
**Centre for Clean Energy Technology & School of Chemistry
and Forensic Science
Faculty of Science**

**Graphene-based Nanocomposite Materials
for High-performance Supercapacitors and
Lithium Rechargeable Batteries**

A Thesis Presented in Fulfillment of the Requirements for the

Degree of

Doctor of Philosophy

By

Bei Wang, B. Sc., M. Eng

University of Technology Sydney

2012

Certificate of Authorship/Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Student

Production Note:
Signature removed prior to publication.

July 2012

Acknowledgement

First, I would like to express my sincere gratitude to my supervisor, Prof. Guoxiu Wang, who has been guiding and supporting me wholeheartedly through rigorous but fruitful supervision and financial funding for over five years since I started my research career in 2007. Dr. Jane Yao is also greatly acknowledged for all the administrative assistance and lab management, as well as figure processing and enhancement.

Special thanks are given to all my colleagues in the research team at the Centre for Clean Energy Technology for all the valuable discussions, kind co-operation and assistance. It is a pleasure to have worked with all of you and I really appreciate everyone's efforts in creating an intimate atmosphere for the research work.

I am also grateful for the assistance and patience of Rochelle Seneviratne, the Research and Development Officer, Faculty of Science, who always responds to my enquires and sorts out all the administrative issues. Relevant training in the research facilities from Dr. Ronald Shimmon, Dr. Linda Xiao, and all the MAU staff are much appreciated as well. Assoc. Prof. Alison Ung deserves real gratitude for her contribution to reviewing my manuscript and the priceless discussions. I would also like to acknowledge the editorial assistance from Dr. Fiona MacIver for proofreading this thesis.

Deep gratitude is to be expressed to my wife, my parents and my relatives, who have been caring and sustaining me over these years. Without your continuous support, I could not have finalized my PhD study and become a mature and responsible person. My upcoming baby fills me with joy. This thesis is also for you, my son. Thank you for bringing luck and happiness to me and to our family.

Table of Contents

Certificate of Authorship/Originality	i
Acknowledgement	ii
Table of Contents	iii
List of Schemes, Tables and Figures	ix
Abstract	xviii
Chapter 1 — Introduction	2
Chapter 2 — Literature Review	8
2.1 History and Development of Graphene.....	8
2.2 Preparation of Graphene	10
2.2.1 Exfoliation and Cleavage	10
2.2.2 Chemical Method.....	11
2.2.3 Electrolytic Exfoliation	13
2.2.4 Other Methods.....	14
2.3 Graphene and Graphene-based Materials for Energy Storage Applications	14
2.3.1 Supercapacitors	16
2.3.1.1 History and Development	16

2.3.1.2 Energy Storage Mechanism	17
2.3.1.3 Electrode Materials	20
2.3.2 Lithium-Ion Batteries	24
2.3.2.1 History and Development	24
2.3.2.2 Energy Storage Mechanism	26
2.3.2.3 Electrode Materials	27
2.4 Summary	32
Chapter 3 — Materials Characterization and Electrochemical Techniques	34
3.1 Materials and Chemicals	34
3.2 Materials Synthesis	36
3.2.1 In-situ Reduction.....	36
3.2.2 Co-precipitation.....	37
3.2.3 Hydrothermal and Solvothermal	37
3.2.4 Simple Incorporation.....	38
3.3 Materials Characterization	39
3.3.1 X-ray Diffractometry	39
3.3.2 Scanning Electron Microscopy and Transmission Electron Microscopy	40
3.3.3 Atomic Force Microscopy.....	42

3.3.4 Raman Spectroscopy	44
3.3.5 Brunauer-Emmett-Teller Surface Area and Barrett-Joyner-Halenda Pore Size and Volume Analysis	45
3.3.6 Thermogravimetric Analysis.....	46
3.4 Electrode Fabrication and Cell Assembly	47
3.4.1 Electrode Fabrication	47
3.4.2 Cell Assembly	47
3.5 Electrochemical Testing.....	49
3.5.1 Cyclic Voltometry.....	49
3.5.2 Galvanostatic Charge/Discharge.....	51
3.5.3 Electrochemical Impedance Spectroscopy.....	52
Chapter 4 — Sn/Graphene Nanocomposite with 3D Architecture for Enhanced Reversible Lithium Storage in Lithium-Ion Batteries.....	55
4.1 Introduction.....	55
4.2 Experimental	56
4.2.1 Material Synthesis.....	56
4.2.2 Materials Characterization	56
4.2.3 Electrochemical Testing.....	57
4.3 Results and Discussion.....	57

4.4 Conclusions	67
Chapter 5 — Mn₃O₄ Nanoparticles Embedded into Graphene Nanosheets: Preparation, Characterization, and Electrochemical Properties for Supercapacitors	69
5.1 Introduction	69
5.2 Experimental	70
5.2.1 Material Synthesis	70
5.2.2 Material Characterization	71
5.2.3 Electrochemical Testing	72
5.3 Results and Discussion	73
5.4 Conclusions	84
Chapter 6 — In-situ Synthesis of Co₃O₄/Graphene Nanocomposite Material for Lithium-Ion Batteries and Supercapacitors with High Capacity and Supercapacitance	86
6.1 Introduction	86
6.2 Experimental	87
6.2.1 Material Synthesis	87
6.2.2 Material Characterization	88
6.2.3 Electrochemical Testing	89
6.3 Results and Discussion	90

6.4 Conclusions	106
Chapter 7 — Superior Electrochemical Performance of Sulfur/Graphene Nanocomposite Material for High-Capacity Lithium-Sulfur Batteries.....	108
7.1 Introduction	108
7.2 Experimental	111
7.2.1 Material Synthesis	111
7.2.2 Material Characterization.....	111
7.2.3 Electrochemical Testing.....	112
7.3 Results and Discussion.....	112
7.4 Conclusions	124
Chapter 8 — Graphene-Supported SnO₂ Nanoparticles Prepared by a Solvothermal Approach for an Enhanced Electrochemical Performance in Lithium-Ion Batteries	127
8.1 Introduction	127
8.2 Experimental	128
8.2.1 Material Synthesis	128
8.2.2 Material Characterization.....	129
8.2.3 Electrochemical Testing.....	129
8.3 Results and discussion	130

8.4 Conclusions	141
Chapter 9 — Solvothermal Synthesis of CoS₂/Graphene Nanocomposite Material for High-Performance Supercapacitors	143
9.1 Introduction	143
9.2 Experimental	143
9.2.1 Materials Synthesis	143
9.2.2 Materials Characterization	144
9.2.3 Electrochemical Testing.....	144
9.3 Results and Discussion.....	146
9.4 Conclusions	159
Chapter 10 — General Conclusions	162
Appendix A List of Acronyms and Abbreviations	166
Appendix B List of Publications	171
References	174

List of Schemes, Tables and Figures

Schemes

Scheme 2-1 Graphene and other carbon allotropes: graphene (top left), graphite (top right), carbon nanotube (bottom left), buckminsterfullerene (C_{60} , bottom right).

Scheme 2-2 Schematic illustrations of (a) dried graphene and (b) graphene with modified nanoparticles.

Scheme 2-3 Schematic illustration of the charge/discharge mechanism of a lithium-ion battery.

Scheme 2-4 Schematic representation of the processes during charge/discharge of $LiFePO_4$.

Scheme 4-1 Schematic diagram of the synthesis of the Sn/GNS nanocomposite with a 3D architecture.

Scheme 6-1 Schematic of the reaction mechanism for the formation of Co_3O_4 /GNS nanocomposite.

Scheme 7-1 Schematic illustration of the sandwich structure of S/GNS nanocomposite.

Scheme 8-1 Schematic diagram of the formation of SnO_2 /GNS nanocomposite.

Tables

Table 3-1 Materials and chemicals used in the research project.

Table 5-1 Elemental analysis for GNS-60 and GNS-450 (wt%)

Figures

Fig. 3-1 An X-ray diffractometer (Siemens D5000 model). (Image captured from the Science Faculty Resource Manage System, UTS)

Fig. 3-2 An FE-SEM facility (Zeiss Supra 55VP). (Image captured from the Science Faculty Resource Manage System, UTS)

Fig. 3-3 A commercial TEM setup (JEOL 2011 model).

Fig. 3-4 A MFP-3D-SA AFM facility manufactured by Asylum Research.

Fig. 3-5 A Renishaw inVia Raman Microscope. (Image captured from the Science Faculty Resource Manage System, UTS)

Fig. 3-6 A TriStar II Surface Area Analyzer.

Fig. 3-7 A TGA/DTA Analyzer (SDT 2960 model, TA Instruments). (Image captured from the Science Faculty Resource Manage System, UTS)

Fig. 3-8 A Unilab glove box, manufactured by MBraun, Germany.

Fig. 3-9 An electrochemistry workstation (CHI660D model).

Fig. 3-10 A set of Neware battery testers.

Fig. 4-1 (a) XRD pattern of Sn/GNS nanocomposite. (b) Raman spectrum of Sn/GNS nanocomposite.

Fig. 4-2 FE-SEM image of Sn/GNS nanocomposite. The inset is the high magnification FE-SEM image, in which Sn nanoparticles are clearly visible.

Fig. 4-3 (a) Low magnification TEM image of the Sn/GNS nanocomposite, showing the homogeneous distribution of the Sn nanoparticles on the graphene nanosheets. The inset is the SAED pattern. (b) High magnified TEM image of the Sn/GNS nanocomposite, from which the average particle size of Sn can be measured. (c) HRTEM image of the Sn/GNS nanocomposite, showing that the Sn nanoparticles are surrounded by wavy strips of graphene nanosheets. (d) Lattice resolved HRTEM image of Sn/GNS. The inset contains the lattice image of a Sn nanoparticle.

Fig. 4-4 AFM image of Sn nanoparticles anchored on graphene nanosheets. The line scan shows the peaks arising from Sn nanoparticles and the height of graphene at the edge of two pieces of stacked graphene sheets.

Fig. 4-5 (a) Cyclic voltammograms of the Sn/GNS electrode. (b) Charge/discharge profiles of Sn/GNS electrode in lithium-ion cells.

Fig. 4-6 Reversible lithium storage capacity *vs.* cycle number for Sn/GNS nanocomposite electrode, bare graphene electrode, and bare Sn electrode.

Fig. 5-1 X-ray diffraction patterns (a) vacuum dried graphene nanosheets, and (b) $\text{Mn}_3\text{O}_4/\text{GNS}$ nanocomposites showing the diffraction lines of Hausmannite Mn_3O_4 and graphene nanosheets.

Fig. 5-2 FE-SEM images of the as-prepared $\text{Mn}_3\text{O}_4/\text{GNS}$ nanocomposites: (a) low magnification image, showing the general morphology of graphene nanosheets with embedded Mn_3O_4 nanoparticles and (b) high magnification image, illustrating Mn_3O_4 nanoparticles on graphene nanosheets.

Fig. 5-3 TEM images of the as-prepared Mn₃O₄/GNS nanocomposites: (a) a low magnification TEM image showing dense Mn₃O₄ nanoparticles deposited on a large area of graphene nanosheets and the SAED pattern (inset) displaying graphene (0 0 2) and Mn₃O₄ (1 0 3), (2 1 1), and (2 2 0) diffraction rings; (b) an HRTEM image illustrating the *d*-spacing of Mn₃O₄ nanoparticles, which were evaluated to be around 10 nm in size.

Fig. 5-4 AFM images of the as-prepared Mn₃O₄/GNS nanocomposites: (top) an image taken in a scan area of 500 nm by 500 nm, displaying graphene nanosheets (indicated by arrows) with embedded Mn₃O₄ nanoparticles (indicated by circles); (bottom) height profile across the examined area, as indicated by the red line, from which the particle size was determined to be 9.7 nm and 12.6 nm for particles (a) and (b), respectively.

Fig. 5-5 CV curves of dried graphene nanosheets at a 5 mV s⁻¹ scan rate in (a) 1 M Na₂SO₄ and (b) 6 M KOH, and CV curves of Mn₃O₄/GNS nanocomposite powders at scan rates of 5 mV s⁻¹, 10 mV s⁻¹, 20 mV s⁻¹, and 50 mV s⁻¹ in (c) 1 M Na₂SO₄ and (d) 6 M KOH.

Fig. 6-1 (a) XRD pattern and (b) Raman spectrum of the as-prepared Co₃O₄/GNS nanocomposite material.

Fig. 6-2 (a) XRD and (b) Raman spectrum of pure graphene nanosheets.

Fig. 6-3 FE-SEM images of the Co₃O₄/GNS nanocomposite obtained under GB-HR mode: (a) numerous curly graphene nanosheets observed at a low magnification, and (b) a higher magnification image, displaying the distribution of Co₃O₄ nanoparticles on graphene nanosheets. The embedded Co₃O₄ nanoparticles are ~20 nm in size.

Fig. 6-4 TEM images of the $\text{Co}_3\text{O}_4/\text{GNS}$ nanocomposite material: (a) a low magnification image showing Co_3O_4 nanoparticles dispersed on graphene nanosheets; (inset) the SAED pattern within this examined region; (b) an HRTEM image focusing on a single Co_3O_4 nanoparticle.

Fig. 6-5 AFM images covering an area of 400 nm by 400 nm: (a) surface evidence of graphene nanosheets and deposited Co_3O_4 nanoparticles; (b) height profile across the red line; the particle size of the single Co_3O_4 nanoparticle on the line is 17.8 nm.

Fig. 6-6 TGA curve of the $\text{Co}_3\text{O}_4/\text{GNS}$ nanocomposite.

Fig. 6-7 CV curves of $\text{Co}_3\text{O}_4/\text{GNS}$ anode over a voltage range of 0.01–3 V at a scan rate of 0.1 mV s^{-1} in the 1st, 2nd and 50th cycles.

Fig. 6-8 Charge/discharge profiles of $\text{Co}_3\text{O}_4/\text{GNS}$ anode at a current of 55 mA g^{-1} in the 1st, 2nd and 50th cycles.

Fig. 6-9 Cycling performance of $\text{Co}_3\text{O}_4/\text{GNS}$ nanocomposite material, Co_3O_4 nanoparticles, and bare graphene nanosheets as anode materials at a current of 55 mA g^{-1} .

Fig. 6-10 CV curves of $\text{Co}_3\text{O}_4/\text{GNS}$ as working electrode in a supercapacitor cell in 2 M KOH over a voltage range of -0.25 – 0.55 V at scan rates of 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , and 50 mV s^{-1} , respectively.

Fig. 6-11 CV curves of (a) pure graphene nanosheets and (b) commercial Co_3O_4 powders ($< 50 \text{ nm}$) in 2 M KOH electrolyte at a scan rate of 5 mV s^{-1} .

Fig. 6-12 N_2 adsorption/desorption isotherms of $\text{Co}_3\text{O}_4/\text{GNS}$ nanocomposite.

Fig. 7-1 (a) Pure sulfur crystalline, pure graphene nanosheets, and S/GNS nanocomposite. (b) A high resolution FESEM image showing general morphology of the S/GNS nanocomposite material.

Fig. 7-2 (a) A low-magnification FESEM image of S/GNS nanocomposite material. (b) Elemental mapping of carbon, and (c) elemental mapping of sulfur.

Fig. 7-3 Raman spectra of crystalline sulfur, pure graphene nanosheets, and S/GNS nanocomposite at an extended range from 100 to 3500 cm^{-1} .

Fig. 7-4 TGA curve of the S/GNS nanocomposite material, ranging from room temperature to 1000 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$ in air.

Fig. 7-5 CV curves of the S/GNS nanocomposite electrode in the 1st, 2nd, and 5th cycle. The scanning rate is 0.1 mV s^{-1} .

Fig. 7-6 The charge/discharge profiles of S/GNS nanocomposite electrodes in the first cycle at current rates of 0.05 C, 1 C, and 2 C, respectively.

Fig. 7-7 Cycling performance of S/GNS nanocomposite electrodes at 0.05 C, 1 C, and 2 C, for 100 cycles.

Fig. 7-8 EIS spectra of the S/GNS nanocomposite electrode before cycling, and after 5 and 50 cycles. The inset shows magnified EIS spectra at high frequency region.

Fig. 7-9 FE-SEM images showing morphologies of the S/GNS nanocomposite electrodes. (a) and (b) are FE-SEM images before cycling test; (c) and (d) are FE-SEM images after 100 cycles.

Fig. 8-1 XRD pattern of (a) SnO_2/GNS nanocomposite and (b) GNS.

Fig. 8-2 Raman spectra of SnO₂/GNS nanocomposite and bare GNS from 200 to 2000 cm⁻¹. The inset shows magnified views of the spectra in the range of 400 to 900 cm⁻¹.

Fig. 8-3 TGA curve of SnO₂/GNS nanocomposite.

Fig. 8-4 FE-SEM images of SnO₂/GNS nanocomposite: (a) a low magnified image showing flower-like microstructure of graphene nanosheets and (b) a high magnified image focusing on a large graphene flake.

Fig. 8-5 TEM images of SnO₂/GNS nanocomposite: (a) a low magnified image exhibiting homogenous distribution of SnO₂ nanoparticles on graphene nanosheets. The inset shows the corresponding SAED ring pattern, where crystal planes (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 1 0) of SnO₂ are indexed; (b) an HRTEM image focusing on a few SnO₂ nanoparticles with indexed (1 0 0) and (1 1 0) crystal planes.

Fig. 8-6 CV curves of the SnO₂/GNS nanocomposite electrode at the 1st, 2nd and 5th cycle at a sweep rate of 0.1 mV s⁻¹.

Fig. 8-7 Charge/discharge profiles of the SnO₂/GNS nanocomposite electrode at a current rate of 0.1 C.

Fig. 8-8 Cycling performances of SnO₂/GNS nanocomposite, GNS, and SnO₂ nanoparticles.

Fig. 8-9 Multiple-step cycling characteristic of the SnO₂/GNS nanocomposite electrode at different current rates.

Fig. 8-10 AC impedance spectra of the SnO₂/GNS nanocomposite electrode (a) before cycling, (b) after 5 cycles, and (c) after 100 cycles.

Fig. 9-1 XRD patterns of (a) CoS₂/GNS nanocomposite and (b) bare GNS.

Fig. 9-2 Raman spectra of CoS₂/GNS and bare GNS in the range of 200 to 2000 cm⁻¹.

Fig. 9-3 FE-SEM and TEM observations of the CoS₂/GNS nanocomposite: (a) a low magnification SEM image exhibiting general morphology of the nanocomposite; (b) a higher magnification SEM image with detailed CoS₂ nanoparticle distribution, (c) a TEM image showing CoS₂ nanoparticles dispersed on a single graphene nanosheet. The inset shows the SAED pattern with indexed diffraction rings; (d) an HRTEM image presenting lattice-resolved information of CoS₂ nanoparticles. The inset displays the (1 1 1) crystal planes of CoS₂ nanoparticles with a *d*-spacing of 0.31 nm.

Fig. 9-4 (a) N₂ adsorption–desorption isotherms of the CoS₂/GNS nanocomposite. The inset is the pore size distribution; (b) TGA curves of CoS₂ and GNS in air ranging from room temperature to 1000 °C.

Fig. 9-5 CV curves of (a) CoS₂/GNS, (b) GNS, (c) CoS₂ nanoparticles; and (d) the corresponding specific capacitances at sweep rates of 5, 10, 20, and 50 mV s⁻¹ in 6 M KOH solution.

Fig. 9-6 (a) low and (b) high magnified FE-SEM images of the CoS₂ nanoparticles.

Fig. 9-7 Charge/discharge profiles of CoS₂/GNS, GNS and CoS₂ nanoparticles at (a) 0.5 A g⁻¹ and (b) 1 A g⁻¹ in 6 M KOH.

Fig. 9-8 Cycling performances of CoS₂/GNS, GNS and CoS₂ nanoparticles at 0.5 A g⁻¹ and 1 A g⁻¹ in 6 M KOH for 1000 cycles.

Fig. 9-9 Charge/discharge profiles of CoS₂/GNS, GNS and CoS₂ nanoparticles at (a) 0.5 A g⁻¹ and (b) 1 A g⁻¹ in 1 M LiClO₄ in PC.

Fig. 9-10 Cycling performances of CoS₂/GNS, GNS and CoS₂ nanoparticles at 0.5 A g⁻¹ and 1 A g⁻¹, respectively in 1 M LiClO₄ in PC for 1500 cycles.

Abstract

Human activity and energy supplies mainly rely on the consumption of non-regenerative fossil fuels. With the gradual decrease of these carbon-based energy sources and the increase in environmental pollution, finding alternative green and sustainable energies has become critical. Therefore, innovative and renewable energy technologies must be developed to combat global warming and climate change.[1, 2] Extensive research has been performed on the development of solar cells,[3, 4] fuel cells,[5] lithium-ion batteries[6, 7] and supercapacitors[8, 9] to replace carbon-based energy.

Graphene has been considered a promising electrode material for energy storage applications due to its ultrahigh surface area ($2600 \text{ m}^2 \text{ g}^{-1}$),[10] excellent electric conductivity,[11] and one-atom thick two-dimensional sp^2 carbon arrangement.[12] However, the surface area of graphene nanosheets (GNS) is often dramatically reduced because monolayer GNS always stack to multilayer in the dry state. The stacking of GNS leads to unexposed surface area, which hinders the ion diffusion from the electrolyte to the electrode, resulting in a low electrochemical performance.

To prevent the re-stacking of GNS, and thus maintain well-exposed surface area, nanocrystals can be inserted between graphene layers to form nanocomposite materials. With the above motivation, graphene-based nanocomposite materials have been intensively studied in this thesis. All the materials examined were prepared via different synthesis techniques and well characterized. Their electrochemical properties were evaluated for supercapacitors and/or lithium rechargeable batteries. Sn/GNS is shown to have a very high reversible specific capacity of 785 mAh g^{-1} . $\text{Mn}_3\text{O}_4/\text{GNS}$ shows a specific capacitance of 256 F g^{-1} , almost double that of pure GNS. Of the examined

materials, $\text{Co}_3\text{O}_4/\text{GNS}$ presents the highest supercapacitance of 478 F g^{-1} and a rechargeable specific capacity of 722 mAh g^{-1} . S/GNS generates ultra-high specific capacity of up to 1580 mAh g^{-1} and excellent rate capability. SnO_2 nanoparticles supported by GNS deliver a specific capacity of 830 mAh g^{-1} with well maintained cycling stability. CoS_2/GNS yields high capacitances of 314 F g^{-1} in an aqueous electrolyte and 141 F g^{-1} in an organic electrolyte. The enhanced overall electrochemical performances of these nanocomposite materials can be attributed to the dual contributions of the decorating materials, creating enlarged interlayer spacing, and graphene itself, with its facility for flexible nanolayered structure. The results of this study of these graphene-based nanocomposite materials indicate their great potential for application to practical energy storage devices.