Sn alloy formation. The first anodic scan also showed two main peaks at ~ 0.5 V and ~ 1.2 V, which could be explained by Li-Sn de-alloying and Sn oxidation, respectively [71-73]. The second and third cycles showed similar CV scans, except that the first cathodic peak shifted to a higher potential of ~ 1.1 V. The GCD (Figure 5.25b) profile of SnO_2 nanosheets agreed with the CV scans. The first cycle showed a huge capacity loss due to SEI formation during the initial discharge, which resulted in a low Coulombic efficiency

of ~52%. In the subsequent two cycles, specific discharge capacities of ~1121 and ~1071 were achieved, with Coulombic efficiencies of 87% and 89%, respectively.

Figure 5.25. (a) CV curves conducted at 0.1 mV/s, and (b) GCD profile at 0.08 A/g of SnO₂ nanosheets synthesized at 400 °C/1 h/air.

5.2.2.1.1.5 NiO and Co₃O₄ Nanosheets

CV profile of NiO nanosheets (350 °C/1 h air) demonstrated one major cathodic peak at ~0.4 V during the first discharge (Figure 5.26a), which corresponded to NiO decomposition to metallic Ni and SEI formation. In subsequent cycles, NiO decomposition took place at ~1 V. Anodic processes occurred at ~1.4 V and ~2.2 V, corresponding to partial SEI oxidation and Ni oxidation, respectively [2, 26, 74]. Specific capacities of ~1682, ~1231 and ~1185 mAh/g were achieved in the first 3 cycles (Figure 5.26b), with Coulombic efficiencies of ~71%, ~93% and ~95%, respectively. The low Coulombic efficiency in the first cycle was attributed to the SEI formation, and its improvement in subsequent cycles indicated electrode reversibility.

Figure 5.26. (a) CV curves conducted at 0.1 mV/s, and (b) GCD profile at 0.1 A/g of NiO nanosheets synthesized at 350 °C/1 h/air.

The CV profile of Co_3O_4 nanosheets (350 °C/1 h air) showed similar electrochemical behavior as NiO nanosheets (Figure 5.27a). A large cathodic peak appeared in the first discharge at ~ 0.75 V, which could be attributed to Co_3O_4 decomposition, accompanied by SEI formation. The anodic Co oxidation reaction occurred at ~ 2.1 V. The cathodic peak position shifted to ~ 1 V in subsequent cycles, while the anodic peak showed no shift. This agreed with previously reported results [75], and was corroborated by the GCD profile (Figure 5.27b). Similar to other conversion reaction-based oxides, Co_3O_4 nanosheets had a large initial discharge capacity of ~ 1107 mAh/g that decreased to ~ 890 and ~ 838 mAh/g in the second and third cycles, respectively, with Coulombic efficiencies of $\sim 78\%$ for the first cycle and $\sim 91\%$ for the second and third cycles.

Figure 5.27. (a) CV curves conducted at 0.1 mV/s, and (b) GCD profile at 0.1 A/g of Co_3O_4 nanosheets synthesized at 350 °C/1 h/air.

5.2.2.1.2 Stability and Rate Performance

5.2.2.1.2.1 Nb₂O₅ and Nb₂O₅/rGO Nanosheets

Nb₂O₅ nanosheets with different degrees of crystallinity were first tested to determine the effect of crystallinity on Nb₂O₅ performance (Figure 5.28a). Cycling stability was conducted at 1C. 1C for Nb₂O₅ was previously assumed to be 100 mAh/g [76]. In this work, it was assumed to be 150 mAh/g. However, currently it is the norm in the literature to assume 1C = 200 mAh/g. When comparing the results to the literature, C-rates were converted to current densities in A/g.

Amorphous Nb₂O₅ nanosheets synthesized at 350 °C/1 h/air and 450 °C/1 h/air achieved ~41 and ~46 mAh/g after 200 cycles. Crystalline Nb₂O₅ nanosheets calcined at 500 °C/1 h/air and 600 °C/1 h/air have capacities of 89.4 and 88.7 mAh/g, respectively, with the former having very high Coulombic efficiency of 99–100% after the first few cycles.

Figure 5.28. (a) Cycling and (b) rate performances of Nb₂O₅ nanosheets, calcined in air for 1 h at the calcination temperatures (°C) specified.

Ex situ TEM (Figure 5.29a–e) and XRD (Figure 5.29f) were conducted to assess the crystalline Nb₂O₅ nanosheet stability during cycling. It was found that Nb₂O₅ nanosheets maintained their morphology and phase after the first discharge and charge, and even after prolonged cycling, which agreed with their stable performance.

Rate performance showed similar trend (Figure 5.28b), where the crystalline nanosheets achieved enhanced rate performance, with ~ 76 mAh/g at 5C. However, it was found that the nanosheets calcined at 600 °C/1 h/air could not tolerate higher current densities, with rapid performance deterioration at 10C, as compared to ~ 40 mAh/g still retained by the nanosheets calcined at 500 °C/1 h/air. These results suggested that crystallinity improved the energy storage performance of Nb₂O₅ nanosheets. This agreed with previously reported results, and could be attributed to the rapid Faradic reactions permitted by the orthorhombic crystal structure, especially along the vacant sites between the (001) planes [38, 77]. The poor high-rate performance of Nb₂O₅ nanosheets calcined at 600 °C/1 h/air could be explained by their thicker compact structure, and low surface area and pore volume, which affected charge transport and reduced contact with the electrolyte. Based on the results above, Nb₂O₅ nanosheets calcined at 500 °C/1 h/air (Nb₂O₅-500) showed the best performance, offering a balance between crystallinity and structural properties, which are both critical for high-performance LIB electrodes.

Figure 5.29. *Ex situ* (a–c) TEM images, (d–e) HRTEM images, and (f) XRD patterns of Nb₂O₅ nanosheets synthesized at 500 or 600 °C/1 h/air after (a, d, f) 1st discharge, (b, e, f) 1st charge, and (c, f) 200 cycles. * in (f) indicates carbon additives peak.

Although Nb₂O₅-500 nanosheets had very good performance, there was still room for improvement. Several approaches were investigated to improve the electrode conductivity in an effort to enhance its capacity and rate capability, such as rGO incorporation and Ti doping. The modified nanosheets demonstrated improved performance (Figure 5.30a), where Nb₂O₅/rGO-OCM (22.9 wt%), Nb₂O₅/rGO (29 wt% rGO) and Ti-doped Nb₂O₅ (2 at% Ti) nanosheets achieved ~143, ~138, ~131 mAh/g after 100 cycles at 1C, as compared to ~99 mAh/g achieved by the pristine Nb₂O₅-500 nanosheets. The performance enhancement was more obvious at high C-rates (Figure 5.30b), where Nb₂O₅/rGO, Nb₂O₅/rGO-OCM and Ti-Nb₂O₅ achieved ~120, ~69, ~45 mAh/g, respectively at 20C, as compared to ~9 mAh/g retained by Nb₂O₅-500. The improved performance of the modified nanosheets could be explained by the enhanced conductivity that facilitated electronic transfer. The better rate performance of Nb₂O₅/rGO nanosheets, as compared to Nb₂O₅/rGO-OCM nanosheets could be attributed to the simultaneous oxide formation and GO reduction in the case of Nb₂O₅/rGO, which might have led to better contact between Nb₂O₅ and rGO.

The high capacities of ~179 and ~120 mAh/g at 5C (0.75 A/g) and 20C (3 A/g), respectively, achieved by Nb₂O₅/rGO nanosheets are superior to those shown by Nb₂O₅@C nanocrystals [78], Nb₂O₅ macroporous nanostructures [79], Nb₂O₅ nanosheets [17] and Nb₂O₅ 3D nanowire superstructure [80], which achieved ~100, ~111, ~90 and ~135 mAh/g at 3, 1.6, 1 and 0.5 A/g, respectively. Although Nb₂O₅/rGO nanosheets had lower rate performance than Nb₂O₅ nanowires [63] and mesoporous Nb₂O₅/C nanostructures [64] that showed ~160 and ~115 mAh/g at 5 A/g, they have better performance at lower rates. A comparison of Nb₂O₅/rGO nanosheet performance to previously reported results is summarized in Table 5.4.

Figure 5.30. (a) Cycling and (b) rate performances of Nb₂O₅-500, Nb₂O₅/rGO-OCM, Nb₂O₅/rGO and Ti-doped Nb₂O₅ (2 at% Ti) nanosheets.

5.2.2.1.2.2 TiO₂ and TiO₂/rGO Nanosheets

TiO₂-500 nanosheets (500 °C/1 h/air) showed excellent cycling stability (Figure 5.31a) and rate performance (Figure 5.31b). The nanosheets achieved an initial capacity of ~243 mAh/g (1C = 168 mAh/g), and ~172 mAh/g after 100 cycles, retaining ~71% of the initial capacity. They also demonstrated a very high Coulombic efficiency of 99–100% over cycling. The nanosheet morphology and anatase phase were maintained after cycling (Figure 5.31c–e), which helped to explain the high stability of the nanosheets. TiO₂-500 nanosheets also showed very good rate performance, retaining ~85 mAh/g at 20C (Figure 5.31b).

TiO₂ nanosheets were modified by rGO incorporation and Nb doping to improve their electrochemical properties. Nanosheet modification did not improve the electrode performance at a moderate C-rate of 1C (Figure 5.31a). However, at high C-rates, they showed some improvement (Figure 5.31b); TiO₂/rGO-OCM (23.6 wt% rGO) and Nb-doped TiO₂ (10 at% Nb) nanosheets achieved ~98 and ~102 mAh/g at 20C, respectively. The performance of TiO₂ nanosheets was compared to previous studies. Nb-TiO₂ nanosheets achieved ~268, ~161, ~133 and ~102 mAh/g at 1C, 5C, 10C and 20C, respectively, which is better than that achieved by TiO₂ microboxes [81], TiO₂ cubes [82], TiO₂ hollow microspheres [83], TiO₂ mesoporous microspheres [84] and 3D TiO₂/graphene network [85], which have capacities of ~63, ~96, ~88, ~100 and ~105

mAh/g at 20C, 2C, 20C, 10C and 12C, respectively. Hierarchically porous TiO_2 microspheres achieved ~ 166 and ~ 130 mAh/g at 1C and 20C, respectively [67], showing lower capacity than TiO_2 nanosheets at low rates, but better rate capability. A comparison of the TiO_2 nanosheet performance to the literature is summarized in Table 5.4.

Figure 5.31. (a) Cycling and (b) rate performances of TiO_2 -500, $\text{TiO}_2/\text{rGO-OCM}$ and Nb-doped TiO_2 (10 at% Nb) nanosheets. *Ex situ* (c) TEM image, (d) HRTEM image, and (e) XRD pattern of TiO_2 -500 nanosheets after 100 cycles. * in (e) indicates carbon additives peak, while the blue arrows point to anatase TiO_2 peaks.

5.2.2.1.2.3 Iron Oxide and Iron Oxide/rGO Nanosheets

The cycling stability of iron oxide nanosheets (325 °C/1 h/air) was investigated at 1 A/g (Figure 5.32a). They had an initial discharge capacity of ~ 1358 mAh/g, which decreased sharply to ~ 86 mAh/g after 50 cycles, then slightly increased, ending with ~ 129 mAh/g after 300 cycles. The nanosheet structure was still retained after cycling (Figure 5.34a, b), but it was composed of small particles that formed as a result of iron oxide decomposition and re-formation during cycling. It was found that the iron oxide

nanosheets with little rGO content (7.4 wt%) could not overcome cycling-induced pulverization and contact loss. The carbon additives within the electrode were not enough to provide a conductive support that could keep the active material in contact with the current collector. This was not surprising since conversion reaction-based Li^+ storage is known to involve active material decomposition and reformation, with large volume change and severe pulverization.

To tackle this problem, iron oxide/rGO nanosheets (38.3 wt% rGO) were synthesized by mild calcination (300 °C/1 h/air), so that rGO sheets would provide a highly conductive matrix, buffer volume change and prevent contact loss during cycling. Incorporation of rGO sheets improved iron oxide performance dramatically (Figure 5.32a). The nanocomposite suffered from gradual capacity loss to ~664 mAh/g after the first 20 cycles, then its capacity increased at a rapid pace to ~1328 mAh/g at the 200th cycle. After the 200th cycle, the capacity stabilized showing slight increase over further cycling reaching ~1394 mAh/g at the 300th cycle, with a high Coulombic efficiency of 99–100%.

Figure 5.32. (a) Cycling stability, (b) rate performance, and (c) Nyquist plots of iron oxide and iron oxide/rGO nanosheets.

The contribution of rGO in the electrode capacity had to be considered because rGO is an active Li^+ storage material below 1 V [86]. Control rGO had a capacity of ~ 561 and ~ 598 mAh/g after 200 and 300 cycles, respectively (Figure 5.33a). The rGO contribution to the capacity of iron oxide/rGO nanosheets was calculated to be $\sim 16\%$ at the 200th and 300th cycles. This clearly showed that the dramatic capacity increase was due to the activation of the metal oxide nanosheets, rather than direct Li^+ storage by rGO sheets. rGO acted as a conductive support that buffered iron oxide volume change during cycling, ensured its contact with the current collector and mitigated pulverization-induced contact loss. This could be inferred from the nanoparticles that were still anchored to the rGO sheets after cycling (Figure 5.34c, d), and the lower charge transfer resistance of the nanocomposite, as determined by the smaller semi-circle diameter in the Nyquist plot (Figure 5.32c).

Figure 5.33 (a) Cycling and (b) rate performances of control rGO.

Iron oxide/rGO nanosheets showed a very high capacity, beyond the theoretical capacity of the nanocomposite (~ 917 mAh/g, assuming the theoretical capacity of graphene to be 774 mAh/g [87]). They also showed an increasing capacity over cycling, especially during the first 200 cycles. These observations agreed with the results discussed in Chapter 4, Section 4.2.2.1, and with previous reports investigating iron oxide and other conversion reaction-based LIB anodes. There are several explanations for the increasing capacity over cycling, the most established of which is the catalytically-enhanced electrolyte decomposition at low potential, leading to the formation of a gel-like polymer, which would dissolve during charging [88-90]. This phenomenon has been shown to cause capacity increase over cycling, exceeding the theoretical capacity of the active

material. Another hypothesis is that irreversible Li_2O formation would take place during the initial cycles, which would be followed by gradual Li_2O activation over cycling, leading to capacity increase [91]. The activation of Li_2O has been attributed to the metallic nanoparticles generated during the initial cycles. Another possible mechanism for capacity increase is the continuous pulverization and particle size reduction during cycling that would expose more electrochemically active sites, leading to capacity increase [92]. A recent study also proposed that LiOH formed on the metal oxide surface reacted with Li^+ to produce Li_2O and LiH , which increased the capacity [93]. It should be noted that the presence of a conductive support would enhance all of these proposed mechanisms, because it would facilitate electron transfer during the electrochemical reactions.

The rate performance of iron oxide/rGO nanosheets was studied at various current densities ranging from 0.5 to 7 A/g (Figure 5.32b). They showed an excellent rate capability achieving ~453 and ~346 mAh/g at 5 and 7 A/g, respectively, while iron oxide nanosheets showed only ~29 mAh/g at 5 A/g. The contribution of rGO would only account for ~21% of the total capacity of iron oxide/rGO nanosheets at 7 A/g, as calculated from the control rGO rate study (Figure 5.33b), which further confirmed that the higher performance upon rGO introduction was mainly due to the activation of iron oxide. rGO sheets could stabilize iron oxide at high rates by preventing its detachment and ensuring adequate electronic transfer that would be critical at such high current densities.

The performance of iron oxide/rGO nanosheets was compared to the literature. The iron oxide/rGO nanosheets achieved ~715 and ~453 mAh/g at 2 and 5 A/g, respectively, which was better than iron oxide nanoparticles/carbon nanotubes [70] and iron oxide@C [94], which attained ~320 and ~370 mAh/g at 2 and 4 A/g, respectively. Iron oxide/rGO nanosheet performance was comparable to or relatively lower than that of iron oxide/carbon nanofibers [69], iron oxide/graphene [95] and yolk-shell iron oxide@C [96], which achieved ~491, ~500 and ~575 mAh/g at 5 A/g. A comparison of iron oxide/rGO nanosheet performance to the literature is summarized in Table 5.5.

Figure 5.34. *Ex situ* TEM images of (a, b) iron oxide and (c, d) iron oxide/rGO nanosheets after cycling.

5.2.2.1.2.4 SnO₂ and SnO₂/rGO Nanosheets

SnO₂ nanosheets (400 °C/1 h/air) suffered rapid capacity decay during cycling at 0.8 A/g (Figure 5.35a). They showed a very high initial discharge capacity of ~1772 mAh/g, which decayed during the first 100 cycles to ~180 mAh/g, and then further declined slowly to ~129 mAh/g after 300 cycles. The reason behind capacity decay is similar to iron oxide nanosheets, where drastic volume change and pulverization resulted in contact loss of the active materials. The nanosheet morphology could still be observed after cycling (Figure 5.36a, b), even with SnO₂ nanocrystals clearly seen. However, the absence of a conductive support rendered them isolated and out of contact with the current collector.

On the other hand, SnO₂/rGO nanosheets (40.3 wt% rGO) synthesized at 375 °C/1 h/air showed much better stability (Figure 5.35a). Capacity declined over the first 10 cycles to ~959 mAh/g, and then increased slowly to ~1271 mAh/g at the 300th cycle, with very

high Coulombic efficiency of 99–100% over cycling. The contribution of rGO was calculated to be ~16%. This showed that the enhanced performance of the nanocomposite was mainly due to SnO_2 stabilization by buffering volume change, enhancing conductivity and mitigating contact loss. This could be inferred from the TEM images of the SnO_2/rGO nanosheets after cycling (Figure 5.36c, d), which showed that the nanoparticles were still anchored to the rGO sheets. In addition, the charge transfer resistance of the nanocomposite was lower than that of pure SnO_2 nanosheets as determined from the smaller semi-circle diameter in the Nyquist plot (Figure 5.35c).

Figure 5.35. (a) Cycling stability, (b) rate performance, and (c) Nyquist plots of SnO_2 and SnO_2/rGO nanosheets.

SnO_2/rGO nanosheets showed a capacity increase over cycling. Similar to iron oxide/rGO nanosheets, the reason might be the formation of a gel-like polymer due to the low operation potential. However, the capacity increased slowly and did not show a sharp change as in the case of iron oxide/rGO nanosheets. This might be due to the difference

in the mechanism of Li^+ storage between iron oxide and SnO_2 , where the former stores Li^+ by conversion reaction, while the latter stores Li^+ mainly by alloying/de-alloying mechanism, and partially by conversion reaction. This means that in the case of SnO_2/rGO nanosheets, the decomposition of Li_2O during de-lithiation only occurred partially and was not the main de-lithiation reaction. Therefore, Li_2O activation following initial cycling, which has been proposed to increase the capacity in the case of conversion reaction-based oxides, was only partially valid in the case of SnO_2 .

SnO_2/rGO nanosheets displayed an excellent rate performance (Figure 5.35b). The nanocomposite achieved ~ 775 and ~ 713 mAh/g at 3.2 and 4 A/g, respectively, with rGO contribution calculated to be $\sim 23\%$ at 4 A/g. SnO_2 nanosheets achieved only ~ 172 and ~ 73 mAh/g at 3.2 and 4 A/g, respectively. This demonstrated the ability of rGO to stabilize SnO_2 , helping it to cope with the high current densities, while achieving impressive Li^+ storage.

The Li^+ storage performance of SnO_2/rGO nanosheets was compared to the literature. SnO_2/rGO nanosheets achieved ~ 918 and ~ 713 mAh/g at 1.6 and 4 A/g, respectively, which is better than $\text{SnO}_2/\text{graphene}$ [72], $\text{SnO}_2/\text{graphene}/\text{polyaniline}$ [97], 3D $\text{SnO}_2/\text{graphene}$ foam [98] and $\text{SnO}_2@\text{C}$ submicroboxes [99], which had ~ 790 , ~ 240 , ~ 480 and ~ 583 mAh/g at 1, 2, 3 and 1 A/g, respectively. However, the rate performance of SnO_2/rGO nanosheets was lower than that of SnO_2 quantum dots/graphene [100] which achieved ~ 932 mAh/g at 3.9 A/g. A comparison of SnO_2/rGO nanosheet performance to the literature is summarized in Table 5.5.

Figure 5.36. *Ex situ* TEM images of (a, b) SnO_2 and (c, d) SnO_2/rGO nanosheets after cycling. Red circles in (b) encircle SnO_2 crystals.

5.2.2.1.2.5 NiO , NiO/rGO , Co_3O_4 and $\text{Co}_3\text{O}_4/\text{rGO}$ Nanosheets

NiO and Co_3O_4 nanosheet ($350^\circ\text{C}/1\text{ h}/\text{air}$) cycling stabilities were studied at 1 A/g (Figure 5.37a, c). NiO nanosheets had an initial capacity of $\sim 1289\text{ mAh/g}$ that decreased to $\sim 85\text{ mAh/g}$ after 50 cycles, and then increased slowly to $\sim 139\text{ mAh/g}$ after 300 cycles. Capacity decline occurred in a similar manner as iron oxide and SnO_2 nanosheets, whereby electrode pulverization caused contact loss and capacity fading. Co_3O_4 nanosheets have an initial capacity of $\sim 968\text{ mAh/g}$ that decreased after the first 10 cycles to $\sim 310\text{ mAh/g}$. Interestingly, Co_3O_4 nanosheets showed capacity increase reaching $\sim 1066\text{ mAh/g}$ after 400 cycles. It was not clear why only Co_3O_4 nanosheets were able to maintain high capacity over cycling without rGO. This might be attributed to the higher

ability of Co nanoparticles formed during discharge to catalyze the decomposition of Li_2O during charging. However, this would need to be further investigated.

Figure 5.37. (a, c) Cycling and (b, d) rate performances of (a, b) NiO and NiO/rGO nanosheets, and (c, d) Co_3O_4 and $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets.

NiO/rGO (325 °C/1 h/air, 42.9 wt% rGO) and $\text{Co}_3\text{O}_4/\text{rGO}$ (325 °C/0.7 h/air, 21.9 wt% rGO) nanosheets had improved cycling performances (Figure 5.37a, c). NiO/rGO nanosheets showed initial capacity decline, followed by capacity increase reaching ~1624 mAh/g after 300 cycles. $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets also showed initial decline, then capacity increased reaching ~1642 mAh/g after 400 cycles, ~576 mAh/g higher than that achieved by Co_3O_4 nanosheets. The contribution of rGO was calculated to be ~16% and ~9% in the case of NiO/rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets at the 300th and 400th cycle, respectively.

NiO/rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheet rate performances were investigated (Figure 5.37b, d). NiO/rGO nanosheets achieved ~311 mAh/g at 5 A/g, as compared to ~24 mAh/g

attained by NiO nanosheets. $\text{Co}_3\text{O}_4/\text{rGO}$ and Co_3O_4 nanosheets retained ~ 113 and ~ 21 mAh/g, respectively, at 5 A/g. The contribution of rGO in the capacities of NiO/rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets at 5 A/g was calculated to be $\sim 44\%$ and 62% , respectively. The low rate performance of $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets might be attributed to the pronounced capacity decline it endured during the first 200 cycles, which overlapped with the rate performance test. This could have been caused by the relatively low rGO content in the nanocomposite.

NiO/rGO nanosheets achieved ~ 1039 , ~ 503 ~ 361 and ~ 311 mAh/g at 0.5, 2, 4 and 5 A/g respectively, which is comparable to NiO nanosheets/C [26] and NiO nanosheets/graphene [2], which have capacities of ~ 824 and ~ 492 mAh/g at 0.8 and 3.6 A/g, respectively, and better than NiO/graphene nanocomposites reported by Mai *et al.* [101] and Kottegoda *et al.* [102], which retained ~ 369 mAh/g at 0.8 A/g, and ~ 200 mAh/g at 3 A/g, respectively. $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets achieved ~ 986 , ~ 304 , ~ 150 and ~ 113 mAh/g at 0.5, 2, 4 and 5 A/g, respectively. These results are better than or comparable to those achieved by other $\text{Co}_3\text{O}_4/\text{graphene}$ nanocomposites, which have ~ 484 at 0.5 A/g [103], ~ 600 [104] and ~ 295 [105] mAh/g at 1 A/g. However, graphene-wrapped Co_3O_4 hollow spheres had better performance, achieving ~ 259 mAh/g at 5 A/g [75]. A comparison of NiO/rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheet performance to previously reported results is summarized in Table 5.6.

Insertion-based metal oxide nanosheets that operate by Li^+ intercalation/de-intercalation, such as Nb_2O_5 and TiO_2 nanosheets, have shown high capacity and very good cycling stability. Their performance, especially rate capability, was improved by rGO incorporation and doping. The excellent performance of the nanosheets could be attributed to the high surface area that improved contact with the electrolyte, the 2D nanostructure that helped to mitigate the mechanical damage caused by the continuous volume change, the small thickness that shortened Li^+ and electron diffusion paths, and the micron-sized lateral dimensions that provided continuous charge-transfer pathway. The improvement of rate performance upon rGO incorporation and doping could be

ascribed to the enhanced conductivity, where rGO sheets could facilitate electronic transfer at high current densities.

The metal oxide nanosheets operating by conversion reaction-based and alloying/de-alloying mechanisms suffered from rapid capacity decay, which is commonly observed for such materials. The nanosheet structure was not effective in mitigating the active material contact loss due to continuous pulverization. Metal oxide/rGO nanosheets synthesized by the mild calcination method showed dramatically improved performance, including capacity, cycling stability and rate capability. This was ascribed to the high conductivity of rGO sheets and their ability to buffer volume change and maintain electric contact with the current collector during cycling, thus mitigating pulverization-induced capacity loss.

5.2.2.2 Supercapacitors

Mn₃O₄ nanosheets (350 °C/1 h/air) demonstrated high capacitance and very good cycling stability as supercapacitor electrode (Figure 5.38a). The specific capacitance of Mn₃O₄ nanosheets increased during the initial 250 cycles, and then stabilized at ~140 F/g for 3000 cycles at 10 A/g. Mn₃O₄ activation over cycling has been reported previously, and was linked to the insertion/extraction processes taking place in crystalline Mn₃O₄ [106, 107].

CV (Figure 5.38b) and GCD (Figure 5.38c) were conducted after Mn₃O₄ nanosheet activation, at a potential range of 0–1 V vs. Ag/AgCl. The CV curves had symmetric rectangular shapes, indicating reversible capacitive behavior. GCD also showed pseudocapacitive curves, typical of Mn₃O₄. Specific capacitances were calculated based on the discharge curves after IR drop [15, 108] to be ~156, ~152, ~145 and ~133 F/g at 3, 5, 10 and 20 A/g, respectively (Figure 5.38d).

Manganese oxide/rGO nanosheets (325 °C/1 h/air, 25 wt% rGO) were also studied in an effort to improve the pseudocapacitive performance of manganese oxide. Although manganese/rGO nanosheets had better capacitance in the initial cycles, probably due to

the higher surface area, their activity degraded over cycling (data not shown). This could be attributed to the amorphous nature of manganese oxide in the nanocomposite, which was not able to undergo the insertion/extraction reaction-based activation process.

The performance of Mn_3O_4 nanosheets was compared to the literature. Activated Mn_3O_4 nanosheets had better performance, as compared to Mn_3O_4 nanocrystals [106] and Mn_3O_4 nanorods/graphene [109], which achieved ~ 46 and ~ 83 F/g, respectively, at 20 A/g. However, they have comparable or lower performance, as compared to Cr-doped Mn_3O_4 nanocrystals [106] and $\text{Mn}_3\text{O}_4/\text{C}$ nanoparticles [110], which achieved ~ 150 and ~ 180 F/g, respectively, at 10 A/g. A comparison of Mn_3O_4 nanosheet supercapacitor performance to the literature is summarized in Table 5.7.

The excellent performance of Mn_3O_4 nanosheets could be attributed to the high surface area, good contact with the electrolyte, fast charge transport and crystalline nature that allowed activation during the initial cycles.

Figure 5.38. (a) Cycling performance at 10 A/g, (b) CV curves, (c) GCD profiles, and (d) specific capacitance vs. current density plot of Mn_3O_4 nanosheets.

Table 5.4. Comparison of optimized Nb₂O₅ and TiO₂ nanosheet battery performance with the literature.

Material	Morphology	Current density (mA/g)	Specific capacity (mAh/g)	Reference
Nb ₂ O ₅ /rGO	Nanosheets	150	216	This work
		3000	120	
Nb ₂ O ₅ /C	Nanocrystals	200	160	[78]
		3000	100	
Nb ₂ O ₅	Nanosheets	200	184	[17]
		1000	90	
Nb ₂ O ₅	3D nanowire superstructure	200	165	[80]
		500	135	
Nb ₂ O ₅	Nanowires	100	209	[63]
		2000	175	
Nb ₂ O ₅ /C	Mesoporous nanocomposite	100	180	[64]
		5000	115	
Nb-TiO ₂ (10 at% Nb)	Nanosheets	85	338	This work
		168	268	
		3360	105	
TiO ₂	Microboxes	168	205	[81]
		3360	63	
TiO ₂	Cubes	85	201	[82]
		336	96	
TiO ₂	Hollow microspheres	85	215	[83]
		3360	88	
TiO ₂	Mesoporous microspheres	85	160	[84]
		1680	100	
TiO ₂ /G ^a	3D network	200	185	[85]
		2000	105	
TiO ₂	Porous microspheres	168	166	[67]
		3360	130	

^aG: Graphene

Table 5.5. Comparison of iron oxide/rGO and SnO₂/rGO nanosheet battery performance with the literature.

Material	Morphology	Current density (mA/g)	Specific capacity (mAh/g)	Reference
Iron Oxide/rGO	Nanosheets	500	1070	This work
		4000	480	
		5000	450	
Fe ₂ O ₃ /MWCNT ^a	Nanoparticles	500	400	[70]
		2000	320	
Iron oxide@C	Yolk-shell	200	820	[94]
		4000	370	
Iron oxide/G	Nanoparticles	1000	730	[95]
		5000	500	
Fe ₂ O ₃ /C	Bubble nanorods	500	913	[69]
		5000	491	
Fe ₃ O ₄ @C	Yolk-shell boxes	500	890	[96]
		5000	575	
SnO ₂ /rGO	Nanosheets	400	1131	This work
		1600	918	
		4000	713	
SnO ₂ /G	Nanoparticles in 3D foam	500	672	[98]
		3000	480	
SnO ₂ /G	Nanoparticles	500	1090	[72]
		1000	790	
SnO ₂ /G/polyaniline	Nanoparticles	500	530	[97]
		2000	240	
SnO ₂ @C	Submicroboxes	1000	583	[99]
		5000	372	
SnO ₂ /G	Quantum dots	780	1100	[100]
		3900	932	

^aMulti-walled carbon nanotubes.

Table 5.6. Comparison of NiO/rGO and Co₃O₄/rGO nanosheet battery performance with the literature.

Material	Morphology	Current density (mA/g)	Specific capacity (mAh/g)	Reference
NiO/rGO	Nanosheets	500	952	This work
		2000	503	
		5000	311	
NiO/C	Nanosheets	200	1043	[26]
		800	824	
NiO/G	Nanosheets	700	872	[2]
		3600	492	
NiO/G	Nanoparticles	400	509	[101]
		800	369	
NiO/G	Nanoparticles	450	400	[102]
		3000	200	
Co ₃ O ₄ /rGO	Nanosheets	500	986	This work
		2000	304	
		4000	150	
Co ₃ O ₄ /G	Nanoparticles	500	484	[103]
Co ₃ O ₄ /G	Nanoparticles	500	800	[104]
		1000	600	
Co ₃ O ₄ /G	Fibers	300	754	[105]
		1000	295	
Co ₃ O ₄ /G	Hollow spheres	1000	692	[75]
		5000	259	

Table 5.7. Comparison of Mn_3O_4 nanosheet supercapacitor performance with the literature.

Material	Morphology	Current density (mA/g)	Specific capacitance (F/g)	Reference
Mn_3O_4	Nanosheets	3000	156	This work
		10,000	145	
		20,000	133	
Mn_3O_4	Nanocrystals	10,000	55	[106]
		20,000	45	
$\text{Mn}_3\text{O}_4/\text{G}$	Nanorods	10,000	88	[109]
		20,000	83	
Cr-doped Mn_3O_4	Nanocrystals	10,000	150	[106]
		20,000	125	
$\text{Mn}_3\text{O}_4/\text{C}$	Nanoparticles	5000	250	[110]
		10,000	180	

5.3 Conclusion

A novel and generalized strategy for binary oxide nanosheet synthesis was developed using GO template. The facile nanosheet synthesis approach requires neither hydro/solvothermal reactions nor template removal processes. The GO planar-confined growth strategy was employed for the synthesis of a wide range of binary and doped binary oxide nanosheets, with their properties controlled by the synthesis conditions. The binary oxide nanosheets were used in energy storage applications, due to the unique energy storage capability of the 2D nanostructure. Insertion-based binary oxide nanosheets have shown impressive performance as LIB anodes, which was further improved by rGO incorporation and doping. Conversion reaction- and alloying/de-alloying-based binary oxide nanosheets suffered from capacity decay, which was reversed upon rGO incorporation, achieving very good LIB anode cycling stability and rate performance. Mn_3O_4 nanosheets have shown very promising pseudocapacitive activity, demonstrating high capacitance and excellent cycling stability and rate capability.

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Chapter 6

Synthesis of Ternary Oxide Nanosheets for High-Performance Li-Ion Battery Anodes

This chapter presents the extension of the nanosheet synthesis methodology discussed in Chapter 5 to include ternary oxide nanosheets. It demonstrates the applicability of the synthesis strategy to produce various ternary oxide nanosheets with controlled properties and rGO content. This is followed by discussion of the electrochemical characterization and performance evaluation of the ternary oxide nanosheets as Li-ion battery anodes. The nanosheet synthesis strategy showed remarkable versatility, such as producing TiNb_2O_7 and $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ ternary phases for the first time as nanosheets. The nanosheets showed very good energy storage performance.

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6.1 Introduction

Ternary oxides are promising Li-ion battery (LIB) anode materials as they offer new phases with unique Li^+ storage characteristics. For example, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been demonstrated as a safe and highly stable LIB anode with excellent rate capability [1]. Another recent example is TiNb_2O_7 , which was introduced in 2011 [2] as a safe LIB anode operating at > 1 V vs. Li^+/Li . TiNb_2O_7 has a high theoretical specific capacity of 387.6 mAh/g, which arises from its ability to intercalate 5 Li^+ per unit formula, making use of $\text{Ti}^{4+}/\text{Ti}^{3+}$, $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples [3]. In addition, ternary oxides, such as NiCo_2O_4 and MnCo_2O_4 , have better electrochemical and mechanical properties, as compared to binary oxides [4-7]. These ternary oxides store Li^+ by conversion reaction; hence, they are not regarded as new materials with unique Li^+ storage properties because the ternary phase decomposes during the first discharge leading to the formation of two different binary oxides. However, it has been argued that the presence of mixed oxides would improve LIB anode performance synergistically [8]. Ternary oxides can also reduce overall material cost and toxicity by partially substituting expensive and toxic metals such as Co with less expensive and more environmentally friendly metals, such as Ni and Mn [7-10].

Ternary oxide nanomaterials and nanocomposites have shown promising Li^+ storage performance. TiNb_2O_7 nanoparticles synthesized using SBA-15 template could retain 175 mAh/g after 300 cycles at 1C, and ~76 mAh/g at 10C [11]. Li *et al.* reported TiNb_2O_7 nanoparticles anchored to graphene sheets, which showed a remarkable rate performance, with a capacity of 136 mAh/g at 8C [12]. NiCo_2O_4 /reduced graphene oxide (rGO) nanocomposite has a stable performance at 0.1 A/g, achieving 816 mAh/g after 70 cycles. It could retain 396 mAh/g at 0.8 A/g [13]. MnCo_2O_4 nanosheet arrays have shown superior full-cell performance, as compared to Co_3O_4 nanosheets, mainly due to their lower average potential that resulted in higher full-cell output voltage [14]. MnCo_2O_4 /graphene nanocomposite achieved a capacity of ~865 mAh/g after 50 cycles at 0.2 A/g, and ~462 mAh/g at 4 A/g [15]. Graphene incorporation could improve the performance of ternary oxides by enhancing electrode conductivity, buffering volume change and preventing contact loss [12, 13, 15].

Ternary oxide energy storage performance could be improved by adopting the nanosheet morphology. This is due to the unique properties of the two-dimensional (2D) nanostructure that enhance the electrode electrochemical activity and stability [16-22]. For example, NiCo_2O_4 nanosheets, grown on rGO, showed very good LIB anode performance, achieving ~ 437 mAh/g at 1 A/g [23]. However, the synthesis of ternary oxide nanosheets is more difficult than that of binary oxide nanosheets, due to their more complex composition. For example, no report could be found for TiNb_2O_7 nanosheets, in spite of being a very promising LIB anode material. Facile methods for the synthesis of ternary oxide nanosheets need to be developed to advance their energy storage applications.

Several approaches have been previously reported for the synthesis of ternary oxide nanosheets. Exfoliation was used to synthesize ternary oxide nanosheets from their layered bulk counterparts. Titanium niobium oxide nanosheets, such as TiNbO_5^- and $\text{Ti}_2\text{NbO}_7^-$, were prepared by exfoliating protonated cation-exchangeable layered oxides, such as KTiNbO_5 and $\text{CsTi}_2\text{NbO}_7$, using tetra(n-butylammonium) hydroxide [24-26]. $[\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}]\text{O}_2$ nanosheets were synthesized by proton exchange of $\text{Li}[\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}]\text{O}_2$, followed by exfoliation using tetramethylammonium hydroxide [27]. Another strategy for ternary oxide nanosheet synthesis is the solvothermal approach, where the precursors are dissolved in an appropriate solvent such as hydroethanolic solution or ethylene glycol, and then reacted in autoclave forming an intermediate product, which is calcined to form the desired oxide [8, 14, 28]. Ternary oxide nanosheets were also synthesized by electrodeposition on conductive substrates. NiCo_2O_4 nanosheets were electrodeposited on Ni foam at a potential of -1.0 V vs. saturated calomel electrode, where Ni and Co reacted with OH^- that was formed during the electrochemical reaction, leading to the synthesis of nickel cobalt hydroxide, which was converted to the corresponding oxide by calcination [20]. Similar electrochemical deposition process was also reported for the synthesis of MnCo_2O_4 nanosheets [29].

Despite the promising energy storage performance of ternary oxide nanosheets, their current synthesis methods suffer from several limitations. Exfoliation is time consuming;

the process may take up to one month. It is also not environmentally friendly since it involves a protonation step using a concentrated acid solution [24, 25, 27]. In addition, this synthesis process is only limited to intrinsically layered oxides, such as TiNbO_5^- and $\text{Ti}_2\text{NbO}_7^-$. The solvothermal and electrodeposition methods are difficult to scale up and do not provide a general platform for ternary oxide nanosheet synthesis. Therefore, there is a lack of generalized methodology for the synthesis of ternary oxide nanosheets. Although several methods for the generalized synthesis of binary oxide nanosheets have been reported [30-35], they have not been extended to cover the more complex ternary oxides.

Herein, the GO planar-confined growth strategy was extended to synthesize ternary oxide nanosheets for LIB anodes. Metal oxide precursors were mixed with GO oxide at the desired ratios, followed by washing, drying and calcination, leading to the formation of ternary oxide nanosheets. The metal oxide precursor ratio and calcination conditions were used to control the composition, phase, crystallite size, surface area and porosity of the nanosheets. Ternary oxide/rGO nanosheets were also synthesized by mild calcination and opposite-charge method (OCM). The ternary oxide nanosheets were investigated as LIB anodes, with very good performance obtained.

6.2 Results and Discussion

6.2.1 Materials Characterization

6.2.1.1 Titanium Niobium Oxide Nanosheets

6.2.1.1.1 TiNb_2O_7 Nanosheets

TiNb_2O_7 nanosheets were synthesized using the GO planar-confined growth approach. It was shown in Chapter 5 that Nb_2O_5 nanosheets could be doped with Ti up to 25 at% Ti. It was observed that when Ti at% increased to ~33 at%, the phase changed from orthorhombic Nb_2O_5 to monoclinic TiNb_2O_7 (JCPDS #01-077-1374), with no remnant Nb_2O_5 phase or additional TiO_2 phase formation, as determined by X-ray diffractometry (XRD) (Figure 6.1g). The nanosheet morphology was shown by transmission electron microscopy (TEM) (Figure 6.1a), however, it appeared relatively thick and dense, which

could be attributed to the high calcination temperature of 700 °C. The TiNb_2O_7 phase was confirmed by high-resolution TEM (HRTEM) (Figure 6.1b), which showed its (110) plane, as well as by selected area electron diffraction (SAED) pattern (Figure 6.1c). Energy dispersive X-ray spectroscopy (EDX) mapping showed the uniform distributions of Ti (Figure 6.1e) and Nb (Figure 6.1f), confirming the absence of phase separation. X-ray photoelectron spectroscopy (XPS) Ti core level spectrum (Figure 6.1i) showed a peak doublet at 464.6 eV and 458.9 eV (separated by 5.7 eV), corresponding to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ of Ti^{4+} state, respectively [36, 37]. Nb core level spectrum (Figure 6.1j) showed a peak doublet at 210.0 eV and 207.3 eV (separated by 2.7 eV), corresponding to Nb $3d_{3/2}$ and Nb $3d_{5/2}$ of Nb^{5+} , respectively [38]. The chemical states of Ti and Nb agreed with previously reported results of TiNb_2O_7 [39]. The nanosheets were free from residual rGO content as shown by the thermogravimetric analysis (TGA) profile (Figure 6.1h). The thick and dense structure observed using TEM agreed with the fairly large crystallite size of 14.9 nm, the relatively low surface area of 23.8 m^2/g (Figure 6.2a) and low pore volume of 0.1 cm^3/g (Figure 6.2b). This was also reflected in the atomic force microscopy (AFM) analysis (Figure 6.2c), which showed that the nanosheets had a relatively large thickness of ~3.5 nm.

The ability of the GO planar-confined growth strategy to produce ternary oxide nanosheets showed that GO not only served as a template, but also as a substrate on which metal oxide precursors could react to form complex phases, while growing into a 2D nanostructure.

To the best of my knowledge, this is the first report of the synthesis of TiNb_2O_7 nanosheets. It shows the significance of the synthesis methodology; its broad applicability and versatility allow the facile synthesis of complex oxides as nanosheets for potential applications in various fields.

Figure 6.1. (a) TEM image, (b) HRTEM image, (c) SAED pattern, (d) STEM image, (e, f) EDX mapping images, (g) XRD pattern, (h) TGA profile, (i) XPS Ti 2p spectrum, and (j) XPS Nb 3d spectrum of TiNb_2O_7 nanosheets.

Figure 6.2. (a) Nitrogen adsorption-desorption isotherm, (b) pore size distribution, and (c) AFM profile of TiNb_2O_7 nanosheets.

6.2.1.1.2 $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ Nanosheets

The GO planar-confined growth methodology has shown much versatility, with nanosheet properties controllable by the synthesis conditions. It was previously demonstrated that calcination conditions could be tuned to control the nanosheet crystallinity. In this section, it is shown that they could also control the crystal structure of the nanosheets.

Upon using the same precursor ratio and synthesis conditions for TiNb_2O_7 nanosheets, but changing calcination conditions from 700 °C/ 1 h/ air to 700 °C/2 h/Ar, a different phase was obtained. Under the oxygen deficient conditions, $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO}$ nanosheets with tetragonal $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ phase were synthesized. This could be

attributed to the inert atmosphere that prevented further oxidation to TiNb_2O_7 . TEM (Figure 6.3a, b) showed the nanosheet morphology of the nanocomposite, which is composed of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanoparticles anchored to rGO sheets. The $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ phase (JCPDS #00-047-0024) was determined using XRD (Figure 6.3d), and was confirmed by HRTEM (Figure 6.3c) that showed its (110) plane. The full rGO content was retained in the nanocomposite because of the inert calcination conditions, and it was calculated to be 36.1 wt% using TGA (Figure 6.3e). XPS Ti (Figure 6.3f) and Nb (Figure 6.3g) core level spectra shifted to higher binding energies. This has been previously reported for rGO-incorporated nanocomposites, and has been attributed to the interaction between the residual oxygenated groups on rGO and the metal species, which resulted in electron density withdrawal from the metal species, leading to peak shift to higher binding energies [37, 40]. Ti core level spectrum showed the main peak doublet at 465.6 eV and 459.8 eV, corresponding to Ti $2p_{1/2}$ and Ti $2p_{3/2}$, respectively. Ti $2p_{3/2}$ peak was deconvoluted into two peaks at 459.9 eV and 458.9 eV, which could be assigned to Ti^{4+} and Ti^{3+} , respectively [41]. Nb core level spectrum doublet appeared at 210.8 eV and 208.1 eV, corresponding to Nb $3d_{3/2}$ and Nb $3d_{5/2}$, respectively. Nb $3d_{5/2}$ was deconvoluted into two peaks at 208.1 eV and 207.1 eV, which could be attributed to Nb^{5+} and Nb^{4+} , respectively [38]. The presence of the lower Ti and Nb oxidation states agreed with the oxygen deficient phase.

Pure $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets could be synthesized by removing rGO. This could be done by calcining the nanocomposite at 500 °C/1 h/air, which was enough to remove the rGO, leaving behind pure $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets (Figure 6.4a), free from residual rGO (Figure 6.4h). Interestingly, the $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ phase was still stable after calcination in air at 500 °C, as shown by XRD pattern (Figure 6.4g), HRTEM (Figure 6.4b) and SAED pattern (Figure 6.4c). EDX analysis showed the uniform distribution of Ti (Figure 6.4e) and Nb (Figure 6.4f) throughout the nanosheets. $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets have a relatively small crystallite size of 8 nm, and were mesoporous with an average pore size of 5 nm (Figure 6.4j). They also displayed a large pore volume of 0.23 cm^3/g and a high specific surface area of 98.7 m^2/g (Figure 6.4i). As far as I know, $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ tetragonal phase was not previously synthesized as nanosheets.

Figure 6.3. (a, b) TEM images, (c) HRTEM image, (d) XRD pattern, (e) TGA profile, (f) XPS Ti 2p spectrum, and (g) XPS Nb 3d spectrum of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO}$ nanosheets. Red arrow in (b) points to rGO sheet.

Figure 6.4. (a) TEM image, (b) HRTEM image, (c) SAED pattern, (d) STEM image, (e, f) EDX mapping images, (g) XRD pattern, (h) TGA profile, (i) nitrogen adsorption-desorption isotherm, and (j) pore size distribution of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets.

6.2.1.1.3 Titanium Niobium Oxide/rGO Nanosheets

TiNb₂O₇/rGO and Ti_{0.61}Nb_{1.29}O₄/rGO nanosheets were synthesized using OCM. TiNb₂O₇ and Ti_{0.61}Nb_{1.29}O₄ nanosheets had negative surface charges of ~-40 mV and ~-45mV, respectively. They reacted electrostatically with the positively charged GO-PDDA, followed by calcination in Ar, resulting in the formation of TiNb₂O₇/rGO and Ti_{0.61}Nb_{1.29}O₄/rGO nanosheets. The intimate contact between the metal oxide and rGO sheets is clearly observed in the TEM (Figure 6.5a, b) and EDX mapping images (Figure 6.5d–f, h–j). The monoclinic and tetragonal phases of TiNb₂O₇ and Ti_{0.61}Nb_{1.29}O₄, respectively, were not changed after rGO incorporation (Figure 6.5k, l). The rGO content was calculated using TGA (Figure 6.5m) to be 23.8 and 27.0 wt% for TiNb₂O₇/rGO-OCM and Ti_{0.61}Nb_{1.29}O₄/rGO-OCM, respectively.

6.2.1.2 Ni_xCo_{3-x}O₄ and Ni_xCo_{3-x}O₄/rGO Nanosheets

Ni_xCo_{3-x}O₄ nanosheets of different compositions were synthesized using the GO planar-confined growth strategy at 400 °C/1 h/ air. The nanosheet morphology was observed at all compositions (Figure 6.6a–d), and the uniform elemental distribution was confirmed by EDX mapping (Figure 6.6e–l). It was found that the Ni_xCo_{3-x}O₄ nanosheets synthesized using Ni:Co precursor molar ratios of 0.5, 1, 2 and 4 have actual Ni:Co molar ratios of 0.08, 0.22, 0.38 and 0.75, respectively, as calculated using EDX analysis. The discrepancy could be explained by the different affinity of both precursors to the GO surface, which led to different amounts of the precursors being retained after washing. These results showed that cobalt acetyl acetonate has ~5 times higher affinity than nickel acetyl acetonate towards the GO surface. XRD showed that Ni_{0.22}Co_{2.78}O₄ (Ni/Co = 0.08) crystallized into Co₃O₄ phase (JCPDS # 00-042-1467) (Figure 6.6m), while the compositions with higher Ni content crystallized into NiCo₂O₄ (JCPDS # 00-020-0781) phase (Figure 6.6n). In Ni_{0.22}Co_{2.78}O₄, Ni ions only replaced a portion of the cobalt ions in the Co₃O₄ phase. As the Ni/Co ratio increased, a phase change to NiCo₂O₄ (JCPDS # 00-020-0781) was necessary to accommodate more Ni ions. The ability to control the composition of the ternary oxide nanosheets demonstrated the versatility of the synthesis method, which allowed fine tuning of the composition for the intended application.

Figure 6.5. (a) TEM image, (c) STEM image, (d–f) EDX mapping images, (k) XRD pattern, and (m) TGA profile of $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets. (b) TEM image, (g) STEM image, (h–j) EDX mapping images, (l) XRD pattern, and (m) TGA profile of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ nanosheets. Red arrows in (a) and (b) point to rGO sheets.

$\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets were further synthesized using lower calcination conditions (350 °C/1 h/air and 325 °C/0.8 h/air) to obtain smaller crystallite size and higher rGO content. The nanosheet morphology was confirmed using TEM at both synthesis conditions (Figure 6.7a, d). The nanosheets synthesized at 350 °C/1 h/air crystallized into the NiCo_2O_4 phase as shown by XRD (Figure 6.7g), HRTEM (Figure 6.7b) and SAED (Figure 6.7c). They have a small crystallite size of 4.5 nm, however, they were almost devoid of rGO (Figure 6.7h). The nanosheets synthesized at 325 °C/0.8 h/air showed the oxide nanoparticles anchored to rGO sheets (Figure 6.7e). The rGO content was determined by TGA to be much higher (31.3 wt%) (Figure 6.7h). They showed relatively low crystallinity as demonstrated by the weak XRD peaks (Figure 6.7g) and faint SAED pattern (Figure 6.7f), however, their crystalline phase could still be determined to be NiCo_2O_4 , with a crystallite size of 4.2 nm.

6.2.1.3 $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ Nanosheets

$\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanosheets were synthesized at 500 °C/1 h/air using Mn/Co molar ratios of 0.05, 0.1, 0.15 and 0.2, with actual Mn/Co molar ratios of 0.56 and 1.12, 1.67 and 2.33, respectively. These results indicated the very high affinity of manganese acetyl acetonate to GO, where the actual Mn/Co molar ratio was always ~11 times that of the precursor molar ratio. TEM showed that the nanosheet morphology was obtained at all compositions (Figure 6.8a–d), and EDX mapping images demonstrated the uniform distribution of the elements (Figure 6.8e–l). The nanosheets crystallized into cubic Co_2MnO_4 (JCPDS #00-001-1130) and MnCo_2O_4 (JCPDS #00-023-1237) phases for $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ and $\text{Mn}_{1.58}\text{Co}_{1.42}\text{O}_4$, respectively (Figure 6.8m), and into tetragonal $(\text{Co},\text{Mn})(\text{Co},\text{Mn})_2\text{O}_4$ phase (JCPDS # 00-018-0408) for $\text{Mn}_{1.88}\text{Co}_{1.12}\text{O}_4$ and $\text{Mn}_{2.10}\text{Co}_{0.90}\text{O}_4$ (Figure 6.8n).

Figure 6.6. (a–d) TEM images, (e–l) EDX mapping images, and (m, n) XRD patterns of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanosheets synthesized at 400 °C/1 h/air.

Figure 6.7. (a) TEM image, (b) HRTEM image, (c) SAED pattern, (g) XRD pattern, and (h) TGA profile of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets synthesized at 350 °C/1 h/air. (d, e) TEM images, (f) SAED pattern, (g) XRD pattern, and (h) TGA profile of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ nanosheets synthesized at 325 °C/0.8 h/air.

$\text{Mn}_{1.88}\text{Co}_{1.12}\text{O}_4$ and $\text{Mn}_{2.10}\text{Co}_{0.90}\text{O}_4$ nanosheets showed some aggregation when calcined at 500 °C/1 h/air. However, this was prevented by synthesizing the nanosheets at the lower calcination conditions of 400 °C/1 h/air (Figure 6.9a, b). Interestingly, it was found that the nanosheets did not crystallize into the tetragonal spinel phase at the lower synthesis conditions. They crystallized into the cubic MnCo_2O_4 phase instead (Figure 6.9c). This implied that the cubic phase was crystallized first, followed by transition to the tetragonal phase at higher temperature. The important role of the synthesis conditions in the determination of the crystalline phase of spinel-type oxides has been previously reported [42].

Figure 6.8. (a–d) TEM images, (e–l) EDX mapping images, and (m, n) XRD patterns of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanosheets synthesized at 500 °C/1 h/air.

$\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets were selected for application as Li-ion battery anode. They were further characterized by HRTEM (Figure 6.10a) and SAED (Figure 6.10b) confirming their cubic MnCo_2O_4 phase. In addition, lower synthesis conditions of 325 °C/0.3 h/air were used for rGO incorporation. The nanosheets synthesized at 325 °C/0.3

h/air are shown in Figure 6.10c; a closer look revealed that the oxide nanoparticles were anchored to rGO sheets (Figure 6.10d). XRD (Figure 6.10e), HRTEM (Figure 6.10d: inset) and SAED (Figure 6.10c: inset) showed their cubic spinel phase. The crystallite size was calculated to be 5.3 nm, as compared to 6.3 nm for the nanosheets synthesized at 500 °C/1 h/air. The rGO content was calculated using TGA (Figure 6.10f), with 38.4 wt% rGO retained in the nanocomposite, as compared to ~2.9 wt% for the nanosheets synthesized at 500 °C/1 h/air.

Figure 6.9. (a, b) TEM images and (c) XRD patterns of $\text{Mn}_{1.88}\text{Co}_{1.12}\text{O}_4$ and $\text{Mn}_{2.10}\text{Co}_{0.90}\text{O}_4$ nanosheets synthesized at 400 °C/1 h/air.

The synthesis conditions and properties of TiNb_2O_7 , $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$, $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanosheets are summarized in Table 6.1.

Figure 6.10. (a) HRTEM image, (b) SAED pattern, and (f) TGA profile of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets synthesized at 500 °C/1 h/air. (c) TEM image (inset: SAED pattern), (d) magnified TEM image (inset: HRTEM image), (e) XRD pattern, and (f) TGA profile of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ nanosheets synthesized at 325 °C/0.3 h/air.

Table 6.1. Synthesis conditions and properties of ternary oxide nanosheets.

Metal oxide	Precursor	Calcination conditions ^a	Crystal structure	Crystallite size (nm) ^b	rGO content (wt%)	BET specific surface area (m ² /g)
TiNb ₂ O ₇	Ti(IV) butoxide Nb(V) ethoxide	700 °C/1 h	Monoclinic	14.9	0.0	23.8
Ti _{0.61} Nb _{1.29} O ₄	Ti(IV) butoxide Nb(V) ethoxide	500 °C/1 h ^c	Tetragonal	8.0	0.0	98.7
Ni _{1.29} Co _{1.71} O ₄ / rGO	Ni(II) + Co(II) acetylacetonate	325 °C/0.8 h	Cubic	4.2	31.3	85.9
Ni _{1.29} Co _{1.71} O ₄	Ni(II) + Co(II) acetylacetonate	350 °C/1 h	Cubic	4.5	3.0	67.8
Mn _{1.08} Co _{1.92} O ₄ / rGO	Mn(II) + Co(II) acetylacetonate	325 °C/0.3 h	Cubic	5.3	38.4	49.4
Mn _{1.08} Co _{1.92} O ₄	Mn(II) + Co(II) acetylacetonate	500 °C/1 h	Cubic	6.8	2.9	41.5

^aCalcination in air. ^bBased on (020) peak of TiNb₂O₇ and strongest peak of the other ternary oxides. ^cPre-calcined at 700 °C/2 h/Ar.

6.2.2 Electrochemical measurements

6.2.2.1 TiNb₂O₇ and TiNb₂O₇/rGO Nanosheets

Cyclic voltammetry (CV) was conducted at 1–3 V to study the redox processes of TiNb₂O₇ and TiNb₂O₇/rGO-OCM (23.8 wt% rGO) nanosheets. It was observed that the cathodic peaks of TiNb₂O₇ underwent negative shift over cycling, indicating electrode polarization (Figure 6.11a). This was absent after the introduction of rGO (Figure 6.11b), possibly due to the enhanced conductivity, as inferred from the electrochemical impedance spectroscopy (Figure 6.11c), where TiNb₂O₇/rGO-OCM had smaller semi-circle and higher slope in the middle and low frequency regions, indicating lower charge transfer resistance and better Li⁺ diffusion, respectively. The main cathodic and anodic peaks appeared at 1.49 V and 1.74 V, respectively, which were assigned to Nb⁵⁺/Nb⁴⁺ redox couple. A weak pair of redox peaks could be seen at 1.83 V and 1.97 V,

corresponding to $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple. The redox reactions involving $\text{Nb}^{4+}/\text{Nb}^{3+}$ couple could take place at 1–1.4 V. The prominence of the $\text{Nb}^{5+}/\text{Nb}^{4+}$ redox peaks, and the weakness of those of $\text{Ti}^{4+}/\text{Ti}^{3+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples agreed with previously reported results [12].

Figure 6.11. (a, b) CV curves conducted at 0.1 mV/s, (c) Nyquist plots, and (d) GCD profile at 1C of (a, c, d) TiNb_2O_7 and (b, c) $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets.

Galvanostatic charge-discharge (GCD) profile of TiNb_2O_7 nanosheets was studied at 1C (Figure 6.11d), with the sloping GCD curves in agreement with the broad CV peaks. TiNb_2O_7 nanosheets had an initial discharge capacity of ~ 255 mAh/g at 1C ($1\text{C} = 387$ mAh/g), which decreased to ~ 242 and ~ 234 mAh/g for the second and third cycles, respectively, while showing high Coulombic efficiency of 97–98%. Charge storage mechanism was determined by the analysis of CV data at increasing scan rates using Eq. 3.4. It was found that the b -value = 0.67 and 0.76 for TiNb_2O_7 and $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets, respectively (Figure 6.12). This showed that the charge storage mechanism is both diffusion-controlled and capacitive. The capacitive contribution indicated good rate

performance [43], and its enhancement upon rGO introduction predicted its ability to improve the rate capability.

Figure 6.12. Log anodic peak current vs. log scan rate plots of TiNb_2O_7 and $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets.

TiNb_2O_7 nanosheets had a relatively stable cycling performance at 1C (Figure 6.13a), showing a capacity of ~144 mAh/g after 100 cycles, which slightly improved upon rGO incorporation, reaching ~151 mAh/g. The high Coulombic efficiency of 99–100% shown by $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets after the first few cycles indicated very good stability profile. The rate study (Figure 6.13b) showed that TiNb_2O_7 and $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets had similar performance at the relatively low rates of 0.5C and 1C, however, $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets have better performance at higher rates, achieving ~137, ~103 and ~84 mAh/g, as compared to ~120, ~83 and ~63 mAh/g shown by TiNb_2O_7 nanosheets, at 5C, 10C and 15C, respectively. This could be ascribed to the higher conductivity of $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets.

$\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets showed better performance than TiNb_2O_7 nanofibers [44] and TiNb_2O_7 nanoparticles [11] (which achieved ~150 and ~76 mAh/g at 2.6C and 10C, respectively), and have comparable performance to $\text{TiNb}_2\text{O}_7/\text{graphene}$ nanocomposite [12] and $\text{TiNb}_2\text{O}_7/\text{C}$ microwires [45] (which have capacities of 136 and ~75 mAh/g at 8C and 15C, respectively) (Table 6.2). However, $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets' rate capability was lower than that of TiNb_2O_7 microspheres [46] and nanoporous TiNb_2O_7 [47], which achieved ~100 and 195 mAh/g at 20C.

Figure 6.13. (a) Cycling and (b) rate performances of TiNb_2O_7 and $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets.

6.2.2.2 $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO}$ Nanosheets

After the introduction of TiNb_2O_7 as Li-ion battery anode, several other titanium niobium oxides such as $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ [43, 48, 49], $\text{TiNb}_6\text{O}_{17}$ [50] and $\text{Ti}_2\text{Nb}_2\text{O}_9$ [51] were reported. Although some of these oxides have very promising performance, for example $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (theoretical capacity = 396 mAh/g) achieved 132 and 50 mAh/g at 20C (7.9 A/g) and 50C (19.8 A/g), respectively [43], studies on these materials remained limited.

$\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ with the tetragonal $\text{Ti}_{0.95}\text{Nb}_{1.95}\text{O}_4$ crystal structure has not been previously studied as LIB anode. However, it is a promising material due to its high theoretical capacity of 401.5 mAh/g, assuming the involvement of $\text{Nb}^{5+}/\text{Nb}^{4+}$, $\text{Nb}^{4+}/\text{Nb}^{3+}$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couples. In this section, $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ nanosheets as LIB anodes were examined.

CV of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets showed two main peaks at 1.55 V and 1.82 V (Figure 6.14a, b), which could be attributed to $\text{Nb}^{5+}/\text{Nb}^{4+}$ redox couple, as previously shown for TiNb_2O_7 . However, no other peaks were observed, which could be due to their broad and weak nature. Interestingly, the charge storage mechanism also involved a capacitive contribution as indicated by the b-value of 0.69, which increased to 0.77 upon rGO incorporation (Figure 6.14c). $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets had a sloping GCD profile at 0.5C (Figure 6.14d), with an initial discharge capacity of ~253 mAh/g that decreased to ~189,

~184 and ~182 mAh/g in subsequent cycles. A high Coulombic efficiency of 94–97% was maintained after the first cycle, showing the reversibility of Li^+ insertion/extraction processes.

Figure 6.14. (a, b) CV curves conducted at 0.1 mV/s, (c) log anodic peak current vs. log scan rate plots and (d) GCD profile at 1C of (a, c, d) $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ and (b, c) $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ nanosheets.

$\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets showed a very promising LIB performance. They had a stable cycling performance at 0.5C (Figure 6.15a), reaching ~149 mAh/g after 100 cycles. rGO incorporation did not improve the electrode performance at low rates, however, $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ has better performance at high rates (Figure 6.15b), achieving ~66 and ~40 mAh/g, as compared to ~47 and ~20 mAh/g obtained by pure $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets, at 15C and 25C, respectively. $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ has a comparable rate performance as $\text{TiNb}_2\text{O}_7/\text{rGO-OCM}$ nanosheets, indicating that $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ is a very promising LIB anode material.

Figure 6.15. (a) Cycling and (b) rate performances of $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4/\text{rGO-OCM}$ nanosheets.

6.2.2.3 $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ Nanosheets

$\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets synthesized at 350 °C/1 h/air were analyzed using CV (Figure 6.16a) and GCD (Figure 6.16b). The main cathodic CV peak appeared at ~0.72 V during the initial discharge, which was ascribed to the decomposition of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ forming metallic Ni and Co within Li_2O matrix, and also to SEI formation [52]. This peak showed marked decrease in intensity and shifted to ~1 V during the second and third cycles. The lower intensity is due to the irreversible SEI formation taking place during the first cycle, while the peak shift could be due to an initial activation process [23]. The anodic peaks at ~1.5 V and ~2.2 V were attributed to partial SEI decomposition [53] and metallic Ni and Co oxidation [8], respectively. GCD profile showed discharge and charge plateaus in agreement with the CV cathodic and anodic peaks, respectively. On the basis of this analysis, the reactions taking place during lithiation and de-lithiation could be expressed as follows [8, 52],

$\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets had a high initial discharge capacity of ~ 1528 mAh/g at 0.1 A/g, but with a low Coulombic efficiency of $\sim 70\%$ due to SEI formation. The second and third cycles showed discharge capacities of ~ 1108 and ~ 1062 mAh/g, with relatively high Coulombic efficiencies of $\sim 93\%$ and $\sim 95\%$, respectively, indicating better stability.

Figure 6.16. (a) CV curves conducted at 0.1 mV/s and (b) GCD profile at 0.1 A/g of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets.

$\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets had a poor cycling stability profile at 1 A/g (Figure 6.17a). Capacity declined rapidly during the initial 50 cycles, reaching ~ 116 mAh/g. Similar to other conversion reaction-based materials discussed in Chapter 5, introduction of rGO (31.3 wt%) to $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ by adjusting the calcination conditions to $325^\circ\text{C}/0.8$ h/air dramatically improved the cycling performance. The capacity initially declined to ~ 360 mAh/g during the first 30 cycles, and then it increased to ~ 1454 mAh/g after 300 cycles, while maintaining a high Coulombic efficiency of 98–100%. The contribution of rGO to the capacity of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ nanosheets was calculated to be $\sim 13\%$ at the 300th cycle. Capacity increase over cycling has been previously discussed in Section 5.2.2.1.2.3.

Rate capability of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ nanosheets was studied at a current density range of 0.5–5 A/g (Figure 6.17b). They retained ~ 128 and ~ 48 mAh/g, which improved to ~ 291 and ~ 147 mAh/g upon rGO incorporation, at 2 and 4 A/g, respectively.

$\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ has a high capacity of ~ 913 mAh/g at 0.5 A/g, which was better than or comparable to that achieved by other $\text{NiCo}_2\text{O}_4/\text{rGO}$ nanocomposites [13, 23, 52]. $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ nanosheets had comparable or slightly lower performance at higher rates, where the NiCo_2O_4 nanoplates/rGO [13], NiCo_2O_4 nanosheets/multiwall carbon nanotubes [52] and NiCo_2O_4 nanosheets/rGO [23] achieved 396, 392 and ~ 437 mAh/g at 0.8 A/g, 1 A/g and 1 A/g, respectively (Table 6.2). However, $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ nanosheet rate capability would still need improvement, which could be achieved by reducing the large capacity decline observed during the initial cycles, by further increasing the rGO content or tuning the Ni/Co molar ratio.

Figure 6.17. (a) Cycling and (b) rate performances of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ nanosheets.

6.2.2.4 $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ Nanosheets

$\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets synthesized at $500^\circ\text{C}/1$ h/air were electrochemically studied using CV and GCD. The initial CV cathodic scan (Figure 6.18a) showed a broad peak at ~ 1.4 V and a sharp peak at ~ 0.55 V. The former was attributed to Li^+ insertion into the lattice and reduction of Co^{3+} to Co^{2+} , while the latter was ascribed to the decomposition of the material forming Li_2O with embedded metallic Mn and Co [6, 15]. The cathodic reduction potential shifted to ~ 0.88 V during the second cycle as a result of material activation [6, 54]. The anodic peaks at ~ 1.5 and ~ 2 V could be due Mn and Co oxidation, respectively [6, 9, 55]. The entire electrochemical process could be expressed as follows [6, 9, 54],

GCD of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets (Figure 6.18b) showed a large initial discharge capacity of ~ 1818 mAh/g, with a low Coulombic efficiency of $\sim 64\%$ due to SEI formation. Capacity decreased to ~ 1254 and ~ 1160 mAh/g during the second and third cycles, with Coulombic efficiencies of $\sim 87\%$ and $\sim 90\%$, respectively.

Figure 6.18. (a) CV curves conducted at 0.1 mV/s and (b) GCD profile at 0.1 A/g of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets.

$\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets had poor cycling stability at 1 A/g (Figure 6.19a), which is similar to other conversion reaction-based materials. The capacity declined rapidly over the initial 50 cycles reaching ~ 177 mAh/g, and then it slightly increased over cycling reaching ~ 265 mAh/g after 300 cycles. $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ nanosheets synthesized at $325^\circ\text{C}/0.3$ h/air with 38.4 wt% rGO were employed to improve the cycling stability. The initial capacity decline occurred as well, but to a lower extent, with a capacity of ~ 400 mAh/g retained after 50 cycles. This was followed by capacity increase reaching ~ 1497 mAh/g after 300 cycles, with a high Coulombic efficiency of 99–100% maintained over cycling.

Rate capability of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets was improved by rGO incorporation (Figure 6.19b). A low rate performance was shown by $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets, which achieved ~ 178 , ~ 63 and ~ 45 mAh/g at 2, 4 and 5 A/g, respectively. The performance was improved upon rGO introduction to ~ 372 , ~ 196 and ~ 160 mAh/g, respectively. However,

the rate performance was still relatively low compared, for example, to $\text{MnCo}_2\text{O}_4/\text{graphene}$ nanocomposite, which achieved $\sim 462 \text{ mAh/g}$ at 4 A/g [15] (Table 6.2). The rate performance could be further improved by reducing the capacity decline during initial cycling.

Figure 6.19. (a) Cycling and (b) rate performances of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ nanosheets.

Ternary oxide nanosheets operating by intercalation/de-intercalation mechanism have shown very promising performance. TiNb_2O_7 and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets showed stable cycling and very good rate capability, which were attributed to the small thickness and 2D structure that facilitated charge transport and mitigated volume change. In addition, the incorporation of rGO allowed for a better performance at high rates.

The conversion reaction-based ternary oxide nanosheets had low cycling stability, which was improved by rGO incorporation. $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets showed similar performance to Co_3O_4 nanosheets discussed in Chapter 5, where they suffered from severe capacity decay, leading to low cycling stability. This was mitigated by rGO incorporation; ternary oxide/rGO nanosheets showed less capacity decline, followed by capacity increase. The enhanced cycling performance was mainly due to the ability of rGO sheets to prevent pulverization-induced contact loss and improve conductivity. Nevertheless, the initial capacity decline still resulted in low performance during the rate studies. Thus, further improvement would be needed to reduce the initial capacity decline and improve the rate capability. Although $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and

$\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets did not show performance improvement, as compared to Co_3O_4 nanosheets, the toxic and expensive cobalt was partially replaced with more affordable and environmentally friendly metals, which was one of the objectives of using ternary oxides. In addition, the relatively lower average redox potential of $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ could increase the output voltage in a full cell.

6.3 Conclusion

The GO planar-confined growth strategy was used for the synthesis of ternary oxide nanosheets. The synthesis methodology was used for the production of various types of nanosheets, demonstrating its broad applicability for ternary oxide nanosheet synthesis, which is rare in previously reported methods. In addition, the synthesis conditions were used to control the nanosheet properties, such as composition, phase and rGO content, demonstrating versatility and adaptability to the intended application. LIB anode insertion-based ternary oxide nanosheets, including TiNb_2O_7 and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ achieved high capacity and stable performance, which was further improved by rGO incorporation, especially at high current densities. Conversion reaction-based ternary oxide nanosheets, including $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ showed pulverization-induced capacity decay, which was mitigated by rGO incorporation, achieving high capacities over prolonged cycling and better rate capability. However, their rate capability would need further improvement, such as by tuning the ratio between the metal constituents, and increasing the rGO content.

Table 6.2. Comparison of ternary oxide nanosheet battery performance with the literature.

Material	Morphology	Current density (mA/g)	Specific capacity (mAh/g)	Reference
TiNb ₂ O ₇ /rGO	Nanosheets	194	263	This work
		1940	150	
		5810	89	
TiNb ₂ O ₇ /G ^a	Nanoparticles	1550	156	[12]
		3100	136	
TiNb ₂ O ₇	Nanoparticles	1940	130	[11]
		3870	76	
TiNb ₂ O ₇	Nanofibers	200	240	[44]
		1000	150	
TiNb ₂ O ₇ @C	Microwires	2000	140	[45]
		6000	75	
TiNb ₂ O ₇	Microspheres	194	270	[46]
		7750	100	
TiNb ₂ O ₇	Nanoporous framework	1940	236	[47]
		7740	195	
Ni _{1.29} Co _{1.71} O ₄ /rGO	Nanosheets	500	913	This work
		2000	291	
NiCo ₂ O ₄ /MWCNTs ^b	Nanosheets	100	836	[52]
		1000	392	
NiCo ₂ O ₄ /rGO	Nanoplates	500	521	[13]
		800	396	
NiCo ₂ O ₄ /rGO	Nanosheets	100	1200	[23]
		1000	437	
NiCo ₂ O ₄	Nanowire arrays on carbon textiles	1000	800	[7]
		3000	600	
Mn _{1.08} Co _{1.92} O ₄ /rGO	Nanosheets	500	1020	This work
		2000	372	
		4000	196	
MnCo ₂ O ₄	Spheres	800	571	[6]
MnCoO _x	Microspheres	500	698	[55]
		1500	417	
MnCo ₂ O ₄	Microspheres	400	814	[9]
		1800	513	
MnCo ₂ O ₄ /G ^a	Nanoparticles	1000	853	[15]
		4000	462	

^aG: graphene. ^bMWCNTs: multiwall carbon nanotubes.

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Chapter 7

Discussion and Future Work

This chapter interlinks the concepts and strategies used throughout the thesis, and reflects on the results obtained. The motivation and research work are briefly summarized, followed by a deep reflection on the results, emphasizing the validity of the concepts guiding the dissertation, and the suitability of the approaches used. Future work is suggested based on questions and opportunities presented by the results. In situ transmission electron microscopy analysis would be a useful tool to help us understand the performance of the conversion-based metal oxide nanosheets. The promising pseudocapacitive activity shown by the nanosheets has sparked an interest in investigating other metal oxide compositions as supercapacitors. The high rate performance achieved by the insertion-based metal oxide nanosheets renders them very promising for hybrid supercapacitors. The new contributions of this thesis are the development of novel and facile methods for the synthesis of nickel sulfide and graphene-wrapped nickel sulfide nanopyramids, in addition to a wide variety of binary, doped binary and ternary oxide nanosheets, including ternary phases being reported for the first time as nanosheets, with optimized characteristics for energy storage.

7.1 Discussion

This thesis is an attempt to address the world's energy problem by the synthesis of high-performance energy storage materials. We are facing great challenges due to oil production instability, heavy urban pollution and accelerated global warming. This has resulted in a major shift in energy policies towards renewable energy and green transport. Enhancing the contribution of wind and solar energy to the power grid, and reducing vehicle emissions would help to reduce dependence on oil, alleviate urban pollution and decelerate global warming. One of the main bottlenecks of going green is energy storage, which is needed to store the intermittent renewable energy and power electric vehicles. The energy storage problem can be further narrowed down to energy storage materials, which are the main impediment to a greener future.

Li-ion batteries (LIBs) and supercapacitors (SCs) are promising energy storage systems. LIBs have evolved since the 1970's to become the dominant technology for portable energy storage, mainly due to their large energy density. SCs provide a complementary technology, which is suitable for special applications requiring high power density, such as vehicle acceleration.

Electrode materials of LIBs and SCs need improvement. The electrode materials are responsible for the energy and power densities of the system. Current LIB electrode materials are limited in terms of storage capacity and rate capability. For example, the conventional graphite anode can store only 372 mAh/g, in addition, it has poor rate performance, and suffers from safety issues. SC electrode materials have limited energy density that hinders their practical application. There is a need for the development of novel high-performance energy storage materials, with improved capacity, stability and rate capability.

Size, morphology and carbon incorporation are key in the quest for high-performance energy storage. It has been found that material synthesis at the nanoscale has several advantages for energy storage, including enhanced charge transport, higher contact with the electrolyte and better strain accommodation. Morphology is another important aspect

when optimizing material performance. For example, it can help to improve charge transport and stabilize cycling performance, as in the case of two-dimensional (2D) materials. In addition, designing a secondary structure that is composed of primary nanoparticles can help to overcome some of the limitations of nanoparticles, such as instability, loose inter-particle contact and low density. Carbon is a necessary pillar for building a high-performance energy storage electrode, as it provides a conductive matrix that improves conductivity, buffers volume change, and prevents contact loss during cycling.

The main aim of this thesis is to synthesize nanomaterials and nanocomposites with controlled morphology and properties for high-performance energy storage. Although many studies have investigated nanomaterials for energy storage, nanomaterial synthesis and performance optimization are still challenging. Further work is needed to synthesize nanomaterials and nanocomposites with the desired structures using facile methods, and to optimize their properties to achieve high-performance energy storage, in terms of capacity, cycling stability and rate capability.

In this thesis, nanomaterials and nanocomposites with controlled characteristics have been synthesized using novel and facile methods, and applied as LIB anodes and SC electrodes with very promising performance. In Chapter 4, nickel sulfide and graphene-wrapped nickel sulfide nanopyramids were synthesized using a one-pot colloidal approach, showing very promising energy storage performance. In Chapter 5, a wide variety of binary oxide nanosheets were synthesized using a template-assisted method. They have shown very good energy storage performance, which was further optimized by tuning the nanosheets' properties, such as composition, crystallinity, surface area and reduced graphene oxide (rGO) content. In Chapter 6, the nanosheet synthesis methodology was extended to produce ternary oxide nanosheets. The ability of the method to control the compositions and phases of such complex oxides was demonstrated, and their properties were optimized for enhanced LIB anode performance.

7.1.1 Reflection on the Synthesis and Energy Storage Performance of Nickel Sulfide and Graphene-Wrapped Nickel Sulfide Nanopyramids

Nickel sulfide is a very promising energy storage material, with high LIB anode capacity and very good pseudocapacitive activity. Several reports have demonstrated its promising energy storage performance. However, it was found that most of the reported synthesis methods used the hydro/solvothermal approach, which resulted in non-uniform and relatively large particles, or special methods such as spray pyrolysis and electrospinning. Moreover, the synthesis procedure was sometimes complicated by additional steps for precursor synthesis and sulfurization.

The colloidal synthesis approach is promising for energy storage applications. It is able to synthesize monodisperse nanoparticles with controlled morphology and high crystallinity. The organic medium used in the synthesis may also result in the formation of a thin carbon coating upon calcination in inert conditions. These make the colloidal approach appealing for the synthesis of energy storage materials. For example, iron, cobalt and copper sulfides have achieved very good performance when synthesized by the colloidal synthesis method.

In Chapter 4, nickel sulfide nanopyramids were synthesized using a colloidal thermal decomposition method. Monodisperse nanocrystals with nanopyramidal shape were produced in a facile one-step method. The surface-adsorbed organic moieties were carbonized by calcination in Ar. Moreover, the nanocrystals were uniformly anchored to graphene surface using the same method. The nickel sulfide nanopyramids and nickel sulfide/graphene nanocomposite were used as LIB anodes and supercapacitor electrodes.

Nickel sulfide nanopyramids achieved a very high initial capacity as LIB anode; however, they suffered from severe capacity decay due to electrode pulverization. This problem was solved by anchoring the nanocrystals to graphene sheets, which buffered volume change and prevented contact loss, resulting in enhanced cycling performance and rate capability. Nickel sulfide nanopyramids also have very good pseudocapacitive activity, which was shown to be better than that of many of the reported nickel sulfide

nanomaterials. The performance at high rates was further improved upon the introduction of the graphene sheets.

Although nickel sulfide nanopyramids showed fast capacity decay as LIB anode, requiring graphene wrapping to improve their performance, they have very good pseudocapacitive activity, even without introducing graphene. This could be explained by the different mechanisms involved in the two energy storage systems. Nickel sulfide stores Li^+ by conversion reaction-based mechanism that involves its reduction to metallic Ni during discharge and oxidation during charge, which puts much stress on the material, resulting in electrode pulverization and contact loss from the current collector. On the other hand, as SC, nickel sulfide stores charge through Faradaic reactions occurring mostly on the surface, without a major change in the chemical composition or physical properties, resulting in greater stability over cycling. Nevertheless, the nanocrystal anchoring to graphene helped to improve the SC performance at high current densities, which could be attributed to enhanced electronic conductivity, rather than the ability of graphene to stabilize the material during cycling.

Nanomaterial structure played an important role in energy storage performance optimization. It was shown that anchoring the nickel sulfide nanopyramids to graphene sheets enhanced their energy storage performance. The graphene sheets provided a highly conductive 2D platform on which the well-dispersed nickel sulfide nanoparticles have good contact with the electrolyte, high inter-particle contact and improved contact with the current collector. The use of nanocomposite, which has good contact between its constituents, solved the material stability problem that was associated with the LIB anode, and improved the rate capability of the SC electrode.

The colloidal thermal decomposition approach led to nickel sulfide nanopyramids with nanosize, uniform size distribution and high crystallinity. These nanoparticles were also well dispersed when anchored to the graphene sheets. These material characteristics resulted in very promising energy storage performance. It would be of interest to extend

the colloidal approach to synthesize other metal sulfide and oxide nanomaterials with controlled size, morphology and phase for various applications.

7.1.2 Reflection on the Generalized Synthesis of Binary Oxide Nanosheets for Energy Storage

The nanosheet morphology is able to enhance material electrochemical performance by buffering volume change during cycling, improving charge transport and increasing contact with the electrolyte. These characteristics have driven the investigation of the nanosheet morphology of different materials for energy storage, including metal oxides. Metal oxide nanosheets have demonstrated very promising performance as LIB anodes and supercapacitors.

Establishing a generalized synthesis method for binary oxide nanosheets is quite challenging. Several methods have been investigated, such as exfoliation and hydro/solvothermal methods; however, these methods are material-specific and not easily scalable. Template-assisted synthesis is promising for generalized metal oxide nanosheet synthesis; however, the current methods are laborious and not easily scalable.

A generalized strategy for the synthesis of binary oxide nanosheets was demonstrated in Chapter 5. The method is facile, involving the deposition of metal oxide precursors on the surface of GO template, followed by air calcination, which promotes the growth of oxide in 2D nanostructure and removes the carbonaceous template simultaneously. The GO planar-confined growth strategy could produce a wide variety of binary oxide and doped binary oxide nanosheets. Moreover, the nanosheets' attributes could be tuned by varying the calcination conditions.

The binary oxide nanosheets demonstrated very good cycling performance and rate capability as high-voltage LIB anodes, operating through Li^+ intercalation/de-intercalation. As for the materials operating through conversion and/or alloying/de-alloying mechanisms (high-capacity anodes), the nanosheets achieved high initial capacity; however, the capacity declined rapidly due to severe volume change, electrode

pulverization and contact loss. Mn_3O_4 nanosheets demonstrated high capacitance, cycling stability and rate capability as SC.

The nanosheets' properties were optimized to enhance their energy storage performance. High-voltage anodes were modified by rGO incorporation and doping, which improved their LIB anode performance, especially at high current densities. High-capacity anode nanosheets were modified by rGO incorporation, which minimized rapid capacity fading and improved cycling stability dramatically. The rate capability of the nanocomposites was superior to that of the nanosheets, and very promising capacities were attained at high current densities.

The nanosheet synthesis methodology was versatile and could be used to synthesize various binary oxide nanosheets, and also to introduce dopants at the desired levels. Moreover, the nanosheets' characteristics such as crystallinity, crystallite size, surface area, porosity and rGO content could be controlled simply by changing the calcination conditions. The versatility enables the production of metal oxide nanosheets with the desired properties for different applications. For example, the LIB anode performance of the nanosheets was improved by doping and rGO incorporation, which was done simply by introducing the dopant precursors to the synthesis mixture and varying the calcination conditions, respectively.

The nanosheet synthesis can be scaled up easily. Although the yield of binary oxide nanosheets varied depending on the metal oxide and the precursor used, this could be worked around by recycling the excess precursors.

7.1.3 Reflection on the Synthesis of Ternary Oxide Nanosheets for LIB Anodes

Ternary oxide nanosheets are very promising Li^+ storage materials, but challenging to synthesize. Ternary oxide phases have shown unique Li^+ storage properties, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiNb_2O_7 . They were also reported to be more electrochemically active than binary oxides, which make them promising LIB anode materials. Adopting the nanosheet morphology could further improve the ternary oxide's electrochemical properties.

However, the lack of facile and generalized synthesis of ternary oxide nanosheets was an obstacle to their widespread applications in energy storage.

In Chapter 6, the GO planar-confined growth strategy was used for the synthesis of various types of ternary oxide nanosheets, which showed high performance as LIB anodes. The versatile synthesis method allowed for the formation of complex ternary phases, while retaining the nanosheet morphology. Moreover, the synthesis conditions could be varied to control the nanosheets' crystal structure, and to optimize their characteristics, such as rGO content. High-voltage anode nanosheets (TiNb_2O_7 and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$) showed very good energy storage performance, and their high-rate capacities were improved by rGO incorporation. $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets suffered from rapid capacity decay, as shown previously by other conversion reaction-based materials, which was alleviated by rGO incorporation to yield very good cycling stability. However, $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ nanosheets showed relatively low rate performance, similar to that shown by $\text{Co}_3\text{O}_4/\text{rGO}$ nanosheets, which was attributed to the deep and prolonged initial capacity decline.

In the cases of $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets, pulverization induced initial decline in capacity. This might have masked the electrochemical activity of these ternary oxide phases, resulting in relatively low rate performance (as for Co_3O_4 nanosheets). However, the partial replacement of cobalt ions with less expensive and more environmentally friendly Ni and Mn ions was a positive feature of these nanosheets. In addition, the relatively lower average potential shown by $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$ nanosheets, as compared to Co_3O_4 , can increase the full-cell output voltage.

GO planar-confined synthesis methodology could advance ternary oxide nanosheet-based applications. For example, the GO planar-confined growth strategy allowed the synthesis of TiNb_2O_7 and $\text{Ti}_{0.61}\text{Nb}_{1.29}\text{O}_4$ nanosheets, which showed very promising performance as LIB battery anodes. To the best of my knowledge, this is the first report of the synthesis of TiNb_2O_7 and $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ phases as nanosheets. It is also the first report of the investigation of $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ phase as LIB anode. It demonstrates the potential of the

ternary oxide nanosheets in energy storage, and opens the door for their investigation in other applications.

7.2 Future Work

7.2.1 *In Situ* TEM of High-Capacity Anode Materials

High-capacity anodes, which refer to nanomaterials operating by conversion and/or alloying/de-alloying mechanisms, have shown intriguing electrochemical behavior. In this thesis, several high-capacity anode materials were studied, including nickel sulfide, iron oxide, SnO_2 , NiO , Co_3O_4 , $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4$. They all showed rapid capacity decline that was mitigated upon rGO introduction. They also demonstrated capacity increase over cycling, often exceeding their theoretical capacities. In addition, some differences and exceptions were noted. $\text{Co}_3\text{O}_4/\text{rGO}$, $\text{Ni}_{1.29}\text{Co}_{1.71}\text{O}_4/\text{rGO}$ and $\text{Mn}_{1.08}\text{Co}_{1.92}\text{O}_4/\text{rGO}$ showed greater and more prolonged initial capacity decline, as compared to the other high-capacity anodes, which could be due to slower Li_2O activation. Also, in contrast to other rGO-free high-capacity anodes, rGO-free Co_3O_4 nanosheets were activated after ~ 100 cycles, where the initial capacity decline was reversed, achieving a very high and relatively stable performance up to 400 cycles.

The cycling behavior of high-capacity anodes was explained based on *ex situ* transmission electron microscopy (TEM) analysis and the previous literature. The rGO-incorporated nanomaterials showed metal oxide and sulfide nanoparticles still anchored to the rGO sheets after cycling, indicating minimized contact loss, which might explain the enhanced performance. *Ex situ* TEM analysis of graphene-wrapped nanopyrramids after 3 and 30 cycles showed particle disintegration over cycling, which could explain the increasing capacity, in agreement with previously reported results [1]. Electrolyte decomposition [2-4], Li_2O gradual activation [5] and LiOH formation [6] were also probable explanations for the capacity increase over cycling. Further investigation is required for deeper understanding of the high-capacity anode's cycling performance, and to explain the differences between the behaviors of different nanomaterials.

In situ TEM analysis may help to further elucidate the cycling behavior of the high-capacity anodes. It has been used to study a material's electrochemical behavior during operation, thus eliminating sample contamination that may occur with *ex situ* analysis, and allowing *in operando* material characterization during lithiation and de-lithiation. *In situ* TEM not only probes morphological change, but also monitors the phase evolution by selected area electron diffraction and valence state changes by electron energy loss spectroscopy [7-10]. Hence, it is capable of revealing the chemical reactions taking place during cycling, and relating them to the morphological changes observed. *In situ* TEM can clarify the role of rGO in improving the cycling performance, validate the assumptions made regarding capacity increase over cycling, and correlate the cycling behavior of the nanomaterials with their morphological, structural and chemical changes.

7.2.2 Metal Oxide Nanosheets as SCs

Metal oxide nanosheets of various compositions can be investigated as SCs. Mn_3O_4 nanosheets have shown high capacitance, excellent cycling stability and very good rate capability. This promising performance prompts further investigation of other metal oxide nanosheets as SCs. GO planar-confined synthesis strategy is useful for obtaining various binary, doped binary and ternary oxide nanosheets with tunable properties, allowing for the performance of different metal oxides to be optimized and compared.

Several binary oxide nanosheets can be investigated as SCs. Co_3O_4 [11], NiO [12] and Fe_2O_3 [13] have been reported to have good pseudocapacitive performance, with the electrochemical activity affected to a great extent by the material morphology. The metal oxide nanosheets with their unique 2D nanostructure and nanoparticle building blocks are expected to show very good pseudocapacitive performance, where the nanothickness and small crystallite size may improve electrode kinetics, while the micron-sized lateral dimensions may maintain electrode stability during cycling.

Doping and ternary oxide compositions can further enhance the pseudocapacitive performance of the nanosheets. It was demonstrated that transition-metal-ion doping of binary oxides could improve phase stability and charge transfer, resulting in better

cycling performance and rate capability [14]. Ternary oxides, having better electrochemical activity and conductivity than binary oxides, were also shown to achieve very promising pseudocapacitive performance [15-17]. Their enhanced activity is expected to be more obvious than in the case of LIBs, because the structural decomposition and capacity decline caused by conversion reaction in the latter can mask the improvement in electrochemical activity. The GO planar-confined growth approach is capable of doping binary oxide nanosheets at the desired levels, and synthesizing ternary oxide nanosheets with different compositions. Thus, it would be suitable for the synthesis of a variety of nanosheets for pseudocapacitive applications.

7.2.3 Metal Oxide Nanosheets as Hybrid Supercapacitors

Hybrid supercapacitor is a relatively novel energy storage system that bridges LIBs and SCs. LIBs and SCs have always been regarded as two different energy storage systems with distinct charge storage principles, and thus different energy and power capabilities. LIBs operate through bulk Faradaic reactions, which result in high energy densities up to 200 Wh/kg, but low power density of < 1000 W/kg, and low stability. On the other hand, SCs store charge mainly on the surface, either by physical adsorption or surface Faradic reactions. This results in a high power density of up to 10,000 W/kg and good cycling stability, but low energy storage capacity of 3–10 Wh/kg. Hybrid SC is a relatively novel concept that combines both systems in one device, whereby a LIB anode is assembled with a carbonaceous SC cathode, using an organic electrolyte containing Li salt. The combination of the high-energy anode and high-power cathode can improve the overall performance of the device [18].

Hybrid supercapacitors have been hindered by a serious challenge. The unmatched kinetics between the two electrodes results in lower energy density and deterioration of the device performance. The power capability of the anode needs to be enhanced to improve the hybrid supercapacitor performance. High-voltage anode materials operating by lithium-insertion mechanism (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Nb_2O_5 , TiO_2 and TiNb_2O_7) have been investigated as promising anode materials for hybrid SCs due to their good safety profile, stability and fast Li^+ insertion kinetics [18-21].

High-voltage anode nanosheets are promising candidates for hybrid SC anodes. Nb_2O_5 , TiO_2 and TiNb_2O_7 nanosheets synthesized using the GO planar-confined growth strategy have demonstrated high capacity and very good stability as LIB anodes. Moreover, the rGO-incorporated nanosheets have enhanced rate capabilities that were superior to many of the previously reported results. The high-voltage anode nanosheets may be applied in hybrid SCs to achieve high energy and power densities.

7.3 Novel Contributions

1. Development of a facile one-pot method for the synthesis of nickel sulfide and graphene-wrapped nickel sulfide nanopyramids, with high energy storage performance

The synthesis methodology produced uniform nanocrystals that could be homogeneously anchored to the surface of graphene sheets, in contrast to the relatively large and non-uniform nanoparticles synthesized using the conventional hydro/solvothermal approach. These characteristics resulted in high energy storage capability.

2. Generalized synthesis of binary oxide nanosheets using a facile template-assisted method, and optimization of their characteristics for enhanced energy storage performance

The synthesis methodology utilized a GO template to direct the metal oxide growth into 2D nanostructure. It involves neither hydro/solvothermal reactions nor template-removal processes. It is also a general approach that can produce a very wide variety of binary oxide and doped binary oxide nanosheets. Moreover, it has shown interesting versatility, with the nanosheets' characteristics easily controlled by varying the synthesis conditions, allowing for the optimization of energy storage performance of the nanosheets.

3. Extension of the novel nanosheet synthesis strategy for the production of various ternary oxide nanosheets, and tuning of their properties for enhanced LIB anode performance

The nanosheet synthesis methodology was extended to include ternary oxide nanosheets. To the best of my knowledge, this is the first report of ternary oxide nanosheet synthesis using a general methodology. It is also the first report of the synthesis of nanosheets with TiNb_2O_7 and $\text{Ti}_{0.95}\text{Nb}_{0.95}\text{O}_4$ crystal structures, with the latter phase tested as LIB anode for the first time. The synthesis method allowed for tuning the nanosheets' characteristics for optimized LIB anode performance.

7.4 Conclusion

High-performance energy storage was achieved by the synthesis of nanomaterials and nanocomposites with controlled morphology, crystal structure and composition. Two novel and facile approaches were developed for the synthesis of size-, shape- and phase-controlled nanomaterials and nanocomposites, addressing problems in the existing synthesis methods. The colloidal approach showed very good control of the nickel sulfide size and morphology, while the GO planar-confined growth strategy allowed for the facile synthesis of a wide range of metal oxide nanosheets, including complex phases for the first time. The nanomaterials and nanocomposites derived through these methods showed superior energy storage performance, as compared to many reports in the literature, demonstrating the significance of size and structure control, the critical role played by carbonaceous materials, and the efficacy of the synthesis methods developed in producing nanomaterials and nanocomposites with the desired characteristics.

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List of Publications

Journal Articles

[1] A. A. AbdelHamid, Y. Yu, J. Yang and J. Y. Ying, GO-templated synthesis of ternary oxide nanosheets for high-performance Li-ion battery anodes. Manuscript in preparation.

[2] A. A. AbdelHamid, Y. Yu, J. Yang and J. Y. Ying. Generalized synthesis of metal oxide nanosheets and their application as Li-ion battery anodes. *Adv. Mater.* Accepted manuscript.

[3] A. A. AbdelHamid, X. Yang, J. Yang, X. Chen and J. Y. Ying. Graphene-wrapped nickel sulfide nanoprisms with improved performance for Li-ion battery anodes and supercapacitors. *Nano Energy*. **2016**, 26, 425-437.

Patents

[1] J. Y. Ying and A. A. AbdelHamid. Generalized synthesis of metal oxide nanosheets and their application as Li-ion battery anodes. **2016**, Singapore Patent Application No. 10201608827X.