



**UNIVERSITI PUTRA MALAYSIA**

***FABRICATION OF CARBON-BASED NANOSTRUCTURED FLEXIBLE  
SUPERCAPACITOR***

**CHEE WEI KIT**

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**FABRICATION OF CARBON-BASED NANOSTRUCTURED FLEXIBLE  
SUPERCAPACITOR**

**By**

**CHEE WEI KIT**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
In Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

**March 2018**

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

## **FABRICATION OF CARBON-BASED NANOSTRUCTURED FLEXIBLE SUPERCAPACITOR**

By

**CHEE WEI KIT**

March 2018

**Chair: Associate Professor Janet Lim Hong Ngee, PhD**  
**Faculty: Science**

This research essentially focuses on the fabrication of a carbon-based flexible energy storage devices via the development of highly flexible electrode material. In the first study where polypyrrole/ graphene oxide/ zinc oxide nanocomposite was directly electrodeposited on a nickel foam by an electrodeposition technique, a free-standing flexible supercapacitor was fabricated by sandwiching a potassium hydroxide/ polyvinyl alcohol hydrogel electrolyte between two layers of the as-prepared ternary nanocomposite electrodes. A specific capacitance of  $123.8 \text{ Fg}^{-1}$  at  $1 \text{ Ag}^{-1}$  was achieved with excellent flexibility. However, the cycling stability of the ternary nanocomposite showed a sensitive behavior towards types of electrolyte used, at which a favorable specific capacitance retention of more than 90.0% using a mild alkaline electrolyte.

In order to improve the stability performance, electrospinning technique is employed at which a flexible and conductive nanofiber membranes were fabricated. Initial attempt by introducing graphene oxide to envelop the carbon nanofibers resulted poor electrochemical performance as the effect of pore blockage by graphene oxide. Whereby second attempt with addition of graphene nanoplatelets resulted in enhancement of electrochemical performance, however with in-distinctive trend as the effect of phase separation presence between CNF/ GnP components. Further modification was made at which graphene oxide was functionalized to induce hydrophobicity by using a photo-polymerization approach, at which it was successfully dispersed in the precursor polymeric solution. The electrochemical performance of the reduced graphene oxide-modified carbon nanofibers resulted in a specific capacitance of  $140.10 \text{ Fg}^{-1}$  at a current density of  $1 \text{ Ag}^{-1}$  with capacitance retention of 96.2%, however with a significant increase in charge transfer resistance, which was not favorable in electrochemical devices.

A final attempt was made via electrospun polyacrylonitrile membranes with reinforcement of metallic contents, which induced a unique morphology with integration of metal oxides with the polymer structure upon carbonization. When the nanofibers were constructed into a supercapacitor device, a specific capacitance of more than  $100 \text{ Fg}^{-1}$  was recorded at  $1 \text{ Ag}^{-1}$ , along with minimal resistance as compared to any other counterparts, achieved with reinforcement of nickel oxide nanoparticles. Furthermore, the fabricated device retained a capacitive retention of as high as 93.9% even after 2000 cycles of vigorous galvanostatic charging/ discharging process, with a minimal value of 0.05 V voltage drop. Additionally, the device successfully demonstrated excellent flexibility by recording no deviation in performance even subjected to bending and curvatures. These studies concluded that the fabrication of flexible electrode materials is the determining role in the fabrication of a highly flexible energy storage device.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

## **PENYEDIAAN SUPERKAPASITOR FLEKSIBEL BERASASKAN KARBON STRUKTUR NANO**

Oleh

**CHEE WEI KIT**

Mac 2018

**Pengerusi: Professor Madya Janet Lim Hong Ngee, PhD**  
**Fakulti: Sains**

Penyelidikan ini secara khususnya memberi tumpuan kepada fabrikasi peranti penyimpanan tenaga fleksibel berasaskan karbon melalui penyediaan bahan elektrod yang mempunyai ciri fleksibel. Dalam kajian pertama di mana komposit nano polypyrrole / graphene oksida / zink oksida secara langsung electro-deposit pada permukaan nikel, kemudiannya supercapacitor fleksibel yang terhasil dibentuk melalui elektrolit kalium hidroksida / gel polyvinyl alkohol di antara dua lapisan electrode. Kapasitif  $123.8 \text{ Fg}^{-1}$  pada  $1 \text{ Ag}^{-1}$  dicapai dengan daya lentur yang sangat baik oleh peranti tersebut. Walau bagaimanapun, kestabilan kitaran cas nanokomposit yang dihasilkan menunjukkan tingkah laku yang sensitif kepada jenis elektrolit yang digunakan, di mana pengekaln kapasitif yang direkod adalah lebih daripada 90.0% apabila elektrolit alkali yang lemah digunakan.

Untuk meningkatkan prestasi kestabilan, teknik elektrospinning digunakan, di mana membran yang terdiri daripada gentian nanokarbon yang konduktif dan fleksibel telah dihasilkan. Percubaan awal dengan memperkenalkan graphene oksida untuk menyelubungi gentian nanokarbon telah menyebabkan prestasi elektrokimia yang lemah akibat daripada liang-liang pada gentian tersebut terhalang oleh graphene oksida. Dengan percubaan kedua di mana penambahan platlet nano graphene menghasilkan peningkatan prestasi elektrokimia, namun tiada hasil yang memberangsangkan akibat kesan kehadiran fasa pemisahan antara komponen gentian nano dan platlet nano graphene. Graphene oksida telah kemudian diubahsuai untuk mendorong sifat hidrofobik dengan menggunakan kaedah pempolimeran foto, di mana graphene oksida terubahsuai berjaya disebarkan dalam larutan polimer hidrofobik. Prestasi elektrokimia gentian nanokarbon yang ditambah graphene oksida terubahsuai menghasilkan daya kapasitif  $140.10 \text{ Fg}^{-1}$  pada ketumpatan arus  $1 \text{ Ag}^{-1}$  dengan pengekaln kapasiti setinggi 96.2%, namun dengan peningkatan ketara dalam rintangan pemindahan caj.

Percubaan terakhir dilakukan melalui membran gentian nano poliakrilonitril dengan tambahan kandungan logam, di mana morfologi yang unik telah dihasilkan dimana integrasi oksida logam dengan struktur polimer semasa proses karbonisasi. Apabila gentian nano tersebut digunakan sebagai peranti supercapacitor, daya kapasitif yang melebihi  $100 \text{ Fg}^{-1}$  dicatatkan pada daya arus  $1 \text{ Ag}^{-1}$ , berserta dengan rintangan minima berbanding dengan peranti supercapacitor lain yang terhasil. Penambahbaikan tersebut dicapai dengan oleh pengukuhan nanopartikel nikel oksida pada permukaan gentian nanokarbon. Selain itu, peranti tersebut dapat mengekalkan daya kapasitif setinggi 93.9% walaupun selepas 2000 kitaran proses pengecasan / discas galvanostatik, dengan arus bocor pada tahanan yang minima  $0.05 \text{ V}$ . Di samping itu, peranti itu berjaya menunjukkan fleksibiliti yang sangat baik di mana tiada pengurangan dalam prestasi walaupun dilentur kepada pelbagai sudut. Kajian-kajian ini menyimpulkan bahawa bahan-bahan elektrod yang fleksibel memainkan peranan yang penting dalam menentukan penghasilan alat simpanan tenaga yang fleksibel.



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I certify that a Thesis Examination Committee has met on 28 March 2018 to conduct the final examination of Chee Wei Kit on his thesis entitled "Fabrication of Carbon-Based Nanostructured Flexible Supercapacitor" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

**Gwendoline Ee Cheng Lian, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Mansor bin Hj Ahmad @ Ayob, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Taufiq Yap Yun Hin, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Robert A.W. Dryfe, PhD**

Professor  
University of Manchester  
United Kingdom  
(External Examiner)



---

**NOR AINI AB. SHUKOR, PhD**  
Professor and Deputy Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date: 24 May 2018

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

**Lim Hong Ngee, PhD**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Zulkarnain Zainal, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Ian Harrison, PhD**

Professor  
Faculty of Engineering  
The University of Nottingham Broga Campus  
(Member)

**Yoshito Ando, PhD**

Professor  
Graduate School of Life Science and Systems Engineering  
Kyushu Institute of Technology Japan  
(Member)

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**ROBIAH BINTI YUNUS, PhD**

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## LIST OF ABBREVIATIONS

AC	Activated Carbon
Ag/AgCl	Silver/ silver chloride referenc electrode
Ag <sup>-1</sup>	Ampere per Gram
A-SC	Aerogel Supercapacitor
ATR	Attenuated Total Reflectance
Au	Gold
CB	Carbon Black
CC	Charge/ Discharge
CCG	Chemically Converted Graphene
CDC	Charge/ Discharge
cMWCNT	Multi-walled Carbon Nanotube
CNF	Carbon Nanofibers
CNP	Carbon Paper
CNTs	Carbon Nanotubes
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
E	Specific Energy Density
EDLC	Electric Double-Layer Capacitor
EDX	Energy Dispersive X-Ray
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
fGO	Functionalized Graphene Oxide
fGO	functionalized Graphene Oxide
FT-IR	Fourier Transform Infrared Spectroscopy
GnP	Graphene Nanoplatlets
GO	Graphene Oxide
GSC	Graphite Sheet/ Cellophane Tape

IL-CMG	ionic liquid functionalized-chemically modified graphene film
IR	Voltage Drop
ITO	Indium-Tin Oxide
kPa	Kilo Pascal
LED	Light Emitting Diode
LSG	Laser-reduced Graphene Film
M	Molarity
MMA	Methyl Methacrylate
MO	Metal Oxides
MSSC	Meso-structured Solar Cell
Mw	Weight-Average of Molecular Weight
NMR	Nuclear Magnetic Resonance
OMC	ordered mesoporous carbon
P	Specific Power Density
PAAK	Potassium Polyacrylate
PANI	Polyaniline
PEDOT	Poly (3,4-ethylenedioxythiophene)
PET	Poly(ethylene terephthalate)
PMMA	Poly(methyl methacrylate)
PPy	Polypyrrole
PPy/GO	Polypyrrole/ Graphene Oxide
PPy/GO/ZnO	Polypyrrole/ Graphene Oxide/ Zinc Oxide
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl Alcohol
PVDF	Polyvinylidene Fluoride
$R_{ct}$	Charge Transfer Resistance
rGO	Reduced Graphene Oxide
rGO-en-CNF	Graphene Encapsulated Carbon Nanofibers
RMGO	Reduced Multilayer Graphene Oxide

RPM	Revolutions Per Minute
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Analyzer
ZnO	Zinc Oxide



# CHAPTER 1

## INTRODUCTION

### 1.1 Overview of Supercapacitors

Flexible electronics has expanded to become one of the most popular research fields over the last few decades. Rapid developments in electronics such as flexible displays, wearable devices, flexible cellular phones, and energy devices (battery anodes and supercapacitor electrodes) open up a wide demand for flexible devices that theoretically possess excellent flexibility, a light weight, softness, high transparency, and good mechanical strength, which are impossible to obtain with the integrated circuits commonly available today (Sun et al., 2014).

Generally, supercapacitors are divided into two main categories: electric double layer capacitors (EDLC) and pseudocapacitors. An EDLC primarily utilizes the charges accumulated on the interfacial electrolyte/electrode surface, which mainly involves carbon-based materials with a high specific surface area. The latter possessed similar electrochemical signature of a capacitive electrode (Brousse et al., 2015), however utilizes faradaic mechanisms to store charges (C. Liu et al., 2010). On the other hand, the actual performance of a supercapacitor device frequently being measured by the power density and energy density of the system. Both are commonly used to characterize and compare the electrochemical performances of different supercapacitor devices (Fan et al., 2011a; Winter & Brodd, 2004).

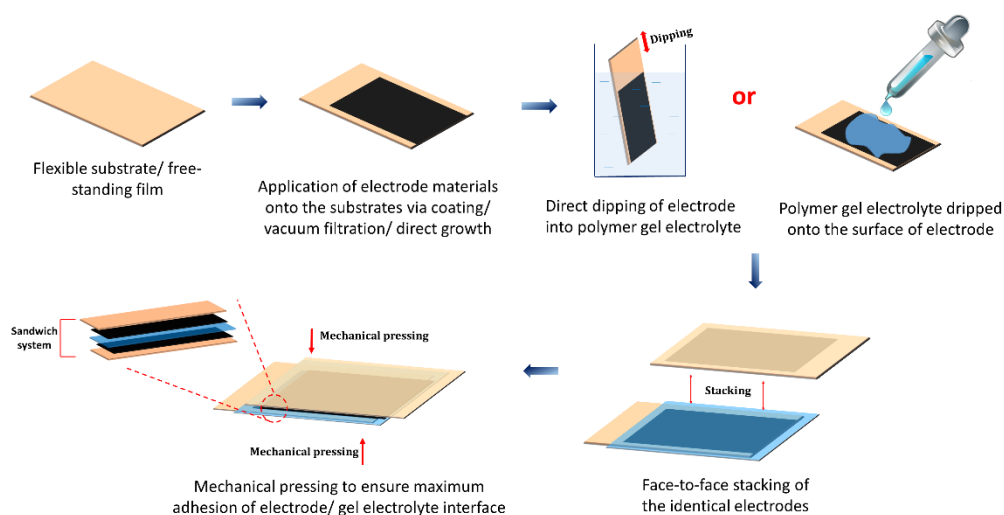
The recent research on supercapacitor devices has heavily focused on the mechanical flexibility of solid-state devices, with the goal of maintaining their high electrochemical performance while following the significant trend of portable and wearable electronics becoming small, thin, lightweight, and flexible, which brings new challenges for energy storage systems (Nyholm et al., 2011; Rogers et al., 2010). Numerous attempts to fabricate a graphene-based flexible supercapacitor system have been reported, with and without the addition of binders, as summarized in Table 1.1. A simple illustration on the fabrication technique for a flexible solid-state supercapacitor device is summarized in Figure 1.1.

**Table 1.1: A summary on the fabricated graphene-based supercapacitor devices.**

Electrode Materials	Current Collectors	Binder	Highest specific Capacitance	Current Density ( $\text{Ag}^{-1}$ )	Capacitance basis	Areal mass loading ( $\text{cm}^2$ )	Electrolyte	Ref.
rGO/ carbon black	Au coated PET	Carbon black	$79 \text{ Fg}^{-1}$	1	Whole electrode	1	PVA/ $\text{H}_2\text{SO}_4$	(Y. Wang et al., 2014)
Mesoporous graphene/ PTFE	Coin cell	PTFE	$100\text{-}250 \text{ Fg}^{-1}$	1	N/A	1.3 (coin cell)	Celgard membrane/ EMIMBF <sub>4</sub>	(C. Liu et al., 2010)
Graphene/ PANI	-	-	$261 \text{ Fg}^{-1}$	0.38	Active material	N/A	PVA/ $\text{H}_3\text{PO}_4$	(Y. Xie et al., 2014)
Graphene/ PANI nanofibers	-	-	$210 \text{ Fg}^{-1}$	0.30	Whole electrode	N/A	Filter paper/ $\text{H}_2\text{SO}_4$	(Q. Wu et al., 2010)
PPy/ graphene	-	-	$237 \text{ Fg}^{-1}$	$0.01 \text{ Vs}^{-1}$ (CV)	Whole electrode	N/A	KCl	(Davies et al., 2011)
rGO/ cMWCNT – CFP/PPy	-	-	$82.4 \text{ Fg}^{-1}$	0.5	Active material	N/A	PAAK/KCl	(C. Yang et al., 2014)
Multilayer rGO	Au-sputterd	-	$247.3 \text{ Fg}^{-1}$	0.176	Whole electrode	0.4	PVA/ $\text{H}_3\text{PO}_4$	(Yoo et al., 2011)
MnO <sub>2</sub> -coated graphene fiber	-	-	$9.1\text{-}9.6 \text{ mFcm}^{-2}$	$2 \times 10^{-4} \mu\text{A}$	Whole electrode	N/A	PVA/ $\text{H}_2\text{SO}_4$	(Q. Chen et al., 2014)
$\beta\text{-Ni(OH)}_2$ / graphene	Au-coated PET	-	$3304 \mu\text{Fcm}^{-2}$	$0.1/ \text{m}^2$	Area of single electrode	1	PVA/ KOH	(J. Xie et al., 2013)
Laser-scribed rGO	-	-	$4.04 \text{ mFcm}^{-2}$	1	Whole electrode	N/A	PVA/ $\text{H}_2\text{SO}_4$	(El-Kady et al., 2012)

Graphene-coated MnO <sub>2</sub>	-	-	29.8 Fg <sup>-1</sup>	1.5 mA/ cm <sup>2</sup>	Whole electrode	N/A	Membrane separator/ Na <sub>2</sub> SO <sub>4</sub>	(He et al., 2012)
CNT-Mn <sub>3</sub> O <sub>4</sub> / graphene	-	-	72.6 Fg <sup>-1</sup>	0.5	Active material	N/A	PAAK/ KCL	(H. Gao et al., 2012)
IL-CMG/ RuO <sub>2</sub> -IL-CMG	-	-	167 Fg <sup>-1</sup>	1	Active material	N/A	PVA/ H <sub>2</sub> SO <sub>4</sub>	(Choi et al., 2012)
Graphene-cellulose nanofibers aerogel	-	-	203 Fg <sup>-1</sup>	0.7	Active material	0.02	PVA/ H <sub>2</sub> SO <sub>4</sub>	(K. Gao et al., 2013)
MnO <sub>2</sub> / rGO	CNF	Ethylene glycol	-	-	Active material	28	PVA/ NaNO <sub>3</sub>	(Sawangphruk et al., 2013)
Graphene hydrogel	Au-coated PI	-	186 Fg <sup>-1</sup>	1	Active material	N/A	PVA/ H <sub>2</sub> SO <sub>4</sub>	(Y. Xu et al., 2013)
OMC-graphene/ Ag NWs	-	-	213 Fg <sup>-1</sup>	1	Electrode material	N/A	Filter paper/ KOH	(J. Zhi et al., 2014)
CNT-graphene/ Fe <sub>3</sub> O <sub>4</sub> nanoparticle	Au-coated PET	-	200 <sup>-1</sup>	0.1 Vs <sup>-1</sup> (CV)	Electrode material	1	Filter paper/ Na <sub>2</sub> SO <sub>4</sub>	(Cheng et al., 2013)

\*Non-available: N/A



**Figure 1.1: Schematic diagram of fabrication of flexible supercapacitor device.**

## 1.2 Problems Statement

Although various approaches had been reported in the development of flexible supercapacitors, the progress in developing a high-performance and cost-effective flexible devices is yet remain as a challenge. Parallely, the successful fabrication of flexible supercapacitor electrodes without the addition of binders or additives still rely heavily on the electrical conductivity of the composite material itself, not forgetting that mechanical strength of the fabricated electrode films is required as reinforcement to withstand the stress load on the fabricated devices during bending or twisting.

Therefore, there is a need in the development of cost effective, simple, and high performance flexible supercapacitor electrode in order to meet the expectation in the application in future electronic devices which requires fabricated energy devices that are thin, flexible, and lightweight. The fabrication of highly flexible electrode materials with optimum electrochemical performance serves an ultimate role in determining the final outcome of the fabricated supercapacitor device.

## 1.3 Hypothesis of Study:

- The fabricated graphene-based ternary nanocomposites has enhanced electrochemical performance and stability in the fabrication of flexible devices.
- The synergistic combination of electrospinning and additives successfully generated a facile route in the production of highly flexible electrode materials with enhanced electrochemical performance to be incorporated into a high flexibility energy storage device.

#### 1.4 Research Objectives

1. To fabricate graphene based nanocomposite-deposited nickel foam as flexible supercapacitor electrode via electrodeposition technique.
2. To fabricate flexible conductive carbon nanofiber via carbonization of electrospun polymer nanofibers
3. To evaluate the addition of various additives in electrospun carbon nanofibers as the function of electrochemical performance enhancement
4. To fabricate and characterize the flexible solid-state supercapacitors based on prepared electrode materials





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