



**UNIVERSITI PUTRA MALAYSIA**

***PREPARATION OF GRAPHENE DERIVATIVES FOR SUPERCAPACITOR  
APPLICATION***

**SYAZWAN AFIF MOHD ZOBIR**

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**PREPARATION OF GRAPHENE DERIVATIVES FOR SUPERCAPACITOR  
APPLICATION**

By

**SYAZWAN AFIF MOHD ZOBIR**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra  
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Doctor of Philosophy**

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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

## **PREPARATION OF GRAPHENE DERIVATIVES FOR SUPERCAPACITOR APPLICATION**

By

**SYAZWAN AFIF MOHD ZOBIR**

**May 2018**

**Chairman : Associate Professor Suraya Abdul Rashid, PhD**  
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The research on the carbon nanomaterials has begun since the world war one. Various types of carbon nanomaterials such as fullerenes, activated carbon, carbon nanotubes are subjected to intense research. The main advantage of nanomaterials over the conventional counterparts is their tiny size which provides higher surface area to volume ratio, which is very useful in wide applications. The depletion of fossil fuels as the main source for energy has prompted intense search for alternative energy storage such as batteries and supercapacitors. The main advantage of supercapacitors is their ability to rapidly store and release energy and is very useful for portable devices and shows promising potential to replace fossil fuels in automotive industries. However, the current generation of supercapacitors which is made of graphite has poor energy storage capacity due to poor ion adsorption/desorption between the electrolyte and active sites of the carbon electrode. In addition, it also known that graphite has poor fast ion transport which is essential for high current density application such as heavy industries and automotive applications. However, the discovery of monolayer carbon lattice of graphene which has superlative properties encourages an intense research to exploit its properties, especially for supercapacitor application. In this work, a suitable method was developed to prepare various nanographene derivatives and their nanohybrids. The work also covers the determination of their physical, chemical and electrochemical properties for supercapacitor application.

The preparation of various sizes of nanographene derivatives such as graphene oxide, nanographene oxide and graphene oxide quantum dots (GOQD) by a combination of chemical oxidation and step by step centrifugation speeds were carried out. Locally produced, herringbone

graphite nanofibers (HGNF) was used as the starting material. Particle size distribution (PSD) study shows micron-, nano- and quantum dots graphene oxide (GO) were obtained. Importantly, the formation mechanism was identified due to pitted and peeled out of HGNF into smaller carbon fragments. In addition, the formation of various functional groups was recorded on the FTIR and XPS spectra. Interestingly, the photoluminescence (PL) results indicate the GO with 100 nm lateral size starts to exhibit the fluorescence property. The huge differences in the physical and chemical properties between GOQD and GQD were observed in this work. The morphological analysis indicates that the GOQD was agglomerated while GQD was well dispersed. Similarly, the FTIR and XPS studies show huge percentage difference of C-C/C-O between GOQD and GQD, which is 40% and 60%, respectively. It is believed that this percentage difference has affected the emitted colour of the quantum structure from blue at 425 nm to green at 450 nm. This is due to the shifted of the emission wavelength from lower to higher wavelength as shown by the PL studies. After the study on the individual component of these graphene derivatives was accomplished, then the preparation of two types of nanohybrids, namely nanographene/graphene quantum dots and graphene oxide/graphene quantum dots were carried out.

The electrochemical studies were carried out to determine the supercapacitor performances of the nanographene derivatives. It was found that the specific capacitance values were increased for smaller sizes of the graphene sheets. This is due to better ion adsorption/desorption between electrolyte and smaller sizes of nanographene derivatives as the electrode. This is in agreement with the higher integrated area of cyclic voltammograms and longer discharging time in charge/discharge profiles for smaller sizes of nanographene derivative. More importantly, it was found that the availability of abundant edges of GOQD is essential for fast ion transport which crucial for high current density supercapacitor application. The impedance spectroscopy also indicates lower resistances as the sizes were decreased. Moreover, the electrochemical studies also indicate better supercapacitor performances were obtained when some functional groups were removed from the quantum dots particles. In addition, a computational modeling study using density functional theory (DFT) was carried out for the graphene oxide quantum dots and the graphene quantum dots to predict its charge density distribution mapping.

Generally, it was found that superior supercapacitor performances were obtained for the both types of nanohybrids. The double layer capacitor (DLC) characteristic was also observed for the *in situ* formation of nanographene/GQD nanohybrid. It is believed that the coexistent of both GQD and nanographene provided abundant active sites for ions adsorption/desorption interactions between the electrolyte and the nanohybrid. Interestingly, this nanohybrid could retain more than 300 F/g of specific capacitance values, even at high current densities. The formation of random-stacked GQD and individual GQD played a crucial role to retain the

impressive capacitor performance. In addition to good retention, the nanohybrid has shown a remarkable improvement for specific energy and specific power. Another type of nanohybrid also was prepared using the wet chemical method by mixing GO and GOQD. A hybrid characteristic was observed in the cyclic voltammetry analysis, which is due the presence of GOQD and GO. Generally, the nanohybrid exhibits superior capacitor performance compared to the individual components. This is due to better ions adsorption/desorption interactions as more ions were allowed to diffuse. The charge/discharge profiles indicated the superiority of the capacitor performances of the nanohybrid at different current densities. In addition, it was also found an improvement in the specific energy and specific power of the resulting nanohybrid.



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## **PENYEDIAAN TERBITAN GRAFEN UNTUK KEGUNAAN SUPERKAPASITOR**

Oleh

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Penyelidikan tentang bahan nano karbon telah bermula sejak perang dunia pertama. Penyelidikan menggunakan pelbagai jenis bahan nano karbon seperti fulleren, karbon teraktif, karbon nanotub telah pun dijalankan. Kelebihan utama bahan nano berbanding karbon konvensional adalah saiznya yang kecil yang memberikan nisbah luas permukaan terhadap isipadu yang lebih tinggi dan ia sangat berguna dalam pelbagai jenis aplikasi. Kekurangan bahan api fosil sebagai sumber utama tenaga telah mendorong pencarian untuk penyimpanan tenaga alternatif seperti bateri dan superkapasitor. Kelebihan utama superkapasitor adalah keupayaannya untuk menyimpan dan melepaskan tenaga dengan cepat dan ia amat berguna untuk peranti mudah alih dan menunjukkan potensi yang tinggi untuk menggantikan bahan bakar fosil dalam industri automatif. Walaubagaimanapun, superkapasitor generasi kini yang diperbuat daripada grafit mempunyai kapasiti penyimpanan tenaga yang rendah kerana penjerapan/nyah-jerapan ion yang lemah antara elektrolit dan karbon yang digunakan sebagai elektrod. Selain daripada itu, grafit juga mempunyai kadar pengaliran ion yang lemah dan tidak sesuai untuk aplikasi arus kepadatan tinggi seperti bagi industri berat dan aplikasi automotif. Walaubagaimanapun, penemuan kekisi karbon ekalapis grafen dengan ciri-ciri superlatif menggalakkan penyelidikan yang meluas untuk digunakan bagi aplikasi superkapasitor. Dalam kajian ini, kaedah yang sesuai telah dibangunkan untuk menyediakan pelbagai terbitan nanograpfen dan nanohibrid mereka. Kajian ini juga meliputi penentuan sifat-sifat fizik, kimia dan elektrokimia mereka untuk aplikasi superkapasitor.

Penyediaan pelbagai saiz terbitan nanografen seperti grafen oksida, nanografen oksida dan titik kuantum grafen oksida (GOQD) dengan kaedah pengoksidaan kimia diikuti dengan pengemparan langkah demi langkah telah dijalankan. Nanofiber grafit tulang *herring* (HGNF) yang dihasilkan oleh syarikat tempatan telah digunakan sebagai bahan permulaan. Hasil kajian taburan saiz zarah (PSD) menunjukkan pelbagai saiz seperti titik mikron, nano dan kuantum grafen oksida (GO) telah diperolehi. Apa yang penting ialah mekanisma pembentukannya telah dikenalpasti, iaitu disebabkan oleh lekukan rongga dan terkupasnya HGNF menjadi serpihan karbon yang lebih kecil. Di samping itu, pembentukan pelbagai kumpulan berfungsi telah juga diperhatikan daripada spektrum FTIR dan XPS. Menariknya, hasil kajian pendafosfor (PL) menunjukkan GO dengan saiz 100 nm mula menunjukkan sifat pendarfluor. Seterusnya, perbezaan besar dalam sifat fizikal dan kimia antara GOQD dan GQD juga telah diperhatikan. Analisis morfologi menunjukkan bahawa GOQD mengumpul manakala GQD tersebar dengan baik. Begitu juga, kajian FTIR dan XPS menunjukkan perbezaan peratusan besar bagi C-C/C-O antara GOQD dan GQD, masing-masing dengan nilai 40% dan 60%. Adalah dipercayai bahawa perbezaan peratusan ini telah mempengaruhi warna emulsi struktur kuantum daripada biru pada 425 nm ke hijau pada 450 nm. Ini adalah disebabkan oleh anjakan pancaran panjang gelombang daripada pendek kepada lebih panjang seperti yang ditunjukkan oleh kajian PL. Setelah kajian mengenai komponen individu terbitan grafen ini dicapai, maka penyediaan dua jenis nanohibrid, iaitu nanografen/titik kuantum nanografen dan grafen oksida/titik kuantum grafen telah dijalankan.

Seterusnya, kajian elektrokimia telah dijalankan untuk menentukan prestasi superkapasitor bagi terbitan nanografen. Hasil kajian menunjukkan bahawa nilai kapasitan spesifik bertambah bagi lapisan saiz grafen yang lebih kecil. Ini adalah disebabkan oleh penjerapan/penyah-jerapan ion yang lebih baik antara elektrolit dan saiz terbitan nanografen yang lebih kecil sebagai elektrod. Ini adalah selaras dengan luas kawasan kamiran voltammogram kitaran yang lebih tinggi dan masa nyah caj yang lebih lama untuk profil caj/nyah-caj untuk saiz yang lebih kecil bagi terbitan nanografen. Lebih penting lagi, didapati bahawa kewujudan banyak birai/tepi bagi GOQD adalah penting untuk pengangkutan ion yang cepat, yang mana ini adalah penting untuk kegunaan superkapasitor ketumpatan arus tinggi. Spektroskopi impedan juga menunjukkan rintangan yang lebih rendah apabila saiznya berkurangan. Selain daripada itu, kajian elektrokimia juga menunjukkan performan superkapasitor yang lebih baik telah diperolehi kerana sebahagian kumpulan berfungsi telah disingkirkan daripada zarah titik kuantum. Selain daripada itu, kajian pemodelan komputer menggunakan teori fungsi kepadatan (DFT) telah dijalankan untuk titik-titik kuantum grafen oksida dan titik-titik kuantum grafen untuk meramalkan pemetaan ketumpatan casnya.

Pada umumnya didapati bahawa prestasi superkapasitor yang lebih baik telah diperolehi untuk kedua-dua jenis nanohibrid. Ciri-ciri kapasitor lapisan ganda (DLC) juga telah diperhatikan untuk pembentukan nanografen/GQD nanohibrid secara *in situ*. Adalah dipercayai bahawa kewujudan bersama kedua-dua GQD dan nanografen menyediakan tapak aktif yang banyak untuk interaksi jerapan/nyahjerapan ion antara elektrolit dan nanohibrid. Menariknya, nanohibrid ini dapat mengekalkan lebih daripada 300 F/g nilai kapasitansi spesifik, walaupun pada arus kepadatan tinggi. Pembentukan GQD tersusun secara rawak dan GQD individu memainkan peranan penting untuk mengekalkan prestasi kapasitor yang mengagumkan. Sebagai tambahan kepada pengekalannya yang baik, nanohibrid telah menunjukkan peningkatan yang luar biasa untuk tenaga spesifik dan kuasa spesifik. Satu lagi jenis nanohibrid juga telah disediakan dalam kajian ini ialah dengan menggunakan kaedah kimia basah, dengan mencampurkan GO dan GOQD. Ciri-ciri hibrid telah diperhatikan dalam analisis voltammetri kitaran, yang disebabkan oleh kehadiran GOQD dan GO. Pada umumnya, nanohibrid tersebut mempamerkan prestasi kapasitor yang lebih baik berbanding dengan komponen individunya. Ini adalah disebabkan oleh interaksi jerapan/nyahjerapan ion yang lebih baik kerana lebih banyak ion dibenarkan untuk meresap. Profil caj/nyah-caj menunjukkan prestasi kapasitor nanohibrid yang lebih baik pada kepadatan arus yang berbeza. Di samping itu, didapati juga peningkatan dalam tenaga spesifik dan kuasa spesifik bagi nanohibrid yang telah dihasilkan.



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I certify that a Thesis Examination Committee has met on 28 May 2018 to conduct the final examination of Syazwan Afif Mohd Zobir on his thesis entitled "Preparation of Graphene Derivatives for Supercapacitor Application" 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.

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## LIST OF ABBREVIATIONS

$\Omega$	Ohm
0D	Zero dimensional
2D	Two dimensional
3D	Three dimensional
A	Ampere
AFM	Atomic force microscope
BET	Bruneuar-Emmett-Teller
CDC	Charge/discharge profile
CNT	Carbon nanotubes
$C_s$	Specific capacitance
CV	Cyclic voltammetry/voltammogram
CVD	Chemical vapour deposition
DLS	Dynamic light scattering
DFT	Density functional theory
DLC	Double layer capacitor/capacitance
E	Specific energy
EC	Electrochemical capacitor
EIS	Electrochemical impedance spectroscopy
EMIM	1-ethyl-3-methylimidazoliumtetrafluoroborate
F	Farad
FESEM	Field emission scanning electron microscope/micrograph
FTIR	Fourier-transform infrared
GNF	Graphite nanofiber

GO	Graphene oxide
GO <sub>11500</sub>	Graphene oxide obtained at centrifugation speed of 11500 rpm
GO <sub>4000</sub>	Graphene oxide obtained at centrifugation speed of 4000 rpm
GO <sub>8000</sub>	Graphene oxide obtained at centrifugation speed of 8000 rpm
GOQD	Graphene oxide quantum dots
GQD	Graphene quantum dots
H	Hour
HGNF	Herringbone graphite nanofiber
HRTEM	High resolution transmission electron microscope
I <sub>G</sub> /I <sub>D</sub>	Ratio of the intensity of the G to the D band of the Raman spectrum
IOT	Internet of things
K	Potassium
KDa	KiloDalton
Kg	Kilogram
M	Minute
MOSFET	Metal-oxide semiconductor field-effect transistor
MWCNT	Multi-walled carbon nanotubes
NPGO	Nanoporous graphene oxide
P	Specific power
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol

PET	Polyethylene-terephthalate
PL	Photoluminescence
PLD	Pulse laser deposition
Ppy	Polypyrrole
PSD	Particle size distribution
PVDF-co-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
R	Resistance
$R_{ct}$	Faradaic transfer resistance
$R_{ESR}$	Equivalent series resistance
RGO	Reduced graphene oxide
$R_s$	Electrolyte resistance
s	Second
SEM	Scanning electron microscope
SRAM	Static random-access memory
UC	Ultracapacitor
UV	Ultraviolet
UV-VIS	ultraviolet-visible
V	Volt
W	Watt
XPS	X-ray photoelectron spectroscopy/spectra
$Z'$	Real part of impedance of Nyquist plot
$Z''$	Imaginary part of impedance of Nyquist plot

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

The research on carbon nanomaterials began with the work on fullerenes and related compounds in the 1970s, and subsequently a tremendous increase of the research activity in the field has emerged. Since then, new classes of carbon nanomaterials such as carbon nanotubes, carbon onions and nanoscale diamond have been introduced. However, the appearance of graphene in 2010 discovered by Nobel prize winners was a major turning point which was spurred by the understanding of the properties and chemistry and the development of reliable production methods. This paved way to new applications for carbon nanomaterials in general and graphene and their products in particular (Chabot et al., 2014; Pirnat et al., 2014 and Sun et al., 2008).

Lately, carbon nanomaterials and many carbon-rich organic materials are available to the scientific community in excellent quality and suitable amounts for the investigation of fundamental properties and prospective applications. This has led to the emergence of a new community of scientists working in an interdisciplinary area from materials science to agriculture and from biomedical science to engineering. Such interdisciplinary collaborations especially on graphene and their derivative products has opened the possibility of a broad range of applications including catalysis, electronics and optoelectronics, biomedical applications and of particularly important is the energy conversion and storage.

#### 1.2 Graphene and nanographene

Graphene is a two dimensional (2D), one atom thick sheet of carbon lattice which has become the subject of intense research lately due to their unique properties and their potential applications in various technologies. Graphene is a crystalline allotrope of carbon, with a dense  $sp^2$  bonded hexagonal arrangement of carbon lattice. Due to its monolayer structure, this material is transparent, has remarkable strength, highly conductive and has a very high specific surface area. These superlative properties of graphene have attracted many intense researches on various graphene-derivative products such as graphene, graphene oxide (GO), reduced graphene oxide (rGO), and various graphene nanocomposite materials. The resulting products have great potential in wide range of applications such as for energy storage in solar cells and supercapacitor batteries (Chabot et al., 2014; Pirnat et al., 2014; and

Zhang et al., 2012), drug delivery systems and other medical applications (Yang et al., 2015 and Sun et al., 2008).

On the other hand, nanographene can be defined as graphene sheets which have lateral sizes of less than 100 nm. Recently, the formation of one type of nanographene which is graphene quantum dots (GQDs) by chemical cutting of graphene sheets via hydrothermal method was reported (Pan et al., 2009). GQDs have recently received a lot of attention due to their unique chemical, electronic and optical properties as a result of their quantum confinement and edge effects batteries (Chabot et al., 2014; Pirnat et al., 2014). It also shows stable photoluminescence, low cytotoxicity, high water solubility and excellent biocompatibility (Roy, et al., 2015).

GQD can be defined as a zero-dimensional (0D) graphene with lateral dimensions of less than 10 nm. Due to its unique properties, GQD is considered to be promising nanomaterial for applications in photocatalyst, sensor, bioimaging, etc. (Yang et al., 2015). Most of the works on GQDs were emphasized on the theoretical predictions of their formations and their interesting PL behaviour. However, the electrochemical studies for supercapacitor application using GQD-based materials were not well reported.

Nanohybrids can be defined as materials which are composed of different shapes but of the same elements. Numerous works have been reported on the preparation of various nanohybrids for various applications. Examples of nanohybrids are carbon nanotubes/graphene, carbon nanotubes/activated carbon, etc. Previous works have shown that the co-existent of both carbonaceous materials could enhance the desired properties in many applications of interest.

### **1.3 Energy storage**

The depletion of fossil fuels as the main resource for energy has prompted intense search for alternative energy storage. In addition, wars involving major fossil fuel exporters could easily cause crude oils price to hike which consequently leads to economic instability. While escalating power demands are due to more sophisticated electronic devices which require huge amounts of energy to be used for various operations. Therefore, energy storage has become more prominent as consumers prefer portable, easy to use devices compared to plug-in electronic devices, especially for various internet of thing (IOT) applications. This is because energy storages are required for these portable electronic devices.

Recently, electric vehicles have been touted as the future technology for clean transportation. The main advantage of using electric vehicles is that it does not require fossil fuel as the energy source, which leads to zero emission of carbon as the by product, therefore pollution can be minimized. However, the real challenge for this technology to be feasible is the time consumption for charging the energy. The current technology still requires a lot of time for charging electric vehicles. This is due to the lack of developments of energy storage which can be used at high energy density. Generally, energy storage can be classified into several categories such as capacitors, supercapacitors, batteries and fuel cells. Capacitors and supercapacitors have superior specific power but lacks in specific energy compared to its counterparts. It is believed that high current density supercapacitors will become the next generation of supercapacitors as it is able to rapidly store and release energies.

#### **1.4 Supercapacitors**

Generally, a capacitor can be defined as a passive two-terminal electrical component which stores electrical energy in an electric field. Thus a supercapacitor is a high-capacity capacitor with a significant capacitance values than the capacitors. Supercapacitors are usually able to store about 100 times more energy per unit volume or mass than the capacitor. The main advantage of supercapacitors as the energy storage is, it can accept and deliver charge much faster than batteries and fuel cells. In addition, supercapacitors are commonly referred to as 'electrochemical capacitor (EC)', 'double layer capacitor (DLC)' or ultracapacitor (UC) due to their unique characteristics which fill the gap between batteries and capacitors.

There are a few common types of electrochemical capacitors; double-layer capacitors, pseudocapacitors and hybrid capacitors. Owing to the formation of 'double layer' at the electrode/electrolyte interface, a significant capacitance performance can be achieved for DLC supercapacitors. This type of capacitor stores the electrical energy between the electrode and the electrolyte solution. The polarized electrode which causes charge rearrangement will generate a current. On the other hand, the charge storage for pseudocapacitor involves a fast faradaic redox reaction, which is due to the chemical reactions between various metal oxides, conducting polymers and carbonaceous material as the electrode and the electrolyte. The hybrid capacitor is a combination of these two characteristics as mentioned above.

Supercapacitors have been used in many applications due to their ability to rapidly store and release energy. For smaller unit energy, supercapacitors are primarily used as memory backup for random-access memory (SRAM) for computational devices. Portable electronic devices such as mobile phones, digital cameras and televisions usually require low units of energy ranging from 1-150 F. Intermediate unit energy requirements range from 300 - 350 F

and they are usually needed for industrial applications. On the other hand, higher unit energy is usually found for automotive sectors, trains, rails and busses for public transports, and many other applications.

## **1.5 Problem statement**

The main advantage of supercapacitors is their ability to rapidly store and release energy. Currently, commercially available supercapacitors are made of graphite. The multiple layers of graphite were found very useful to store a small amount of charges and the storage capacity is sufficient as supercapacitors for backup-power for less powered-electronic devices. As the technology progresses and increase in power demand, this multiple layers of graphitic sheets and has been considered relatively poor supercapacitor performance. This is due to inadequate active sites for ion adsorption/desorption between the electrolytes and the carbonaceous materials. In addition, graphite has poor fast ion transport for high current densities for various supercapacitor applications.

The emergence of graphene technology has revolutionised the research on supercapacitors. Recent reports showed that the graphene-based supercapacitors exhibit superior performance and have a huge potential to be the main energy storage for various electronic devices. This is due to its higher surface area for ion adsorption/desorption between electrolytes and carbon electrodes.

More recently, ultrafine carbonaceous particles sizes of GQD could be prepared using the top-down approach by chemical oxidation method (Rashid et al., 2015). It is believed that more economical way was achieved to produce GQD particles using this method. However, the lack of reports on the electrochemical properties of GQD and its nanocomposites for supercapacitor application warrants further studies.

## **1.6 Hypothesis**

Theoretically, as the particle size decreases, the specific surface area will increase. A higher surface area will allow more active sites for ion adsorption/desorption of charge between electrolytes and carbonaceous material. The improvement of the charge transport through the active layers of nanographene derivatives will improve supercapacitor performance. In addition, it is also believed that by combining the GQD particles with other types of carbon such as graphene and graphene oxide forming a nanohybrid would further improve the supercapacitor performance.

## **1.7 Significance of study**

Low production cost could be achieved for the preparation of various nanographene derivatives and their nanohybrids via the top down approach. A novel combination of chemical oxidation method followed by step by step centrifugation process at different speeds was carried out in this work. A locally produced herringbone graphite nanofiber (HGNF) was used as the starting material. The proposed formation mechanism of various sizes of nanographene derivatives was determined from their physical and chemical properties. In addition, the electrochemical properties of these nanographene derivatives provide crucial information on how to improve the supercapacitor performance. In addition, the findings on the unique properties of the graphene nanohybrids will provide superior supercapacitor performance and finally can be used as a stepping stone for further development of advanced supercapacitors.

## **1.8 Research objectives**

Experimental work has been planned accordingly to ensure the smooth accomplishment of the research work. The objectives of this study are listed below:

1. To develop suitable method for preparation of various nanographene derivatives.
2. To investigate the physical and chemical properties of nanographene derivatives and nanographene hybrids
3. To determine the electrochemical properties of nanographene derivatives and their hybrids for supercapacitor application.

## **1.9 Scope of work**

The scope of work is listed below in order to achieve the research objectives which were mentioned earlier. The scope of work covers:

- 1.1 The preparation, and physico-chemical characterizations of various sizes of nanographene derivatives such as graphene oxide, nanographene oxide and graphene quantum dots prepared by modified Hummer's method and step-by step centrifugation using herringbone graphite nanofibers (HGNF) as the precursor.
- 1.2 The comparison of physico-chemical properties of GOQD and GQD.
- 2.1 The preparation and physico-chemical characterizations of two types of nanohybrids; nanographene/graphene quantum dots and graphene oxide/graphene quantum dots for supercapacitor application.

- 3.1 The study on the electrochemical properties of various graphene derivatives which was prepared in Section 1.1.
- 3.2 The comparison of the electrochemical properties of GOQD and GQD for supercapacitor application. A computational modeling study using density functional theory (DFT) is carried out for the graphene oxide quantum dots and the graphene quantum dots.
- 3.3 The study on the electrochemical properties of the nanohybrids which were prepared in Section 2.1



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