Development of polyaniline nanostructures using bio-soft-template approaches and graphene-based composites for supercapacitor applications

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**DEVELOPMENT OF POLYANILINE NANOSTRUCTURES
USING BIO-SOFT-TEMPLATE APPROACHES AND
GRAPHENE-BASED COMPOSITES FOR
SUPERCAPACITOR APPLICATIONS**

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Summary

The focus of the current work is to develop a supercapacitor that has energy density which is comparable with high energy batteries, but with the advantages of supercapacitors such as high power density and long rechargeable cycle life. The selected approach was to enhance both the electrical double-layer capacitance and pseudo-capacitance. To achieve these, electrodes based on a graphene/polyaniline composite system that has the appropriate morphology, microstructure and composition to provide the optimum properties were developed.

The 2D graphene sheets have the tendency to aggregate or stack which reduces the available surface area and limits the ion transport during electrochemical process. This makes it difficult for the stacked graphene assembly to achieve optimum device performance. Thus, we report a strategy to solve these problems by transforming the aggregated graphene sheet into an open assembly structure by introducing a spacer (*p*-phenylenediamine (PPD)) between the layers by covalent functionalization. Compared to stacked graphene sheet, the modified graphene sheet (GPPD) is capable of delivering a much higher specific capacitance and energy density of 232.96 F/g and 32.38 Wh/kg (almost 2-fold), respectively at the current density of 500 mA/g in aqueous 1 M H₂SO₄ solution. The retention of capacitance of this electrode was found to be 92.92% after 1000 charge-discharge cycles.

Polyaniline (PANI) nanostructures (viz. nanotubes and nanofibers) networks with different morphology were synthesized by chemical oxidative polymerization method using the bio-molecules like vitamin C and heparin. We report the discovery of an unprecedented behavior of vitamin C which forms a rod-like assembly through hydrogen-

bonding in water, which produced PANI nanotubes upon the addition of aniline monomer. The tubular growth of PANI at the nanometer scale can be controlled by the variation of molar ratio of vitamin C to aniline. The polymerization rate became slower at higher molar ratio, whereas at lower molar ratio of 0.25 (i.e. [Vitamin C]/[Aniline] = 0.25), uniform nanotubes (PANIV-0.25) were observed. The outer diameter of the nanotube was in the range of 80 - 120 nm. Surprisingly, no polymerization was observed at an equal molar ratio of vitamin C to aniline. Besides this, with heparin template, uniform nanofibers were also synthesized when the weight ratio of heparin to aniline was 0.25 (PANIH-0.25). The uniform nanofibers obtained had average diameters of between 80 - 110 nm. No uniform PANI nanofibers were formed at other weight ratios.

We have further studied the novelty of PANI nanotubes and nanofibers as nanostructured electrode materials for supercapacitor applications. The PANIV-0.25 nanotube based electrodes showed higher capacitance and energy density values of 619.76 F/g and 86.14 Wh/kg at 500 mA/g current density in aqueous 1 M H₂SO₄ solution, respectively, with a cyclic stability of 76.74% capacitance retention after 1000 cycles. On the other hand, the PANI nanofiber electrode (PANIH-0.25) yielded a higher specific capacitance and energy density values of 732.18 F/g and 101.77 Wh/kg, respectively, where the retention of capacitance was 72.28% after 1000 cycles at the same current density. The observed capacitances were also elucidated and justified based on theoretical considerations, which showed the good agreement between the observed and theoretical values.

The graphene/PANI nanostructures (nanotubes and nanofibers) based composites were then fabricated and evaluated. The graphene nanosheet/PANI nanotube composites

were fabricated by in situ chemical oxidative polymerization of aniline using vitamin C as a template. The G20PNT80 composite showed the best current-voltage response and the maximum specific capacitance was found to be 671.79 F/g at 500 mA/g current density in aqueous 1 M H₂SO₄ solution. The composite presented an excellent cycle life with 89.33% specific capacitance retention after 1000 cycles. The specific energy density was calculated to be 93.38 Wh/kg.

Next, graphene/PANI nanofibers composites were synthesized using a novel in situ chemical oxidative polymerization of aniline using heparin as a template. The novel G25PNF75 composite showed a high specific capacitance of 690.68 F/g and an excellent energy density of 96 Wh/kg at a discharge current density of 500 mA/g. When the current density was reduced to 250 mA/g, the composite showed specific capacitance and energy density values of 890.79 F/g and 123.81 Wh/kg, respectively. This energy density is comparable to that of high energy batteries. Moreover, the composite exhibited excellent cycle life with 88.78% specific capacitance retained after 1000 cycles. The significantly improved specific capacitance is due to the synergistic effect in the composite. The excellent cyclic stability over the entire cycle life can be attributed to the good mechanical stability of the composite electrode. Thus, this composite with such a high specific capacitance is a very promising electrode material for supercapacitor applications.

List of Publications

1. **Md Moniruzzaman Sk** and Chee Yoon Yue, Layer-by-layer (LBL) assembly of graphene with *p*-phenylenediamine (PPD) spacer for high performance supercapacitor applications, *RSC Advances*, 2014, 4 (38), 19908-19915. (*Chapter 4*)
2. **Md Moniruzzaman Sk** and Chee Yoon Yue, Synthesis of polyaniline nanotubes using the self-assembly behavior of vitamin C: a mechanistic study and application in electrochemical supercapacitors, *Journal of Materials Chemistry A*, 2014, 2, 2830-2838. (*Chapter 5*)
3. **Md Moniruzzaman Sk**, Chee Yoon Yue and Rajeeb Kumar Jena, Facile growth of heparin-controlled porous polyaniline nanofiber networks and their application in supercapacitors. *RSC Advances*, 2014, 4, 5188-5197. (*Chapter 5*)
4. **Md Moniruzzaman Sk**, Chee Yoon Yue and Rajeeb Kumar Jena, Synthesis of graphene/vitamin C template-controlled polyaniline nanotubes composite for high performance supercapacitor electrode. *Polymer*, 2014, 55, 798-805. (*Chapter 6*)
5. **Md Moniruzzaman Sk**, Chee Yoon Yue and Rajeeb Kumar Jena, Graphene/heparin template-controlled polyaniline nanofibers composite for high energy density supercapacitor electrode. *Materials Research Express*, 2014, 1, 045051. (*Chapter 6*)

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Abbreviations & Notations

A

AAO - Anodized alumina oxide

ACA - 9-anthracene carboxylate ion

AOT - Sodium bis(2-ethylhexyl) sulfosuccinate

APS - Ammonium persulfate

APTS - 3-aminopropyltriethoxysilane

B

BC - Bacterial cellulose

BET - Brunauer-Emmett-Teller

BJH - Barret-Joyer-Halenda

[BMIM]Cl - 1-Butyl-3-methylimidazolium chloride

[BMIM]PF₆ - 1-butyl-3-methylimidazolium hexafluorophosphate

C

C_{pseudo} - Pseudo-capacitance

C_{sp} - Specific capacitance

CC - Carbon cloth

CCD - Cyclic charge-discharge

(C₂H₅)₄N⁺BF₄⁻ - Tetraethyl ammonium tetrafluoroborate

CNT - Carbon nanotube

CP - Conducting polymer

CTAB - Cetyltrimethylammonium bromide

CV - Cyclic voltammetry

D

3D-RGO - 3D reduced graphene oxide

DTAB - Dodeyltrimethylammonium bromide

E

$E_{\max}$ - Energy density

EDL - Electrical doublelayer

EDLC - Electrical double-layer capacitor

EIS - Electrochemical impedance spectroscopy

EMImBF₄ -1-ethyl-3-methylimidazolium tetrafluoroborate

[EMIM]EtOSO₃ -1-Ethyl-3-methylimidazolium ethylsulfate

ESR - Equivalent series resistance

F

FESEM - Field emission scanning electron microscopy

FTIR - Fourier transform infrared

G

GO - Graphene oxide

GP - Graphene paper

GPPD - PPD modified graphene

H

HRTEM - High resolution transmission electron microscopy

I

IHP - Inner Helmholtz plane

IL - Ionic liquid

L

LAH - Lithium aluminium hydride

LBL - Layer-by-layer

M

[MTEOA]MeOSO₃ - Tris(2-hydroxyethyl)methylammoniummethylsulfate

MWCNT - Multi-walled carbon nanotube

N

NDSA - Naphthalene disulfonic acid

NSA - Naphthalene sulfonic acid

O

OD - Outer diameter

OHP - Outer Helmholtz plane

OTAB - Octyltrimethylammonium bromide

P

P_{max} - Power density

PANI - Polyaniline

PEDOT - Poly(3,4-ethylenedioxythiophene)

PEO - Polyethylene oxide

PFOSA - Perfluorooctane sulfonic acid

PFSEA - Perfluorosebacic acid

PPD - *p*-phenylenediamine

PPy - Polypyrrole

PTh - Polythiophene

PVA - Poly(vinyl alcohol)

R

R_i - Equivalent series resistance

R_w - Warburg resistance

RG - Reduced graphene oxide

S

SA - Sodium alginate

SS - Stainless-steel

SWCNT - Single-walled carbon nanotube

X

XPS - X-ray photoelectron spectroscopy

Chapter 1 Introduction

1.1 Background

The energy crisis is one of several global issues that have to be tackled in the next fifty years. In this regard, the technical challenges are the conversion, storage and distribution of energy. These are closely connected with the development of several key technologies such as electronics, transportation, communication and defense. Recently, considerable focuses have been paid on climate changes and rising depletion of fossil fuel, leading to ample concern on the investigation and development of the alternative and renewable resources. There is increase research in the creation of renewable energy from wind and sun, as well as the making of electric cars with low CO₂ emissions [1]. Electrical energy storage systems have played a significant role in our daily lives due to their quick availability on demand. The focus has been on the development of energy storage systems that have higher power density as well as higher energy density for both existing and new applications.

At the forefront of these, nowadays fuel cells [2, 3], batteries [2], conventional capacitors, and supercapacitors [2, 4, 5] are commonly used energy storage devices. The specific energy and power capabilities of these energy storage and conversion systems are shown in the Ragone plot in Figure 1.1. Also, a comparison between batteries, traditional capacitors and supercapacitors are shown in the Table 1.1. It is apparent that an electrochemical energy storage device that can have both high power and high energy densities is essential to meet many future demands.

Conventional capacitors store energy as positive and negative charges on two parallel sheets made of conductive materials, which offers a high power density. However, it provides a low energy density which prevents it to use for many applications. Batteries have been the favored storage device for most applications due to their ability to produce high energy. However, where the application demands high power, then the supercapacitor has been the best choice to fulfill this purpose. New battery technology such as those based on lithium-ion and other advanced secondary batteries [6, 7] has been developed to increase power density as well as energy density but still it did not solve the need for high power. The electrochemical performance of batteries is determined by the reaction kinetics of active materials and mass transport. Therefore, batteries generally yield high energy densities (150 Wh/kg for Li-ion batteries). However, such batteries have rather low power densities and limited rechargeable cycle life.

Figure 1.1 Ragone plot of specific energy and power capabilities for various energy storage and conversion devices [8].

In that context, today supercapacitors have become a topic of great technical interest in the green energy world. It has attracted rapidly growing consideration due to their unique features, such as moderately high energy density, high power density, long cycle life and low cost. Supercapacitors have higher specific power than batteries and they are extensively used in power applications [2, 4, 5]. Some other common applications include wind turbines, electronic vehicles, satellite propulsion, pulse power, aerospace and military applications. The way to achieve the enormous increase in power density in supercapacitors compared to traditional capacitors is to utilize an electrode having high surface area in addition with the high charge storage capability at the interface and the bulk of the electrode.

The configuration of a typical supercapacitor consists of a couple of polarizable electrodes with current collectors, a separator, and an electrolyte (for 2-electrode system), similar to that of a battery. The basic difference between supercapacitors and batteries lies in the mechanism that energy is physically stored in an electrochemical capacitor by means of ion adsorption at the electrode/electrolyte interface known as electrical double-layer capacitors (EDLCs). Although, the supercapacitors store energy by two mechanisms, namely; EDL capacitance and reversible Faradaic reactions (called as pseudo-capacitance). Carbon based materials [5, 9, 10] with large surface area and good electrical conductivity are usually recognized as good electrode materials for EDLCs. The metal oxides, [11-13], conducting polymers (CPs) [14, 15] are generally used as redox electrode materials for pseudo-capacitors.

Table 1.1 A comparison between batteries, traditional capacitors and supercapacitors [2, 4, 5]

Property	Batteries	Traditional Capacitors	Supercapacitors
Power density	Low	Extremely High	High
Energy density	High	Extremely Low	Moderately High
Lifetime	Low	High	High

Metal oxides [11-13] like manganese dioxide (MnO_2), ruthenium oxide (RuO_2), iridium(IV) oxide (IrO_2), cobalt oxide (Co_3O_4), molybdenum trioxide (MoO_3), titanium dioxide (TiO_2) and nickel oxide (NiO) with various oxidation states have been used for electrodes with pseudo-capacitive properties for the electrochemical supercapacitors. Various conducting polymers (CPs) [14, 15] like polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and Poly(3,4-ethylenedioxythiophene) (PEDOT) have been widely studied as electrode materials for supercapacitors because of their good electrochemical properties, easy synthesis and low cost. Among the carbon materials, carbon nanotubes (CNTs) [10, 16] have received much importance due to their unique structural, mechanical and electronic properties. There are primarily two types of nanotube, namely; single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Recently, graphene [17] a new carbon based material with 2D nanostructure, has generated great curiosity because of its large specific surface area, remarkable mechanical strength, good electrical conductivity and very high thermal stability.

In order to avoid the drawbacks of a single component based electrode material, researchers developed composite based electrode materials for coupling the advantages of the EDLCs and pseudo-capacitors. The combination of CPs (possess large capacitance)

and graphene (possess high conductivity and mechanical strength) are known to enhance the supercapacitor performance due to the ability to store charges via the two charge storage mechanisms [18, 19] and the synergistic effect [18].

The commonly used electrolytes for supercapacitors are aqueous or organic. The aqueous electrolyte offers a low internal resistance but it has the limitation in low operating potential window (about 1.0 V). Organic electrolytes with a broader electrochemical window (2.3 - 3.0 V) can significantly enhance the performance in supercapacitors but it produces high internal resistance.

1.2 Objectives and scope of thesis

The objective of the present work is to develop high-performance supercapacitors by addressing some fundamental issues that control the energy density and cycle life of the supercapacitor electrodes. Currently, the energy density of commercially available carbon based electrochemical supercapacitors is much lower than that of conventional batteries (35 - 40 Wh/kg for conventional batteries and 150 Wh/kg for the Li-ion batteries). Although metal oxide or CP based electrodes exhibit high-energy supercapacitors that are comparable to batteries, they suffer from poor cycling stability. This is a critical problem that needs to be resolved if composite based electrode materials are to be utilized.

The choice of electrolytes has a profound impact on the energy density of supercapacitors. In general, organic electrolytes and ionic liquids and a broad operating voltage window (2.3 - 3.4 V) offer relatively high energy density compared to aqueous electrolytes. However, organic electrolytes with poor electrical conductivity require strict control on environmental safety because of their toxic nature, while ionic liquids are cost-

ineffective. The specific capacitance is also lower because of the larger size of their ions which cannot diffuse into the smaller pores of the porous electrode materials. Hence, the entire surface area is not utilized rendering both types of electrolytes to be unsuitable for practical applications as they produce high internal resistance. On the other hand, aqueous electrolytes have advantages over organic electrolytes because they are environment friendly and have low cost, and are thus desirable for use in smart supercapacitors with appropriate electrode materials. The development of advanced electrode materials with appropriate electrolytes is the key to develop high-performance supercapacitors.

Based on the above considerations, this work outlined in this thesis aims to develop a supercapacitor based on a carbon reinforced conducting polymer composite which has enhanced electrochemical performance in an aqueous electrolyte that will have high specific capacitance, high energy density and good cycling stability (as the high power density is not an issue in existing supercapacitors, so this will not be addressed here). The carbon reinforcement based graphene is not only a good material for EDLC but can potentially enhance the mechanical properties of the reinforced CP so as to improve the cycle life. Moreover, the capacity for the CP to function as an effective pseudo-capacitor that can store many charged ions can be greatly enhanced by controlling its morphology. Therefore, the specific issues to be addressed include:

(a) Study ways to modify graphene and to identify the influence of such effects on the electrochemical properties. Specifically, effective and simple techniques to increase the surface area of the graphene by creating an open assembly structure between adjacent graphene layers will be developed. This will enhance the EDL capacitance properties.

(b) Study to develop techniques to synthesize polyaniline (PANI) nanostructures with different controlled morphology like nanotubes and nanofibers. In particular, a suitable biomolecules-based soft-template approach will be developed to make these conducting polymer nanostructures. The influence of the PANI morphology on the electrochemical properties in supercapacitor applications will be studied.

(c) Finally, the design of nanocomposite materials consisting of reduced graphene oxide (RG) and PANI nanostructures like nanotubes and nanofibers for high-performance supercapacitors will be considered. It is believed that a supercapacitor with good electrochemical properties will be developed.

1.3 Structure of this thesis

The Chapter 1 presents a short introduction and the scope of the study about the supercapacitors. The Chapter 2 discusses a comprehensive literature review on the working principles, the commonly used techniques for evaluating the electrochemical properties of supercapacitors, the electrode materials, the electrolytes, a brief description about the various template approaches for the synthesis of polymer nanostructures, and literature review on CPs based graphene composites for their supercapacitors applications. Chapter 3 gives the experimental part which includes chemicals and general equipments, and experimental methods used in this project.

Chapter 4 discusses the graphene based electrode for high performance supercapacitor applications.

Chapter 5 presents the synthesis of bio-molecule based soft template approach for the synthesis of PANI nanostructures (nanotubes and nanofibers) for electrochemical supercapacitor applications.

Chapter 6 deals with the synthesis of graphene and PANI nanostructures based composite for high performance supercapacitor electrodes.

Finally, Chapter 7 deals with the conclusions and recommendations for future work.

Chapter 2 Literature review

A comprehensive literature review on issues pertaining to the development of a supercapacitor based on a carbon reinforced conducting polymer composite with excellent electrochemical performance in an aqueous electrolyte will be reviewed. Firstly, the working principles and the common techniques for assessing the electrochemical properties of supercapacitors will be considered. Then some common electrode materials and electrolytes will be covered. Existing approaches in using templates for the synthesis of polymer nanostructures will be discussed. A review of conducting polymers and their graphene composites in supercapacitors applications will be presented.

2.1 Energy storage and classification of supercapacitors

Today, energy conversion and storage has become prime concerns in the world. Different types of energy storage devices have been invented. Fossil fuels, nuclear heat, renewable energies can be used to produce electrical energy, however, there is a great need to develop reliable storage devices such as supercapacitors. Such storage devices will enable excess energy that is produced to be stored for use at future usage when required. Carbons based materials, nanostructured CPs, metal oxides and their composites have been studied as promising materials in such electrode based supercapacitors for energy storage devices.

As indicated in Chapter 1, supercapacitors store energy by two mechanisms, namely; ion adsorption at the electrode-electrolyte interface (commonly called EDLC), and reversible Faradaic reactions (commonly called pseudo-capacitor). In order to realize

the full advantages of EDLCs and pseudo-capacitors, the third type of capacitor composed of these two mechanisms called hybrid capacitor [2] was also invented. The details of energy storage principle in all type of supercapacitors are described in the following sections.

2.1.1 Electric double-layer capacitors (EDLCs)

The double-layer capacitance was first discovered by Helmholtz. According to the Helmholtz theory, the creation of electrical double layer (EDL) is due to the buildup of charges of opposite signs across the electrode/electrolyte interface, and reversible ion adsorption onto the electrode is accountable for the energy storage in supercapacitors [2, 4]. Capacitance in pure EDLC is solely electrostatic and non-Faradaic in nature as there is no charge transfer occurs between electrode and electrolyte. This kind of charge storage mechanism occurs mainly in carbon based electrodes where no redox reactions occur and the cyclic voltammetry (CV) curve for this type of electrode is rectangular (see Figure 2.3a). By using porous electrodes with larger surface area, a higher capacitance can be obtained through the double-layer mechanism. The charge-discharge process in EDLC happens readily and also highly reversible. The double layer capacitance (C_{dl}) can be calculated by using following equation [20] as follows:

$$C_{dl} = \frac{A\epsilon_0\epsilon_r}{d} \dots\dots\dots (2.1)$$

Where, A (m^2/g) is the accessible specific surface area of the electrode, ϵ_0 (F/m) is the permittivity of free space, ϵ_r (a dimensionless constant) is the relative permittivity, and d

(m) is the thickness of EDL. The charge storage mechanism in EDL is schematically described in Figure 2.1 [20].

Figure 2.1 The charge storage mechanism in EDLC [20].

The double layer formation mechanism at the interface is not fully understood and several models have been proposed. Helmholtz first proposed the model of EDL which was further developed by Gouy and Chapman [21]. After this, Stern combined Helmholtz's model with the Gouy-Chapman model to clearly recognize two layers of ion distribution: the compact layer (often called as Stern layer) and the diffuse layer. The EDL model is shown in Figure 2.2. In Figure 2.2, the inner Helmholtz plane (IHP) indicates the distance of closest approach of specifically adsorbed ions (generally anions) and the outer Helmholtz plane (OHP) represents the non-specifically adsorbed ions, d is the thickness of EDL, ψ_0 and ψ are the potentials generated at the electrode surface and the

electrode/electrolyte interface, respectively. According to this model - (i) the inner layer which is defined as the compact layer that deals with the counter ions adsorbed in the charged electrode, and (ii) the diffusive layer where the counter ions are not specifically adsorbed, but are adsorbed due to the long range electrostatic attractions between the charged electrodes and solvated ions [22]. Thus, for an ideal EDLC, the specific capacitance of each electrode is generally assumed to be a parallel-plate capacitor and is made of contributions from the compact layer and the diffuse layer. The total charge density of the EDL is assumed to be the combination of charge density of the inner layer as well as the charge density of excessive ions in the diffusive layer [23].

Figure 2.2 EDL models: (a) the Helmholtz model, (b) the Gouy-Chapman model and (c) the Stern model [21].

2.1.2 Pseudo-capacitors

Pseudo-capacitance is produced when Faradaic charge transfer takes place across the electrode/electrolyte interface due to the occurrence of redox reactions [12]. This type of capacitance is predominant in CPs and metal oxide based supercapacitor electrodes. In pseudo-capacitors, the charge transfer occurs across the double layer of the electrode and in the bulk of the electrode. The pseudo-capacitance (C_{sp}) is calculated by following equation [24]:

$$C_{sp} = \frac{\Delta q}{\Delta V} \dots\dots\dots (2.2)$$

where, Δq is an amount of charge stored and ΔV is the potential difference.

In pseudo-capacitance, the redox reactions by electrolyte ions absorption in the electrode result from changes in the oxidation state in transition metals based electrodes or reversible doping/de-doping redox reactions in the CPs. There are many factors like the porosity of materials, particle sizes, conductivity of electrode materials as well as the surface area of the electrode which may influence the pseudo-capacitance of the materials. The capacitance obtained from pseudo-capacitance is generally much higher than EDL capacitance; however, pseudo-capacitors have lower cycle life. During the insertion/de-insertion process of the counter ions, the swelling or shrinkage of the materials causes volume distortion. This causes the partial sealing of pores and loss the adhesion between the electrode materials and the current collector of the materials, thus lowering the cycle life of the electrodes.

It should be noted that if only double layer capacitance exists, the CV curve should be approximately rectangular in shape (as shown in Figure 2.3a) but if there is a

contribution of pseudo-capacitance, then the shape of the curve will no longer be rectangular due to the influence of oxidation/reduction reactions. The latter effect causes the shape of the curve to be changed (for example, see Figure 2.3b) according to the nature of the chemical reactions which are also characteristic of the property of the composite where at least one component is pseudo-capacitive material.

Figure 2.3 Typical cyclic voltammograms of (a) EDLC and (b) pseudo-capacitor.

2.1.3 Hybrid capacitors

Hybrid capacitors utilize the advantages of both EDL capacitance and pseudo-capacitance to obtain large improvement in the overall performance of supercapacitors [25]. The hybrid system delivers high energy density and power density without lowering the cycle life drastically because the energy storage mechanism in hybrid supercapacitors depends on both Faradic and non-Faradic processes. In hybrid capacitors, electrodes are commonly made from either composite electrodes with carbon-based materials and CPs or metal oxides. The combination of carbon based electrode materials (which exhibit EDL

capacitance) with CPs (which exhibit pseudo-capacitance) has gained much importance due to the great improvement in overall electrochemical performance.

2.2 Experimental methods for evaluation of electrochemical properties

To evaluate the electrochemical performance of supercapacitors, cyclic voltammetry (CV), cyclic charge-discharge (CCD), and electrochemical impedance spectroscopy (EIS) are the most commonly used techniques. The electrochemical characterization of supercapacitors can be carried out using either a two-electrode system or three-electrode system. In a three-electrode supercapacitor system, there are three electrodes, namely; a working electrode, a counter electrode and a reference electrode. The voltage is applied between the working and reference electrode and the corresponding current is measured between the working and counter electrode. The reference electrode has a constant potential against which the other potentials are measured, including the working electrode at which the cell phenomenon takes place. The counter electrode is actually used to complete the electrical circuit and is typically made of electrochemically inert materials such as gold and platinum. The choice of a suitable reference electrode has a crucial role to the realization of any experimental program.

The specific capacitance (C_{sp} , F/g) can be calculated from the constant current charging-discharging curve using the following relationship [26, 27]

$$C_{sp} = (I \times dt)/(dV \times m) \dots\dots\dots (2.3)$$

where, I is the constant current, dt is the total discharging time, dV is the discharge voltage range (excluding ohmic drop at the beginning of the discharging curve), and m is the mass of the active electrode material.

The specific capacitance (C_{sp}) can also be calculated by using following equations [28, 29] from the CV curve:

$$C_{sp} = i/(s \times m) \dots \dots \dots (2.4)$$

$$\text{and } C_{sp} = C/m = \frac{\int_{V_2}^{V_1} i(V) dV}{(V_1 - V_2) V_m} \dots \dots \dots (2.5)$$

where, i is average cathodic current of the CV loop and s is the scan rate.

And in the second equation, the term in the numerator represents the area of I-V curve and V_1 , V_2 are the switching potentials in CV curve.

The energy density and power density are two important parameters to evaluate the efficiency of a supercapacitor electrode. The energy density is the capacity to perform work and the power density provide the information how fast the energy is delivered. The energy density can be determined from a cyclic charge-discharge curve in which the potential range is fixed and the upper limit is determined based on the types of electrolytes used.

The energy density (E_{max} , Wh/kg) of a supercapacitor can be calculated by the following equation [26]:

$$E_{max} = 1/2 C_{sp} V_i^2 \dots \dots \dots (2.6)$$

where, C_{sp} = specific capacitance and V_i = operating voltage range.

From the above equation, it can be inferred that the energy density depends essentially on voltage, i.e., on the electrolyte stability window. Thus, the type of electrolyte used has a critical role in achieving the energy density of the electrode system.

Furthermore, power density (P_{max} , W/kg) can be calculated by the following equation [30]:

$$P_{max} = V_i^2/4R_i \dots\dots\dots (2.7)$$

where, R_i = equivalent series resistance (ESR), V_i = operating voltage range.

The power density (P_{max}) can also be calculated by the following equation [31]:

$$P_{max} = E_{max}/t \dots\dots\dots (2.8)$$

where, E_{max} is the energy density and t is the discharge time.

2.3 Electrode materials for supercapacitors

The electrode materials are the key component of a supercapacitor. The electrode thickness and the accessible surface area are the main factors for optimum electrochemical performance. The electrochemical performance is also influenced by the adhesion of the electrode materials to the current collector surface. There are different types of electrode materials such as

- Carbon based electrodes (activated carbons, CNTs, graphene)
- Metal oxides based electrodes
- CPs based electrodes
- CNTs/CPs composite based electrodes
- Graphene/CPs composite based electrodes

2.3.1 Carbon based electrodes

2.3.1.1 Activated carbon based electrodes

In supercapacitors, activated carbon is used as an electrode material because of its high surface area (e.g. about 2500 m²/g) [5]. However, it is a poor electrical conductor and thus the conductivity of activated carbon needs to be improved by adding small amounts of a

more conductive carbon which may include conducting grade carbon black, graphite or glassy carbon. Double-layer capacitance is directly related to the accessible carbon surface area available. To enhance the double-layer capacitance, researchers have developed high-surface area carbon with a porous morphology which provides good accessibility for the electrolyte ions. Typical commercially available activated carbons have a specific capacitance (EDL capacitance) in the range of 70 - 120 F/g based on organic electrolytes and ionic liquids (ILs) [5, 32]. However, this value depends upon the precursor and the type of electrolytes. Wei et al. [32] reported a higher specific capacitance with the activated carbon using PPy as the precursor in ILs as electrolyte and the typical CV curves are shown in Figure 2.4. They have achieved a maximum specific capacitance of 300 F/g using this activated carbon in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) ionic liquid (IL) electrolyte at the current density of 10 A/g and showed 5 - 8% performance improvement after 10000 charge-discharge cycles.

Figure 2.4 Morphology of PPy-based activated carbons: (a) Scanning electron microscope (SEM) and (b) Transmission electron microscope (TEM) images of the carbon activated at the temperature of 700 °C, and (c, d) CV study of carbon activated at the temperature of 700 °C in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) ionic liquid at the temperature of 20 °C and 60 °C, respectively [32].

2.3.1.2 CNTs based electrodes

There are primarily two types of nanotubes, namely; single walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Their conductivity range varies depending on the diameter and length of the nanotube. In supercapacitors, the presence of mesopores in carbon nanotubes (CNTs) serve as easy access points for the electrolyte ions to the electrode/electrolyte interface for the EDL formation as well as pseudo-Faradaic reactions upon varying the functionality of the nanotube surface. Also the specific capacitance values greatly depend on the type of electrolytes, type of CNTs-

growth processes, accessible surface area by the electrolyte ions, and the diameter and length of CNTs. Although CNTs possess longer cycle life, however the capacitance values of CNTs are very limited; it mainly possesses an EDL capacitance of only up to 135 F/g [10, 16].

2.3.1.3 Graphene based electrode

Recently, graphene [17, 33, 34] which has a 2D nanostructure, has attracted great interest in various research fields. Owing to its large surface area, outstanding mechanical strength and electrical conductivity; graphene has been proposed for potential applications in the field of nanoelectronics like electrochemical supercapacitors. The structure, preparation methods and charge storage mechanisms as well as performance of graphene in supercapacitors are discussed below:

Structures and properties of graphene

The chemistry of graphene oxide (GO) provides valuable insight into its reactivity and ultimately its properties, as well as those of graphene that are derived therefrom. The actual chemical structure of GO has been the subject of extensive debate in recent years.

Various structural models of GO can be outlined as follows:

1. Hofmann and Holst's model (Figure 2.5a) in which epoxy groups are present across the basal planes of graphite with sp^2 hybridization [35].
2. Ruess projected a variation of this model which incorporated hydroxyl groups into the basal plane. Ruess's model (Figure 2.5b) also modified the basal plane structure to a sp^3 hybridized system. The Ruess model still assumed a repeat unit,

however, where $1/4^{\text{th}}$ of the cyclohexanes contained epoxy groups and hydroxyl groups [36].

3. Another model (Figure 2.5c) was suggested by Nakajima and Matsuo relied on the assumption of a lattice framework similar to poly(dicarbon monofluoride), $(\text{C}_2\text{F})_n$ [37].
4. The most recent models of GO have rejected the lattice based model and have focused on a nonstoichiometric, amorphous structure. Certainly, the most well-known model is proposed by Anton Lerf and Jacek Klinowski (Figure 2.5d & e) [34].

In this model, GO contains two segments - 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 carboxylic groups along the edge [33, 34]. The presence of these functional groups in GO leads to the graphene sheets with versatile functionalization abilities which will be discussed in Chapter 4.

The breaking strength of graphene is 200 times higher than steel. Room temperature electrical conductivity of graphene is $>1200 \text{ S/m}$. Graphene is aromatic in nature possessing highly dense π -electron clouds. Thus, electrophilic substitution of graphene is much easier than nucleophilic substitution. The reaction in graphene destruct the sp^2 structure leads to the formation of defects and loss of electrical conductivity.

Figure 2.5(a) Hofman, (b) Ruess, (c) Nakajima-Matsuo and (d & e) Lerf-Klinowski model structures of GO showing the presence of oxygen functionalities above and below the basal plane [35] [36] [37] [34].

Preparation methods

Several approaches have been developed to synthesize graphene-based materials, which includes:

1. Epitaxial growth and chemical vapor deposition (CVD) growth of graphene on SiC and matched metal surfaces [38-41].
2. Micromechanical exfoliation of graphite [42, 43].

3. Exfoliation of graphite in organic solvents [44].
4. Substrate free gas-phase synthesis of graphene platelets in a microwave plasma reactor [45].
5. Arc-discharge synthesis of multi-layered grapheme [46].
6. Reduction from GO, which is synthesized by Staudenmaier [47] and Hummers methods [48].

The most important method to prepare graphene-based materials is the chemical exfoliation of graphite to GO, followed by controllable reduction of GO to reduced graphene (RG).

The reduction process is one of the most important reactions employed for the GO because of the similarities between properties of reduced graphene (RG) and pure graphene. The GO are electrically less conducting due to their disrupted sp^2 bonding networks. However, the RG can recover the electrical conductivity of the materials by restoring the π -network. It should be mentioned that the surface functionality greatly weakens the interactions between the graphene sheets. A variety of reagent may be used to reduce GO. The most commonly used reagent for the reduction of GO is by hydrazine monohydrate [49]. Reduction of GO may also be done with extremely strong reducing agents, such as lithium aluminium hydride (LAH). However, it remains a challenge with LAH due to the side reactions with water which is a commonly used solvent for dispersing GO. In a recent report, sodium borohydride ($NaBH_4$) was confirmed to function more effectively than hydrazine as a reductant of GO [50]. Other reductants have been used for the chemical formation of graphene includes hydroquinone [51] and strongly alkaline solutions [52].

GO can also be reduced to RG via thermal exfoliation of GO. It has been reported that GO can be exfoliated into RG when the temperature is higher than 550 °C at normal pressure [53] [54]. However, a low temperature method is more convenient, which has been proved by Yang's group. They proposed a high-vacuum environment that produced RG at low temperature (200 °C).

Recently, Xu et. al. [55] proposed a novel 3D self-assembled graphene hydrogel prepared by chemical reduction of the aqueous GO dispersion with sodium ascorbate. Zhang and co-workers [56] prepared another kind of graphene hydrogels via hydrothermal reduction of GO dispersions followed by further reduction with hydrazine or hydroiodic acid.

After the chemical reduction of GO in the aqueous solution, the loss of oxygen-functional groups lower the electrostatic repulsions between GO sheets, leading the RG to agglomerate. This agglomeration not only decreases the surface area, but also prevents the access of the graphene surface by electrolyte ions. Thus, stabilizer or spacers are generally used to ensure the high electrochemical utilization of graphene sheets through open architectures. An example of using spacer is reported in Chapter 4 as a part of our work.

Charge-storage mechanism

The high surface area is the key to have high specific capacitance of graphene. The porous 3D curved graphene networks or open structures create interconnected channels favorable for fast ion transport contributing to an excellent rate performance (see Figure 2.6). The high specific capacitance and good cyclic performance of the porous graphene electrode could be ascribed to the following reasons:

(a) The presence of wrinkled and folded regions on the graphene surface effectively prevent the facile aggregation and restacking, maintaining relatively high surface area and improving the utilization of intrinsic high surface area of graphene.

(b) The hierarchical open pore texture composed of micropores, mesopores and macropores provides high surface area for efficient electrical charge storage process. It also facilitates the penetration of electrolyte ions, and greatly shortens the diffusion length of electrolyte ions, thereby decreasing the internal resistance and ensuring good electrochemical performance. Large pore volume in the mesoporous structure provides rich sites to adsorb electrolyte ions and facilitates the electron transfer.

Large graphene surface in direct contact with liquid electrolyte are capable of rapidly and reversibly capturing ions through surface adsorption and/or surface redox reaction. A pair of redox peaks may be found in RG based electrode materials, which is due to the quinone/hydroquinone groups in carbon materials. The residual polar oxygen functional groups are also actively involved in Faradaic redox reactions contributing to pseudo-capacitance. Additionally, the oxygen functional groups on reduced graphene can also enhance hydrophilicity property, which in turn, improves the electrode-electrolyte contact to facilitate the ion transport phenomenon.

Figure 2.6 Charge storage mechanism in graphene based supercapacitor electrode [57].

Performance of graphene in supercapacitors

The specific capacitance of graphene based electrode which is up to 135 and 99 F/g, respectively in aqueous and organic electrolytes, as reported by Stoller et al. [58], is rather limited for practical applications. Chen et al. [59] found that partially reduced GO using hydrobromic acid showed the maximum capacitance values of 348 and 158 F/g at a current density of 0.2 A/g in 1 M H_2SO_4 and 1-butyl-3-methylimidazolium hexafluorophosphate, respectively. A comprehensive literature review of graphene based electrode materials will be outlined in Chapter 4 in order to give an in-context comparison of our result.

2.3.2 Metal oxides based electrodes

Transition metal oxides [11, 13, 60] are widely used as active pseudo-capacitive electrode materials in supercapacitor applications. The capacitance in a metal oxide [11-13] based electrode is due to the redox reactions occurring in the metallic oxides giving rise to the redox pseudo-capacitance. Metal oxides have good electrochemical properties; however, they are not easily available and thus have high cost. The metal oxides that are commonly used for electrode materials are RuO_2 , IrO_2 , MnO_2 , Co_3O_4 , TiO_2 , NiO and MoO_3 . Although RuO_2 provides very high specific capacitance, the major drawbacks are its toxicity and high cost. The highest value of specific capacitance reported for an amorphous hydrated RuO_2 synthesized by the sol-gel process was 720 F/g [12]. Sugimoto et al. [61] synthesized hydrated RuO_2 nanosheets which showed a capacitance value of 658 F/g. The specific capacitance obtained using the other metal oxides have so far been much poorer than RuO_2 . Currently, electrode materials based on porous transition metal oxides such as MnO_2 , Co_3O_4 and NiO are being actively evaluated for supercapacitors. This is especially so for NiO based electrodes because of their comparatively low cost and low toxicity.

2.3.3 Conducting polymer (CPs) based electrodes

The CPs [14, 15] have received much attention not only due to their electronic properties but also for their reversible redox behavior, ionic transport and tunable doping properties. During electrochemical performance, the oxidation/reduction phenomenon occurs in the CPs chains which then store the charge and produced the capacitance. The charge storage mechanism of a CPs based electrode is electrochemical redox reactions. Therefore, the

pseudo-capacitance by Faradaic redox process is dominant and only 2 - 10% is EDL capacitance type. CPs based electrode materials are much cheaper than metal oxides or other electrode materials like CNTs based supercapacitors. However, they do not possess long-term cyclic stability during electrochemical performance because of shrinkage, cracking or damage of the electrode materials during service. Some most commonly used CPs include polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh). The structures of these polymers are shown below in Figure 2.7. Also, a comprehensive literature study on the specific capacitance of PANI is given in Chapter 5.

Figure 2.7 Chemical structures of PANI, PPy and PTh.

2.3.4 CNT/CP composite based electrodes

The inorganic-organic or organic-organic composite materials of CPs are currently under intensive research. The polymeric nanocomposites [27, 62] based on CNTs, have successfully been prepared and evaluated for potential use as electrode materials in supercapacitors. This is because CNT/CP composites, which have superior mechanical properties compared to the neat CPs, can withstand the volumetric changes during the

doping/de-doping process without affecting their electrochemical performance. The considerable interest of CNT/CP composites is due to the good electronic transport properties of CPs in presence of CNT. It also improves the stability during electrochemical performance and minimizes shrinkage.

A CNT/CP composite based electrode can combine the beneficial characteristics of EDL type capacitance and pseudo-capacitance. The low specific capacitance of a neat CNT based supercapacitor is a serious drawback to its potential application. Consequently, there has been much interest in synthesizing CNT/CP composite based supercapacitor electrodes which have the ability to deliver high specific capacitance. Gupta et al. [63] reported a SWCNT/PANI composite which had a high specific capacitance of 463 F/g at the current density of 10 mA/cm². Mi et al. [64] showed an enhanced specific capacitance of 322 F/g was obtained for the PANI composite at the current density of 1 mA/cm², which was about 12 times that of the specific capacitance value of MWCNTs. Recently, the fabrication of hierarchical PANI-functional MWCNTs (FMWNTs) composite with high specific surface area is reported [65]. The maximum specific capacitances of 568, 473 and 395 F/g were obtained at current densities of 10, 20 and 50 A/g, respectively for these electrodes, indicating a better storage capacity of the MWCNT based composite electrode.

2.3.5 Graphene/CPs composites based electrodes

In order to avoid the drawbacks of CNT/CP based electrode (possess lower capacitance value), it is viable to develop composite based electrode materials with other two components - graphene and CPs. The combination of CPs nanostructures (which have

large capacitance) and graphene sheets (which possess good cyclic stability) have been proved to enhance the supercapacitor performance due to the ability to store charges via two charge storage mechanisms [18, 19] - EDL capacitance and pseudo-capacitance. A comparative study on the graphene based CPs (like PPy and PEDOT) composite will be shown later in this chapter. Also, a literature review on graphene/PANI composite electrodes for supercapacitors application will be outlined in Chapter 6.

2.4 Electrolytes for supercapacitors

One of the important components in a supercapacitor cell is the electrolyte which plays a crucial role during supercapacitor performance. It supplies the ions and carries the electric charges between the electrodes of opposite polarities. Therefore the choice of the electrolyte leads to strategic decisions in the supercapacitor design because it has great impact on the capacitance, energy density and power density. There are three kinds of primary electrolytes in supercapacitors, namely aqueous electrolytes, organic electrolytes and ionic liquids. The basic requirement of an electrolyte is to provide the highest ionic conductivity in the entire operating temperature range and it must neither freeze nor vaporize during the charge-discharge process.

2.4.1 Aqueous electrolytes

The selection of electrolytes depends on several parameters including the ESR, the size of potential window and the capacitance. For a given electrochemical measurement condition, the ESR in aqueous electrolyte is much smaller than in organic electrolyte. Aqueous electrolytes which have higher ionic conductance, tend to diminish the ESR but

provide higher power density. On the other hand, aqueous electrolytes limit the low operating voltage ($V = 1.0\text{ V}$) because a voltage above 1.23 V corresponds to the decomposition potential of the water molecules as follows:

Thus, redox reactions will occur which diminishes the energy density. The aqueous electrolytes have the advantage over organic toxic electrolytes because aqueous electrolytes are environmentally friendly and have lower cost. The most commonly used aqueous electrolytes are sulphuric acid (H_2SO_4), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), potassium hydroxide (KOH), potassium chloride (KCl), sodium hydroxide (NaOH) and sodium sulphate (Na_2SO_4) in water solvent.

2.4.2 Organic electrolytes

The advantage of an organic electrolyte is its large potential window ($2.3 - 3.0\text{ V}$). The final choice of an organic electrolyte leads to an increment of the energy and power density by several times. However, it requires control of the environmental safety. The ionic conductivity of an organic electrolyte is provided by the addition of a salt in the organic solvent or by organic liquids. Some common organic electrolytes include quaternary ammonium salts – $\text{R}_4\text{N}^+\text{Cl}^-$, where, $\text{R} = -\text{CH}_3$, $-\text{C}_2\text{H}_5$, and LiClO_4 in acetonitrile solvent. The tetraethyl ammonium tetrafluoroborate $(\text{C}_2\text{H}_5)_4\text{N}^+\text{BF}_4^-$ is another commonly used industrial organic electrolyte. Each molecule of this electrolyte dissociates into a positive cation $(\text{C}_2\text{H}_5)_4\text{N}^+$ and a negative anion BF_4^- , and forms an EDL at the porous electrode surface. However, an organic electrolyte reduces the maximum useable power because it increases the ESR. The specific capacitance is also reduced

because of the larger size of ions which cannot diffuse into the pores of the porous electrode materials and hence the entire surface area is not utilized.

2.4.3 Ionic electrolytes

Ionic electrolytes contain bulky organic cations with different anions. They have the highest operating voltage window (3.4 V) of the electrochemical supercapacitors. The commonly used ionic liquids are 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆), 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-Ethyl-3-methylimidazolium ethylsulfate ([EMIM]EtOSO₃) and tris(2-hydroxyethyl)methylammoniummethanesulfate ([MTEOA]MeOSO₃). There are no solvent molecules in an ionic liquid unlike other electrolytes which dissolves salts in molecular solvents. At room temperature, it is generally liquid with high thermal and electrochemical stability with negligible vapor pressure. Due to the higher operating potential, the ionic electrolytes exhibit high energy density and power density. However, ionic electrolytes have limited use in commercial supercapacitors because of their high cost and higher ESR due to the larger sizes of ions.

2.5 Template methods for synthesis of CP nanostructures

In recent years, there has been significant progress in the synthesis of 1D nanostructures with nanoscale and molecular level characteristics that have the desired properties. For example, CNTs, inorganic semiconductors, metallic nanotubes or nanowires, and CP nanofibers and nanotubes can be tailored and produced to possess required properties. These nanostructured materials have interesting physical and chemical properties over a

wide range of applications in the field of electronics, optics, and energy conversion/storage [66, 67] due to their beneficial characteristics at the nanometer level [68, 69].

So far, different CPs nanostructured morphologies have been fabricated by various synthesis routes. Existing chemical methods of fabricating nanostructures can be categorized into those techniques based on hard-templates [70-74] and soft-templates [75-79]. In the hard-template approach, researchers have mainly employed templates based on porous membranes [74] and zeolite channels [73]. Although the dimensions and morphology of polymer nanostructures can easily be tuned, these approaches require some form of post-treatment of the samples to remove the hard template. Such post-treatments are often not straightforward and may damage the soft polymeric nanoarchitectures. Therefore, much attention has been paid to produce nanostructures with the aid of various structure-directing soft-template approach like micelles [76], vesicles [77], aniline oligomers [79, 80] eliminating the use of hard-templates. The details of the various synthesis routes are discussed in the following sections.

2.5.1 Hard-template method

In the hard-template method [70-74], a physical template is generally required to grow the nanostructures within the pores or channels of the hard-template, leading to complete control of nanostructures. The porous membrane is the most important part of the hard-template method. A schematic diagram of the hard-template synthesis of CP nanostructures is shown in Figure 2.8. In Figure 2.8a, the porous membrane is used as the hard-template to produce CP nanotubes and nanowires where firstly, the growth of the

polymer occurs within the pores or channels of the membrane, and then the templates are removed after complete polymerization to leave behind nanotubes and nanofibers. In Figure 2.8b, the nanofibers are used as the hard-template to produce CP nanotubes. In the first step, the growth of CPs occurs on to the nanofiber template, and then the nanofibers are removed by dissolving or de-polymerizing to obtain nanotubes. In Figure 2.8c, the colloidal particles are used as the hard-template to produce nanoporous membranes. The monomers polymerize in the voids between colloidal particles, and a porous 3D CP structure is obtained when the colloidal particles are removed. The nanostructure synthesized by the template synthesis approach showed improved physical properties that exhibit great potential for applications in energy storage devices like a supercapacitor. The advantages of the hard-template method can be outlined as follows:

- (a) Uniform CP nanostructures can readily be produced. For example, arrays of CP nanowires/-tubes which improve ionic change of electrode materials and electronic transport to the current collector can readily be made.
- (b) Nanostructures can also be made using composite materials. Such composite nanostructures have been made and utilized for improved performance in supercapacitors and batteries.

On the other hand, there are some disadvantages of the hard-template method which are as follows:

- (a) Using a hard-template requires post-processing to remove the template, which often damage or distort the wall of the formed nanostructures and thus complicates the preparation process.

(b) The quantity of the nanostructures produced by this route is limited by the size of the template, which thus limits the production of large-scale nanostructure.

Figure 2.8 Schematic diagram of the hard-template synthesis of CP nanostructured morphology: (a) CP nanotubes and nanowires fabricated by porous membrane as the hard-template, (b) CP nanotubes fabricated by using nanofibers as the hard-template and (c) nanoporous membranes fabricated using colloidal particles as the hard-template [81].

In the hard-template method, the CP nanostructures are prepared by chemical or electrochemical polymerization. Chemical hard-template synthesis is carried out by immersing a membrane in a solution of the specific monomer, dopant, and oxidant followed by the polymerization within the pores [82, 83]. By controlling the polymerization time, various types of nanostructures can be produced [75]. On the other hand, for an electrochemical hard-template synthesis, a metal film coated on one surface of the membrane is required for the polymerization of a particular monomer within the

pores of the membrane [84]. In comparison to chemical hard-template method, the electrochemical hard-template route is more complex and expensive, but it is more controllable through proper control of parameters like the polymerization time, current density and applied voltage.

The most commonly commercially available hard templates may include anodized alumina oxide (AAO) membrane [85], zeolite [73], radiation track-etched polycarbonate membranes [86, 87], and mesoporous carbon [88]. Martin's group [84, 86, 89] has synthesized CP nanotubes using the AAO template, and for instance a well-ordered array of PPy nanotubes obtained using an AAO template (shown in Figure 2.9). Zhang et al. [90] first reported a direct one-step bulk chemical synthetic route to make CP nanofibers using pre-existing nanofiber seed as a template where it served as both the hard-template as well as the oxidant simultaneously, which eliminates the post-process of removing the template.

Figure 2.9 TEM image of the PPy nanotubes fabricated using the AAO membrane as hard-template [86].

Other types of membranes, such as highly oriented hydrolytic graphite [91], colloidal particles [92-94], porous silicate [95], lipid tubule edges [96] and electro-spun polymer fibers [97] have also been used as the templates to prepare CP nanostructures. Lahav et al. [98] reported the synthesis of a core-shell and segmented polymer-metal composite nanostructures by sequential deposition of PANI and Au by an electrochemical route. Some mesoporous materials with open nanochannels can also be employed as templates to produce CP nanofiber/composites. Wu's group [95] synthesized conducting PANI filaments (with aniline vapor) in the hexagonal aluminosilicate MCM-41 channel (3 nm wide).

In the synthesis of the CP nanostructures using micro-/nanoparticles as templates, the target material was first polymerized on the surface of the micro-/nanoparticles (templates), which formed a core-shell structure [99, 100], and after elimination of the template, nanotubes or hollow nanocapsules were obtained [101]. Monodispersed inorganic oxide nanoparticles [102] and polymer microspheres [103] are other commonly used materials for such hard-templates. These kind of templates are advantageous because uniform nanostructures can be made through the use of nanoparticles with narrow size distributions. However, the post-processing for the removal of template is tedious and often affects the hollow nanostructures, which discourages the use of such templates.

In another work, Zhang et al. [104] discovered octahedral or micro-spherical cuprous oxide (Cu_2O) as a hard-template to synthesize analogous hollow structures of PANI (see Figure 2.10) in presence of phosphoric acid (H_3PO_4) and oxidizing agent ammonium persulfate (APS). Compared with other commonly used hard-templates, the Cu_2O template not only excludes post-template elimination process through solubilization

of Cu^{2+} ions, it also provided a unique octahedral structures. The morphology and conductivity of the hollow microstructures can be tuned by altering the molar ratio of oxidant to aniline monomer. Zhu et al. [105] has also reported a unique method using an aniline/citric acid salt as the hard-template in combination with a gas/solid reaction to fabricate brain-like PANI nanostructures.

Figure 2.10 (a) SEM and (b) TEM images of octahedral PANI nanostructure synthesized at $[\text{An}]/[\text{H}_3\text{PO}_4] = 2:1$, $[\text{Cu}_2\text{O}]/[\text{An}] = 1:2$, and $T = 0 - 5^\circ\text{C}$; where, An = aniline[104].

2.5.2 Soft-template method

The soft-template method [75-79], which is also known as the self-assembly method, is a relatively simple, cost-effective, and reliable process for fabricating CP nanostructures. Recently, micelles, surfactants, colloidal particles, liquid crystalline phases, structure-directing molecules and aniline oligomers have aided as soft-templates. Various other soft-template approaches have been developed like interfacial polymerization [106], emulsion polymerization [107], dilute polymerization [108], template-free method [76, 78], rapid mixing polymerization [109], reverse emulsion polymerization [110] and

ultrasonic irradiation [111]. These methods are usually based on self-assembly mechanisms due to hydrogen bonding, van der Waals forces, stacking and electrostatic interactions as driving forces. The advantage of the soft-template method is that no post-synthesis process is required in order to exclude the template. The disadvantage of this method is poor control of the nanostructures, orientation and diameter of the CP nanostructures. A schematic diagram of the mechanism of the soft-template synthesis of CP nanostructures is shown in Figure 2.11. In Figure 2.11a, the micelles are used as the soft-templates for the formation of CP nanotubes, where the micelles were formed by the self-assembly of dopants and then the polymerization was induced on the surface of the micelles. In Figure 2.11b, the nanowires are formed by the protection of dopants and the polymerization takes place inside the micelles, and in Figure 2.11c, the monomer droplets acts as soft-templates in the formation of CP micro-spheres. Figure 2.11d illustrates polymerization that occurs on the substrate producing aligned nanowire arrays and the nanowires that were protected by the dopants with preferential polymerization occurring at the tips of nanowires.

Figure 2.11 Schematic diagram of the mechanism of the soft-template synthesis of CP nanostructured morphology: (a) micelles as soft-templates used in the formation of CP nanotubes, (b) nanowires formed by dopants and the polymerization takes place inside the micelles, (c) monomer droplets acted as soft-templates in the formation of micro-sphere and (d) polymerization occurs on the substrate to fabricate aligned nanowire arrays [81].

Wan and coworkers [78, 112] developed a self-assembly method without an external template for the synthesis of CP nanostructures. With protonic acids as dopants, and by tuning synthesis conditions like temperature and molar ratio of monomer to dopant, PANI and PPy nanostructures could be synthesized by in situ doping polymerization. In this approach the self-assembled micelles formed by dopant and/or monomer act as soft templates for the formation of nanotubes/-wires. Zhang et al. [113] also reported that PANI nanotubes (see Figure 2.12) can be prepared by in situ doping polymerization in existence of naphthalene sulfonic acid (NSA) as the dopant in the absence of any external substance. Here, the -HSO_3 group of NSA acts as dopant as well

as surfactant at the same time, which then self-assembled to form the nanostructures. The morphologies and diameters of the CP nanostructures (like micro-/nanotubes, hollow micro-spheres) generated by template-free synthesis are affected by nature of the dopant, monomer, oxidant and the polymerization conditions. Ding et al. [114] found that the PANI nanofibers with well-defined diameters could be prepared by direct oxidation using various oxidants without any soft-template and acidic dopant.

Further, the self-assembling ability of surfactants in a bulk solution produces the possibility of surfactant micelles serving as soft-templates to form CP nanostructures. The favored aggregate morphology of a surfactant in a solution is spherical, cylindrical, or flat bi-layer depending on the volume and length of the surfactant tail within the hydrophobic core of the aggregate and the effective area occupied by each surfactant head group at the surface of the aggregate. The PPy nanostructures like nanowire, nanoribbon, and nanosphere have been fabricated by using various surfactants as soft-templates [115] in the presence of oxidizing agents like ammonium persulfate (APS) or ferric chloride (FeCl_3). The surfactants used in this study were cetyltrimethylammonium bromide (CTAB), dodeyltrimethylammonium bromide (DTAB) and octyltrimethylammonium bromide (OTAB). The surfactants and oxidizing agents used here have played a key role in defining the PPy nanostructures.

Figure 2.12 FESEM images of PANI nanotubes doped with different naphthalene sulfonic acid at [dopant] = 0.0125 M: (a) PANI-(α -NSA), (c) PANI-(β -NSA) and (e) PANI-(1,5-NDSA); and TEM images of PANI nanotubes doped with different naphthalene sulfonic acid at [dopant] = 0.0125 M: (b) PANI-(α -NSA), (d) PANI-(β -NSA) and (f) PANI-(1,5-NDSA); where, NDSA = naphthalene disulfonic acid [113].

Reverse micro-emulsion is another common method for the preparation of micro-/ nanostructures of CP where an aggregation of surfactant molecules occurs with a nanometer-sized water pool in the oil phase. The most commonly used surfactant to form

reverse micelles [116] is an anionic surfactant like sodium bis(2-ethylhexyl) sulfosuccinate (AOT) with two hydrophobic tail-groups. The AOT molecules favorably form reverse micelles in the oil phase due to the bulky hydrophobic tail-groups compared with the hydrophilic head-groups in AOT. In the literature, many reports are available on the chemical polymerization of CP nanostructures in the presence of AOT. For example, PPy nanotubes were prepared by using AOT reverse cylindrical micelles as the soft-templates [116]. Zhang et al. [117] also shown PEDOT nanotubes prepared using a hexane/water reverse micro-emulsion comprising of AOT cylindrical micelles as the soft-template.

Furthermore, the 3D microstructures can be created with 1D nanostructures via a self-assembly process where micelles as soft-templates and molecular interactions as the driving forces combine together. Using this process, conductive superhydrophobic hollow rambutan-like spheres [118], hollow dandelion-like [119] and hollow cube box-like 3D-microstructures [120] were synthesized successfully in the presence of perfluorooctane sulfonic acid (PFOSA) or perfluorosebacic acid (PFSEA) as the dopant. Here the dopant serve as the doping agent, soft-template and hydrophobic functions at the same time. For example, the hydrophilic $-\text{SO}_3\text{H}$ group in PFOSA or the two hydrophilic $-\text{COOH}$ end groups in PFSEA can act as the dopant and soft-template at the same time, whereas the per-fluorinated carbon moiety in both PFOSA and PFSEA acts as the hydrophobic functions. Zhu et al. [121] also reported the synthesis of the rose-like 3D-microstructures of PANI by a template-free method using APS as both oxidant and dopant at a high relative humidity (80%).

Huang et al. [106, 122] reported a simple chemical polymerization method to produce high-quality PANI nanofibers (see Figure 2.13) under ambient conditions using aqueous/organic interfacial polymerization. In this method the oxidative polymerization of aniline monomer takes place only at the interface of the organic/water phase. The organic phase consists of aniline whereas oxidant is in water phase, and the product enters into the water phase due to the hydrophilicity of the polymerized product. Like other soft-template routes, both the synthesis and the purification in the interfacial polymerization method are quite simple and no post-process is required to get the final products.

Figure 2.13 SEM images of PANI nanofibers synthesized by interfacial polymerization in a water/methylene chloride system with the acids in the aqueous phase: (a) HCl, (b) H₂SO₄, (c) HNO₃, and (d) HClO₄ [106].

Huang and coworkers [109] also developed an excellent rapid mixing route by which a large quantity of PANI nanofibers with no/minimum secondary growth on the nanofibers are found (see Figure 2.14). Due to the even distribution of aniline monomers and oxidant molecules in solution, all of the initiator molecules were rapidly consumed after the start of the polymerization. Consequently, PANI secondary growth was limited due to the lack of available reactants in the reaction container. Compared to the nanofibers prepared by a conventional slow reaction or an interfacial polymerization, the product obtained in the rapidly mixed reaction consisted of pure nanofibers with a relatively uniform size distribution.

For optimal properties, alignment of nanofibers is generally highly desirable. Chiou et al. [108] developed a unique dilute polymerization process to fabricate aligned PANI nanofibers in bulk solutions where the polymerization of aniline occurred at substantially lower than usual concentrations of aniline and oxidant. The proposed two step mechanism for the development of the aligned PANI nanofibers could be understood. The first step is between two possible nucleation sites in bulk solution and on solid substrates. The heterogeneous nucleation occurs first on solid substrates, therefore, most active nucleation sites are produced on the solid substrates at a relatively faster rate at the starting of polymerization. The second step then follows during the nanofiber fabrication process, as the consumption of reactive aniline cation-radicals and oligomer intermediates results in the suppression of the growth of PANI on the solid substrates. Consequently, PANI starts to grow only vertically from the active nucleation centers created at the initial stage of polymerization.

Figure 2.14 SEM images showing the morphology of PANI synthesized from (a) a rapidly mixed reaction and (b) a slowly mixed reaction [109].

Molecular template-guided synthesis is another effective approach for the preparation of nanostructures with well-controlled diameters. For example, PANI-sodium alginate nanofibers with 40 - 100 nm diameters have been synthesized (see Figure 2.15) by a molecular template-guided process in a solution of sodium alginate (SA) [123]. This study demonstrated that the formation of nanofibers with SA depended on the reaction conditions, and in the absence of SA, only spherical nanoparticles were formed [124]. DNA has also been used as a template to prepare CP nanostructures [125] and the chiral nature of DNA creates the possibility that DNA template based synthesis of CP nanostructures can produce stereo-selectively without the assistance of chiral groups [126].

Figure 2.15 SEM images of PANI-sodium alginate nanofibers synthesized with different concentrations of aniline at 0 °C for 48 hours: (a) $[An] = 0.04$ M, (b) $[An] = 0.06$ M, (c) $[An] = 0.08$ M and (d) $[An] = 0.10$ M. The content of SA is 0.2 wt.%, and the molar ratio of APS to aniline is 1 : 1 [100].

2.5.3 Other methods

Electrospinning is a very effective method to fabricate long uniform CP fibers with diameter from micrometers to a few nanometers range by using strong electrostatic forces [127]. In the electrospinning process, the polymer, ceramic, metallic, and composite fibers are obtained from the solution or molten liquid as a liquid jet accelerates through a high voltage (30 - 50 kV) electric field. Through an improved or modified electrospinning device, nanofibers with good orientation could be prepared. By now, micro-/nanoscale fibers of PANI/polyethylene oxide (PEO) [128], PPy/PEO [129], pure PANI [130], pure

PPy [131], PANI/PEO/CNTs [132] and poly(3-hexyl-thiophene)/PEO [133] have been fabricated by this technique, which are used in various applications like field-effect transistor and chemical sensor. Compared with other synthetic methods, the electrospinning process appears to be the only method that can mass-produce continuous long nanofibers. However, in order to assist in the fiber formation, some non-CPs or reagents (e.g. PEO) are usually added into the spinning solution, which may have adverse effects on the conductivity/quality of the electrospun composite fibers. It was found that through reducing or eliminating PEO content [134] or embedding carbon nanotubes in the fibers [132], their conductivity or quality could be improved by several fold. However, this process is limited to produce nanofibers only, which is a serious limitation of this type of process.

Nanoimprint lithography has also been employed to fabricate high-density CP nanostructures [135] and in the literature, many reports are available on the synthesis of CP nanostructures by this method. For example, poly(4-styrenesulfonate) doped conducting PEDOT was synthesized in the form of nanowires on a glass or a Si wafer by micro-molding in capillaries [136]. Nanowires and 2D nanodots of semiconducting polymer have also been synthesized by a liquid embossing method. In addition, Hu et al. [137] reported that arrays of CPs nanowires with internal preferential alignment can be developed by a simple embossing process. Samitsu et al. [138] reported the fabrication of self-assembled CP nanofibers by a whisker method using anisotropic crystallization in a nematic liquid crystal, which produced large-scale aligned nanofibers.

2.6 Graphene/CPs based previous works on the supercapacitors

This section deals with the literature review on the nanocomposites of graphene and CPs. Many studies have been carried out on graphene/CPs nanocomposites for supercapacitor applications. Xu et al. [139] demonstrated the conductive nanocomposite membranes of PPy/bacterial cellulose (PPy/BC) by in situ oxidative polymerization of pyrrole with iron (III) chloride as an oxidant and BC as a template. The PPy/BC showed a maximum specific capacitance of 459.5 F/g at a discharge current of 0.16 A/g in 1 M NaCl solution. Si et al. [140] reported a novel porous nano platelet composite of graphene/PPy prepared by electrochemical method with specific surface area of 136.5 m²/g. The composite material achieved the maximum specific capacitance of 285 F/g at a discharge current of 0.5 A/g in 0.5 M Na₂SO₄ solution. Furthermore, it showed specific capacitance retention of 90% after 1000 charge-discharge cycles. Zhang et al. [141] synthesized graphene/PPy nanocomposite through in situ polymerization process in the presence of graphene nanosheet suspension and pyrrole, and highest capacitance value of 482 F/g was achieved by the composite at the current density of 0.5 A/g in 1 M H₂SO₄ aqueous solution. In another study, Chang et al. [142] reported the electrochemical synthesis of reduced graphene oxide/PPy nanocomposite which exhibited a maximum specific capacitance of 424 F/g at a current density of 1 A/g in 1 M aqueous H₂SO₄ solution.

Xiaomiao's group [143] reported a simple electrodeposition method for the fabrication of graphene/PPy composite film which exhibited a maximum specific capacitance of 355 F/g in 1 M H₂SO₄ solution at 1 A/g current density. The authors also reported the cycle life of the composite electrode where 85% specific capacitance retention was found after 1000 cycles. Bose et al. [144] synthesized poly(sodium 4-

styrenesulfonate) modified graphene/PPy nanocomposite through in situ polymerization process which showed a highest specific capacitance of 417 F/g for the composite at 10 mV/s scan rate in 2 M H₂SO₄ solution with the capacitance retention of almost 90% after 500 charge-discharge cycles. They found the energy density and power density to be 94.93 Wh/kg and 3797.2 W/kg, respectively for the composite. Davies et al. [145] found a flexible uniform graphene/PPy composite film by pulsed electro-polymerization method, which exhibited specific capacitance of 237 F/g at a scan rate of 0.01 V/s in 1 M aqueous KCl solution. The composite exhibited an energy density and power density of 32.9 Wh/Kg and 1184 W/Kg, respectively at the same scan rate.

Zhang et al. [1] reported the in situ polymerization of aniline monomer with graphene oxide under acid conditions to prepare the supercapacitor electrode material based on chemically reduced graphene and PANI. The composite showed the highest specific capacitance of 480 F/g at a current density of 0.1 A/g in 2 M H₂SO₄ solution. It was seen that more than 70% of the initial capacitance was retained after 400 cycles. Liu et al. [146] prepared composite films based on sulfonated graphene and PPy through an electrochemical deposition process using dodecylbenzene sulfonic acid (DBSA) which exhibited a specific capacitance of 285 F/g at a discharge current of 0.5 A/g in 1 M KCl solution with 40 wt.% of sulfonated graphene. The composite film also maintained the retention of capacitance of 92% after 800 charging-discharging cycles at a charge-discharge current density of 2 A/g.

Xu et al. [147] synthesized novel hierarchical graphene/PPy nanosheet composite through an in situ oxidative polymerization method and the composite exhibited a maximum specific capacitance of 318.6 F/g at a scan rate of 2 mV/s. The composite also

displayed the potentiality with almost 95% specific capacitance retention after 1000 cycles at the scan rate of 100 mV/s. Pham et al. [148] demonstrated highly conductive reduced graphene oxide/PPy composite through in situ photo-polymerization of pyrrole in a graphene oxide suspension. The specific capacitance was found to be 376 F/g at 25 mV/s scan rate in 1 M H₂SO₄ solution. The charge-discharge curves show that the composite also displayed excellent cyclic stability with almost 94% capacitance retention after 1000 cycles at 1 A/g current density. Yu et al. [149] reported the self-assembled PEI-modified graphene sheets/acid-oxidized MWCNTs hybrid carbon film for the electrochemical performances which revealed average specific capacitance of 120 F/g at the high scan rate of 1 V/s in 1 M H₂SO₄ solution.

Mi et al. [150] reported the synthesis of a core-shell PPy/PANI composite electrode material for supercapacitors applications. The composite exhibited a maximum specific capacitance of 416 F/g in 1 M H₂SO₄ electrolyte and 291 F/g in 1 M KCl electrolyte. Further, it displayed almost 91% specific capacitance retention at a current density of 15 mA/cm² in 1 M H₂SO₄ electrolyte. Li's group [151] reported the growth of PPy nanowire on the surface of graphene oxide. The composite was fabricated by in situ polymerization technique using APS as oxidant. It exhibited a high specific capacitance of 633 F/g at a current density of 1 A/g. The electrode also retained the specific capacitance of 94% after 100 cycles at the same current density. Liu et al. [152] fabricated a novel composite by PPy nanotubes with chemically reduced graphene sheets for the supercapacitor electrodes. The maximum specific capacitance of 400 F/g was obtained for the composite at a current density of 0.3 A/g and 324 F/g at a current density of 1.5 A/g.

Chu et al. [153] synthesized the PEDOT-modified graphene composite materials, where conducting flexible and porous carbon cloth (CC) and graphene paper (GP)-modified CC (GP/CC) were used as substrates on which the PEDOT was electrodeposited. The specific capacitance of PEDOT on the CC was 118.40 F/g and a maximum specific capacitance of the PEDOT on the GP/CC was 714.93 F/g at 50 mV/s scan rate in 0.5 M H_2SO_4 solution. Han et al. [154] reported the preparation of PEDOT/sulfonic acid-functionalized graphene composite hydrogel using in situ polymerization. The composite hydrogel showed a maximum specific capacitance of 135 and 220 F/g at a current density of 5 A/g in KI and $\text{K}_3\text{Fe}(\text{CN})_6\text{-H}_2\text{SO}_4$ solution electrolytes, respectively. Wang et al. [155] showed the fabrication of a ternary electrode material, based on graphene, tin oxide (SnO_2) and PEDOT via one-pot synthesis for supercapacitors. For this composite the maximum specific capacitances of 184 F/g in 1 M H_2SO_4 and 181 F/g in 1 M Na_2SO_4 , respectively were obtained at the 1 mV/s scan rate. Alvi et al. [156] presented the chemical oxidative polymerization synthesis of graphene-PEDOT nanocomposite as electrode material for supercapacitor applications. This showed the specific capacitance of 374 F/g in 0.01 A/g in 2 M HCl electrolyte.

Furthermore, much research have been carried out on PANI nanostructures as an electrode material either in its pure form or in the form of its composite of graphene. The specific capacitance obtained from the PANI nanostructures and its graphene composite obtained by different synthetic approach will be discussed in the relevant chapters.

2.7 Summary

In summary, in this chapter, a comprehensive literature review on various energy storage processes and its mechanisms is discussed. Supercapacitors store energy by two

mechanisms, namely; ion adsorption at the electrode-electrolyte interface (known as EDLC), and Faradaic reactions (known as pseudo-capacitor). Besides these, the third type of energy storage process in which EDLCs and pseudo-capacitors combined together to produce hybrid capacitors was also discussed. To evaluate the electrochemical performance of electrode materials, cyclic voltammetry (CV), cyclic charge-discharge (CCD), and electrochemical impedance spectroscopy (EIS) techniques were used. The electrochemical characterizations of supercapacitors were carried out using three-electrode system.

Some common electrode materials and electrolytes are also presented in this chapter. The electrode materials are the key component of a supercapacitor, which were discussed in detail. In the literature, it is reported that carbon based materials with large surface area and good electrical conductivity are excellent electrode materials for EDLCs. The metal oxides, conducting polymers are generally used as redox electrode materials for pseudo-capacitors. The combination of CPs and graphene to produce graphene/CPs composite based electrodes, are known to enhance the supercapacitor performance due to the ability to store charges via the two charge storage mechanisms, and the synergistic effect.

One of the important components in a supercapacitor cell is the electrolyte which plays a crucial role during supercapacitor performance. There are three kinds of primary electrolytes for supercapacitors that have been reported in the literature, namely; aqueous electrolytes, organic electrolytes and ionic liquids. The basic requirement of an electrolyte is to provide the highest ionic conductivity in the entire operating temperature range and it must be stable during the charge-discharge process. The aqueous electrolytes have the

advantage over toxic organic or ionic electrolytes because aqueous electrolytes are environmentally friendly and have lower cost.

As the present work is based on the template synthesis technique, therefore, a detail literature review is given on the formation of various kinds of nanostructures using template synthesis route. Existing approaches in using templates for the synthesis of polymer nanostructures are discussed in detail in this chapter. In recent years, there has been significant advancement in the synthesis of 1D nanostructures. The nanostructured materials have fascinating physical and chemical properties over a broad range of applications in the field of electronics due to their nanoscale and molecular level characteristics. Different CP nanostructured morphologies have been produced by various synthesis routes. Existing chemical methods of fabricating nanostructures can be classified into those techniques based on hard-templates and soft-templates. In the hard-template approach, researchers have mainly employed templates based on porous membranes and zeolite channels. Although the dimensions and morphology of polymer nanostructures can easily be adjusted by hard-templates, these approaches require some form of post-treatment of the samples to remove the hard-templates. Such post-treatments are cost-ineffective and also, may destroy the soft polymeric nanostructures. Therefore, much attention has been paid to produce nanostructures with the aid of various structure-directing soft-template approaches like vesicles, micelles, aniline oligomers.

A literature review of conducting polymers and their graphene composites for supercapacitors applications is presented using various electrolytes. In the literature, various template synthesis routes are reported to synthesize the PANI nanotubes; however, the route demonstrated for the synthesis of PANI nanotube using a biomolecule - vitamin C has not

been reported. Furthermore, Shi et al. reported that heparin biomolecule based nanostructured PPy can be synthesized by electrochemical deposition on to the tin-doped indium oxide (ITO). However, the synthesis of PANI nanofiber using heparin template is not reported in the literature. Therefore, in our work vitamin C and heparin are used for the synthesis of PANI nanostructures. The fabrication of nanocomposite structures using these two templates in combination with graphene has not been reported in the literature for the electrochemical supercapacitor applications. These will be carried out in our present work. The review on what have been done in the literature is provided in the respective chapters in order to facilitate comparison with our results.

Chapter 3 Materials & experimental

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

3.1 Chemicals and general equipments

The chemical used in this work are listed below:

Table 3.1 List of chemicals

<i>Chemical name</i>	<i>Supplier name</i>
Graphene oxide (GO) (99%, thickness: 0.7 - 1.2 nm)	CheapTubes, USA
Aniline (reagent grade, 99%)	Sigma-Aldrich, Singapore
Heparin ($M_w = 6,000$ g/mol) (Grade I-A, ≥ 180 USP units/mg, BioReagent)	Sigma-Aldrich, Singapore
Vitamin C (reagent grade, $\geq 99.5\%$)	Sigma-Aldrich, Singapore
Ammonium persulphate (APS) (reagent grade, 98%)	Sigma-Aldrich, Singapore
Nafion solution (5 wt.% in ethanol)	Sigma-Aldrich, Singapore
Carbon black ($\geq 99\%$)	Age D'orPte Ltd, Singapore
<i>p</i> -phenylenediamine (PPD) (reagent grade, $\geq 99\%$)	Sigma-Aldrich, Singapore
Hydrazine monohydrate (reagent grade, $\geq 98\%$)	Sigma-Aldrich, Singapore
Sulphuric acid (H_2SO_4)	Sigma-Aldrich, Singapore
Hydrochloric acid (HCl)	Sigma-Aldrich, Singapore

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

1. Hot plate & magnetic stirrer (MR 3002, Heidolph)
2. Oven (Binder FD240, Fisher Scientific)
3. Furnace (Mettler GmbH & Co. KG)
4. Centrifuge (Thermo IEC, 220/240)
5. Ultrasonicator (MISONIX, Sonicator 3000)

3.2 Experimental

3.2.1 Field emission scanning electron microscopy (FESEM)

FESEM (JEOL JSM 7600) was used to examine the surface morphology of the electrode materials with varying accelerating voltage and different magnifications. For the preparation of sample, a small amount of the material was adhered onto the sample holder using the double sided carbon tape and then gold coated for about 15 - 30 seconds (the coating time is higher for non-conducting samples and less for moderately conducting samples). The gold coating was done under 1×10^{-1} mbar vacuum pressure with sputtering voltage of 1.0 kV and sputtering current of 10 mA. Next, the sample is put into the equipment chamber and then images were taken.

3.2.2 High resolution transmission electron microscopy (HRTEM)

TEM (JEOL JEM 2010) study was performed to know the bulk morphology of the materials with different magnifications. A small amount of the sample was put in the water and sonicated for 15 min in an ultrasonic bath. Then a drop of this dispersed

solution was put onto the copper grid and dried in oven at 55 °C for 10 minutes for HRTEM analysis.

3.2.3 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra for the samples were recorded with a Nicolet 8700 FTIR spectrometer within the range of 650 - 4000 cm^{-1} . A total of 32 scans were performed with a resolution of 4 cm^{-1} . The molecular and functional structures of the electrode materials were characterized by FTIR spectroscopy using a KBr-sample mixture pallet. Firstly, in a mortar, a small amount of dry sample is mixed with dry KBr powder (where amount of KBr $\gg$ sample) to make a homogeneous mixture. Then, a little amount of mixture is put in the sample holder and the sample mixture is pressed with 2 MPa pressure with the help of a hydraulic press. Next, the KBr-sample mixture pallet (which is fixed with the sample holder) put in the FTIR instrument for analysis.

3.2.4 X-ray photoelectron spectroscopy (XPS)

The XPS study was performed for the samples using the Kratos Axis-ULTRA XPS analyzer after plasma cleaning in the XPS chamber pressure at about 4×10^{-8} Pascal for 300 s. In order to confirm the elemental and bonding environment of the samples, the X-ray photoelectron spectroscopic (XPS) analysis was done within the binding energy range of 0 - 1200 eV. For the preparation of sample, first a little amount of sample is adhered with the two sided carbon tape whose one side is fixed with aluminum foil of the dimension of 0.3 mm $\times$ 0.5 cm $\times$ 0.5 cm. This is then fixed with the sample holder for XPS analysis.

3.2.5 Raman spectroscopy

The structure of the samples was investigated using Raman spectroscopy (Renishaw 1000) having a He-Ne laser (632 nm) over the range of 800 - 2000 cm^{-1} . The spectral resolution of 1 cm^{-1} and a spatial resolution of 1 μm were used for the experiments. For the preparation of sample, first a small amount of sample was put into water and sonicated for 15 min in an ultrasonic bath. Then a drop of this dispersed solution was put onto the silicon wafer of the dimension of 0.5 mm $\times$ 0.5 cm $\times$ 0.5 cm for Raman study. The silicon wafer was cut with diamond cutter with fixed dimension. The sample is then dried in oven to dry it properly and then analyzed by Raman spectroscopy.

3.2.6 Conductivity measurement

Electrical conductivities of the samples are measured using a Keithley 2000 (Keithley Instruments Inc., USA) apparatus by the four probe method. First, a little amount of dry sample is put in the sample holder and pressed the sample mixture with 5 MPa pressure with the help of hydraulic press. Next, after releasing the pressure, the pallet is separated from the sample holder and then the measurement was done using the sample pallet. The thickness (t) and radius (r) of the sample were 0.07 and 0.3 cm, respectively. The density (d) can be calculated by the following formula:

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

The conductivity was measured by the following equations:

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

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

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

3.2.7 Surface area measurement and pore size distribution

The Brunauer-Emmett-Teller (BET) surface area, Barret-Joyer-Halenda (BJH) pore size and pore size distributions of the materials were characterized by nitrogen adsorption-desorption using a surface area and porosity analyzer (Micromeritics, ASAP 2020). To prepare the sample, first, about 150 mg dry powder sample is placed into the sample holder and degassed for 6 hours. Next, the sample is weighed again and the reading is recorded. Then, the sample and the sample holder is put in the equipment for nitrogen adsorption-desorption, and the graph and data obtained were analyzed. The original sample weight is obtained by subtracting the weight of sample holder from the sample and holder weight.

To calculate the BET surface area, following equation is used:

$$\frac{1}{v \left[\left(\frac{P_0}{P} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c} \quad \dots\dots\dots(3.1)$$

where, P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (in volume unit), and v_m is the monolayer adsorbed gas quantity, c is the BET constant. Using this equation, v_m is calculated. Next, the number of molecules contained in v_m is calculated which is then multiplied by the area occupied by a nitrogen molecule to get the total BET surface area.

3.2.8 Electrochemical performance

The electrochemical study of the materials was investigated using the three-electrode cell in galvanostat/potentiostat (Gamry Reference 3000). The electrochemical performance for

each sample was determined in 1 M H_2SO_4 solution using cyclic voltammetry (CV), cyclic charge-discharge (CCD) and Electrochemical impedance spectroscopy (EIS) experiments. The materials were tested using the glassy carbon electrode as the working electrode, platinum as the counter electrode and a silver/silver chloride (Ag/AgCl) as the reference electrode.

3.2.8.1 Cyclic voltammetry (CV)

The CV study is a widely used technique for acquiring qualitative information about electrochemical phenomenon such as the reaction mechanisms involved in supercapacitors. The current-voltage response of the electrode was examined by CV experiment using a three-electrode electrochemical cell within the potential range of 0 - 1.0 V in an aqueous 1 M H_2SO_4 electrolyte.

3.2.8.2 Cyclic charge-discharge (CCD)

The CCD study was used to examine the charge-discharge phenomenon of the electrode materials. A three electrode based CCD experiment of the electrodes was carried out within the potential range of 0 - 1.0 V. The experiment was done by keeping the current constant while monitoring the varying potential developed during the charging-discharging process with respect to the time.

3.2.8.3 Electrochemical impedance spectroscopy (EIS)

The EIS is an informative tool to evaluate the charge transport phenomena of materials. To demonstrate the impedance characteristics of the electrode material, EIS was carried

out in 1 M aqueous H_2SO_4 electrolyte. The impedance spectroscopy measurement was performed using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 1 Hz.

3.2.9 Electrode preparation

The electrodes were prepared with 2 mg of composite using few drops of nafion solution (5 wt.% in ethanol) & 10 wt.% carbon black to make a homogeneous paste and it was then applied on to the glassy carbon electrode (diameter 3 mm). Next, all the electrodes were dried in the oven at 90 °C after which they were used in the experiments.

Chapter 4 Layer-by-layer (LBL) assembly of graphene with *p*-phenylenediamine (PPD) spacer for high performance supercapacitor electrode

4.1 Introduction

Due to its high electrical conductivity and high surface area [17, 157, 158], recently graphene has attracted significant interest in many potential applications like batteries [2], and supercapacitors [2, 4, 5]. However, the aggregation nature of graphene sheets causes it to stack readily to form a compact structure which limits the use of graphene in many fields. This adversely affects the device performance by reducing the accessible surface area of graphene sheets by hindering electrolyte ion transport. To make scalable devices, one would need to solve the aggregation problem so that the optimum device performance can be achieved.

The modification of graphene sheets through GO by chemically tuning the surface charge [157] is an efficient way to prepare a desired well-defined structures for various applications. These would prevent the aggregation of graphene sheets and produce highly accessible surface area [159, 160]. It is well known that GO contains two segments: (i) the sp^2 -hybridized aromatic regions and (ii) the oxidized regions that include carbon with oxy-generated functional groups such as hydroxyl, epoxy groups on the basal plane and carboxylic groups along the edge [33, 34]. The presence of these functional groups in GO offer the graphene sheets with versatile functionalization abilities.

Chemical functionalization is one of the most commonly employed route for the modification of graphene. This process is related to the covalent attachment of functional groups onto the functional groups already present on the GO. Veca et al. [161] reported that a pre-formed poly(vinyl alcohol) (PVA) was attached to carbodiimide-activated carboxylic acid groups of GO platelets via ester linkages using a grafting approach. Stankovich et al. [162] synthesized the hydrophilic GO nanosheets into hydrophobic by using isocyanates. Niyogi et al. [163] modified the GO through the grafting with octadecylamine (ODA). Liu et al. [164] grafted branched, biocompatible polyethylene glycol onto the GO through amide bond. The epoxy groups can easily be modified through ring-opening reactions under various conditions. Wang et al. [165] reported the epoxide ring-opening reaction by the addition of octadecylamine to GO. Yang's group [166] demonstrated the covalent attachment of 3-aminopropyltriethoxysilane (APTS) to GO platelets where silane moieties are grafted via a nucleophilic S_N2 displacement reaction between the epoxide and the amine groups of APTS.

GO can also exhibit non-covalent binding by pi-pi stacking, cation-pi or van der Waals interactions on the graphene sheets in which the groups are not oxidized or engaged in hydrogen bonding. Lu and coworkers [167] reported a DNA sensor that utilized a non-covalent binding interaction between DNA or proteins and GO sheets. Recently, Khanra et al. [168] showed a green approach for the non-covalent method via electrochemical exfoliation of graphite where the 9-anthracene carboxylate ion (ACA) was used as an electrolyte and was adsorbed on the surface of graphene through non-covalent interaction.

In this chapter, we discuss a route to modify the graphene by transforming the aggregated graphene sheet into an open assembly structure by introducing a spacer between the layers. The PPD is covalently functionalized onto GO nanosheets through the reaction between two amine groups of PPD and the epoxy groups on the basal plane of GO to form a layer-by-layer assembly of graphene sheets (GPPD) that has improved electrochemical performance. It will be shown that the GPPD based electrode with open structure possess much higher capacitance than electrodes based on the stacked graphene sheets.

4.2 Experimental

4.2.1 Surface modification of graphene

Initially, 500 mg of GO was dispersed in 250 ml distilled water by ultrasonication for 1 hour. Then, 1 g of PPD was dissolved in 100 ml distilled water before the PPD solution was added slowly to the GO dispersion. The resulting mixture was then stirred for 24 hours at 70 °C. Next, the hydrazine monohydrate (5.0 ml) was added to the GO-PPD solution and the temperature was raised to 100 °C [49]. Stirring was continued for another 24 hours, after which the mixture was cooled to room temperature. Then, the product was obtained by centrifugation (at 10000 rpm) and washed several times using distilled water to remove excess PPD and hydrazine monohydrate. The resulting product was dried under vacuum at 60 °C for 72 hours and stored. The chemically functionalized graphene sample was denoted as GPPD. The RG was also prepared separately by treating 500 mg GO with hydrazine monohydrate (5.0 ml) at the temperature of 100 °C [49].

4.2.2 Characterization techniques

The morphological properties of samples were characterized by using FESEM and HRTEM techniques. The molecular characterizations were performed using FTIR and XPS techniques. Electrical conductivities of the samples are measured using four probe method. The surface area and pore size distributions of the sample were characterized by nitrogen adsorption-desorption using a surface area and porosity analyzer. The electrochemical performance was determined in aqueous 1 M H₂SO₄ solution using CV, CCD and EIS experiments. As discussed before, the electrochemical study of the samples were investigated using the three-electrode cell by using a galvanostat/potentiostat (Gamry Reference 3000) at different scan rates within the potential range of 0 - 1.0 V. The same potential range was also used in the CCD measurements at various discharge currents. From the discharging curve, the specific capacitance was calculated from equation 2.3 and the energy density was calculated using equation 2.6. The impedance spectroscopy measurements were done using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 1 Hz. The experimental conditions for all these techniques were outlined in Chapter 3.

4.3 Results and discussion

4.3.1 Mechanism of the covalent functionalization with amine (-NH₂) groups

The presence of functional groups (such as the carboxylic acids which decorate the edges of GO, and epoxy and hydroxyl groups on their basal planes) provides the GO sheets with many functionalization abilities. The chemical interaction between amine groups and GO has been widely debated in the literature [34, 169-172]. Bourlinos et al. [170] suggested

the treatment of GO with amine can lead to derivatization of both the edge carboxyl and surface epoxy functional groups through the covalent bonding of amine and epoxy groups. As discussed before, Yang's group [166] studied the covalent attachment of APTS to GO sheets where the authors claimed that silane moieties were grafted via a nucleophilic S_N2 displacement reaction between the epoxide and the amine groups of APTS. Matsuo et al. [169] reported the hydrogen bonding between amines and hydroxyl groups on the basal plane and Lerf et al. [34] stated that interaction of the amine with carboxyl groups along the GO sheet edge where amine groups exist can cause them to react with carboxylic acid groups of GO through the amidation process.

However, in our study, it is believed that the functionalization of PPD with the GO is achieved through multiple reactions which occur simultaneously. Most importantly, the reaction occurs through the epoxy groups, as it can easily be modified through ring-opening reactions. In PPD due to the presence of two $-NH_2$ groups (see Figure 4.1), the GO sheets can cross-link via the epoxy groups of two or more sheets, stitching them together to yield an ordered nanostructure (see Scheme 4.1 & Figure 4.2b).

Figure 4.1 Chemical structure of *p*-phenylenediamine (PPD).

Scheme 4.1 Reaction scheme for the modification of GO.

4.3.2 Morphological investigations

4.3.2.1 FESEM and HRTEM studies

Figure 4.2 showed the FESEM and HRTEM micrographs of the structure of stacked graphene and the functionalized graphene sheets. As expected, the flat graphene sheets pack like a stack of papers (Figure 4.2a). In contrast, it can be seen from the modified graphene sheets (Figure 4.2b & d) that there is free space between each individual graphene sheet in GPPD due to the functionalization. It is evident that the treated graphene is less dense and more open compared to the untreated flat sheets. Thus, the treated graphene sheets should be more favorable for the ionic flow and electron transport for supercapacitor electrodes during the electrochemical performance.

Figure 4.2 FESEM images of (a) RG and (b) GPPD; HRTEM images of (c) RG and (d) GPPD.

4.3.3 Molecular characterizations

4.3.3.1 FTIR spectroscopy study

The FTIR spectra in Figure 4.3 showed the characteristic peaks of PPD, GO and GPPD. The two bands near 3400 cm^{-1} was assigned to the stretching vibration of 1° amine and the band at 3009 cm^{-1} was assigned to the aromatic C-H stretching vibration in PPD. The peak at 1630 and 1509 cm^{-1} were due to the C=C stretching for aromatic ring in PPD. The FTIR spectrum of GO (Figure 4.3b) shows the presence of epoxy groups, C=O groups and C=C groups at 1226 , 1703 and 1635 cm^{-1} , respectively [173, 174]. Besides, the broad

peak centered at 3452 cm^{-1} indicates the presence of -OH groups in the GO. In Figure 4.3c, the disappearance of the doublet near 3400 cm^{-1} indicates the successful functionalization of PPD onto the GO where the 1° amine is converted into the 2° amine and a new C-N bond is formed which is assigned by the band at 1272 cm^{-1} [175] (which is not present in GO). The more obvious peak at 1226 cm^{-1} in GO compared to the GPPD indicates that the epoxide attached to the basal plane of GO was reacted through the $\text{S}_{\text{N}}2$ reaction between the -NH_2 groups in PPD and the epoxide in GO, this mechanism also supports the work done by Yang's group (discussed in section 4.3.1) [166]. The small peak at 1698 cm^{-1} may be due to the formation of amide-carbonyl (-NHCO-) bonds between the -COOH groups in graphene sheets and the PPD molecule. The peaks at 3009 and 1167 cm^{-1} that indicated aromatic C-H stretching and C-H in-plane bending, respectively, may be due to the presence of aromatic segment in PPD [175], which was also shown by pure PPD (Figure 4.3a).

Figure 4.3 FTIR spectra of (a) pure PPD, (b) GO and (c) GPPD.

4.3.3.2 XPS study

In order to confirm the elemental analysis, the wide scan XPS analysis (Figure 4.4) was done within 0 - 1200 eV for the GO and GPPD samples. In the XPS analysis for GO (Figure 4.4a), the contents of C and O were found to be 82.33% and 17.77%. However, in GPPD (Figure 4.4b), the contents of C, O and N were found to be 84.15%, 9.56% and 6.29%. This indicates the successful attachment of PPD to graphene sheets (this is also supported by FTIR spectrum) as a new peak is appeared for N 1s at about 400 eV (Figure 4.4b). The PPD contents in GPPD were calculated using XPS analysis as follows:

In order to calculate the percentage of PPD content in GPPD, let GPPD was 100 mg.

So, the total amount of N atoms present in GPPD = $(100 \times 6.29) / 100 = 6.29 \text{ mg} = (6.29 \text{ mg} / 14 \text{ g mole}^{-1}) / 1000 = 0.0004492 \text{ mole}$ (Molar mass of N is 14 g mole^{-1})

In GPPD, 2 moles of N atoms are present in 1 mole PPD.

So, content of PPD in GPPD = $0.0004492 \text{ mole} / 2 = 0.0002246 \text{ mole}$

= $0.0002246 \text{ mole} \times 108.14 \text{ g mole}^{-1} \times 1000$ (Molar mass of PPD is $108.14 \text{ g mole}^{-1}$)

= 24.288 mg = **24.288%** (as 100 mg GPPD was taken).

Figure 4.4 XPS spectra of (a) GO (wide scan) and (b) GPPD (wide scan).

4.3.4 Surface area measurements and pore size distributions

The surface area and pore-size characterization of the RG and GPPD electrode were verified by measuring the nitrogen adsorption-desorption isotherms as shown in Figure 4.5. According to the IUPAC classification, both exhibited the combined characteristics of type-II and type-IV isotherms [176, 177] (Figure 4.5a & b). The surface areas of RG and GPPD were found to be 122.86 and 456.23 m²/g, respectively. Furthermore, the pore volume distribution curves as a function of the pore size calculated by the BJH method that are presented in the Figure 4.6c demonstrates the development of a mesoporous structure in the GPPD material after the modification. It can also be seen from the peaks

Figure 4.5 Nitrogen adsorption-desorption isotherm: (a) BET surface area and BJH pore size distribution of graphene (RG), (b) BET surface area measurement of GPPD and (c) BJH pore size distribution of GPPD.

in Figure 4.5c that, although a pore size distribution exists in GPPD electrode, there were many pores with pore sizes of 4.21 and 6.02 nm. The existence of a pore size distribution in the open structure is also supported by the FESEM and HRTEM (see Figure 4.2). The large surface area found in GPPD is very desirable for effective ions transportation during electrochemical tests, which produced a larger capacitance value.

4.3.5 Conductivity measurements

The conductivity was measured by four-probe method, where the average values of five different measurements were taken. In our study, during the measurement the thickness (t) of the pallets was 0.07 cm and radius (r) of the pallet was 0.3 cm. Masses (m) of the samples were 71.302 mg and 73.236 mg for RG and GPPD, respectively. The densities of the pallets were found to be 3.604 g/cm^3 for RG and 3.072 g/cm^3 for GPPD.

The conductivity of the graphene (RG) and GPPD were found to be 63.2 and 38.7 S/m, respectively. This high conductivity value of graphene can reduce the equivalent series resistance during the impedance measurement study. However, in case of the GPPD, equivalent series resistance increased slightly (showed by EIS study, section 4.3.6.3) because of little lower conductivity compared to RG. The decrease of the conductivity in GPPD after the functionalization compared to RG may be explained below:

- (a) The RG has the minimum defect site and thus it possess a regular ring structure in the graphene sheet. On the other hand, in GPPD due to the functionalization, the defect site are more relative to RG as during functionalization the continuity of conjugated system will be disturbed. Thus, the electron flow will be disturbed due

to the discontinuity of the conjugated double bond in GPPD and conductivity will be reduced.

- (b) The RG existed in the compact form; and on the other hand, the GPPD doesn't have a compact structure, rather it possesses an open morphology (proved by FESEM study). Thus, the continuity of electron flow from one graphene sheet to another (due to the good connectivity among the sheets in compact structure) will be easier in RG compared to GPPD. Therefore, the conductivity of GPPD is lower than the RG.

4.3.6 Electrochemical characterizations

4.3.6.1 CV study

Cyclic voltammograms for the RG and GPPD samples are shown in Figure 4.6 in the potential range of 0 - 1.0 V vs. (Ag/AgCl) in a 1 M aqueous H₂SO₄ electrolyte at the scan rates of 1, 5, 10, 20, 50, 100 and 200 mV/s. Figure 4.6a & b demonstrated that the PPD modified graphene electrode showed much improved electrochemical performance compared to the stacked graphene sheets (this is also apparent from the next section from the CCD experiment). The CV profiles of GPPD electrode at various scan rates clearly show excellent electrochemical behavior due to the existence of its open morphology. The deviation from rectangularity and the appearance of peaks at lower scanning rates in the CV curves may be attributed to the pseudo-capacitance contribution through redox changes of some remaining functional groups in RG, and PPD which is embedded between the graphene sheets [178] in GPPD (the rectangular type curve is the characteristic of pure graphene through EDL mechanism). It can be seen from Figure 4.6b

that the GPPD electrode displayed high current values of 0.00516 A at 200 mV/s whereas for RG (in Figure 4.6a) it was 0.00354 A at 200 mV/s. On the basis of the above results, it can be inferred that transforming the stacked graphene sheets into the open nanostructure is highly favorable for achieving scalable supercapacitor performance.

Figure 4.6 Cyclic voltammograms of (a) RG and (b) GPPD electrode in aqueous 1 M H_2SO_4 electrolyte at various scan rates.

4.3.6.2 CCD study

The galvanostatic charge-discharge method was employed to determine the specific capacitance of the materials. Typical charge-discharge curves of RG and functionalized graphene sheets (GPPD) based electrode materials are shown in Figure 4.7. The experiments (shown in Figure 4.7a) on GPPD were accomplished with four different charge-discharge currents of 2500, 1000, 500 and 375 mA/g. The galvanostatic charge-discharge experiment (Figure 4.7b) for the pristine graphene was also carried out at 500 mA/g current value for comparison purposes. It was found that the GPPD electrode had a

specific capacitance of 232.96 F/g at 500 mA/g constant charge-discharge current, whereas, the specific capacitance for the stacked graphene sheet at the same charge-discharging current was 133.86 F/g. Also, the energy density of GPPD electrode was much higher (32.38 Wh/kg) compared to the untreated graphene sheets (only 18.6 Wh/kg) at the same discharge current. From the different current levels used on the GPPD electrode, it is found that as the current was decreased, the specific capacitance showed an increase in capacitance from 205.01 F/g at 2500 mA/g to 282.33 F/g at 375 mA/g (and 216.34 F/g at 1000 mA/g). The similar trend was also found for the energy density. The energy densities for the GPPD electrode at different current densities were found to be 28.5, 30.07 and 39.24 Wh/kg at 2500, 1000 and 375 mA/g discharge current, respectively.

In order to compare our result with the reported results in the literature, we have included a literature review in this section. It is evident from the comparison below that our results are either comparable or better than most of the results reported in the literature. Based on the electrostatic interactions between negatively charged GO and positively charged mesoporous carbon CMK-5 platelets, Lei et al. [179] prepared RGO/CMK-5 electrode. The RGO/CMK-5 electrode exhibited a maximum specific capacitance of 144.4 F/g at a current density of 0.2 A/g in 1-ethyl-3-methylimidazolium tetrafluoroborate electrolyte. Zhang et al. [56] prepared the graphene hydrogels via hydrothermal reduction of GO and it exhibited a high specific capacitance of 220 F/g at 1 A/g. Liu et al. [180] reported that a high specific capacitance of 326.8 F/g was found for graphene sheets-cotton cloth composite fabric at 10 mV/s in 6 M KOH electrolyte. Lei and co-workers [181] reported a facile and green route to reduce GO using urea as the reducing agent. They obtained maximum specific capacitances of 255 and 100 F/g at

current densities of 0.5 and 30 A/g, respectively. Hu et al. [182] reported that a mesoporous graphene with 3D wrinkled structure that was prepared using a simple solvent treatment and modified Hummers method. This exhibited a specific capacitance of 341 F/g in 6 M KOH aqueous solution and 166 F/g in 1.5 M $\text{NEt}_4^+\text{BF}_4^-$ acetonitrile solution at the scan rate of 1 mV/s. Furthermore, Xiao et al. [183] reported a simple approach to fabricate the nitrogen-modified few-layer graphene directly from graphite flakes which exhibited a much higher specific capacitance of 227 F/g at the discharge current of 1 A/g than that of reduced GO (133 F/g) at the same current density.

It can be seen from Figure 4.8b that at the current density of 500 mA/g, a lower internal resistance (also called ohmic drop, at the beginning of the discharging curve) was observed for the modified graphene (GPPD) (0.0947 V) compared to the stacked graphene (0.1446 V). The open structure of GPPD exhibited easy ion accessibility which consequently produced lower internal resistance and higher capacitance value. Furthermore, although all the curves for GPPD electrode showed (Figure 4.8a) the internal resistance, this was smaller at a lower charge-discharge current of 375 mA/g (0.0692 V) compared to that at the higher current value of 2500 mA/g (0.372 V). This lowering of ohmic drop and increase in specific capacitance at lower current value may be attributed to the slow electrochemical process in which the electrolyte ions accessed the deeper pores beneath the surface of the electrode (i.e. ions had accessibility of entire electrode surface area both on and underneath the surface). On the other hand, at higher charge-discharge currents (fast electrochemical process), the electrolyte ions only accessed the outer surface area of the electrode which produced the lower capacitance

value [184, 185]. Therefore, it is evident that the morphological difference in graphene sheet has profound impact on its capacitance performance.

Figure 4.7 Cyclic charge-discharge graphs of (a) GPPD at various discharge current densities and (b) RG and GPPD at the discharge current density of 500 mA/g in aqueous 1 M H₂SO₄ electrolyte.

4.3.6.3 EIS study

The EIS technique [4, 186] was used to study the electron and ion transport phenomena in the graphene based electrode. Figure 4.8 showed the typical Nyquist plots of impedance spectra which were recorded over the frequency range of 100 kHz to 1 Hz. The first intersections of the curves with the real axis at high frequency indicate the equivalent series resistance (ESR) of the materials, which includes; (a) the ionic resistance of the electrolyte within the electrode, (b) the intrinsic resistance of the material, and (c) the contact resistance at the active material/current collector interface [187]. An ESR of 6.56 ohm was found for the GPPD electrode after the first cycle, whereas for stacked graphene (RG), it was 5.62 ohm. The slightly higher resistance in both the samples may be due to

the existence of the some oxygen functional groups which may remain after the reduction of GO [168]. These functional groups take part in the development of redox pseudo-capacitance which consequently produces resistance due to the occurrence of redox reactions. However, the slight decrease in resistance of graphene compared to GPPD is due to the higher conductivity of the graphene. Furthermore, the presence of a semicircular shape in the high to medium frequency region in Figure 4.8 is due to the interfacial charge transfer resistance (R_{ct}) in the electrodes. Typically, semicircles with smaller radii indicate lower resistance (which is the case in graphene due to the higher conductivity) in charge transfer (R_{ct}) and a larger semicircle indicates higher charge-transfer resistance in the electrode. The slope of the tails extending beyond the semicircle in the low frequency region (Figure 4.8) provides a measure of the electrolyte diffusion resistance which is also known as Warburg resistance (R_w). If there is no diffusion resistance (R_w) [1, 58], the tails at the low frequency region should be vertical and normal to the real axis. In the GPPD electrode, the slope of the Nyquist plot at the low frequency region was slightly higher (after the semicircle) (indicating lower R_w resistance) compared to that for the untreated graphene indicating the good ion diffusion within the electrode in the former due to the open morphology.

Figure 4.8 Nyquist plots of (a) RG and (b) GPPD electrodes in aqueous 1 M H₂SO₄ electrolyte.

4.3.6.4 Cyclic stability study

The cycle life efficiency of the GPPD electrode was assessed by performing continuous charge-discharge cycles at a constant current density of 500 mA/g (Figure 4.9). The cyclic stability of the treated graphene (GPPD) was found to be 92.82% after 1000 charge-discharge cycles, demonstrating excellent reversibility of the electrodes. This clearly shows that the open morphology of the electrode enables facile ion transport, which is the key to both high specific capacitance and the high cyclic stability of the electrode. Furthermore, the enhanced cycling stability of the GPPD electrode may result from the low resistance due to the little redox reaction, because its primary source of the capacitance is the electrical double layer.

Figure 4.9 Cyclic stability of GPPD electrode at 500 mA/g discharge current in aqueous 1 M H_2SO_4 electrolyte.

4.4 Summary

In summary, we have developed a novel route to fabricate the LBL assembly of graphene sheets through the covalent functionalization of GO. The aggregation-resistant properties of the aromatic spacers (PPD) and the conversion of the aggregated graphene sheets into an open morphology allowed them to maintain highly accessible surface areas. The increased accessible free space inside and between the sheets can facilitate charge transport, leading to high specific capacitance and cyclic stability. The capacitance obtained in the present study for the GPPD was found to be much higher than that for the graphene-based electrode. Such synthesized graphene sheets may inspire many curiosity-driven discoveries and applications at the interfaces of chemistry, materials science, and other disciplines.

Chapter 5 Polyaniline (PANI) nanostructures based electrode materials

The unique properties of CPs [14, 15] have made possible a wide range of applications in the leading edge of energy conversion/storage [66, 67] due to their nanostructured morphology. The properties of these materials are dependent on their size and shape (i.e. nanoparticles, nanofibers, nanotubes) when their dimensions are minimized to the nanoscale [188]. PANI is one of the most useful CPs due to its high conductivity, environmental stability and interesting redox behavior [189, 190]. Nanostructured PANI has received much more attention over its bulk counterpart because of its many potential applications. So far different PANI morphologies have been fabricated by varying the synthesis route. Existing chemical methods of fabricating PANI nanostructures (particles, wires, fibers, tubes) can be categorized mainly as techniques which utilize hard-templates [70-74] and soft-templates [75-79], which were discussed in detail in Chapter 2, section 2.5. Because of the disadvantages (i.e. require some form of post-treatment after the synthesis) in the hard-template based methods, today the soft-template based methods have become a popular way to synthesize CP nanostructures. In particular, nowadays, the biomolecules based soft-template is very promising for the synthesis of CPs nanostructures due to its availability and environment friendly property. In this chapter, in the next two sections, we will discuss the use of vitamin C and heparin biomolecules based soft-template approaches for synthesizing PANI nanotubes and nanofibers, respectively.

5.1 Synthesis of PANI nanotubes with vitamin C based soft-template using self-assembly process and its electrochemical supercapacitor applications

5.1.1 Introduction

Here, we discuss the development of a soft-template based technique which is an easy and highly reproducible synthetic route capable of producing uniform PANI nanotubes in presence of an easily available and low cost biological molecule, vitamin C (*l*-enantiomer of ascorbic acid). Vitamin C is an important biological antioxidant that protects the cell from detrimental radicals [191]. In the literature [192, 193], it was reported that the vitamin C derivatives produce the self-assembled supramolecular aggregates like monolayers, micelles, vesicles, microemulsions or liposomes. For example, the octanoyl-ascorbic acid forms nearly spherical micelles in water solution [192].

However, in our study, it was discovered that vitamin C molecules self-assemble together forming a rod-like structure through H-bonding, which can be used as a new and reliable model for the single step synthesis of PANI nanotubes. The detailed postulated mechanisms for the formation of nanotubes that includes the effect of concentration of vitamin C on the overall morphology have been investigated carefully. The electrochemical study was carried out on this novel PANI nanotube as a potential efficient electro-active material for the supercapacitor based model energy-storage device.

5.1.2 Experimental

5.1.2.1 Synthesis of PANI nanotubes

For the synthesis of PANI nanotubes, 35 ml distilled water was treated in a beaker with vitamin C and stirred for 1 hour at room temperature. Then 151 μL (a constant amount for all the samples) of aniline was added and again stirred for about 30 minutes. Next, 5 ml of 0.378 g aqueous solution of APS (mole ratio of aniline : APS = 1 : 1) was added drop by drop into the reaction mixture and the resultant solution was allowed to stand for 24 hours. Then, the resulting precipitate was washed several times with distilled water to remove the core part (template) of the vitamin C/PANI composite. After this, 2 ml of 1 M HCl was added to the product in order to ensure complete doping (previously doped by acidic H^+ ions from vitamin C forming anilinium ions). Finally, the pure PANI nanotube product was dried in an oven at 55 $^{\circ}\text{C}$ overnight and stored. Six different molar ratios of $[\text{Vitamin C}]/[\text{Aniline}] = 1, 0.5, 0.25, 0.1, 0.05$ and 0.01 were used to demonstrate the effect of concentration on the PANI morphology. For the molar ratios of $[\text{Vitamin C}]/[\text{Aniline}] = 0.5, 0.25, 0.1, 0.05$ and 0.01 , the corresponding samples were denoted as PANIV-0.5, PANIV-0.25, PANIV-0.1, PANIV-0.05 and PANIV-0.01, respectively. For the parallel sample, pure PANI was synthesized following the same procedure without template.

5.1.2.2 Characterization techniques

The morphological properties of samples were characterized by using FESEM and HRTEM techniques. The molecular characterizations were performed using FTIR and XPS techniques. Surface area measurements and pore size distributions were measured

according to nitrogen adsorption-desorption isotherms. The electrochemical performances were determined in aqueous 1 M H₂SO₄ solution using CV, CCD and EIS experiments. The experimental conditions for all these techniques were discussed in Chapter 3.

5.1.3 Results and discussion

5.1.3.1 Molecular characterizations

5.1.3.1.1 FTIR spectroscopy study

The molecular structure of the pure vitamin C, vitamin C/PANI composite (a product obtained before washing) at the molar ratio of 0.25 and PANI nanotubes at the molar ratio of 0.25 were characterized by FTIR spectroscopy as shown in Figure 5.1. The characteristic peaks (Figure 5.1c) at about 1583 and 1498 cm⁻¹ in PANI nanotube (PANIV-0.25) were attributed to the C=C stretching for quinoid ring and the C=C stretching vibration mode for benzenoid rings, respectively indicating the presence of PANI [194, 195]. The presence of these characteristic bands implied that the PANI has the amine and imine nitrogen units in its backbone. In Figure 5.1c, the aromatic C-H bending in the plane (1130 cm⁻¹) and out-of-plane (824 cm⁻¹) for a 1,4-disubstituted aromatic ring indicates a linear structure for PANI chains. The characteristic peak (Figure 5.1c) appeared at about 1296 cm⁻¹ was due to the C-N stretching of a secondary amine in the PANI. The PANI at other molar ratios showed the similar characteristics peaks in FTIR spectroscopy which are shown in Figure A1 in Appendix.

The peaks that appeared at 1760, 1322 and 1117 cm⁻¹ in the FTIR spectra (Figure 5.1a) were the characteristics of C=O stretching, enol hydroxyl group and C-O-C stretching in pure vitamin C, respectively [196-198]. In Figure 5.1a, the sharp peaks near

3500 cm^{-1} were attributed to the hydroxyl group without H-bonding, and a peak at 1634 cm^{-1} may be due to the C=C bonds in vitamin C. It should be noted that the C=C stretching in PANI is located at 1583 cm^{-1} (Figure 5.1c) whereas in vitamin C this peak is at 1634 cm^{-1} (Figure 5.1a). The lowering of wave number in PANI is due to the delocalization of conjugated C=C bonds (in PANI). The FTIR study (Figure 5.1b) of vitamin C/PANI composite was also carried out in order to demonstrate the involvement of functional groups in H-hydrogen bonding, and the electron transfer mechanism (antioxidant property) of vitamin C in the reaction retardation. It is interesting to note that the C=C stretching band of pure vitamin C at 1634 cm^{-1} has disappeared in the vitamin C/PANI composite. This peak disappearance that occurred in vitamin C is probably due to the transfer of 2 electrons and 2 protons forming total 3 -C(=O)- groups [199] in the 5-membered ring (see Appendix, Scheme SA2). Furthermore, in the vitamin C/PANI composite the -C(=O)- peak was shifted to a lower vibrational energy (1735 cm^{-1}) (Figure 5.1b) compared to pure vitamin C (1760 cm^{-1}) (Figure 5.1a). Also, the broad peak (compared to pure vitamin C in Figure 5.1a) of -OH group with a shoulder at higher wave number (Figure 5.1b) was due to the polarity changes of the -OH group in the presence of H-bonding. These observations demonstrated the existence of significant intermolecular H-bonding between the -OH and -C(=O)- groups in vitamin C which resulted in the formation of a rod-like assembly.

Figure 5.1 FTIR spectra of (a) pure vitamin C, (b) PANI/vitamin C composite system at the molar ratio of 0.25 without washing and (c) pure PANI nanotube (PANIV-0.25) at the molar ratio of 0.25 after washing. On right side is the enlarged spectrum of pure vitamin C.

5.1.3.1.2 XPS study

In order to confirm the elemental and bonding environment within the pure vitamin C and PANI nanotubes, XPS analysis (Figure 5.2) was done for the samples. The XPS spectrum of pure vitamin C showed the presence of C and O elements and the PANIV-0.25 showed the presence of C, O and N elements (Figure 5.2a & b). An N 1s narrow scan core-level spectrum (Figure 5.2c) showed that most of the nitrogen atoms were in the form of amine (-NH- , 70.56%) centered at 400.04 eV in benzenoid amine or amide groups [1, 188]. Two small additional peaks [1, 188] (Figure 5.2c) suggested that some nitrogen atoms existed as imine (=N- , 16.27%) form centered at 399.3 eV and positively charged nitrogen (N^+ , 13.17%) form centered at 401.08 eV. The wide scan spectra of PANIV-0.5, PANIV-0.1, PANIV-0.05, PANIV-0.01 and pure PANI (synthesized without template) are shown in Figure A2 in Appendix.

Figure 5.2 XPS spectra of (a) pure vitamin C (wide scan), (b) PANIV-0.25(wide scan)and (c) XPS spectrum of N 1s of PANIV-0.25 (narrow scan).

5.1.3.2 Morphological investigations and postulated mechanism

To synthesize the PANI nanotubes, six different molar ratios of [Vitamin C]/[Aniline] were used with a fixed molar ratio of [Aniline]/[APS] = 1:1 and the same reaction temperature (room temperature). Nanotubes with different morphologies were obtained. It was found that the size and uniformity of PANI nanotubes could be appropriately adjusted by tuning the concentration of aniline and vitamin C. Except at a molar ratio of [Vitamin C]/[Aniline] = 1 (where no polymerization occurred), all the other ratios produced PANI with different morphologies depending on the ratio used. The length of the nanotube was significantly influenced by the [Vitamin C]/[Aniline] ratio and the average length varied from a few nanometers to several micrometers when the molar ratio was varied from 0.5

to 0.01. The longer (several micrometers) and uniform nanotubes (outer diameter (OD): 80 - 120 nm) (as can be seen in Figure 5.3 & Figure 5.4) were found at the molar ratio of $[\text{Vitamin C}]/[\text{Aniline}] = 0.25$. It is noteworthy that, in addition to this, uniform nanotubes were also produced at the molar ratio of 0.1. However, the length of the nanotubes for the ratio 0.25 was longer than that obtained at 0.1. These results indicated that a molar ratio in the range of 0.1 - 0.25 was favorable for the formation of PANI nanotubes, and the optimum was obtained at a 0.25 ratio.

Shorter length nanotubes or random aggregates of thick polymer layer were formed at the ratios of 0.5, 0.05 and 0.01 (Figure 5.3 & Figure 5.4). This may be due to presence of either very high or very low concentrations of vitamin C in the reaction medium whereupon proper association of vitamin C molecules can't take place in both cases. At higher concentration (see Figure 5.3a & Figure 5.4a) it appeared that many rod-like vitamin C assemblies fused together, which destroyed the orientation of individual assembly. And at lower concentration (see Figure 5.3e & Figure 5.4e), the deficiency of vitamin C seems to have created an improper assembly that resulted in the formation of random aggregates of PANI. A pure PANI (a parallel sample) was also synthesized in the absence of template by the conventional oxidative polymerization method. It is apparent that this produced a random aggregate of thick polymer morphology (see Figure 5.3f & Figure 5.4f).

It was observed that no reaction occurred at a molar ratio of 1. The presence of equal amounts of oxidant and antioxidant ($[\text{APS}]/[\text{Vitamin C}] = 1$ i.e. $[\text{oxidant}]/[\text{antioxidant}] = 1$) in the reaction medium probably caused the rate of oxidation reaction of APS and the reduction reaction of vitamin C to be the same at this molar ratio

such that it cancelled out the net oxidation of aniline monomer for further polymerization (see Scheme 5.1). A delay in response in the polymerization reactions (recognized by color change that occurred in the reaction medium) was observed at each different molar ratio after the addition of initiator (APS). This may be due to the antioxidant properties of vitamin C which partially reduced the anilinium radical ions that were previously produced due to the presence of APS. Each synthesis (with each different molar ratio) was repeated 6 times and the delay in reaction times were recorded (Figure 5.5). It can be seen from Figure 5.5 that, at lower molar ratio, the delay time of the reaction after addition of APS was negligible, whereas at higher concentration, this was longer.

From equation (1) we get, $r_1 = d[\text{An}^+]/dt = k_1[\text{An}][\text{APS}]$ ----- (3)

and from equation (2) we get, $r_2 = d[\text{An}]/dt = -d[\text{An}^+]/dt = k_2[\text{An}^+][\text{Vit C}]$ ----- (4)

Case-I: If $[\text{An}] : [\text{APS}] : [\text{Vit C}] = 1 : 1 : 1$, then

$$\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} = \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 1}$$

No polymerization takes place due to the absence of excess An^+ .

Case-II: If $[\text{APS}]/[\text{An}] = 1$ and $[\text{Vit C}]/[\text{An}] = x$, where $x = 0.5, 0.25, 0.1, 0.05$ & 0.01

Then, $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} < 1}$

Polymerization takes place due to the availability of An^+ .

i.e. (a) $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 0.5}$

(b) $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 0.25}$

(c) $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 0.1}$

(d) $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 0.05}$

(e) $\{d[\text{An}^+]/dt\}_{\{[\text{APS}]/[\text{An}]\} = 1} > \{d[\text{An}]/dt\}_{\{[\text{Vit C}]/[\text{An}]\} = 0.01}$

Scheme 5.1 Reaction kinetics in presence of vitamin C and APS in aniline polymerization.

Figure 5.3 FESEM images of (a) PANIV-0.5, (b) PANIV-0.25, (c) PANIV-0.1, (d) PANIV-0.05, (e) PANIV-0.01 and (f) pure PANI (synthesized without template).

Figure 5.4 HRTEM images of (a) PANIV-0.5, (b) PANIV-0.25, (c) PANIV-0.1, (d) PANIV-0.05, (e) PANIV-0.01 and (f) pure PANI (synthesized without template).

Figure 5.5 Molar ratio vs. reaction delay time response for (a) PANIV-0.5, (b) PANIV-0.25, (c) PANIV-0.1, (d) PANIV-0.05 and (e) PANIV-0.01.

Scheme 5.2 Schematic diagram for the formation of PANI nanotubes.

The probable mechanism for the formation of nanotube can be postulated from the observed development of the aggregation of vitamin C molecules into solid rod-like assemblies (Scheme 5.2) through intermolecular H-bonding among several -OH/-C(=O)- groups. After the addition of aniline monomer, it (monomer) interacts on the outer surface of the rod-shaped vitamin C to form an aniline wrapped vitamin C composite assembly. Due to the shape-persistent features and fixed orientation of non-covalent interaction sites in aniline molecule, it was self-assembled into the tubular structures, which was governed by H-bonding between the oxygen of -OH/-C(=O)- groups in vitamin C and the protonated anilinium ions (and aniline molecules if present). The enolic -OH group is more acidic (due to keto-enol tautomerization) than the typical -OH groups and upon the addition of aniline monomer in the solution of vitamin C, it abstracted H^+ ions to form anilinium ions. The aniline monomer also abstracted one more proton (per molecule) from vitamin C (see Appendix, Scheme SA1). This anilinium ion could then initiate the polymerization reaction in the presence of APS.

The H-bonding mechanism was verified using the following approaches utilizing a fixed molar ratio of $[Vitamin\ C]/[Aniline] = 0.25$:

A) *Effect of solvent polarity*: The polymerization was carried out in different solvents like ethanol, 2-propanol and acetone at the molar ratio of $[Vitamin\ C]/[Aniline] = 0.25$ under the same condition as water medium. The FESEM micrographs (see Appendix, Figure A3) of each product (final product after washing) were taken and it was observed that no nanotubes were found which supported the important role of the H-bonding mechanism. This may be explained as the H-bond formation tendency is higher in a more polar solvent than in a less-polar/non-polar solvent. Herein, the polarity and H-bond formation tendency

of the different solvents used are increased in the order of acetone < 2-propanol < ethanol < water. At the initial stage, the more polar solvent (water) formed intermolecular H-bonding with the vitamin C, which changed the polarity of the -OH or -C(=O)- groups (in vitamin C). This change of polarity consequently facilitated the association of vitamin C through intermolecular H-bonding (among vitamin C) which was not the case in other solvents. Thus, only water solvent produced the PANI nanotubes.

B) *Effect of dilution:* At higher dilution with increased solvent (water) amount from 40 ml to 250 ml in vitamin C & aniline mixture, no formation of nanotube was observed (see Appendix, Figure A4) and instead, the formation of random aggregates of PANI was found. This may be due to the low concentration of vitamin C in water which caused high dilution and disallowed the efficient formation of H-bonding.

C) *Nature of intermediate products:* Furthermore, a careful investigation of the reaction mechanism was carried out at different stages of the reaction at the selected molar ratio of [Vitamin C]/[Aniline] = 0.25 in water in order to derive some insightful understanding of the reaction mechanism. After the addition of initiator (APS), the reaction products at various reaction times ($t = 10$ minutes, $t = 1$ hour, $t = 4$ hours and $t = 24$ hours) were collected, washed and dried after which they were examined under the HRTEM (see Figure 5.6). At $t = 10$ minutes, a very narrow vitamin C/PANI nanofibers composite was formed and continuous assemble of aniline onto the vitamin C occurred, at $t = 1$ hour the vitamin C/PANI nanofibers composite formation was complete and this was also same as at $t = 4$ hours. At $t = 24$ hours, after washing the core part vitamin C (water soluble), the PANI nanotubes were obtained. This continuous monitoring of the reaction as the reaction

progressed, strongly supported the association of vitamin C through the intermolecular H-bonding.

Figure 5.6 FESEM images of the intermediate products after addition of initiator (a) 10 minutes, (b) 1 hour, (c) 4 hours and (d) final step after washing.

5.1.3.3 Surface area measurements and pore size distributions

Nitrogen adsorption-desorption isotherms of pure PANI (synthesized without template), PANIV-0.5, PANIV-0.25, PANIV-0.1, PANIV-0.05 and PANIV-0.01 are shown in Figure 5.7. According to the IUPAC classification these exhibited type-IV isotherms [200] and specified the formation of mesoporous (2 - 50 nm) structures. A sharp increase in the adsorbed volume of N₂ and a hysteresis loop at a high relative pressure ($P/P^\circ \approx 0.95$) are the typical characteristics of mesoporous materials [201]. The specific surface areas calculated by the BET equation for pure PANI (synthesized without template), PANIV-0.5, PANIV-0.25, PANIV-0.1, PANIV-0.05 and PANIV-0.01 were 15.39, 18.01, 39.75, 29.08, 25.24 and 22.57 m²/g, respectively. Therefore it can be inferred that the specific surface area in PANI-0.25 was increased significantly compared to pure PANI (increased about 3-fold) which was synthesized without any template. Furthermore, pore volume distribution curves as a function of the pore size calculated by the BJH method are presented in the inset in Figure 5.7 which demonstrated the development of nanoporous structure of PANIV-0.25 material. The larger surface area found in PANIV-0.25 is very much desirable for effective ions transportation during electrochemical tests, which would lead to a larger capacitance value.

Figure 5.7 Nitrogen adsorption-desorption isotherms: BET surface area measurements of (a) pure PANI (synthesized without template), (b) PANIV-0.5, (c) PANIV-0.25, (d) PANIV-0.1, (e) PANIV-0.05 and (f) PANIV-0.01. Inset is the BJH pore size distributions.

5.1.3.4 Conductivity measurements

The conductivity was measured by four-probe method, where the average values of five different measurements were taken. In our study, during the measurement the thickness (t) of the pellets was 0.07 cm and radius (r) of the pellet was 0.3 cm. Mass (m) of PANIV-0.25 (best nanotube) sample was 75.142 mg. The density of the pellet was found to be 3.8 g/cm³. The conductivity of PANIV-0.25 sample was found to be 0.95 S/cm.

5.1.3.5 Electrochemical characterizations

5.1.3.5.1 CV study

As surface area has the crucial role to achieve the high capacitance value, thus based on the surface area obtained in our samples we have done the CV experiment for PANIV-0.25 sample where highest surface area (39.75 m²/g) was achieved (see section 5.1.3.3). Also, for the comparison purpose the CV study is done for pure PANI (without template). The current-voltage response of pure PANI (synthesized without template) and PANIV-0.25 nanotubes at the scan rates of 5, 10, 20, 50 and 100 mV/s are shown in Figure 5.8a & b. The lack of symmetry (i.e. deviation from rectangularity) in the CV curves (Figure 5.8) was largely due to the pseudo-capacitive property of PANI. Faradaic reactions occur between PANI and the ions of the electrolyte [202] i.e. the nitrogen atoms of the PANI backbone and H⁺ ions (from H₂SO₄). Since nitrogen atoms have basic characters, H⁺ ions would accumulate on the electrode surface and pseudo-capacitive interactions would occur (see Scheme 5.3). No obvious peaks were observed at higher scan rates for both the samples, which may be attributed to the fast electrochemical process which is not able to display the detailed electrochemical phenomena [184]. It should be noticed that for the

pure PANI, the peak appeared at very low current which may be due to the fact that, at this low scan rate only, complete activation occurred for this electrode material. On the other hand, in PANIV-0.25 at some higher scan rate of ≤ 50 mV/s, some peaks appeared due to the active participation of electrolyte and electrode occurred during the test.

It is noticeable from Figure 5.8 that the peak intensity gradually increased as we moved towards higher scan rates. The appearance of a peak at lower scan rate was probably due to the electronic transition between different oxidation states of PANI chains. A pair of broad redox peaks (each pair consisting of an anodic and a cathodic peak) was found for both the samples at the lower scan rate (Figure 5.8). In general, PANI shows two redox processes [188, 203], namely; (i) leucoemeraldine (LE)/emeraldine salt (ES) transition and (ii) emeraldine salt (ES)/pernigraniline (P) transition. Herein, the observed broad redox peaks (obvious in Figure 5.8b at 5 mV/s) originated from the overlap of the two redox processes [188]. Therefore, in order to derive more details on electrochemical mechanisms, a lower scan rate is always more preferable.

For the PANIV-0.25 based electrode, the CV profiles proved to show good electrochemical behavior than the pure PANI (synthesized without any template) which was apparent from Figure 5.8b which exhibited a high current values of 0.00802 A at 100 mV/s. However, on the other hand, for the pure PANI (Figure 5.8a) the peak current obtained was 0.00296 A at 100 mV/s scanning rate. Furthermore, as seen in Figure 5.8c, both the anodic and cathodic peak currents increased linearly with scan rate, implying good reversible stability and fast response to oxidation/reduction on the current changes due to surface-controlled redox process [188, 200]. The redox process has been found to

take place at the surface of the electrode, which was most likely due to the low dimension of the PANI nanotubes.

Figure 5.8 Cyclic voltammograms of (a) pure PANI synthesized without any template and (b) PANIV-0.25 in aqueous 1 M H₂SO₄ electrolyte; and (c) plots of the peak current (the anodic peak current, I_{pa}; the cathodic peak current, I_{pc}) vs the scan rate for PANIV-0.25.

Scheme 5.3 Charge-discharge mechanism in PANI

5.1.3.5.2 CCD study

The galvanostatic charge-discharge experiments for the PANIV-0.25 electrode and a comparison between the charge-discharge curves of pure PANI and PANIV-0.25 are shown in Figure 5.9. The experiments for PANIV-0.25 were accomplished with three different charge-discharge currents of 500, 375 and 250 mA/g. The nanotube electrode was found to have a specific capacitance of 619.76 F/g at 500 mA/g constant charge-discharge current. However, for the pure PANI the specific capacitance was found to be 124.29 F/g at the charge-discharge current of 500 mA/g. The specific capacitance was found to increase with decreasing current. For PANIV-0.25 electrode, when the current was decreased from 500 to 250 mA/g, the specific capacitance showed an increase in capacitance from 619.76 to 714.68 F/g, respectively. The capacitance was 643.18 F/g when the current was 375 mA/g. The nanotubular structure of PANI greatly assists to the formation of ionic channel during the study. To the best of our knowledge, no such

electrochemical study has been carried out on the PANI nanotube based electrode and thus a literature review on the PANI nanofiber based materials is given (please see section 5.2.3.4.2). An excellent energy density of 99.34 Wh/kg was also obtained for PANIV-0.25 electrode at a discharge current of 250 mA/g. Also, at the discharge currents of 375 and 500 mA/g, the energy density values were 89.4 and 86.14 Wh/kg, respectively.

Although all the curves showed the ohmic drops (due to the internal resistance) at the beginning of the discharging phase, however this was reduced at the lower charge-discharge current of 250 mA/g (0.2927 V at 250 mA/g compared to 0.3717 V at 500 mA/g). Still, at the lower discharge current the ohmic drop is a little high which may be due to the randomly oriented nanotubes with respect to current collector, which may restrict ionic flow into the electrode. However, the increase in specific capacitance and lowering of ohmic drop at lower current value may be attributed to the slow electrochemical process in which the electrolyte ions accessed the deep pores (in the inner surface of the nanotubes) of the electrode. It is important to note that the ions had accessibility of the entire electrode surface area (both the outer surface and inner surface). On the other hand, at higher charge-discharge current (fast electrochemical process), the electrolyte ions only have time to access the outer surface area of the electrode which leads to a lower capacitance value [184, 185]. Furthermore, as discussed in a following section, the maximum theoretical value for the nanotube electrode can be calculated and correlated with the observed experimental value.

Figure 5.9 Cyclic charge-discharge graphs of (a) PANIV-0.25 at various scan rates and (b) pure PANI and PANIV-0.25 at the discharge current of 500 mA/g in aqueous 1 M H₂SO₄ electrolyte.

5.1.3.5.3 Justification between theoretical and observed capacitance values

The high specific capacitance value of 714.68 F/g reported above can be justified through theoretical considerations. The maximum theoretical capacitance can be calculated by considering Faradaic reactions or pseudo-capacitance in parallel to the EDL capacitance for a porous CP electrode, leading to an upper limit of the capacitance value. Although the actual combination of the two elements (pseudo-capacitance & EDL capacitance) could be more complicated, the maximum theoretical specific capacitance (C_{max}) can be estimated using the following formula [204, 205]:

$$C_{max} = \alpha \cdot F / dV \cdot M + C_{dl} \cdot A \dots \dots \dots (5.1.1)$$

where α is the fraction of electron shared on each monomer unit, F is the Faraday constant (96485.3 C/mol), dV is the voltage range, M is the molecular weight of aniline repeat units (91.1 g/mol), A is the specific surface area and C_{dl} is the EDL capacitance. The maximum value of α is 1 in PANI. The average C_{dl} of PANI was reported to be about 30

$\mu\text{F}/\text{cm}^2$. The average specific surface area for the PANIV-0.25 was found to be $39.75 \text{ m}^2/\text{g}$ by BET measurement (which was about 3-fold higher than the pristine PANI synthesized without template) (see Figure 5.7). Therefore, the theoretical C_{max} was estimated to be 1071.039 F/g within the potential of 1.0 V , wherein the pseudo-capacitance contribution was 1059.114 F/g and the EDL capacitance was only 11.925 F/g .

According to the well-studied redox mechanism of PANI, 1 electron per monomer (i.e. $\alpha = 1$) is needed to oxidize the polymer from its fully reduced leucoemeraldine state (LE) to its fully oxidized pernigraniline (P) state. The value of α is known to be related to the insulating-to-conducting phase transition in the polymer. When $\alpha = 1$, this phase transition is low in electrochemical reversibility [206]. This α value varies through the conversion from LE to emeraldine state (ES) with $0 < \alpha < 0.5$ and ES to P with $0.5 < \alpha < 1$. The more reversible conversion between LE and ES involves 0.5 electron per monomer (i.e. $\alpha = 0.5$).

However, in our experiment, the specific capacitances were found to be 619.76 F/g at 500 mA/g , 643.18 F/g at 375 mA/g and 714.68 F/g at 250 mA/g which are all lower than the maximum possible value of 1071.039 F/g . Based on the observed capacitance values and using equation-5.1.1, the degree of oxidations per monomer α at the different discharge currents were calculated and the results are as shown in Table 5.1. It is apparent from Table 5.1 that at 500 mA/g discharge current, 57.39% electron transfer occurred per monomer (i.e. $\alpha = 0.5739$) in PANI. This implies that only 57.39% of electrons were active for the redox capacitance. At 250 mA/g , the proportion of active electrons increased to 66.35% (i.e. $\alpha = 0.6835$). This demonstrated that at a lower discharge current and higher oxidation level, the capacitance value was increased.

The lower observed value of 714.68 F/g (at 250 mA/g) compared to the theoretical value of 1071.039 F/g can be accounted by the lower experimentally observed α value (i.e. $\alpha < 1$). The theoretical capacitance in our experiment can probably be achieved at some very low discharge current when $\alpha = 1$ (i.e. when all the PANI chains are accessible and are in a highly doped state). Although the high pseudo-capacitance value of the PANI nanotube could push the total capacitance to the theoretical value at an extremely low current density (where $\alpha \approx 1$), however, such a low current defeats the primary purpose of using a supercapacitor in various applications.

Furthermore, the lower observed capacitance value could be explained by the ion transport phenomenon within the nanotube electrode. Typically, the PANI nanotubes are randomly oriented (this is the case in our study) with respect to the current collectors in a supercapacitors electrode [207, 208]. In such cases, the electrolyte ions are often limited from penetrating far inside the PANI chains. This lowers the complete utilization of the electrode surface area. It has been reported that ion diffusion parallel to the orientation of nanotube can be exceedingly fast which consequently produces large capacitance value [207, 208].

Table 5.1 Calculation of α values

Discharge current density (mA/g)	Max. observed capacitance value (F/g)	α
500	619.76	0.5739
375	643.18	0.5966
250	714.68	0.6635

5.1.3.5.4 EIS study

To demonstrate the impedance characteristics [4, 186] of pure PANI and mesoporous PANIV-0.25 electrode, EIS study was carried out in 1 M aqueous H_2SO_4 electrolyte. The Nyquist plot (Figure 5.10) contain two segments, namely: a lower frequency region on the upper right portion, and a high frequency region on the lower left portion of the plot. Both the graphs exhibited a semi-circle (for the comparison see the inset for graph (b)) at the high frequency range followed by a linear slope in the low frequency region. The resistance characterized by the semi-circle is commonly known as charge transfer resistance (R_{ct}) which originates at the electrode/electrolyte interface. A small semi-circle for the electrode suggested very low ($R_{ct} = 0.78 \text{ ohm}$) interfacial charge-transfer resistance due to the good electrode/electrolyte contact. However, for the pure PANI electrode, the R_{ct} was found to be 62 ohm. This very high resistance may be due to the obstruction of ions movement into the compact pure PANI electrode.

The intercept at Zreal along the X-axis at very high frequencies is known as the ESR. As discussed before, this resistance originates from a combination of: (a) ionic resistance of the electrolyte within the electrode, (b) intrinsic resistance of the electrode material, and (c) contact resistance at the active material/current collector interface [187]. The lower ESR (14.32 ohm) found for PANIV-0.25 was probably due to the large surface area of the nanostructured electrode. However, for the pure PANI, the ESR in the cell increased to 25 ohm. The increase in resistance can probably be attributed to the low surface area or compact layer of pure PANI structure. The part of the curve with 45° slope (at low frequency zone) called the Warburg resistance (R_w), is a consequence of the frequency dependence of the ion diffusion/transport process. The resistance to ionic

diffusion is proportional to the slope of the impedance curves in the low frequency region. A more vertical line indicates that the electrode is closer to an ideal capacitor and a large deviation from the vertical line indicates a higher R_w . The slope of the plots in Figure 5.10 decreased for pure PANI, thereby indicating only an increase in ionic diffusion resistance due to the obstruction in ion diffusion in the compact PANI layer. This demonstrated the excellent supercapacitive performance of the PANIV-0.25 electrode. Thus, the nanotubular morphology of PANI is very promising for improved electrochemical performance.

Figure 5.10 Nyquist plots of (a) pure PANI and (b) PANIV-0.25 in aqueous 1 M H_2SO_4 electrolyte.

5.1.3.5.5 Cyclic stability study

The cycle life efficiency of pure PANI and PANIV-0.25 electrode was assessed by subjecting the sample to 1000 continuous charge-discharge cycles at a constant charge-discharge current of 500 mA/g. The retention of capacitance over a number of charge-

discharge cycles is a crucial parameter for long term power-delivery supercapacitors. Herein, the PANIV-0.25 electrode showed capacitance retention of 76.74% (Figure 5.11) after 1000 continuous charge-discharge cycles whereas for pure PANI it was only 37.12%. The substantial reduction of capacitance in pure PANI may be due to the compact microstructures of pure PANI which doesn't have space to accommodate volume changes occurred during the cycling, and consequently the performance of the electrode materials was reduced. The slight reduction in capacitance of PANIV-0.25 after 1000 cycles may be explained by the loss of adhesion of some active material with the current collector or volumetric change which may cause partial blockage of the regular pore structure [209]. This can lead to a slower ionic transfer rate at higher number of cycles which eventually caused the slight reduction in capacitance value.

Figure 5.11 Cyclic stability of (a) pure PANI and (b) PANIV-0.25 in aqueous 1 M H_2SO_4 electrolyte.

5.1.4 Summary

In summary, we have successfully demonstrated a novel strategy to produce long uniform PANI nanotubes using the chemical oxidative polymerization method through the use of a biomolecule, vitamin C. The nanotubes were several micrometers long and had an outer diameter in the range of 80 - 120 nm. It was observed that the morphology of the PANI changed when the molar ratio of vitamin C was varied. A delay in the onset of reaction was observed at higher molar ratios of vitamin C. No reaction occurred at an equal molar ratio of vitamin C to aniline due to the antioxidant property of vitamin C. The intermolecular H-bonding amongst the vitamin C molecules was responsible for the rod-like assembly leading to the formation of PANI nanotubes. The PANIV-0.25 electrode showed excellent capacitive behavior with good cycling stability. Such a PANI nanotube based electrode with good electrochemical behavior has excellent potential for various applications in nanoelectronics including supercapacitors.

5.2 Synthesis of PANI nanofiber networks with heparin based soft-template approach and its applications in electrochemical supercapacitors

5.2.1 Introduction

The objective of this work is to ascertain how the properties and stability of the electrode materials based on PANI nanotubes (in section 5.1) compares with those based on PANI nanofibers. Shi et al. [210] synthesized heparin (a biomolecule) based nanostructured PPy by electrochemical deposition on to the tin-doped indium oxide (ITO). However, this process requires some external substance for the electrochemical deposition which is not often straightforward. Thus, here we have proposed a heparin biomolecule based simple chemical oxidative polymerization route for the synthesis of PANI nanofibers.

The heparin molecule acts as a template for forming PANI nanofibers due to their chain-shaped structure in which the functional groups on their surface serves as morphology-directing sites. The possible growth mechanism of PANI nanofibers on to the heparin and the effects of the concentration on the morphology of nanostructures have been investigated carefully. The potential of this novel PANI nanofiber as an efficient electrode material for supercapacitor applications has also been evaluated.

5.2.2 Experimental

5.2.2.1 Synthesis of PANI nanofibers

For the synthesis of PANI nanofibers, various concentrations of heparin were treated with distilled water for the synthesis of three PANI samples, namely; PANIH-0.5

([Heparin]/[Aniline] = 0.5 wt.%), PANIH-0.25 ([Heparin]/[Aniline] = 0.25 wt.%) and PANIH-0.1 ([Heparin]/[Aniline] = 0.1 wt.%). The solutions were then stirred for about 30 minutes with a magnetic stirrer to prepare the homogeneous aqueous solutions of heparin. A constant amount of 0.91 ml aniline monomer in 10 ml of 1 M HCl was added to the solution of each of the samples and stirred for about 4 hours. Next, 100 ml distilled water containing 2.28 g ammonium persulphate (APS) (mole ratio of aniline : APS = 1 : 1) was added slowly to each solution as an initiating agent and the mixtures were well stirred for another 10 minutes. Then, the reaction mixtures were left standing at room temperature for 24 hours. The resulting precipitates were filtered and washed with distilled water several times, and then dried at 60 °C for 12 hours.

5.2.2.2 Characterization techniques

The morphological properties of samples were characterized by using FESEM and HRTEM techniques. The molecular characterizations were performed using FTIR and XPS techniques. Surface area measurements and pore size distributions were measured according to nitrogen adsorption-desorption isotherms. The electrochemical performances were determined in aqueous 1 M H₂SO₄ solution using CV, CCD and EIS experiments. The experimental conditions for all these techniques were discussed in Chapter 3.

5.2.3 Results and discussion

5.2.3.1 Morphological investigations and nanofiber formation mechanism

In this study, we have used heparin which is a bio-macromolecule that is generally used as an anticoagulant agent, as a template for the synthesis of PANI nanofibers. The

mechanism for the formation of the PANI nanofibers was investigated through the participation of chemical functional groups present in the template (heparin). As shown in Scheme 5.4, heparin consists of a linear block co-polymer of glucosamine and uronic acid bearing many sulphonic groups ($-\text{SO}_3^-$) and carboxyl groups ($-\text{COO}^-$) (here a low molecular weight heparin molecule is shown). The chain-shaped structure and the functional groups ($-\text{SO}_3^-$ and $-\text{COO}^-$) in the heparin backbone would play an important role in the formation of PANI nanostructures. The bio-macromolecule is negatively charged, and the strong electrostatic repulsion among $-\text{SO}_3^-$ and $-\text{COO}^-$ leads to the expanded structure of the heparin chains [210, 211]. These $-\text{SO}_3^-$ and $-\text{COO}^-$ groups interact with the nitrogen atoms of aniline monomer through hydrogen bond/electrostatic force to form biopolymer-monomer (heparin-aniline) complexes due to the site selective nature of aniline. This caused the aniline monomers to be aligned into chain-shaped intermediate anilines [123] and thus act as a template to regulate the growth of PANI nanofibers. The aniline monomers bonded on the $-\text{SO}_3^-$ and $-\text{COO}^-$ groups would then be polymerized sequentially along the heparin backbone to form PANI nanofibers upon the addition of initiator (APS) (Scheme 5.5). It should be mentioned that the length of the resulting PANI nanofibers is dependent on the contour length of the heparin molecules [210].

Scheme 5.4 A low molecular weight heparin sodium salt.

Scheme 5.5 Schematic diagram for the formation of PANI nanofibers.

To obtain an in-depth understanding of the nanofiber formation mechanism, the effect of different concentrations of heparin on the PANI morphology was investigated thoroughly. It was observed that the morphology and length of the PANI nanofibers can be controlled easily by changing the concentration of heparin. At an optimum

concentration of heparin (i.e. $[\text{Heparin}]/[\text{Aniline}] = 0.25 \text{ wt.}\%$), long uniform PANI nanofibers (see Figure 5.12b & Figure 5.13b) were formed. This may be due to the proper association of aniline monomers with the heparin molecule which caused the monomer to be aligned along the length of the heparin. This led to proper head-to-tail coupling of aniline monomers onto the heparin molecules, which in turn promoted the growth of uniform and long nanofibers. The nanofibers may be longer than the corresponding heparin molecules. This is due to the propagation of polymerization reaction between the aniline free radicals that may reside at the end of the different heparin molecules, which would happen if two or more heparin molecules meet end to end in the reaction container [210]. When the concentration of heparin was 0.1 (i.e. $[\text{Heparin}]/[\text{Aniline}] = 0.1 \text{ wt.}\%$), PANI nanostructure with irregular fiber-like morphology with many secondary growths was obtained. This may be attributed to the deficiency of heparin molecules for alignment of the aniline molecules, and consequently secondary growth of PANI occurred readily (see Figure 5.12c & Figure 5.13c). At a higher concentration of heparin (i.e. $[\text{Heparin}]/[\text{Aniline}] = 0.5 \text{ wt.}\%$), the PANI morphology was also found to be non-uniform with many secondary growth (see Figure 5.12a & Figure 5.13a). This may be due to fusion of several heparin molecules that were in close proximity in the reaction container due to the higher concentration of heparin.

From the above discussion, it can be seen that there is a remarkable relation between the concentration of heparin and the formation of the PANI nanofibers. The PANI morphology with the porous network is believed to be very suitable for the electrochemical supercapacitor applications [212] and this will be studied in the present chapter.

Figure 5.12 FESEM images of (a) PANIH-0.5, (b) PANIH-0.25 and (c) PANIH-0.1.

Figure 5.13 HRTEM images of (a) PANIH-0.5, (b) PANIH-0.25 and (c) PANIH-0.1.

5.2.3.2 Molecular characterizations

5.2.3.2.1 FTIR study

The molecular structure of the pure heparin and PANIH-0.25 was confirmed by FTIR study which is shown in Figure 5.14. In Figure 5.14b, the peak at about 1577 cm^{-1} was attributed to the C=C stretching vibrational mode for quinoid ring and at about 1499 cm^{-1} was assigned to the C=C stretching vibrational mode for benzenoid rings indicating the presence of emeraldine form of PANI [194, 195]. The existence of these bands

demonstrated that the polymer possessed amine and imine nitrogen units in its backbone. The strong absorption at 1298 cm^{-1} was due to the C-N stretching of aromatic amines. The absorption peak at 1141 cm^{-1} is caused by the in plane deformation vibration. The out-of-plane bending mode located at 818 cm^{-1} , which is a characteristic for para-disubstituted aromatic rings [195]. The weak bands located near 695 and 750 cm^{-1} can be assigned to C-H out-of-plane deformation vibrations of mono-substituted aromatic rings.

Figure 5.14 FTIR spectra of (a) pure heparin and (b) PANIH-0.25.

The characteristic absorption peaks at about 1141 and 1234 cm^{-1} were assigned to the symmetric and asymmetric stretching vibrating of $\text{O}=\text{S}=\text{O}$ group [213], respectively in the heparin template (Figure 5.14a). The peak at 1234 cm^{-1} also attributed to the C-O stretch in $-\text{COOH}$ in the heparin molecule (Figure 5.14a). It is obvious that the peak due to the aromatic C-H bending in the plane (1141 cm^{-1}) for a 1, 4 disubstituted aromatic ring

in the PANI superimposed with the peak appeared due to the presence of symmetric stretching of O=S=O vibration (1141 cm^{-1}) in heparin based PANI nanofibers (Figure 5.14a & b). Also, the band at 1026 cm^{-1} was attributed to the $-\text{SO}_3$ group [214] of heparin (Figure 5.14a). Thus, the presence of trace amount of heparin molecules in the PANIH-0.25 is evident. The FTIR spectra of PANIH-0.5 and PANIH-0.1 are shown in Figure A5 in Appendix, which also demonstrated nearly the same spectral features as PANIH-0.25.

5.2.3.2.2 XPS study

The XPS analysis was done for the PANIH-0.25 in order to confirm the chemical and bonding environment of the sample. Figure 5.15a showed the wide scan spectra of PANIH-025, which were recorded between 0 - 1200 eV. The spectra demonstrated the existence of C, O and N elements in the sample. Figure 5.15b showed the N 1s spectra in which the peak at 399.1, 400.22 and 402.08 eV revealed the presence of imine nitrogen ($=\text{N}-$) (13.72%), amine nitrogen ($-\text{NH}-$) (75.14%) and protonated nitrogen (N^+) (11.14%), respectively, in the PANI backbone [1, 188, 215]. This observation demonstrated that the PANI existed in a physical mixture of emeraldine salt (ES) and protonated leucoemeraldine (LE) form. The XPS spectra of PANIH-0.5 and PANIH-0.1 are shown in Figure A6 in Appendix.

Figure 5.15 XPS spectra of (a) PANIH-0.25 (wide scan) and (b) N 1s of PANIH-0.25 (narrow scan).

5.2.3.3 Surface area measurements and pore size distributions

In Figure 5.16, the PANIH-0.1, PANIH-0.25 and PANIH-0.5 exhibited N₂ adsorption-desorption isotherms with type-IV hysteresis loops [200] at $P/P_0 \approx 0.95$, a typical characteristic of large pore mesoporous materials. The specific surface areas of the samples were calculated by BET method and the values were found to be 33.73, 53.20 and 28.64 m²/g for PANIH-0.1, PANIH-0.25 and PANIH-0.5, respectively. This high value in PANIH-0.25 is attributed to the presence of mesoporous PANI nanofibers networks [201]. The BET surface area of PANIH-0.25 (53.20 m²/g) is much larger than that of pure PANI (15.39 m²/g). This increase in the surface area in PANIH-0.25 results in the high electrochemical utilization of PANI during the tests and produces in the larger capacitance values. The pore size distributions were calculated using the BJH model according to the desorption isotherm and are shown in the Figure 5.16 (inset). There is a

wide hump located near 30 nm for the samples indicating the presence of mesopores in the materials.

Figure 5.16 Nitrogen adsorption-desorption isotherms: BET surface area measurements of (a) PANIH-0.1, (b) PANIH-0.25 and (c) PANIH-0.5. Inset is the BJH pore size distributions.

5.1.3.4 Conductivity measurements

The conductivity was measured by four-probe method, where the average values of five different measurements were taken. In our study, during the measurement the thickness (t) of the pallets was 0.07 cm and radius (r) of the pallet was 0.3 cm. Mass (m) of PANIH-

0.25 (best nanofiber) sample was 74.055 mg. The density of the pallet was found to be 3.743 g/cm^3 . The conductivity of PANIH-0.25 sample was found to be 1.02 S/cm .

5.2.3.5 Electrochemical characterizations

5.2.3.5.1 CV study

As to achieve the high capacitance, the higher surface area is very crucial, thus based on the surface area obtained in our sample we have carried out the CV experiment for PANIH-0.25 sample where highest surface area ($53.20 \text{ m}^2/\text{g}$) was achieved (see section 5.2.3.3). We have also shown the CV study of PANIH-0.1 sample. To evaluate the electrochemical characteristics of the electrode materials, CV study was performed in aqueous $1 \text{ M H}_2\text{SO}_4$ electrolyte at the scan rates of 5, 10, 20, 50 & 100 mV/s within the potential window of 0 - 1.0 V. The CV curves of PANIH-0.1 & PANIH-0.25 are shown in Figure 5.17. This revealed the non-rectangular shape of the curve which indicates the pseudo-capacitive properties of the PANI. The electrochemical capacitance is proportional to their CV curve area and the peak current (I_{max}) in the CV curve. The near linear dependence of the peak current on the scan rate for PANI-0.25 electrode (Figure 5.17c) indicates the fast response to oxidation/reduction processes as the current changes [200]. This fast response may arise from the nanoelectrode materials that have many advantages - higher electrode/electrolyte contact area which enhance charge-discharge rates and short path lengths for electrolyte ions transport.

It can be seen from Figure 5.16 and Figure 5.7 that in comparison to pure PANI, the nanostructured network of PANIH-0.25 has a higher specific surface area ($53.20 \text{ m}^2/\text{g}$) which is favorable for electrolyte ions transport and fast redox reactions [200]. Thus the

PANIH-0.25 specimen exhibited a highest $I_{\max}$ (0.01162 A at 100 mV/s) in CV curve compared to pure PANI synthesized without template (see Figure 5.17 & Figure 5.8). The redox reactions occur between the nitrogen atoms of the PANI backbone and H^+ ions from H_2SO_4 (see Scheme 5.2) [202]. There is a possibility that the total capacitance of the electrode may be affected by the presence of any trace amount of heparin in the PANIH-0.25 (confirmed by FTIR in Figure 5.14b). However, this can be neglected because the CV response of heparin (see Figure A7, Appendix) is very poor ($I_{\max} = 0.000152$ A at 100 mV/s).

Figure 5.17 Cyclic voltammograms of (a) PANIH-0.1 and (b) PANIH-0.25 at various scan rates in aqueous 1 M H_2SO_4 electrolyte; and (c) plots of the peak current (the anodic peak current, I_{pa} ; the cathodic peak current, I_{pc}) vs the scan rate for PANIH-0.25.

5.2.3.5.2 CCD study

The galvanostatic charge-discharge curves of pure PANI, PANIH-0.1 & PANIH-0.25 electrodes at the current density of 500 mA/g are shown in Figure 5.18. The specific capacitances were calculated from the discharging phase of the charge-discharge curve. The specific capacitance of the PANIH-0.25 was as high as 732.18 F/g at a current density of 500 mA/g while that of pure PANI & PANIH-0.1 were 124.29 & 415.21 F/g, respectively. The specific energy densities of the samples were found to be 17.28, 57.71 and 101.77 Wh/kg for pure PANI, PANIH-0.1 and PANIH-0.25, respectively at 500 mA/g discharge current. This implied that the PANIH-0.25 electrode promotes much faster redox reaction and more rapid ion diffusion than the pure PANI electrode due to the higher accessible surface area in the former nanostructures.

The above specific capacitance is comparable to the previously reported results. Mi et al. [216] reported the doped PANI nanofibers fabricated by the seed template method in presence of ferric chloride (FeCl_3) and APS as the oxidant with the help of organic composite of methyl orange/ FeCl_3 (MO/ FeCl_3) as template. The PANI fiber obtained a maximum specific capacitance of 428 F/g at a current density of 2 mA/cm² in 1 M H_2SO_4 solution. Li and coworkers [217] showed that the synthesis of PANI nanofiber on modified stainless-steel (SS) electrode (PANI/SS), exhibited a maximum specific capacitance of 524.9 F/g in 1 M H_2SO_4 solution which was only 26% of the theoretical value. Kim et al. [218] showed that PANI nanofibers fabricated by the rapid mixing polymerization which were used to produce a flexible supercapacitor electrode had a specific capacitance of 235 F/g at 100 mV/s scan rate in 1 M H_2SO_4 solution. Wang et al. [219] reported the synthesis of an ordered whiskerlike PANI grown on the surface of

mesoporous carbon where the capacitance of the composite was 768 F/g at a discharge current density of 5 A/g in 1 M H₂SO₄ solution. Guan et al. [67] has shown that PANI nanofibers obtained by interfacial polymerization for high-rate supercapacitors in the presence of *p*-phenylenediamine (PPD), had a maximum specific capacitance of 548 F/g, a specific power value of 127 W/kg and a specific energy value of 36 Wh/kg at a constant discharge current density of 0.18 A/g in 1 M H₂SO₄ solution. Gupta et al. [220] showed the electrochemical deposition of a random nanofiber network of PANI and reported a capacitance value of 562 F/g was obtained at the scan rate of 200 mV/s in 1 M H₂SO₄ electrolyte. They have also stated that PANI nanowires synthesized by electrochemical polymerization process showed a specific capacitance of 742 F/g at 6 mA/cm² current density [221]. Furthermore, in another study by Zhou's group [222], the PANI nanofiber was synthesized by the pulse galvanostatic method on a stainless steel substrate. The highest specific capacitance obtained from charge-discharge study for this nanofiber was 609 F/g at a discharge current density of 1.5 mA/cm² in NaClO₄ and HClO₄ mixed electrolyte solution.

Figure 5.18 Cyclic charge-discharge graphs of (a) pure PANI, (b) PANIH-0.1, (c) PANIH-0.25 at a constant current of 500 mA/g in aqueous 1 M H₂SO₄ electrolyte.

In the present study, it is believed that the extensive amount of microchannels and pores in the PANIH-0.25 nanostructure become accessible for diffusion and accumulation of electrolyte ions. In comparison, fewer electrolyte ions can freely transport into the macroscopic polymer (e.g. pure PANI) to conduct cyclic adsorption/desorption process because the compact packing morphology is hardly accessible. Furthermore, the low internal resistance (produced due to the ohmic drop) is of great importance in energy-storage devices because that will produce unwanted heat during charge-discharge process [223]. The ohmic drops in PANIH-0.25 was found to be smaller compared to both the pure PANI and PANIH-0.1 samples, which is the result of mesoporous network morphology of PANIH-0.25 that is favorable for the easy ion transport during the electrochemical test.

5.2.3.5.3 Justification between theoretical and observed capacitance values

The maximum theoretical specific capacitance ($C_{\max}$) can be estimated from the equation 5.1.1 [204, 205]. Based on the specific surface area, the theoretical $C_{\max}$ were estimated for each sample as shown in Table 5.2.

Table 5.2 Calculation of α values

Sample	Max. observed capacitance value (F/g)	α
Pure PANI	124.29	0.1129
PANIH-0.1	415.21	0.3824
PANIH-0.25	732.18	0.6761

As discussed in section 5.1.3.4.3, according to the redox mechanism of PANI, 1 electron per monomer (i.e. $\alpha = 1$) is required to oxidize the PANI from its fully reduced LE to fully oxidized P state. The condition $\alpha = 1$ is known to be responsible for the insulating-to-conducting phase transition in the PANI chain and this phase transition is low in electrochemical reversibility [206]. This α value varies throughout the conversion from LE state to ES with $0 < \alpha < 0.5$ and ES to P with $0.5 < \alpha < 1$. The more reversible conversion between LE and ES involves 0.5 electron per monomer (i.e. $\alpha = 0.5$) [206].

However, in our experiment, the specific capacitances were found to be 124.29, 415.21 and 732.18 F/g for pure PANI, PANIH-0.1 and PANIH-0.25, respectively. From the observed capacitance values, the α values i.e. the degree of oxidations per monomer were calculated using equation 5.1.1 as shown in Table 5.2. It can be seen from Table 5.2 that for the pure PANI, 11.29% electron transfer occurred per monomer (i.e. $\alpha = 0.1129$) i.e. only this amount was active for the redox capacitance and for PANIH-0.25, it

increased to 67.61% (i.e. $\alpha = 0.6761$). It is already proved previously that with the lowering of discharge current values the observed capacitance value can be pushed towards the theoretical value. The lowering of observed capacitances compared to the theoretical values could also be explained by the ion transport phenomenon within the nanofiber electrode. If the nanofibers are randomly oriented with respect to the current collector, then the electrolyte ions may not penetrate far inside the electrode. This lowers the complete utilization of the electrode surface area. This is consistent with the reported observation that ion diffusion parallel to the orientation of the nanofiber is fast which in turn produces large capacitance value [207, 208]. Thus, it is proved that with the material with more accessible surface area can push the observed capacitance value towards the theoretical value.

5.2.3.5.4 EIS study

The EIS is one of the principal methods to examine the impedance behavior and ion diffusion in the mesoporous electrode materials for supercapacitors [4, 186]. Figure 5.19 showed the Nyquist plots obtained in the frequency range from 100 kHz to 1 Hz at AC amplitude of 10 mV. The Nyquist plots of impedance contain two segments - the upper right portion in the graph indicated the low frequency region and the lower left portion indicated the high frequency region. The high frequency region represents a diffusion process and low frequency region represents capacitive behavior [224]. The interfacial charge transfer resistance (R_{ct}) originates at the electrode/electrolyte interface corresponds to the diameter of the semicircle along the X-axis. The R_{ct} can be quantitatively estimated by the diameter of curvature in Nyquist plot.

In pure PANI, the R_{ct} was found to be 62 ohm (see Figure 5.10), this high resistance may be due to the obstruction of ions movement into the compact pure PANI electrode. However, in PANIH-0.25 (see Figure 5.19) the absence of semicircle at high frequency region demonstrated to the negligible charge transfer resistance (R_{ct}) caused by the development of excellent electrode/electrolyte interface due to the mesoporous structure. A better compatibility between the electrode and electrolyte assisted easy accumulation of charges on the porous electrode surface and provided higher specific capacitance. Hence, the differences of their impedance behavior at high frequency range can mainly be ascribed to the limitation of interfacial charge transfer between the electrode and electrolyte.

At very high frequencies, the intercept at Z_{real} along the X-axis known as the ESR which is due to the combinational resistance of ionic resistance of the electrolyte, intrinsic resistance of the material and contact resistance at the electrode material/current collector interface [187]. For the PANIH-0.25 electrode, a lower ESR of 11.8 ohm was obtained, which was due to the high accessibility of specific surface area whereas the pure PANI showed (see Figure 5.10) very high ESR value (25 ohm) due to the low surface area or compact layer. The PANIH-0.1 electrode which had a moderate surface area, had an ESR of 15.2 ohm.

The slope of the 45° portion of the curve called as the Warburg resistance (R_w) is a result of the frequency dependence of ion diffusion/transport to the electrode surface [58]. Ideal supercapacitors have vertical impedance curve with respect to the Y-axis and the more the deviation from the vertical line, the higher is the Warburg resistance (R_w). The impedance curve of PANIH-0.25 (see Figure 5.19) was almost vertical to the Y-axis

implying an ideal supercapacitor behavior compared to the pure PANI (see Figure 5.10) and PANIH-0.1 samples. Thus, the variation of the slope is very dependent on the morphology of PANI in the different samples.

Figure 5.19 Nyquist plots of (a) PANIH-0.1 and (b) PANIH-0.25 in aqueous 1 M H_2SO_4 electrolyte.

5.2.3.5.5 Cyclic stability study

The cycle-life test of the PANI based electrode was performed at a constant current of 500 mA/g for 1000 cycles. After 1000 cycles, the retention of capacitances of the PANIH-0.1 and PANIH-0.25 were 51.34 and 72.28%, respectively while for pure PANI, it was 37.12% (see Figure 5.20 & Figure 5.11). At the cycle-life experiment, the multiple insertion/de-insertion of electrolyte ions of the electrolyte into or from the PANI chains results in the swelling and shrinkage of the CP [209]. In comparison to the pure PANI electrode, the excellent cycle life of PANIH-0.25 even after 1000 cycles may be attributed to the mesoporous PANI nanofiber networks. The significant reduction of capacitance in

pure PANI may be due to the compact structures of pure PANI which hinders the volume change accommodation during cycling. The slight reduction in capacitance in PANIH-0.25 after 1000 cycles may be due to the partial blockage of regular pore structure caused by swelling and contraction of polymer which slows down the ionic rate transfer during the test [209].

Figure 5.20 Cyclic stability of (a) PANIH-0.1 and (b) PANIH-0.25 electrode in aqueous 1 M H_2SO_4 electrolyte.

5.2.4 Summary

We have synthesized a new class of novel uniform PANI nanofiber networks (PANIH-0.25) with an average diameter of 80 - 110 nm by the template induced oxidative polymerization method. It was observed that the morphology of the PANI varied with the variation of molar ratios of heparin. The site selective interaction between the heparin molecules and aniline was responsible for the formation of nanofibers. The nanostructured PANIH-0.25 electrode demonstrated a good reversible stability and fast response to

oxidation/reduction and an excellent electrochemical capacitance. This kind of PANI nanofiber based electrode with their good electrochemical behavior has excellent potential as electro-active material for various applications in nanoelectronics like supercapacitors. Moreover, we believe that this could be an ideal synthesis route for the large scale production of PANI nanostructures in a very simple, controlled, pollution-free way.

5.3 Comparison of PANI nanotube electrode materials with PANI nanofiber electrode materials

A comparison between the PANI nanotube electrode materials and the PANI nanofibers electrode materials is outlined below:

- i. The surface areas obtained in PANI nanofibers (28.64, 53.20 and 33.73 m²/g for PANIH-0.5, PANIH-0.25 and PANIH-0.1, respectively) were higher than the PANI nanotubes (18.01, 39.75, 29.08, 25.24 and 22.57 m²/g for PANIV-0.5, PANIV-0.25, PANIV-0.1, PANIV-0.05 and PANIV-0.01, respectively), which is advantageous for the electrochemical supercapacitor applications.
- ii. From the electrochemical study, it is evident that the nanofibers showed the superior electrochemical performance than the nanotubes which is probably due to the higher surface area in nanofibers than in the nanotubes. The nanotube showed the specific capacitance of 619.76 F/g whereas for nanofiber it was 732.18 F/g at 500 mA/g discharge current. Further, the energy density for the nanotube was 86.14 Wh/kg, whereas for the nanofibers, it was a higher value of 101.77 Wh/kg at the same current density.
- iii. In both the cases, at [template/aniline] = 0.25 (molar ratio for vitamin C and wt.% ratio for heparin based synthesis), the best nanotubes and nanofibers were obtained with vitamin C and heparin, respectively.
- iv. The template used in producing the nanotubes is vitamin C which is cheaper than the template used in producing nanofibers, heparin. Therefore, large scale

production of nanotubes by vitamin C is possible where with heparin template it is not possible due to the cost factor.

- v. In both the cases the nanotubes and the nanofibers obtained are randomly oriented with respect to the current collector, and probably thus it haven't achieved the theoretical values.
- vi. The nanotubes showed little higher cyclic stability of 76.74% than the nanofibers with the cyclic stability of 72.28% after 1000 charge-discharge cycles at 500 mA/g discharge current. This may be caused by the reason that as the cycling going on, the ions can create the channels on the surface of the nanotubes and the ions have the accessibility of the inner surface of the nanotubes. However, this is not the case with nanofibers, although the initial specific capacitance is higher in heparin based supercapacitor electrode material than the vitamin C based electrode material.

Chapter 6 Graphene and polyaniline (PANI) nanostructures based composite electrode materials

In Chapter 4, it has been shown that although the graphene based electrode showed high cyclic stability, however, its poor specific capacitance limits many practical application. On the other hand, in Chapter 5, it has been seen that although PANI based nanostructures produce high specific capacitance, it suffers from poor cyclic stability during the charge-discharge process. Thus, in order to avoid the drawbacks of a single phase electrode material, it is viable to develop composite based electrode materials for coupling the advantages of the EDLC and pseudo-capacitor. The combination of PANI nanostructures (possess large capacitance) and graphene sheets (possess good cyclic stability) can enhance the supercapacitor performance due to the ability to store charges via two charge storage mechanisms [18, 19]; EDL and Faradaic reactions. The inclusion of graphene sheet maximizes the unique potential of PANI nanostructure for the supercapacitor through the synergistic effect [18]. In this chapter, we will discuss the fabrication of graphene/PANI nanostructures (nanotubes and nanofibers) based electrode materials for supercapacitor applications.

6.1 Synthesis of graphene/vitamin C template-controlled PANI nanotubes composite for high performance supercapacitor electrode

6.1.1 Introduction

In Chapter 5 (section 5.1), we have shown the fabrication and the application of PANI nanotubes for supercapacitor applications. However, the desired performance was not achieved with this electrode material, especially in terms of cyclic stability. Thus, for better electrochemical performance, we have fabricated the graphene/vitamin C-controlled PANI nanotubes composite as a superior electrode material for such applications. It will be shown that the composite material possess excellent electrochemical activity along with superior cyclic stability.

6.1.2 Experimental

6.1.2.1 Synthesis of composite

Firstly, the PANI nanotubes was synthesized according to the previous route discussed in Chapter 5 (section 5.1.2.1) with $[\text{Vitamin C}]/[\text{Aniline}] = 0.25$ (best nanotubes were obtained at this molar ratio). Then, the GO solution in water (which had been sonicated for 30 minutes) was added to the vitamin C-PANI solution for the preparation of composite (GO : PANI = 20 : 80) and stirred for 2 hours. Chemical conversion of GO to RG was then achieved according to the reported method [49], through the addition of 0.1 ml hydrazine monohydrate followed by heating the mixture at 95 °C for 1 hour. During this conversion, the PANI in the composite may have also been reduced, so re-oxidation

and re-protonation are required to recover the conductive PANI nanostructure after the reduction of GO [1]. Therefore, the reduced composite was then stirred with 10 ml 1 M HCl solution in the presence of APS at room temperature overnight. Next, the resulting mixture was washed several times with distilled water to remove the core part (template) of the vitamin C-PANI complex and the excess hydrazine monohydrate. Sufficient washing was required for the complete removal of template (vitamin C) in order to produce the PANI nanotubes. Finally, the graphene/PANI nanotube composite (G20PNT80) product was dried in an oven at 55 °C overnight and stored. In the similar way, we have also synthesized composites with the ratio (wt.%) of GO : PANI = 15 : 85 and GO : PANI = 25 : 75 in order to examine the detail effect of the inclusion of graphene within the PANI nanotubes which were denoted as G15PNT85 and G25PNT75, respectively.

6.1.2.2 Characterization techniques

The morphological properties of samples were characterized by using FESEM and HRTEM techniques. The molecular characterizations were performed using FTIR, XPS and Raman spectroscopy techniques. Surface area measurements and pore size distributions were measured according to nitrogen adsorption-desorption isotherms. The electrochemical performances were determined in aqueous 1 M H₂SO₄ solution using CV, CCD and EIS experiments. The experimental conditions for all these techniques were discussed in Chapter 3.

6.1.3 Results and discussion

6.1.3.1 Morphological investigations

6.1.3.1.1 FESEM and HRTEM studies

The morphology of the pure PANI nanotube was confirmed using FESEM and HRTEM micrographs in the Chapter 5 (see Figure 5.3 & Figure 5.4). In this chapter, various composites which were made with the uniform nanotubes obtained at the molar ratio of [Vitamin C]/[Aniline] = 0.25 (as shown in Figure 5.3b & Figure 5.4b) with various ratios of graphene will be discussed. The FESEM and HRTEM micrographs of these composites are shown in Figure 6.1(a-f), which demonstrated the distribution of graphene sheets into the PANI nanotubes matrix where the PANI nanotubes were incorporated into the graphene sheets (also see Scheme 6.1). Since the capacitive performances of electrode materials were strongly dependent on their microstructures, the tubular network of the graphene composite with PANI nanotube is believed to be desirable for the applications in supercapacitors. This will be ascertained experimentally in a later section.

Figure 6.1 FESEM images of (a) G15PNT85 composite, (c) G20PNT80 composite and (e) G25PNT75 composite; and HRTEM images of (b) G15PNT85 composite, (d) G20PNT80 composite and (f) G25PNT75 composite.

Scheme 6.1 Schematic diagram for the synthesis of graphene/vitamin C-controlled PANI nanotubes composite.

6.1.3.2 Molecular characterizations

6.1.3.2.1 FTIR spectroscopy study

The structure of all the graphene/PANI nanotube composites was confirmed by FTIR spectroscopy (Figure 6.2(a-c)). The absorption peaks in Figure 5.1c (Chapter 5) at about 1583 and 1498 cm^{-1} in PANI nanotube component were attributed to the C=C stretching for quinoid ring and the C=C stretching vibrational mode for benzenoid rings in PANI [194, 195]. They indicate the presence of the amine and imine nitrogen units in its backbone. However, in the composite (Figure 6.2 (a-c)), the peaks near C=C bond stretching zone were due to the presence of two different kind of C=C bonds in PANI nanotubes. In Figure 6.2(a-c), the peak at about 1141 cm^{-1} was due to the in plane

vibrational mode of aromatic C-H bending. The out-of-plane bending mode peak located at about 826 cm^{-1} for a para-disubstituted aromatic ring indicates a linear structure of PANI [195] in graphene/PANI nanotube composite. The characteristic peak in Figure 6.2(a-c) appearing at about 1298 cm^{-1} was due to the C-N stretching of an aromatic secondary amine in the PANI nanotubes. Comparing the spectrum of composite in Figure 6.2(a-c) & pure PANI in Figure 5.1c, the peak shift to lower wave number that occurred for the C=C group in the composite may be attributed to the interaction between the graphene surface and the PANI nanotubes. This kind of interaction has the prime role in enhancing the cyclic stability of the composite electrode material through the improvement of mechanical stability and conductivity of the composite during the electrochemical study. These peaks were shifted slightly towards lower wave number for the G20PNT80 composite compared to other two composites (G15PNT85 and G25PNT75), which is highly desirable for the high performance supercapacitor as it causes the synergistic effect. The absence of a peak (in Figure 6.2(a-c)) in the carbonyl zone demonstrates the successful reduction of GO to RG nanosheets in the presence of hydrazine monohydrate.

Figure 6.2 FTIR spectra of (a) G15PNT85 composite, (b) G20PNT80 composite and (c) G25PNT75 composite.

6.1.3.2.2 XPS study

In order to ascertain the elemental and bonding environment in G15PNT85, G20PNT80 and G25PNT75 composites, the XPS analysis (Figure 6.3) was carried out within the binding energy range of 0 - 1200 eV. The XPS spectra of all the three samples showed the presence of C, O and N elements (Figure 6.3a, b & c). An N 1s narrow scan core-level spectrum (Figure 6.3d) of G20PNT80 composite showed that most nitrogen atoms are in the form of amine (-NH- , 58.81%) centered at 400.1 eV in benzenoid amine or amide groups [188]. Two small additional shoulder peaks (Figure 6.3d) revealed that a lower percentage of nitrogen atoms existed in the imine (=N- , 15.43%) form centered at 398.4 eV and the positively charged nitrogen (N^+ , 25.76%) form centered at 401.7 eV [1, 188].

Figure 6.3 XPS spectra of (a) G15PNT85 composite (wide scan), (b) G20PNT80 composite (wide scan), (c) G25PNT75 composite (wide scan) and (d) N 1s in G20PNT80 composite (narrow scan).

6.1.3.2.3 Raman spectroscopic study

Raman spectroscopy is one of the most widely used tool to characterize the carbon based materials, particularly to distinguish ordered/disordered crystal structures and defect density. In general, Raman spectrum of graphene is characterized by two main bands; namely, the G band and the D band. In the Raman spectrum, the D band represents the breathing modes of rings or K-point phonons of A_{1g} symmetry and the G band signifies

Figure 6.4 Raman spectra of (a) GO, (b) G15PNT85 composite, (c) G20PNT80 composite and (d) G25PNT75 composite.

the in-plane bond-stretching motion of the pairs of C sp^2 atoms for the E_{2g} phonons. Figure 6.4 showed the Raman spectroscopy of GO and the composites, G15PNT85, G20PNT80 and G25PNT75. A broad D band at 1346 cm^{-1} and G band at 1603 cm^{-1} were observed in the Raman spectra for GO. The intensity ratio (I_D/I_G) of D band to G band for all the composites is decreased compared to that of pristine GO, explains the minimum defect sites in graphene in the composite after the reduction and lowering of oxygen based functional groups [225].

6.1.3.3 Surface area measurements and pore size distributions

The surface area and pore structure of the composite electrodes were characterized by BET and BJH study, respectively by nitrogen sorption analysis. Figure 6.5 showed the nitrogen sorption isotherms and pore size distributions (inset). This exhibits a type-IV isotherm with a significant slope at higher relative pressures [200]. The steep increase in adsorption at $P/P_0 \approx 0.95$ relative pressure indicates the characteristic for mesoporous materials of the composite [201]. The BET surface areas of the G15PNT85, G20PNT80 and G25PNT75 composites were found to be 41.84, 43.12 and $45.78\text{ m}^2/\text{g}$, respectively. It should be noted that the large surface area in the graphene based composite compared to the pure PANI nanotubes ($39.75\text{ m}^2/\text{g}$) may be due to the presence of graphene components in the composite. Furthermore, the large surface area in the G25PNT75 composite compared to the other two composites may be due to the higher percentage of graphene in the composite.

Figure 6.5 (a) Nitrogen adsorption-desorption isotherms: BET surface area measurements of (a) G15PNT85 composite, (b) G20PNT80 composite and (c) G25PNT75 composite. Inset is the BJH pore size distributions.

6.1.3.4 Conductivity measurements

The conductivity was measured by four-probe method, where the average values of five different measurements were taken. In our study, during the measurement the thickness (t) of the pallets was 0.07 cm and radius (r) of the pallet was 0.3 cm. Mass (m) of G20PNT80 composite sample was 74.542 mg. The density of the pallet was found to be 3.768 g/cm³. The conductivity of G20PNT80 composite sample was found to be 17.87 S/cm.

6.1.3.5 Electrochemical characterizations

6.1.3.5.1 CV study

The CV experiment was conducted for the graphene based PANI nanotube composite electrode with a potential from 0 - 1.0 V in 1 M H₂SO₄ aqueous solution. Figure 6.6 showed the CV curves of the composites at the scan rates of 1, 5, 10, 20, 50 and 100 mV/s. It is observed that with increasing scanning rate from 1 to 100 mV/s, the redox current increases for each composite. At 100 mV/s scanning rate, the peak currents for G15PNT85, G20PNT80 and G25PNT75 composite were 0.0079, 0.0095 and 0.0074 A, respectively. The high current value in G20PNT80 composite compared to G15PNT85 and G25PNT75 composite can be explained as - (i) with increasing the amount of graphene in the PANI matrix, the conductivity and surface area of the composite will increase as it is known that the conductivity and surface area of graphene is high compared to pure PANI. Thus, considering the conductivity and surface area factors, the peak current of the composite should increase as the graphene content increases, (ii) however, on the other hand, two other factors like capacitance contribution (EDL capacitance and pseudo-capacitance) and the synergistic effect has to be taken into consideration. As the graphene content increases the EDL capacitance will increase and the pseudo-capacitance will decrease. For a given amount of material, it was shown that the EDL capacitance is much less than the pseudo-capacitance. Thus, the gradual increase in graphene content may not follow the trend of increase of the peak current. Also, from the FTIR spectra it is clear that the composite G20PNT80 showed better synergistic effect compared to other two composites, which will enhance the charge transfer process in this

composite. Thus, overall the above explanation validates the observed current-voltage response in G20PNT80 composite.

The voltammetric curves of the G20PNT80 composite electrode represent the behavior of a synergistic combination [18] of both redox capacitance (from PANI nanotubes) and EDL capacitance (from graphene sheets). It is worthy to note that the deviation from rectangularity in the CV curves (apparent from Figure 6.6) is largely due to the pseudo-capacitive profile of PANI. The pseudo-capacitance of the composite originated from the redox reaction of PANI where upon doping electron delocalization occurred along the polymer chains to enable high conductivity [226]. These doping charges can be retrieved after the polymer is de-doped by reduction.

Figure 6.6 Cyclic voltammograms of (a) G15PNT85 composite, (b) G20PNT80 composite and (c) G25PNT75 composite in aqueous 1 M H_2SO_4 electrolyte.

The peak intensity increased gradually as we move from higher to lower scanning rate. The appearance of peaks was probably due to the electronic transition between the different oxidation states of PANI chains. Usually PANI based electrodes exhibit two pairs of redox waves which are indicative of an active pseudo-capacitive characteristic of PANI [188, 203]. In Figure 6.6, a pair of broad redox peaks (each pair consists of anodic and cathodic peak) was found for the composite electrodes at the lower scan rate. The observed broad redox peaks originated from the overlapping of the two redox processes [188] which were discussed in detail in Chapter 5.

6.1.3.5.2 CCD study

The CCD experiment is a very reliable method for evaluating the electrochemical capacitance of materials under controlled current conditions. Based on the CV experiments it was found that the G20PNT80 composite showed the maximum current values among all the three composites. Thus, the CCD study was carried out for this composite, G20PNT80. Figure 6.7 showed the galvanostatic charge-discharge graphs of this composite at various current densities. It was found that the specific capacitances of the G20PNT80 composite were 756.65, 717.93 and 671.79 F/g at the discharge current densities of 250, 375 and 500 mA/g, respectively. The composite revealed better electrochemical performance which was due to the better synergistic effect between the components in the composite. The corresponding energy densities were found to be 105.17, 99.79 and 93.38 Wh/kg for the discharge currents of 250, 375 and 500 mA/g, respectively.

The specific capacitance of the composite is much higher than that of the individual components at the same discharging current. The G20PNT80 composite produced the specific capacitance of 671.79 F/g at a discharge current of 500 mA/g, reaching about five times enhancement in comparison with graphene (133.86 F/g) and also much higher than the pure PANI nanotube (619.76 F/g) at the same discharge current. The improved capacitance in this composite is mainly due to the following two factors [223]. First, the incorporation of PANI nanotubes into graphene sheets (see Figure 6.1) greatly improved the EDL capacitance of graphene in the G20PNT80 composite by forming a porous structure. Second, the pseudo-capacitance of PANI nanotube in the composite was enhanced by its highly conductive graphene sheet, which favors the redox

reaction of PANI component. This kind of nanostructure with PANI nanotubes in graphene assisted in the formation of an efficient EDL and dynamic charge propagation throughout the whole bulk composite by contributing a smaller resistance and shorter diffusion pathways. The adsorption of redox PANI nanotubes on to the graphene sheet not only effectively inhibited the stacking/agglomeration of graphene resulting in high EDL capacitance, but also exhibited enhanced electrode/electrolyte interface areas through the nanostructures of both the components [18]. The highly conductive pathways generated by graphene sheets in the composite also provided for electron transport during the charge-discharge processes and facilitated the rapid transport of the electrolyte ions into the electrode.

To the best of our knowledge, no study on the electrochemical characteristics of PANI nanotube based graphene composite has been reported in the literature. The specific capacitance obtained in our experiments on nanotube composites is either higher or comparable to the other studies with PANI nanofiber based graphene composites. Zhang et al. [1] observed a specific capacitance of 480 F/g for PANI nanofiber-graphene composite at a current density of 0.1 A/g in 1 M H₂SO₄ electrolyte. However, they have obtained the specific capacitance of 260 F/g at the current density of 0.5 A/g. Wu et al. [223] prepared graphene and PANI nanofiber based supercapacitor electrode which exhibited a specific capacitance of 210 F/g at a discharge rate of 0.3 A/g in 1 M H₂SO₄ electrolyte. Gómez et al. [227] showed a maximum specific capacitance of 500 F/g at a current density of 0.1 A/g with graphene-PANI nanocomposite material in 2 M H₂SO₄ electrolyte. Cao et al. [228] fabricated the graphene microspheres with a 3D porous structure by spray drying of graphene nanosheets suspensions that were used as a template

to synthesize PANI/GMS (modified graphene sheets) composite by in situ polymerization. The PANI/GMS composite exhibited a maximum specific capacitance of 261 F/g at the current density of 0.5 A/g in 1 M H₂SO₄ electrolyte. Graphene-wrapped PANI nanofibers were prepared by Zhou's group [229] by direct co-assembly of the positively charged aqueous dispersible PANI nanofibers and negatively charged GO in an aqueous dispersion followed by reduction of GO by hydrazine. The hybrid composite showed a specific capacitance of 250 F/g at a current density of 0.5 A/g in 1 M Et₄N⁺.BF₄⁻/propylene carbonate electrolyte in an organic non-proton electrolyte. Meng et al. [230] designed a 3D reduced graphene (3D-RGO) based PANI composite (3D-RGO/PANI) which showed the specific capacitance of 385 and 362 F/g at the current density of 0.5 and 1 A/g, respectively in 1 M H₂SO₄ solution. Further, Luo et al. [231] reported the fabrication of self-assembled hierarchical graphene/PANI nanoworm composite using GO and aniline as the starting materials. The supercapacitor electrode produced the specific capacitance of 601.4 and 488.2 F/g at 0.4 and 0.5 A/g discharge currents, respectively in 1 M H₂SO₄ solution.

It should be noted from Figure 6.7 that the discharging curves show two voltage stages, an initial fast discharging stage (which includes sharp potential drop, also known as ohmic drop) followed by a slow discharging stage. For the former stage, the relatively short discharging duration is ascribed to the EDL capacitance originated largely from graphene and a smaller percentage of PANI in the composite [226]. However, for the later stage, it showed good performance of the electrode materials due to the much longer discharging duration that is associated with the combination of EDL capacitance of graphene and PANI plus large pseudo-capacitance of PANI nanotubes in the composite

[226]. Thus, it is believed that the high specific capacitance and energy density in the composite originated from the Faradaic reactions of PANI. Furthermore, a synergistic factor of the composite play an important role in order to achieve this higher specific capacitance and energy density [18] through the redox capacitance (from PANI nanotubes) and EDL capacitance (from graphene sheets).

Figure 6.7 Cyclic charge-discharge graphs of G20PNT80 composite at various discharge current in aqueous 1 M H_2SO_4 electrolyte.

6.1.3.5.3 EIS study

To investigate the electrochemical impedance behavior the electrodes, EIS study was carried out for the materials [4, 186]. Figure 6.8 showed the Nyquist plots of the composites. The Nyquist plot of G20PNT80 and G25PNT75 composites do not exhibit a semicircular shape at the high-frequency region, probably because of the very low interfacial charge-transfer resistance (R_{ct}) through the creation of excellent electrode/electrolyte contact [1]. However, for the G15PNT85 composite specimen, the

small semi-circle for the electrode suggested very low ($R_{ct} = 1.59 \text{ ohm}$) interfacial charge-transfer resistance which may be due to the poor synergistic effect between the components in the composite, which created a poor electrode/electrolyte contact. The intersection of the curves at the real axis (X-axis) in the range of high-frequency represents the ESR [1] which were about 5.65 and 6.32 ohm for the G25PNT75 and G15PNT85 composites, respectively. However, for the G20PNT80 composite, it was only 2.02 ohm. This lower ESR of G20PNT80 composite may be attributed to the nanostructured composite material with higher synergistic effect in the composite, which facilitated the efficient access of electrolyte ions to the electrode surface.

Figure 6.8 Nyquist plots of (a) G15PNT85 composite, (b) G20PNT80 composite and (c) G25PNT75 composite in aqueous 1 M H_2SO_4 electrolyte.

It should be noted that supercapacitors usually behave as pure resistors at high frequencies and typical capacitors at low frequencies. As discussed before, a straight line with 45° angle between the low and high frequency region is commonly known as

Warburg resistance (R_w) and this is a combination of both resistive and capacitive behavior [1] resulting from the diffusion behavior of ions in the electrode pores. The vertical profile of the sloped line represents an ideal capacitive behavior with fast ion diffusion. It is apparent from Figure 6.8 that among the three composites, the G20PNT80 composite electrode exhibited a steeper slope at low-frequency in contrast to the high frequency region, illustrating better capacitive behavior and lower diffusion resistance of ions at the low frequency region for this nanotube based graphene composite.

6.1.3.5.4 Cyclic stability study

As the composite G20PNT80 showed the better capacitive behavior, thus, the cycle life of the composite G20PNT80 was investigated by charge-discharge study for 1000 cycles at 500 mA/g as presented in Figure 6.9. The G20PNT80 electrode exhibited excellent cyclic stability over the entire cycle testing period. After 1000 cycles, the capacitance decreased by only 10.77% of the initial value, demonstrating that the G20PNT80 electrode possesses long-term electrochemical stability. This slight loss may be attributed to the randomly oriented nanotubes in the composite, which is not easily accessible to the electrolytes. During the insertion/de-insertion process of the counter ions, the swelling or shrinkage of PANI causes volume distortion, and consequently destroys the polymer backbone. However, due to the presence of graphene sheets in the substrate, the swelling and shrinkage of PANI during charge-discharge processes is efficiently prevented. For this reason, our new hybrid material is more adaptable and can withstand volumetric changes due to the redox reactions resulting in significant improvement in cycling stability [19, 62, 226].

Figure 6.9 Cyclic stability of G20PNT80 composite in aqueous 1 M H_2SO_4 electrolyte.

6.1.4 Summary

In summary, graphene/polyaniline nanotube composites have been synthesized using a novel in situ polymerization process based on the chemical oxidative polymerization of aniline using vitamin C as a soft-template. The inclusion of graphene sheets within the PANI nanotubes matrix made the composite more electrochemically active through the enhancement of conductivity of the composite which then improved the ionic transport within the electrode. The significantly improved specific capacitance is due to the synergistic effect of the composite of both the components. It showed excellent cyclic stability compared to pure PANI nanotube over the entire cycles which can be attributed to the good mechanical stability of the composite electrode. Thus, the novel G20PNT80 composite can be considered as the potential electrode material for supercapacitor applications.

6.2 Synthesis of graphene/heparin template-controlled PANI nanofibers composite for high performance supercapacitor electrode

6.2.1 Introduction

In Chapter 5 (section 5.2), we have discussed about the development of heparin bio-molecule based soft-template route for the synthesis of PANI nanofibers. In this chapter, we will discuss the fabrication and characterizations of graphene/heparin-controlled PANI nanofibers composite materials for the supercapacitor applications.

6.2.2 Experimental

6.2.2.1 Synthesis of composite

The composites were prepared with the PANI nanofibers and the GO. Firstly, the PANI nanofibers were synthesized according to the route described in Chapter 5, section 5.2.2.1. Then, the GO solution in water (which had been sonicated for 30 minutes) was added to the heparin-PANI solution for the preparation of composite (with the weight ratio of GO : PANI = 25 : 75) and stirred for 2 hours. Then, chemical conversion of GO to RG was done according to the reported method [49] through the addition of 0.1 mL of hydrazine monohydrate, and the mixture was heated at 95 °C for 1 hour (see Scheme 6.2). As the PANI nanofibers in the composite may have also been reduced during this reaction, so re-oxidation and re-protonation are required to recover the conductive PANI nanofibers after the reduction of GO [1]. Therefore, the reduced composite was stirred with 10 ml 1 M HCl solution in the presence of APS at room temperature overnight. Next, the resulting

mixture was washed several times with distilled water to remove the heparin template from the heparin-PANI complex and any trace amount of hydrazine monohydrate. Finally, the graphene/PANI nanofiber composite product (marked as G25PNF75) was dried overnight in an oven at 55 °C and stored in a glass vial. Other composites with the (wt.%) ratios of GO : PANI = 30 : 70 and GO : PANI = 20 : 80 were also synthesized and the samples were designated as G30PNF70 and G20PNF80, respectively.

Scheme 6.2 Schematic diagram for the synthesis of graphene/heparin-controlled PANI nanofibers composite.

6.2.2.2 Characterization techniques

The morphological properties of samples were characterized by using FESEM and HRTEM techniques. The molecular characterizations were performed using FTIR, XPS and Raman spectroscopy techniques. Surface area measurements and pore size

distributions were measured according to nitrogen adsorption-desorption isotherms. The electrochemical performances were determined in aqueous 1 M H₂SO₄ solution using CV, CCD and EIS experiments. The experimental conditions for all these techniques were discussed in Chapter 3.

6.2.3 Results and discussion

6.2.3.1 Morphological investigations

6.2.3.1.1 FESEM and HRTEM studies

As discussed in Chapter 5, the morphology of the PANI nanofiber was confirmed using FESEM and HRTEM micrographs (see Figure 5.12 & Figure 5.13). The FESEM and HRTEM micrographs of three composites are shown in Figure 6.10(a-f), which demonstrated the distribution of graphene sheets into the PANI nanofibers matrix where the PANI nanofibers were incorporated into the graphene sheets (see Scheme 6.2). Depending on the amount of PANI nanofiber and the graphene used, the composites show different distribution of PANI nanofiber into the graphene sheets. The interaction between the PANI nanofibers and the graphene sheets will cause the synergistic effect which will consequently provide better capacitive behavior.

Figure 6.10 FESEM images of (a) G20PNF80 composite, (c) G25PNF75 composite and (e) G30PNF70 composite; and HRTEM images of (b) G20PNF80 composite, (d) G25PNF75 composite and (f) G30PNF70 composite.

6.2.3.2 Molecular characterizations

6.2.3.2.1 FTIR spectroscopy study

The molecular structure of various graphene/PANI nanofiber composites were characterized by FTIR spectroscopy (Figure 6.11). In the G30PNF70 and G20PNF80 composites, the peaks at about 1575 and 1493 cm^{-1} were due to the presence of two different kind of C=C bonds (benzonoid and quinoid) in PANI nanofibers. However, the G25PNF75 composite showed the peaks at 1567 and 1487 cm^{-1} , this slight lowering of wave number compared to the other two composites may be due to the extensive interaction between the components. In Figure 6.11, it is apparent that the aromatic C-H bending in the plane and out-of-plane vibration are at about 1143 and 822 cm^{-1} , respectively for a para-disubstituted aromatic ring which indicated a linear structure of PANI in all the composite [195]. The characteristic peak appearing at about 1293 cm^{-1} was due to the C-N stretching of an aromatic secondary amine in the PANI nanofibers. Also, comparing the spectrum of pure PANI nanofiber (shown in Chapter 5, Figure 5.14), the peak shift to lower wave number that occurred for the C=C group in the composite may be attributed to the non-covalent interaction between the graphene surface and the PANI nanofibers. This kind of interaction has the prime role in enhancing the cyclic stability of the composite electrode material through the improvement of mechanical stability of the composite during the electrochemical study. As discussed before, this kind of interaction was higher in G25PNF75 composite compared to other two composites, which will produce better synergistic effect between the components in G25PNF75 composite. Also, the absence of a peak in the carbonyl zone demonstrates the successful reduction of GO to graphene nanosheets in the presence of hydrazine monohydrate.

Figure 6.11 FTIR spectra of (a) G20PNF80 composite, (b) G25PNF75 composite and (c) G30PNF70 composite.

6.2.3.2.2 XPS study

For the structural information in G20PNF80, G25PNF75 and G30PNF70 composites, the XPS analysis (Figure 6.12) was done within the binding energy range of 0 - 1200 eV. The XPS spectra of all the sample specimens show the presence of C, O and N elements (Figure 6.12a, b & c). An N 1s narrow scan core-level spectrum of G25PNF75 composite (Figure 6.12d) showed that most nitrogen atoms are in the form of amine (-NH- , 59.49%) centered at 400.1 eV in benzenoid amine or amide groups [188]. Also, the two small additional peaks (Figure 6.12d) suggested that a lower percentage of nitrogen atoms existed in the imine (=N- , 14.96%) form centered at 398.4 eV and the positively charged nitrogen (N^+ , 25.55%) form centered at 401.7 eV [1, 188].

Figure 6.12 XPS spectra of (a) G20PNF80 composite (wide scan), (b) G25PNF75 composite (wide scan), (c) G30PNF70 composite (wide scan) and (d) N 1s in G25PNF75 composite (narrow scan).

6.2.3.2.3 Raman spectroscopic study

The reduction of GO in the composite was confirmed by Raman spectroscopy. Figure 6.13 showed the Raman spectra of GO and all the three composites G20PNF80, G25PNF75 and G30PNF70. For GO a broad D band centered at 1346 cm^{-1} and G band centered at 1603 cm^{-1} were observed in the Raman spectrum. As discussed earlier, in the

Raman spectrum, the D band signifies the breathing modes of rings or K-point phonons of A_{1g} symmetry and the G band implies the in-plane bond-stretching motion of the pairs of $C sp^2$ atoms for the E_{2g} phonons. The intensity ratio (I_D/I_G) of D band to G band for all the composites is decreased compared to that of pristine GO. This demonstrates the minimum defect sites in graphene in the composite after the reduction and lowering of oxygen based functional groups [225]. The presence of minimum defect sites in graphene in the composite is beneficial for the superior supercapacitor properties.

Figure 6.13 Raman spectra of (a) GO, (b) G20PNF80 composite, (c) G25PNF75 composite and (d) G30PNF70 composite.

6.2.3.3 Surface area measurements and pore size distributions

In Figure 6.14, the hysteresis loop at the relative pressure of $P/P_0 \approx 0.95$ in N_2 adsorption-desorption isotherms revealed the presence of mesoporous structure of the composite [200, 201]. The corresponding pore size distributions given in the inset in Figure 6.14 demonstrated the presence of prominent mesopores. The isotherms exhibit type-IV curves and the specific surface areas of the G20PNF80, G25PNF75 and G30PNF70 composites were calculated using the BET equation to be 56.82, 61.43 and 64.22 m^2/g , respectively. The large surface area in the graphene based composite compared to the pure

Figure 6.14 Nitrogen adsorption-desorption isotherms: BET surface area measurements of (a) G20PNF80 composite, (b) G25PNF75 composite and (c) G30PNF70 composite. Inset is the BJH pore size distributions.

PANI nanofibers ($53.20 \text{ m}^2/\text{g}$) may be attributed to the presence of graphene (possess high surface area) components in the composite. The large surface area in the G30PNF70 and G25PNF75 composites compared to the G20PNF80 is due to the higher percentage of graphene in the composite, which is beneficial for high performance electrode materials.

6.1.3.4 Conductivity measurements

The conductivity was measured by four-probe method, where the average values of five different measurements were taken. In our study, during the measurement the thickness (t) of the pellets was 0.07 cm and radius (r) of the pellet was 0.3 cm. Mass (m) of G25PNF75 composite sample was 74.542 mg. The density of the pellet was found to be 3.768 g/cm^3 . The conductivity of G25PNF75 composite sample was found to be 20.68 S/cm.

6.2.3.5 Electrochemical characterizations

6.2.3.5.1 CV study

The CV experiments were carried out for all the composite electrodes using a potential window from 0 - 1.0 V in 1 M H_2SO_4 aqueous solution. Figure 6.15 illustrated the CV curves of the composites at the scan rates of 1, 5, 10, 20, 50 & 100 mV/s. The maximum current obtained for the G25PNF75 was 0.0127A at 100 mV/s scanning rate, which indicates good electrochemical behavior of the material. However, for the G20PNF80 and G30PNF70 composite the peak current at 100 mV/s scanning rate were found to be 0.0078 and 0.00469 A, respectively. The high current value in G25PNF75 composite compared to G20PNF80 and G30PNF70 composite can be explained by four factors - conductivity, surface area, capacitance contribution (EDL capacitance and pseudo-

capacitance) and the synergistic effect. This has been explained in section 6.1.3.4.1. However, the voltammetric curves of the composite electrode represent the behavior of a synergistic combination [18] of both redox capacitance from PANI nanofibers and EDL capacitance from graphene. It is apparent from the Figure 6.15 that for the G20PNF80 and G25PNF75 composite samples, the peak appearance started at 50 mV/s. However, this is not the case for the G30PNF70 composite. Thus, it can be inferred that the former two composites are more electrochemically active than the later; and therefore the later produced a lower current compared to other two composites. Moreover, the lower current in G30PNF70 may be attributed to the higher percentage of EDL capacitance due to the existence of graphene in the composite. For a given material, the EDL capacitance is lower than the redox capacitance. Now, the higher current in G25PNF75 composite among all the composites may be due to the better synergistic effect between the components. Usually the PANI based electrodes exhibit two pairs of redox waves which are indicative of a typical pseudo-capacitive characteristic of PANI [188, 203] which has been discussed before.

Figure 6.15 Cyclic voltammograms of (a) G20PNF80 composite, (b) G25PNF75 composite and (c) G30PNF70 composite in aqueous 1 M H₂SO₄ electrolyte.

6.2.3.5.2 CCD study

The galvanostatic charge-discharge experiments were carried out to investigate the electrochemical properties of materials. Figure 6.16 showed the galvanostatic charge-discharge graphs of the G25PNF75 composite at various charge-discharge currents like 250, 375 and 500 mA/g. It was found that the specific capacitance of G25PNF75 composite was found to be higher than the other two composites. The specific capacitances of G25PNF75 composite were 890.79, 825.8, 690.68 F/g at the discharge currents of 250, 375 and 500 mA/g, respectively. This higher specific capacitance of this

composite structure may be due to the good conductivity of the composite due to the presence of the graphene sheets, and the synergistic effect between the components where an effective charge transfer occurs. In addition to this, the layered and fibrous structures of the composite shorten the diffusion lengths of the electrolyte ions and offer high electroactive regions, thus improving the utilization of PANI. The specific energy densities of this composite at various discharge currents were 123.81, 114.79 and 96 Wh/kg at 250, 375 and 500 mA/g currents, respectively.

In the literature, the specific capacitance values on the graphene based PANI composite are found to be comparable to our work. Some literature reviews on the other graphene based PANI nanofiber composite were given previously in this chapter.

In addition, Zhang et al. [232] prepared the GO/PANI composite by the one-step electrochemical co-deposition method. Different ratios of GO were utilized to improve the electrochemical performances. They achieved the maximum specific capacitance for GO/PANI composite of 1136.4 F/g with a GO concentration of 10 mg/L at a scan rate of 1 mV/s. They have also found that GO/PANI composite showed good cycling stability, retaining over 89% of its initial capacitance after 1000 cycles. Kumar et al. [233] found that the specific capacitance of graphene-PANI nanocomposite was as high as 338 F/g at the scan of 5 mV/s in 1 M H₂SO₄ solution. Jin et al. [234] reported an easy and one-pot synthesis process for the preparation of sulfonated graphene/PANI nanofiber (SGEPA) composites by interfacial polymerization. A high specific capacitance of 962 F/g was

Figure 6.16 Cyclic charge-discharge graphs of G25PNF75 composite at various discharge current in aqueous 1 M H_2SO_4 electrolyte.

obtained at a potential scan rate of 2 mV/s in 6 M KOH electrolyte. Also, retention of the capacitance value of about 78% was obtained after 1000 cycles. It also exhibited a high energy density of 68.86 Wh/kg at a power density of 102 W/kg. Li et al. [18] found that the graphene nanosheets/PANI nanofibers (GNS/PANI) composites synthesized via in situ polymerization of aniline monomer in HClO_4 solution, showed a high specific capacitance of 1130 F/g obtained at a scan rate of 5 mV/s in 1 M H_2SO_4 solution. Moreover, the GNS/PANI composite showed excellent long cycle life with 87% specific capacitance retained after 1000 charge-discharge cycles.

Mao et al. [226] showed the fabrication of PANI nanofibers by in situ polymerization of aniline in the presence of surfactants such as tetrabutylammonium

hydroxide and sodium dodecyl benzenesulfonate stabilized graphene under acidic condition. Then, a graphene composite was prepared where a homogeneous dispersion of individual graphene sheets within the polymer matrix was achieved. The composite showed a maximum specific capacitance of 526 F/g at a current density of 0.2 A/g. Li et al. [235] fabricated the sandwich like graphene/PANI/graphene composite by chemical oxidation polymerization where they achieved a maximum specific capacitance of 775 F/g at a discharge current density of 1 A/g in 1 M H₂SO₄ electrolyte. Wang et al. [236] demonstrated that a flexible graphene/PANI hybrid material as a supercapacitor electrode was synthesized by an in situ polymerization process. A high specific capacitance of 1126 F/g was obtained for the electrode at the scan rate of 1 mV/s in 1 M H₂SO₄ electrolyte with a retention capacitance of 84% after 1000 cycles.

6.2.3.5.3 EIS study

The EIS [4, 186] technique is a complementary to galvanostatic charge-discharge measurements which provides information on the electrochemical behavior of the system where the redox reaction resistance and ESR can be studied. Figure 6.17 showed the Nyquist plot of the three composites. The resistance at the semi-circular portion at the high frequency range is commonly known as charge transfer resistance (R_{ct}). None of the composite samples exhibited a Nyquist plot with an obvious semicircular shape at the high-frequency region, probably because of the very low interfacial charge-transfer resistance through the creation of excellent electrode/electrolyte contact [1]. The intersection of the curves at the real axis (X-axis) in the range of high-frequency represents the ESR [1] which is about 1.85 ohm for the G25PNF75 composite (2.57 ohm

for G20PNF80 and 3.05 ohm for G30PNF70). This lower ESR of G25PNF75 composite may be attributed to the nanostructured composite material which facilitated the efficient access of electrolyte ions to the electrode surface and the enhanced conductivity due to the presence of graphene sheets. The G25PNF75 electrode exhibited little steeper slope compared to other two composites at low-frequency in contrast to the high frequency region, illustrating lower Warburg resistance (W_R), better capacitive behavior and lower diffusion resistance of ions at the low frequency region.

Figure 6.17 Nyquist plots of (a) G20PNF80 composite, (b) G25PNF75 composite and (c) G30PNF70 composite in aqueous 1 M H_2SO_4 electrolyte.

6.2.3.5.4 Cyclic stability study

The long-term cyclic stability of the electrode was evaluated by repeating CCD testing in 1 M H_2SO_4 electrolyte at a discharge current of 500 mA/g for the G25PNF75 composite for 1000 cycles. As shown in Figure 6.18, the composite presented excellent cycling behavior and only a slight capacitance loss of about 11% occurred after 1000 cycles. This

is attributed to the charge storage mechanism of the composite due to the existence of graphene sheets that store charge through EDL. This slight loss may also be attributed to the randomly oriented nanofibers in the graphene composite, which is not easily accessible to the electrolyte. It has been demonstrated that the pure PANI nanofiber shows the specific capacitance retention of 72.28% after 1000 charge-discharge cycles. The better stability of graphene based PANI nanofiber composite (G25PNF75) is derived from the supporting effect of the RG and the synergistic effect of the RG and PANI nanofibers [237]. The graphene nanosheets hinder the mechanical deformation caused by the swelling and shrinking of the nanostructures during the long term charge-discharge practices. Thus, it is suggested that the higher stability of the composite materials compared to the pure PANI component may be due to the - (a) inclusion of graphene sheets within the PANI nanofiber matrix which increase the mechanical stability of the composite during the electrochemical performance, and the conductivity, (b) highly porous nature of the composite which makes it easy to accommodate the volume change and (c) the synergistic combination of both the components in the composite [19, 62, 226].

Figure 6.18 Cyclic stability of G25PNF75 composite in aqueous 1 M H_2SO_4 electrolyte.

6.2.4 Summary

In summary, graphene/PANI nanofiber composites have been synthesized using in situ polymerization process based on the chemical oxidative polymerization of aniline using heparin as a soft-template. The homogeneous dispersion of individual graphene sheet within the polymer nanofibers matrix enhanced the kinetics for both charge transfer and ion transport throughout the electrode and consequently produced higher specific capacitance. Also, the cyclic stability of the composite (G25PNF75) is much improved after the inclusion of graphene component and this is about 16% higher than the pure PANI nanofibers. The significantly improved specific capacitance and cyclic stability were due to the synergistic effect of the composite of both the components and the mechanical stability. Thus, the composite electrode material with such high specific capacitance and specific energy density is very promising for supercapacitor applications.

6.3 Comparison of PANI nanotube composite electrode materials with PANI nanofiber composite electrode materials

A comparison between the PANI nanotube composite electrode materials and the PANI nanofibers composite electrode materials is outlined below:

- i. The surface areas obtained in PANI nanofiber composites (56.82, 61.43 and 64.22 m^2/g for G20PNF80, G25PNF75 and G30PNF70 composites, respectively) were higher than the PANI nanotube composites (41.84, 43.12 and 45.78 m^2/g for G15PNT85, G20PNT80 and G25PNT75 composites, respectively). This is desirable as it can be inferred that the electrochemical properties of the nanofiber composite will be more superior than the nanotube based composites.
- ii. From the electrochemical study, it was evident that the nanofiber based composites showed better electrochemical performance than the nanotube based electrode, which is probably due to the higher surface area in nanofiber composites than in the nanotube composites. An optimum ratio for the best electrochemical properties existed in the composites. In nanofiber based composite, the composite G25PNF75 showed the best electrochemical performance, whereas in nanotube based composite, the composite G20PNT80 showed best performance. The nanotube based graphene composite G20PNT80 showed the specific capacitance of 671.79 F/g, whereas for nanofiber based graphene composite G25PNF75, it was 690.68 F/g at the discharge current of 500 mA/g. Furthermore, the energy densities were found to be 93.38 Wh/kg and 96 Wh/kg for G20PNT80 and G25PNF75 composites, respectively at the discharge current of 500 mA/g.

However, at the low discharge current (250 mA/g), the specific capacitance and energy density of G20PNT80 were found to be 756.65 F/g and 105.17 Wh/kg, respectively. On the other hand at this current for the G25PNF75 composite, the specific capacitance and energy density were found to be 890.79 F/g and 123.81 Wh/kg, respectively.

- iii. It should be noted that, although at the higher discharge current the specific capacitance and the energy density in both the composites (nanotube and nanofiber) are nearly the same; however, at the lower discharge currents the specific capacitance and the energy density of nanofiber based composite is higher than the nanotube based composite. This is probably due to the reason that at the lower current the nanofiber based graphene composite is more active in electrochemical performance than that of nanotube based graphene composite.
- iv. The nanotube based composite electrode G20PNT80 showed almost same cyclic stability of 89.33% as the nanofiber based composite G25PNF75 with the cyclic stability of 88.77% after 1000 charge-discharge cycles at 500 mA/g discharge current.

Chapter 7 Conclusions and future work

7.1 Conclusions

We have modified the graphene sheets by LBL assembly using an organic spacer. The PANI nanotubes and nanofibers were synthesized using a biomolecule-based soft-template approach. Furthermore, we have fabricated the graphene based PANI nanostructures composite and evaluated their electrochemical characteristics and properties.

From the study, the following conclusions may be drawn:

- i. The modification of graphene into RG that had an open structure (GPPD) enhanced the electrochemical performance. The LBL assembly of graphene sheets through the covalent functionalization of GO using the PPD organic spacer enabled the conversion of aggregated graphene sheets into an open morphology. This allowed the graphene sheets to maintain highly accessible surface area leading to great potential for improved electrochemical performance.
- ii. The morphology of the PANI nanostructures can be tuned by controlling the monomer to template ratio, where an optimum ratio produced the uniform PANI nanostructures (nanotubes and nanofibers). It was observed that, in case of vitamin C template, no reaction occurred at an equal molar ratio of vitamin C to aniline due to the antioxidant property of vitamin C.

- iii. The site selective interaction between the aniline monomers and the template, through intermolecular H-bonding and the participation of chemical functional groups present in the template are responsible for the formation of nanostructures.
- iv. The morphology and type of PANI nanostructures have a profound impact on the electrochemical performance. The PANI nanotubes exhibit lower specific capacitance values compared to the nanofibers. Also, the surface area of PANI nanotube is lower than the nanofibers. This concludes that the synthetic route and the surface area have great impact on the electrochemistry of the nanostructures.
- v. From the CV curves, it can be inferred that the redox peak for the PANI is more obvious at lower scanning rate than at higher scanning rate. Thus, in order to derive the complete electrochemical behavior of any electrode material, lower scanning rate should preferably be used. This is because the slower electrochemical process at low scanning rates allows sufficient time and more complete electrochemical phenomenon to occur in the system. In contrast, this is not the case with fast electrochemical process at higher scanning rates.
- vi. The specific capacitance and the cyclic stability of the graphene based composite materials are higher than that of the 'pure PANI nanostructures' based electrodes. The dispersion of individual graphene sheet within the nanostructured matrix enhanced the kinetics for both charge transfer and ion transport throughout the electrode. The significantly improved specific capacitance in the composite compared to the pure PANI nanostructures based electrodes is mainly due to the synergistic effect of both components in the composite. The excellent cyclic stability over the entire cycle life can be attributed to the good mechanical stability

of the composite electrode due to the presence of the reinforcing graphene component.

- vii. The randomly oriented nanostructures (viz. nanotubes and nanofibers) with respect to the current collector provide more resistance which is obvious from the ohmic drop at the beginning of discharge curve. Thus, vertically-oriented nanostructures with respect to the current collector are preferable in order to minimize the resistance for good electrochemical performance.
- viii. The low energy density and the poor cyclic stability were the prime concerns in supercapacitor based electrode. Although the energy density of the pure PANI nanostructure based electrode was reasonably good, however, the cyclic life was very poor. It has been found that using the above composite materials, it is possible to achieve the high energy density which is comparable to that of batteries. The cyclic life is also higher with composite based electrode than the electrode based on pure PANI. Thus, the overall energy density and the cyclic stability of the composite based electrode were superior.

7.2 Recommendations for future work

Electrode materials are one of the key components in high-performance supercapacitors. Thus, incorporation of graphene into the polymer matrices enhances the electrochemical performances of the nanocomposites.

The effect of covalent and non-covalent functionalization of graphene on the electrochemical performances in aqueous and organic electrolytes can be studied in future. The functionalized graphene/CP composite or functionalized graphene/metal

oxide composite can be fabricated in order to attain optimum electrochemical properties. The CP or metal oxide can be grown as the nanostructures onto the functionalized graphene sheets.

Ternary nanocomposites based on graphene, CP and metal oxide can be studied further as electrode materials for supercapacitors. Also, the CPs and metal oxide can also be grown vertically together onto the graphene surface in order to produce maximum specific capacitance as the vertical alignment of the nanostructures on to the substrate will be highly accessible for the electrolytes ions.

Various other hard-templates can be used for the fabrication of nanostructures of metal oxides or CPs, without substrate or onto the graphene surface for the vertical growth. The vertical growth of nanostructures has been proven to provide the highest capacitance values compared to the randomly oriented nanostructures (nanofibers/nanowires/nanotubes). Soft-template based process is another facile approach for the fabrication of above mentioned nanostructures. As the electrochemical properties are highly dependent on the synthetic route, therefore, the choice of template is very critical for the fabrication of nanostructures.

Furthermore, so far very few studies have been found on the redox electrolyte based supercapacitors. Thus, the redox electrolyte can be used for the electrochemical study with some graphene based composite electrode materials. The result obtained from this study with redox electrolytes can be compared with the aqueous and organic electrolytes.

The flexible supercapacitor is one of the most important research areas in the supercapacitors. Thus, the graphene or functionalized graphene and its composite with metal oxide or CP can be studied further for the optimum device performance.

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Appendix

Figure A1 FTIR spectra of (a) PANIV-0.5, (b) PANIV-0.1, (c) PANIV-0.05, (d) PANIV-0.01 and (e) pure PANI (synthesized without template).

Figure A2 XPS spectra (wide scan) of (a) PANIV-0.5, (b) PANIV-0.1, (c) PANIV-0.05, (d) PANIV-0.01 and (e) pure PANI (synthesized without template).

Figure A3 FESEM images of PANI in (a) ethanol, (b) 2-propanol and (c) acetone solvents.

Figure A4 FESEM image of PANI in dilute condition.

Figure A5 FTIR spectra of (a) PANIH-0.5 and (b) PANIH-0.1.

Figure A6 XPS spectra (wide scan) of (a) PANIH-0.5 and (b) PANIH-0.1.

Figure A7 Cyclic voltammograms (CV) of pure heparin.

Scheme SA1 Electron transfer mechanism in vitamin C.