Development of 3D porous graphene/manganese dioxide/polyaniline hybrid film for flexible all-solid-state asymmetric supercapacitor

Ghosh, Kalyan

2018

Ghoshi, K. (2018). Development of 3D porous graphene/manganese dioxide/polyaniline hybrid film for flexible all-solid-state asymmetric supercapacitor. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/74102>

<https://doi.org/10.32657/10356/74102>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**DEVELOPMENT OF 3D POROUS GRAPHENE/MANGANESE
DIOXIDE/POLYANILINE HYBRID FILM FOR FLEXIBLE ALL-
SOLID-STATE ASYMMETRIC SUPERCAPACITOR**

KALYAN GHOSH

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2018

**DEVELOPMENT OF 3D POROUS GRAPHENE/MANGANESE
DIOXIDE/POLYANILINE HYBRID FILM FOR FLEXIBLE ALL-
SOLID-STATE ASYMMETRIC SUPERCAPACITOR**

KALYAN GHOSH

School of Mechanical and Aerospace Engineering

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

2018

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.

....18/04/2018.....
Date

Kalyan Ghosh

Acknowledgements

It gives me a great pleasure to appreciate and acknowledge all the people who have been an integral part of my PhD journey. Firstly, I would like to express my heartily gratitude to my supervisor **Prof. Yue Chee Yoon**, Associate Provost (Graduate Education) and full professor in the Mechanical and Aerospace Engineering, Nanyang Technological University, for his valuable insights, guidance and inspiration. My knowledge has been lifted several degrees by his immense help and enthusiastic encouragement at each and every step of the present work. It will be my great pleasure to tell that I am extremely fortunate to work under his supervision.

I would also like to thank all the lab technicians of Materials Lab 1 & 2 and Chemical Lab of the Mechanical & Aerospace Engineering, NTU, Ms. Yong Mei Yoke, Ms. Yeong Peng Neo Sandy, Mr. Leong Kwok Phui, Mr. Lew Sui Leung Thomas and Ms. Koh Joo Luang, for their cooperation and valuable time during my project work.

After all, I would like to convey my warmest thanks to my project-team members, Dr. Md Moniruzzaman, Dr. R. K. Jena, Dr. Bi Shuguang and Mr. Swaroop Narayan for their all kinds of help, guidance and valuable suggestions. Also, I would like to express my sincere thanks to my fiancée Dr. Suparna Sadhukhan for her continuous support and encouragement. Although, it is difficult to find an appropriate word, still I would like to express my deepest gratitude from the beneath of my heart to my beloved mother, father, sister and brothers who inspired and encouraged me constantly throughout my study.

My sincere thanks also go to Nanyang Technological University, Singapore for proving me the scholarship for my research work. Without the financial support, the journey would not have started in the first place. So, I am truly thankful to the Singapore Government, and equally thankful to MAE NTU for granting the privilege to pursue PhD candidature in this esteemed institution.

Lastly, I would like to thank to all my friends who helped me to finish my research work.

Table of Contents

Contents	Page No.
Acknowledgements -----	IV
Table of contents -----	V
Abstract -----	XI
List of figures -----	XIII
Abbreviations & notations -----	XXII
Publications -----	XXVII
Chapter 1 Introduction -----	1
1.1 Background-----	1
1.2 Objectives and scope of the report -----	4
1.3 Structure of the report-----	5
Chapter 2 Literature review -----	6
2.1 Development of Supercapacitor -----	6
2.2 Working principles of supercapacitors (SCs) -----	7
2.2.1 Principle of electrochemical double-layer capacitors-----	7
2.2.2 Principle of pseudocapacitors-----	9
2.2.3 Principle of hybrid capacitors-----	10
2.3 Supercapacitor cell components -----	10
2.3.1 Electrode materials-----	10
2.3.1.1 Carbon materials -----	10

2.3.1.1.1 Activated carbon (AC) and carbon nanotubes (CNTs) -----	10
2.3.1.1.2 Graphene -----	11
2.3.1.2 Metal oxides -----	14
2.3.1.2.1 RuO ₂ -----	14
2.3.1.2.2 MnO ₂ -----	14
2.3.1.2.3 MoO ₃ -----	17
2.3.1.2.4 Other metal oxides -----	20
2.3.1.3 Conducting polymers (CPs) -----	20
2.3.1.3.1 Polyaniline (PANI) -----	21
2.3.1.3.2 Polypyrrole (PPy) -----	22
2.3.1.3.3 Polythiophenes (PTh) -----	23
2.3.1.4 Hybrid materials -----	23
2.3.1.4.1 MnO ₂ –PANI based composite electrode -----	24
2.3.1.4.2 MnO ₂ –graphene based composite electrodes -----	25
2.3.2 Electrolytes for supercapacitors -----	26
2.3.2.1 Aqueous electrolytes -----	27
2.3.2.2 Organic electrolytes -----	27
2.3.2.3 Ionic electrolytes -----	27
2.3.2.4 Polymer gel electrolytes -----	28
2.3.3 Separators -----	29
2.3.4 Current collectors -----	29
2.4 Electrochemical cell systems and measurements -----	29
2.4.1 Electrode cell systems and measurement methods -----	29
2.4.2 Cyclic voltammetry (CV) study -----	30
2.4.3 Cyclic charge–discharge (CCD) study -----	31
2.4.4 Electrochemical impedance spectroscopy (EIS) study -----	33
2.4.5 Cycle lifetime -----	34
2.5 Supercapacitor device type -----	35
2.6 Techniques of 3D macroporous graphene fabrication -----	36
2.6.1 Hydrothermal method -----	37
2.6.2 Template guided approach -----	38

2.6.2.1 Soft-template approach-----	38
2.6.2.2 Hard-template approach-----	39
2.6.2.3 Others approaches-----	40
2.7 Flexible solid-state supercapacitors -----	41
2.7.1 Electrode materials for flexible solid-state supercapacitors -----	42
2.7.1.1 Carbon-based flexible electrode-----	42
2.7.1.2 Pseudocapacitive material based flexible electrode -----	42
2.7.1.3 Composite materials based flexible electrode -----	42
2.7.2 Flexible solid-state symmetric supercapacitors (SSCs) -----	43
2.7.2.1 Carbon materials based SSCs -----	43
2.7.2.1.1 CNTs -----	43
2.7.2.1.2 Graphene-----	43
2.7.2.2 Conducting polymers (CPs) based SSCs-----	44
2.7.2.3 Hybrid materials based SSCs-----	44
2.7.3 Flexible solid-state asymmetric supercapacitors (ASCs) -----	46
2.8 Application of flexible solid-state supercapacitors-----	47
2.9 Basis of materials selection and perspective of the current research work-----	49
2.10 Summary -----	49
Chapter 3 Materials and experimental details -----	51
3.1 Chemicals and general equipment-----	51
3.2 Experimental -----	52
3.2.1 Field emission scanning electron microscopy (FESEM)-----	52
3.2.2 Transmission electron microscopy (TEM)-----	53
3.2.3 Fourier transform infrared (FTIR) spectroscopy -----	53
3.2.4 X-ray diffraction (XRD)-----	53
3.2.5 X-ray photoelectron spectroscopy (XPS) -----	53
3.2.6 Raman spectroscopy -----	54
3.2.7 Thermogravimetric analysis (TGA)-----	54
3.2.8 Surface area measurement and pore size distribution -----	54

3.2.9 Conductivity measurement-----	55
3.2.10 Electrochemical performance -----	55
3.2.11 Fabrication of electrode and polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel electrolyte-----	56
Chapter 4 Development of 3D urchin-shaped coaxial MnO₂@PANI composite and self-assembled 3D pillared graphene foam for flexible all-solid-state asymmetric supercapacitor -----	57
4.1 Introduction -----	57
4.2 Experimental section-----	58
4.2.1 Preparation of 3D graphene foam (GF) -----	58
4.2.2 Synthesis of MnO ₂ nanostructures -----	59
4.2.3 Preparation of MnO ₂ @PANI composite -----	59
4.2.4 Fabrication of all-solid-state supercapacitor electrodes -----	60
4.2.5 Characterization techniques-----	60
4.3 Results and discussion -----	61
4.3.1 Graphene foam -----	61
4.3.1.1 Morphological investigation-----	61
4.3.1.2 Molecular characterization-----	63
4.3.1.3 Electrochemical measurements-----	65
4.3.2 MnO ₂ and MnO ₂ @PANI nanomaterials -----	66
4.3.2.1 Morphological investigation-----	66
4.3.2.2 Molecular characterization-----	69
4.3.2.3 MnO ₂ @PANI coaxial microurchin formation mechanism -----	73
4.3.2.4 Electrochemical measurements-----	75
4.3.3 Asymmetric hybrid supercapacitor-----	76
4.3.4 Comparison with other results -----	83
4.4 Summary-----	85

Chapter 5 Development of 3D porous graphene/MnO₂@polyaniline hybrid film and 3D graphene aerogel for all-solid-state flexible asymmetric supercapacitor----- 86

5.1 Introduction -----	86
5.2 Experimental -----	88
5.2.1 Synthesis of porous RGO/MnO ₂ @PANI hybrid film -----	88
5.2.2 Preparation of graphene aerogel-----	89
5.2.3 Fabrication of flexible all-solid-state supercapacitor cells -----	89
5.2.4 Characterization techniques-----	90
5.3 Results and discussion -----	90
5.3.1 Graphene Aerogel -----	90
5.3.1.1 Morphological investigation-----	90
5.3.1.2 Molecular characterization-----	92
5.3.1.3 Electrochemical measurements-----	95
5.3.2 Graphene/MnO ₂ @Polyaniline (RGO/MnO ₂ @PANI) film -----	96
5.3.2.1 Morphological investigation-----	96
5.3.2.2 Molecular characterization-----	98
5.3.2.3 Electrochemical measurements-----	100
5.3.3 Asymmetric hybrid supercapacitor-----	102
5.3.4 Comparison with other results -----	107
5.4 Summary-----	110

Chapter 6 Novel all-solid-state flexible asymmetric supercapacitor based on ternary 3D heterogeneous structures - polyaniline decorated porous MnO₂–graphene electrode and MoO₃/graphene aerogel --- 111

6.1 Introduction -----	111
6.2 Experimental -----	112
6.2.1 Synthesis of sandwich-type PANI/(MnO ₂ –RGO)/PANI porous film -----	112
6.2.2 Preparation of MoO ₃ /graphene aerogel-----	113
6.2.3 Fabrication of all-solid-state supercapacitor -----	113
6.2.4 Characterization techniques-----	113

6.3 Results and discussion -----	114
6.3.1 MoO ₃ /GF composite materials -----	114
6.3.1.1 Molecular characterization-----	114
6.3.1.2 Morphological analysis-----	117
6.3.1.3 Electrochemical analysis and performance -----	120
6.3.2 PANI/(MnO ₂ -RGO)/PANI hybrid film -----	123
6.3.2.1 Molecular characterization-----	123
6.3.2.2 Morphological analysis-----	125
6.3.2.3 Electrochemical measurements-----	127
6.3.3 Asymmetric hybrid supercapacitor-----	129
6.3.4 Comparison with other results -----	133
6.4 Summary-----	134
Chapter 7 Conclusions and suggestions for future work -----	136
7.1 Conclusions -----	136
7.2 Suggestions for future work-----	139
References-----	141
Appendix -----	164

Abstract

There is increasing demand for safe, environmentally benign energy storage devices in portable electronic appliances, wearable gadgets, flexible displays, and other personal multimedia devices. The flexible solid-state supercapacitor can be used as an energy storage device to meet these future needs. Carbonaceous electrode materials such as activated carbon, carbon nanotubes, and graphene are recognized as promising electrode materials for flexible solid-state supercapacitor due to their high power density and long cyclic stability. However, their energy storage is limited to the electrochemical double-layer mechanism that cannot provide the required high energy density. This is in contrast to other materials such as metal oxides and conducting polymers that can support high energy densities through the pseudocapacitive energy storage mechanism. However, most metal oxides are costly and toxic, while conducting polymers suffer from poor long-term cyclic stability. Thus, for this work, MnO_2 is selected due to its inexpensive and non-toxic in nature. Furthermore, it is essential to synthesize and develop hybrid electrode materials in which the disadvantages of each constituent component material can be mitigated. This work focuses on the synthesis and development of novel 3D ternary composite materials based on reduced graphene oxide (RGO), MnO_2 , and polyaniline (PANI). Our studies revealed that the morphology and microstructure of the 3D ternary composite system can be optimized to develop high performance flexible solid-state asymmetric supercapacitors.

At first, a novel 3D hollow urchin-shaped coaxial manganese dioxide@polyaniline (MnO_2 @PANI) composite and a 3D graphene foam (GF) were synthesized for use as positive and negative electrodes, respectively to fabricate an all-solid-state flexible asymmetric supercapacitor (ASC). Polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel was used as the electrolyte. The selection of KOH based electrolyte over acidic electrolyte was to prevent the Ni foam current collector from the corrosive effect of acidic electrolyte. Moreover, PVA/KOH electrolyte shows high ionic mobility. The coaxial MnO_2 @PANI composite was synthesized by employing a hydrothermal route followed by oxidation aniline without the use of an external

oxidant The solid-state asymmetric supercapacitor ($\text{MnO}_2\text{@PANI//GF}$) had a high energy density of 37 Wh kg^{-1} at a power density of 0.386 kW kg^{-1} and a good cyclic stability with $\sim 11\%$ capacitance loss was observed after 5000 cycles.

A hybrid film comprising of novel ternary composite 3D porous RGO/ $\text{MnO}_2\text{@PANI}$ hybrid material was successfully developed as the positive electrode material for the ASC device. The flexible composite film was synthesized by vacuum filtration of the graphene oxide (GO) and $\text{MnO}_2\text{@PANI}$ dispersion, followed by chemical reduction of the residue film in a hydrothermal autoclave. To increase the energy density of the negative electrode material 3D graphene aerogel with high surface area was synthesized using a nonionic triblock copolymer Pluronic F-68 solution as a soft-template following the hydrothermal route. The pluronic copolymer had dual roles, firstly it enabled effective dispersion of GO in water, and secondly, it assisted the formation of a stable 3D pillared hydrogel assembly. The solid-state ASC (graphene aerogel//RGO/ $\text{MnO}_2\text{@PANI}$) had a very high energy density of 38.12 Wh kg^{-1} at a power density of 1.191 kW kg^{-1} and 85.8% capacitance retention after 5000 cycles.

Finally, the approach to significantly increase energy density of the supercapacitor by enlarging operating voltage window through the use of two metal oxides that have a large difference in work function was investigated. Through the use of MnO_2 and MoO_3 in the positive and negative electrodes respectively, and adopting a 3D heterogeneous composite based on PANI and RGO, the operating voltage window was successfully widened to 0–1.6 V. A ternary composite of sandwich-type PANI decorated 3D porous $\text{MnO}_2\text{--RGO}$ hybrid film ($\text{PANI}/(\text{MnO}_2\text{--RGO})/\text{PANI}$) was synthesized as the positive electrode, while a 3D molybdenum oxide/graphene aerogel (MoO_3/GF) composite material was developed to use as the negative electrode material. The asymmetric supercapacitor ($\text{MoO}_3/\text{GF//PANI}/(\text{MnO}_2\text{--RGO})/\text{PANI}$) exhibited a dramatically high energy density of 51.91 Wh kg^{-1} at a power density of 0.838 kW kg^{-1} . The asymmetric cells were flexible, and three cells connected in series could illuminate a green LED for 62 s. This showed that the novel 3D ternary composite materials developed in the current work can be employed to fabricate a flexible ASC that is reliable and has very high energy density.

List of Figures

Figure 1.1 Ragone plot of conventional capacitors, supercapacitors, batteries and fuel cells [8].....	1
Figure 2.1 Schematic illustration of charge storage of a static capacitor [5].....	7
Figure 2.2 EDL models: (a) the Helmholtz model, (b) the Gouy-Chapman model and (c) the Stern model [35].	8
Figure 2.3 Schematic illustration of charging and discharging of double-layer capacitor [36].	9
Figure 2.4 Crystal structure of graphene [44].	12
Figure 2.5 (a & b) Lerf-Klinowski model structures of GO showing the presence of oxygen functionalities above and below the basal plane [47] [45].....	12
Figure 2.6 Charge storage mechanism in grapheme based supercapacitor electrode [54].....	13
Figure 2.7 Typical crystal structures of MnO_2 [58].	15
Figure 2.8 ((a), (b)) TEM images of the as-prepared $\alpha\text{-MnO}_2$ nanorods; the inset shows the corresponding SAED pattern. ((c), (d)) HRTEM images of the $\alpha\text{-MnO}_2$ nanorods [66]. Adapted with permission from Ref. 66, Copyright (2013), IOP publishing.	16
Figure 2.9 Morphologies of the products obtained by hydrothermal reaction for 12 h: (a and b) low magnification; (c and d) profile images of $\alpha\text{-MnO}_2$ hollow urchins [65]. Adapted with permission from Ref. 65, Copyright (2007), American Chemical Society.	17
Figure 2.10 (a) – (d) SEM images of MoO_3 nanorods [73].	18
Figure 2.11 FESEM of h- MoO_3 (a and b), FE-SEM of $\alpha\text{-MoO}_3$ (c and d) [74].	19

Figure 2.12 SEM micrographs of (a) the MoO ₃ nanoplates and (b) the bulk MoO ₃ [72]. Adapted with permission from Ref. 72, Copyright (2011), The Royal Society of Chemistry.....	19
Figure 2.13 Chemical structures of PANI, PPy and PTh [89].	21
Figure 2.14 General chemical structure of polyaniline [89].	21
Figure 2.15 Conversion of PANI emeraldine form to PANI emeraldine base [90].	22
Figure 2.16 Reversible redox reaction of polypyrrole [92].	22
Figure 2.17 The oxidized and reduced chemical forms of PEDOT structure [89].	23
Figure 2.18 (a) SEM images for MnO ₂ –PANI nanofibers synthesized with rapid mixing and using MnO ₂ as the seed at magnification of 2.00 μm, (b) SEM images for MnO ₂ –PANI nanofibers synthesized with rapid mixing and using MnO ₂ as the seed at magnification of 1.00 μm [96]. Adapted with permission from Ref. 96, Copyright (2013) Elsevier.	24
Figure 2.19 (a–c) SEM image of MnO ₂ NW, MnO ₂ /PANI coaxial NW and PANI; (d and e) TEM image of MnO ₂ NW and MnO ₂ /PANI coaxial NW, and (f) TEM-EDS analysis of MnO ₂ /PANI coaxial NW [25]. Adapted with permission from Ref. 25, Copyright (2012), The Royal Society of Chemistry.....	25
Figure 2.20 (a) FESEM image of 3D nickel foam substrate. (b) FESEM image of 3D graphene foam without nickel substrate. (c) Low magnification FESEM image of MnO ₂ /3D graphene foam hybrid. (d) MnO ₂ deposited on the surface of 3D graphene foams at high magnifications [100]. Adapted with permission from Ref. 100, Copyright (2012), Elsevier.	26
Figure 2.21 a) CV plot of an ideal EDLC and b) Typical CV plot of a pseudocapacitor [89].	31
Figure 2.22 General representation of CCD cycles [118].	32
Figure 2.23 General representation of Nyquist plot [41].	34
Figure 2.24 Work functions of transition metal oxides [32].	35

- Figure 2.25** (a) Photographs of a 2 mg mL⁻¹ homogeneous GO aqueous dispersion before and after a hydrothermal reduction at 180 °C for 12 h, (b) photographs of a strong GF allowing easy handling and supporting weight, and (c) SEM images of the SGH interior microstructures [122]. Adapted with permission from Ref. 122, Copyright (2010), American Chemical Society.....37
- Figure 2.26** (a) Schematic drawings illustrating the leavening process to prepare RGO foams, (b) Cross-sectional SEM image of RGO foams formed after 10 h in an autoclave at 90 °C with 80 µL hydrazine monohydrate and freestanding paper-like RGO foam (inset), (c) Schematic diagram of the flexible RGO foam supercapacitor where the distance between two sides of the RGO foam supercapacitor characterizes its bending degree and (d) Optical image of the flexible RGO foam supercapacitor [127]. Adapted with permission from Ref. 127, Copyright (2012), WILEY-VCH Verlag GmbH & Co. KGaA.....38
- Figure 2.27** SEM images of (a) 3D graphene network grown on nickel foam after CVD process and (b) 3D graphene networks after removal of the nickel foam [141]. Adapted with permission from Ref. 141, Copyright (2011), WILEY-VCH Verlag GmbH & Co. KGaA.40
- Figure 2.28** Schematic illustration of a solid-state SC [147].41
- Figure 2.29** The upper left image is the optical photographs of the fabricated solid-state supercapacitor device. The square indicates the capacitance region. The bottom left images show the flexibility of the device. The right image shows a light-emitting-diode (LED) lit by a device composed of three SCs connected in series [107]. Adapted with permission from Ref. 107, Copyright (2011), American Chemical Society.....45
- Figure 2.30** (a) Upper: schematic diagram illustrating the growth processes of H-TiO₂@MnO₂ and H-TiO₂@C core-shell nanowires. Lower: SEM image of the H-TiO₂@MnO₂ core-shell nanowires grown on a carbon cloth substrate. Inset: a red LED (1.5 V) powered by a solid-state ASC device. (b) CV curves collected at a scan rate of 100 mV s⁻¹ for the ASC device under flat, bent, and twisted conditions. Insets are the device pictures under test conditions [30]. Adapted with permission from Ref. 30, Copyright (2013), WILEY-VCH Verlag GmbH & Co. KGaA.....47

Figure 2.31 (a–c) Practical applications of solid-state SCs [189, 191, 192]. Adapted with permission from Ref. 189, Copyright (2014), WILEY-VCH Verlag GmbH & Co. KGaA; Ref. 191, Copyright (2014), The Royal Society of Chemistry and Ref. 192 Copyright (2013) American Chemical Society.....	48
Figure 4.1 (a) GO dispersion in water, (b) 3D self-assembled GO hydrogel, (c) FESEM image of the graphene foam at lower magnification (inset shows GF after heat treatment) and (d) FESEM image of the graphene foam at higher magnification.	62
Figure 4.2 (a) The N ₂ adsorption–desorption isotherm loop and (b) pore volume distribution plot of 3D GF.....	63
Figure 4.3 Raman spectroscopy of GF and GO.....	64
Figure 4.4 XRD analysis of GF and GO.....	64
Figure 4.5 (a) CV curves at different scan rates and (b) CCD curves at different current densities of GF//GF solid-state supercapacitor.....	66
Figure 4.6 (a) Low- and (b) high-magnification FESEM images of MnO ₂ ; (d) low- and (e) high magnification FESEM images of MnO ₂ @PANI (@ 0.02 M HCl); (c) MnO ₂ and (f) MnO ₂ @PANI (@ 0.02 M HCl) TEM images.....	67
Figure 4.7 (a) FESEM and (b) TEM images at 0.002 M HCl; (c) FESEM and (d) TEM images at 0.2 M HCl concentrations of MnO ₂ @PANI composites.	69
Figure 4.8 XRD patterns of (i) MnO ₂ and (ii) MnO ₂ @PANI composite materials....	70
Figure 4.9 Raman spectra of (i) MnO ₂ and (ii) MnO ₂ @PANI, and inset (<i>i'</i>) magnified MnO ₂ materials.	71
Figure 4.10 FTIR spectra for (i) MnO ₂ and (ii) MnO ₂ @PANI materials.....	72
Figure 4.11 XPS spectra of (a) Mn 2p of MnO ₂ ; (b) N 1s and (c) C 1s spectrum of MnO ₂ @PANI composite.	73
Figure 4.12 (a) Schematic diagram of MnO ₂ @PANI core–shell structure formation, and (b) schematic presentation of PANI-coating formation on a dissolute MnO ₂ surface at an optimized [H ⁺] concentration.....	74

Figure 4.13 (a) CV curves at different scan rates and (b) CCD curves at different current densities of MnO ₂ @PANI composite.....	76
Figure 4.14 (a) Schematic presentation of GF//MnO ₂ @PANI flexible solid-state ASC, (b) CV curves for MnO ₂ @PANI and GF materials by three-electrode cell measurement at 100 mV s ⁻¹ , (c) CV curves in different voltage windows at a scan rate of 100 mV s ⁻¹ , (d) CV curves at different scan rates from 10–500 mV s ⁻¹ , (e) CCD curves at different current densities of GF//MnO ₂ @PANI ASC, and (f) specific capacitance comparison with current densities for SSCs and ASC.....	78
Figure 4.15 (a) Coulombic efficiency of GF//MnO ₂ @PANI ASC; (b) Ragone plots, (c) cyclic stability performance over 5000 cycles; and (d) Nyquist plots of GF, MnO ₂ @PANI SSCs, and GF//MnO ₂ @PANI ASC (the inset of panel presents the schematic diagram of the Nyquist plot); (e) CV curves for ASC at different bending states (the inset optical images show the bending states); and (f) CCD curves of ASC where two and three cells are connected in series (the inset shows a red LED that was powered by the tandem ASC).	80
Figure 4.16 FESEM images MnO ₂ @PANI microstructure (a) before and (b) after 5000 cyclic charge –discharge test.	83
Figure 5.1 (a) GO dispersion in water, (b) 3D Self-assembled GO hydrogel; (c) at lower magnification and d) at higher magnification FESEM image of the GF20 graphene aerogel.	91
Figure 5.2 (a) The N ₂ adsorption–desorption isotherm loop of GF0, GF10 and GF40 aerogels, (b) Pore volume distribution plot of GF0, GF10, GF20 and GF40 aerogels.	92
Figure 5.3 Raman spectroscopy (i) GO, (ii) raw-GF20 and (iii) GF20 aerogel.	93
Figure 5.4 XRD analysis of (i) GO, (ii) raw-GF20 and (iii) GF20 aerogel.	94
Figure 5.5 TGA of raw-GF20.	94
Figure 5.6 (a) CV curves of GF20 SSC for scan rates of 10–100 mV s ⁻¹ ; (b) CCD curves of the GF0, GF10, GF20 and GF40 SSCs at 1 A g ⁻¹ ; and (c) CCD curves at different current densities of the GF40 SSC.	96

Figure 5.7 (a) and (d) normal photographs of RGO/M@P25 film; (b) FESEM micrograph of the cross-sectional edge of RGO/M@P25 film at lower magnification; (c), (e) and (f) magnified FESEM images of RGO/M@P25 film highlighting different positions.	97
Figure 5.8 Schematic presentation of (a) GO/M@P25 film and (b) RGO/M@P25 film.	98
Figure 5.9 XRD patterns of (i) MnO ₂ @PANI and (ii) RGO/M@P25 film.	99
Figure 5.10 Raman spectra of (i) GO film, (ii) RGO film (iii) MnO ₂ @PANI and (iv) RGO/M@P25 film.	100
Figure 5.11 (a) CV profiles at different scan rates and (b) CCD profiles at different current densities of RGO/M@P25 SSC.	101
Figure 5.12 Comparison of CCD profiles of RGO, RGO/M@P10, RGO/M@P25 and RGO/M@P40 SSCs at 1 A g ⁻¹ current density.	102
Figure 5.13 (a) Schematic presentation of flexible solid-state GF40//RGO/M@P25 ASC; (b) CV curves for RGO/M@P25 and GF40 materials from the three-electrode system at 100 mV s ⁻¹ ; (c) CV curves at different voltage windows at a scan rate of 100 mV s ⁻¹ , (d) CV curves at different scan rates from 10–100 mV s ⁻¹ and (e) CCD curves at different current densities of GF40//RGO/M@P25 ASC; and (f) Ragone plot of RGO/M@P25 SSC and GF40//RGO/M@P25 ASC [Inset : red LED was powered by the ASC].	104
Figure 5.14 (a) Nyquist plots of GF40, RGO/M@P25 SSCs and GF40//RGO/M@P25 ASC [Inset presents schematic diagram of the Nyquist plot]; (b) Cyclic stability performance over 5000 cycles, (c) Coulombic efficiency of GF40//RGO/M@P25ASC for 5000 cycles [Inset: Figure represents the charge–discharge behavior for last 10 cycles]; (d) CV curves for ASC at different bending states [Inset optical image shows the bent sample]; (e) CCD curves of GF40//RGO/M@P25 where two and three ASC cells are connected in series [Inset: green LED was powered by the ASC]; (f) Photographs of green- and red-LED lighted up by 2 and 3 ASC cells connected in series, respectively.	106
Figure 6.1 XRD patterns of GO, GF, MoO ₃ and MoO ₃ /GF5, respectively.	114

Figure 6.2 Raman spectra of GO, GF, MoO ₃ and MoO ₃ /GF5, respectively (inset shows magnified Raman spectra of GO, GF, and MoO ₃ /GF5).	115
Figure 6.3 FTIR of GF, MoO ₃ and MoO ₃ /GF5 materials.	116
Figure 6.4 (a) XPS survey spectra; (b) deconvolution of Mo 3d; (c) deconvolution of C 1s spectra of GO and (d) deconvolution of C 1s spectra of MoO ₃ /GF5 composite.	117
Figure 6.5 (a) Transformation of (MoCl ₃ /GO) mixture to MoCl ₃ /GF hydrogel column; (b) FESEM images of pristine MoO ₃ , (c) TEM image of MoO ₃ /GF5 composite; FESEM images of (d) MoO ₃ /GF2.5, (e) MoO ₃ /GF5 and (f) MoO ₃ /GF10 composites, respectively.	118
Figure 6.6 The N ₂ adsorption–desorption isotherm loop of GF, MoO ₃ /GF5 and MoO ₃ /GF10 materials.	118
Figure 6.7 (a) Schematic illustration of coordination bond formation between MoCl ₃ and GO sheet in MoCl ₃ /GF hydrogel and (b) distribution of MoO ₃ nanocrystals in graphene matrix of MoO ₃ /GF5 composite.	119
Figure 6.8 TGA analysis of MoCl ₃ in O ₂ atmosphere.	120
Figure 6.9 (a) CV plots at different scan rates and (b) CCD at different current densities of MoO ₃ /GF5 SSC; (c) comparison CCD plots of MoO ₃ /GF2.5, MoO ₃ /GF5 and MoO ₃ /GF10 SSCs at 1 A g ⁻¹ current density, (d) EIS of GF SSC and MoO ₃ /GF5 SSC and (e) cyclic stability of MoO ₃ /GF5 SSC.	122
Figure 6.10 XRD patterns of GO, MnO ₂ , MnO ₂ –RGO and P/(M–R)/P materials. .	124
Figure 6.11 Raman spectra of MnO ₂ –GO, MnO ₂ –RGO and P/(M–R)/P materials.	125
Figure 6.12 Cross-sectional side-view FESEM images of (a) MnO ₂ –GO film and (b) MnO ₂ –RGO film; (c) magnified FESEM image of inside layer of MnO ₂ –RGO film, (d) magnified side view of MnO ₂ –RGO film, (e) top view FESEM image of P/(M–R)/P film at low magnification (inset: normal photograph of P/(M–R)/P film), and (f) magnified top view FESEM images of P/(M–R)/P film; (g) TEM image of PANI, and (h) normal photograph of P/(M–R)/P film in bending state.	126

Figure 6.13 Schematic illustration for synthesis steps of sandwich-type PANI/(MnO ₂ -RGO)/PANI film.....	127
Figure 6.14 CV studies at different scan rates, (b) CCD plots at different current densities of P/(M-R)/P SSC, (c) EIS comparison of RGO film SSC and P/(M-R)/P film SSC and (d) cyclic stability curve of P/(M-R)/P film SSC.	129
Figure 6.15 (a) Schematic presentation of the flexible solid-state ASC, (b) three-electrode measurement of MoO ₃ /GF25 and P/(M-R)/P electrode materials, (c) CV study with increasing potential windows from 0–1.0 to 0–1.7 V at the scan rate 100 mV s ⁻¹ , (d) CCD study with increasing potential window from 0–1.0 to 0–1.8 V at 5 A g ⁻¹ current density, (e) CV study at different scan rates of 5–200 mV s ⁻¹ , and (f) CCD study at different current densities of MoO ₃ /GF5//P/(M-R)/P ASC.	131
Figure 6.16 (a) Ragone plots of P/(M-R)/P film SSC and MoO ₃ /GF5//P/(M-R)/P ASC, (b) cyclic stability, Inset: CCD plots of last 10 cycles of the ASC, (c) CV performances at different bending angles, and (d) CCD study of series connected 2 cells and 3 cells, Inset: green-LED light up by series connected 3 cells.	132

List of Tables

Table 3.1 List of chemicals used.....	51
Table 4.1 Typical results obtained from flexible solid-state symmetric and asymmetric supercapacitors.	84
Table 5.1 Comparison of electrochemical performance of solid-state symmetric supercapacitors.....	108
Table 5.2 Comparison of electrochemical performance of solid-state asymmetric supercapacitor.	109
Table 6.1 A comparison of the energy density, power density and cyclic stability performances of ASC.....	134
Table 7.1 Comparison of electrochemical performances of the fabricated ASC devices.....	138

Abbreviations & Notations

A

AC – Activated carbon

APS – Ammonium persulfate

ASC – Asymmetric supercapacitor

B

BET – Brunauer–Emmett–Teller

BJH – Barrett–Joyner–Halenda

C

CCD – Cyclic charge–discharge

α -CD – α -Cyclodextrin

C_{dl} – Double-layer capacitance

C_{diff} – Diffusive layer capacitance

C_H – Compact double-layer capacitance

CNT – Carbon nanotube

Co_3O_4 – Cobalt oxide

CP – Conducting polymer

CV – Cyclic voltammetry

CVD- Chemical vapor deposition

C_{sp} – Specific capacitance

D

1D – One dimensional

2D – Two dimensional

3D – Three dimensional

E

E_{cell} – Energy density

EDL – Electrical double-layer

EDLC – Electrical double-layer capacitor

EIS – Electrochemical impedance spectroscopy

ESR – Equivalent series resistance

F

FESEM – Field emission scanning electron microscopy

FTIR – Fourier transform infrared

G

GA – Graphene aerogel

GF – Graphene foam

GO – Graphene oxide

H

HCl – Hydrochloric acid

H₂SO₄ – Sulphuric acid

TEM – Transmission electron microscopy

I

IHP – Inner Helmholtz plane

K

KOH – Potassium hydroxide

KCl – Potassium chloride

KMnO₄ – Potassium permanganate

L – Light-Emitting-Diode

M

MnO₂ – Manganese di-oxide

MWCNT – Multi-walled carbon nanotube

N

NiO –Nickel oxide

Na₂SO₄ – Sodium sulfate

O

OCV – Open circuit voltage

OD – Outer diameter

OHP – Outer Helmholtz plane

P

P_{cell} – Power density

PANI – Polyaniline

PDMS – Poly(dimethyl siloxane)

PEDOT – Poly(3,4-ethylenedioxythiophene)

PEO – Poly(ethylene oxide)

PMMA – Poly(methyl methacrylate)

PPy – Polypyrrole

PTh – Polythiophene

PVA – Poly(vinyl alcohol)

PVDF – Poly(vinylidene difluoride)

PVP – Polyvinylpyrrolidone

PET – Polyethylene terephthalate

R

RGO – Reduced graphene oxide

R_{ct} – Charge transfer resistance

R_s – Combined series resistance

R_w – Warburg resistance

RuO_2 – Ruthenium oxide

S

SDBS – Sodium dodecyl benzene sulphonate

SC – Supercapacitor

SWCNT – Single-walled carbon nanotube

SSC – Symmetric supercapacitor

V

V_2O_5 – Vanadium oxide

W

Wt – weight

X

XPS – X-ray photoelectron spectroscopy

XRD – X-ray diffraction

Publications

1. **Kalyan Ghosh**, Chee Yoon Yue, Md Moniruzzaman Sk and Rajeeb Kumar Jena, Development of 3D urchin-shaped coaxial MnO_2 @PANI composite and self-assembled 3D pillared graphene foam for asymmetric all-solid-state flexible supercapacitor application *ACS Appl. Mater. Interfaces* 9.18 (2017), 15350-15363. (Chapter 4)
2. **Kalyan Ghosh**, Chee Yoon Yue, Md Moniruzzaman Sk and Rajeeb Kumar Jena, Development of 3D porous graphene/ MnO_2 @polyaniline hybrid paper for all-solid-state flexible asymmetric supercapacitor –*Sustainable Energy Fuels* 2, (2018), 280-293). (Chapter 5)
3. **Kalyan Ghosh and** Chee Yoon Yue, Novel all-solid-state flexible asymmetric supercapacitor based on ternary 3D heterogeneous structures - PANI decorated porous MnO_2 –Graphene electrode and MoO_3 /graphene aerogel. (Just accepted in *Electrochim. Acta* (Chapter 6)
4. Md Moniruzzaman Sk, Chee Yoon Yue, **Kalyan Ghosh** and Rajeeb Kumar Jena, Review on advances in porous nanostructured nickel oxides and their composite electrodes for high-performance supercapacitors, *J. Power Sources*. 308 (2016), 121-140.
5. Rajeeb Kumar Jena, Chee Yoon Yue, Md Moniruzzaman Sk, and **Kalyan Ghosh**, A novel high performance poly (2-methyl thioaniline) based composite electrode for supercapacitors application, *Carbon* 115 (2017), 175-187.

Chapter 1 Introduction

1.1 Background

The fast rising need for portable electronic devices such as wearable electronics, electronic papers, roll-up displays, mobile phones, flexible biosensors and flexible displays [1, 2], has made it essential to develop lightweight flexible high performance and safe power sources [3, 4]. Supercapacitors [5-7] (SCs) are reliable alternate energy storage sources compared to batteries and capacitors, because of their moderate energy density, high power density, long cycle life and safety in use [5]. The energy and power density plot of capacitors, supercapacitors, batteries, and fuel cells is shown in Figure 1.1 [8]. It shows that supercapacitor engulfs the gap between a battery and a conventional capacitor in terms of both energy density and power density.

Figure 1.1 Ragone plot of conventional capacitors, supercapacitors, batteries and fuel cells [8].

The earlier SCs were basically centered on liquid based aqueous, organic or ionic electrolytes [9, 10]. These SCs suffered from two major limitations. Firstly, due to possible leakage of electrolyte which is basically toxic and corrosive, it is necessary to use high cost packaging materials. Secondly, it is difficult to make the supercapacitor flexible when using liquid electrolyte due to problems in packaging. In recent years, flexible all-solid-state SCs have become a new category of energy storage devices [11-13]. These flexible SCs have important advantages compared to conventional SCs. These are small size, light weight, easy to carry, and have no chance of electrolyte leakage, and can be used in a wide range of temperature. Hence, these SCs hold great impact for use in flexible and portable electronics.

SCs can be classified in terms of the energy storage mechanism into two types: electrical double-layer capacitor (EDLC) and pseudocapacitor [14]. EDL capacitance arises from charge accumulation arising from electrode double-layer formation at the electrode–electrolyte interface. In contrast, pseudo-capacitance is based on the faradic charge transfer reactions and reversible redox reactions that occur at the surface of electro-active species.

Carbon-based supercapacitors have stood out as an emerging energy storage device because of their high power density and long cyclic stability [15]. Among the carbon based materials, graphene is attracted mostly due to its high conductivity, high surface area, and high flexibility [16]. There is an attempt to prepare graphene films for flexible electrode materials by integrating individual graphene sheet into the macroscopic structure. However, the energy storage mechanism in this work was limited to electrochemical double-layer capacitance. Recently, researchers have been working on incorporating pseudocapacitive materials [17-19] into graphene film.

Among all transition metal oxides, manganese dioxide (MnO_2) has been regarded as the most attractive oxide material in the field of supercapacitor due to its high theoretical specific capacitance (C_{sp}) (1370 F g^{-1}) [20], natural profusion, low cost, and it's environmentally benign nature [21]. However due to its poor electrical conductivity, the experimental C_{sp} of MnO_2 is very low [21], in the range of 100–250 F g^{-1} . To improve the electrochemical performance, the conductivity of MnO_2 -based electrode materials have been improved by adding conducting agents like carbonaceous materials [22-24] and conducting polymers (CPs) [25] which facilitated faster ion transportation. However, as the capacitance of most carbonaceous materials

is not high, the C_{sp} of MnO_2 -carbon hybrid materials are relatively low. CPs such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) have been mixed with MnO_2 to increase the electron and ion exchange rate in the electrode material [26]. Among all CPs, PANI has been identified as the most impactful conducting material due its high conductivity, very facile synthesis procedure, low cost and environmentally benign nature [6, 27].

Although MnO_2 -PANI binary composites have been fabricated to overcome the poor conductivity of MnO_2 and the poor stability of PANI, one key problem is the lack of good contact between MnO_2 and PANI. Therefore, it is essential to develop a new approach to improve the interaction between these two components. It is believed that improved interaction can be obtained by developing a suitable ternary composite of graphene, MnO_2 and PANI with the desired morphology to enhance the C_{sp} of the SC cell, whereby the contributions of both pseudocapacitive and electrochemical double-layer (EDL) capacitive materials can be attained. This is the approach taken in the present work on the development of a flexible SC cell.

It can be seen that the energy density (E_{cell}) of a supercapacitor depends on two critical factors, specific capacitance (C_{sp}) and operating voltage window (ΔV), which is obvious from the equation $E_{cell} = 1/2 C_{sp} \Delta V^2$ [28]. Hence, the energy density of the supercapacitor can be increased either by increasing the C_{sp} or ΔV values. To obtain high energy density, organic and ionic liquid electrolytes have been used for supercapacitor since they can provide for a higher voltage window (~ 3.0 V). However, these organic and ionic electrolytes are toxic and costly. Another way to expand the potential window is by asymmetric combination of the electrode materials, whereby the voltage window can be expanded to reach up to 2.0 V [29-31]. The latter approach will be considered in present work.

The operating potential window in the asymmetric supercapacitor (ASC) can be expanded by increasing the work function difference between the positive and negative electrode materials. This is achieved when the negative and positive electrodes contain metal oxides with the largest work function difference [32]. Among transition metal oxides, the highest work function difference was found between MoO_3 ($\psi = 6.9$ eV) and MnO_2 ($\psi = 4.4$ eV) [32]. This hypothesis will be put to the test in the current work by utilizing MnO_2 in the positive electrode and MoO_3 in the

negative electrode, to amplify the overall capacitance by creating the largest possible work function difference between the electrodes.

1.2 Objectives and scope of the report

The objective of the current research is to study how the three promising constituents, namely; PANI, MnO_2 and graphene, can be combined to develop an inexpensive high performance solid-state flexible supercapacitor that has high energy density and cyclic stability. In particular, a ternary 3D MnO_2 -PANI-graphene system with the appropriate morphology will be developed in order to improve the overall capacitance and energy density of the solid-state symmetric supercapacitor (SSC) via the EDL and pseudocapacitive mechanisms. Furthermore, the possibility of increasing the energy density of the SC by increasing the operating voltage window will be studied. This will be attempted by utilizing an asymmetric cell that employs suitable metallic oxides such MnO_2 and MoO_3 as electrode materials.

The approaches are as follows:

- (a) To investigate the structures that can be obtained in a binary MnO_2 @PANI system. It will be shown that a novel MnO_2 @PANI coaxial microrouchin can be synthesized via a simple and green approach without any surfactant and additional oxidant. This MnO_2 @PANI microrouchin system will be used as an electrode material in a flexible all-solid-state asymmetric supercapacitor and the electrochemical properties will be studied.
- (b) Next, composite nanostructures based on the ternary MnO_2 @PANI and reduced graphene oxide (RGO) system will be developed and evaluated. It will be demonstrated that a novel 3D RGO/ MnO_2 @PANI porous hybrid film can be synthesized using GO and MnO_2 @PANI nanoparticles. This will be utilized as an electrode material in a flexible solid-state SSC, and also in an ASC together with graphene aerogel as a negative electrode. The electrochemical properties of both flexible solid-state SSCs and ASC will be studied.
- (c) Finally, an approach to improve the energy density by enlarging the operating voltage window by employing negative and positive electrodes that contain

metal oxides with the largest work function difference will be attempted. It will be demonstrated that a novel flexible all-solid-state asymmetric supercapacitor with very high energy density can be obtained by enlarging the operating voltage window to 0–1.6 V through the use of MnO_2 and MoO_3 in the positive and negative electrodes, respectively, and adopting a 3D heterogeneous composite based on PANI and graphene.

1.3 Structure of the report

The objectives and scope of this research on ternary composites systems based on PANI, MnO_2 and graphene-based for energy storage in supercapacitors are outlined in Chapter 1.

Chapter 2 comprises a comprehensive literature review on supercapacitors including the working principles, common electrode materials, and synthesis methods of 3D graphene. A brief literature review on solid-state symmetric and asymmetric supercapacitors is also included.

The experimental details including the chemicals, general equipment and procedures used are contained in Chapter 3.

Chapter 4 presents studies on the binary MnO_2 –PANI system and the synthesis of PANI coated MnO_2 coaxial microrouchins (MnO_2 @PANI) and their asymmetric solid–state cell with 3D graphene foam are considered to analyze their electrochemical performances.

Chapter 5 outlines the development of the ternary composite system. Specifically, the development of RGO/ MnO_2 @PANI film based SSC, template guided graphene aerogel based SSC and their asymmetric combination to fabricate a solid-state ASC of graphene aerogel//RGO/ MnO_2 @PANI are discussed.

Chapter 6 deals with the issue of enhancing energy density by widening the operating voltage window by incorporating MnO_2 and MoO_3 in the electrode materials of the ASC. In particular, the development of high energy density flexible solid-state ASC by developing a sandwich-type 3D PANI/(MnO_2 –RGO)/PANI porous film and 3D MoO_3 /graphene aerogel is considered in detail. Finally, the summary of conclusions and recommendations for future work are given in Chapter 7.

Chapter 2 Literature review

2.1 Development of Supercapacitor

The conventional capacitor which store energy in an electrostatic field comprises of two parallel plates (electrode) separated by a dielectric [33]. A potential difference is applied across the plates to migrate the positive and negative charges towards the surfaces of the electrodes of opposite polarity as illustrated in Figure 2.1. This causes storage of charges in the capacitor. The capacitance (C) of the capacitor is the ratio of electric charge (Q) stored on each electrode to the potential difference (V) between them as shown by the Equation 2.1 [33].

$$C = \frac{Q}{V} \dots\dots\dots (2.1)$$

The capacitance C depends on to the permittivity of the dielectric, area (A) of each electrode and distance (d) between the two electrodes, which can be denoted by the Equation 2.2 [33].

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \dots\dots\dots (2.2)$$

where, ϵ_0 is the permittivity of the free space and ϵ_r is the dielectric constant of the material placed in between the plates.

Figure 2.1 Schematic illustration of charge storage of a static capacitor [5].

An electrochemical capacitor (EC), which follows the same principle of conventional capacitors, comprises electrodes with high specific surface area and a thinner dielectric that is governed by thickness of the double layer. When the capacitance of an EC is rated as high as ten hundred thousand farads per device, the capacitor is called a supercapacitor or ultracapacitor [5, 33].

2.2 Working principles of supercapacitors (SCs)

In terms of their energy storage mechanism, SCs can be classified in two classes namely; electrochemical double-layer capacitors (EDLCs) and pseudocapacitors [14], which will be discussed in the following sections.

2.2.1 Principle of electrochemical double-layer capacitors

The concept of double-layer was first developed and modeled by Von Helmholtz in the nineteenth century. In Helmholtz double-layer model, opposite charges accumulates at the electrode–electrolyte interface by electrostatic attraction. The opposite charge is separated by an atomic distance as shown in Figure 2.2a. Later, the

Helmoltz model was refined as the Gouy–Chapman model which describes two oppositely charged layers that are formed at the electrode–electrolyte interface. Later, Stern [34] combined Helmholtz model with the Gouy–Chapman model. In the Stern model, two distinct regions are identified in the electrolyte which are the compact layer (or stern layer) and the diffuse layer. The stern layer developed at the electrode–electrolyte interface comprises solvated ions that are adsorbed by the electrode. In the diffuse layers, cations and anions are distributed in solution by thermal motions as described in Figure 2.2c [33, 34].

Figure 2.2 EDL models: (a) the Helmholtz model, (b) the Gouy–Chapman model and (c) the Stern model [35].

Therefore, the double layer capacitance (C_{dl}) can be regarded to have two components, the compact double-layer capacitance (C_H) and the diffusive layer capacitance (C_{diff}). Hence the overall double layer capacitance (C_{dl}) can be obtained from the following relationship:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \dots\dots\dots (2.3)$$

The electrical double-layer (EDL) capacitance ultimately depends on the following factors; the conductivity of electrode material, accessibility of the electrode surface, the electric field across the electrodes and the electrolyte properties like ion sizes, dipole moments and ion pair vicinity. The charging and discharging of an EDLC is shown in Figure 2.3. The EDL capacitance is solely electrostatic and non-faradic in nature since no charge transfer occurs. This kind of charge storage phenomena occurs mainly in carbon-based materials and the charging–discharging behavior is highly reversible in nature.

Figure 2.3 Schematic illustration of charging and discharging of double-layer capacitor [36].

2.2.2 Principle of pseudocapacitors

In 1970s, Conway and Trasatti introduced a new concept of charge storage principle called pseudocapacitance [5] whereby charge storage is based on the faradic charge transfer process between the electrode material and electrolyte ions. The charge transfer happens by the reversible redox reaction, and intercalation or electrosorption processes on the surface of the electrodes. The principle of energy storage is somewhat similar to a battery. The most commonly studied pseudocapacitive materials are transition metal oxides such as RuO_2 , MnO_2 , Co_3O_4 , TiO_2 , V_2O_5 , Mo_3O_4 and iron oxide Fe_3O_4 , and CPs such as polyaniline (PANI), polythiophene (PTh) and polypyrrole (PPy) [5, 33].

2.2.3 Principle of hybrid capacitors

Hybrid electrode materials are commonly made from a combination of EDL-capacitive and pseudocapacitive materials. Hybrid capacitors utilize the advantages of both EDL capacitance and pseudocapacitance to obtain large improvement in the overall performance of supercapacitors [37]. The advantage of a hybrid system is that it delivers high energy and power density without lowering its cycle life. The charge storage principle in hybrid supercapacitors depends on both the Faradic and non-Faradic (electrostatic) processes.

2.3 Supercapacitor cell components

A supercapacitor have four basic components, namely: (1) electrodes materials, (2) electrolytes, (3) separators and (4) current collectors. Details studies of the supercapacitor cell components are discussed below:

2.3.1 Electrode materials

There are three major categories of electrode materials are found in the field of supercapacitor. They are carbon-based materials, transition metal oxides, and conducting polymers (CPs). These materials have their respective advantages and limitations for use as supercapacitor electrode materials. Hybrid materials comprising a combination of the above three materials have been found to be promising electrode materials [5].

2.3.1.1 Carbon materials

2.3.1.1.1 Activated carbon (AC) and carbon nanotubes (CNTs)

Activated carbons (ACs) are regarded as the most widely utilized carbon materials in commercial EDLCs because of their stable supply and ease of fabrication procedures, low cost and environmentally benign nature. They can provide a wide variety of capacitance depending on their pore sizes, surface area, electrical conductivity and chemical composition. In general, the reported capacitance values of ACs in an

aqueous electrolyte have been found to be around $100\text{--}400\text{ F g}^{-1}$ and about $120\text{--}150\text{ F g}^{-1}$ in organic or ionic liquid [33].

Carbon nanotubes (CNTs) have been regarded as another promising carbon material for EDLCs because of its 1D geometry, high electrical conductivity, high surface area light weight and high chemical stability [5, 33]. There are primarily two types of nanotubes, namely; single walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). Their conductivity range varies depending on the diameter and length of the nanotubes. The presence of mesopores (pore diameter $2\text{--}50\text{ nm}$) in carbon nanotubes (CNTs) provide as easy access points for the electrolyte ions to the electrode–electrolyte interface for the EDL formation. The C_{sp} values depend on the CNT-growth process used which affects the accessible carbon surface area, and the diameter and length of the CNTs. Although CNTs possess longer cycle life, the capacitance values of CNTs are low with an EDL capacitance of only up to 135 F g^{-1} [38, 39].

2.3.1.1.2 Graphene

Graphene, a 2D sp^2 hybridized carbon skeleton has been recognized as promising electrode material among carbon based materials because of its high electrical conductivity ($\sim 200\text{ S m}^{-1}$) [40, 41], very large surface area ($2650\text{ m}^2\text{ g}^{-1}$), unique charge-carrier mobility, high electrocatalytic activity and mechanical strength [42, 43]. The graphene is aromatic in nature possessing highly dense π -electron clouds. The crystal structure of graphene is represented in Figure 2.4. The graphene can be synthesized in large amounts at low cost through reduction of graphene oxide (GO). Usually, reduced graphene oxide (RGO) is treated as equivalent to pristine graphene.

Figure 2.4 Crystal structure of graphene [44].

In recent years various structural models of GO have been proposed. Among these, the model proposed by Anton Lerf and Jacek Klinowski (Figure 2.5a & Figure 2.5b) [45]) is the most widely accepted. In this model, GO contains two segments – (i) the sp^2 -hybridized aromatic rings, and the oxidized regions that include carbon with oxy-generated functional groups such as hydroxyl, epoxy groups on the basal plane and (ii) carboxylic groups along the edge [45, 46].

Figure 2.5 (a & b) Lerf-Klinowski model structures of GO showing the presence of oxygen functionalities above and below the basal plane [47] [45].

The high surface area of graphene is the key reason for its high intrinsic specific capacitance. The theoretical capacitance of graphene is 526 F g^{-1} [42, 43]. However, the obtained capacitance of RGO electrodes in aqueous, organic, and ionic liquid electrolytes is lower and have been reported to be 135, 99, and 75 F g^{-1} , respectively [48]. The lower capacitance values obtained are due to the agglomeration or stacking of graphene sheets into graphite-like structure. There are several approaches to overcome the graphene sheets stacking problem. One way is to develop a 3D porous form of graphene sheet that is commonly known as 3D graphene. In 3D graphene, the accessible surface area for electrolyte ions is greatly increased leading to a large enhancement in the experimental capacitance. The charge storage mechanism of graphene based electrode is shown in Figure 2.6. The most common techniques for preparing 3D graphene preparation are by chemical vapor deposition (CVD), epitaxial growth, chemical exfoliation and [49, 50] and mechanical exfoliation of graphene oxide [51-53].

Figure 2.6 Charge storage mechanism in graphene based supercapacitor electrode [54].

2.3.1.2 Metal oxides

Transition metal oxides are very important pseudocapacitive materials due to the fast reversible redox reactions that can occur at their surfaces. Notable metal oxides which have been studied include RuO_2 , MnO_2 , Co_3O_4 , NiO , and V_2O_5 . There are two basic requirements for a metal oxide in an SC are; (i) it must possess good electrical conductivity, and (ii) it must exist in two or more oxidation states without any phase change. The basic principles and charge storage mechanism of the commonly used metal oxides are discussed below.

2.3.1.2.1 RuO_2

Among all transition metal oxides RuO_2 is the most widely studied material which gives the highest capacitance because of its high reversible redox reaction, presence of three distinct oxidation states, wide potential window, metallic type conductivity and high thermal stability [55].

The charging mechanism for RuO_2 in an acidic condition is presented as follows:

According to Equation 2.4, the fast exchange between proton and electron are in favor of reversible redox reaction. It was reported that $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ had a high C_{sp} of 900 F g^{-1} [55].

2.3.1.2.2 MnO_2

Even though RuO_2 shows very high specific capacitance, its application in commercial supercapacitor is limited as it is very toxic and costly. MnO_2 had been found to be a suitable alternative material because of its high theoretical capacitance (1370 F g^{-1}) [56], environmentally benign nature and low cost. However, the reported C_{sp} of MnO_2 of $100\text{--}200 \text{ F g}^{-1}$ is very low due to its poor electrical conductivity and

poor ions mobility. The proposed charging mechanism of MnO_2 can be expressed as follows:

where, $\text{D}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$ and H^+ . In an alkaline medium, the first electron discharge of MnO_2 , which is called the electron-proton mechanism, can be expressed as follows:

Crystallinity and structural water content are important factors that might affect the electrochemical performance of the MnO_2 . It is well known that high crystallinity can enhance the conductivity; however it reduces the specific surface area. On the other hand, low crystallinity can result in a porous microstructure of MnO_2 , but electronic conductivity would be reduced. Extensive research [21, 57, 58] had unveiled that MnO_2 had several typical crystal structures, such as α -, β -, and δ - MnO_2 . Both α - and β - MnO_2 have tunnel structures, while δ - MnO_2 has a layered structure as shown in Figure 2.7. It was apparent that different crystal structures of MnO_2 can be obtained by employing different synthesis conditions. With increasing the precursor acidity, the crystal structures of MnO_2 can progress from layered structured δ - MnO_2 , to subsequently become tunnel structured α - and β - MnO_2 .

Figure 2.7 Typical crystal structures of MnO_2 [58].

Different techniques have been used to prepare MnO_2 nanoparticles including: the (1) thermal decomposition process, (2) hydrothermal process, (3) sol-gel process, (4) electrochemical deposition process, (5) physical vapor deposition process and (6)

sonochemistry method. So far, various crystalline structures of MnO_2 comprising those with 1D (nanorods, nanowires and nanotubes) [59-61], 2D (nanosheets and nanoflakes) [62, 63], and 3D (nanospheres and nanoflowers) [64, 65] features have been synthesized. Hongen et al. [66] synthesized $\alpha\text{-MnO}_2$ nanorods (shown in Figure 2.8) through the hydrothermal method using potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4) as the precursors. The nanorods were formed through the dissolution–recrystallization mechanism which is commonly known as Ostwald ripening process.

Similarly, Xu [65] et al. synthesized hollow spheres and hollow urchins of $\alpha\text{-MnO}_2$ through hydrothermal reaction of KMnO_4 and H_2SO_4 . The obtained morphology of the $\alpha\text{-MnO}_2$ urchins is shown in Figure 2.9.

Figure 2.8 ((a), (b)) TEM images of the as-prepared $\alpha\text{-MnO}_2$ nanorods; the inset shows the corresponding SAED pattern. ((c), (d)) HRTEM images of the $\alpha\text{-MnO}_2$ nanorods [66]. Adapted with permission from Ref. 66, Copyright (2013), IOP publishing.

Figure 2.9 Morphologies of the products obtained by hydrothermal reaction for 12 h: (a and b) low magnification; (c and d) profile images of α - MnO_2 hollow urchins [65]. Adapted with permission from Ref. 65, Copyright (2007), American Chemical Society.

2.3.1.2.3 MoO_3

Other than MnO_2 , molybdenum trioxide (MoO_3) has been regarded as a promising electrode material replacing RuO_2 in the field of SC due to its high electrochemical activity, low cost and environmentally benign nature [67]. MoO_3 acts like an n-type semiconductor. MoO_3 exist in three different polymorphs, which are: orthorhombic α - MoO_3 , monoclinic β - MoO_3 , and hexagonal h- MoO_3 . Among these, α - MoO_3 is the thermodynamically stable phase, and h- MoO_3 the low temperature metastable phases [68]. The α - MoO_3 has attracted most interest due to its anisotropic layered structure. This layered structure provides for a large accessible area for the mobility of electrolyte ions (H^+ or K^+) during electrochemical measurements [69, 70]. On the other hand, its poor ionic and electronic conductivity limits its electrochemical performance. The theoretical specific capacity of α - MoO_3 was found to be 1111 mAh g^{-1} [71]. The charge-discharge lithiation reaction of MoO_3 electrode can be presented by the following reaction [72]:

In recent years, various nanostructures such as, nanobelts, nanorods and nanoplates of MoO_3 have been synthesized utilizing the hydrothermal method, the chemical bath deposition method and the sol-gel process. For example, Khandare et al. [73] synthesized $\alpha\text{-MoO}_3$ nanorods (shown in Figure 2.10) through the hydrothermal method using ammonium heptamolybdate tetrahydrate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$ and nitric acid (HNO_3).

Figure 2.10 (a) – (d) SEM images of MoO_3 nanorods [73].

Desai et al. [74] synthesized h-MoO_3 and $\alpha\text{-MoO}_3$ nanocrystal (see Figure 2.11) through the chemical bath deposition technique using similar constituents of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and HNO_3 .

Figure 2.11 FESEM of h-MoO₃ (a and b), FE-SEM of α-MoO₃ (c and d) [74].

Tang et al. [72] followed a different technique to synthesize MoO₃ nanoplates as the anode materials for SCs through the sol-gel process using molybdenum (Mo) powder and hydrogen peroxide (H₂O₂) as precursors. The obtained morphology of the MoO₃ nanoplates is shown in Figure 2.12.

Figure 2.12 SEM micrographs of (a) the MoO₃ nanoplates and (b) the bulk MoO₃ [72]. Adapted with permission from Ref. 72, Copyright (2011), The Royal Society of Chemistry.

2.3.1.2.4 Other metal oxides

NiO has also been considered as another promising electrode material for SC in alkaline solution owing to its low cost, low toxicity and high theoretical C_{sp} of 3750 F g⁻¹ [75]. However, the experimentally obtained NiO possess low C_{sp} of 170–250 F g⁻¹ due to its poor electrical conductivity. The charging mechanism of NiO in KOH electrolytes can be presented as follows [76]:

Another known candidate is Co₃O₄ due to its excellent reversible redox behavior, large surface area and good chemical stability [77]. Wang et al. [78] fabricated mesoporous Co₃O₄ microspheres that showed a C_{sp} of 102 F g⁻¹. The charging mechanism of Co₃O₄ as an electrode material of pseudocapacitor is as follows [79]:

Many other materials, such as SnO₂ [80, 81], IrO₂ [82], MoO₂ [83], NiCo₂O₄ [84, 85] and MnCo₂O₄ [86] have also been studied. However, their high synthesis cost limits their applications as electrode materials.

2.3.1.3 Conducting polymers (CPs)

The CPs [87, 88] are promising pseudocapacitive materials as they can support reversible redox reactions. The CPs are useful electrode materials due to their high electrical conductivity, easy synthesis procedure, good ionic transportation and can readily be doped. CPs are cheaper than the metal oxides and other EDL based electrode materials such as CNT and graphene. However, they show poor performance when subjected to prolonged cyclic charge-discharge processes due to shrinkage, cracking or damage of the electrode material. Some most commonly used

CPs includes polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh). The structures of these polymers are shown below in Figure 2.13:

Figure 2.13 Chemical structures of PANI, PPy and PTh [89].

2.3.1.3.1 Polyaniline (PANI)

PANI is the most promising pseudocapacitance material among all CPs due its ease of synthesis, high electrical conductivity, low cost and environmentally benign nature [6, 27]. PANI can be synthesized through polymerization of aniline by a chemical oxidant or by electrochemical polymerization. Different nanostructures of PANI such as nanotubes, nanofibers, nanosphere and nanorods can be synthesized by emulsion polymerization, seeding polymerization and template methods. A general chemical structure of PANI which includes amine and imine forms is shown in Figure 2.14.

Figure 2.14 General chemical structure of polyaniline [89].

PANI exists in four well-known states which show different chemical and physical properties. These are emeraldine salt, emeraldine base, leucoemeraldine and pernigraniline base. The most common state is emeraldine (protonated state) with dark green color, which has a conductivity of $2\text{--}10\text{ S cm}^{-1}$ [89]. The protonated PANI can be converted to nonconductive blue emeraldine base (blue color) upon treating with ammonium hydroxide. The fully reduced state is known as leucoemeraldine with pale brown color [89]. The oxidation process of PANI is shown below in Figure 2.15:

Figure 2.15 Conversion of PANI emeraldine form to PANI emeraldine base [90].

2.3.1.3.2 Polypyrrole (PPy)

PPy is another promising CP used widely in supercapacitor. Bolto et al. in 1963 first developed conductive iodine doped PPy by chemical polymerization [91]. PPy and its derivative have attracted interest in the field of SC due to their stable oxidation states, high conductivity, interesting redox properties and easy synthesis procedure. The reversible redox reaction of PPy is shown in Figure 2.16.

Figure 2.16 Reversible redox reaction of polypyrrole [92].

2.3.1.3.3 Polythiophenes (PTh)

PTh also has been considered as a promising material in SC application. The derivative of PTh, poly(3,4-ethylenedioxythiophene) (PEDOT) has been successfully utilized due to its good electrical conductivity, excellent environmental stability and transparency in thin oxidized films [93]. PEDOT can be synthesized by electrochemical polymerization, liquid phase polymerization and vapor phase polymerization. The oxidation and reduction processes of PEDOT are illustrated in Figure 2.17.

Figure 2.17 The oxidized and reduced chemical forms of PEDOT structure [89].

2.3.1.4 Hybrid materials

Various hybrid materials were synthesized in recent years for supercapacitor electrode materials comprising of carbon materials with metal oxides, carbon materials with conducting polymers, metal oxides with conducting polymers, and ternary composites of carbon materials, metal oxides and conducting polymers. Here, those published works that pertain to MnO_2 , PANI and graphene based composite electrode materials will be briefly discussed.

2.3.1.4.1 MnO₂–PANI based composite electrode

In order to address the disadvantage of the low electronic conductivity of MnO₂, conductive polymers such as PANI are synthesized together with MnO₂ to make binary composites that can provide a conductive network to promote faster transfer of the electrons and ions. Chen et al. [94] prepared hybrid films of PANI and MnO₂ by the electrodeposition and electro-copolymerization methods. It should be noted that the morphology of MnO₂ in the above composites was in the shape of particles. Liu et al. [95] electrochemically synthesized MnO₂ nanoparticles embedded in a 3D matrix of PANI doped polymers. Iranagh et al. [96] synthesized MnO₂–PANI nanofiber composites (as shown in Figure 2.18) by utilizing MnO₂ nanofibers as ‘seeds’. The MnO₂ nanofiber prepared from a chemical precipitation method was used as the seeds to facilitate the polymerization of aniline.

Figure 2.18 (a) SEM images for MnO₂–PANI nanofibers synthesized with rapid mixing and using MnO₂ as the seed at magnification of 2.00 μm, (b) SEM images for MnO₂–PANI nanofibers synthesized with rapid mixing and using MnO₂ as the seed at magnification of 1.00 μm [96]. Adapted with permission from Ref. 96, Copyright (2013) Elsevier.

Sumboja et al. [25] developed manganese dioxide/polyaniline coaxial nanowire (MnO₂/PANI) networks using a double surfactant method. They first prepared MnO₂ nanorods through the hydrothermal route using manganese nitrate Mn(NO₃)₂ and KMnO₄ as the precursors, and next synthesized MnO₂/PANI coaxial nanowire using the surfactants polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) to coaxially grow PANI on MnO₂ nanowire through polymerization of aniline using ammonium persulfate (APS). The morphology of the obtained coaxial MnO₂/PANI nanowires is shown in Figure 2.19.

Figure 2.19 (a–c) SEM image of MnO₂ NW, MnO₂/PANI coaxial NW and PANI; (d and e) TEM image of MnO₂ NW and MnO₂/PANI coaxial NW, and (f) TEM-EDS analysis of MnO₂/PANI coaxial NW [25]. Adapted with permission from Ref. 25, Copyright (2012), The Royal Society of Chemistry.

2.3.1.4.2 MnO₂–graphene based composite electrodes

Like PANI, graphene has also been incorporated with MnO₂ to increase its capacitance, rate capability and cycle life. An GO sheets supported needle-like MnO₂ nanocrystals (GO–MnO₂ nanocomposites) was synthesized through a soft chemical route in a water–isopropyl alcohol system [97]. The oxygenate groups on the surface of GO sheets acted as centers for anchoring manganese ions and their subsequent nucleation and growth. With the assistance of microwave heating, the redox reaction between carbon and permanganate ions was used to deposit MnO₂ on graphene (RGO) sheets [98]. The RGO–MnO₂ composite exhibited enhanced capacitive performance mainly due to the synergistic effect of the high conductivity of RGO sheets and the redox reaction of manganese oxides. Cheng et al. [99] fabricated MnO₂–graphene composites as an electrode material by anodic electrodeposition on a graphene sheet. Dong et al. [100] synthesized the 3D free-standing supercapacitor

electrode hybrid material comprising MnO_2 and graphene foam (see Figure 2.20) utilizing nickel foam as the sacrificial template.

Figure 2.20 (a) FESEM image of 3D nickel foam substrate. (b) FESEM image of 3D graphene foam without nickel substrate. (c) Low magnification FESEM image of MnO_2 /3D graphene foam hybrid. (d) MnO_2 deposited on the surface of 3D graphene foams at high magnifications [100]. Adapted with permission from Ref. 100, Copyright (2012), Elsevier.

2.3.2 Electrolytes for supercapacitors

The electrolyte is a critical component in SCs, and the performance of the SC depends on the type of electrolytes used. It supplies the ions to the electrodes and carries the ionic charges. The choice of electrolyte is in great concern as it affects the C_{sp} , energy density and power density. There are four basic types of electrolytes. They are aqueous electrolyte, organic, ionic and polymer gel electrolytes. The requirements of an electrolyte are high ionic conductivity, be stable in the operating temperature range, and should not vaporize or freeze during the electrochemical process.

2.3.2.1 Aqueous electrolytes

Aqueous electrolytes are widely used in supercapacitor. Some common aqueous electrolytes are sulfuric acid (H_2SO_4), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), potassium hydroxide (KOH), potassium chloride (KCl), sodium hydroxide (NaOH) and sodium sulfate (Na_2SO_4) in water solvent. The advantages of using aqueous electrolytes are: (i) its lower ESR compared to organic or ionic electrolyte, (ii) its higher ionic conductance and (iii) it provides higher power density. The major problem of using aqueous electrolytes is its low operating potential window ($\Delta V \sim 1.0$ V). Water molecules dissociates above 1.23 V potential which is depicted by the equation $2 \text{H}_2\text{O} (l) = \text{O}_2 (g) + 4\text{H}^+ + 4\text{e}^-$. As the energy density is proportional to the square of the potential window, the obtained energy density in aqueous electrolyte tends to be on the lower side.

2.3.2.2 Organic electrolytes

The advantage of using an organic electrolyte is its large potential window (2.3–3.0 V) which eventually increases the energy density of the SCs. However, organic electrolytes are costly and toxic in nature. Some commonly used organic electrolytes are tetraethyl ammonium tetrafluoroborate $(\text{C}_2\text{H}_5)_4\text{N}^+\text{BF}_4^-$, and quaternary ammonium salts – $\text{R}_4\text{N}^+\text{Cl}^-$, where, $\text{R} = -\text{CH}_3$ and $-\text{C}_2\text{H}_5$, exists in acetonitrile solvent. The organic electrolyte has high ESR which reduces the C_{sp} . The C_{sp} is also reduced due to the large size of the ion which cannot diffuse into the inner pores of the electrode materials. Hence, the entire surface of electrode cannot be utilized by the electrolyte ions, which eventually decreases the C_{sp} value.

2.3.2.3 Ionic electrolytes

The ionic electrolyte contains bulky cations. The operating voltage window is about 3.4 V which increases the energy density. However, due to the bulky ion sizes, the entire surface of electrode cannot be accessed. Moreover, the electrolyte is costly and toxic in nature. It has a higher ESR which decreases the C_{sp} value. Some common ionic electrolytes are: 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}]\text{PF}_6$), 1-Butyl-3-methylimidazolium chloride ($[\text{BMIM}]\text{Cl}$), 1-Ethyl-3-

methylimidazolium ethylsulfate ([EMIM]EtOSO₃) and tris(2-hydroxyethyl)methylammoniummethylsulfate ([MTEOA]MeOSO₃).

2.3.2.4 Polymer gel electrolytes

The polymer gel electrolyte is one of the key components for solid-state supercapacitor. Polymer gel electrolyte is very easy to handle, there is no danger of any leakage of electrolyte after packaging and it can be used in the wider temperature range. The polymer gel electrolytes are low cost, nontoxic in nature, very stable and safe in use. The electrolyte usually consists of polymer framework, a solvent and an electrolytic salt. Some most common polymers used for gel electrolytes are polyvinyl alcohol (PVA) [12], poly(methyl methacrylate) (PMMA) [101], poly(vinylidene fluoride) (PVdF), poly(ethylene oxide) (PEO) [102], polyacrylate (PAA) [103], polyacrylonitrile (PAN) and poly(amine-ester) (PAE) [104]. Either organic or aqueous solvent can be used in gel electrolyte. The three major types of gel polymer electrolyte are (1) lithium ion gel polymer electrolytes, (2) proton conducting gel polymer electrolytes and (3) alkaline gel polymer electrolytes. Brief information on each electrolyte is outlined below.

(1) *The lithium ion gel polymer electrolytes:* These are prepared by dissolving the polymer and Li salt in organic electrolyte and they are suitable for a wide operating temperature range of 70–170 °C. The commonly used lithium ion gel electrolytes are PVA/LiClO₄ [105], PMMA/LiClO₄ [101], PVA/LiCl [30] and PAN-b-PEG-b-PAN/LiClO₄ [106].

(2) *Proton conducting gel polymer electrolytes:* As the proton has higher mobility than Li⁺ ions, the proton conducting gel polymer electrolyte can be very effective in SC application. The commonly used gel polymer electrolytes are PVA/H₂SO₄ [12], PVA/H₃PO₄ [107], PVA/H₃PO₄/silicotungstic acid [108]. The gel electrolyte is usually prepared by dissolving the polymer and proton donor acid with a polar solvent. Usually H₂SO₄ and H₃PO₄ are commonly used as the proton donor solvent.

(3) *Alkaline gel polymer electrolytes:* These are emerging electrolytes where potassium hydroxide (KOH) is dissolved with polymer gel in aqueous solvent. The common alkaline gel polymer electrolytes are PVA/KOH [109, 110], PAAK/KOH

[111, 112] and PEO/KOH [113]. Amongst these, the PVA/KOH gel electrolyte has a high ionic conductivity of the order of $10^{-2} \text{ S cm}^{-1}$.

2.3.3 Separators

Separators comprise of non-conducting thin paper or polymer or ceramic materials, that are used with aqueous or organic electrolyte in-between the two electrodes. The separator should transport the electrolyte ions very easily by electrophoresis and should have sufficient mechanical resistance. In a solid-state supercapacitor, the solid-state gel electrolyte between two electrodes acts as a separator and hence it is not necessary to use any external material as a separator in solid-state SC fabrication.

2.3.4 Current collectors

Current collectors are usually made of metals and alloys which have high electrical conductivity. Ni, Cu, Al and Pt sheets or foams are commonly. Recently, researchers have developed graphene film to utilize as both an electrode material as well as a current collector due its high conductivity and mechanical stability. In flexible SCs, the current collector should be very flexible and have sufficient mechanical strength to withstand cyclic bending. It should be thin and lightweight so that the whole supercapacitor unit is light and easy to handle.

2.4 Electrochemical cell systems and measurements

2.4.1 Electrode cell systems and measurement methods

In a three-electrode cell system, there is one working electrode, one reference electrode and one counter electrode. Usually a carbon electrode or glass electrode is used as the working electrode, Ag/AgCl or calomel electrode ($\text{Hg}_2\text{Cl}_2/\text{Hg}$) is used as the reference electrode, and platinum wire is commonly used as the counter electrode.

In a two-electrode cell system, Ni or Cu or Pt sheets/foils are used as working electrodes as well as the current collector. The SC cell is prepared by assembling two working electrodes.

The performance of a supercapacitor can be evaluated using the following electrochemical techniques, namely: cyclic voltammetry (CV), cyclic charge–discharge (CCD) and electrochemical impedance spectroscopy (EIS) which are outlined below.

2.4.2 Cyclic voltammetry (CV) study

In the CV technique, a linear voltage ramp between two voltage limits is applied to an electrode or a cell and the resulting current is measured.

The capacitance C (in F) can be expressed by the Equation 2.8 [114]:

$$C = \frac{Q}{\vartheta} = \frac{\int_{V_1}^{V_2} i(V) dV}{\vartheta(V_2 - V_1)} \dots\dots\dots(2.8)$$

where, the term in the numerator of Equation 2.8 represents the area of I – V curve (Figure 2.21), ϑ is the scan rate, and V_1 and V_2 are the switching potentials in the cyclic voltammetry test.

In the three-electrode cell system, the measured capacitance is just the capacitance per electrode. On the other hand, in the two-electrode cell system, the measured capacitance is the capacitance of a SC cell. In this system, the two capacitors are assumed to be connected in series such that the measured total capacitance value is multiplied by 2 to determine the electrode capacitance [115].

$$\frac{1}{C_{tot}} = \frac{1}{C_1} + \frac{1}{C_2} \dots\dots\dots(2.9)$$

where, C_1 and C_2 are the capacitances of the individual electrodes, C_{tot} is the total capacitance obtained from the experiment.

Assuming, $C_1 = C_2 = C$, where, C = capacitance per single electrode.

$$\text{So, } \frac{1}{C_{tot}} = \frac{2}{C} \text{ or, } C = 2C_{tot} \dots\dots\dots (2.10)$$

The specific capacitance of SC cell for the two-electrode system was evaluated from the following Equation 2.11 [114]:

$$C_{sp} = \frac{C_{tot}}{m} \dots\dots\dots (2.11)$$

where, C_{sp} is the specific capacitance (F g^{-1}) and m (g) is the mass of the total active material.

It should be noted that an EDL type capacitive material shows a rectangular CV curve as shown in Figure 2.21a. In contrast, a pseudocapacitive type material exhibits a curve that has a maxima and a minima that correspond to the oxidation/reduction peaks (E_p^a & E_p^c) for reversible redox reactions as shown in Figure 2.21b

Figure 2.21 a) CV plot of an ideal EDLC and b) Typical CV plot of a pseudocapacitor [89].

2.4.3 Cyclic charge–discharge (CCD) study

This is the most widely used technique for measuring the electrochemical performance of a SC cell because it can be extended from the laboratory to an

industrial scale. In this technique, the voltage output is measured under a constant applied current.

The C_{sp} of the SC cell can also be calculated from the constant current from the charging–discharging curve using the following Equation 2.12 [116, 117]:

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \dots\dots\dots (2.12)$$

where, C_{sp} is the specific capacitance (F g^{-1}), I is the constant discharge current (A), Δt is the total discharging time (s), ΔV is the discharge voltage range (excluding ohmic drop at the beginning of the discharging curve), and m is the total mass of the active electrode materials.

The Coulombic efficiency (η) which is the ratio of discharging time to charging time can be calculated by using Equation 2.13 [117].

$$\eta = \left(\frac{t_d}{t_c} \right) \times 100 \dots\dots\dots (2.13)$$

where, t_c and t_d are the charging and discharging times (s). A typical CCD plot is shown in Figure 2.22, which depicts the charge–discharge profile of (a) an EDL materials and (b) a pseudocapacitive materials

Figure 2.22 General representation of CCD cycles [118].

The energy density (E_{cell} , Wh kg⁻¹) of a supercapacitor can be calculated from the following Equation 2.14 [116]:

$$E_{cell} = \frac{1}{2} C_{sp} \Delta V^2 \dots\dots\dots (2.14)$$

Where, C_{sp} = specific capacitance and ΔV = operating voltage range.

The power density (P_{cell} , kW kg⁻¹) can be calculated from the following Equation 2.15 [119]:

$$P_{cell} = \frac{E_{cell}}{t} \frac{3600}{1000} \dots\dots\dots (2.15)$$

where, E_{cell} is the energy density (Wh kg⁻¹) and t is the discharge time (s).

2.4.4 Electrochemical impedance spectroscopy (EIS) study

EIS is very useful technique to understand the interfacial behavior of the electrochemical system, such as the equivalent series resistance, charge transfer resistance, mass transfer and diffusion control. The Nyquist plots of impedance contain two segments – the lower-frequency region which is indicated by the upper right portion and the higher-frequency region which is indicated by the lower left portion. A schematic Nyquist curve is shown in Figure 2.23 to illustrate different parts of the impedance curve [41].

Figure 2.23 General representation of Nyquist plot [41].

In the higher-frequency region, the intercept at Z_{real} axis at point A, represents the equivalent series resistance (R_s) which includes the contact resistance between the current collector and the electrode material, the intrinsic resistance of the active material, the contact resistance at the electrode–electrolyte interface and the ionic resistance of the electrolyte [120]. In the medium-frequency region (denoted as B), the diameter of the semicircle provides a measure of the charge-transfer resistance (R_{ct}) at the electrode–electrolyte interface [41]. In the lower-frequency region (denoted as C), the 45° slope portion of the curve depicts the Warburg resistance (R_w) which is a measure of ionic diffusion of the electrolyte ions towards the electrodes. The higher slope of the line indicates higher diffusion rate and a lower R_w [7, 120]. The straight line close to 90° indicates a pure EDL-capacitive behavior [41].

2.4.5 Cycle lifetime

The cyclic stability test is usually performed by conducting repetitive CCD or CV tests for many cycles. SC usually shows high cyclic stability since charge storage is controlled electrostatically for EDL materials. In case of pseudocapacitors, a reversible redox reaction results in high cyclic stability, but irreversibility in the redox reaction reduces the lifetime.

2.5 Supercapacitor device type

SC devices can be fabricated by symmetric combination or by the asymmetric combination of the electrodes materials. Symmetric supercapacitors (SSCs) are assembled using two similar electrode materials, whereas asymmetric supercapacitors (ASC) are designed by assembling two dissimilar electrode materials. The advantage of the latter is that the operative cell potential window is enhanced and enlarged. The ASC functions like a battery, where one electrode acts as a positive electrode and the other electrode acts as a negative electrode. The degree of enlargement of the potential window of an ASC depends on the work function difference between two electrode materials used [32]. Thus, the size of the potential window of an ASC can be changed by selecting different combinations of transition metals for the positive and negative electrodes. The work functions of transition metal oxides are shown in Figure 2.24.

Figure 2.24 Work functions of transition metal oxides [32].

The potential window of an ASC can be fixed by the complementary potential windows of positive and negative electrodes. This is obligate to balance the charges stored at the positive and negative electrodes to obtain the potential window of an ASC. The charge stored (Q) in an electrode can be calculated by the following Equation 2.16:

$$Q = C_{spe} \times \Delta V \times m \dots\dots\dots (2.16)$$

where, C_{spe} is the specific capacitance of the electrode, ΔV is the potential window and m is the mass of the active electrode material. Hence, the equation can be written by comparing the equivalent amount of charges stored in the positive and negative electrodes in following way [121]:

$$\frac{m_+}{m_-} = \frac{C_{sp-}\Delta V_-}{C_{sp+}\Delta V_+} \dots\dots\dots (2.17)$$

where, “+” and “-” signs corresponding to the positive and negative electrodes. To fabricate the ASC device, the mass ratio of the positive and negative electrode materials is calculated by the above Equation 2.17. The positive and negative electrodes of an ASC could be i) redox//redox ($\text{Fe}_2\text{O}_3//\text{MnO}_2$) ii) redox//double-layer type ($\text{MnO}_2//\text{AC}$) or iii) double-layer//double-layer type (AC//graphene).

2.6 Techniques of 3D macroporous graphene fabrication

The 3D macroscopic graphene architectures that are synthesized to resolve the problem of re-stacking and self-aggregation of graphene sheets are commonly known as 3D graphene. The 3D graphene foam typically has a macroporous morphology where the accessible surface area for ions is increased immensely. The pore sizes of graphene are in the range of sub-micrometer to several micrometers. This porous nature of graphene foam makes it ultralight with excellent adsorption capability. It also has high mechanical strength and high conductivity. The porous structures allow easy transportation of electrolyte ions in multi-directions resulting in high electrochemical performance. The different fabrication techniques of 3D graphene materials are outlined below.

2.6.1 Hydrothermal method

Xu et al. reported the development of self-assembled graphene foam by the hydrothermal route at 180 °C for 12 h [122]. The interconnected porous network was formed by partial overlapping or coalescing of graphene sheets or by π - π interaction of individual graphene sheet (Figure 2.25). The morphology of the 3D building block depends on the GO precursor concentration and the time of hydrothermal reduction. The C_{sp} of graphene foam was found to be 175 F g⁻¹ in aqueous electrolyte. Zhang and coworkers [123] developed the more conductive graphene foam using a reducing agent hydroiodic acid or hydrazine in the same hydrothermal treatment. This assists to increase the electrochemical capacitance which was found to be 220 F g⁻¹. Graphene foam has also been fabricated by using noble-metal nanocrystal as linker to strengthen the GO foam. The noble-metal linker sites help to self-assemble of 3D building block [124]. Transition metal oxides and hydroxides have also been incorporated into graphene foam to increase the C_{sp} [125, 126]. The metal oxides decrease the contact resistance among nanosheets and help in faster electron and ion transmission, and also shorten the transport path of the ions.

Figure 2.25 (a) Photographs of a 2 mg mL⁻¹ homogeneous GO aqueous dispersion before and after a hydrothermal reduction at 180 °C for 12 h, (b) photographs of a strong GF allowing easy handling and supporting weight, and (c) SEM images of the SGH interior microstructures [122]. Adapted with permission from Ref. 122, Copyright (2010), American Chemical Society.

Niu et al. [127] synthesized porous graphene paper with continuous crosslinked structure through hydrothermal reduction of GO films using hydrazine monohydrate. The chemical reduction of GO releases gaseous by-products (e.g. H₂O

and CO_2), which were entrapped by the compact layers (Figure 2.26). The open networking and porous structure of graphene film helps to prevent restacking. Recently, several other reducing agents like sodium bisulfite, vitamin C, sodium ascorbate, hydroiodic acid, hydroquinone, ethylene diamine, hydrophosphoric acid/iodine have been used for reduction of GO [128-131].

Figure 2.26 (a) Schematic drawings illustrating the leavening process to prepare RGO foams, (b) Cross-sectional SEM image of RGO foams formed after 10 h in an autoclave at 90 °C with 80 μL hydrazine monohydrate and freestanding paper-like RGO foam (inset), (c) Schematic diagram of the flexible RGO foam supercapacitor where the distance between two sides of the RGO foam supercapacitor characterizes its bending degree and (d) Optical image of the flexible RGO foam supercapacitor [127]. Adapted with permission from Ref. 127, Copyright (2012), WILEY-VCH Verlag GmbH & Co. KGaA.

2.6.2 Template guided approach

2.6.2.1 Soft-template approach

In the soft-template approach, graphene sheets and soft-templates are assembled spontaneously into 3D hydrogel architecture. The soft-templates are mostly amphiphilic in nature. The 3D porous graphene aerogel is formed when the solvent is removed by freeze-drying or by supercritical drying from the hydrogel. This is an

efficient approach of removing solvent from 3D hydrogel. Lu et al. [132] synthesized 3D graphene foam under the support of water soluble template polyfluorene-grafted-poly(sulfobetaine methacrylate) (PF-g-PSBMA) through reduction of GO by hydrazine. The stiff backbone and flexible branched chains facilitated the dispersion of the hydrophobic graphene sheets in aqueous medium. Zu et al. [133] synthesized supramolecular hydrogel of RGO by using pluronic copolymer poly(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide (PEO-b-PPO-b-PEO) and α -cyclodextrin (α -CD). Graphene hydrogel can also be fabricated by utilizing the assistance of amphiphilic molecules such as poly(vinyl alcohol) (PVA) [134], poly(vinylidene fluoride) (PVDF) [135], poly(vinylpyrrolidone) (PVP) [136], poly(ethyleneimine) (PEI) [136], and poly(N, N-dimethylacrylamide)-b-poly(N-isopropylacrylamide) (AZOPDMA-b-PNIPAM) [137]. Biomolecules such as DNA and hemoglobin can also be used for assembling of graphene in 3D macroporous structure.

2.6.2.2 Hard-template approach

In the hard-template method graphene macrostructures were synthesized through the deposition of graphene sheets larger than 50 nm on inorganic/organic particles or by in situ growth of graphene sheets on a porous framework that may be subsequently removed. Nickel foam is a commonly used porous metal framework that is retained and not removed. This is because the nickel foam can be used as the current collector in the supercapacitor.

Qiu et al. [138] developed corklike graphene monolith after freeze-drying an aqueous dispersion of GO. Ice is regarded as the hard-template when an aqueous dispersion of GO is subjected to freeze-drying. A 3D macroporous structure is obtained after sublimation of the ice crystal. Polymer microspheres can also serve as a hard-template for macroporous graphene fabrication. For example, polystyrene (PS) and poly(methyl methacrylate) (PMMA) microspheres have been used to fabricate macroporous graphene foam [139, 140]. Choi et al. [139] synthesized a graphene film by vacuum filtration of a mixture of GO and PS spheres at a pH of 2, followed by removal of the PS spheres using toluene. Su et al. [140] developed 3D macroporous graphene film by vacuum filtration of a mixture of PMMA spheres and dispersed GO,

followed by calcination of the air dried film at 800 °C to remove the PMMA template and simultaneously subject the GO to thermal reduction.

The nickel foam is one of the typical sacrificial hard-templates for *in situ* growth of graphene sheets by the CVD technique [141]. The as-prepared 3D graphene sheets consist of very high quality graphene that can be used for the fabrication of graphene-based composites. The graphene foam can easily be fabricated by the chemical method or hydrothermal method. However, they suffer from poor electrical conductivity due to the presence of defects in the graphene sheets. On the other hand, the CVD was found to be an alternate technique for effective fabrication of 3D graphene but this is a very costly process. The FESEM micrographs of 3D graphene synthesized from the CVD technique are shown in Figure 2.27b.

Figure 2.27 SEM images of (a) 3D graphene network grown on nickel foam after CVD process and (b) 3D graphene networks after removal of the nickel foam [141]. Adapted with permission from Ref. 141, Copyright (2011), WILEY-VCH Verlag GmbH & Co. KGaA.

2.6.2.3 Others approaches

Macroporous graphene can also be synthesized without the use of any template. Chen et al. [142] reported that macroporous graphene can be synthesized by electrochemical reduction of a highly concentrated GO aqueous dispersion ($\geq 3 \text{ mg mL}^{-1}$) during cyclic voltammetry in a 0.15 M LiClO_4 electrolyte. The as-prepared graphene foam showed very high specific surface area of $1000 \text{ m}^2 \text{ g}^{-1}$. High temperature treatment of a carbon-rich polymer is also another alternative way to synthesize macroporous graphene [143, 144]. For example, Biener et al. [143]

developed monolithic carbon foam through carbonization of resorcinol and formaldehyde at 1050 °C. The resorcinol and formaldehyde was synthesized by the acid-catalyzed sol–gel polymerization.

2.7 Flexible solid-state supercapacitors

The flexible solid-state SCs usually consist of two flexible electrodes/current collectors, electrode materials and a solid-state electrolyte. Flexible solid-state SCs differ from conventional SCs in two ways. Firstly, the electrolyte in the former is in solid form. Secondly, the electrodes and electrolyte are flexible in nature. The solid-state electrolyte also acts as a separator. Bendable plastic films of polyethylene terephthalate (PET), ethylene/vinyl acetate copolymer (EVA), and polydimethylsiloxane (PDMS) are used for packaging of the solid-state SCs. A schematic illustration of a solid-state SC is shown in Figure 2.28. The electrochemical performance of a solid-state SCs depend largely on the type of electrode materials used. Carbon-based materials have been widely studied for flexible electrode preparation. This is because carbon-based materials have good electrical conductivity, high power density, excellent cycling stability and exceptional mechanical properties [145, 146]. In the following section, a discussion on recently developed flexible electrode materials and their flexible cell as solid-state symmetric SCs (SSCs) and asymmetric SCs (ASCs) will be outlined.

Figure 2.28 Schematic illustration of a solid-state SC [147].

2.7.1 Electrode materials for flexible solid-state supercapacitors

2.7.1.1 Carbon-based flexible electrode

Among various carbon-based materials, graphene and their composites are regarded as promising candidate for fabrication of flexible electrode materials due to their good electrical conductivity, excellent mechanical properties and large surface area. Different fabrication techniques have been used for solid-state SCs. The easiest approach is to grow or coat the carbon materials on a porous flexible substrate [148]. Hu et al.[149] developed a flexible electrode by depositing ink on office paper. The office paper acts as flexible substrate to absorb the CNT inks. Zheng et al. [150] developed similar graphene paper electrode by painting graphene on cellulose paper. Hu et al. [151] reported the fabrication of a flexible CNT–cotton electrode using a simple dipping and drying process.

2.7.1.2 Pseudocapacitive material based flexible electrode

As mentioned above, pseudocapacitive materials such as metal oxides and CPs shows higher C_{sp} than carbon materials. Hence to obtain high energy density, the flexible electrode have been fabricated to incorporate various pseudocapacitive materials such as MnO_2 [152, 153], NiCo_2O_4 [85], NiO [154], PANI [155, 156] and PPy [105].

2.7.1.3 Composite materials based flexible electrode

It should be noted that metal oxides have poor electrical conductivity and CPs have poor cyclic stability. Therefore, it is essential to develop a composite electrode material whereby the limitations of these constituent component materials can be overcome. There are two basic types of carbon-based composite materials and metal oxides-based composite materials. In carbon-based composites, carbon materials like CNT and graphene are incorporated with metal oxides (such as MnO_x [157, 158], RuO_2 [18, 159], VO_x [160, 161] and CoO_x [162]), or CPs (such as PANI [163-166], PPy [167, 168] and PEDOT [169]) to ensure high energy density and high cyclic stability. Similarly, to obtain high capacitance and energy density, both metal oxide

and conducting polymers are combined together. Solid-state SSCs and ASCs based on composite materials will be highlighted in following sections.

2.7.2 Flexible solid-state symmetric supercapacitors (SSCs)

2.7.2.1 Carbon materials based SSCs

2.7.2.1.1 CNTs

Flexible solid-state SSCs based on carbon nanoparticles, carbon nanotubes and graphene have been widely studied due to their light behavior, low cost and ease of handling. Fu et al. [170] developed flexible fiber SSC by using pen ink as active material on carbon fiber, which showed a C_{sp} of 0.504 mF cm^{-1} . Kaempgen et al. [11] fabricated an SSC by assembling two SWCNTs electrodes utilizing PVA/H₃PO₄ gel electrolyte. The SWCNT electrode was prepared by spraying SWCNTS network on a polyethylene terephthalate film (PET) which acted as an electrode as well as the current collector. The C_{sp} of the SSC device was found to be 36 F g^{-1} . Kang et al. [171] fabricated a flexible SSC by assembling two CNT/paper electrodes utilizing PVA/LiCl gel electrolyte. The CNT/paper electrode was developed by depositing CNTs on the office paper through a drop-dry method. The CNT/paper flexible SSC had a maximum energy density of 35 Wh kg^{-1} . Kang et al. [172] a fabricated flexible SSC by assembling bacterial nanocellulose/carbon nanotube electrodes using ionic liquid based gel electrolyte. The SSC operates in a wider potential window of 3.0 V and had a high energy density of 15.5 Wh kg^{-1} . Niu et al. [173] fabricated a highly stretchable SSC by developing stretchable SWCNT film which was prepared by combining polydimethylsiloxane (PDMS) with directly grown SWCNT film. The device shows exceptional electrochemical properties without losing its properties when it was stretched by 120%.

2.7.2.1.2 Graphene

Graphene is widely regarded as one of the most promising carbon materials among all carbon based materials such as, AC, carbon nanoparticles, and CNTs [174, 175]. The pure graphene film has an intrinsic capacitance of 21 mF cm^{-2} [176]. Yoo et al. [174]

developed an SSCs based on pristine graphene using PVA/H₃PO₄ gel electrolyte, which showed a C_{sp} of 80 mF cm⁻². To maximize the C_{sp} , Choi et al. [177] fabricated a thin flexible SSC by synthesizing nafion functionalized RGO (f-RGO). The f-RGO based SSC had a C_{sp} of 118.5 F g⁻¹ at 1 A g⁻¹ whereas a pure graphene based SSC has a C_{sp} of 62.3 F g⁻¹ at 1 A g⁻¹. This suggested that nafion functionalization enhances the C_{sp} of graphene. Recently, Gao et al. [178] developed cellulose nanofiber based graphene hybrid aerogel as an electrode material to fabricate a solid-state SSC device which had an energy density of 20 mW h cm⁻².

2.7.2.2 Conducting polymers (CPs) based SSCs

CPs such as PANI, PPy and PEDOT have been well studied for solid-state SSCs. Meng et al. [105] fabricated a flexible solid-state SSC comprising PPy/Au electrode material utilizing PVA/HClO₄ gel as the electrolyte. The PPy/Au electrode was prepared by depositing PPy on the porous Au electrochemically. The C_{sp} of the PPy/Au electrode material was found to be 270 F g⁻¹ at a current density of 0.6 A g⁻¹. Yuan et al. [179] fabricated a flexible solid-state SSC by developing PANI/Au/paper electrode material through the facile electrochemical deposition method. The device had a high C_{sp} and the energy density of 10 mW h cm⁻³ at a power density of 3 W cm⁻³ and superior cyclic stability without dropping its capacitance after 10000 cycles.

2.7.2.3 Hybrid materials based SSCs

The electrode materials for SSCs have been synthesized widely by hybridizing EDL and pseudocapacitive materials. Meng et al. [12] developed an SSC comprising CNT/PANI composite films assembled with PVA/H₂SO₄ electrolyte. The SSC had a C_{sp} of 31.4 F g⁻¹ with excellent cyclic performance. The flexible transparent solid-state SSC was developed by assembling PANI/MWCNTs composite electrodes utilizing PVA/H₃PO₄ as the gel electrolyte. The SSC exhibited a C_{sp} of 112 F g⁻¹ at 0.3 A g⁻¹. Chen et al. [159] fabricated an SSC by first synthesizing a SWCNT thin film on an PET substrate and carbon cloths, and then integrating RuO₂ nanowires on it with the help of a commercial inkjet printer using SWNT ink. A PVA/H₃PO₄ gel electrolyte was used together with the SWCNT/RuO₂ nanowires electrode material.

The SSC exhibited a C_{sp} of 138 F g⁻¹ and an energy density of 18.8 Wh kg⁻¹ at a power density of 96 kWkg⁻¹. Sellers et al. [180] synthesized MWCNT/RuO₂ composite by functionalization of MWCNT with RuO₂ following direct redox reaction with potassium perruthenate (KRuO₄). The MWCNT/RuO₂ SSC had a C_{sp} of 96 F g⁻¹ at 1.0 A g⁻¹ with good cyclic performance. However, RuO₂ is very costly and have low natural profusion, and is toxic.

Most recent studies have focused on cheaper naturally found transition metal oxides such as MnO₂, MoO₃, Co₃O₄, NiO and VO_x. Among these, MnO₂ has been recognized as the most attractive alternative material to RuO₂. Numerous solid-state SSC that are based on MnO₂ have been established in recent years [107, 181-185]. However, the low electrical conductivity (10⁻⁵ to 10⁻⁶ S cm⁻¹) of MnO₂ has limited its application [147]. To overcome this limitation, the electrical conductivity has been improved by mixing MnO₂ with conductive carbon materials such as CNT, graphene or CPs. Yuan et al. [107] fabricated a highly flexible SSC by assembling two carbon nanoparticles/MnO₂ (CNps/MnO₂) hybrid electrodes that were prepared through flame synthesis followed by electrochemical deposition of MnO₂ on the CNps (Figure 2.29). The SSC shows excellent capacitance and cyclic stability with a capacitance retention of 97% after 10000 cycles. Yang et al. [183] fabricated an SSC device by assembling ZnO@MnO₂ core-shell nanowire electrodes utilizing PVA/LiCl gel electrolyte that had an areal capacitance of 26 mF cm⁻².

Figure 2.29 The upper left image is the optical photographs of the fabricated solid-state supercapacitor device. The square indicates the capacitance region. The bottom left images show the flexibility of the device. The right image shows a light-emitting-diode (LED) lit by a device composed of three SCs connected in series [107]. Adapted with permission from Ref. 107, Copyright (2011), American Chemical Society.

2.7.3 Flexible solid-state asymmetric supercapacitors (ASCs)

Some solid-state SCs which have an asymmetric combination of electrode materials have also been fabricated. Choi et al. [18] developed a solid-state ASC by using ionic liquid functionalized chemically modified graphene (IL-CMG) film as the negative electrode and a hydrous RuO_2 -IL-CMG composite film as the positive electrode. The energy density of the RuO_2 -IL-CMG//IL-CMG ASC was found to be 19.7 Wh kg^{-1} at a power density of 0.5 kW kg^{-1} in a wide potential window of 1.8 V [18]. The ASC shows excellent cyclic stability in the bending state as well as in the twisted state. Gao et al. [186] fabricated an ASC by assembling carbon nanotube/graphene (CNTG) paper as a negative electrode and Mn_3O_4 nanoparticles/graphene (MG) paper material as the positive electrode utilizing potassium polyacrylate/KCl gel electrolyte. The CNTG//MG ASC had a high energy density of 32.7 Wh kg^{-1} at 0.5 A g^{-1} in the operating potential window of 1.8 V . Similarly, Shao et al. [187] fabricated a solid-state ASC by using graphene/ MnO_2 nanorod thin film as the positive electrode and a graphene/Ag thin film as the negative electrode. The ASC device displayed a maximum energy density of 50.8 Wh kg^{-1} at the power density of 101.5 W kg^{-1} . These graphene films based ASC always have to be packaged using PET film in order to prevent cracking of the graphene film, which usually limits the flexibility of the device. The strong van der Waals interactions restack the graphene film resulting in a decrease in specific surface area.

Another promising approach is to deposit the active materials on a carbon cloth which is flexible and conductive. The carbon cloth provides a 3D scaffold to support the electrode material. Lu et al. [30] developed hydrogen treated TiO_2 nanowires on a carbon cloth with the electrochemically deposited MnO_2 forming a core-shell which showed excellent performance as an electrode for an asymmetric device. (Figure 2.30) The $\text{H-TiO}_2@\text{MnO}_2$ and $\text{H-TiO}_2@\text{C}$ electrodes exhibited C_{sp} values of 449.6 and 253.4 F g^{-1} at a scan rate of 10 mV s^{-1} , respectively. The high C_{sp} value of $\text{H-TiO}_2@\text{MnO}_2$ electrode was resulted from the core-shell morphology, large accessible surface area, and binder free nature. Xiao et al. [67] fabricated a solid-state ASC device based on $\text{MoO}_{3-x}@\text{WO}_{3-x}$ as the anode material, and PANI nanowire as the cathode material. The ASC operates in a voltage window of 1.9 V and showed a high energy density of 1.9 mW h cm^{-3} at 0.04 W cm^{-3} . Zilong et al. [188] developed the ASC by using $\text{ZnO}@\text{MnO}_2$ as the cathode material and RGO as

the anode material utilizing LiCl/PVA gel electrolyte. The ASC showed a high volumetric capacitance of 0.52 F cm^{-3} at 0.5 mA cm^{-2} . Duay et al. [101] fabricated a flexible solid-state ASC by using MnO_2 /PEDOT as the cathode material and PEDOT nanowire arrays as the anode material utilizing PMMA/ LiClO_4 gel. The MnO_2 /PEDOT//PEDOT ASC operated in the large voltage window of 1.7 V and had an energy density of 9.8 Wh kg^{-1} at a power density of 850 W kg^{-1} .

Figure 2.30 (a) Upper: schematic diagram illustrating the growth processes of H-TiO_2 @ MnO_2 and H-TiO_2 @C core-shell nanowires. Lower: SEM image of the H-TiO_2 @ MnO_2 core-shell nanowires grown on a carbon cloth substrate. Inset: a red LED (1.5 V) powered by a solid-state ASC device. (b) CV curves collected at a scan rate of 100 mV s^{-1} for the ASC device under flat, bent, and twisted conditions. Insets are the device pictures under test conditions [30]. Adapted with permission from Ref. 30, Copyright (2013), WILEY-VCH Verlag GmbH & Co. KGaA.

2.8 Application of flexible solid-state supercapacitors

Flexible solid-state SCs have high energy density, high power density, excellent cyclic stability and high flexibility. They can be used directly as power sources. The flexible solid-state SC can be used to light up light-emitting-diode (LED) displays [30, 107, 109, 173, 181] (Figure 2.31a). Lu et al. [189] verified that a tandem cell of three MnO_2 // Fe_2O_3 devices in series can charge a mobile HTC, A320e. (Figure 2.31b) Moreover, the solid-state flexible device can be integrated with clothing and textile materials using adhesive, thus making it possible to exploit the SC for many potential applications. Jost et al. [190] stitched an SSC device with cloth and demonstrated its

stable performance at different bending states. Secondly, flexible solid-state SCs can be used to store energy produced from other energy sources. The SSC can also be integrated with [181] renewable energy sources too. For example, Yuan et al. [179] demonstrated a that a PANI SSC could be combined with a piezoelectric generator which produced direct current for charging the SSC. The flexible device can be used in wearable electronics, bio-implantable systems, flexible displays, flexible mobile phones and wireless sensors.

Figure 2.31 (a–c) Practical applications of solid-state SCs [189, 191, 192]. Adapted with permission from Ref. 189, Copyright (2014), WILEY-VCH Verlag GmbH & Co. KGaA; Ref. 191, Copyright (2014), The Royal Society of Chemistry and Ref. 192 Copyright (2013) American Chemical Society.

2.9 Basis of materials selection and perspective of the current research work

The performance of the solid-state SCs needs to be expanded further for use in numerous practical applications. The flexible electrodes are mostly made from carbon based composites where carbon materials constitutes the major component. To improve the energy density of the SC cell, it is essential to incorporate more pseudocapacitive materials, specifically metal oxides with carbon based materials. However, the power density of the SC will be decreased due to poor conductivity of the metal oxides. Thus, it is essential to design the composite morphology by integrating the benefits of all the individual constituent materials.

The possibility exists that 3D porous carbon materials could provide a solution for the development of SCs with a high mass loading of pseudocapacitive materials. For this purpose, graphene will be selected as a primary material due to its high electrical conductivity, and high cyclic stability due to its EDL type charge storage mechanism. As outlined in Section 2.6, 3D macroporous graphene has been developed by employing suitable template-based methods to resolve the problem of re-stacking of the individual graphene sheets. Substantial research is still needed to realize the full potential of 3D graphene macro-assemblies that incorporates MnO_2 and PANI conductive polymer. Moreover, a solid-state asymmetric supercapacitor (ASC) will be developed by selecting suitable combinations of positive and negative electrode materials. This is to extend the working potential window in order to increase the energy density and power density. This will be attempted by using metal oxides with a large work function difference in the electrode materials for the anode and cathode. In particular, MoO_3 will be selected for the negative electrode material and MnO_2 for the positive electrode. This is because MnO_2 and MoO_3 shows largest work function difference among the transition metal oxides (see in Figure 2.24).

2.10 Summary

In this chapter, a comprehensive literature review on various energy storage mechanisms and the characteristics and requirements of electrode materials for supercapacitors have been provided. The details of the key components of a supercapacitor, and the fundamental principles of the techniques utilized to evaluate the electrochemical performance of a supercapacitor such as cyclic voltammetry,

cyclic charge–discharge and electrochemical impedance spectroscopy tests have been discussed. Existing work on the fabrication of 3D macroporous graphene and its relevance to flexible solid-state SCs has been reviewed. Moreover, issues pertaining to various solid-state symmetric supercapacitors and asymmetric supercapacitors have been addressed.

Chapter 3 Materials and experimental details

This chapter deals with the materials used in this research and a brief description of different characterization techniques employed in the work.

3.1 Chemicals and general equipment

The chemicals used in the studies are listed below:

Table 3.1 List of chemicals used.

Chemical name	Supplier name
Graphene oxide (GO) (99%, thickness: 0.7-1.2 nm)	CheapTubes, USA
Potassium permanganate (KMnO ₄)	Sigma-Aldrich, Singapore
Aniline (reagent grade, 99%)	Sigma-Aldrich, Singapore
Hydrochloric acid (HCl)	Sigma-Aldrich, Singapore
Ammonium persulfate (APS) (reagent grade, 98%)	Sigma-Aldrich, Singapore
Molybdenum (III) chloride (MoCl ₃)	Sigma-Aldrich, Singapore
Poly(vinylidene fluoride) (PVDF) (powder form)	Sigma-Aldrich, Singapore
Dimethylformamide (DMF) (99.8%)	Sigma-Aldrich, Singapore
Conductive carbon black ($\geq 99\%$)	Age D'orPte Ltd, Singapore
Hydrazine monohydrate (reagent grade, $\geq 98\%$)	Sigma-Aldrich, Singapore
Potassium hydroxide (KOH)	Sigma-Aldrich, Singapore
Pluronic [®] F-68 solution (concentration 10%)	Sigma-Aldrich, Singapore
Polyvinyl alcohol (PVA)	Sigma-Aldrich, Singapore
Sodium dodecyl benzenesulfonate (SDBS)	Sigma-Aldrich, Singapore

The nickel (Ni) foam (1000 mm length $\times$ 300 mm width $\times$ 1.6 mm thickness) was purchased from MTI Corporation. Anodisc filter paper (pore $\varnothing$ 0.2 μ m) was obtained from Newton 101 Pte. Ltd. The copper (Cu) grid (300 mesh) was supplied by Jeol Asia Pte Ltd.

The general equipment used in this work (during synthesis of materials) are listed below:

1. Hot plate & magnetic stirrer (MR 3002, Heidolph)
2. Teflon-lined stainless-steel hydrothermal autoclave (Latech)
3. Electric Oven (Binder FD240, Fisher Scientific)
4. Vacuum oven (Binder , Fisher Scientific)
5. Centrifuge (Thermo IEC, 220/240)
6. Furnace (MettlerGmbH & Co. KG)
7. Freeze dryer (Scanvac coolsafe)
8. Ultrasonicator (MISONIX, Sonicator 3000)

3.2 Experimental

3.2.1 Field emission scanning electron microscopy (FESEM)

The surface morphology of the electrode materials was examined using the field emission scanning electron microscope JEOL-JSM-7600. To capture the FESEM images, a small amount of powder sample was placed on a double sided carbon tape whose other side was attached to the sample holder. The sample was then coated with gold in a Sputter coater. In general, a coating time of 50 s was used, and the actual coating time for the different types of specimens varied according to their conductivity. The sputter coating was carried out in the chamber under a vacuum of 1×10^{-1} mbar pressure with a voltage of 10 kV and a current of 10 mA. After gold coating, the sample was placed inside the microscope chamber and the surfaces of the sample were examined at an accelerating voltage of 5–10 kV.

3.2.2 Transmission electron microscopy (TEM)

The bulk morphology of the samples was analyzed on a transmission electron microscope JEOL-JEM-2010. To prepare the sample, at first a small amount of sample was dispersed in water for 10 min in an ultrasonic bath. The sample was drop casted on a Cu grid and dried for 6 h at 70 °C in an electric oven. Next, the Cu grid was placed into the microscope chamber and the sample was analyzed at a High Tension (HT) of 200 kV and a current of 107 μ A at different magnifications.

3.2.3 Fourier transform infrared (FTIR) spectroscopy

The Nicolet 8700 FTIR spectrometer was used to analyze the FTIR spectra of the materials. The analysis was carried out in the range of 400–4000 cm^{-1} with a total of 32 scans using a KBr/sample pallet. To prepare a sample pallet, the powder sample and KBr were first dried in a vacuum oven at 90 °C for 12 h. Next, a small amount of sample was mixed with KBr (~10 times higher amount). The KBr/sample mixture was placed in the sample holder and the mixture was compressed up to 2 MPa in a hydraulic press. The KBr/sample pallet was then ready for analysis in the FTIR instrument.

3.2.4 X-ray diffraction (XRD)

A PANalytical XRD, with Cu $K\alpha$ radiation with $\lambda=0.15418$ nm, was used for X-ray diffraction analysis of the samples. The equipment was operated at 40 kV and 40 mA at a scanning speed of 1.00 ($^{\circ}$ /min). The compacted powder sample was scanned in the range from $5^{\circ} < \theta < 90^{\circ}$ with a step size of 0.01.

3.2.5 X-ray photoelectron spectroscopy (XPS)

A Kratos Axis-ULTRA XPS analyzer was used to carry out the XPS study of the samples under a chamber pressure of 4×10^{-8} Pascal. A monochromatic Al $K\alpha$ line ($h\nu = 1486.71$ eV) powered with 10 mA and 15 kV was used as the X-ray source. The analysis was carried out within the binding energy range of 0–1200 eV. The sample

was prepared by placing a small amount of sample on a double-sided carbon tape that was attached to a silicon wafer of dimensions 5 mm x 5 mm x 0.3 mm. The silicon wafer with the sample was then fixed onto the sample holder and placed in the XPS chamber for analysis.

3.2.6 Raman spectroscopy

Raman spectroscopy was conducted using the Renishaw inVia Raman microscope with a laser source of 518 nm in the range of 100–4000 cm^{-1} . To prepare the samples, a small amount of sample material was first dispersed in water by water-bath sonication for about 10 min. The dispersed sample was then drop-casted on a silicon wafer of the dimension of 5 mm x 5mm x 0.3 mm. The sample was dried for 6 h at 70 °C in a vacuum oven before it was analyzed in the Raman microscope.

3.2.7 Thermogravimetric analysis (TGA)

TGA analysis was carried out using a TGA Q500 (Universal V4.5A TA Instruments). About 10 mg of sample was placed in the TGA pan and the experiment was carried out in an oxygen atmosphere at a heating rate of 10 °C min^{-1} in the temperature range from 25 to 500 °C.

3.2.8 Surface area measurement and pore size distribution

The surface area and porosity analysis were carried out based on the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods through nitrogen adsorption–desorption measurements using a Micromeritics, ASAP 2020. To carry out the measurement, about 100 mg of sample material was first dried in a vacuum oven for 12 h, before it was placed in the sample holder. The sample was degassed for 12 h and data obtained was analyzed using the ASAP 2020. The BET surface area was calculated using the BET equation as follows:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \dots\dots\dots (3.1)$$

where, p_0 and p are the saturation pressure and equilibrium pressure of the adsorbates, respectively; c is the BET constant, v is the adsorbed gas quantity, and v_m is the monolayer adsorbed gas quantity.

3.2.9 Conductivity measurement

For electrical conductivity measurement, a pellet (radius 3 mm and thickness 0.05 mm) was first prepared by compressing the powder specimen contained in a sample holder at 5 MPa pressure using a hydraulic press. The sample was then assessed using a Keithley 2000 (Keithley Instruments Inc., USA) apparatus following the four-point probe method.

The density (d) can be calculated using the following formula:

$$d = m/v; \text{ where, } m = \text{mass of the sample, and } v = \text{volume of the sample} = \pi r^2 t.$$

The conductivity was determined using the following equations:

$$\text{Resistivity } (\rho, \text{ ohm-cm}) = \pi t / \ln 2 (V/I) = 4.53 \times t \times \text{resistance}$$

where, V = measured voltage and I = applied current.

$$\text{Conductivity } (\sigma, \text{ S/cm}) = 1/\rho$$

The conductivity of each sample was the average value obtained from five different measurements.

3.2.10 Electrochemical performance

The galvanostat–potentiostat (Gamry Reference 3000) was used to analyze the electrochemical performance of the electrode materials by the conventional three-electrode and two-electrode cell systems [193] at room temperature. In the three-electrode system, a platinum (Pt) wire and a silver/silver chloride (Ag/AgCl) electrode were used as the counter and reference electrodes, respectively, and a glassy carbon electrode was used as the working electrode in a 6 M aqueous KOH. For the two-electrode system, the assembled solid-state supercapacitor cell was used where Ni foam acted as the electrode as well as the current collector [194]. The electrochemical

performances were determined using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and the cyclic charge–discharge (CCD) experiments.

3.2.11 Fabrication of electrode and polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel electrolyte

In case of three-electrode cell system, to prepare the working electrode, 80 wt% of electrode material, 15 wt% of carbon black and 5 wt% of PVDF in DMF (considering the total mass of 2 mg) were mixed to make a homogeneous paste. The paste was then applied on to a glassy carbon electrode (inner diameter 5 mm). Next, the electrode was dried in the oven at 90 °C for 6 h, after which it was used in the experiment. Here, PVDF acts as a binder which has very little effect on the electrochemical performances of the electrode materials [195]. Conductive carbon black was added to enhance the surface conductivity of electrode materials and to compensate the non-conductive nature of PVDF. The two-electrode cell preparation will be outlined in the respective chapters.

The PVA/KOH gel electrolyte [194] was prepared by first dissolving 4 g of PVA in 40 mL of deionized water at 85 °C, after which 4 g of KOH beads were added and stirred vigorously to obtain a clear solution. Next, the as-prepared gel was cooled to room temperature and used for fabricating the electrodes.

Chapter 4 Development of 3D urchin-shaped coaxial MnO_2 @PANI composite and self-assembled 3D pillared graphene foam for flexible all-solid-state asymmetric supercapacitor

4.1 Introduction

Carbon-based materials are known to be promising electrode materials in the field of flexible SCs. Carbon-based SCs have excellent features including a long cycle life and high power density. Graphene is the most promising electrode materials amongst all carbon-based materials due to its high specific surface area, high mechanical strength and high conductivity [16, 120]. However, graphene sheets have a tendency to restack together in a graphite-like structure due to strong van der Waals interactions between the individual graphene sheets. This has a negative impact on the accessible surface area and flexibility. Therefore, much effort has been made to synthesize graphene-based materials into 3D foams and gels that have an open structure with large accessible surface area. Among all methods, the self-assembly of graphene oxide into a 3D macroporous architecture by hydrothermal method has been attractive due to ease of preparing 3D graphene foam [122, 123, 196] using this technique. The 3D graphene foam obtained has extensive surface area that is readily accessible by ions.

However, a SC device based on the 3D graphene foam (GF) alone cannot provide sufficiently high capacitance. The 3D graphene foam electrode has to be utilized in conjunction with another suitable electrode material that is pseudocapacitive in nature, to make an ASC device with improved energy density by enlarging the operating potential window. Based on the literature review, pseudocapacitive transition metal oxide MnO_2 is selected as a key constituent material for the new electrode material to be synthesized. The poor conductivity of MnO_2 will be mitigated by combining it with the conducting polymer (CP) like PANI.

In the literature, conducting agents such as carbonaceous materials [22-24] and conducting polymers [25] have been utilized to improve the electrochemical performance of MnO_2 -based electrode materials. However, because the capacitance of most carbonaceous materials is not high, the use of CPs such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) are preferred [26]. Among these CPs, PANI is commonly used due its very facile synthesis procedure and because it is inexpensive, environmentally friendly, and highly conductive nature [6, 27]. Researchers have synthesized MnO_2 -PANI binary composites to overcome the poor conductivity of MnO_2 and poor stability of PANI. However, one key problem in MnO_2 -PANI binary composites is the lack of good contact between MnO_2 and PANI. It is essential to develop a new approach to improve the interaction between MnO_2 and PANI. Therefore, a core-shell morphology was developed in which highly ordered 3D hollow urchin-shaped MnO_2 had been synthesized first, following which coaxial PANI was grown on the MnO_2 surface using a controlled oxidation process.

Therein, in this report, a novel 3D hollow MnO_2 @PANI coaxial microurchin was synthesized. This novel material was used as the positive electrode material together with 3D GF as the negative electrode material utilizing PVA/KOH gel electrolyte to fabricate a flexible all-solid-state asymmetric supercapacitor (ASC). The positive electrode material was fabricated via a facile approach without the use of any additional oxidant. In an acidic condition, the MnO_2 microurchin initiates the polymerization of aniline monomers on its nascent activated surface by acting both as an oxidant and template. The negative electrode material was fabricated through self-assembly of graphene sheet by vitamin C as the reducing agent via a one-step hydrothermal reaction. These provide a facile, inexpensive and environmentally friendly approach to fabricate a flexible all-solid-state ASC using 3D MnO_2 @PANI composite and 3D GF, which is potentially useful in high-tech applications.

4.2 Experimental section

4.2.1 Preparation of 3D graphene foam (GF)

Graphene oxide (GO) directly was used as purchased to synthesize the graphene foam (GF). To prepare GF, 50 mg of GO was dispersed by ultrasonication in 25 mL of

distilled water for 20 min. Next, 100 mg of vitamin C was added in GO dispersion medium and stirred for 10 min. Then the as-prepared dispersion was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept for 6 h at 150 °C. The autoclave was allowed to cool to room temperature, and graphene hydrogel was collected. It was found that the hydrogel assembled as a 3D cylindrical building block. Then, the excess ions and impurities from the hydrogel were removed by dialysis. After freeze-drying, the foam was heat treated at 400 °C for 4 h with the heating rate of 5 °C min⁻¹. The heat treatment was carried out to eliminate any residual organic compounds and volatile functional groups from graphene aerogel. This heat treatment actually improves the purity of the graphene foam sample and also improves the thermal and electrical properties of graphene. The sample was stored then for characterization.

4.2.2 Synthesis of MnO₂ nanostructures

To prepare the MnO₂ nanostructure, 2 mmol of KMnO₄ and 650 mL of concentrated HCl were added into 35 mL of deionized water and stirred for 30 min at 300 rpm. The solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was then placed in an electric oven at 140 °C for 12 h, after which the autoclave was taken out and cooled under room atmosphere conditions. The precipitate formed was filtered using Whatman filter paper (Ø-185 mm), and the possible impurities were removed by washing several times with deionized water. Finally, the as-prepared brown color sample was dried in an electric oven at 70 °C for 12 h and stored in a glass vial for further use.

4.2.3 Preparation of MnO₂@PANI composite

The as-prepared 160 mg of MnO₂ was dispersed in 60 mL of 0.02 M HCl aqueous solution by stirring at 300 rpm with cooling in an ice bath. Separately, 40 mL of 0.02 M HCl aqueous was added to a beaker containing 200 µL of aniline monomers and cooled in an ice bath for 30 min. The latter solution was rapidly added into the first beaker containing the MnO₂ solution and stirred in the ice bath for 6 h. Next, the precipitate was filtered using Whatman filter paper (Ø-185 mm), and the residue was

washed with deionized water several times to remove impurities before it was dried in an electric oven at 70 °C for 12 h.

4.2.4 Fabrication of all-solid-state supercapacitor electrodes

At first, Ni foam (30 mm × 15 mm × 1.6 mm) were pressed under a weight of 1 ton for 1 min and then cleaned with acetone for 10 min and washed several times with deionized water. These pressed Ni foam sheets were used as the current collector. For fabrication of the MnO₂@PANI electrode, 80 wt% of the electrode material, 15 wt% of conductive carbon black and 5 wt% of PDVF solution in DMF (considering the total mass of 2 mg) were mixed to obtain a homogeneous paste. The paste was then embedded in the Ni sheet (area of 15 mm × 15 mm) and dried in an electric oven at 65 °C for 6 h. After drying, a 1 ton of weight was applied on the Ni sheet/sample again to ensure good binding of the electro-active samples in the electrode. Next, the prepared electrodes (Ni sheet/sample) were immersed into PVA/KOH gel solution (preparation method outlined in section 3.2.11) for 60 min and taken out. The two electrodes were dried for 1 h and then assembled together. The assembled cell was kept for 24 h to allow the gel to solidify. Finally, a robust all-solid-state MnO₂@PANI//MnO₂@PANI symmetric supercapacitor (SSC) cell was formed.

The GF electrode was prepared following the same amount (wt%) as mentioned for MnO₂@PANI electrode. Then the solid-state GF//GF SSC cell was fabricated following the same procedure as outlined above. The ASC cell was fabricated by assembling the MnO₂@PANI electrode with the GF electrode. A schematic presentation for the solid-state cell assembly is shown in Figure A1 (see in Appendix).

4.2.5 Characterization techniques

The morphology of the MnO₂, MnO₂@PANI nanoparticles and graphene foam was analyzed using the FESEM and TEM techniques. The molecular structures of the as prepared samples were characterized by XRD, XPS, FTIR and Raman spectroscopy. The surface area and porosity analysis was carried out by Brunauer–Emmett–Teller

(BET) and Barrett–Joyner–Halenda (BJH) methods. The electrical conductivity of the samples was measured utilizing the four-probe method. The electrochemical performances of the electrode materials and SC cells were characterized using the CV, CCD and EIS techniques. The details of all the characterization techniques are outlined in Chapter 3.

4.3 Results and discussion

4.3.1 Graphene foam

4.3.1.1 Morphological investigation

Herein, a 3D self-assembled building block was prepared via the chemical reduction of exfoliated GO by vitamin C through hydrothermal autoclave reaction. It not only provides a simple way to fabricate porous structures from GO, but also shows that the GO can self-assemble into more complicated 3D structures. The optical images in Figure 4.1a and 4.1b show that transformation of GO dispersion into a self-assembled free standing pillared structure had occurred. The optical image of the aerogel (Figure 4.1c inset) shows a loose sponge-like pillared column as the trapped water molecules were removed by freeze-drying. The freeze dried sample was analyzed by FESEM as shown in Figure 4.1c and 4.1d. It can be seen that a well-defined and interconnected 3D network has been formed which is clearly confirmed from the higher magnified image in Figure 4.1d. A wide distribution of pore size was observed where the graphene nanosheets are randomly cross-linked and intertwined to form the 3D network. The formation of this self-supported porous 3D pillared structure can be attributed to the coalescing or combining of the flexible reduced GO sheet by van der Waals forces, π – π interactions and H-bonding [128, 129].

Figure 4.1 (a) GO dispersion in water, (b) 3D self-assembled GO hydrogel, (c) FESEM image of the graphene foam at lower magnification (inset shows GF after heat treatment) and (d) FESEM image of the graphene foam at higher magnification.

During hydrothermal reaction, GO was gradually reduced by vitamin C and assembled together to form a 3D interconnected cross-linked structure. The porous structure was characterized by N_2 adsorption–desorption isotherm, as shown in Figure 4.2a, b. The BET specific surface areas was found to be $296 \text{ m}^2 \text{ g}^{-1}$, and the BJH adsorption and desorption cumulative pore volumes were found to be 0.580 and $0.639 \text{ cm}^3 \text{ g}^{-1}$, respectively. The BJH pore size distribution indicated the existence of mesoporosity in 3D GF with adsorption and desorption pore radii of 5.63 and 3.18 nm , respectively. This highly porous structure and wide distribution of pores facilitate the easy ion adsorption and desorption process when it is used as an electrode material for supercapacitor application.

Figure 4.2 (a) The N₂ adsorption–desorption isotherm loop and (b) pore volume distribution plot of 3D GF.

4.3.1.2 Molecular characterization

Raman spectroscopy is one of the key analytical techniques for characterizing the carbon materials. The Raman spectrum shows that the GO has been well reduced by hydrothermal reaction with vitamin C. The Raman spectrum of GO shows two prominent peaks, G bands at 1590 cm^{-1} and D bands at 1350 cm^{-1} corresponding to the E_{2g} phonon of sp²-bonded carbon atoms in a 2D hexagonal lattice, and the presence of defects as well as disorder of carbon in the graphite layers [197], respectively, as shown in Figure 4.3. GF also shows the peaks at 1582 and 1325 cm^{-1} corresponding to same G- and D-band. As usual, the peak intensity ratio (I_D/I_G) was higher compared to that in the GO. It is well-known that upon reduction of GO, oxygen containing functional groups are removed and the conjugated graphene domain is redeveloped [198]. The increase of I_D/I_G ratio in GF can be explained by the development of smaller-size graphene domains that are numerous in numbers as compared to the graphene domain present in GO [193, 199, 200]. This suggests that GO has been reduced by vitamin C during the hydrothermal treatment.

Figure 4.3 Raman spectroscopy of GF and GO.

XRD was used to analyze the structural changes of graphene oxide. Figure 4.4 presents the XRD pattern of GO and GF. GO shows a diffraction peak at $2\theta = 10.92^\circ$, where the interlayer d-spacing is 0.809 nm, corresponding to (001) crystal plane, indicating the presence of carboxyl, hydroxyl and epoxide groups in GO [201]. The XRD pattern of GF shows a broad diffraction peak at 25.52° corresponding to the interlayer d-spacing of 0.365 nm without showing any peak at 10.92° . These results prove that GO has been successfully reduced by vitamin C [202].

Figure 4.4 XRD analysis of GF and GO.

The electrical conductivity of GF shows a high conductivity of 1.5 S m^{-1} . This high conductivity allows GF to be a promising electrode material for SC application.

4.3.1.3 Electrochemical measurements

The capacitance performance of the solid-state GF//GF symmetric supercapacitor (SSC) was measured using CV, CCD and EIS tests. The CV curves with different scan rates from 5 to 500 mV s⁻¹ are presented in Figure 4.5a. The CV curves show nearly rectangular behavior which indicated ideal capacitive behavior in the GF system. The shape of CV curves with increasing scan rates is similar, indicating that the contact resistance is low in the SC. The CV results are also justified by the CCD test. The CCD curves at different current densities are shown in Figure 4.5b. The charge and discharge curves are linear and symmetric at high current densities in the voltage window of 0–1.0 V. It is observed that charging at low current density (0.5 A g⁻¹) took more time than the discharge time, and that the CCD profile deviated from the symmetrical shape. The shorter discharge time at 0.5 A g⁻¹ is possibly due to the self-discharge of GF//GF supercapacitor cell at very low current when the device gets more time for self-discharging [203]. At higher current densities, the difference between charging and discharging time are lower due to the faster charge-discharge rate. From the slope of discharge curves, the C_{sp} of GF//GF SSC was calculated to be 82.1, 81.3, 80.4 and 76.2 F g⁻¹ at 0.5, 0.75, 1 and 2 A g⁻¹ current densities, respectively according to Equation 2.12 (Chapter 2). The energy density value of GF//GF SSC were found to be 11.40 Wh kg⁻¹ at a power density of 255 W kg⁻¹. The results indicate that GF//GF flexible solid-state SSC shows very high rate capability because 92.8% capacitance maintained at 2 A g⁻¹, compared to that obtained at a current densities of 0.5 A g⁻¹. The 3D porous structure and improved conductivity of GF led to the high capacitance value. This high capacitance value can be attributed to the higher accessible surface area due to the mesopores of 3D building blocks.

Figure 4.5 (a) CV curves at different scan rates and (b) CCD curves at different current densities of GF//GF solid-state supercapacitor.

4.3.2 MnO_2 and MnO_2 @PANI nanomaterials

4.3.2.1 Morphological investigation

The morphology of the hydrothermally synthesized MnO_2 is shown in Figure 4.6. It can be seen from the panoramic FESEM image (Figure 4.6a) of the synthesized MnO_2 that it consisted of spiky spherical microstructures. At higher magnification (see Figure 4.6b), the MnO_2 microspheres look like natural urchins with diameters of 3–5 μm and numerous nanospines radiating randomly outward, except that the microsphere has a hollow core. The hollow interior holds 30–40% (by volume) in the urchin and the shell nanospines have diameters of about 80–100 nm and lengths of 600–700 nm. The spines are actually tubes, as confirmed from the TEM images in Figure 4.6c.

Figure 4.6d represents the FESEM image of the MnO_2 @PANI composite, in which the PANI is uniformly coated on urchin-shaped MnO_2 . Figure 4.6e clearly shows that urchin-shaped MnO_2 @PANI coaxial composites are hollow. The diameter of MnO_2 nanospines of the MnO_2 @PANI coaxial microurchins appears to be similar to that of the spines of MnO_2 microurchin. This is not surprising because the MnO_2 works as an oxidant and template during synthesis. The TEM image in Figure 4.6f shows the core-shell morphology of the MnO_2 @PANI microurchin. It is clear from the figure that the outer PANI layer has a thickness of about 10–20 nm and an inner

layer comprising a thin-walled MnO₂ microurchin. This confirms the successful preparation of MnO₂@PANI coaxial microurchin.

The chemical reaction for the synthesis of MnO₂ can be depicted by Equation 4.1.

Figure 4.6 (a) Low- and (b) high-magnification FESEM images of MnO₂; (d) low- and (e) high magnification FESEM images of MnO₂@PANI (@ 0.02 M HCl); (c) MnO₂ and (f) MnO₂@PANI (@ 0.02 M HCl) TEM images.

Thus, the development of hollow MnO₂ microurchin [204] can be explained by following Figure A2 (see in Appendix). First, through the hydrothermal reaction between KMnO₄ solution and HCl, rose-like MnO₂ microspheres were formed (Figure A2a in Appendix). Gradually, nanospines grew from the surface of microspheres due to the 1D growth habit of the α-MnO₂ crystal, at the expense of inside cores of the spheres because of higher surface energy in the core compared to the outer surface (Figure A2b in Appendix). Finally, hollow microurchins were formed when the solid cores were completely consumed (Figure A2c in Appendix). The formation mechanism of hollow microurchin can be explained by the well-known

Ostwald ripening process [65]. In this process, initially tiny crystalline nuclei are formed in a supersaturated medium and then gradually the crystal grows. Due to the energy difference between the surface and the core, the surface structure grows at the expense of core structure [205].

The morphology and microstructure of the MnO_2 @PANI coaxial microurchins (Figure 4.6) can be optimized to maximize its electrochemical properties. For synthesizing of MnO_2 @PANI coaxial microurchins, MnO_2 by itself can not initiate the polymerization of aniline monomers, and HCl is required to initiate the instant reaction. This proves that hydrogen ions (H^+) perform a critical role in the polymerization reaction. It was observed that the thickness of PANI shell of the MnO_2 @PANI coaxial microurchins was dependent on the HCl concentration during the reaction.

A pH-dependent experiment was performed to better comprehend the development of MnO_2 @PANI coaxial microurchin. It was found that the morphology of the MnO_2 @PANI composite could be varied by changing the concentration of HCl. Figure 4.7 shows FESEM and TEM images of MnO_2 @PANI microurchin at 0.2 and 0.002 M HCl concentration. As the polymerization reaction was conducted in 0.002 M HCl concentration, a negligible PANI layer (Figure 4.7a, b) was formed on the MnO_2 microurchin surface. This is because only a few of the aniline monomers can be polymerized by MnO_2 with the fewer H^+ ions at lower concentration (0.002 M). Moreover, the polymerization rate can also be increased by increasing the amount of the H^+ ions. When the concentration of HCl increased to 0.2 M, due to higher H^+ concentration, MnO_2 partly dissolved in the acid medium, and the 1D MnO_2 nanostructures were partially damaged, as shown in Figure 4.7c, d; a thick PANI coating was observed on the unreacted MnO_2 template. Therefore, it is apparent that a well-defined core-shell nanostructure can be synthesized via in situ polymerization of aniline monomer using MnO_2 microurchin as an oxidant and template at an optimized HCl concentration of 0.02 M (Figure 4.6e, f).

Figure 4.7 (a) FESEM and (b) TEM images at 0.002 M HCl; (c) FESEM and (d) TEM images at 0.2 M HCl concentrations of MnO_2 @PANI composites.

4.3.2.2 Molecular characterization

The crystalline phase of the MnO_2 and MnO_2 @PANI were analyzed by XRD, as shown in Figure 4.8. The diffraction peaks of MnO_2 appeared at $2\theta = 12.73^\circ$, 18.11° , 28.82° , 37.57° , 42.96° , 49.95° , 56.77° , 60.36° , 65.18° , and 69.36° , correspond to the expected diffraction peaks of (110), (200), (310), (211), (301), (411), (600), (521), (002), and (741) crystal planes of α - MnO_2 standard data, respectively, following the JCPDS card PDF file no. 44-0141 [205]. No peaks for other types of MnO_2 are observed, indicating that the as-prepared products composed only of one tetragonal α - MnO_2 phase. The XRD pattern of the MnO_2 @PANI coaxial microurchin sample (Figure 4.8ii) showed peaks that were similar to those MnO_2 , except that the peak intensities were lower. This can be attributed to the presence of uniform coating of PANI on the MnO_2 microurchin. The diffraction pattern of PANI at ~ 20 – 22° is suppressed by high intensity of peak of MnO_2 in the MnO_2 @PANI composite. Chen et al. also reported similar observation for MnO_2 /PANI composite material [206].

Figure 4.8 XRD patterns of (i) MnO₂ and (ii) MnO₂@PANI composite materials.

Raman spectroscopic study was carried out to ensure the presence of MnO₂ and PANI in the MnO₂@PANI composite by investigating the vibration properties of the as-prepared samples. In the Raman spectrum of MnO₂@PANI (Figure 4.9ii), the band at 1489 cm⁻¹ was assigned to the C=N stretching of the emeraldine base. The band at 1577 cm⁻¹ corresponds to the C=C stretching of quinone ring. The bands at 1175 and 1255 cm⁻¹ correspond to the C-H bending and C-N stretching vibration of the quinoid ring, respectively. The band at 1366 cm⁻¹ can be assigned to the C-N⁺ stretching modes of delocalized polaronic charge carriers of protonated imine form of PANI [207]. The bands observed at 820 and 531 cm⁻¹ correspond to bipolaronic quinoid ring and bipolaronic amine deformations, respectively. The band that appeared at 416 cm⁻¹ was attributed to polaronic C-N-C torsion. The same characteristic bands are observed in pure PANI [208]; however, some of the bands were shifted slightly from the characteristic band of PANI, i.e. 1168 to 1175 and 1345 to 1366 cm⁻¹. The slight shifting in the bands confirms the interactions between MnO₂ and PANI. The Raman spectrum of MnO₂ shows a peak at 637 cm⁻¹ (as shown in inset Figure 4.9i'), assigned to the symmetric stretching vibration (Mn-O) of the MnO₆ groups [209], which is also present in MnO₂@PANI at 608 cm⁻¹. This confirms that MnO₂ has been successfully coated by PANI.

Figure 4.9 Raman spectra of (i) MnO₂ and (ii) MnO₂@PANI, and inset (i') magnified MnO₂ materials.

Further to confirm that the MnO₂ microurchin was successfully coated with PANI, an FTIR study was carried out, and a comparison of the spectra of MnO₂ and MnO₂@PANI are depicted in Figure 4.10. In Figure 4.10i, the characteristic peak of MnO₂ at about 725 cm⁻¹ pertained to Mn–O vibrations of MnO₆ octahedra in MnO₂ nanostructure [210, 211]. The peaks at 1637 and 1400 cm⁻¹ are related to O–H vibrational mode, which comes from absorbed water and the stretching of the O–H group that is attached to the Mn atom [94]. These peaks are also observed in the MnO₂@PANI coaxial microurchin (Figure 4.10ii); however, the peak intensities decreased. The additional peaks, which are observed at 1286, 1240, 1585, and 1483 cm⁻¹, correspond to the C–N stretching vibration of aromatic amine, the C–N⁺ stretching vibration of the polaron structure, and the quinoid and benzenoid ring stretching vibration, respectively [25]. This shows that PANI is in its emeraldine state [6, 7]. Thus, the MnO₂@PANI coaxial microurchin also shows identical pure PANI characteristic peaks [212]. The characteristic peak of MnO₂ at 725 cm⁻¹ was shifted to 710 cm⁻¹ for MnO₂@PANI composite, which also revealed similar H-bonding interactions between two components. This observation demonstrated that a layer of PANI has been coated on to the surface of MnO₂ spines.

Figure 4.10 FTIR spectra for (i) MnO₂ and (ii) MnO₂@PANI materials.

The existence of a PANI coating on the MnO₂ microurchin was further confirmed by XPS analysis of MnO₂ and MnO₂@PANI composite. The analysis is shown in Figure 4.11. The characteristic Mn 2p peaks of MnO₂ are shown in Figure 4.11a. The characteristic peaks of N 1s are shown in Figure 4.11b, where the peaks at 399.4, 400.7 and 402.5 eV correspond to the benzenoid amine peak and the polaron and bipolaron states of positive charged nitrogen, respectively. The weak peak at 403.9 eV may be due to the N 1s shakeup satellite of the ionized nitrogen atoms in the PANI molecular chain [25, 213]. After deconvolution the C 1s spectrum of MnO₂@PANI composite displays three peaks centered at 285.2, 287.3 and 289.3 eV as shown Figure 4.11c. The main peak at 285.2 eV is ascribed to carbon backbone (C–C/C–H groups) of the polymer. The peaks at 287.3 and 289.3 eV are ascribed to C–N groups, and the residual carbon comes from the environment, respectively [214, 215]. These strongly indicate the existence of PANI in MnO₂@PANI coaxial microurchins, where MnO₂ has been coated with PANI.

The conductivity of MnO₂ and MnO₂@PANI composite were found to be 6.87×10^{-3} and $2.89 \times 10^{-1} \text{ S m}^{-1}$ respectively. This large increase in conductivity of the MnO₂@PANI composite is due to the encapsulation of MnO₂ microurchin by the conductive PANI layer.

Figure 4.11 XPS spectra of (a) Mn 2p of MnO₂ ; (b) N 1s and (c) C 1s spectrum of MnO₂@PANI composite.

4.3.2.3 MnO₂@PANI coaxial microurchin formation mechanism

The formation mechanism of PANI coating on the MnO₂ microurchin can be explained by considering the chemical oxidation potential of MnO₂ (1.23 V) [56], which is sufficient to make aniline monomers to polymerize on the MnO₂ nascent microurchin surface in an acidic medium because the chemical oxidation potential of aniline monomer reaches up to 1.04 V [216]. During the redox reaction, the MnO₂ microurchin surface is sacrificed while the aniline monomers that are being polymerized surround its surface, leading to the formation of PANI coating on the MnO₂ microurchin. Based on the above results, a schematic presentation of MnO₂@PANI coaxial composite formation can be made as shown in Figure 4.12a. It is clear from the FESEM and TEM micrographs of Figure 4.6 and 4.7 that the MnO₂@PANI microurchin shows a core-shell structure in which MnO₂ microurchin

is a core and PANI is the shell. A redox reaction happens when the MnO_2 microurchin surface comes in contact with aniline monomers in acidic medium. At first, a solid–liquid interface was formed by absorbing the aniline monomers on the exposed surface of the MnO_2 microurchin followed by the redox reaction between MnO_2 and aniline monomers in the acidic medium. This results in the formation of a PANI layer on the undissolved surface of MnO_2 microurchin. Here, the first electron-transfer reaction occurs between the lone pair electron of aniline monomer and 3d metal ion center, which eventually forms a $[\text{An}^\bullet]^+$ radical cation that interacts with another $[\text{An}^\bullet]^+$ and then propagates as usual [217]. The polymerization process of PANI could self-terminate once the exposed surfaces of the MnO_2 nanospines were completely covered, which helped to prevent random incorporation of PANI in the composite. For better understanding of the dissolution of MnO_2 and the formation of PANI, a schematic representation is shown in Figure 4.12b that shows the competition between MnO_2 dissolution and PANI formation with increasing H^+ ion concentration. At an optimum H^+ ion concentration, MnO_2 is fully coated with PANI, keeping the inner core structure unchanged.

Figure 4.12 (a) Schematic diagram of MnO_2 @PANI core–shell structure formation, and (b) schematic presentation of PANI-coating formation on a dissolute MnO_2 surface at an optimized $[\text{H}^+]$ concentration.

4.3.2.4 Electrochemical measurements

The capacitive performance of the flexible solid-state MnO₂@PANI//MnO₂@PANI SSC was determined by CV and CCD techniques within the potential window of -0.3 to $+0.7$ V. The CV was carried out at various scan rates of 5, 10, 25, 50, 75, 100, 200, and 500 mV s⁻¹ as shown in Figure 4.13a. The shapes of CV curves of MnO₂@PANI represent a combination of the pseudocapacitive properties of both MnO₂ and PANI. With increasing scan rates, the peak current density was increased whilst keeping consistent shapes of the CV curves which indicates good reversible redox ability and good rate capability of the composite [218]. The CV curves deviated from usual rectangular shape due to the combined pseudocapacitive effects of PANI and MnO₂. Redox reactions take place with PANI and electrolyte ions [219], which are known as (i) leucoemeraldine–emeraldine salt transition and (ii) emeraldine salt–pernigraniline transition [220, 221]. Here, the broad peaks (in Figure 4.13a) arise from the MnO₂ and PANI redox processes [220]. The specific capacitance (C_{sp}) of the supercapacitor was calculated from the CV study, as mentioned in section 2.4.2 (Chapter 2). The obtained C_{sp} of MnO₂@PANI//MnO₂@PANI solid-state SSC was found to be 132 F g⁻¹ at 5 mV s⁻¹. The C_{sp} value gradually decreased with increasing scan rates. At higher scan rate, the electrolyte ions cannot access all the active surface areas due to fast scan rates, which make poor interaction between the ions of the electrolytes and the electrode, and hence, capacitance values decreased gradually [6]. However, higher scan rate reduces the available diffusion time, resulting in decreased interactions of ions with the active surface area of the electrode. As a result, the capacitance decreases at high scan rates.

Figure 4.13 (a) CV curves at different scan rates and (b) CCD curves at different current densities of MnO₂@PANI composite.

The constant current charge–discharge curves (CCD) of MnO₂@PANI/MnO₂@PANI SSC at different current densities (0.5, 0.75, 1 and 2 A g⁻¹) were obtained at a fixed voltage window of -0.3 and +0.7 V as shown in Figure 4.13b. The C_{sp} (F g⁻¹) of SSC was calculated from the discharge curve using Equation 2.12 (Chapter 2). The calculated C_{sp} of MnO₂@PANI solid-state SSC at 2, 1, 0.75, and 0.5 A g⁻¹ current densities were found to be 55.7, 85.3, 100.4, and 129.2 F g⁻¹, respectively and the obtained energy density at a 0.5 A g⁻¹ constant current density was 17.9 Wh kg⁻¹. Such a good electrochemical performance of 3D urchin-shaped MnO₂@PANI coaxial composite can be attributed to following factors:

- (1) The existence of electrically conductive PANI coating over MnO₂ nanospines facilitates faster electron transport, which helps to overcome the limitations of poor conductivity and low charge–discharge rates of MnO₂. [222].
- (2) PANI has good electrochemical pseudocapacitive properties [223].
- (3) H-bond interaction between MnO₂ and PANI may decrease the electron-transfer barrier and increase the C_{sp} [224].

4.3.3 Asymmetric hybrid supercapacitor

A solid-state asymmetric supercapacitor (ASC) was fabricated with the GF as the negative electrode and the MnO₂@PANI composite as the positive electrode materials

utilizing PVA/KOH gel electrolyte. A schematic presentation of ASC is given in Figure 4.14a. At first, CV test was carried out in a conventional three-electrode system with Pt wire as the counter electrode and Ag/AgCl as the reference electrode in 6 M aqueous KOH electrolyte. It was found that the stable potential windows for GF and MnO₂@PANI electrodes were between -8.0 to $+0.2$ and -0.3 to $+0.7$ V, respectively, as shown in Figure 4.14b. Thus, the cell voltage for ASC can be obtained by the sum of the potential windows of GF and MnO₂@PANI electrodes in the three-electrode system. The effective potential window for GF//MnO₂@PANI ASC could be 0 – 1.5 V considering the overlapping region in Figure 4.14b. Now, it is obligatory to balance the charges stored at the positive and negative electrodes to obtain the 0 – 1.5 V potential window in aqueous electrolyte. The charges stored in the positive and negative electrodes were balanced following the Equation 2.17 (Chapter 2), and the mass ratio of positive electrode to negative electrode materials (m_+/m_-) was found to be 0.94 .

To find the best working range for solid-state GF//MnO₂@PANI ASC, a CV study was carried out by gradually increasing the potential windows of 0 – 1.0 , 0 – 1.2 , 0 – 1.4 , 0 – 1.5 and 0 – 1.6 V at 100 mV s^{-1} (Figure 4.14c). The solid-state GF//MnO₂@PANI ASC exhibited a stable potential window of 0 – 1.5 V. The CV plots from 10 to 500 mV s^{-1} are shown in Figure 4.14d. The CV curves shows similar behavior, where current density increased in a proportional manner with increasing scan rates indicating that the ASC has very good electrochemical stability.

Figure 4.14e shows the charge–discharge curves (CCD) of the solid-state GF//MnO₂@PANI ASC. The symmetrical charge and discharge profile and linear discharge behavior also indicate good I – V characteristics and rate capability. The C_{sp} of the ASC at 1 A g^{-1} was calculated to be 95.3 F g^{-1} . At a high current density of 5 A g^{-1} , the capacitance was found to be 71.4 F g^{-1} . Figure 4.14f depicts the specific capacitance versus current density plot of SSCs and ASC, which shows the high rate capability of the GF//GF SSC system. The GF//MnO₂@PANI ASC shows moderate rate capability through the combined effects from the positive and negative electrodes.

Figure 4.14 (a) Schematic presentation of GF// $\text{MnO}_2\text{@PANI}$ flexible solid-state ASC, (b) CV curves for $\text{MnO}_2\text{@PANI}$ and GF materials by three-electrode cell measurement at 100 mV s^{-1} , (c) CV curves in different voltage windows at a scan rate of 100 mV s^{-1} , (d) CV curves at different scan rates from 10–500 mV s^{-1} , (e) CCD curves at different current densities of GF// $\text{MnO}_2\text{@PANI}$ ASC, and (f) specific capacitance comparison with current densities for SSCs and ASC.

The Coulombic efficiency of the asymmetric cell is shown in Figure 4.15a. It has been seen from the figure that the asymmetric cell shows high Coulombic efficiency of about 97% at 5 A g⁻¹ current density. The Coulombic efficiency decreases with lower current density where ~89% efficiency was observed for 1 A g⁻¹ current density. The dissipation of Coulombic efficiency decrease could be due to slower rate of charge–discharge at low current density.

A Ragone chart that depicts the relationship between power density and energy density is plotted for both SSCs and ASC, as shown in Figure 4.15b. It can be seen from the figure that the energy density of the GF//MnO₂@PANI ASC is higher than that of the MnO₂@PANI//MnO₂@PANI and GF//GF SSCs at the same power density. The energy density was increased about 2.5-times with respect to the MnO₂@PANI//MnO₂@PANI and GF//GF SSCs at a current density of 1 A g⁻¹. The high energy density of 37 Wh kg⁻¹ was obtained at power density of 0.386 kW kg⁻¹. When the power density was increased to 4.018 kW kg⁻¹, the energy density of GF//MnO₂@PANI still reached 22.3 Wh kg⁻¹ at a current density of 5 A g⁻¹.

From the cyclic stability test, it can be seen that the ASC device possess very good capacitance retention after 5000 cycles, as shown in Figure 4.15c. It shows 88.6% capacitance retention after 5000 cycles at a 2 A g⁻¹ current density. A comparative cyclic stability study was also carried out between SSCs and ASC. The MnO₂@PANI//MnO₂@PANI SSC showed 84.7% retention of capacitance after 5000 cycles. The good cyclic life can be ascribed to the hollow spine configuration of the MnO₂ core, which serves as a backbone to limit the degradation of PANI due to volumetric change during cycling. The crystal structure of α -MnO₂ has a tunnel structure (Figure 2.7), and electrolyte ions can be easily inserted into or de-inserted from this tunnel structure during cyclic charge-discharge test. The tunnel volume of α -MnO₂ nanospine is large enough to buffer the big volume change of PANI shell during doping/de-doping processes and hence maintain a good electrical and mechanical stability. The synergic effect between MnO₂ and PANI inhibits the dissolution of MnO₂ and PANI, and consequently improve the electrochemical reversibility and stability of the composite electrode. The uniform PANI coating on MnO₂ microurchin surface helps to prevent dissolution of MnO₂ by acting as a protective layer, which favors the retaining of the higher capacitance after cyclic test.

Figure 4.15 (a) Coulombic efficiency of GF// $\text{MnO}_2\text{@PANI}$ ASC; (b) Ragone plots, (c) cyclic stability performance over 5000 cycles; and (d) Nyquist plots of GF, $\text{MnO}_2\text{@PANI}$ SSCs, and GF// $\text{MnO}_2\text{@PANI}$ ASC (the inset of panel presents the schematic diagram of the Nyquist plot); (e) CV curves for ASC at different bending states (the inset optical images show the bending states); and (f) CCD curves of ASC where two and three cells are connected in series (the inset shows a red LED that was powered by the tandem ASC).

The GF//GF SSC shows 89% capacitance retention after 5000 cycles. This high cyclic stability could be explained by the pure EDL behavior of GF//GF SSC, in which capacitance was obtained only from the ion adsorption desorption mechanism on the surface of 3D porous GF.

Although the GF//MnO₂@PANI and GF//GF SCs showed similar capacitance retention after 5000 cycles, the initial rate of capacitance loss of the GF//MnO₂@PANI ASC was a bit faster (2–3%) compared to the MnO₂@PANI SSC for only the first few 100 cycles. This is due to the asymmetric combination of the cell preparation in which GF acted as the negative electrode and MnO₂@PANI as the positive electrode. The negative-electrode GF shows a high degree of reversibility, which does not mean that the asymmetric supercapacitor would follow the same trend; rather, pseudocapacitive material would likely control the supercapacitor cycle life [225]. At the beginning of cyclic stability test, GF remains as a compact material in which electrolyte ions cannot access the whole surface area; the device performance was fully limited by MnO₂@PANI, and the capacitance loss was higher. After passing a few cycles, the charge–discharge phenomenon became stable, and gradually, ions could access the interior pores of the GF material. Hence, the presence of EDL type component (GF) on the other electrode makes the cyclic performance to be better than the MnO₂@PANI SSC after 5000 cycles.

Electrochemical impedance spectroscopy (EIS) was used to examine the different resistance of the SSC and ASCs in the frequency range of 100 kHz to 1 Hz. The Nyquist plots of the GF//GF and MnO₂@PANI//MnO₂@PANI and GF//MnO₂@PANI solid-state SCs are shown in Figure 4.15d. The intercept on Z_{real} (along the X-axis) in higher-frequency region implies equivalent series resistance (R_s), which include the current collector–electrode material contact resistance, intrinsic resistance of active material and electrolyte resistance [6]. The diameter of the semicircle arc is related to the charge-transfer resistance (R_{ct}) at the electrode–electrolyte interface [41, 226]. It is observed from Figure 4.15d that the resistance R_s for GF, MnO₂@PANI SSCs and GF//MnO₂@PANI ASC are 0.5, 34 and 30 ohm. This trend can be explained by the high conductivity of GF, which makes lower contact resistance at the active material–current collector interface compared to MnO₂@PANI. The GF electrode material has a lower R_{ct} as compared to the

MnO₂@PANI composite electrode material, which is evident from the smaller diameter of the semicircle arc in the Nyquist plot. The lower R_{ct} is due to the fact that the conductive GF enables faster charge transfer between the electrolyte and active material. The $\sim 45^\circ$ slope portion of the curve at the lower-frequency region, which is commonly known as the Warburg resistance (R_w), is a measure of ionic diffusion/transport from the electrolyte to the surface of the electrode [41, 226]. The slope toward 90° specifies a pure capacitive behavior and low diffusion resistance of the electrolyte ions [41]. The GF electrode exhibits a steeper straight line than the MnO₂@PANI electrode because of pure EDL-type charge transfer process in the GF electrodes. The ASC shows an in-between slope at the low-frequency region with respect to GF//GF and MnO₂@PANI//MnO₂@PANI SSCs due to the combined effect of the negative and positive electrode materials.

The flexibility of the device was confirmed by the CV measurements at different bending angles 0, 120 and 150° . It can be seen that the CV curves remained unchanged and stable (Figure 4.15e), which indicates high flexibility and good electrochemical stability. The device could be bent several times and still keep almost the same performance. To further justify the device performance in the bent condition, the CCD tests were carried out in cyclic bending conditions in which the first 100 cycles were in the flat state and next 100 cycles were in bending state (90°) successively for 1000 cycles at 5 A g^{-1} current density. After the cyclic bending test, the difference of capacitance loss was about 1% of the value obtained for a flat specimen after 1000 cycles.

To demonstrate the real application of the ASC device, three cells were connected in series and charged up to 4.5 V at a constant current of 8 mA by 59 s. It was then connected to a red-light-emitting-diode (red-LED) of 1.8 V and was observed to successfully light up the LED for 30 s, as shown in Figure 4.15f.

The FESEM images of MnO₂@PANI microstructure are compared with before and after cyclic charge-discharge test for 5000 cycles, as shown in Figure 4.16. It seems that the MnO₂@PANI nanostructures are agglomerated and have little change of morphology after 5000 cycles. These changes might be due to mechanical degradation happened during ions insertion de-insertion for several times in prolonged

charge-discharge cycles. However, the core-shell structures are undamaged after the test.

Figure 4.16 FESEM images MnO_2 @PANI microstructure (a) before and (b) after 5000 cyclic charge –discharge test.

4.3.4 Comparison with other results

A comparison of the energy density, power density and cyclic stability performances by all-solid-state supercapacitors from published data and this work is presented in Table 4.1.

Table 4.1 Typical results obtained from flexible solid-state symmetric and asymmetric supercapacitors.

Materials	Electrolyte	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Cyclic stability (% of capacitance retention)	Ref.
Solid-state symmetric supercapacitor (SSCs)					
Graphene hydrogel film	H ₂ SO ₄ /PVA gel	0.61	0.670	91.6 (after 10000 cycles)	[227]
CNTs/bacterial nano-cellulose paper	PS-PEO-PS/[EMIM][NTf ₂]	15.5	1.500	99.5 (after 5000 cycles)	[172]
PANI/CNT	H ₂ SO ₄ /PVA gel	7.1	2.200	91.9 (after 1000 cycles)	[12]
Graphene @carbon cloth	H ₂ SO ₄ /PVA gel	1.64	0.670	--	[228]
MnO ₂ @PANI	PVA/KOH gel	17.9	0.261	84.7 (after 5000 cycles)	this work
GF	PVA/KOH gel	11.4	0.255	89 (after 5000 cycles)	this work
Solid-state asymmetric supercapacitors (ASCs)					
Graphene (IL-CMG)//RuO ₂ -IL-CMG	H ₂ SO ₄ /PVA gel	19.7	6.800	95 (after 2000 cycles)	[18]
MnO ₂ @ poly(3,4-ethylene-dioxythiophene)//poly(3,4-ethylene-dioxythiophene)	LiClO ₄ /PMMA gel	9.8	0.850	86 (after 1250 cycles)	[101]
CNTs/MnO ₂ //CNTs/PANI	Na ₂ SO ₄ /PVP gel	24.8	0.120	--	[229]
GF//MnO ₂ @PANI	PVA/KOH gel	37.0	0.386	88.6 (after 5000 cycles)	this work

It can be seen from the table, compared to other literature data for solid-state SSCs and ASCs, the as synthesized GF//MnO₂@PANI ASC possesses very good overall properties in terms of energy density, power density, and cyclic stability.

4.4 Summary

A 3D hollow urchin-shaped coaxial MnO₂@PANI composite was made from the redox active materials, in which the MnO₂ and PANI phases mutually protect and enhance their capacitive performance. This MnO₂@PANI composite can be made using a facile single-step process without the addition of any surfactant and oxidizing agents, that is very simple and easy to implement. This composite can be used as the positive electrode material for a SC. Additionally; a self-assembled 3D graphene hydrogel foam was synthesized using environmentally friendly vitamin C utilizing the hydrothermal autoclave system. This 3D graphene foam can be used as the negative electrode material. An asymmetric supercapacitor with excellent properties was made using a 3D graphene foam and 3D MnO₂@PANI composite that had a wide working potential range of 0–1.5 V. It displays a remarkable high energy density of 37 Wh kg⁻¹ at a power density of 0.386 kW kg⁻¹ and stable cycling performance. The asymmetric supercapacitor can be used as a portable energy storage device.

For the symmetric supercapacitors studied, the solid-state flexible symmetric graphene foam (GF) supercapacitors had an energy density of 11.4 Wh kg⁻¹ at a power density of 0.255 kW kg⁻¹, while the MnO₂@PANI symmetric supercapacitor showed a high energy density of 17.9 Wh kg⁻¹ at a power density of 0.261 kW kg⁻¹.

Chapter 5 Development of 3D porous graphene/MnO₂@polyaniline hybrid film and 3D graphene aerogel for all-solid-state flexible asymmetric supercapacitor

5.1 Introduction

Among carbon-based materials, graphene has been attractive mostly due to its high surface area, high conductivity and high flexibility [16]. It has been reported that reduced graphene oxide (RGO) has better properties than graphene oxide (GO). Dikin et al. prepared free-standing graphene oxide paper using the vacuum filtration method [230]. The specific capacitance (C_{sp}) of pure graphene film was reported to be only 57 F g⁻¹ which is very low due to poor access of ions to the entire surface [166]. In contrast, Niu et al. prepared reduced graphene oxide porous paper, obtaining a C_{sp} of 110 F g⁻¹ in 1 M H₂SO₄ electrolyte [127]. Weng et al. [2] synthesized graphene-cellulose paper which shows the C_{sp} of 120 F g⁻¹ at 1 mV s⁻¹ in 1 M H₂SO₄ electrolyte. Wang et al. prepared graphene film by introducing carbon black as spacers within graphene sheets and obtained a C_{sp} of 138 F g⁻¹ at 10 mV s⁻¹ in 6 M aqueous KOH electrolyte [231]. The limitation of the above systems is that their energy storage mechanism is limited to electrochemical double-layer capacitance. Recently, researchers have been engrossed with fabricating graphene film by incorporating pseudocapacitive materials [17-19]. In this chapter, the previous work will be extended to develop RGO based materials for solid state SCs with the expectation that even better electrochemical properties will be obtained.

The coaxial MnO₂@PANI microurchin developed in Chapter 4, which looks like a sea-urchin will be used as the spacer here to create channels in the inside layers of GO film to facilitate ion access. The urchin-shaped MnO₂@PANI also provides high pseudocapacitive value by the synergistic effect of MnO₂ and PANI. There are two procedural steps that exfoliate the final film. Firstly, the gas released during chemical reduction of GO causes significant exfoliation of the dough GO film, thus making the film highly porous. Secondly, MnO₂@PANI micro-urchins act as a spacer

that prevents the GO sheets from collapsing and attaching to each other. Hence, the overall cell capacitance could be increased greatly via the contributions of both pseudocapacitive and electrochemical double-layer (EDL) capacitive materials. Hence, 3D porous reduced graphene oxide/MnO₂@PANI (RGO/MnO₂@PANI) hybrid film can be proposed here to use as a positive electrode material, in conjunction with graphene as the negative electrode material, for the fabrication of an asymmetric supercapacitor.

In order to prevent the collapse and restacking of graphene sheets in the negative electrode, a 3D self-assembled structure can be designed. The 3D open structure will serve to increase the accessible surface area. The self-assembling of graphene into a 3D pillared structure by using conventional hydrothermal method is an important and significant strategy. During the hydrothermal treatment, the GO sheets are crosslinked together by H-bonds, strong van der Waals forces and π - π interactions to ultimately form a 3D pillared structure.

Xu et al. synthesized self-assembled graphene foam using hydrothermal method, showing C_{sp} of 175 F g⁻¹ in aqueous electrolyte [122]. Zu and Han developed supramolecular graphene hydrogel by using Pluronic copolymer [133]. Zhao et al. prepared 3D graphene foam by using pyrrole that had a C_{sp} of 350 F g⁻¹ in at 1.5 A g⁻¹ in aqueous NaClO₄ electrolyte [232]. Recently, Jiang et al. fabricated self-assembled 3D reduced graphene oxide by divalent ions (Ca²⁺, Ni²⁺, or Co²⁺) as linker [233]. However, there is still lack of 3D self-assembly graphene preparation and their application in gel electrolyte based supercapacitor. Moreover, the surface area of graphene aerogel can still be improved significantly.

A soft-template will be used to build a stable hydrogel column. The soft-template which can be removed easily eventually will leave pores and voids in the aerogel matrix. Hence, herein a 3D graphene aerogel column will be developed with the help of a soft-template Pluronic F-68 solution which is a nonionic triblock copolymer poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly-(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) to increase the surface area of graphene aerogel.

An all-solid-state flexible asymmetric supercapacitor (ASC) was fabricated utilizing the unique 3D porous RGO/MnO₂@PANI hybrid film as the positive electrode and 3D graphene aerogel as the negative electrode material. The positive

electrode material was developed through the preparation of a hybrid film by vacuum filtration of GO and MnO₂@PANI mixture followed by reduction of the film by hydrazine vapor in a hydrothermal autoclave. The negative electrode material was synthesized through self-assembly of the graphene sheet using a soft-template Pluronic copolymer where vitamin C was used as a reducing agent via a one-step hydrothermal reaction. These provide a facile, economic and green approach to fabricate a flexible all-solid-state ASC from 3D porous RGO/MnO₂@PANI hybrid film and 3D graphene aerogel.

5.2 Experimental

5.2.1 Synthesis of porous RGO/MnO₂@PANI hybrid film

Details of the synthesis of urchin-shaped coaxial MnO₂@PANI particles have been outlined in Chapter 4. In the present work, the as-prepared MnO₂@PANI coaxial urchin-shaped particles were used to fabricate the porous RGO/MnO₂@PANI hybrid paper. At first, GO (20 mg) was dispersed in 20 mL deionized water by ultrasonication for 20 min. Next, 5 mg (25% wt ratio to GO) of urchin-shaped coaxial MnO₂@PANI particles was dispersed in GO solution by adding a few drops of SDBS (1 mg mL⁻¹) surfactant. After that, the mixture was filtered by vacuum filtration using anodisc membrane (pore diameter 0.2 μm). A very thin compact layer was formed, which was dried in a vacuum oven at 80 °C. Next, the thin film was peeled off from the membrane and reduced by hydrazine vapor. The film was hanged in a 100 mL Teflon-lined stainless-steel autoclave containing 200 μL hydrazine monohydrate and kept in an electric oven at 110 °C for 10 h. The reduced film was then stored for characterization purposes. Four similar films were fabricated by varying the amount of MnO₂@PANI (0, 10, 25 and 40% wt ratio to GO) to optimize the performance of the film. The four as-prepared films are labeled as RGO, RGO/M@P10, RGO/M@P25 and RGO/M@P40.

5.2.2 Preparation of graphene aerogel

At first, 50 mg of GO was dispersed in 25 mL of deionized water by ultrasonication and then stirred with 5 mL of F-68 solution (20% volume ratio to GO solution (2 mg mL⁻¹)) for 30 min. Next, 100 mg of vitamin C was added in the mixture and stirred for another 20 min. The whole solution was then poured into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was kept in an electric oven at 150 °C for 12 h. After that, the autoclave was removed from the oven and allowed to cool down to room temperature naturally. A 3D graphene hydrogel column was formed by the hydrothermal reaction. Dialysis of the 3D column was conducted for 12 h to remove impurities and excess ions. The final hydrogel was freeze-dried and then heat-treated in a furnace at 500 °C in oxygen atmosphere for 4 h. The aerogels before and after the heat-treatment are labeled as raw-GF20 and GF20, respectively. To optimize the surface area and porosity of the graphene aerogel, different hydrogel columns were prepared by varying the volume ratio of F-68 solution to GO (2 mg mL⁻¹) as 0, 10, 20, 40 and 50%. The final aerogels are labelled as GF0, GF10, GF20, GF40 and GF50.

5.2.3 Fabrication of flexible all-solid-state supercapacitor cells

A Ni foam of (40 mm × 20 mm × 1.6 mm) was pressed using a 1 ton weight to make flexible Ni sheet and then washed several times by acetone and deionized water. Before fabrication of the RGO/MnO₂@PANI electrode, the hybrid film was dipped overnight in 6 M KOH solution which contained a few drops of SDBS solution (1 mg mL⁻¹). As the surface of the film was hydrophobic in nature, surfactant was added to enhance wetting during soaking in the KOH solution. Next, 2 mg of RGO/MnO₂@PANI film sample was placed on the Ni foam and pressed with a 0.05 ton weight. PVA/KOH gel electrolyte was then applied on top of the sample. This was kept in the fume-hood for 6 h to enable water to evaporate from the gel. The two electrodes were then assembled and held together for 24 h while the gel electrolyte solidified completely. In this way, the robust all-solid-state flexible RGO/MnO₂@PANI SSC cells were created.

The solid-state graphene aerogel SSC cells were fabricated following the same procedure as outlined in section 4.2.4 (Chapter 4). The ASC cell was fabricated by assembling one RGO/MnO₂@PANI electrode and one graphene aerogel electrode.

5.2.4 Characterization techniques

Same characterization techniques and procedures were used to characterize all the electrode materials and SC devices as outlined in Chapter 4 (section 4.2.5).

5.3 Results and discussion

5.3.1 Graphene Aerogel

5.3.1.1 Morphological investigation

The transformation of GO suspension into a 3D graphene hydrogel cylindrical block can be seen in Figure 5.1a, b. The optical image (Figure 5.1b) clearly shows that water is entrapped by the graphene sheets in the hydrogel cylindrical block, and the height and diameter of the blocks are 17 and 15 mm, respectively. This confirmed that a 3D pillared graphene hydrogel was developed via a facile one-step hydrothermal method using a Pluronic copolymer (PEO-*b*-PPO-*b*-PEO). The triblock copolymer facilitates easy formation of 3D pillared structure. The hydrophobic PPO segment binds onto the hydrophobic part of graphene and the hydrophilic PEO parts of the copolymer spread into water [133]. Here, the triblock copolymer plays a dual role. Firstly, it aids easy dispersion of GO in water, and secondly, it assists the formation of the 3D building block.

Figure 5.1 (a) GO dispersion in water, (b) 3D Self-assembled GO hydrogel; (c) at lower magnification and d) at higher magnification FESEM image of the GF20 graphene aerogel.

After freeze-drying, the 3D sample shows spongy behavior which is formed due to sublimation of entrapped ice during freeze-drying. The microstructure of a 3D porous graphene aerogel specimen was observed under the FESEM, and it can be seen from Figure 5.1c that the aerogel had a 3D interconnected porous network structure comprising numerous micropores and mesopores. The porous structure of 3D graphene aerogel is apparent in Figure 5.1d. This work has revealed that the pore diameter, pore volume and surface area can be adjusted by varying the amount of Pluronic F-68 solution. The surface area and pore size distribution were analyzed by BET and BJH method through nitrogen adsorption and de-adsorption methods. The nitrogen porosimetry data indicated that Pluronic F-68 solution had a significant impact on the variation of the mesoporous structure of the aerogel. The BET surface area significantly increased when the amount of F-68 solution was high (40% volume ratio to GO). A comparison of the adsorption–desorption plots of GF0, GF10 and GF40 aerogels is shown in Figure 5.2a. The BET surface area for GF0, GF10, GF20, GF40 and GF50 aerogels were found to be 295, 310, 377, 635 and 638 m² g⁻¹, respectively. The similarity in specific surface area of the GF40 and GF50 specimens indicated that the GF40 aerogel has reached its optimum level of porosity. Figure 5.2b shows how the distribution of incremental pore volume varies with pore diameter.

The pore size distribution and the peak pore volume increased with the incorporation of triblock copolymer to form a highly porous graphene aerogel.

Figure 5.2 (a) The N₂ adsorption–desorption isotherm loop of GF0, GF10 and GF40 aerogels, (b) Pore volume distribution plot of GF0, GF10, GF20 and GF40 aerogels.

5.3.1.2 Molecular characterization

Raman spectroscopy studies were employed to confirm the reduction of GO by vitamin C and the removal of F-68 copolymer from the aerogel after heat-treatment. The Raman spectrum of GO, raw-GF20 and GF20 are shown in Figure 5.3. GO shows two prominent peaks at 1345 and 1586 cm⁻¹ corresponding to the D- and G- bands, respectively. The D-band is assigned to structural defects and disorders of carbon in graphite layers, and the G-band corresponds to the E_{2g} phonon of sp² C atoms, which are well documented in literature [197]. The raw-GF20 and GF20 also shows similar peaks corresponding D- and G- bands. The I_D/I_G intensity ratio increased gradually from GO to raw-GF20 and then to GF20, which confirms the reduction of GO by vitamin C. Upon reduction of GO, more numerous smaller graphene domains were reestablished which eventually increases the I_D/I_G ratio [193, 199, 200]. The lower intensity (I_D/I_G) ratio of raw-GF20 with respect to the GF20 would be due to the presence of copolymer in the graphene matrix. The higher I_D/I_G ratio of GF20 confirms that the copolymer has been removed after the heat treatment.

Figure 5.3 Raman spectroscopy (i) GO, (ii) raw-GF20 and (iii) GF20 aerogel.

The XRD graphs of the crystal phase of GO, raw-GF20 and GF20 are as shown in Figure 5.4. In Figure 5.4i, the sharp peak at $2\theta = 10.8^\circ$ corresponds to the (001) plane of GO with a d spacing of 0.215 Å. The raw-GF20 (Figure 5.4ii) shows peaks at $2\theta = 19.8^\circ$, 23.4° and 26.5° . The sharp peaks at 19.8° and 23.4° correspond to the crystalline structure of PEO chains with interlayer d-spacing of 3.74 and 3.83 Å, respectively [234]. The characteristic broad peak at 26.5° corresponds to graphene with a d-spacing 3.41 Å. Figure 5.4iii represents the XRD for GF20 and the single broad peak at 26.4° typifies graphene sheet with a d-spacing of 3.25 Å. The peak intensity ratio was higher for GF20 compared to raw-GF20. No other peak corresponding to PEO chains was observed, which confirms that F-68 copolymer has been removed after heat treatment of the template.

Figure 5.4 XRD analysis of (i) GO, (ii) raw-GF20 and (iii) GF20 aerogel.

The heat stability of raw aerogel (freeze-dried samples) was assessed in a TGA at the heating rate of 10 °C min⁻¹ up to 500 °C temperature in an oxygen atmosphere. It can be seen from Figure 5.5 that the raw-GF20 shows ~3% weight loss at the beginning due to evaporation of adsorbed water and organic residues. The major weight loss at around 310 °C is associated with the combustion of Pluronic copolymer. The weight loss remained stable at ~19% when the temperature reached 500 °C.

Figure 5.5 TGA of raw-GF20.

5.3.1.3 Electrochemical measurements

CV, CCD and EIS tests were performed to measure the capacitive performance of GF20//GF20 solid-state symmetric supercapacitor (SSC). The CV plots for scan rates from 10–100 mV s⁻¹ are as shown in Figure 5.6a. The CV curves look nearly rectangular and symmetrical in shape which follows the ideal capacitive behavior by carbon based materials. It can be seen that the current density increased with increasing the scan rates, which is indicative of the very good intrinsic *I-V* characteristic of the electrode material.

A comparison of the CCD profiles for the GF0, GF10, GF20 and GF40 aerogel-based SSCs are shown in Figure 5.6b. The specific capacitance (C_{sp}) of GF0, GF10, GF20 and GF40 -based SSCs were found to be 81, 87, 95, 111 F g⁻¹ at 1 A g⁻¹, respectively. These results are in line with the basic EDL mechanism where higher surface area produces higher capacitance and higher energy density values. Hence, GF40 aerogel was selected for further study in asymmetric supercapacitor.

The CCD study of GF40//GF40 SSC was carried out at different current densities of 5, 4, 2, and 1 A g⁻¹ as shown in Figure 5.6c. It can be seen that the charging and discharging times decreased with increasing current density. The C_{sp} and energy density of the GF40//GF40 SSC were calculated from the discharge curve based on Equation 2.12 and 2.14 (Chapter 2). The C_{sp} of GF40//GF40 SSC were found to be 87, 91, 107, and 111 F g⁻¹ at current densities of 5, 4, 2 and 1 A g⁻¹, respectively. The energy density was found to be 15.41 Wh kg⁻¹ at the power density 0.523 kW kg⁻¹, and 12.08 Wh kg⁻¹ at the high power density of 2.967 kW kg⁻¹. It is apparent that the highly porous structure of the copolymer induced aerogel is responsible for the high energy density and high capacitance of the GF40//GF40 SSC.

Figure 5.6 (a) CV curves of GF20 SSC for scan rates of 10–100 mV s⁻¹; (b) CCD curves of the GF0, GF10, GF20 and GF40 SSCs at 1 A g⁻¹; and (c) CCD curves at different current densities of the GF40 SSC.

5.3.2 Graphene/MnO₂@Polyaniline (RGO/MnO₂@PANI) film

5.3.2.1 Morphological investigation

Using a facile technique, a 3D RGO/M@P25 porous film (Figure 5.7a) was obtained after reduction of the GO/M@P25 film by hydrazine vapor in the hydrothermal autoclave. The GO sheet contains epoxy, hydroxyl and carboxyl groups in its basal plane and edges, which promote anchoring of the MnO₂@PANI nanostructures onto the surfaces of GO sheets. The advantage of this technique is that the MnO₂@PANI produced, acts as a spacer in between graphene sheets, thus preventing the sheets from aggregating. Moreover, during the reduction process, gaseous products (H₂O (g) and CO₂ (g)) are formed inside the GO layers [127]. The released gases serve to exfoliate the RGO film and make it porous. The top view of the hybrid film as shown

in Figure 5.7a shows curved surface regions where exfoliation had occurred due to the entrapment of gas bubbles within the film. The cross-sectional side view FESEM image of the RGO/M@P25 film is shown in Figure 5.7b. The magnified image in Figure 5.7e confirms that the films are decorated with many pores and channels. The magnified cross-sectional side view images of the film in Figure 5.7c and Figure 5.7f clearly highlight the RGO exfoliation and the presence of an even distribution of MnO₂@PANI in the RGO matrix. Figure 5.7d shows that the RGO/M@P25 film remains intact after bending and folding thus indicating its remarkable flexibility. It is clear from Figure 5.8a and 5.8b that the GO/M@P25 film has been expanded by ~3.5 times after the reduction process step. The schematic presentation in Figure 5.8 shows the distribution of MnO₂@PANI particles and gas entrapment (H₂O (g) and CO₂ (g)) in the RGO matrix. This high exfoliation and the MnO₂@PANI spacer particles provide for more surface area to be accessible for ions diffusion, leading to higher charge transfer and higher capacitance. It was found that the flexibility of the film decreased when the amount of MnO₂@PANI spacer particles increased.

Figure 5.7 (a) and (d) normal photographs of RGO/M@P25 film; (b) FESEM micrograph of the cross-sectional edge of RGO/M@P25 film at lower magnification; (c), (e) and (f) magnified FESEM images of RGO/M@P25 film highlighting different positions.

Figure 5.8 Schematic presentation of (a) GO/M@P25 film and (b) RGO/M@P25 film.

5.3.2.2 Molecular characterization

The structure of the MnO₂@PANI based graphene films and the RGO/M@P25 film can be evaluated by comparing their X-ray diffraction patterns (see Figure 5.9). It can be seen from Figure 5.9i that MnO₂@PANI exhibits 2 θ peaks at 12.7°, 18.1°, 28.8°, 37.5°, 42.1°, 49.9°, 56.7°, 60.3° and 69.7° that correspond to the diffraction peaks of (110), (200), (310), (211), (301), (411), (600), (521) and (541) crystal planes, respectively. These data are well matched with α -MnO₂ standard data JCPDS no. 44-0141 [205]. The diffraction peaks for RGO/M@P25 film are shown in Figure 5.9ii. The peaks which appeared at 2 θ = 11.6°, 28.8°, 37.9°, 42.5°, 46.9°, 47.9°, 56.3° and 60.4° matched with the expected diffraction peaks of α -MnO₂ crystalline phase. However, the peak intensity decreased due to the complex nature of the ternary composite system. In the RGO/M@P25 film, a new broad peak appeared at 2 θ = ~25° which corresponds to the crystal plane of RGO, confirming the reduction of GO to RGO [201, 202].

Figure 5.9 XRD patterns of (i) MnO₂@PANI and (ii) RGO/M@P25 film.

Raman spectroscopy was used to confirm the reduction of GO to RGO, and the presence of interaction between MnO₂@PANI and RGO in the RGO/M@P25 hybrid film. Figure 5.10i and 5.10ii display the Raman spectra of GO and RGO films which show the peaks corresponding to D-band and G-band [197]. The I_D/I_G intensity ratio became higher when GO was transformed to RGO due to the formation of more numerous but smaller graphene networks [193, 199, 200]. This increase in I_D/I_G ratio confirms that GO has been successfully reduced by the hydrazine vapor. The Raman spectra of MnO₂@PANI and RGO/M@P25 film are shown in Figure 5.10iii and 5.10iv respectively. MnO₂@PANI shows all the characteristic peaks of MnO₂ and PANI as mentioned in the previous work (Chapter 4) [235]. The Raman spectra of RGO/M@P25 film shows peaks corresponding to the characteristic D-band and G-band graphene as well as the peaks corresponding to MnO₂@PANI, which overlap in some regions. Moreover, there is a change of peak intensities in the RGO/M@P25 film relative to that for the MnO₂@PANI composite and the RGO film, which indicates that there is an interaction between MnO₂@PANI and RGO film.

Figure 5.10 Raman spectra of (i) GO film, (ii) RGO film (iii) MnO₂@PANI and (iv) RGO/M@P25 film.

5.3.2.3 Electrochemical measurements

The electrochemical performance of the solid-state RGO/M@P25 SSC was determined from CV, CCD and EIS measurements. The CV study was carried out within the potential range of 0–1 V at various scan rates of 10, 25, 50, 75, and 100 mV s⁻¹, respectively as shown in Figure 5.11a. With the gradual increase of scan rates, current density increased, which indicate good capacitive behavior of the SSC. The CV curves deviate from rectangular shape due to the presence of the pseudocapacitive materials MnO₂ and PANI in the porous composite film. The C_{sp} of the supercapacitor cell was found to be 166 F g⁻¹ at 10 mV s⁻¹ scan rate. The excellent electrochemical performance of RGO/M@P25 hybrid film comes from the combined effect of conductive porous graphene and coaxial pseudocapacitive material MnO₂@PANI. The combination of graphene layer and MnO₂@PANI particles facilitates diffusion of ions from the electrolyte and increases the overall capacitance.

The constant current cyclic charge-discharge study of RGO/M@P25 SSC was measured within the voltage window of 0–1.0 V, at the various current densities of 1, 2 and 5 A g⁻¹, as shown in Figure 5.11b. The C_{sp} values of the RGO/M@P25 SSC at current densities of 5, 2, and 1 A g⁻¹ were found to be 80, 103, 125, and 132 F g⁻¹, respectively. The energy density was found to be 18.33 Wh kg⁻¹ at the power density

of 0.388 kW kg⁻¹. At low current densities, the increase in C_{sp} value was small. This is probably due to the slower charge-discharge of electrolyte ions. In general, the C_{sp} values follow the same trend as obtained through the CV study.

Figure 5.11 (a) CV profiles at different scan rates and (b) CCD profiles at different current densities of RGO/M@P25 SSC.

CCD studies were carried out for the RGO, RGO/M@P10, RGO/M@P25 and RGO/M@P40 hybrid films to determine which had the best performance (Figure 5.12). The RGO, RGO/M@P10, RGO/M@P25 and RGO/M@P40 SSCs were found to have C_{sp} values of 82, 104, 125 and 110 F g⁻¹ respectively. It is evident that the C_{sp} values increased when the contents of the pseudocapacitive MnO₂ and PANI materials increased. The conductive PANI layer on the MnO₂ spikes enables easy ion transport from the coaxial microurchin composite to the RGO matrix which provides good double-layer capacitance. This serves to increase the overall capacitance due to the synergistic effect from pseudocapacitive and EDL-capacitive materials. Moreover, the 3D porous graphene film provides higher surface area for ready access of electrolyte ions which ultimately increase the capacitance value.

Figure 5.12 Comparison of CCD profiles of RGO, RGO/M@P10, RGO/M@P25 and RGO/M@P40 SSCs at 1 A g⁻¹ current density.

It can be seen that the MnO₂@PANI particle here has a dual role. Firstly, it acts as a spacer between the graphene layers preventing stacking from occurring. Secondly, it contributes to the high pseudocapacitive properties of the composite. Although C_{sp} increased with increasing MnO₂@PANI content, the RGO/M@P40 sample showed a lower capacitance than the RGO/M@P25 sample which was counter intuitive. However, detailed studies of the sample morphology revealed that at the higher ratio of MnO₂@PANI, the microurchins tend to agglomerate which inhibits their even distribution in the graphene matrix. This was the reason why the gravimetric capacitance could not increase further. Thus, for the asymmetric device, the RGO/M@P25 porous film was selected as it has the highest capacitance and energy density.

5.3.3 Asymmetric hybrid supercapacitor

A flexible all-solid-state asymmetric supercapacitor (ASC) was fabricated using the GF40 aerogel as the negative electrode and the RGO/M@P25 composite film as the positive electrode. A schematic diagram of the solid-state ASC is depicted in Figure 5.13a. To determine the best working potential window, separate CV studies in three-

electrode system were first carried out for the GF40 and RGO/M@P25 electrode materials respectively, as shown Figure 5.13b. It is apparent that the best working range for negative electrode was 0 to -0.8 V, and that for the positive electrode was 0 to $+1.0$ V. Hence, the maximum potential window for the asymmetric supercapacitor cell can reach up to 1.8 V. To attain the potential window of 1.8 V, it is essential to balance the charge stored at the positive and negative electrodes. The charge was balanced following the Equation 2.17 (Chapter 2), and the mass ratio of positive to negative electrode material (m_+/m_-) was found to be 0.79 .

To determine the optimal working window of the solid-state GF40//RGO/M@P25 ASC, the CV study was carried out at the range of $0-1.0$, $0-1.2$, -1.4 , $0-1.5$ and $0-1.6$ V at 100 mV s^{-1} as shown in Figure 5.13c. It is apparent that the ASC shows a stable potential window in the range of $0-1.5$ V. Next, to determine the optimal scan rate, CV studies were conducted at scan rates from 10 to 100 mV s^{-1} within the potential range of $0-1.5$ V (see Figure 5.13d). It can be seen from Figure 5.13d that the potential window remained stable at all the scan rates. The current density was found to increase with increasing scan rate.

The charge-discharge curves (CCD) of the solid-state GF40//RGO/M@P25 ASC, within the potential range of $0-1.5$ V, at current densities of 5 , 4 , 3.5 , 3 , 2.5 , 2 , and 1.5 A g^{-1} are shown in Figure 5.13e. It was found that a high C_{sp} of 122 F g^{-1} was obtained at the current density of 1.5 A g^{-1} .

The Ragone chart, which shows the relationship between power density and energy density, was plotted for both the SSCs and ASC, as shown in Figure 5.13f. It can be seen that, at the same power density, the GF40//RGO/M@P25 ASC has higher energy density than the RGO/M@P25//RGO/M@P25 SSC and the GF40//GF40 SSC. The highest energy density was found to be 38.12 Wh kg^{-1} at a power density of 1.191 kW kg^{-1} . The ASC cell still maintained a high energy density of 28.12 Wh kg^{-1} even at a power density of 4.490 kW kg^{-1} .

Figure 5.13 (a) Schematic presentation of flexible solid-state GF40//RGO/M@P25 ASC; (b) CV curves for RGO/M@P25 and GF40 materials from the three-electrode system at 100 mV s⁻¹; (c) CV curves at different voltage windows at a scan rate of 100 mV s⁻¹, (d) CV curves at different scan rates from 10–100 mV s⁻¹ and (e) CCD curves at different current densities of GF40//RGO/M@P25 ASC; and (f) Ragone plot of RGO/M@P25 SSC and GF40//RGO/M@P25 ASC [Inset : red LED was powered by the ASC].

Electrochemical impedance spectroscopy (EIS) test was carried out in the 100 kHz to 1 Hz frequency range for all the symmetric and asymmetric supercapacitors. Figure 5.14a depicts the Nyquist plot of the GF40//GF40 and RGO/M@P25//RGO/M@P25 SSCs and the GF40//RGO/M@P25 ASC. The inset in Figure 5.14a describes a typical Nyquist plot to facilitate analysis of different parts of the curve. The equivalent series resistance (R_s) of the GF40//GF40 and RGO/M@P25//RGO/M@P25 SSCs were found to be 0.47 and 11.0 ohm respectively. In comparison, the GF40//RGO/M@P25 ASC had an R_s of 7.38 ohm. The higher R_s value for RGO/M@P25 SSC is due to the high intrinsic resistance and contact resistance of the porous substrate. The low R_s value for the GF40 aerogel is consistent with its high conductivity. The low value also indicates that there is good bonding with the Ni foam. The Warburg resistance (R_w) which is a measure of ionic diffusion of electrolyte ions towards the electrodes was determined from the $\sim 45^\circ$ slope portion of the Nyquist plot at lower-frequency region. The RGO/M@P25 SSC shows higher R_w due to the presence of pseudocapacitive MnO₂ and PANI materials. The GF40 aerogel, which exhibits EDL-capacitive behavior, has the highest slope in the lower frequency region. The slope of the ASC was in between that of the GF40 and RGO/M@P25 SSCs because the combined effect from the pure EDL-capacitive graphene aerogel, and pseudocapacitive MnO₂ and PANI materials produced lower diffusion rate than GF40 SSC.

Cyclic stability tests were carried out for both SSCs and ASC at a current density of 5 A g⁻¹ for 5000 cycles. It can be seen in Figure 5.14b that the percentage capacitance retention with respect to cycling is high for the SSCs and ASC. The GF40//GF40 SSC shows a high capacitance retention of 88.6%. The high cyclic stability of this SSC can be explained by the pure EDL-capacitive behavior of 3D porous foam, where capacitance was obtained only from the ions adsorption-desorption mechanism on the surface of porous foam. The RGO/M@P25//RGO/M@P25 SSC showed 83.9% capacitance retention, whereas, the GF40//RGO/M@P25 ASC had a capacitance retention of 85.8%. In this SSC and the ASC, degradation of the urchin-shaped MnO₂@PANI during charge-discharge cycling, is mitigated by the RGO film matrix which covers and protects the MnO₂@PANI phase. The GF40/RGO/M@P25 ASC shows stable Coulombic efficiency $\sim 98\%$ up to 5000 cycles (see Figure 5.14c). This is especially evident from

Figure 5.14 (a) Nyquist plots of GF40, RGO/M@P25 SSCs and GF40//RGO/M@P25 ASC [Inset presents schematic diagram of the Nyquist plot]; (b) Cyclic stability performance over 5000 cycles, (c) Coulombic efficiency of GF40//RGO/M@P25ASC for 5000 cycles [Inset: Figure represents the charge–discharge behavior for last 10 cycles]; (d) CV curves for ASC at different bending states [Inset optical image shows the bent sample]; (e) CCD curves of GF40//RGO/M@P25 where two and three ASC cells are connected in series [Inset: green LED was powered by the ASC]; (f) Photographs of green- and red-LED lighted up by 2 and 3 ASC cells connected in series, respectively.

the inset in Figure 5.14c which depicts the last 10 cycles of the charge-discharge pattern of the GF40/RGO/M@P25 ASC.

The ASC device could withstand bending to different angles without being physically damaged or have an impairment in electromechanical properties. This is attested by the CV profiles obtained when the ASC is held at different angles as shown in Figure 5.14d. It is evident that there is little or no deviation in the CV curves of the ASC that was physically deformed to different bending angles. This was observed even after the ASC was subjected to reversible bending between 0° and 90° for 20 times. Thus, the ASC can be utilized in a bent condition without any loss in performance. The photographs of the ASC device at different bending states are shown in Figure A3 (see in Appendix).

To validate the performance of the ASC cell in practical application, two and three ASC cells were connected in series, and were charged up to a potential window of 0–3.0 V and 0–4.5 V, respectively. The charge-discharge profiles, at 20 mA constant current, of the cells that were connected in series are shown in Figure 5.14e. The three ASC cells that were connected in series could light up the red-light-emitting diode (red-LED-1.8 V) successfully for 45 s. The photographs of two cells and three cells in series lighting up the green- and red-LEDs are shown in Figure 5.14f.

5.3.4 Comparison with other results

A comparison of the energy density, power density and cyclic stability by all-solid-state symmetric and asymmetric supercapacitors from the literature are presented in Table 5.1 and Table 5.2, respectively. Although some of the related works are already reported in Table 4.1 (Chapter 4), for the comprehension purpose, in addition to other works, few of them are reported here too. It is evident that the synthesized GF40//RGO/M@P25 ASC has higher energy density and power density with high cycle performance compared to other ASCs mentioned in literature.

Table 5.1 Comparison of electrochemical performance of solid-state symmetric supercapacitors.

Materials	Electrolyte	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Cyclic stability (% of capacitance retention)	Ref.
Graphene hydrogel film	H ₂ SO ₄ /PVA gel	0.61	0.67	91.6 (after 10000) cycles	[227]
RCF/MnO ₂ /PEDOT	PVA/KCl gel	19.17	0.500	83 (after 10000 cycles)	[236]
CNTs/bacterial nanocellulose paper	PS-PEO-PS/[EMIM][NTf ₂]	15.5	1.500	99.5 (after 5000 cycles)	[172]
PANI/CNT	H ₂ SO ₄ /PVA gel	7.1	2.2	91.9 (after 1000 cycles)	[12]
Graphene @carbon cloth	H ₂ SO ₄ /PVA gel	1.64	0.670	--	[228]
Polypyrrole nanofiber/RGO	PVA/H ₃ PO ₄ gel	20.6	1.280	79.8 (after 1000 cycles)	[237]
RGO/MnO ₂ @PANI (RGO/M@P25) film	PVA/KOH gel	18.33	0.388	83.9 (after 5000 cycles)	this work
Graphene aerogel- (GF40)	PVA/KOH gel	15.41	0.523	88.6 (after 5000 cycles)	this work

Table 5.2 Comparison of electrochemical performance of solid-state asymmetric supercapacitor.

Materials	Electrolyte	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Cyclic stability (% of capacitance retention)	Ref.
Graphene (IL-CMG)//RuO ₂ -IL-CMG	H ₂ SO ₄ /PVA gel	19.7	6.800	95 (after 2000 cycles)	[18]
N-doped graphene/layered MnO ₂ //AC	PVA/LiCl gel	31.67	0.222	90.5 (after 1500 cycles)	[238]
MnO ₂ @ poly(3,4-ethylene-dioxythiophene)//poly(3,4-ethylene-dioxythiophene)	LiClO ₄ /PMMA gel	9.8	0.850	86 (after 1250 cycles)	[101]
GNR//GNR-MnO ₂	PAAK/KCl gel	29.4	12.1	88 (after 5000 cycles)	[239]
CNTs/MnO ₂ //CNTs/ PANI	Na ₂ SO ₄ /PVP gel	24.8	0.120	--	[229]
TiN@GNS//Fe ₂ N@GNS	PVA/LiCl gel	15.4	6.4	~98 (after 20000 cycles)	[13]
GF40//RGO/M@P25	PVA/KOH gel	38.12	1.191	85.8 (after 5000 cycles)	this work

5.4 Summary

A novel all-solid-state flexible asymmetric supercapacitor (ASC) was fabricated comprising a 3D graphene based composite, whereby high energy density was achieved by enlarging the operational potential window. This novel ASC system utilizes a novel 3D porous reduced graphene oxide/MnO₂@polyaniline (RGO/MnO₂@PANI) hybrid film as the positive electrode, and self-assembled 3D pillared graphene aerogel as the negative electrode material. The ASC which uses PVA/KOH as the gel electrolyte operates in a wide potential window of 0–1.5 V. The self-assembled free-standing 3D graphene aerogel was synthesized using Pluronic copolymer as template. A special feature of the positive electrode material was presence of microurchin MnO₂@PANI particles that acted as spacers to mitigate agglomeration of the 3D RGO layers to maximize the surface area for ion transfer. The MnO₂@PANI particles also contribute to pseudocapacitive performance to the cell. The asymmetric supercapacitor has a very high energy density of 38.12 Wh kg⁻¹ at a power density of 1.191 kW kg⁻¹ and stable cycling stability with 85.8% capacitance retention after 5000 cycles. The solid-state asymmetric supercapacitor exhibits high flexibility in bending and can be deployed in various portable devices.

Chapter 6 Novel all-solid-state flexible asymmetric supercapacitor based on ternary 3D heterogeneous structures - polyaniline decorated porous MnO₂-graphene electrode and MoO₃/graphene aerogel

6.1 Introduction

In Chapter 5, MnO₂, PANI, and graphene based ternary composites as a flexible electrode material which shows high energy density. However, it is believed that the energy density of the graphene, MnO₂ and PANI based solid-state SC can be increased further by synthesizing ternary composite having the appropriate architecture. It would be beneficial if architecture of the ternary composite can be developed such that the shortcoming of each electrode material is mitigated. Moreover, the energy density can be increased by enlarging the operating voltage window via asymmetric combination of the electrode materials.

The operating potential window in an asymmetric supercapacitor (ASC) can be expanded by increasing the work function difference between the positive and negative electrode materials. This can be achieved when the negative and positive electrodes contain metal oxides with the largest work function difference to give the highest potential window.[32] Hence, a positive electrode comprising PANI/(MnO₂-RGO)/PANI can be used in conjunction with a suitable negative electrode material. MoO₃ has emerged as an alternate potential oxide material to MnO₂, because of its high activity to electrochemical reactions, low-price and environmentally friendly nature [67, 72, 240]. Among transition metal oxides, the highest work function difference was found between MoO₃ ($\psi = 6.9$ eV) and MnO₂ ($\psi = 4.4$ eV) [32]. Therefore, MoO₃ will be incorporated as a constituent material in the negative electrode in order to create the largest possible work function difference between the positive and negative electrodes. This way, higher possible operative voltage window can be obtained and the overall capacitance can be realized.

Herein, in this report, a flexible all-solid-state ASC was prepared using a unique PANI/(MnO₂-RGO)/PANI material as the positive electrode and MoO₃/GF material as the negative electrode material utilizing PVA/KOH gel electrolyte. It will be demonstrated that, using the principles outlined above, a flexible all-solid-state ASC with very high energy density can be fabricated using a facile, economic and green approach.

6.2 Experimental

6.2.1 Synthesis of sandwich-type PANI/(MnO₂-RGO)/PANI porous film

Details of the synthesis of the MnO₂ nanoparticles have been outlined in Chapter 4. In the present work, the as-prepared MnO₂ urchin-shaped particles were used to fabricate the porous RGO-MnO₂ hybrid film. At first, GO (20 mg) was dispersed in 20 mL of deionized water by ultrasonication for 20 min. Next, 5 mg (25% wt. ratio to GO) of MnO₂ particles was dispersed in GO solution by ultrasonication. After that, the MnO₂ and GO suspension was filtered through an anodisc membrane (pore diameter - 0.2 μ m) using the vacuum filtration method. The residue film was dried in a vacuum oven at 80 °C, after which it was peeled off from the membrane. Next, this MnO₂-GO film was reduced by hydrazine vapor. The film was hung in a Teflon-lined stainless steel autoclave containing 200 μ L of hydrazine monohydrate, and kept in an electric oven at 110 °C for 10 h. The reduced film (MnO₂-RGO) was then dried in air. Next, the as-prepared MnO₂-RGO film was immersed in a solution mixture made up of 20 mL deionized water to 1 mL of anionic surfactant SDBS (1mg mL⁻¹). After dipping for 6 h, 20 μ L of aniline and a few drops of HCl (1 M) were added in the container with continuous shaking. After this, 100 mg of ammonium persulfate (APS) was added. The container was kept in a shaking tray for 2 h after which it was taken out and left overnight inside the fume hood. The film was washed thoroughly with deionized water few times to remove loosely bound PANI from the film surface. Then it was dried in a vacuum oven at 70 °C for 12 h. Finally, the sandwich-type PANI/(MnO₂-RGO)/PANI film was stored for characterization. The amount of PANI in the PANI/(MnO₂-RGO)/PANI film was calculated to be 7 mg.

6.2.2 Preparation of MoO_3 /graphene aerogel

Initially, GO solution was prepared by dispersing 50 mg of GO powder in 25 mL of deionized water by ultrasonication, and then stirred with 25 mg of MoCl_3 (50% wt ratio to GO) for 30 min. Then vitamin C was added and stirred for another 20 min. Next, the whole solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was then placed in an electric oven at 150 °C for 12 h. After that, the autoclave was allowed to cool down to room temperature naturally. A 3D MoCl_3 /graphene hydrogel column was formed by the hydrothermal reaction. The hydrogel was freeze-dried and then heat-treated in a furnace at 400 °C in oxygen atmosphere. The final product (MoO_3 /GF) was collected and stored for characterization. MoCl_3 also was heat treated separately at 400 °C in an oxygen atmosphere to promote the formation of MoO_3 . Different MoO_3 /graphene aerogel composites were prepared by varying the weight ratio of MoCl_3 to GO, where the weight ratios were set at 0, 25, 50, and 100%, and the final composites were labelled as GF, MoO_3 /GF2.5, MoO_3 /GF5 and MoO_3 /GF10, respectively.

6.2.3 Fabrication of all-solid-state supercapacitor

The flexible all-solid-state PANI/(MnO_2 -RGO)/PANI symmetric supercapacitor (SSC) and the MoO_3 /GF SSC cells were fabricated following the same techniques as applied for MnO_2 @PANI/RGO film and graphene aerogel electrodes, respectively (see section 5.2.3, Chapter 5). The solid-state ASC cell was fabricated by assembling one PANI/(MnO_2 -RGO)/PANI film electrode and one MoO_3 /GF electrode following the same technique as mentioned before.

6.2.4 Characterization techniques

The electrode materials and SC devices were characterized following the same techniques and procedures as mentioned in Chapter 4 (section 4.2.5).

6.3 Results and discussion

6.3.1 MoO₃/GF composite materials

6.3.1.1 Molecular characterization

The XRD plots for the GO, GF, MoO₃ and MoO₃/GF5 materials are as shown in Figure 6.1. The MoO₃ nanoparticles show diffraction peaks at $2\theta = 12.9^\circ, 23.5^\circ, 25.8^\circ, 27.5^\circ, 33.9^\circ, 39.1^\circ, 46.2^\circ, 49.5^\circ, 53.0^\circ, 55.3^\circ, 56.5^\circ, 58.0^\circ, 59.0^\circ$ and 64.3° . The MoO₃/GF5 exhibits the diffraction peaks at $12.7^\circ, 22.9^\circ, 25.3^\circ, 26.9^\circ, 33.3^\circ, 38.6^\circ, 45.5^\circ, 48.6^\circ, 54.8^\circ, 58.5^\circ$ and 64.5° . These peaks correspond to the diffraction peaks of α -MoO₃ (JCPDS No.65-2421). The intensity of the α -MoO₃ peaks decreased in MoO₃/GF5 composite as expected. The peaks for pure GO which correspond to the interlayer d-spacing of 8.89 Å at the 10.8° region has disappeared and the new broad peak corresponding to (002) plane was observed in GF. This peak was not very apparent in MoO₃/GF5 composite since the high intensity peaks of MoO₃ overlapped in the same region. This confirms that the GO has been reduced by vitamin C during hydrothermal treatment.

Figure 6.1 XRD patterns of GO, GF, MoO₃ and MoO₃/GF5, respectively.

The Raman spectroscopy study was used to analyze the structural behavior of the MoO₃/GF composites. The Raman spectra of GO, GF, MoO₃ and MoO₃/GF5 materials are presented in Figure 6.2. GO shows peaks at 1355 and 1602 cm⁻¹

corresponding to the D-band and G-band, respectively. The GF and $\text{MoO}_3/\text{GF5}$ show similar peaks corresponding to the D-band and G-band. The I_D/I_G ratios were increased from 0.95 (for GO) to 1.11 and 1.09 for GF and $\text{MoO}_3/\text{GF5}$, respectively. This increase of intensity ratio can be explained by the reestablishment of smaller graphene domains that are more numerous in numbers after reduction [193, 199, 200]. $\text{MoO}_3/\text{GF5}$ shows additional peaks at 151, 284, 339, 661, 821 and 996 cm^{-1} which were observed very prominently in MoO_3 . The peaks appearing at $100\text{--}400\text{ cm}^{-1}$ can be attributed to the different bending modes of $\alpha\text{-MoO}_3$ crystal. The peak at 661 cm^{-1} is due to asymmetric stretching vibration of the O-Mo-O bonds. Moreover, the peaks at 821 and 996 cm^{-1} can be ascribed to the symmetrical and asymmetrical stretching vibration of the terminal Mo-O bonds. However, the peak intensities values were lower than that for the pure MoO_3 . These confirm that MoCl_3/GF has fully converted into MoO_3/GF composite after heat treatment.

Figure 6.2 Raman spectra of GO, GF, MoO_3 and $\text{MoO}_3/\text{GF5}$, respectively (inset shows magnified Raman spectra of GO, GF, and $\text{MoO}_3/\text{GF5}$).

To further confirm the formation of MoO_3 , FTIR study was carried out for the GF, MoO_3 and $\text{MoO}_3/\text{GF5}$ materials and the data can be seen in Figure 6.3. In $\text{MoO}_3/\text{GF5}$, the peaks at 996 and 840 cm^{-1} can be attributed to the stretching vibration of Mo-O and Mo-O-Mo which are seen in pristine MoO_3 . This confirmed the

presence of MoO_3 in the hybrid material. Hence, these results indicate that there is complete formation of MoCl_3 to MoO_3 after the heat treatment.

Figure 6.3 FTIR of GF, MoO_3 and $\text{MoO}_3/\text{GF5}$ materials.

The elemental analysis of the GF and $\text{MoO}_3/\text{GF5}$ hybrid materials was carried out using XPS. The wide scan spectrum of $\text{MoO}_3/\text{GF5}$ reveal the presence of C, Mo and O elements only, and no peak corresponding to Cl was found (Figure 6.4a). This confirms again that MoCl_3 has been converted fully to MoO_3 . The Mo 3d scan is shown in Figure 6.4b which shows two broad peaks for Mo $3d_{5/2}$ and Mo $3d_{3/2}$ at 233.5 and 236.7 eV, respectively corresponding to Mo (VI) of MoO_3 . The C 1s peaks of GO and $\text{MoO}_3/\text{GF5}$ composite were compared by deconvoluting each spectrum which can be seen from Figure 6.4c and 6.4d, respectively. The deconvolution of the C1s peak of $\text{MoO}_3/\text{GF5}$ shows the peaks at 285.2, 286.1, and 289.5 eV corresponding to the non-oxygenated carbon (C-C), ether groups (C-O), and carboxylate carbon (O-C=O). Their peak intensities confirm the reduction of GO by vitamin C during hydrothermal treatment.

Figure 6.4 (a) XPS survey spectra; (b) deconvolution of Mo 3d; (c) deconvolution of C 1s spectra of GO and (d) deconvolution of C 1s spectra of MoO₃/GF5 composite.

6.3.1.2 Morphological analysis

Figure 6.5a illustrates the hydrothermal transformation of MoCl₃/GO suspension into a 3D free standing hydrogel column of MoCl₃/GF. Figure 6.5b, Figure 6.5d, Figure 6.5e and Figure 6.5f display the FESEM images of pristine MoO₃, MoO₃/GF2.5, MoO₃/GF5 and MoO₃/GF10 composites respectively. The length of the MoO₃ rectangular nanocrystals was found to be ~1–1.5 μm and the thickness was 90–100 nm. In the MoO₃/GF5 composite, it is apparent that there is an even distribution of MoO₃ crystals that are anchored on the surface of graphene sheet. The TEM image of MoO₃/GF5 in Figure 6.5c affirmed the attachment and anchoring of the MoO₃ crystals on the graphene sheet. The even distribution of MoO₃ in the MoO₃/GF5 composite enables fast electron transport between the graphene sheets and MoO₃ crystals to improve electrochemical performance. With increasing MoO₃ content, crystal

agglomeration occurred in the GF matrix as observed in Figure 6.5f. It was found that the agglomeration of MoO₃ crystals decrease the porosity and the specific surface area of the composite. The nitrogen adsorption–desorption isotherms of GF, MoO₃/GF5 and MoO₃/GF10 are shown in Figure 6.6. The BET specific surface areas of GF, MoO₃/GF5 and MoO₃/GF10 (calculated using BET equation) were found to be 295, 227 and 104 m² g⁻¹, respectively.

Figure 6.5 (a) Transformation of (MoCl₃/GO) mixture to MoCl₃/GF hydrogel column; (b) FESEM images of pristine MoO₃, (c) TEM image of MoO₃/GF5 composite; FESEM images of (d) MoO₃/GF2.5, (e) MoO₃/GF5 and (f) MoO₃/GF10 composites, respectively.

Figure 6.6 The N₂ adsorption–desorption isotherm loop of GF, MoO₃/GF5 and MoO₃/GF10 materials.

The formation of the MoO₃/GF5 aerogel can be explained as follows. Initially, a 3D free-standing hydrogel column of MoCl₃/GF5 was formed by H-bonding of adsorbed water molecules. The GO sheets are decorated with O containing epoxy, and carbonyl and carboxyl groups which can act as anchoring sites to bind MoCl₃ nanoparticles. Mo ([Kr] 4d⁵ 5s¹) has a vacant 4d orbital. Hence, it is possible for coordination bond formation between MoCl₃ and the O containing functional groups of GO during hydrothermal treatment as shown in Figure 6.7a. During heat treatment of MoCl₃/GF in O₂ atmosphere, MoCl₃ would be converted into MoO₃ and Cl₂. The reaction can be written as follows [241]:

A schematic diagram for the distribution of MoO₃ nanocrystals in graphene matrix is shown in Figure 6.7b. In MoO₃/GF5 composite, the Mo atom of the MoO₃ may bind adjacent graphene sheets together via intermolecular H-bonds or covalent or coordination bonds.

Figure 6.7 (a) Schematic illustration of coordination bond formation between MoCl₃ and GO sheet in MoCl₃/GF hydrogel and (b) distribution of MoO₃ nanocrystals in graphene matrix of MoO₃/GF5 composite.

The weight loss due to the conversion of MoCl₃ to MoO₃ is as shown in the TGA curve in Figure 6.8. Initially, ~4% wt loss occurred at ~100 °C due to

elimination of the adsorbed water. At around 227 °C, ~40% wt loss occurred due to the conversion of MoCl₃ into MoO₃.

Figure 6.8 TGA analysis of MoCl₃ in O₂ atmosphere.

6.3.1.3 Electrochemical analysis and performance

The cyclic voltammetry (CV) plots of the MoO₃/GF5 based solid-state symmetric supercapacitor (SSC) are as shown in Figure 6.9a. The CV analysis was conducted within the 0–1.0 V potential window using scan rates from 5 to 500 mV s⁻¹. It can be seen that the current density increases with increasing scan rates in a symmetric manner, and that the CV plots deviates from the standard rectangular shape due to the presence of pseudocapacitive MoO₃ nanocrystals.

The CCD study was carried out under different current densities of 5, 4, 3, 2 and 1 A g⁻¹ and the curves are as shown in Figure 6.9b. The charge–discharge profiles are symmetric in nature justifying the results obtained in the CV study. It is noted that the discharge curve deviates from a straight line indicating the existence of pseudocapacitive properties that are likely to be due to the anchoring MoO₃ nanocrystals on the graphene sheets. The charging and discharging time increased with decreasing current densities, which is consistent with the fact that the electrochemical phenomena is operationally more effective at low current. The C_{sp} and energy density of the MoO₃/GF SSC were calculated utilizing data from the discharge curve using Equation 2.12 and 2.14. The C_{sp} of MoO₃/GF5 SSC were found

to be 136, 125, 111 and 104 F g⁻¹ at current densities of 1, 2, 4 and 5 A g⁻¹, respectively. The energy density was found to be 18.8 Wh kg⁻¹ at the power density of 0.519 kW kg⁻¹. The obtained energy density was higher than that for pure GF. This increase of energy density can be attributed to the presence of electroactive MoO₃ particles which undergo in reversible redox reaction. Here, the graphene sheets are intertwined and innately attached with MoO₃ nanocrystals serving a dual role. Firstly, it provides conductive network channels and secondly, its large active surface area contributes to EDL capacitance. The MoO₃ nanocrystals shorten the diffusion path of the electrolyte ions and transports electrons continuously in-between graphene sheets. Moreover, the MoO₃ acts as a p-type dopant with graphene which can enhance the charge carrier mobility [242] and eventually increase the capacitance value.

The CCD plots for the pure GF and the MoO₃/GF composite samples (MoO₃/GF2.5, MoO₃/GF5 and MoO₃/GF10) are shown in Figure 6.9c. It was found that the MoO₃/GF2.5 sample that contained MoO₃ nanocrystals had higher capacitance (96 F g⁻¹ at 1 A g⁻¹) than the GF (80 F g⁻¹ at 1 A g⁻¹) sample. The MoO₃/GF5 sample which had higher MoO₃ content and had a uniform distribution of MoO₃ nanocrystals in the matrix had the highest capacitance (136 F g⁻¹ at 1 A g⁻¹). The MoO₃/GF10 composite which exhibited agglomeration of MoO₃ nanocrystals, shows a lower capacitance value about 105 F g⁻¹ (at 1 A g⁻¹) than the MoO₃/GF5 composite. This revealed that the agglomeration of MoO₃ nanocrystals at a higher weight ratio hindered ion transfer between the graphene sheets. Hence, the MoO₃/GF5 composite was selected for further study in ASC.

Electrochemical impedance spectroscopy (EIS) study was carried out for MoO₃/GF5 SSC and GF SSC in the frequency range of 100 kHz to 1 Hz. The Nyquist plots of the GF and MoO₃/GF5 based SSCs are shown in Figure 6.9d. In the high frequency region, the intercept on Z_{real} axis represents the combined resistance (R_s) which are found to be 0.46 and 0.34 ohm for the GF and MoO₃/GF5 SSCs. The lower resistance in the latter is probably due to doping of MoO₃ onto graphene which served to decrease the internal resistance and contact resistance at the interface of active material-current collector as compared to GF. The Warburg resistance (R_w) which is a measure of ionic diffusion/transport from the electrolyte to the surface of the electrode [41] is obtained from the straight line at lower frequency region. The GF

SSC exhibits a steeper straight line than the MoO_3 /GF5 SSC because of pure EDL-type charge transfer process is faster in the GF electrode.

Figure 6.9 (a) CV plots at different scan rates and (b) CCD at different current densities of MoO_3 /GF5 SSC; (c) comparison CCD plots of MoO_3 /GF2.5, MoO_3 /GF5 and MoO_3 /GF10 SSCs at 1 A g^{-1} current density, (d) EIS of GF SSC and MoO_3 /GF5 SSC and (e) cyclic stability of MoO_3 /GF5 SSC.

The MoO₃/GF5 SSC showed high cyclic stability with ~85% capacitance retention after 5000 cycles as seen in Figure 6.9e. The good cyclic life of MoO₃/GF can be attributed to the uniform distribution of MoO₃ nanocrystals in graphene aerogel matrix, which covers the MoO₃ and prevent the degradation during charge-discharge cycling. The graphene coating here acts as a protective layer to prevent faster dissolution of the MoO₃ during the cycling process.

6.3.2 PANI/(MnO₂-RGO)/PANI hybrid film

6.3.2.1 Molecular characterization

The sandwich-type PANI/(MnO₂-RGO)/PANI hybrid film which was labeled as P/(M-R)/P film was prepared in three steps. Firstly, MnO₂ nanoparticle was synthesized through hydrothermal reaction. Secondly, porous MnO₂-RGO film was fabricated by vacuum filtration of MnO₂ and GO suspension followed by reduction with hydrazine vapor. Finally, PANI nanofibers were grown on the surface of the MnO₂-RGO porous film.

The XRD diffraction patterns of the MnO₂ nanoparticles, MnO₂-RGO and P/(M-R)/P films are shown in Figure 6.10. The MnO₂ shows diffraction peaks at $2\theta = 12.7^\circ, 18.1^\circ, 28.8^\circ, 37.5^\circ, 42.1^\circ, 49.9^\circ, 56.7^\circ, 60.3^\circ, 65.1^\circ,$ and 69.3° corresponding to the (110), (200), (310), (211), (301), (411), (600), (521), (002) and (741) crystal planes which are well matched with the of α -MnO₂ standard data (JCPDS card PDF file no. 44-0141) [205], respectively. The MnO₂-RGO composite shows similar diffraction peaks at $2\theta = 12.8^\circ, 18.2^\circ, 28.9^\circ, 37.6^\circ, 42.2^\circ, 49.9^\circ, 56.8^\circ,$ and 60.3° corresponding to the crystal plane of α -MnO₂. However, the peak intensities were lower in the latter. In the MnO₂-RGO composite, the peak located at 10.8° for GO (001) crystal plane corresponding to the d-spacing of 0.321 Å disappeared. A new broad peak appeared corresponding to the crystal plane of RGO at $\sim 26^\circ$, which was not so obvious as the MnO₂ peaks intensity were very high. The sandwich-type P/(M-R)/P film shows a broad peak at $\sim 22^\circ$ corresponding to the crystalline structure of PANI. As the surface of the P/(M-R)/P film was fully covered with PANI, the peaks corresponding to MnO₂ particles and RGO did not appear.

Figure 6.10 XRD patterns of GO, MnO₂, MnO₂-RGO and P/(M-R)/P materials.

Raman spectroscopy was carried out to confirm the presence of PANI, MnO₂ and RGO in the P/(M-R)/P film. Figure 6.11 displays the Raman spectra of MnO₂-GO, MnO₂-RGO and P/(M-R)/P films. The MnO₂-GO shows the peak at 639 cm⁻¹ corresponding to the Mn-O symmetric stretching vibration of the MnO₆ octahedral [209]. The peaks at 1350 and 1585 cm⁻¹ correspond to the characteristic D-band and G-band, respectively. The MnO₂-RGO also shows similar peaks at the same region as in the MnO₂-GO except that the I_D/I_G intensity increased from 0.94 to 1.04 due to reestablishment of more numerous graphene domains upon reduction of GO [193, 199, 200]. The P/(M-R)/P film shows peaks at 1577, 1489, 1366, 1255 and 1175 cm⁻¹ corresponding to the C=C stretching of the quinoid ring, C=N stretching of emeraldine base, C-N⁺ stretching mode of delocalized polaronic charge carriers of protonated imine form, and C-N stretching and C-H bending vibrations of the quinoid ring, respectively. The bands at 820, 531 and 416 cm⁻¹ correspond to the bipolaronic quinoid ring, bipolaronic amine deformations and polaronic C-N-C torsion, respectively. These bands are well matched with the characteristic peaks of the pure polyaniline [235]. Hence, the Raman spectroscopy results confirmed the formation of the PANI network on the surface of the MnO₂-RGO film.

Figure 6.11 Raman spectra of MnO₂-GO, MnO₂-RGO and P/(M-R)/P materials.

6.3.2.2 Morphological analysis

The morphology of MnO₂ nanoparticles are outlined in detail in Chapter 4. Figure 6.12a illustrates the cross-sectional side view FESEM image of the MnO₂-GO film which had been converted into the 3D porous MnO₂-RGO film (Figure 6.12b), where approximately ~3.5 times exfoliation was observed. Figure 6.12c and 6.12d illustrate the higher magnified images of Figure 6.12b, which revealed that the MnO₂-RGO film had been exfoliated by the MnO₂ nanoparticles and the entrapped gaseous species. From Figure 6.12c, it is clear that the MnO₂ nanoparticles are fairly uniformly distributed in the RGO matrix. The magnified image in Figure 6.12d displays the RGO sheet exfoliation through the creation of channels in the micrometer range. The top surface of the P/(M-R)/P film is shown in Figure 6.12e, which shows the wavy film decorated with PANI. The magnified image in Figure 6.12f shows that the numerous PANI nanofibers created a conductive pathway. The porous channels allow easy access by electrolyte ions. The fiber nature of the PANI was confirmed from the TEM image as shown in Figure 6.12g. The P/(M-R)/P film shows remarkable flexibility upon bending and folding as can be seen from Figure 6.12h.

Figure 6.12 Cross-sectional side-view FESEM images of (a) MnO₂-GO film and (b) MnO₂-RGO film; (c) magnified FESEM image of inside layer of MnO₂-RGO film, (d) magnified side view of MnO₂-RGO film, (e) top view FESEM image of P/(M-R)/P film at low magnification (inset: normal photograph of P/(M-R)/P film), and (f) magnified top view FESEM images of P/(M-R)/P film; (g) TEM image of PANI, and (h) normal photograph of P/(M-R)/P film in bending state.

To depict the formation of the hybrid film, schematic illustrations for the synthesis steps of the P/(M-R)/P hybrid film are shown in Figure 6.13. In a MnO₂-GO film, the oxygen containing functional groups of GO assist the MnO₂ nanoparticles to anchor with the GO sheets. The vacant 3d orbital of Mn in MnO₂ may form coordination bonds with O of the GO functional groups. Similarly, H-bonds may also be formed between O of MnO₂ and H of GO functional groups. The formation of these coordination and H-bonds enable the even distribution and anchoring of MnO₂ in the GO matrix. The 3D porous MnO₂-RGO film which was formed by the reduction of MnO₂-GO film was formed, not only by exfoliation due to the MnO₂ nanoparticles, but also by the released gaseous species (CO₂ (g) and H₂O (g)) during reduction by hydrazine vapor. As the obtained MnO₂-RGO film was hydrophobic in nature, it was dipped in SDBS solution for 6 h. The hydrophobic dodecyl part of SDBS facilitates interaction with the hydrophobic RGO surface and the anionic benzenesulfonate faces toward the water molecules. When aniline monomers and HCl were added in the medium, anilinium ions are formed. These

anilinium ions interact with the anionic part of the surfactant and rest on the surface of RGO. Next, the anilinium ions were polymerized by APS, and as a result, PANI nanofibers were formed on top of the MnO₂-RGO hybrid film. The highly exfoliated conductive PANI wrapping will facilitate easy ion diffusion and faster charge transfer, thus leading to high capacitance.

Figure 6.13 Schematic illustration for synthesis steps of sandwich-type PANI/(MnO₂-RGO)/PANI film.

6.3.2.3 Electrochemical measurements

The CV plots of the P/(M-R)/P film based SSC are as shown in Figure 6.14a. The CV study was carried out in a 0–1.0 V voltage window at different scan rates of 5, 10, 25, 50, 75, 100 and 200 mV s⁻¹. It can be observed that current density increased with increasing scan rates showing good capacitance behavior. The CV plots deviate from the regular rectangular shape due to the influence of pseudocapacitive PANI material on top of the MnO₂-RGO film.

The CCD studies were carried out at 0–1.0 V in different current densities of 1, 2, and 5 A g⁻¹ as shown in Figure 6.14b. The C_{sp} of the SSC cell was found to be

148, 117 and 109 F g⁻¹, respectively. The C_{sp} at low current density was higher because the slower charge-discharge rate enables the ions to have longer dwell time on the electrodes. The energy density was found to be 20.5 Wh kg⁻¹ at the power density of 0.521 kW kg⁻¹. The high energy density can be attributed to the porous nature of the sandwich film whereby the pseudocapacitive PANI at the top layer of MnO₂-RGO porous film assists to increase the capacitive value. Moreover, the porous film allowed the electrolyte ions to penetrate into the inside layers to access more surface area. MnO₂ here has a dual role. Firstly, it acts as a spacer between graphene sheets to prevent them from stacking. Secondly, it confers high pseudocapacitive properties to the composite material. The conductive skeleton enables easy and fast ions transfer. The porous RGO film not only served as an effective 3D anchoring site but also provided good double-layer capacitance. These led to an increase in the C_{sp} value.

The Nyquist plots of the RGO and P/(M-R)/P film based SSCs are shown in Figure 6.14c. The combined series resistance (R_s) of the RGO film and P/(M-R)/P film SSCs were found to be 0.34 and 7.58 ohm respectively. The higher R_s value of P/(M-R)/P film SSC is probably due to the higher internal resistance of the active material and higher contact resistance at the interface of active material/current collector as compared to pure RGO film. The P/(M-R)/P film SSC shows higher Warburg resistance (R_w) as indicated by the ~45° slope portion of the curve in the lower frequency region [41]. The RGO film SSC exhibits a steeper straight line than the P/(M-R)/P film SSC due to its pure EDL type behavior where faster diffusion of charge happens. The presence of pseudocapacitive materials (MnO₂ and PANI) increases the diffusion times for P/(M-R)/P film SSC.

Cyclic stability testing was carried out at 5 A g⁻¹ current density for 5000 cycles for the P/(M-R)/P film SSC. The capacitance retention was ~78% after 5000 cycles as shown in Figure 6.14d. The lower capacitance retention of P/(M-R)/P film SSC is due to the relatively faster degradation of the PANI wrapping on the MnO₂-RGO film.

Figure 6.14 CV studies at different scan rates, (b) CCD plots at different current densities of P/(M-R)/P SSC, (c) EIS comparison of RGO film SSC and P/(M-R)/P film SSC and (d) cyclic stability curve of P/(M-R)/P film SSC.

6.3.3 Asymmetric hybrid supercapacitor

A schematic diagram of the all-solid-state flexible ASC is presented in Figure 6.15a, where the ASC is fabricated with the $\text{MoO}_3/\text{GF5}$ material as the negative electrode and the P/(M-R)/P hybrid film material as the positive electrode utilizing PVA/KOH as the gel electrolyte. The best potential window of the each of the positive and negative electrode materials was initially determined from CV studies as shown in Figure 6.15b using the three-electrode test method. The stable potential windows of the negative and positive electrodes were found to be in the range from 0 to -0.9 V and 0 to $+1.0 \text{ V}$, respectively. This indicated that the ASC could be operated in the expanded potential range of 0 to 1.9 V . Now, to obtain $0-1.9 \text{ V}$ potential, it is necessary to balance the charge stored in the positive and negative electrodes. The

charge was balanced following the Equation 2.17 (Chapter 2), and the mass ratio of positive to negative electrode material (m_+/m_-) was found to be 0.88.

To determine the most effective operational working window of the solid-state MoO₃/GF5//P/(M-R)/P ASC, CV studies were carried out in different potential ranges of 0–1.0, 0–1.2, 0–1.4, 0–1.6 and 0–1.7 V at a scan rate of 100 mV s⁻¹ (see Figure 6.15c). It can be seen that the ASC has a stable potential window of 0–1.6 V. This is in agreement with the CCD results in Figure 6.15d. The CCD tests were carried out within the potential windows of 0–1.0, 0–1.2, 0–1.4, 0–1.6, 0–1.7 and 1–1.8 V at a constant current density of 5 A g⁻¹. It is obvious from the Figure 6.15d that the CCD curves are symmetric in nature when the potential window was expanded up to 1.6 V. Hence, the stable operating potential window for the ASC can be considered as 0–1.6 V

The CV plots at different scan rates from 5 to 500 mV s⁻¹ in the potential range of 0–1.6 V are as shown in Figure 6.15e. It can be seen from the CV plots that the current density increases with increasing the scan rates keeping its consistent shape. This indicates that the ASC has very good rate capability towards electrochemical performance.

The CCD tests were conducted utilizing the same potential window of 0–1.6 V. The CCD curves at the current densities of 1, 2, 3, 4, 5, 8 and 10 A g⁻¹ are shown in Figure 6.15f. The charge and discharge profiles are symmetrical in nature indicating good *I*–*V* characteristics and high rate capability. The non-linear charge-discharge curve is due to the presence of the pseudocapacitive materials in the positive and negative electrodes. The C_{sp} values of the ASC at 5, 3, 2 and 1 A g⁻¹ are found to be 107, 118, 123 and 146 F g⁻¹, respectively.

The Ragone chart which relates the power density with the energy density for the P/(M-R)/P SSC and MoO₃/GF5//P/(M-R)/P ASC are shown in Figure 6.16a. The ASC shows a high energy density of 51.91 Wh kg⁻¹ at a power density of 0.838 kW kg⁻¹. The ASC retains its high capacitive performance even at a higher power density, whereby an energy density of 38.15 Wh kg⁻¹ was found at the power density of 4.368 kW kg⁻¹.

Figure 6.15 (a) Schematic presentation of the flexible solid-state ASC, (b) three-electrode measurement of $\text{MoO}_3/\text{GF25}$ and P/(M-R)/P electrode materials, (c) CV study with increasing potential windows from 0–1.0 to 0–1.7 V at the scan rate 100 mV s^{-1} , (d) CCD study with increasing potential window from 0–1.0 to 0–1.8 V at 5 A g^{-1} current density, (e) CV study at different scan rates of 5 – 200 mV s^{-1} , and (f) CCD study at different current densities of $\text{MoO}_3/\text{GF5}/\text{P}/(\text{M-R})/\text{P}$ ASC.

Cyclic stability testing for the ASC was carried out at a current density of 5 A g^{-1} for 5000 cycles and the results are shown in Figure 6.16b. The ASC had 82% capacitance retention after 5000 cycles, whereas it was found that $\text{MoO}_3/\text{GF5}$ SSC and $\text{P}/(\text{M}-\text{R})/\text{P}$ film SSC had ~ 85 and $\sim 78\%$ capacitance retention after 5000 cycles (Figure 6.9e and 6.14d). It is apparent that the capacitance retention of the ASC followed the trend as expected from the positive and negative electrode materials. This is especially evident from the inset in Figure 6.16b which depicts the last 10 cycles of the charge-discharge pattern of the ASC.

Figure 6.16 (a) Ragone plots of $\text{P}/(\text{M}-\text{R})/\text{P}$ film SSC and $\text{MoO}_3/\text{GF5}/\text{P}/(\text{M}-\text{R})/\text{P}$ ASC, (b) cyclic stability, Inset: CCD plots of last 10 cycles of the ASC, (c) CV performances at different bending angles, and (d) CCD study of series connected 2 cells and 3 cells, Inset: green-LED light up by series connected 3 cells.

The above ASC device could retain its electrochemical performance and was not damaged even after it was bent repeatedly by 90° for 20 times. To demonstrate this, CV tests were carried out at different bending angles of 0° , 90° , 120° , 150° , and 20 times cyclic bending at 90° . It can be seen from Figure 6.16c that the electrochemical performance remained the same. This indicates that the ACS device can be used even if it is bent.

The performance of the asymmetric supercapacitor was validated by utilizing it to light up a 1.8 V green-light-emitting diode (green-LED). The charge-discharge profiles of the two and three series connected ASC cells are shown in Figure 6.16d. It can be seen from the Figure 6.16d that the two cells and three cells that were connected in series can run in a potential window of 0–3.2 V and 0–4.8 V, respectively. The three ASC cells connected in series can light up the green-LED for 62 s as demonstrated in the inset of Figure 6.16d.

6.3.4 Comparison with other results

A comparison of the energy density, power density and cyclic stability performances of the present ASC with all-solid-state ASCs from published work is presented in Table 6.1. It is obvious that the fabricated flexible solid-state $\text{MoO}_3/\text{GF5}/\text{P}/(\text{M-R})/\text{P}$ ASC shows the highest performance and can be used in high performance application.

Table 6.1 A comparison of the energy density, power density and cyclic stability performances of ASC.

Materials	Electrolyte	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Cyclic stability (% of capacitance retention)	Ref.
MnO ₂ @ poly(3,4-ethylene-dioxythiophene)// poly(3,4-ethylene-dioxythiophene)	LiClO ₄ /PMMA gel	9.8	0.850	86 (after 1250 cycles)	[101]
TiN@GNS// Fe ₂ N@GNS	PVA/LiCl gel	15.4	6.4	~98 (after 20000 cycles)	[13]
Graphene (IL-CMG)// RuO ₂ –IL-CMG ASCs	H ₂ SO ₄ /PVA gel	19.7	6.800	95 (after 2000 cycles)	[18]
CNTs/MnO ₂ // CNTs/ PANI	Na ₂ SO ₄ /PVP gel	24.8	0.120	--	[229]
GNR//GNR–MnO ₂	PAAK/KCl gel	29.4	12.1	88 (after 5000 cycles)	[239]
N-doped graphene/layered MnO ₂ //AC	PVA/LiCl gel	31.67	0.222	90.5 (after 1500 cycles)	[238]
MoO ₃ /GF5// P/(M–R)/P	PVA/KOH gel	51.91	0.838	82 (after 5000 cycles)	this work

6.4 Summary

An ASC with very high energy density was achieved by extending the working potential range to 0–1.6 V through the use of MnO₂ and MoO₃ in the positive and negative electrodes respectively, and adopting a 3D heterogeneous composite based

on PANI and graphene. Facile methods were used to synthesize the negative and positive electrode materials. The negative electrode comprised a self-assembled 3D MoO₃/graphene hydrogel foam. The positive electrode consisted of a PANI decorated porous 3D MnO₂-RGO composite film which had a sandwich-like structure. The all-solid-state asymmetric supercapacitor was flexible, operated optimally in a wide working potential range of 0–1.6 V and had high cyclic life. The asymmetric supercapacitor had a remarkably high energy density of 51.91 Wh kg⁻¹ at a power density of 0.838 kW kg⁻¹. The asymmetric capacitor showed high stable cycling performance with ~82% capacitance retention even after 5000 cycles. The above asymmetric supercapacitor is very promising in energy storage application for flexible device due to its high energy density, cyclic stability and eco-friendly nature.

Chapter 7 Conclusions and suggestions for future work

From the current research works, it should be noted that the ternary-based composite material comprising MnO_2 , PANI and graphene showed higher capacitance than the binary MnO_2 -PANI composite material. Moreover, the energy density of the ternary composite could be increased further by integrating MnO_2 , graphene and PANI in more effective way in the 3D morphology, as shown in Chapter 6. The soft-template based graphene foam that was developed showed higher energy density due to significant increase in available surface area that was accessible. The incorporation of redox active MoO_3 nanocrystals into the graphene foam served to increase the energy density of the SSC. Furthermore, the ASC showed higher performance when the operating potential window was widened through the use of two different transition metal oxides, namely: MnO_2 and MoO_3 in the positive and negative electrode materials.

7.1 Conclusions

3D graphene, MnO_2 , and PANI based electrode materials were synthesized to fabricate the flexible solid-state symmetric supercapacitors (SSCs) and asymmetric supercapacitors (ASCs). From the study, the following conclusions can be drawn:

1. The MnO_2 @PANI coaxial microurchin was developed without using any external oxidant, and optimized the PANI thickness on the nascent MnO_2 microurchin surface. The synthesis process utilized for the MnO_2 @PANI microurchin is new in the field of MnO_2 -PANI binary composites. The PANI coating effectively enriches the conductivity of the composites, and speeds up the diffusion of electrons and ions. This enabled the fabrication of flexible solid-state ASC utilizing MnO_2 @PANI microurchin and graphene foam (GF) as the positive and the negative electrode materials, respectively, which has been studied for the 1st time through this research work. The solid-state ASC of MnO_2 @PANI//GF is

- advantageous in respect to its high energy density, facile fabrication process, inexpensive, and environmentally friendly nature.
2. The development of the flexible 3D porous graphene hybrid film by incorporating MnO_2 @PANI microrouchins as the spacers in-between the graphene sheets, followed by hydrothermal reduction in the presence of hydrazine vapor, is a new approach to synthesize and fabricate the 3D graphene/ MnO_2 @PANI hybrid film. The solid-state SSC of 3D graphene/ MnO_2 @PANI hybrid film is new in the field of SSCs and it showed high electrochemical performance. The weight percentage of microrouchin spacers in the graphene film was found to have a significant influence on the electrochemical performance of the SSC.
 3. A 3D graphene aerogel was synthesized using amphiphilic block copolymer as a soft-template. This is a facile, inexpensive, and novel way to develop 3D graphene aerogel with high surface area. The volume percentage of the soft-template utilized had an impact on the surface area and pore size distribution of the graphene aerogel. The graphene aerogel which had highest surface area exhibited the highest energy density
 4. The fabrication of the flexible solid-state ASC cell using flexible 3D graphene/ MnO_2 @PANI hybrid film and 3D graphene aerogel is new in the field of solid-state ASC. The ASC device exhibited high energy density showing high flexibility in the bent state making it suitable for usage in various portable devices.
 5. A 3D MoO_3 /graphene composite foam was developed using a new facile method through hydrothermal reaction, followed by the use of combustion techniques. The amount of MoO_3 nanocrystals in the graphene aerogel matrix was found to have a significant influence on the electrochemical performances of the MoO_3 /GF SSC. The solid-state MoO_3 /GF SSC provided higher energy density than the graphene aerogel based SSC due to the presence of electroactive MoO_3 nanoparticles.
 6. A new novel flexible sandwich-type ternary composite (PANI/(MnO_2 -RGO)/PANI) film was synthesized, in which, conductive PANI layer were decorated on the top of graphene film, and MnO_2 nanoparticles were placed in-between the graphene sheets to prevent restacking and agglomeration of the graphene sheets. The solid-state SSC of the PANI/(MnO_2 -RGO)/PANI film showed high electrochemical performance.

7. A flexible solid-state ASC device was fabricated using the PANI/(MnO₂-RGO)/PANI hybrid film as the positive electrode and MoO₃/GF as the negative electrode. This is a new type of ASC device which can operate in a wider potential window, due to the usage of two promising transition metal oxides, MnO₂ and MoO₃, which had a large work function difference. The two transition metals were utilized in the positive and negative electrodes, respectively. The ASC device is very promising in flexible energy storage application as it has high energy density and cyclic stability.

A comparison of energy density, power density, and cyclic stability of the flexible solid-state ASCs utilizing PVA/KOH electrolyte are shown in table 7.1.

Table 7.1 Comparison of electrochemical performances of the fabricated ASC devices

Materials	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Cyclic stability (% of capacitance retention)
GF//MnO ₂ @PANI	37.0	0.386	88.6 (after 5000 cycles)
GF40//RGO/MnO ₂ @PANI25	38.12	1.191	85.8 (after 5000 cycles)
MoO ₃ /GF5//PANI/(MnO ₂ -RGO)/PANI	51.91	0.838	82 (after 5000 cycles)

From the summary, it can be concluded that an increment of energy density was obtained by tailoring the structure of MnO₂, PANI and RGO. The energy density of the ternary composite based materials can be increased by resolving individual materials limitations and obtaining a porous 3D structure. To attain high performance hybrid asymmetric supercapacitor, it is recommended to construct a hybrid nanostructure by optimizing the mass ratio of individual electrode materials accomplishing their shortcoming. An optimum mass ratio of MnO₂, RGO and PANI in PANI/(MnO₂-RGO)/PANI sandwich film was found to be 1:3:1.4, which gives a

high energy density value when in combined with GF/MoO₃ hybrid electrode material which acts as a contrary electrode material of the ASC. However, the cyclic stability of the MoO₃/GF5//PANI/(MnO₂-RGO)/PANI ASC is lower than that of the GF40//RGO/MnO₂@PANI25 or GF//MnO₂@PANI ASC. The drop of cyclic stability in PANI/(MnO₂-RGO)/PANI ASC is due to the pendent PANI nanofibers on top of (MnO₂-RGO) layer, which undergoes mechanical deformation during charge-discharge cycles. The percent of capacitance retention in the GF40//RGO/MnO₂@PANI25 and GF//MnO₂@PANI hybrid materials, do not have much difference as both contains MnO₂@PANI core-shell composite, in which MnO₂ backbone helps to prevent PANI degradation. Henceforth, where very high energy density is the primary requirement, MoO₃/GF5//PANI/(MnO₂-RGO)/PANI ASC can be used in practical application.

7.2 Suggestions for future work

The energy storage device should be flexible enough for easy use in flexible electronic devices. To achieve high flexibility and high electrochemical performance it is essential to have a very thin and flexible current collector, very thin electrode materials and very thin layer of solid state electrolyte which should be well intact to each other. The mechanical strength and flexibility of the synthesized ASC device will be evaluated in our future study. It is also necessary to evaluate how many bending cycles the ASC can tolerate. Moreover, it is essential to check whether there is any separation between the sandwich layers of current collector/electrode materials/gel electrolyte during cyclic bending test and how these will effect on the electrochemical performance. These will be carried out in future study.

It is recommended that a proton donor gel polymer electrolyte such as PVA/H₃PO₄ gel be studied using the as-synthesized graphene-MnO₂-PANI based electrode materials. This is because such an electrolyte would lead to the presence of H⁺ doped PANI which is more conductive nature. Consequently, the electrochemical performance could be enhanced. Moreover, as Ni foam is corrosive in an acid medium, studies could be carried out using conductive carbon cloth as the electrode and current collector.

Carbon cloth is very flexible and can be easily used with wearable garments. Hence, future work can include *in situ* growth of nanomaterials on carbon cloths to reduce the contact resistance between the electrode and the nanomaterials.

Further studies could focus on binary transition metal oxides that have multiple oxidation states as such oxides can potentially give higher capacitance.

Transparent flexible supercapacitors are of great interest due to the development current multimedia devices, such as mobile phone, tablets and flexible displays. Therefore, future work could focus on the development of flexible, transparent solid-state supercapacitor for wearable electronics using 3D graphene and binary metal oxides.

The development of solid-state hybrid supercapacitor-battery for high performance application could also be carried out. The battery gives high energy density whereas the supercapacitor gives high power density and high cyclic life. Hence, such a hybrid system could provide high energy density, high power density and high cycle life.

References

1. Park, S., M. Vosguerichian, and Z. Bao, *A review of fabrication and applications of carbon nanotube film-based flexible electronics*. *Nanoscale*, 2013. **5**(5): p. 1727-1752.
2. Weng, Z., et al., *Graphene–Cellulose Paper Flexible Supercapacitors*. *Advanced Energy Materials*, 2011. **1**(5): p. 917-922.
3. Shi, S., et al., *Flexible supercapacitors*. *Particuology*, 2013. **11**(4): p. 371-377.
4. Koo, M., et al., *Bendable Inorganic Thin-Film Battery for Fully Flexible Electronic Systems*. *Nano Letters*, 2012. **12**(9): p. 4810-4816.
5. Conway, B., *Electrochemical supercapacitor*, in *Scientific Fundamentals and Technological Applications*. 1999, Kluwer Academic/Plenum Publishers New York.
6. Sk, M.M. and C.Y. Yue, *Synthesis of polyaniline nanotubes using the self-assembly behavior of vitamin C: a mechanistic study and application in electrochemical supercapacitors*. *Journal of Materials Chemistry A*, 2014. **2**(8): p. 2830-2838.
7. Sk, M.M., C.Y. Yue, and R.K. Jena, *Facile growth of heparin-controlled porous polyaniline nanofiber networks and their application in supercapacitors*. *RSC Advances*, 2014. **4**(10): p. 5188-5197.
8. Rolison, D.R. and L.F. Nazar, *Electrochemical energy storage to power the 21st century*. *MRS Bulletin*, 2011. **36**(07): p. 486-493.
9. Fic, K., et al., *Novel insight into neutral medium as electrolyte for high-voltage supercapacitors*. *Energy & Environmental Science*, 2012. **5**(2): p. 5842-5850.
10. Cheng, H., et al., *Textile electrodes woven by carbon nanotube-graphene hybrid fibers for flexible electrochemical capacitors*. *Nanoscale*, 2013. **5**(8): p. 3428-3434.

11. Kaempgen, M., et al., *Printable Thin Film Supercapacitors Using Single-Walled Carbon Nanotubes*. Nano Letters, 2009. **9**(5): p. 1872-1876.
12. Meng, C., et al., *Highly flexible and all-solid-state paperlike polymer supercapacitors*. Nano Letters, 2010. **10**(10): p. 4025-4031.
13. Zhu, C., et al., *All Metal Nitrides Solid-State Asymmetric Supercapacitors*. Advanced Materials, 2015. **27**(31): p. 4566-4571.
14. Simon, P. and Y. Gogotsi, *Materials for electrochemical capacitors*. Nature materials, 2008. **7**(11): p. 845-854.
15. Frackowiak, E., *Carbon materials for supercapacitor application*. Physical Chemistry Chemical Physics, 2007. **9**(15): p. 1774-1785.
16. Liu, C., et al., *Graphene-based supercapacitor with an ultrahigh energy density*. Nano Letters, 2010. **10**(12): p. 4863-4868.
17. Sumboja, A., et al., *Large Areal Mass, Flexible and Free-Standing Reduced Graphene Oxide/Manganese Dioxide Paper for Asymmetric Supercapacitor Device*. Advanced Materials, 2013. **25**(20): p. 2809-2815.
18. Choi, B.G., et al., *High performance of a solid-state flexible asymmetric supercapacitor based on graphene films*. Nanoscale, 2012. **4**(16): p. 4983-4988.
19. Li, Z., et al., *Flexible graphene/MnO₂ composite papers for supercapacitor electrodes*. Journal of Materials Chemistry, 2011. **21**(38): p. 14706-14711.
20. Feng, X., et al., *The synthesis of shape-controlled MnO₂/graphene composites via a facile one-step hydrothermal method and their application in supercapacitors*. Journal of Materials Chemistry A, 2013. **1**(41): p. 12818-12825.
21. Wei, W., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews, 2011. **40**(3): p. 1697-1721.
22. Nam, K.-W., et al., *Electrodeposited manganese oxides on three-dimensional carbon nanotube substrate: Supercapacitive behaviour in aqueous and organic electrolytes*. Journal of Power Sources, 2009. **188**(1): p. 323-331.

23. Lin, C.-C. and C.-C. Yen, *Manganese oxide precipitated into activated carbon electrodes for electrochemical capacitors*. Journal of Applied Electrochemistry, 2008. **38**(12): p. 1677-1681.
24. Zhang, J., J. Jiang, and X. Zhao, *Synthesis and capacitive properties of manganese oxide nanosheets dispersed on functionalized graphene sheets*. The Journal of Physical Chemistry C, 2011. **115**(14): p. 6448-6454.
25. Sumboja, A., et al., *Significant electrochemical stability of manganese dioxide/polyaniline coaxial nanowires by self-terminated double surfactant polymerization for pseudocapacitor electrode*. Journal of Materials Chemistry, 2012. **22**(45): p. 23921-23928.
26. Liu, R. and S.B. Lee, *MnO₂/poly (3, 4-ethylenedioxythiophene) coaxial nanowires by one-step coelectrodeposition for electrochemical energy storage*. Journal of the American Chemical Society, 2008. **130**(10): p. 2942-2943.
27. Li, J., et al., *Electrochemical properties of graphene nanosheets/polyaniline nanofibers composites as electrode for supercapacitors*. Journal of Power Sources, 2011. **196**(24): p. 10775-10781.
28. Xu, J., et al., *Flexible asymmetric supercapacitors based upon Co₉S₈ nanorod//Co₃O₄@ RuO₂ nanosheet arrays on carbon cloth*. ACS Nano, 2013. **7**(6): p. 5453-5462.
29. Yan, J., et al., *Advanced asymmetric supercapacitors based on Ni (OH)₂/graphene and porous graphene electrodes with high energy density*. Advanced Functional Materials, 2012. **22**(12): p. 2632-2641.
30. Lu, X., et al., *H-TiO₂@MnO₂//H-TiO₂@C Core–Shell Nanowires for High Performance and Flexible Asymmetric Supercapacitors*. Advanced Materials, 2013. **25**(2): p. 267-272.
31. Chen, P.-C., et al., *Preparation and characterization of flexible asymmetric supercapacitors based on transition-metal-oxide nanowire/single-walled carbon nanotube hybrid thin-film electrodes*. ACS Nano, 2010. **4**(8): p. 4403-4411.

-
32. Chang, J., et al., *Asymmetric supercapacitors based on graphene/MnO₂ nanospheres and graphene/MoO₃ nanosheets with high energy density*. *Advanced Functional Materials*, 2013. **23**(40): p. 5074-5083.
33. Pandolfo, T., et al., *General Properties of Electrochemical Capacitors*, in *Supercapacitors*. 2013, Wiley-VCH Verlag GmbH & Co. KGaA. p. 69-109.
34. Wang, H. and L. Pilon, *Accurate Simulations of Electric Double Layer Capacitance of Ultramicroelectrodes*. *The Journal of Physical Chemistry C*, 2011. **115**(33): p. 16711-16719.
35. Zhang, L.L. and X.S. Zhao, *Carbon-based materials as supercapacitor electrodes*. *Chemical Society Reviews*, 2009. **38**(9): p. 2520-2531.
36. Wu, X.-L. and A.-W. Xu, *Carbonaceous hydrogels and aerogels for supercapacitors*. *Journal of Materials Chemistry A*, 2014. **2**(14): p. 4852-4864.
37. Liu, J., J. Essner, and J. Li, *Hybrid Supercapacitor Based on Coaxially Coated Manganese Oxide on Vertically Aligned Carbon Nanofiber Arrays*. *Chemistry of Materials*, 2010. **22**(17): p. 5022-5030.
38. Frackowiak, E., et al., *Supercapacitor electrodes from multiwalled carbon nanotubes*. *Applied Physics Letters*, 2000. **77**(15): p. 2421-2423.
39. An, K.H., et al., *Supercapacitors Using Single-Walled Carbon Nanotube Electrodes*. *Advanced Materials*, 2001. **13**(7): p. 497-500.
40. Marinho, B., et al., *Electrical conductivity of compacts of graphene, multi-wall carbon nanotubes, carbon black, and graphite powder*. *Powder Technology*, 2012. **221**(0): p. 351-358.
41. Ghosh, A. and Y.H. Lee, *Carbon-Based Electrochemical Capacitors*. *ChemSusChem*, 2012. **5**(3): p. 480-499.
42. Chen, D., L. Tang, and J. Li, *Graphene-based materials in electrochemistry*. *Chemical Society Reviews*, 2010. **39**(8): p. 3157-3180.
43. Pumera, M., *Electrochemistry of graphene: new horizons for sensing and energy storage*. *The Chemical Record*, 2009. **9**(4): p. 211-223.

-
44. Skákalová, V. and A.B. Kaiser, *Graphene: properties, preparation, characterisation and devices*. 2014: Elsevier.
 45. Lerf, A., et al., *Structure of Graphite Oxide Revisited*. The Journal of Physical Chemistry B, 1998. **102**(23): p. 4477-4482.
 46. Gómez-Navarro, C., et al., *Atomic Structure of Reduced Graphene Oxide*. Nano Letters, 2010. **10**(4): p. 1144-1148.
 47. Nakajima, T., A. Mabuchi, and R. Hagiwara, *A new structure model of graphite oxide*. Carbon, 1988. **26**(3): p. 357-361.
 48. Stoller, M.D., et al., *Graphene-based ultracapacitors*. Nano letters, 2008. **8**(10): p. 3498-3502.
 49. Park, S. and R.S. Ruoff, *Chemical methods for the production of graphenes*. Nature nanotechnology, 2009. **4**(4): p. 217-224.
 50. Li, D., et al., *Processable aqueous dispersions of graphene nanosheets*. Nature nanotechnology, 2008. **3**(2): p. 101-105.
 51. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. science, 2004. **306**(5696): p. 666-669.
 52. Berger, C., et al., *Electronic confinement and coherence in patterned epitaxial graphene*. Science, 2006. **312**(5777): p. 1191-1196.
 53. Li, X., et al., *Large-area synthesis of high-quality and uniform graphene films on copper foils*. Science, 2009. **324**(5932): p. 1312-1314.
 54. Yoo, J.J., et al., *Ultrathin Planar Graphene Supercapacitors*. Nano Letters, 2011. **11**(4): p. 1423-1427.
 55. Long, J.W., et al., *Voltammetric characterization of ruthenium oxide-based aerogels and other RuO₂ solids: the nature of capacitance in nanostructured materials*. Langmuir, 1999. **15**(3): p. 780-785.
 56. Yao, W., H. Zhou, and Y. Lu, *Synthesis and property of novel MnO₂@polypyrrole coaxial nanotubes as electrode material for supercapacitors*. Journal of Power Sources, 2013. **241**(0): p. 359-366.

-
57. Brousse, T., et al., *Crystalline MnO₂ as possible alternatives to amorphous compounds in electrochemical supercapacitors*. Journal of The Electrochemical Society, 2006. **153**(12): p. A2171-A2180.
58. Donne, S.W., A.F. Hollenkamp, and B.C. Jones, *Structure, morphology and electrochemical behaviour of manganese oxides prepared by controlled decomposition of permanganate*. Journal of Power Sources, 2010. **195**(1): p. 367-373.
59. Xia, H., et al., *MnO₂ nanotube and nanowire arrays by electrochemical deposition for supercapacitors*. Journal of Power Sources, 2010. **195**(13): p. 4410-4413.
60. Zhang, W., et al., *Large-scale synthesis of β -MnO₂ nanorods and their rapid and efficient catalytic oxidation of methylene blue dye*. Catalysis Communications, 2006. **7**(6): p. 408-412.
61. Yang, Z., et al., *Nanorods of manganese oxides: synthesis, characterization and catalytic application*. Journal of Solid State Chemistry, 2006. **179**(3): p. 679-684.
62. Zhu, H., et al., *Birnessite-type MnO₂ nanowalls and their magnetic properties*. The Journal of Physical Chemistry C, 2008. **112**(44): p. 17089-17094.
63. Yan, D., et al., *Fabrication, in-depth characterization, and formation mechanism of crystalline porous birnessite MnO₂ film with amorphous bottom layers by hydrothermal method*. Crystal Growth and Design, 2008. **9**(1): p. 218-222.
64. Ni, J., et al., *Low-temperature synthesis of monodisperse 3D manganese oxide nanoflowers and their pseudocapacitance properties*. The Journal of Physical Chemistry C, 2008. **113**(1): p. 54-60.
65. Xu, M., et al., *Hydrothermal synthesis and pseudocapacitance properties of α -MnO₂ hollow spheres and hollow urchins*. The Journal of Physical Chemistry C, 2007. **111**(51): p. 19141-19147.
66. Hongen, W., et al., *Single-crystal α -MnO₂ nanorods: synthesis and electrochemical properties*. Nanotechnology, 2007. **18**(11): p. 115616.

-
67. Xiao, X., et al., *WO_{3-x}/MoO_{3-x} Core/Shell Nanowires on Carbon Fabric as an Anode for All-Solid-State Asymmetric Supercapacitors*. Advanced Energy Materials, 2012. **2**(11): p. 1328-1332.
68. Badica, P., *Preparation through the vapor transport and growth mechanism of the first-order hierarchical structures of MoO₃ belts on sillimanite fibers*. Crystal Growth & Design, 2007. **7**(4): p. 794-801.
69. Mai, L.Q., et al., *Lithiated MoO₃ nanobelts with greatly improved performance for lithium batteries*. Advanced Materials, 2007. **19**(21): p. 3712-3716.
70. Zhou, L., et al., *α -MoO₃ nanobelts: a high performance cathode material for lithium ion batteries*. The Journal of Physical Chemistry C, 2010. **114**(49): p. 21868-21872.
71. Xia, X., et al., *Reduced-graphene oxide/molybdenum oxide/polyaniline ternary composite for high energy density supercapacitors: synthesis and properties*. Journal of Materials Chemistry, 2012. **22**(17): p. 8314-8320.
72. Tang, W., et al., *Aqueous supercapacitors of high energy density based on MoO₃ nanoplates as anode material*. Chemical Communications, 2011. **47**(36): p. 10058-10060.
73. Khandare, L., S.S. Terdale, and D.J. Late, *Ultra-fast α -MoO₃ nanorod-based Humidity sensor*. Advanced Device Materials, 2016. **2**(2): p. 15-22.
74. Desai, N., et al., *Chemically Grown MoO₃ Nanorods for Antibacterial Activity Study*. Journal of Nanomedicine & Nanotechnology, 2015. **6**(6): p. 1.
75. Castro, E., S. Real, and L.P. Dick, *Electrochemical characterization of porous nickel–cobalt oxide electrodes*. International Journal of Hydrogen Energy, 2004. **29**(3): p. 255-261.
76. Patil, U., et al., *Chemically deposited nanocrystalline NiO thin films for supercapacitor application*. Applied Surface Science, 2008. **255**(5): p. 2603-2607.
77. Kandalkar, S.G., J. Gunjekar, and C. Lokhande, *Preparation of cobalt oxide thin films and its use in supercapacitor application*. Applied Surface Science, 2008. **254**(17): p. 5540-5544.

-
78. Wang, L., et al., *Preparation and electrochemical properties of mesoporous Co_3O_4 crater-like microspheres as supercapacitor electrode materials*. Current Applied Physics, 2010. **10**(6): p. 1422-1426.
79. Shan, Y. and L. Gao, *Formation and characterization of multi-walled carbon nanotubes/ Co_3O_4 nanocomposites for supercapacitors*. Materials Chemistry and Physics, 2007. **103**(2): p. 206-210.
80. Liu, Y., et al., *Hierarchical SnO_2 nanostructures made of intermingled ultrathin nanosheets for environmental remediation, smart gas sensor, and supercapacitor applications*. ACS Applied Materials & Interfaces, 2014. **6**(3): p. 2174-2184.
81. Li, F., et al., *One-step synthesis of graphene/ SnO_2 nanocomposites and its application in electrochemical supercapacitors*. Nanotechnology, 2009. **20**(45): p. 455602.
82. Grupioni, A.A.F., E. Arashiro, and T.A.F. Lassali, *Voltammetric characterization of an iridium oxide-based system: the pseudocapacitive nature of the $\text{Ir}_{0.3}\text{Mn}_{0.7}\text{O}_2$ electrode*. Electrochimica Acta, 2002. **48**(4): p. 407-418.
83. Rajeswari, J., et al., *One-dimensional MoO_2 nanorods for supercapacitor applications*. Electrochemistry Communications, 2009. **11**(3): p. 572-575.
84. Yuan, C., et al., *Ultrathin mesoporous NiCo_2O_4 nanosheets supported on Ni foam as advanced electrodes for supercapacitors*. Advanced Functional Materials, 2012. **22**(21): p. 4592-4597.
85. Zhang, G. and X.W.D. Lou, *General Solution Growth of Mesoporous NiCo_2O_4 Nanosheets on Various Conductive Substrates as High-Performance Electrodes for Supercapacitors*. Advanced Materials, 2013. **25**(7): p. 976-979.
86. Mondal, A.K., et al., *Mesoporous MnCo_2O_4 with a Flake-Like Structure as Advanced Electrode Materials for Lithium-Ion Batteries and Supercapacitors*. Chemistry-A European Journal, 2015. **21**(4): p. 1526-1532.
87. Nalwa, H.S., *Handbook of Organic Conductive Molecules and Polymers: Conductive polymers : spectroscopy and physical properties*. 1997: Wiley.

-
88. Long, Y.-Z., et al., *Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers*. Progress in Polymer Science, 2011. **36**(10): p. 1415-1442.
89. Basnayaka, P.A., *Development of Nanostructured Graphene/Conducting Polymer Composite Materials for Supercapacitor Applications*. 2013: University of South Florida.
90. Stejskal, J. and R. Gilbert, *Polyaniline. Preparation of a conducting polymer (IUPAC technical report)*. Pure and Applied Chemistry, 2002. **74**(5): p. 857-867.
91. Bolto, B.A., R. McNeill, and D. Weiss, *Electronic conduction in polymers. III. Electronic properties of polypyrrole*. Australian Journal of Chemistry, 1963. **16**(6): p. 1090-1103.
92. Vernitskaya, T.y.V. and O.N. Efimov, *Polypyrrole: a conducting polymer; its synthesis, properties and applications*. Russian Chemical Reviews, 1997. **66**(5): p. 443-457.
93. Pyshkina, O., A. Kubarkov, and V. Sergeyev, *Poly (3, 4-ethylenedioxythiophene): synthesis and properties*. Materials Sciences and Applied Chemistry 2010, vol. 21, p. 51-54, ISSN 1407-7353.
94. Chen, L., et al., *Synthesis and pseudocapacitive studies of composite films of polyaniline and manganese oxide nanoparticles*. Journal of Power Sources, 2010. **195**(11): p. 3742-3747.
95. Liu, F.-J., *Electrodeposition of manganese dioxide in three-dimensional poly (3, 4-ethylenedioxythiophene)-poly (styrene sulfonic acid)-polyaniline for supercapacitor*. Journal of Power Sources, 2008. **182**(1): p. 383-388.
96. Iranagh, S.A., L. Eskandarian, and R. Mohammadi, *Synthesis of MnO₂-polyaniline nanofiber composites to produce high conductive polymer*. Synthetic Metals, 2013. **172**(0): p. 49-53.
97. Chen, S., et al., *Graphene oxide-MnO₂ nanocomposites for supercapacitors*. ACS Nano, 2010. **4**(5): p. 2822-2830.
98. Wang, H., et al., *Effect of graphene oxide on the properties of its composite with polyaniline*. ACS Applied Materials & Interfaces, 2010. **2**(3): p. 821-828.

-
99. Cheng, Q., et al., *Graphene and nanostructured MnO₂ composite electrodes for supercapacitors*. Carbon, 2011. **49**(9): p. 2917-2925.
 100. Dong, X., et al., *Synthesis of a MnO₂-graphene foam hybrid with controlled MnO₂ particle shape and its use as a supercapacitor electrode*. Carbon, 2012. **50**(13): p. 4865-4870.
 101. Duay, J., et al., *Highly flexible pseudocapacitor based on freestanding heterogeneous MnO₂/conductive polymer nanowire arrays*. Physical Chemistry Chemical Physics, 2012. **14**(10): p. 3329-3337.
 102. Sivaraman, P., et al., *Poly (3-methyl thiophene)-activated carbon hybrid supercapacitor based on gel polymer electrolyte*. Electrochemical and Solid-State Letters, 2006. **9**(9): p. A435-A438.
 103. Lee, K.-T. and N.-L. Wu, *Manganese oxide electrochemical capacitor with potassium poly (acrylate) hydrogel electrolyte*. Journal of Power Sources, 2008. **179**(1): p. 430-434.
 104. Hu, X.-L., et al., *A new nanocomposite polymer electrolyte based on poly (vinyl alcohol) incorporating hypergrafted nano-silica*. Journal of Materials Chemistry, 2012. **22**(36): p. 18961-18967.
 105. Meng, F. and Y. Ding, *Sub-Micrometer-Thick All-Solid-State Supercapacitors with High Power and Energy Densities*. Advanced Materials, 2011. **23**(35): p. 4098-4102.
 106. Huang, C.W., et al., *Gel Electrolyte Derived from Poly (ethylene glycol) Blending Poly (acrylonitrile) Applicable to Roll-to-Roll Assembly of Electric Double Layer Capacitors*. Advanced Functional Materials, 2012. **22**(22): p. 4677-4685.
 107. Yuan, L., et al., *Flexible solid-state supercapacitors based on carbon nanoparticles/MnO₂ nanorods hybrid structure*. ACS Nano, 2011. **6**(1): p. 656-661.
 108. Gao, H. and K. Lian, *High rate all-solid electrochemical capacitors using proton conducting polymer electrolytes*. Journal of Power Sources, 2011. **196**(20): p. 8855-8857.

-
109. Lu, X., et al., *Stabilized TiN nanowire arrays for high-performance and flexible supercapacitors*. Nano Letters, 2012. **12**(10): p. 5376-5381.
110. Yang, C.-C. and S. Lin, *Preparation of alkaline PVA-based polymer electrolytes for Ni-MH and Zn-air batteries*. Journal of Applied Electrochemistry, 2003. **33**(9): p. 777-784.
111. Iwakura, C., et al., *New electric double layer capacitor with polymer hydrogel electrolyte*. Electrochemical and Solid-State Letters, 2003. **6**(2): p. A37-A39.
112. Wada, H., et al., *Electrochemical characteristics of electric double layer capacitor using sulfonated polypropylene separator impregnated with polymer hydrogel electrolyte*. Electrochimica Acta, 2004. **49**(27): p. 4871-4875.
113. Lewandowski, A., et al., *Supercapacitor based on activated carbon and polyethylene oxide-KOH-H₂O polymer electrolyte*. Electrochimica Acta, 2001. **46**(18): p. 2777-2780.
114. Giri, S., D. Ghosh, and C.K. Das, *In situ synthesis of cobalt doped polyaniline modified graphene composites for high performance supercapacitor electrode materials*. Journal of Electroanalytical Chemistry, 2013. **697**: p. 32-45.
115. Cheng, Q., et al., *Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density*. Physical Chemistry Chemical Physics, 2011. **13**(39): p. 17615-17624.
116. Girija, T.C. and M.V. Sangaranarayanan, *Analysis of polyaniline-based nickel electrodes for electrochemical supercapacitors*. Journal of Power Sources, 2006. **156**(2): p. 705-711.
117. Gupta, V. and N. Miura, *Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors*. Electrochimica Acta, 2006. **52**(4): p. 1721-1726.
118. Pell, W.G. and B.E. Conway, *Analysis of power limitations at porous supercapacitor electrodes under cyclic voltammetry modulation and dc charge*. Journal of Power Sources, 2001. **96**(1): p. 57-67.
119. Ghosh, D., S. Giri, and C.K. Das, *Synthesis, characterization and electrochemical performance of graphene decorated with 1D NiMoO₄.nH₂O nanorods*. Nanoscale, 2013. **5**(21): p. 10428-10437.

-
120. Sk, M.M. and C.Y. Yue, *Layer-by-layer (LBL) assembly of graphene with p-phenylenediamine (PPD) spacer for high performance supercapacitor applications*. Rsc Advances, 2014. **4**(38): p. 19908-19915.
121. Jagadale, A.D., et al., *Ultrathin nanoflakes of cobalt–manganese layered double hydroxide with high reversibility for asymmetric supercapacitor*. Journal of Power Sources, 2016. **306**: p. 526-534.
122. Xu, Y., et al., *Self-assembled graphene hydrogel via a one-step hydrothermal process*. ACS Nano, 2010. **4**(7): p. 4324-4330.
123. Zhang, L. and G. Shi, *Preparation of Highly Conductive Graphene Hydrogels for Fabricating Supercapacitors with High Rate Capability*. The Journal of Physical Chemistry C, 2011. **115**(34): p. 17206-17212.
124. Tang, Z., et al., *Noble-metal-promoted three-dimensional macroassembly of single-layered graphene oxide*. Angewandte Chemie, 2010. **122**(27): p. 4707-4711.
125. Wu, Z.-S., et al., *3D nitrogen-doped graphene aerogel-supported Fe₃O₄ nanoparticles as efficient electrocatalysts for the oxygen reduction reaction*. Journal of the American Chemical Society, 2012. **134**(22): p. 9082-9085.
126. Chen, S., et al., *Hierarchically porous graphene-based hybrid electrodes with excellent electrochemical performance*. Journal of Materials Chemistry A, 2013. **1**(33): p. 9409-9413.
127. Niu, Z., et al., *A leavening strategy to prepare reduced graphene oxide foams*. Advanced Materials, 2012. **24**(30): p. 4144-4150.
128. Chen, W. and L. Yan, *In situ self-assembly of mild chemical reduction graphene for three-dimensional architectures*. Nanoscale, 2011. **3**(8): p. 3132-3137.
129. Sheng, K.-x., et al., *High-performance self-assembled graphene hydrogels prepared by chemical reduction of graphene oxide*. New Carbon Materials, 2011. **26**(1): p. 9-15.
130. Pham, H.D., et al., *Synthesis of the chemically converted graphene xerogel with superior electrical conductivity*. Chemical Communications, 2011. **47**(34): p. 9672-9674.

-
131. Tien, H.N., et al., *Synthesis of a highly conductive and large surface area graphene oxide hydrogel and its use in a supercapacitor*. Journal of Materials Chemistry A, 2013. **1**(2): p. 208-211.
 132. Lu, X., et al., *Macroporous foam of reduced graphene oxides prepared by lyophilization*. Materials Research Bulletin, 2012. **47**(12): p. 4335-4339.
 133. Zu, S.-Z. and B.-H. Han, *Aqueous dispersion of graphene sheets stabilized by pluronic copolymers: formation of supramolecular hydrogel*. The Journal of Physical Chemistry C, 2009. **113**(31): p. 13651-13657.
 134. Bai, H., et al., *A pH-sensitive graphene oxide composite hydrogel*. Chemical Communications, 2010. **46**(14): p. 2376-2378.
 135. Zha, D.-a., et al., *Superhydrophobic polyvinylidene fluoride/graphene porous materials*. Carbon, 2011. **49**(15): p. 5166-5172.
 136. Bai, H., et al., *On the gelation of graphene oxide*. The Journal of Physical Chemistry C, 2011. **115**(13): p. 5545-5551.
 137. Liu, J., G. Chen, and M. Jiang, *Supramolecular hybrid hydrogels from noncovalently functionalized graphene with block copolymers*. Macromolecules, 2011. **44**(19): p. 7682-7691.
 138. Qiu, L., et al., *Biomimetic superelastic graphene-based cellular monoliths*. Nature Communications, 2012. **3**: p. 1241.
 139. Choi, B.G., et al., *3D macroporous graphene frameworks for supercapacitors with high energy and power densities*. ACS Nano, 2012. **6**(5): p. 4020-4028.
 140. Su, D., *Macroporous 'bubble' graphene film via template-directed ordered-assembly for high rate supercapacitors*. Chemical Communications, 2012. **48**(57): p. 7149-7151.
 141. Cao, X., et al., *Preparation of novel 3D graphene networks for supercapacitor applications*. Small, 2011. **7**(22): p. 3163-3168.
 142. Chen, K., et al., *Three-dimensional porous graphene-based composite materials: electrochemical synthesis and application*. Journal of Materials Chemistry, 2012. **22**(39): p. 20968-20976.

-
143. Biener, J., et al., *Macroscopic 3D nanographene with dynamically tunable bulk properties*. Advanced Materials, 2012. **24**(37): p. 5083-5087.
144. Xiao, X., et al., *Lithographically defined three-dimensional graphene structures*. Acs Nano, 2012. **6**(4): p. 3573-3579.
145. Cheng, Y. and J. Liu, *Carbon nanomaterials for flexible energy storage*. Materials Research Letters, 2013. **1**(4): p. 175-192.
146. Tai, Z., et al., *Enhancement of capacitance performance of flexible carbon nanofiber paper by adding graphene nanosheets*. Journal of Power Sources, 2012. **199**: p. 373-378.
147. Lu, X., et al., *Flexible solid-state supercapacitors: design, fabrication and applications*. Energy & Environmental Science, 2014. **7**(7): p. 2160-2181.
148. Cheng, H., et al., *Textile electrodes woven by carbon nanotube–graphene hybrid fibers for flexible electrochemical capacitors*. Nanoscale, 2013. **5**(8): p. 3428-3434.
149. Hu, L., H. Wu, and Y. Cui, *Printed energy storage devices by integration of electrodes and separators into single sheets of paper*. Applied Physics Letters, 2010. **96**(18): p. 183502.
150. Zheng, G., et al., *Paper supercapacitors by a solvent-free drawing method*. Energy & Environmental Science, 2011. **4**(9): p. 3368-3373.
151. Hu, L., et al., *Stretchable, porous, and conductive energy textiles*. Nano letters, 2010. **10**(2): p. 708-714.
152. Chen, Y.-C., et al., *Highly flexible supercapacitors with manganese oxide nanosheet/carbon cloth electrode*. Electrochimica Acta, 2011. **56**(20): p. 7124-7130.
153. Chou, S.-L., et al., *Electrodeposition of MnO₂ nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors*. Electrochemistry Communications, 2008. **10**(11): p. 1724-1727.
154. Luan, F., et al., *High energy density asymmetric supercapacitors with a nickel oxide nanoflake cathode and a 3D reduced graphene oxide anode*. Nanoscale, 2013. **5**(17): p. 7984-7990.

-
155. Yan, X., et al., *Fabrication of carbon nanofiber–polyaniline composite flexible paper for supercapacitor*. *Nanoscale*, 2011. **3**(1): p. 212-216.
156. Wang, Z.-L., et al., *Polyaniline nanotube arrays as high-performance flexible electrodes for electrochemical energy storage devices*. *Journal of Materials Chemistry*, 2012. **22**(6): p. 2401-2404.
157. Hu, L., et al., *Symmetrical MnO₂–carbon nanotube–textile nanostructures for wearable pseudocapacitors with high mass loading*. *Acs Nano*, 2011. **5**(11): p. 8904-8913.
158. He, Y., et al., *Freestanding three-dimensional graphene/MnO₂ composite networks as ultralight and flexible supercapacitor electrodes*. *ACS nano*, 2012. **7**(1): p. 174-182.
159. Chen, P., et al., *Inkjet printing of single-walled carbon nanotube/RuO₂ nanowire supercapacitors on cloth fabrics and flexible substrates*. *Nano Research*, 2010. **3**(8): p. 594-603.
160. Perera, S.D., et al., *Vanadium Oxide Nanowire–Carbon Nanotube Binder-Free Flexible Electrodes for Supercapacitors*. *Advanced Energy Materials*, 2011. **1**(5): p. 936-945.
161. Boukhalfa, S., K. Evanoff, and G. Yushin, *Atomic layer deposition of vanadium oxide on carbon nanotubes for high-power supercapacitor electrodes*. *Energy & Environmental Science*, 2012. **5**(5): p. 6872-6879.
162. Yuan, C., et al., *Flexible hybrid paper made of monolayer Co₃O₄ microsphere arrays on rGO/CNTs and their application in electrochemical capacitors*. *Advanced Functional Materials*, 2012. **22**(12): p. 2560-2566.
163. Cong, H.-P., et al., *Flexible graphene–polyaniline composite paper for high-performance supercapacitor*. *Energy & Environmental Science*, 2013. **6**(4): p. 1185-1191.
164. Ge, J., G. Cheng, and L. Chen, *Transparent and flexible electrodes and supercapacitors using polyaniline/single-walled carbon nanotube composite thin films*. *Nanoscale*, 2011. **3**(8): p. 3084-3088.

-
165. Wang, K., et al., *Flexible supercapacitors based on cloth-supported electrodes of conducting polymer nanowire array/SWCNT composites*. Journal of Materials Chemistry, 2011. **21**(41): p. 16373-16378.
166. Wu, Q., et al., *Supercapacitors based on flexible graphene/polyaniline nanofiber composite films*. ACS Nano, 2010. **4**(4): p. 1963-1970.
167. Davoglio, R.A., et al., *Flexible and high surface area composites of carbon fiber, polypyrrole, and poly (DMcT) for supercapacitor electrodes*. Electrochimica Acta, 2013. **93**: p. 93-100.
168. Davies, A., et al., *Graphene-based flexible supercapacitors: pulse-electropolymerization of polypyrrole on free-standing graphene films*. The Journal of Physical Chemistry C, 2011. **115**(35): p. 17612-17620.
169. Alvi, F., et al., *Graphene–polyethylenedioxythiophene conducting polymer nanocomposite based supercapacitor*. Electrochimica Acta, 2011. **56**(25): p. 9406-9412.
170. Fu, Y., et al., *Fiber supercapacitors utilizing pen ink for flexible/wearable energy storage*. Advanced Materials, 2012. **24**(42): p. 5713-5718.
171. Kang, Y.J., et al., *All-solid-state flexible supercapacitors based on papers coated with carbon nanotubes and ionic-liquid-based gel electrolytes*. Nanotechnology, 2012. **23**(6): p. 065401.
172. Kang, Y.J., et al., *All-solid-state flexible supercapacitors fabricated with bacterial nanocellulose papers, carbon nanotubes, and triblock-copolymer ion gels*. ACS Nano, 2012. **6**(7): p. 6400-6406.
173. Niu, Z., et al., *Highly Stretchable, Integrated Supercapacitors Based on Single-Walled Carbon Nanotube Films with Continuous Reticulate Architecture*. Advanced Materials, 2013. **25**(7): p. 1058-1064.
174. Yoo, J.J., et al., *Ultrathin planar graphene supercapacitors*. Nano Letters, 2011. **11**(4): p. 1423-1427.
175. El-Kady, M.F., et al., *Laser scribing of high-performance and flexible graphene-based electrochemical capacitors*. Science, 2012. **335**(6074): p. 1326-1330.

-
176. Xia, J., et al., *Measurement of the quantum capacitance of graphene*. Nature Nanotechnology, 2009. **4**(8): p. 505-509.
177. Choi, B.G., et al., *Facilitated ion transport in all-solid-state flexible supercapacitors*. ACS Nano, 2011. **5**(9): p. 7205-7213.
178. Gao, K., et al., *Cellulose nanofiber-graphene all solid-state flexible supercapacitors*. Journal of Materials Chemistry A, 2013. **1**(1): p. 63-67.
179. Yuan, L., et al., *Paper-Based Supercapacitors for Self-Powered Nanosystems*. Angewandte Chemie, 2012. **124**(20): p. 5018-5022.
180. Sellers, M.C., N.P. Zussblatt, and C.P. Marsh, *Potassium perruthenate-treated carbon nanotube sheets for flexible supercapacitors*. Electrochemistry Communications, 2012. **18**: p. 58-61.
181. Lu, X., et al., *WO_{3-x}@Au@MnO₂ Core-Shell Nanowires on Carbon Fabric for High-Performance Flexible Supercapacitors*. Advanced Materials, 2012. **24**(7): p. 938-944.
182. Li, X., et al., *Flexible supercapacitor based on MnO₂ nanoparticles via electrospinning*. Journal of Materials Chemistry A, 2013. **1**(35): p. 10103-10106.
183. Yang, P., et al., *Hydrogenated ZnO core-shell nanocables for flexible supercapacitors and self-powered systems*. ACS Nano, 2013. **7**(3): p. 2617-2626.
184. Xue, M., et al., *Microfluidic etching for fabrication of flexible and all-solid-state micro supercapacitor based on MnO₂ nanoparticles*. Nanoscale, 2011. **3**(7): p. 2703-2708.
185. Xiao, X., et al., *Fiber-based all-solid-state flexible supercapacitors for self-powered systems*. Acs Nano, 2012. **6**(10): p. 9200-9206.
186. Gao, H., et al., *Flexible all-solid-state asymmetric supercapacitors based on free-standing carbon nanotube/graphene and Mn₃O₄ nanoparticle/graphene paper electrodes*. ACS Applied Materials & Interfaces, 2012. **4**(12): p. 7020-7026.

-
187. Shao, Y., et al., *High-performance flexible asymmetric supercapacitors based on 3D porous graphene/MnO₂ nanorod and graphene/Ag hybrid thin-film electrodes*. Journal of Materials Chemistry C, 2013. **1**(6): p. 1245-1251.
188. Zilong, W., et al., *High performance flexible solid-state asymmetric supercapacitors from MnO₂/ZnO core-shell nanorods/specially reduced graphene oxide*. Journal of Materials Chemistry C, 2014. **2**(7): p. 1331-1336.
189. Lu, X., et al., *Oxygen-deficient hematite nanorods as high-performance and novel negative electrodes for flexible asymmetric supercapacitors*. Advanced Materials, 2014. **26**(19): p. 3148-3155.
190. Jost, K., et al., *Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics*. Energy & Environmental Science, 2013. **6**(9): p. 2698-2705.
191. Jost, K., G. Dion, and Y. Gogotsi, *Textile energy storage in perspective*. Journal of Materials Chemistry A, 2014. **2**(28): p. 10776-10787.
192. Lu, X., et al., *High Energy Density Asymmetric Quasi-Solid-State Supercapacitor Based on Porous Vanadium Nitride Nanowire Anode*. Nano Letters, 2013. **13**(6): p. 2628-2633.
193. Gao, H., et al., *High-performance asymmetric supercapacitor based on graphene hydrogel and nanostructured MnO₂*. ACS Applied Materials & Interfaces, 2012. **4**(5): p. 2801-2810.
194. Khattak, A.M., et al., *Three dimensional iron oxide/graphene aerogel hybrids as all-solid-state flexible supercapacitor electrodes*. RSC Advances, 2016. **6**(64): p. 58994-59000.
195. Hu, C.-C. and W.-C. Chen, *Effects of substrates on the capacitive performance of RuO_x·nH₂O and activated carbon-RuO_x electrodes for supercapacitors*. Electrochimica Acta, 2004. **49**(21): p. 3469-3477.
196. Han, Z., et al., *Ammonia solution strengthened three-dimensional macro-porous graphene aerogel*. Nanoscale, 2013. **5**(12): p. 5462-5467.
197. Pimenta, M., et al., *Studying disorder in graphite-based systems by Raman spectroscopy*. Physical Chemistry Chemical Physics, 2007. **9**(11): p. 1276-1290.

-
198. Ji, Z., et al., *In situ synthesis of graphene/cobalt nanocomposites and their magnetic properties*. Materials Science and Engineering: B, 2011. **176**(9): p. 711-715.
199. Stankovich, S., et al., *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*. Carbon, 2007. **45**(7): p. 1558-1565.
200. Ji, Z., et al., *Synthesis of reduced graphene oxide/CeO₂ nanocomposites and their photocatalytic properties*. Nanotechnology, 2013. **24**(11): p. 115603.
201. Liu, Z.-h., et al., *Intercalation of organic ammonium ions into layered graphite oxide*. Langmuir, 2002. **18**(12): p. 4926-4932.
202. Qiao, X., et al., *Phosphorus and nitrogen dual doped and simultaneously reduced graphene oxide with high surface area as efficient metal-free electrocatalyst for oxygen reduction*. Catalysts, 2015. **5**(2): p. 981-991.
203. Ricketts, B.W. and C. Ton-That, *Self-discharge of carbon-based supercapacitors with organic electrolytes*. Journal of Power Sources, 2000. **89**(1): p. 64-69.
204. Yang, W., et al., *Synthesis of reduced graphene nanosheet/urchin-like manganese dioxide composite and high performance as supercapacitor electrode*. Electrochimica Acta, 2012. **69**: p. 112-119.
205. Li, B., et al., *Low-temperature synthesis of α -MnO₂ hollow urchins and their application in rechargeable Li⁺ batteries*. Inorganic chemistry, 2006. **45**(16): p. 6404-6410.
206. Chen, L., et al., *Synthesis and electrochemical performance of polyaniline-MnO₂ nanowire composites for supercapacitors*. Journal of Physics and Chemistry of Solids, 2013. **74**(2): p. 360-365.
207. Bernard, M.C. and A. Hugot-Le Goff, *Quantitative characterization of polyaniline films using Raman spectroscopy: I: Polaron lattice and bipolaron*. Electrochimica Acta, 2006. **52**(2): p. 595-603.
208. Cochet, M., et al., *Theoretical and experimental vibrational study of emeraldine in salt form. Part II*. Journal of Raman Spectroscopy, 2000. **31**(12): p. 1041-1049.

-
209. Ma, S.-B., et al., *Synthesis and characterization of manganese dioxide spontaneously coated on carbon nanotubes*. Carbon, 2007. **45**(2): p. 375-382.
210. Jafri, R.I., A.K. Mishra, and S. Ramaprabhu, *Polyaniline–MnO₂ nanotube hybrid nanocomposite as supercapacitor electrode material in acidic electrolyte*. Journal of Materials Chemistry, 2011. **21**(44): p. 17601-17605.
211. Yuan, A. and Q. Zhang, *A novel hybrid manganese dioxide/activated carbon supercapacitor using lithium hydroxide electrolyte*. Electrochemistry Communications, 2006. **8**(7): p. 1173-1178.
212. Trchová, M. and J. Stejskal, *Polyaniline: The infrared spectroscopy of conducting polymer nanotubes (IUPAC Technical Report)*, in *Pure and Applied Chemistry*. 2011. p. 1803.
213. Zeng, X.-R. and T.-M. Ko, *Structures and properties of chemically reduced polyanilines*. Polymer, 1998. **39**(5): p. 1187-1195.
214. Binkauskienė, E., V. Jasulaitienė, and A. Lugauskas, *Effect of Aspergillus niger Tiegh. L-10 on the physical and chemical properties of a polyaniline coating in the growth substrate*. Synthetic Metals, 2009. **159**(13): p. 1365-1368.
215. Asim, N., S. Radiman, and M.A.b. Yarmo, *Preparation and characterization of core-shell polyaniline/V₂O₅ nanocomposite via microemulsion method*. Materials Letters, 2008. **62**(6–7): p. 1044-1047.
216. Wang, B., J. Tang, and F. Wang, *Proceedings of the International Conference of Science and Technology of Synthetic Metals Electrochemical polymerization of aniline*. Synthetic Metals, 1987. **18**(1): p. 323-328.
217. Biswas, M., S.S. Ray, and Y. Liu, *Water dispersible conducting nanocomposites of poly (N-vinylcarbazole), polypyrrole and polyaniline with nanodimensional manganese (IV) oxide*. Synthetic Metals, 1999. **105**(2): p. 99-105.
218. Yu, L., et al., *Facile synthesis of MnO₂/polyaniline nanorod arrays based on graphene and its electrochemical performance*. Synthetic Metals, 2014. **198**: p. 167-174.

-
219. Subramanian, V., H. Zhu, and B. Wei, *Nanostructured MnO₂: Hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material*. Journal of Power Sources, 2006. **159**(1): p. 361-364.
220. Park, H.W., et al., *Anisotropic growth control of polyaniline nanostructures and their morphology-dependent electrochemical characteristics*. ACS Nano, 2012. **6**(9): p. 7624-7633.
221. Xiong, S., et al., *Covalently bonded polyaniline/fullerene hybrids with coral-like morphology for high-performance supercapacitor*. Electrochimica Acta, 2012. **85**: p. 235-242.
222. Yang, X.-f., et al., *A novel layered manganese oxide/poly(aniline-co-o-anisidine) nanocomposite and its application for electrochemical supercapacitor*. Electrochimica Acta, 2010. **55**(19): p. 5414-5419.
223. Sharma, R.K., A.C. Rastogi, and S.B. Desu, *Manganese oxide embedded polypyrrole nanocomposites for electrochemical supercapacitor*. Electrochimica Acta, 2008. **53**(26): p. 7690-7695.
224. Ni, W., et al., *Fabrication of nanocomposite electrode with MnO₂ nanoparticles distributed in polyaniline for electrochemical capacitors*. Materials Chemistry and Physics, 2010. **124**(2): p. 1151-1154.
225. Pell, W.G. and B.E. Conway, *Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes*. Journal of Power Sources, 2004. **136**(2): p. 334-345.
226. Sk, M.M., C.Y. Yue, and R.K. Jena, *Synthesis of graphene/vitamin C template-controlled polyaniline nanotubes composite for high performance supercapacitor electrode*. Polymer, 2014. **55**(3): p. 798-805.
227. Xu, Y., et al., *Flexible solid-state supercapacitors based on three-dimensional graphene hydrogel films*. ACS Nano, 2013. **7**(5): p. 4042-4049.
228. Wang, S., et al., *Highly porous graphene on carbon cloth as advanced electrodes for flexible all-solid-state supercapacitors*. Nano Energy, 2013. **2**(4): p. 530-536.

-
229. Jin, Y., et al., *Graphene-patched CNT/MnO₂ nanocomposite papers for the electrode of high-performance flexible asymmetric supercapacitors*. ACS Applied Materials & Interfaces, 2013. **5**(8): p. 3408-3416.
230. Dikin, D.A., et al., *Preparation and characterization of graphene oxide paper*. Nature, 2007. **448**(7152): p. 457-460.
231. Wang, G., et al., *Flexible Pillared Graphene-Paper Electrodes for High-Performance Electrochemical Supercapacitors*. Small, 2012. **8**(3): p. 452-459.
232. Zhao, Y., et al., *Highly compression-tolerant supercapacitor based on polypyrrole-mediated graphene foam electrodes*. Advanced Materials, 2013. **25**(4): p. 591-595.
233. Jiang, X., et al., *Self-assembly of reduced graphene oxide into three-dimensional architecture by divalent ion linkage*. The Journal of Physical Chemistry C, 2010. **114**(51): p. 22462-22465.
234. Polu, A.R. and H.-W. Rhee, *Effect of Organic-Inorganic Hybrid Nanoparticles (POSS-PEG($n = 4$)) on Thermal, Mechanical, and Electrical Properties of PEO-Based Solid Polymer Electrolytes*. Advances in Polymer Technology, 2017. **36**(2): p. 145-151.
235. Ghosh, K., et al., *Development of 3-D Urchin Shaped Coaxial MnO₂@PANI Composite and Self-Assembled 3-D Pillared Graphene Foam for Asymmetric All-Solid-State Flexible Supercapacitor Application*. ACS Applied Materials & Interfaces, 2017.
236. Hu, X., et al., *Hierarchical Manganese Dioxide/Poly (3, 4-ethylenedioxythiophene) Core-Shell Nanoflakes on Ramie-Derived Carbon Fiber for High-Performance Flexible All-Solid-State Supercapacitor*. ACS Sustainable Chemistry & Engineering, 2016. **4**(3): p. 1201-1211.
237. Li, S., et al., *Mechanically strong high performance layered polypyrrole nano fibre/graphene film for flexible solid state supercapacitor*. Carbon, 2014. **79**: p. 554-562.
238. Liu, Y., et al., *Layered-MnO₂ nanosheet grown on nitrogen-doped graphene template as a composite cathode for flexible solid-state asymmetric*

-
- supercapacitor*. ACS Applied Materials & Interfaces, 2016. **8**(8): p. 5251-5260.
239. Liu, M., et al., *One-step synthesis of graphene nanoribbon–MnO₂ hybrids and their all-solid-state asymmetric supercapacitors*. Nanoscale, 2014. **6**(8): p. 4233-4242.
240. Tang, W., et al., *An aqueous rechargeable lithium battery of excellent rate capability based on a nanocomposite of MoO₃ coated with PPy and LiMn₂O₄*. Energy & Environmental Science, 2012. **5**(5): p. 6909-6913.
241. Jehn, H., et al., *Gmelin handbook of inorganic chemistry, Mo, Supplement Volume B5*. 8th edition. 1990, Heidelberg Springer. xvii, 391.
242. Xie, L., et al., *Electrical measurement of non-destructively p-type doped graphene using molybdenum trioxide*. Applied Physics Letters, 2011. **99**(1): p. 012112.

Appendix

Figure A1 Schematic presentation of the fabrication of all-solid-state supercapacitor cell.

Figure A2 FESEM images of MnO_2 after (a) 15 min, (b) 30 min and (c) 45 min of hydrothermal reaction.

Figure A3 Different bending states of the all-solid-state GF40//RGO/M@P25 ASC.

A.1 Cyclic voltammetry (CV) and cyclic charge-discharge (CCD) study of RGO-MnO₂ film symmetric supercapacitor SSC

Figure A4 (a) CV and (b) CCD study of RGO-MnO₂ film

The solid-state flexible RGO-MnO₂ film SSC exhibits the specific capacitance of 98 F g⁻¹ and an energy density of 13.61 Wh kg⁻¹ at a power density of 0.526 kW kg⁻¹ current density.