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

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Statement of Originality

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

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Date

Kalyan Ghosh
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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, MnO₂ 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), MnO₂, 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 (MnO₂@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 MnO₂@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 (MnO$_2$@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/MnO$_2$@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 MnO$_2$@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/MnO$_2$@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 MnO$_2$–RGO hybrid film (PANI/(MnO$_2$–RGO)/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 (MoO$_3$/GF//PANI/(MnO$_2$–RGO)/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.
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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$_3$O$_4$ – Cobalt oxide
CP – Conducting polymer
CV – Cyclic voltammetry
CVD- Chemical vapor deposition
$C_{sp}$ – Specific capacitance
<table>
<thead>
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<tbody>
<tr>
<td><strong>D</strong></td>
<td></td>
</tr>
<tr>
<td>1D – One dimensional</td>
<td></td>
</tr>
<tr>
<td>2D – Two dimensional</td>
<td></td>
</tr>
<tr>
<td>3D – Three dimensional</td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td></td>
</tr>
<tr>
<td>$E_{cell}$ – Energy density</td>
<td></td>
</tr>
<tr>
<td>EDL – Electrical double-layer</td>
<td></td>
</tr>
<tr>
<td>EDLC – Electrical double-layer capacitor</td>
<td></td>
</tr>
<tr>
<td>EIS – Electrochemical impedance spectroscopy</td>
<td></td>
</tr>
<tr>
<td>ESR – Equivalent series resistance</td>
<td></td>
</tr>
<tr>
<td><strong>F</strong></td>
<td></td>
</tr>
<tr>
<td>FESEM – Field emission scanning electron microscopy</td>
<td></td>
</tr>
<tr>
<td>FTIR – Fourier transform infrared</td>
<td></td>
</tr>
<tr>
<td><strong>G</strong></td>
<td></td>
</tr>
<tr>
<td>GA – Graphene aerogel</td>
<td></td>
</tr>
<tr>
<td>GF – Graphene foam</td>
<td></td>
</tr>
<tr>
<td>GO – Graphene oxide</td>
<td></td>
</tr>
<tr>
<td><strong>H</strong></td>
<td></td>
</tr>
<tr>
<td>HCl – Hydrochloric acid</td>
<td></td>
</tr>
<tr>
<td>$H_2SO_4$ – Sulphuric acid</td>
<td></td>
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<tr>
<td>TEM – Transmission electron microscopy</td>
<td></td>
</tr>
</tbody>
</table>
Abbreviations & Notations

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
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PANI</td>
<td>Poly(aniline)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane)</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethyleneoxythiophene)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PTh</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene difluoride)</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Combined series resistance</td>
</tr>
<tr>
<td>$R_w$</td>
<td>Warburg resistance</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>Ruthenium oxide</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Sodium dodecyl benzene sulphonate</td>
</tr>
<tr>
<td>SC</td>
<td>Supercapacitor</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>SSC</td>
<td>Symmetric supercapacitor</td>
</tr>
</tbody>
</table>


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*)


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.

![Ragone plot of conventional capacitors, supercapacitors, batteries and fuel cells](image)

**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 (MnO₂) 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 MnO₂ is very low [21], in the range of 100–250 F g⁻¹. To improve the electrochemical performance, the conductivity of MnO₂-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 ($\Delta V$), 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 $\Delta V$ 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, \( \text{MnO}_2 \) 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 \( \text{MnO}_2 \)–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 as \( \text{MnO}_2 \) and \( \text{MoO}_3 \) as electrode materials.

The approaches are as follows:

(a) To investigate the structures that can be obtained in a binary \( \text{MnO}_2 @\text{PANI} \) system. It will be shown that a novel \( \text{MnO}_2 @\text{PANI} \) coaxial microrchin can be synthesized via a simple and green approach without any surfactant and additional oxidant. This \( \text{MnO}_2 @\text{PANI} \) microrchin 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 \( \text{MnO}_2 @\text{PANI} \) and reduced graphene oxide (RGO) system will be developed and evaluated. It will be demonstrated that a novel 3D RGO/\( \text{MnO}_2 @\text{PANI} \) porous hybrid film can be synthesized using GO and \( \text{MnO}_2 @\text{PANI} \) 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 MnO₂ and MoO₃ 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, MnO₂ 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 MnO₂–PANI system and the synthesis of PANI coated MnO₂ coaxial microuchins (MnO₂@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/MnO₂@PANI film based SSC, template guided graphene aerogel based SSC and their asymmetric combination to fabricate a solid-state ASC of graphene aerogel//RGO/MnO₂@PANI are discussed.

Chapter 6 deals with the issue of enhancing energy density by widening the operating voltage window by incorporating MnO₂ and MoO₃ 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/(MnO₂–RGO)/PANI porous film and 3D MoO₃/graphene aerogel is considered in detail. Finally, the summary of conclusions and recommendations for future work are given in Chapter 7.
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].

\[
C = \frac{Q}{V} \quad \text{......................................................... (2.1)}
\]

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].

\[
C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad \text{......................................................... (2.2)}
\]

where, \( \varepsilon_0 \) is the permittivity of the free space and \( \varepsilon_r \) is the dielectric constant of the material placed in between the plates.
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 Helmohltz 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].](image)

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:

\[
\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad \text{(2.3)}
\]
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.

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 RuO₂, MnO₂, Co₃O₄, TiO₂, V₂O₅, Mo₃O₄ and iron oxide Fe₃O₄, and CPs such as polyaniline (PANI), polythiophene (PTh) and polypyrrole (PPy) [5, 33].

Figure 2.3 Schematic illustration of charging and discharging of double-layer capacitor [36].
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 100–400 F g\(^{-1}\) and about 120–150 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 2–50 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 (~200 S m\(^{-1}\)) [40, 41], very large surface area (2650 m\(^2\) g\(^{-1}\)), unique charge-carrier mobility, high electrocatalytic activity and mechanical strength [42, 43]. The graphene is aromatic in nature possessing highly dense \(\pi\)-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.
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 2.4 Crystal structure of graphene [44].](image)

![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].](image)
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].

![Graphene sheet](image)

**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$_3$O$_4$, NiO, and V$_2$O$_5$. There are two basic requirements for a metal oxide in an SC are; (i) it must possess good electrical conductivity, and (ii) it must exists in two or more oxidation states without any phase change. The basics 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:

$$\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_{2-x}(\text{OH})_x$$

According to Equation 2.4, the fast exchange between proton and cation are in favor of reversible redox reaction. It was reported that RuO$_2$·0.5H$_2$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 100–200 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:

\[
\text{MnO}_2 + D^+ + e^- \leftrightarrow \text{MnO}_2 D \quad (2.5)
\]

where, $D^+$ = Li$^+$, Na$^+$, 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:

\[
\text{MnO}_2 + \text{H}_2\text{O} \leftrightarrow \text{MnOOH} + \text{OH}^- \quad (2.6)
\]

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 $\alpha$-, $\beta$-, and $\delta$-MnO$_2$. Both $\alpha$- and $\beta$-MnO$_2$ have tunnel structures, while $\delta$-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 $\delta$-MnO$_2$, to subsequently become tunnel structured $\alpha$- and $\beta$-MnO$_2$.

\[\text{MnO}_2 + \text{H}_2\text{O} \leftrightarrow \text{MnOOH} + \text{OH}^- \quad (2.6)\]

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 MnO₂ 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 α-MnO₂ nanorods (shown in Figure 2.8) through the hydrothermal method using potassium permanganate (KMnO₄) and sulfuric acid (H₂SO₄) 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 α-MnO₂ through hydrothermal reaction of KMnO₄ and H₂SO₄. The obtained morphology of the α-MnO₂ urchins is shown in Figure 2.9.

![Figure 2.8](image_url) **Figure 2.8** ((a), (b)) TEM images of the as-prepared α-MnO₂ nanorods; the inset shows the corresponding SAED pattern. ((c), (d)) HRTEM images of the α-MnO₂ 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-MnO₂ hollow urchins [65]. Adapted with permission from Ref. 65, Copyright (2007), American Chemical Society.

2.3.1.2.3 MoO₃

Other than MnO₂, molybdenum trioxide (MoO₃) has been regarded as a promising electrode material replacing RuO₂ in the field of SC due to its high electrochemical activity, low cost and environmentally benign nature [67]. MoO₃ acts like an n-type semiconductor. MoO₃ exist in three different polymorphs, which are: orthorhombic α-MoO₃, monoclinic β-MoO₃, and hexagonal h-MoO₃. Among these, α-MoO₃ is the thermodynamically stable phase, and h-MoO₃ the low temperature metastable phases [68]. The α-MoO₃ has attracted most interest due to its anisotropic layered structure. This layered structure provides for a large accessible are 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-MoO₃ was found to be 1111 mAh g⁻¹ [71]. The charge-discharge lithiation reaction of MoO₃ electrode can be presented by the following reaction [72]:

\[
\text{MoO}_3 + 2e^- + 2H^+ \rightarrow \text{Mo} + \text{H}_2 \text{O}
\]
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 $\alpha$-MoO$_3$ nanorods (shown in Figure 2.10) through the hydrothermal method using ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O) and nitric acid (HNO$_3$).

$$\text{MoO}_3 + x \text{Li}^+ + xe^- \xrightarrow{\text{charge}} \text{Li}_x\text{MoO}_3 \xrightarrow{\text{discharge}} \text{MoO}_3$$

(2.7)

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

\textbf{Figure 2.10} (a) – (d) SEM images of MoO$_3$ nanorods [73].
Tang et al. [72] followed a different technique to synthesize MoO$_3$ nanoplates as the anode materials for SCs through the sol-gel process using molybdenum (Mo) powder and hydrogen peroxide ($\text{H}_2\text{O}_2$) as precursors. The obtained morphology of the MoO$_3$ nanoplates is shown in Figure 2.12.
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]:

$$\text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + e^- \quad \text{................................................. (2.8)}$$

Another known candidate is Co$_3$O$_4$ due to its excellent reversible redox behavior, large surface area and good chemical stability [77]. Wang et al. [78] fabricated mesoporous Co$_3$O$_4$ microspheres that showed a $C_{sp}$ of 102 F g$^{-1}$. The charging mechanism of Co$_3$O$_4$ as an electrode material of pseudocapacitor is as follows [79]:

$$\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \leftrightarrow 3 \text{CoCOOH} + e^- \quad \text{......................... (2.9)}$$

Many other materials, such as SnO$_2$ [80, 81], IrO$_2$ [82], MoO$_2$ [83], NiCo$_2$O$_4$ [84, 85] and MnCo$_2$O$_4$ [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:

![Chemical structures of PANI, PPy and PTh](image)

**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.

![General chemical structure of polyaniline](image)

**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 $2 \times 10^{-1} \text{ S cm}^{-1}$ [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](image)

**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](image)

**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](image_url)

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 MnO₂, PANI and graphene based composite electrode materials will be briefly discussed.
2.3.1.4.1 MnO$_2$–PANI based composite electrode

In order to address the disadvantage of the low electronic conductivity of MnO$_2$, conductive polymers such as PANI are synthesized together with MnO$_2$ 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 MnO$_2$ by the electrodeposition and electro-copolymerization methods. It should be noted that the morphology of MnO$_2$ in the above composites was in the shape of particles. Liu et al. [95] electrochemically synthesized MnO$_2$ nanoparticles embedded in a 3D matrix of PANI doped polymers. Iranagh et al. [96] synthesized MnO$_2$–PANI nanofiber composites (as shown in Figure 2.18) by utilizing MnO$_2$ nanofibers as ‘seeds’. The MnO$_2$ nanofiber prepared from a chemical precipitation method was used as the seeds to facilitate the polymerization of aniline.

![Figure 2.18](image)

**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.

Sumboja et al. [25] developed manganese dioxide/polyaniline coaxial nanowire (MnO$_2$/PANI) networks using a double surfactant method. They first prepared MnO$_2$ nanorods through the hydrothermal route using manganese nitrate Mn(NO$_3$)$_2$ and KMnO$_4$ as the precursors, and next synthesized MnO$_2$/PANI coaxial nanowire using the surfactants polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) to coaxially grow PANI on MnO$_2$ nanowire through polymerization of aniline using ammonium persulfate (APS). The morphology of the obtained coaxial MnO$_2$/PANI nanowires is shown in Figure 2.19.
2.3.1.4.2 MnO$_2$–graphene based composite electrodes

Like PANI, graphene has also been incorporated with MnO$_2$ to increase its capacitance, rate capability and cycle life. An GO sheets supported needle–like MnO$_2$ nanocrystals (GO–MnO$_2$ 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 MnO$_2$ on graphene (RGO) sheets [98]. The RGO–MnO$_2$ 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 MnO$_2$–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](image)

**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 supercapacitors. Some common aqueous electrolytes are sulfuric acid (H₂SO₄), lithium perchlorate (LiClO₄), lithium tetrafluoroborate (LiBF₄), potassium hydroxide (KOH), potassium chloride (KCl), sodium hydroxide (NaOH) and sodium sulfate (Na₂SO₄) 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 (ΔV ~1.0 V). Water molecules dissociates above 1.23 V potential which is depicted by the equation 2 H₂O (l) = O₂ (g) + 4H⁺ + 4e⁻. 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 (C₂H₅)₄N⁺BF₄⁻, and quaternary ammonium salts − R₄N⁺Cl⁻, where, R = −CH₃ and −C₂H₅, exists in acetonitrile solvent. The organic electrolyte has high ESR which reduces the Cₛₚ. The Cₛₚ 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 Cₛₚ 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 Cₛₚ value. Some common ionic electrolytes are: 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆), 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-Ethyl-3-
methylimidazolium ethylsulfate ([EMIM]EtSO$_3$) and tris(2-hydroxyethyl)methylammoniummethylsulfate ([MTEOA]MeOSO$_3$).

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/LiClO$_4$ [105], PMMA/LiClO$_4$ [101], PVA/LiCl [30] and PAN-b-PEG-b-PAN/LiClO$_4$ [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/H$_2$SO$_4$ [12], PVA/H$_3$PO$_4$ [107], PVA/H$_3$PO$_4$/silicotungstic acid [108]. The gel electrolyte is usually prepared by dissolving the polymer and proton donor acid with a polar solvent. Usually H$_2$SO$_4$ and H$_3$PO$_4$ 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
Among these, the PVA/KOH gel electrolyte has a high ionic conductivity of the order of $10^{-2}$ 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 (Hg$_2$Cl$_2$/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]:

$$C = \frac{1}{\theta} = \frac{\int_{V_1}^{V_2} i(v) \, dv}{\theta (V_2 - V_1)} \tag{2.8}$$

where, the term in the numerator of Equation 2.8 represents the area of $I-V$ curve (Figure 2.21), $\theta$ 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].

$$\frac{1}{C_{\text{tot}}} = \frac{1}{C_1} + \frac{1}{C_2} \tag{2.9}$$

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

Assuming, $C_1 = C_2 = C$, where, $C =$ capacitance per single electrode.
So, \( \frac{1}{C_{tot}} = \frac{2}{C} \) or, \( C = 2C_{tot} \) …………………………… (2.10)

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

\[
C_{sp} = \frac{C_{tot}}{m} \quad …………………………… (2.11)
\]

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](image_url)  
**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]:

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m}$$

where, $C_{sp}$ is the specific capacitance ($\text{F g}^{-1}$), $I$ is the constant discharge current ($\text{A}$), $\Delta t$ is the total discharging time ($\text{s}$), $\Delta V$ 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 ($\eta$) which is the ratio of discharging time to charging time can be calculated by using Equation 2.13 [117].

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

where, $t_c$ and $t_d$ are the charging and discharging times ($\text{s}$). 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].](image)
The energy density \((E_{cell}, \text{Wh kg}^{-1})\) of a supercapacitor can be calculated from the following Equation 2.14 [116]:

\[
E_{cell} = \frac{1}{2} C_{sp} \Delta V^2 \tag{2.14}
\]

Where, \(C_{sp}\) = specific capacitance and \(\Delta V\) = operating voltage range.

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

\[
P_{cell} = \frac{E_{cell} \times 3600}{t \times 1000} \tag{2.15}
\]

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 a 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].
In the higher-frequency region, the intercept at $Z_{\text{real}}$ 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.

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:
\[
Q = C_{spe} \times \Delta V \times m 
\]

where, \( C_{spe} \) is the specific capacitance of the electrode, \( \Delta V \) 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]:

\[
\frac{m_+}{m_-} = \frac{c_{sp^-} \Delta V_-}{c_{sp^+} \Delta V_+} 
\]

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 (Fe₂O₃//MnO₂) ii) redox//double-layer type (MnO₂//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](image-url) (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. H$_2$O
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](image)

**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 \textit{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.](image)

### 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 m$^2$ 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.

![Polymer gel electrolyte and separator](image)

**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$_2$O$_4$ [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/H$_3$PO$_4$ 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] 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/H_3PO_4 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/HClO_4 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/H_2SO_4 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/H_3PO_4 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 RuO_2 nanowires on it with the help of a commercial inkjet printer using SWNT ink. A PVA/H_3PO_4 gel electrolyte was used together with the SWCNT/RuO_2 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/RuO$_2$ composite by functionalization of MWCNT with RuO$_2$ following direct redox reaction with potassium perruthenate (KRuO$_4$). The MWCNT/RuO$_2$ SSC had a $C_{sp}$ of 96 F g$^{-1}$ at 1.0 A g$^{-1}$ with good cyclic performance. However, RuO$_2$ 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 MnO$_2$, MoO$_3$, Co$_2$O$_4$, NiO and VO$_x$. Among these, MnO$_2$ has been recognized as the most attractive alternative material to RuO$_2$. Numerous solid-state SSC that are based on MnO$_2$ have been established in recent years [107, 181-185]. However, the low electrical conductivity ($10^{-5}$ to $10^{-6}$ S cm$^{-1}$) of MnO$_2$ has limited its application [147]. To overcome this limitation, the electrical conductivity has been improved by mixing MnO$_2$ with conductive carbon materials such as CNT, graphene or CPs. Yuan et al. [107] fabricated a highly flexible SSC by assembling two carbon nanoparticles/MnO$_2$ (CNps/MnO$_2$) hybrid electrodes that were prepared through flame synthesis followed by electrochemical deposition of MnO$_2$ 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@MnO$_2$ 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$_3$O$_4$ 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 H-TiO$_2$@MnO$_2$ and H-TiO$_2$@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 H-TiO$_2$@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 MoO$_3$–x@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 ZnO@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](image)

**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\(_2\)O\(_3\) 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 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>
<thead>
<tr>
<th>Chemical name</th>
<th>Supplier name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene oxide (GO) (99%, thickness: 0.7-1.2 nm)</td>
<td>CheapTubes, USA</td>
</tr>
<tr>
<td>Potassium permanganate (KMnO₄)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Aniline (reagent grade, 99%)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Ammonium persulfate (APS) (reagent grade, 98%)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Molybdenum (III) chloride (MoCl₃)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride) (PVDF) (powder form)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Dimethylfomamide (DMF) (99.8%)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Conductive carbon black (≥ 99%)</td>
<td>Age D’orPte Ltd, Singapore</td>
</tr>
<tr>
<td>Hydrazine monohydrate (reagent grade, ≥ 98%)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Potassium hydroxide (KOH)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Pluronic® F-68 solution (concentration 10%)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
<tr>
<td>Sodium dodecyl benzenesulfonate (SDBS)</td>
<td>Sigma-Aldrich, Singapore</td>
</tr>
</tbody>
</table>
The nickel (Ni) foam (1000 mm length × 300 mm width × 1.6 mm thickness) was purchased from MTI Corporation. Anodisc filter paper (pore Ø 0.2 µm) 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 (MemmertGmbH & 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 1x10⁻¹ 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 μA 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 Kα radiation with λ=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 (°/min). The compacted powder sample was scanned in the range from 5° < θ < 90° 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 Kα line (hν = 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
\(^\circ\)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 \(\text{\textdegree}\)C min\(^{-1}\) in the temperature range
from 25 to 500 \(\text{\textdegree}\)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:

\[
\frac{p}{\nu(p_0-p)} = \frac{1}{\nu_mc} + \frac{c-1}{\nu_mc} \frac{p}{p_0} \hspace{1cm} \text{.................. (3.1)}
\]
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 pallet (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:

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

The conductivity was determined using the following equations:

Resistivity ($\rho$, ohm-cm) = $\pi t/\ln2 (V/I) = 4.53 \times t \times \text{resistance}$

where, $V = \text{measured voltage}$ and $I = \text{applied current}$.

Conductivity ($\sigma$, 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 MnO₂-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 MnO₂–PANI binary composites to overcome the poor conductivity of MnO₂ and poor stability of PANI. However, one key problem in MnO₂–PANI binary composites is the lack of good contact between MnO₂ and PANI. It is essential to develop a new approach to improve the interaction between MnO₂ and PANI. Therefore, a core–shell morphology was developed in which highly ordered 3D hollow urchin-shaped MnO₂ had been synthesized first, following which coaxial PANI was grown on the MnO₂ surface using a controlled oxidation process.

Therein, in this report, a novel 3D hollow MnO₂@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 MnO₂ 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 MnO₂@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 MnO\(_2\) nanostructures

To prepare the MnO\(_2\) nanostructure, 2 mmol of KMnO\(_4\) 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 MnO\(_2\)@PANI composite

The as-prepared 160 mg of MnO\(_2\) 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 MnO\(_2\) 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 MnO$_2$@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 MnO$_2$@PANI//MnO$_2$@PANI symmetric supercapacitor (SSC) cell was formed.

The GF electrode was prepared following the same amount (wt%) as mentioned for MnO$_2$@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 MnO$_2$@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 MnO$_2$, MnO$_2$@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].
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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 m$^2$ g$^{-1}$, and the BJH adsorption and desorption cumulative pore volumes were found to be 0.580 and 0.639 cm$^3$ 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 4.1 (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.
Figure 4.2 (a) The N$_2$ 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 and D bands at 1350 cm$^{-1}$ corresponding to the E$_{2g}$ phonon of sp$^2$-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.
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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 $25.52^\circ$ corresponding to the interlayer d-spacing of 0.365 nm without showing any peak at $10.92^\circ$. 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.
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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 looks 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
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layer comprising a thin-walled MnO$_2$ microurchin. This confirms the successful preparation of MnO$_2$@PANI coaxial microurchin.

The chemical reaction for the synthesis of MnO$_2$ can be depicted by Equation 4.1.

\[ 2\text{KMnO}_4 + 8\text{HCl} = 2\text{KCl} + 2\text{MnO}_2 + 3\text{Cl}_2 + 4\text{H}_2\text{O} \]

\[ \text{Equation 4.1} \]

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.

Thus, the development of hollow MnO$_2$ microurchin [204] can be explained by following Figure A2 (see in Appendix). First, through the hydrothermal reaction between KMnO$_4$ solution and HCl, rose-like MnO$_2$ microspheres were formed (Figure A2a in Appendix). Gradually, nanospines grew from the surface of microspheres due to the 1D growth habit of the $\alpha$-MnO$_2$ 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 cannot 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).
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![Figure 4.7](image_url)

**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 $2\theta = 12.73^\circ$, $18.11^\circ$, $28.82^\circ$, $37.57^\circ$, $42.96^\circ$, $49.95^\circ$, $56.77^\circ$, $60.36^\circ$, $65.18^\circ$, and $69.36^\circ$, correspond to the expected diffraction peaks of (110), (200), (310), (211), (301), (411), (600), (521), (002), and (741) crystal planes of $\alpha$-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 $\alpha$-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 $\sim 20–22^\circ$ 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].
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Raman spectroscopic study was carried out to ensure the presence of MnO$_2$ and PANI in the MnO$_2$@PANI composite by investigating the vibration properties of the as-prepared samples. In the Raman spectrum of MnO$_2$@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 MnO$_2$ and PANI. The Raman spectrum of MnO$_2$ shows a peak at 637 cm$^{-1}$ (as shown in inset Figure 4.9i’), assigned to the symmetric stretching vibration (Mn–O) of the MnO$_6$ groups [209], which is also present in MnO$_2$@PANI at 608 cm$^{-1}$. This confirms that MnO$_2$ has been successfully coated by PANI.

**Figure 4.8** XRD patterns of (i) MnO$_2$ and (ii) MnO$_2$@PANI composite materials.
Further to confirm that the MnO$_2$ microurchin was successfully coated with PANI, an FTIR study was carried out, and a comparison of the spectra of MnO$_2$ and MnO$_2$@PANI are depicted in Figure 4.10. In Figure 4.10i, the characteristic peak of MnO$_2$ at about 725 cm$^{-1}$ pertained to Mn–O vibrations of MnO$_6$ octahedra in MnO$_2$ 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 MnO$_2$@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 MnO$_2$@PANI coaxial microurchin also shows identical pure PANI characteristic peaks [212]. The characteristic peak of MnO$_2$ at 725 cm$^{-1}$ was shifted to 710 cm$^{-1}$ for MnO$_2$@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 MnO$_2$ spines.
The existence of a PANI coating on the MnO$_2$ microuchins was further confirmed by XPS analysis of MnO$_2$ and MnO$_2$@PANI composite. The analysis is shown in Figure 4.11. The characteristic Mn 2p peaks of MnO$_2$ 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 MnO$_2$@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 MnO$_2$@PANI coaxial microuchins, where MnO$_2$ has been coated with PANI.

The conductivity of MnO$_2$ and MnO$_2$@PANI composite were found to be 6.87 × 10$^{-3}$ and 2.89 × 10$^{-1}$ S m$^{-1}$ respectively. This large increase in conductivity of the MnO$_2$@PANI composite is due to the encapsulation of MnO$_2$ microuchin by the conductive PANI layer.
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![Figure 4.11](image.png)

**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.

4.3.2.3 MnO$_2$@PANI coaxial microurchin formation mechanism

The formation mechanism of PANI coating on the MnO$_2$ microurchin can be explained by considering the chemical oxidation potential of MnO$_2$ (1.23 V) \[56\], which is sufficient to make aniline monomers to polymerize on the MnO$_2$ 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 MnO$_2$ microurchin surface is sacrificed while the aniline monomers that are being polymerized surround its surface, leading to the formation of PANI coating on the MnO$_2$ microurchin. Based on the above results, a schematic presentation of MnO$_2$@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 MnO$_2$@PANI microurchin shows a core–shell structure in which MnO$_2$ microurchin
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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 [An$^+$]$^+$ radical cation that interacts with another [An$^+$]$^+$ 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.

![Schematic diagram](image)

**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.
4.3.2.4 Electrochemical measurements

The capacitive performance of the flexible solid-state MnO$_2$@PANI//MnO$_2$@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 MnO$_2$@PANI represent a combination of the pseudocapacitive properties of both MnO$_2$ 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 MnO$_2$. 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 MnO$_2$ 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 MnO$_2$@PANI//MnO$_2$@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.
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![Figure 4.13](image)

**Figure 4.13** (a) CV curves at different scan rates and (b) CCD curves at different current densities of MnO$_2$@PANI composite.

The constant current charge–discharge curves (CCD) of MnO$_2$@PANI//MnO$_2$@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 MnO$_2$@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 MnO$_2$@PANI coaxial composite can be attributed to following factors:

1. The existence of electrically conductive PANI coating over MnO$_2$ nanospines facilitates faster electron transport, which helps to overcome the limitations of poor conductivity and low charge–discharge rates of MnO$_2$. [222].

2. PANI has good electrochemical pseudocapacitive properties [223].

3. H-bond interaction between MnO$_2$ 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 MnO$_2$@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 MnO$_2$@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 MnO$_2$@PANI electrodes in the three-electrode system. The effective potential window for GF//MnO$_2$@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//MnO$_2$@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//MnO$_2$@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 show 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//MnO$_2$@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//MnO$_2$@PANI ASC shows moderate rate capability through the combined effects from the positive and negative electrodes.
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**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.
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//MnO\(_2@\)PANI ASC is higher than that of the MnO\(_2@\)PANI//MnO\(_2@\)PANI and GF//GF SSCs at the same power density. The energy density was increased about 2.5-times with respect to the MnO\(_2@\)PANI//MnO\(_2@\)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//MnO\(_2@\)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 MnO\(_2@\)PANI//MnO\(_2@\)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 MnO\(_2\) core, which serves as a backbone to limit the degradation of PANI due to volumetric change during cycling. The crystal structure of α-MnO\(_2\) 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-MnO\(_2\) 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 MnO\(_2\) and PANI inhibits the dissolution of MnO\(_2\) and PANI, and consequently improve the electrochemical reversibility and stability of the composite electrode. The uniform PANI coating on MnO\(_2\) micourchin surface helps to prevent dissolution of MnO\(_2\) by acting as a protective layer, which favors the retaining of the higher capacitance after cyclic test.
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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).
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//MnO$_2$@PANI and GF//GF SCs showed similar capacitance retention after 5000 cycles, the initial rate of capacitance loss of the GF//MnO$_2$@PANI ASC was a bit faster (2–3%) compared to the MnO$_2$@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 MnO$_2$@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 MnO$_2$@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 MnO$_2$@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 MnO$_2$@PANI//MnO$_2$@PANI and GF//MnO$_2$@PANI solid-state SCs are shown in Figure 4.15d. The intercept on $Z_{\text{real}}$ (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, MnO$_2$@PANI SSCs and GF//MnO$_2$@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 MnO$_2$@PANI. The GF electrode material has a lower $R_{ct}$ as compared to the
MnO$_2$@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 ~45° 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 MnO$_2$@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 MnO$_2$@PANI//MnO$_2$@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 MnO$_2$@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 MnO$_2$@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.

![FESEM images MnO$_2$@PANI microstructure (a) before and (b) after 5000 cyclic charge–discharge test.](image)

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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Power density (kW kg⁻¹)</th>
<th>Cyclic stability (% of capacitance retention)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid-state symmetric supercapacitor (SSCs)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene hydrogel film</td>
<td>H₂SO₄/PVA gel</td>
<td>0.61</td>
<td>0.670</td>
<td>91.6 (after 10000 cycles)</td>
<td>[227]</td>
</tr>
<tr>
<td>CNTs/bacterial nano-cellulose paper</td>
<td>PS-PEO-PS/[EMIM] [NTf₂]</td>
<td>15.5</td>
<td>1.500</td>
<td>99.5 (after 5000 cycles)</td>
<td>[172]</td>
</tr>
<tr>
<td>PANI/CNT</td>
<td>H₂SO₄/PVA gel</td>
<td>7.1</td>
<td>2.200</td>
<td>91.9 (after 1000 cycles)</td>
<td>[12]</td>
</tr>
<tr>
<td>Graphene @carbon cloth</td>
<td>H₂SO₄/PVA gel</td>
<td>1.64</td>
<td>0.670</td>
<td>--</td>
<td>[228]</td>
</tr>
<tr>
<td>MnO₂@PANI</td>
<td>PVA/KOH gel</td>
<td>17.9</td>
<td>0.261</td>
<td>84.7 (after 5000 cycles)</td>
<td>this work</td>
</tr>
<tr>
<td>GF</td>
<td>PVA/KOH gel</td>
<td>11.4</td>
<td>0.255</td>
<td>89 (after 5000 cycles)</td>
<td>this work</td>
</tr>
<tr>
<td><strong>Solid-state asymmetric supercapacitors (ASCs)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene (IL-CMG)//RuO₂–IL-CMG</td>
<td>H₂SO₄/PVA gel</td>
<td>19.7</td>
<td>6.800</td>
<td>95 (after 2000 cycles)</td>
<td>[18]</td>
</tr>
<tr>
<td>MnO₂@ poly(3,4-ethylene-dioxythiophene)//poly(3,4-ethylene-dioxythiophene)</td>
<td>LiClO₄/PMMA gel</td>
<td>9.8</td>
<td>0.850</td>
<td>86 (after 1250 cycles)</td>
<td>[101]</td>
</tr>
<tr>
<td>CNTs/MnO₂//CNTs/PANI</td>
<td>Na₂SO₄/PVP gel</td>
<td>24.8</td>
<td>0.120</td>
<td>--</td>
<td>[229]</td>
</tr>
<tr>
<td>GF//MnO₂@PANI</td>
<td>PVA/KOH gel</td>
<td>37.0</td>
<td>0.386</td>
<td>88.6 (after 5000 cycles)</td>
<td>this work</td>
</tr>
</tbody>
</table>
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It can be seen from the table, compared to other literature data for solid-state SSCs and ASCs, the as synthesized GF//MnO$_2$@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 MnO$_2$@PANI composite was made from the redox active materials, in which the MnO$_2$ and PANI phases mutually protect and enhance their capacitive performance. This MnO$_2$@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 MnO$_2$@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 MnO$_2$@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/MnO$_2$@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 H$_2$SO$_4$ 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 H$_2$SO$_4$ 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 MnO$_2$@PANI micourchin 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 MnO$_2$@PANI also provides high pseudocapacitive value by the synergistic effect of MnO$_2$ 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, MnO$_2$@PANI micro-urchins act as a spacer
that prevents the GO sheets from collapsing and attaching to each together. 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/MnO$_2$@PANI (RGO/MnO$_2$@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 $\pi-\pi$ 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 NaClO$_4$ electrolyte [232]. Recently, Jiang et al. fabricated self-assembled 3D reduced graphene oxide by divalent ions (Ca$^{2+}$, Ni$^{2+}$, or Co$^{2+}$) 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/MnO$_2$@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 MnO$_2$@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/MnO$_2$@PANI hybrid film and 3D graphene aerogel.

5.2 Experimental

5.2.1 Synthesis of porous RGO/MnO$_2$@PANI hybrid film

Details of the synthesis of urchin-shaped coaxial MnO$_2$@PANI particles have been outlined in Chapter 4. In the present work, the as-prepared MnO$_2$@PANI coaxial urchin-shaped particles were used to fabricate the porous RGO/MnO$_2$@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 MnO$_2$@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 MnO$_2$@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.
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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 $^\circ$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 $^\circ$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 $\times$ 20 mm $\times$ 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/MnO$_2$@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/MnO$_2$@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/MnO$_2$@PANI SSC cells were created.
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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/MnO$_2$@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.
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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 m$^2$ 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 E₂g 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.
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$^\circ$ and 26.5$^\circ$. The sharp peaks at 19.8$^\circ$ and 23.4$^\circ$ 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$^\circ$ 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$^\circ$ 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 5.3 Raman spectroscopy (i) GO, (ii) raw-GF20 and (iii) GF20 aerogel.
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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 looks 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.
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![Graph showing CV curves and CCD curves for different conditions](image)

**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/MnO$_2$@Polyaniline (RGO/MnO$_2$@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 MnO$_2$@PANI nanostructures onto the surfaces of GO sheets. The advantage of this technique is that the MnO$_2$@PANI produced, acts as a spacer in between graphene sheets, thus preventing the sheets from aggregating. Moreover, during the reduction process, gaseous products (H$_2$O (g) and CO$_2$ (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 MnO$_2$@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 MnO$_2$@PANI particles and gas entrapment (H$_2$O (g) and CO$_2$ (g)) in the RGO matrix. This high exfoliation and the MnO$_2$@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 MnO$_2$@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.
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5.3.2.2 Molecular characterization

The structure of the MnO$_2$@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 MnO$_2$@PANI exhibits 20 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-MnO$_2$ 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 2θ = 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-MnO$_2$ 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 2θ = ~25° which corresponds to the crystal plane of RGO, confirming the reduction of GO to RGO [201, 202].
Raman spectroscopy was used to confirm the reduction of GO to RGO, and the presence of interaction between MnO$_2$@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 MnO$_2$@PANI and RGO/M@P25 film are shown in Figure 5.10iii and 5.10iv respectively. MnO$_2$@PANI shows all the characteristic peaks of MnO$_2$ 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 MnO$_2$@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 MnO$_2$@PANI composite and the RGO film, which indicates that there is an interaction between MnO$_2$@PANI and RGO film.
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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 MnO$_2$ 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 MnO$_2$@PANI. The combination of graphene layer and MnO$_2$@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 MnO\(_2\) and PANI materials increased. The conductive PANI layer on the MnO\(_2\) 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.
It can be seen that the MnO$_2$@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 $C_p$ increased with increasing MnO$_2$@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 MnO$_2$@PANI, the micrurchins 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 ($m_p/m_n$) 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 $0$ to $-1.0$, $0$ to $-1.2$, $-1.4$, $0$ to $-1.5$ and $0$ to $-1.6$ 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 $0$ to $1.5$ 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 $0$ to $1.5$ 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 $0$ to $1.5$ 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$^{-1}$. 

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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 ~45° 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 MnO$_2$ 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 MnO$_2$ 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 MnO$_2$@PANI during charge-discharge cycling, is mitigated by the RGO film matrix which covers and protects the MnO$_2$@PANI phase. The GF40/RGO/M@P25 ASC shows stable Coulombic efficiency ~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.
Chapter 5  Development of 3D porous graphene/MnO₂@polyaniline hybrid film and 3D graphene aerogel for all-solid-state flexible asymmetric supercapacitor

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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Power density (kW kg⁻¹)</th>
<th>Cyclic stability (% of capacitance retention)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene hydrogel film</td>
<td>H₂SO₄/PVA gel</td>
<td>0.61</td>
<td>0.67</td>
<td>91.6 (after 10000 cycles)</td>
<td>[227]</td>
</tr>
<tr>
<td>RCF/MnO₂/PEDOT</td>
<td>PVA/KCl gel</td>
<td>19.17</td>
<td>0.500</td>
<td>83 (after 10000 cycles)</td>
<td>[236]</td>
</tr>
<tr>
<td>CNTs/bacterial nanocellulose paper</td>
<td>PS-PEO-PS/[EMIM][NTf₂]</td>
<td>15.5</td>
<td>1.500</td>
<td>99.5 (after 5000 cycles)</td>
<td>[172]</td>
</tr>
<tr>
<td>PANI/CNT</td>
<td>H₂SO₄/PVA gel</td>
<td>7.1</td>
<td>2.2</td>
<td>91.9 (after 1000 cycles)</td>
<td>[12]</td>
</tr>
<tr>
<td>Graphene @carbon cloth</td>
<td>H₂SO₄/PVA gel</td>
<td>1.64</td>
<td>0.670</td>
<td>--</td>
<td>[228]</td>
</tr>
<tr>
<td>Polypyrrole nanofiber/RGO</td>
<td>PVA/H₃PO₄ gel</td>
<td>20.6</td>
<td>1.280</td>
<td>79.8 (after 1000 cycles)</td>
<td>[237]</td>
</tr>
<tr>
<td>RGO/MnO₂@PANI (RGO/M@P25) film</td>
<td>PVA/KOH gel</td>
<td>18.33</td>
<td>0.388</td>
<td>83.9 (after 5000 cycles)</td>
<td>this work</td>
</tr>
<tr>
<td>Graphene aerogel-(GF40)</td>
<td>PVA/KOH gel</td>
<td>15.41</td>
<td>0.523</td>
<td>88.6 (after 5000 cycles)</td>
<td>this work</td>
</tr>
</tbody>
</table>
Chapter 5  Development of 3D porous graphene/MnO$_2$@polyaniline hybrid film and 3D graphene aerogel for all-solid-state flexible asymmetric supercapacitor

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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Energy density (Wh kg$^{-1}$)</th>
<th>Power density (kW kg$^{-1}$)</th>
<th>Cyclic stability (% of capacitance retention)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene (IL-CMG)//RuO$_2$–IL-CMG</td>
<td>H$_2$SO$_4$/PVA gel</td>
<td>19.7</td>
<td>6.800</td>
<td>95 (after 2000 cycles)</td>
<td>[18]</td>
</tr>
<tr>
<td>N-doped graphene/layered MnO$_2$//AC</td>
<td>PVA/LiCl gel</td>
<td>31.67</td>
<td>0.222</td>
<td>90.5 (after 1500 cycles)</td>
<td>[238]</td>
</tr>
<tr>
<td>MnO$_2$@ poly(3,4-ethylene-dioxythiophene)//poly(3,4-ethylene-dioxythiophene)</td>
<td>LiClO$_4$/PMMA gel</td>
<td>9.8</td>
<td>0.850</td>
<td>86 (after 1250 cycles)</td>
<td>[101]</td>
</tr>
<tr>
<td>GNR//GNR-MnO$_2$</td>
<td>PAAK/KCl gel</td>
<td>29.4</td>
<td>12.1</td>
<td>88 (after 5000 cycles)</td>
<td>[239]</td>
</tr>
<tr>
<td>CNTs/MnO$_2$//CNTs/PANI</td>
<td>Na$_2$SO$_4$/PVP gel</td>
<td>24.8</td>
<td>0.120</td>
<td>--</td>
<td>[229]</td>
</tr>
<tr>
<td>TiN@GNS//Fe$_2$N@GNS</td>
<td>PVA/LiCl gel</td>
<td>15.4</td>
<td>6.4</td>
<td>~98 (after 20000 cycles)</td>
<td>[13]</td>
</tr>
<tr>
<td>GF40//RGO/M@P25</td>
<td>PVA/KOH gel</td>
<td>38.12</td>
<td>1.191</td>
<td>85.8 (after 5000 cycles)</td>
<td>this work</td>
</tr>
</tbody>
</table>
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/MnO$_2$@polyaniline (RGO/MnO$_2$@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 MnO$_2$@PANI particles that acted as spacers to mitigate agglomeration of the 3D RGO layers to maximize the surface area for ion transfer. The MnO$_2$@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 MnO$_2$–graphene electrode and MoO$_3$/graphene aerogel

6.1 Introduction

In Chapter 5, MnO$_2$, 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, MnO$_2$ 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/(MnO$_2$–RGO)/PANI can be used in conjunction with a suitable negative electrode material. MoO$_3$ has emerged as an alternate potential oxide material to MnO$_2$, 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 MoO$_3$ ($\psi = 6.9$ eV) and MnO$_2$ ($\psi = 4.4$ eV) [32]. Therefore, MoO$_3$ 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/(MnO$_2$−RGO)/PANI material as the positive electrode and MoO$_3$/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/(MnO$_2$−RGO)/PANI porous film

Details of the synthesis of the MnO$_2$ nanoparticles have been outlined in Chapter 4. In the present work, the as-prepared MnO$_2$ urchin-shaped particles were used to fabricate the porous RGO–MnO$_2$ 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 MnO$_2$ particles was dispersed in GO solution by ultrasonication. After that, the MnO$_2$ and GO suspension was filtered through an anodisc membrane (pore diameter - 0.2 µm) 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 MnO$_2$–GO film was reduced by hydrazine vapor. The film was hung in a Teflon-lined stainless steel autoclave containing 200 µL of hydrazine monohydrate, and kept in an electric oven at 110 °C for 10 h. The reduced film (MnO$_2$–RGO) was then dried in air. Next, the as-prepared MnO$_2$–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 µL 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/(MnO$_2$–RGO)/PANI film was stored for characterization. The amount of PANI in the PANI/(MnO$_2$–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-sate 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 MoO$_3$/GF composite materials

6.3.1.1 Molecular characterization

The XRD plots for the GO, GF, MoO$_3$ and MoO$_3$/GF5 materials are as shown in Figure 6.1. The MoO$_3$ nanoparticles show diffraction peaks at 2θ = 12.9°, 23.5°, 25.8°, 27.5°, 33.9°, 39.1°, 46.2°, 49.5°, 53.0°, 55.3°, 56.5°, 58.0°, 59.0° and 64.3°. The MoO$_3$/GF5 exhibits the diffraction peaks at 12.7°, 22.9°, 25.3°, 26.9°, 33.3°, 38.6°, 45.5°, 48.6°, 54.8°, 58.5° and 64.5°. These peaks correspond to the diffraction peaks of α-MoO$_3$ (JCPDS No.65-2421). The intensity of the α-MoO$_3$ peaks decreased in MoO$_3$/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 MoO$_3$/GF5 composite since the high intensity peaks of MoO$_3$ overlapped in the same region. This confirms that the GO has been reduced by vitamin C during hydrothermal treatment.

The Raman spectroscopy study was used to analyze the structural behavior of the MoO$_3$/GF composites. The Raman spectra of GO, GF, MoO$_3$ and MoO$_3$/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 MoO$_3$/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 MoO$_3$/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]. MoO$_3$/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 100–400 cm$^{-1}$ can be attributed to the different bending modes of α-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 MoO$_3$/GF5, respectively (inset shows magnified Raman spectra of GO, GF, and MoO$_3$/GF5).](image)

To further confirm the formation of MoO$_3$, FTIR study was carried out for the GF, MoO$_3$ and MoO$_3$/GF5 materials and the data can be seen in Figure 6.3. In MoO$_3$/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.

![FTIR spectrum](image)

**Figure 6.3** FTIR of GF, MoO$_3$ and MoO$_3$/GF5 materials.

The elemental analysis of the GF and MoO$_3$/GF5 hybrid materials was carried out using XPS. The wide scan spectrum of MoO$_3$/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 MoO$_3$/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 MoO$_3$/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.
Chapter 6  Novel all-solid-state flexible asymmetric supercapacitor based - polyaniline decorated porous MnO₂−graphene electrode and MoO₃/graphene aerogel

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 MoO$_3$ crystals decrease the porosity and the specific surface area of the composite. The nitrogen adsorption–desorption isotherms of GF, MoO$_3$/GF5 and MoO$_3$/GF10 are shown in Figure 6.6. The BET specific surface areas of GF, MoO$_3$/GF5 and MoO$_3$/GF10 (calculated using BET equation) were found to be 295, 227 and 104 m$^2$ g$^{-1}$, respectively.

**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.

**Figure 6.6** The N$_2$ adsorption–desorption isotherm loop of GF, MoO$_3$/GF5 and MoO$_3$/GF10 materials.
The formation of the MoO$_3$/GF5 aerogel can be explained as follows. Initially, a 3D free-standing hydrogel column of MoCl$_3$/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 MoCl$_3$ nanoparticles. Mo ([Kr] 4d$^5$ 5s$^1$) has a vacant 4d orbital. Hence, it is possible for coordination bond formation between MoCl$_3$ and the O containing functional groups of GO during hydrothermal treatment as shown in Figure 6.7a. During heat treatment of MoCl$_3$/GF in O$_2$ atmosphere, MoCl$_3$ would be converted into MoO$_3$ and Cl$_2$. The reaction can be written as follows [241]:

$$2\text{MoCl}_3 + 3\text{O}_2 = 2\text{MoO}_3 + 3\text{Cl}_2, \hspace{1cm} \Delta H = -85 \text{ Kcal mol}^{-1}$$

A schematic diagram for the distribution of MoO$_3$ nanocrystals in graphene matrix is shown in Figure 6.7b. In MoO$_3$/GF5 composite, the Mo atom of the MoO$_3$ may bind adjacent graphene sheets together via intermolecular H-bonds or covalent or coordination bonds.

![Figure 6.7](image.png)

*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.

The weight loss due to the conversion of MoCl$_3$ to MoO$_3$ 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 MoCl$_3$ into MoO$_3$.

![TGA analysis of MoCl$_3$ in O$_2$ atmosphere.](image)

**Figure 6.8** TGA analysis of MoCl$_3$ in O$_2$ atmosphere.

### 6.3.1.3 Electrochemical analysis and performance

The cyclic voltammetry (CV) plots of the MoO$_3$/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 MoO$_3$ 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 MoO$_3$ 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 MoO$_3$/GF SSC were calculated utilizing data from the discharge curve using Equation 2.12 and 2.14. The $C_{sp}$ of MoO$_3$/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 MoO\(_3\) particles which undergo in reversible redox reaction. Here, the graphene sheets are intertwined and innately attached with MoO\(_3\) nanocrystals serving a dual role. Firstly, it provides conductive network channels and secondly, its large active surface area contributes to EDL capacitance. The MoO\(_3\) nanocrystals shorten the diffusion path of the electrolyte ions and transports electrons continuously in-between graphene sheets. Moreover, the MoO\(_3\) 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 MoO\(_3\)/GF composite samples (MoO\(_3\)/GF2.5, MoO\(_3\)/GF5 and MoO\(_3\)/GF10) are shown in Figure 6.9c. It was found that the MoO\(_3\)/GF2.5 sample that contained MoO\(_3\) 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 MoO\(_3\)/GF5 sample which had higher MoO\(_3\) content and had a uniform distribution of MoO\(_3\) nanocrystals in the matrix had the highest capacitance (136 F g\(^{-1}\) at 1 A g\(^{-1}\)). The MoO\(_3\)/GF10 composite which exhibited agglomeration of MoO\(_3\) nanocrystals, shows a lower capacitance value about 105 F g\(^{-1}\) (at 1 A g\(^{-1}\)) than the MoO\(_3\)/GF5 composite. This revealed that the agglomeration of MoO\(_3\) nanocrystals at a higher weight ratio hindered ion transfer between the graphene sheets. Hence, the MoO\(_3\)/GF5 composite was selected for further study in ASC.

Electrochemical impedance spectroscopy (EIS) study was carried out for MoO\(_3\)/GF5 SSC and GF SSC in the frequency range of 100 kHz to 1 Hz. The Nyquist plots of the GF and MoO\(_3\)/GF5 based SSCs are shown in Figure 6.9d. In the high frequency region, the intercept on Z\(_{\text{real}}\) axis represents the combined resistance (R\(_s\)) which are found to be 0.46 and 0.34 ohm for the GF and MoO\(_3\)/GF5 SSCs. The lower resistance in the latter is probably due to doping of MoO\(_3\) 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
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SSC exhibits a steeper straight line than the MoO₃/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 MoO₃/GF5 SSC; (c) comparison CCD plots of MoO₃/GF2.5, MoO₃/GF5 and MoO₃/GF10 SSCs at 1 A g⁻¹ current density, (d) EIS of GF SSC and MoO₃/GF5 SSC and (e) cyclic stability of MoO₃/GF5 SSC.
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The MoO$_3$/GF5 SSC showed high cyclic stability with ~85% capacitance retention after 5000 cycles as seen in Figure 6.9e. The good cyclic life of MoO$_3$/GF can be attributed to the uniform distribution of MoO$_3$ nanocrystals in graphene aerogel matrix, which covers the MoO$_3$ and prevent the degradation during charge-discharge cycling. The graphene coating here acts as a protective layer to prevent faster dissolution of the MoO$_3$ during the cycling process.

6.3.2 PANI/(MnO$_2$–RGO)/PANI hybrid film

6.3.2.1 Molecular characterization

The sandwich-type PANI/(MnO$_2$–RGO)/PANI hybrid film which was labeled as (P/(M–R)/P) film was prepared in three steps. Firstly, MnO$_2$ nanoparticle was synthesized through hydrothermal reaction. Secondly, porous MnO$_2$–RGO film was fabricated by vacuum filtration of MnO$_2$ and GO suspension followed by reduction with hydrazine vapor. Finally, PANI nanofibers were grown on the surface of the MnO$_2$–RGO porous film.

The XRD diffraction patterns of the MnO$_2$ nanoparticles, MnO$_2$–RGO and P/(M–R)/P films are shown in Figure 6.10. The MnO$_2$ shows diffraction peaks at $\theta = 12.7^\circ$, 18.1°, 28.8°, 37.5°, 42.1°, 49.9°, 56.7°, 60.3°, 65.1°, 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-MnO$_2$ standard data (JCPDS card PDF file no. 44-0141) [205], respectively. The MnO$_2$–RGO composite shows similar diffraction peaks at $\theta = 12.8^\circ$, 18.2°, 28.9°, 37.6°, 42.2°, 49.9°, 56.8°, and 60.3° corresponding to the crystal plane of α-MnO$_2$. However, the peak intensities were lower in the latter. In the MnO$_2$–RGO composite, the peak located at 10.8° for GO (001) crystal plane corresponding to the d-pacing of 0.321 Å disappeared. A new broad peak appeared corresponding to the crystal plane of RGO at ~26°, which was not so obvious as the MnO$_2$ peaks intensity were very high. The sandwich-type P/(M–R)/P film shows a broad peak at ~22° 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 MnO$_2$ particles and RGO did not appear.
Raman spectroscopy was carried out to confirm the presence of PANI, MnO$_2$ and RGO in the P/(M−R)/P film. Figure 6.11 displays the Raman spectra of MnO$_2$–GO, MnO$_2$–RGO and P/(M−R)/P films. The MnO$_2$–GO shows the peak at 639 cm$^{-1}$ corresponding to the Mn−O symmetric stretching vibration of the MnO$_6$ octahedral [209]. The peaks at 1350 and 1585 cm$^{-1}$ correspond to the characteristic D-band and G-band, respectively. The MnO$_2$–RGO also shows similar peaks at the same region as in the MnO$_2$–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 MnO$_2$–RGO film.
6.3.2.2 Morphological analysis

The morphology of MnO$_2$ nanoparticles are outlined in detail in Chapter 4. Figure 6.12a illustrates the cross-sectional side view FESEM image of the MnO$_2$−GO film which had been converted into the 3D porous MnO$_2$−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 MnO$_2$−RGO film had been exfoliated by the MnO$_2$ nanoparticles and the entrapped gaseous species. From Figure 6.12c, it is clear that the MnO$_2$ 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) 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.

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 MnO$_2$–GO film, the oxygen containing functional groups of GO assist the MnO$_2$ nanoparticles to anchor with the GO sheets. The vacant 3d orbital of Mn in MnO$_2$ may form coordination bonds with O of the GO functional groups. Similarly, H-bonds may also be formed between O of MnO$_2$ and H of GO functional groups. The formation of these coordination and H-bonds enable the even distribution and anchoring of MnO$_2$ in the GO matrix. The 3D porous MnO$_2$–RGO film which was formed by the reduction of MnO$_2$–GO film was formed, not only by exfoliation due to the MnO$_2$ nanoparticles, but also by the released gaseous species (CO$_2$ ($g$) and H$_2$O ($g$)) during reduction by hydrazine vapor. As the obtained MnO$_2$–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 MnO$_2$–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/(MnO$_2$–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 MnO$_2$–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
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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 MnO$_2$–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. MnO$_2$ 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 $\sim$45° slope portion of the curve in the lower frequency region [41]. The RGO film SSC exhibits a steeper straight line than the P/(M–R)/P film SSC due to its pure EDL type behavior where faster diffusion of charge happens. The presence of pseudocapacitive materials (MnO$_2$ 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 $\sim$78% after 5000 cycles as shown in Figure 6.14d. The lower capacitance retention of P/(M–R)/P film SSC is due to the relatively faster degradation of the PANI wrapping on the MnO$_2$–RGO film.
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 MoO$_3$/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 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 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 to found to be 0.88.

To determine the most effective operational working window of the solid-state MoO\(_3\)/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 MoO\(_3\)/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 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.
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 MoO\(_3\)/GF5 SSC and P/(M–R)/P film SSC had ~85 and ~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.

\[\text{Energy density (Wh kg}^{-1}\)]
\[\text{Power density (kW kg}^{-1}\)]

\[\text{MoO}_3\text{/GF5//P/(M–R)/P ASC}
\[\text{P/(M–R)/P SSC}

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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Energy density (Wh kg$^{-1}$)</th>
<th>Power density (kW kg$^{-1}$)</th>
<th>Cyclic stability (% of capacitance retention)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$@ poly(3,4-ethylenedioxythiophene)//poly(3,4-ethylenedioxythiophene)</td>
<td>LiClO$_4$/PMMA gel</td>
<td>9.8</td>
<td>0.850</td>
<td>86 (after 1250 cycles)</td>
<td>[101]</td>
</tr>
<tr>
<td>TiN@GNS//Fe$_2$N@GNS</td>
<td>PVA/LiCl gel</td>
<td>15.4</td>
<td>6.4</td>
<td>~98 (after 20000 cycles)</td>
<td>[13]</td>
</tr>
<tr>
<td>Graphene (IL-CMG)//RuO$_2$–IL-CMG ASCs</td>
<td>H$_2$SO$_4$/PVA gel</td>
<td>19.7</td>
<td>6.800</td>
<td>95 (after 2000 cycles)</td>
<td>[18]</td>
</tr>
<tr>
<td>CNTs/MnO$_2$//CNTs/PANI</td>
<td>Na$_2$SO$_4$/PVP gel</td>
<td>24.8</td>
<td>0.120</td>
<td>--</td>
<td>[229]</td>
</tr>
<tr>
<td>GNR//GNR–MnO$_2$</td>
<td>PAAK/KCl gel</td>
<td>29.4</td>
<td>12.1</td>
<td>88 (after 5000 cycles)</td>
<td>[239]</td>
</tr>
<tr>
<td>N-doped graphene/layered MnO$_2$//AC</td>
<td>PVA/LiCl gel</td>
<td>31.67</td>
<td>0.222</td>
<td>90.5 (after 1500 cycles)</td>
<td>[238]</td>
</tr>
<tr>
<td>MoO$_3$/GF5//P/(M–R)/P</td>
<td>PVA/KOH gel</td>
<td>51.91</td>
<td>0.838</td>
<td>82 (after 5000 cycles)</td>
<td>this work</td>
</tr>
</tbody>
</table>

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 MnO$_2$ and MoO$_3$ in the positive and negative electrodes respectively, and adopting a 3D heterogeneous composite based
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Facile methods were used to synthesize the negative and positive electrode materials. The negative electrode comprised a self-assembled 3D MoO$_3$/graphene hydrogel foam. The positive electrode consisted of a PANI decorated porous 3D MnO$_2$–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 microuchin was developed without using any external oxidant, and optimized the PANI thickness on the nascent MnO$_2$ microuchin surface. The synthesis process utilized for the MnO$_2$@PANI microuchin 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 microuchin and graphene foam (GF) as the positive and the negative electrode materials, respectively, which has been studied for the 1$^{st}$ 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 microrchins 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 microrchin 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.
Chapter 7

Conclusions and suggestions for future work

7. A flexible solid-state ASC device was fabricated using the PANI/(MnO$_2$–RGO)/PANI hybrid film as the positive electrode and MoO$_3$/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, MnO$_2$ and MoO$_3$, 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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Energy density (Wh kg$^{-1}$)</th>
<th>Power density (kW kg$^{-1}$)</th>
<th>Cyclic stability (% of capacitance retention)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF//MnO$_2$@PANI</td>
<td>37.0</td>
<td>0.386</td>
<td>88.6 (after 5000 cycles)</td>
</tr>
<tr>
<td>GF40//@RGO/MnO$_2$@PANI25</td>
<td>38.12</td>
<td>1.191</td>
<td>85.8 (after 5000 cycles)</td>
</tr>
<tr>
<td>MoO$_3$/GF5//PANI/(MnO$_2$–RGO)/PANI</td>
<td>51.91</td>
<td>0.838</td>
<td>82 (after 5000 cycles)</td>
</tr>
</tbody>
</table>

From the summary, it can be concluded that an increment of energy density was obtained by tailoring the structure of MnO$_2$, 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 MnO$_2$, RGO and PANI in PANI/(MnO$_2$–RGO)/PANI sandwich film was found to be 1:3:1.4, which gives a
high energy density value when in combined with GF/MoO$_3$ hybrid electrode material which acts as a contrary electrode material of the ASC. However, the cyclic stability of the MoO$_3$/GF5//PANI/(MnO$_2$–RGO)/PANI ASC is lower than that of the GF40//RGO/MnO$_2$@PANI25 or GF//MnO$_2$@PANI ASC. The drop of cyclic stability in PANI/(MnO$_2$–RGO)/PANI ASC is due to the pendent PANI nanofibers on top of (MnO$_2$–RGO) layer, which undergoes mechanical deformation during charge-discharge cycles. The percent of capacitance retention in the GF40//RGO/MnO$_2$@PANI25 and GF//MnO$_2$@PANI hybrid materials, do not have much difference as both contains MnO$_2$@PANI core-shell composite, in which MnO$_2$ backbone helps to prevent PANI degradation. Henceforth, where very high energy density is the primary requirement, MoO$_3$/GF5//PANI/(MnO$_2$–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/H$_3$PO$_4$ gel be studied using the as-synthesized graphene–MnO$_2$–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


References


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Appendix

Figure A1 Schematic presentation of the fabrication of all-solid-state supercapacitor cell.
Figure A2 FESEM images of MnO₂ 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-MnO$_2$ film symmetric supercapacitor SSC

![Graphs showing CV and CCD study of RGO-MnO$_2$ film](image_url)

**Figure A4** (a) CV and (b) CCD study of RGO-MnO$_2$ film

The solid-state flexible RGO-MnO$_2$ 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.