UNIVERSITI PUTRA MALAYSIA

PREPARATION OF GRAPHENE DERIVATIVES FOR SUPERCAPACITOR APPLICATION

SYAZWAN AFIF MOHD ZOBIR

PREPARATION OF GRAPHENE DERIVATIVES FOR SUPERCAPACITOR APPLICATION

By

SYAZWAN AFIF MOHD ZOBIR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2018

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
Faculty : Engineering

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.

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

PENYEDIAAN TERBITAN GRAFEN UNTUK KEGUNAAN SUPERKAPASITOR

Oleh

SYAZWAN AFIF MOHD ZOBIR

Mei 2018

Pengerusi : **Profesor Madya Suraya Abdul Rashid, PhD**
Fakulti : **Kejuruteraan**

Penyelidikan tentang bahan nano karbon telah bermula sejak perang dunia pertama. Penyelidikan menggunakan pelbagai jenis bahan nano karbon seperti fulleren, karbon teraktif, karbon nanotiub 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 juga diperhatikan. Analisis morfologi menunjukkan bahawa GOQD mengumpal 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/tepian 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 nanograpfen 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 pengekalan 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/nyah-jerapan 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.

ACKNOWLEDGEMENTS

All praises be to Allah, the most gracious, the most merciful. Only by his grace, mercy and help, this thesis can be completed.

It is a pleasure to express my gratitude to whom have helped me throughout this study.

I would like to take this opportunity to express my sincere appreciation to the main supervisor, Associate Professor Dr. Suraya Abdul Rashid for her invaluable advice and guidance and tremendous support throughout this study. I am also grateful to all the co-supervisors and collaborators, Professor Dr. Zulkarnain Zainal, Associate Professor Dr. Lim Hong Ngee, Dr. Shuhazlly Mamat, Dr. Sook-Keng Chang, Dr. Amir Reza and Ms Infazah Ramli for their guidance and suggestions throughout the work. I would also like to thank to Professor Dr. Zulkarnain Zainal, Dr. Asma Shamsudin and Dr. Sook-Keng Chang for giving the permission to use the instruments for electrochemical characterizations and direct/indirect assistant to operate the instruments and data extraction. In addition, I am also like to thank to Associate Professor Dr. Lim Hong Ngee for giving me the opportunity to use the centrifuge machine at the early stage of this work.

I would like to thank Professor Norhisam for giving me the opportunity to take part in the student exchange programme for 14 days at Shinshu University, Nagano, Japan. It was a very good experience for me.

I would like to thank all my friends, Ms P.K. Yaacob, Dr. Saifollah Bullo, Dr. Tumirah, Dr. Asma, Ms. Roza, Ms Infazah Ramli, Ms Rozanna, Mr. Muhammad, Ms Izanne Rahim, Dr. Diana and Ms Norhanisah for the indirect help and invaluable experience as the labmates/friends. I would like to express my gratitude to MPTL and MSCL laboratories staffs especially Mr. Hafis for his help and good experience. I would also like to thank ITMA administrative staffs for their help given during my study.

Last but not least, I deeply owed my deepest gratitude to my parents for their continuous support, care and encouragements throughout my life. To them, I dedicated my work.

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

Suraya Abdul Rashid, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Zulkarnain Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Shuhazlly Mamat, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature:____________________ Date:_______________

Name and Matric No: Syazwan Afif Mohd Zobir, GS37024

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature:
Name of Chairman of Supervisory Committee: Associate Professor Dr. Suraya Abdul Rashid

Signature:
Name of Member of Supervisory Committee: Professor Dr. Zulkarnain Zainal

Signature:
Name of Member of Supervisory Committee: Dr. Shuhazlly Mamat

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ω	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_{11500}	Graphene oxide obtained at centrifugation speed of 11500 rpm
GO_{4000}	Graphene oxide obtained at centrifugation speed of 4000 rpm
GO_{8000}	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_G/I_D	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	Polyanaline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol

PET	Polyethylene-terephtahalate
PL	Photoluminescence
PLD	Pulse laser deposition
Ppy	Polypyrole
PSD	Particle size distribution
PVDF-co-HFP	Poly(vinylidine 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

REFERENCES

Akhavan, E., Ghaderi, E., Aghayee, S., Fereydooni, Y. & Talebi, A. (2012). The use of a glucose-reduced graphene oxide suspension for photothermal cancer therapy. J. Mater. Chem., 22: 13773-13781.

Akhbulut, S., Yilmaz, M., Raina, S., Hsu, S.H., Kang, W.P. (2017). Advanced supercapacitor protype using nanostructured double-ided mno2/cnt electrodes on flexible graphite Foil. J. of Applied Chem. 47(9):1035-1044.

Alvi, M. K. R., Basnayaka, P. A., Stefanakos, E., Goswami, Y. & Kumar, A. (2011). Graphene-polyethylenedioxythiophene conducting polymer nanocomposite based supercapacitor. Electrochim. Acta, 56: 9406-9412.

Amiri, A., Ahmadi, G., Shahbedi, M., Savari, M., Kazi, S.N., & Chew, B.T. (2015). Microwave-assisted synthesis of highly-crumpled, few-layered graphene and nitrogen-doped graphene for use as high-performance electrodes in capacitive deionization. Sci Rep., 5: 17503.

Ananthanarayanan, Y., Wang, Y., Routh, P., Sk, M.A., Than, A., Lin, M., Zhang, J., Chen, J., Sun, H. & Chen, P. (2015). Nitrogen and phosphorus co-doped graphene quantum dots: synthesis from adenosine triphosphate, optical properties and cellular imaging. Nanoscale, 7: 8159-8165.

Andrews, R., Jacques, D., Qian, D. & Rantell, T. (2002). Multiwall carbon nanotubes: synthesis and application. Acc. Chem. Res., 35: 1008-1017.

Aravinda, L.S., Nagaraja, K.K., Hasokoppa, N. & Bhat, B.R. (2013). ZnO/carbon nanotube nanocomposite for high energy density supercapacitors. Electrochim. Acta, 95: 119-124.

Arof, K., Kufian, M.Z., Syukur, M.F., Aziz, M.F., Abdelrahman, A.E., Majid, S.R. (2012). Electrical double layer capacitor using poly(methyl methacrylate)–c4bo8li gel polymer electrolyte and carbonaceous material from shells of mata kucing (dimocarpus longan) fruit. Electrochim. Acta, 74: 39-45.

Artyushkova, K. & Atanassov, P. (2013). X-Ray photoelectron spectroscopy for characterization of bionanocomposite functional materials for energy-harvesting technologies. Chem. Phys. Chem., 14(10): 2071-2080.

Baby, T.T. & Ramaprabhu, S. (2010). Investigation of thermal and electrical conductivity of graphene based nanofluids. J. Appl. Sci., 108: 124308.

Baker, R.T.K. (1989). Catalyctic growth of carbon filaments. Carbon, 27: 315-323.

Baker, R.T.K., Barber, M.A., Harris, P.S., Feates, F.S. & Waite, R.J. (1972). Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene. J. Catal., 26: 51-62.

Baker, R.T.K., Chambers, A., Park, C. & Rodriguez, N.M. (1997). The existence of an unusual reversible deactivation phenomenon associated with preferential surface segregation in bimetallic systems in Catalyst Deactivation, Bartholomew, C.H. & Fuentes, G.A. editors. Elsevier, 593-599.

Bao, L., Zhang, Z.L., Tian, Z.Q., Zhang, L., Liu, C., Lin, Y., Qi, B.P. & Pang, D.W. (2011). Electrochemical tuning of luminescent carbon nanodots: from preparation to luminescence mechanism. Adv. Mater., 23: 5801–5806.

Barzegar, F., Hakeem, A., Damilola, B. & Manyala, M.N. (2015). Effect of conductive additives to gel electrolytes on activated carbon-based supercapacitors. AIP Adv., 5: 097171.

Basnayaka, P.A., Ram, M.K., Stefanakos, E.K. & Kumar, A. (2015). Nanostructured hybrid graphene-conducting polymers for electrochemical supercapacitor electrodes. Handbook of Nanoelectrochemistry, 2: 479-501.

Bhuyan, M.S.A., Uddin, M.N., Islam, M.M., Bipasha, F.A. & Hossain, S.S. (2016). Synthesis of graphene. Inter. Nano Lett., 6: 65-83.

Bolotina, K.I., Sikes, J., Jiang, Z., Klimac, M., Fudenberg, G., Honec, J., Kim, P. & Stomer, H. L. (2008). Ultrahigh electron mobility in suspended graphene. Solid State Comm., 146: 351-355.

Budhiraju, V.S., Sharma, A. & Sivakumar, S. (2017). Structurally stable mesoporous hierarchical NiMoO4 hollow nanofibers for asymmetric supercapacitors with enhanced capacity and improved cycling stability. Chem. Electrochem., 4(12): 3331-3339.

Buron, J.D., Pizzocchero, F., Jensen, P.U., Peterson, D.H., Caridad, J.M., Jessen, B.S., Booth, T.J. & Boggild, P. (2015). Graphene mobility mapping. Sci. Reports, 5: 12305.

Buzea, C., Pacheco, I. & Robbie, K. (2007). Nanomaterials and nanoparticles: sources and toxicity. Biointerphases, 2: 17-71.

Cameron, C.G. (2006). Supercapacitor materials for soldier systems land sustain (12s) thrust advisory group scoping study supercapacitor materials for soldier systems land sustain (12S) thrust advisory group scoping study. Technical Memorandum DRDC Atlantic TM, 1: 1-142.

Camilo, Z., Puech, N., Zakri, C., Grelet, E., Moulton, S.E., Wallace, G.C., Gambhir, S., Blanc, C., Anglaret, E. & Poulin, P. (2012). Liquid crystallinity and dimensions of surfactant-stabilized sheets of reduced graphene oxide. J. Phys. Chem. Lett., 3: 2425–2430.

Cançado, L.G., Jorio, A., Martins Ferreira, E.H., Stavale, F., Achete, C.A., Capaz, R.B., Moutinho, M.V.O., Lombardo, A., Kulmala, T.S. & Ferrari, A.C. (2011). Quantifying defects in graphene via raman spectroscopy at different excitation energies. Nano Lett., 11: 3190–3196.

Cao, H., Zhou, X., Qin, Z., & Liu, Z. (2013). Low temperature preparation of nitrogen-doped graphene for supercapacitors. Carbon, 56: 218-223.

Chabot, V., Higgins, D., Yu, A., Xiao, X., Chen, Z., & Zhang, J. (2014). A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment. Energy Environ. Sci., 7: 1564-1596.

Chang, C., Liu, C., Wu, S. & Tsai, M. (2017). Adsorption and dehydrogenation of ethane, propane and butane on Rh13 clusters supported on unzipped graphene oxide and TiO2 (110) – a DFT study. Phys. Chem. Phys., 19: 4989-4996.

Chen, C., Guo, Y., Huang, L., Xue, Y., Geng, D., Liu, H., Wu, B., Yu., G, Hu, W., Liu, Y. & Zhu, D. (2014). Controllable fabrication of ultrathin free-standing graphene films. Phil. Trans. Roy. Soc. A., 372: 20130017.

Chen, C., Zhu, J., Wu, X., Han, Q., & Wang, X. (2010). Graphene oxide−MnO2 nanocomposites for supercapacitors. ACS Nano, 4: 2822–2830.

Chen, M., Cai, J.H., Huang, Y.S., Lee, K.Y. & Tsai, D.S. (2011). Preparation and characterization of iridium dioxide–carbon nanotube nanocomposites for supercapacitors. IOP Nanotechnol., 22(11): 115706.

Chen, X., Chen, X., Zhang, F., Yang, Z. & Huang, S. (2013). One-pot hydrothermal synthesis of reduced graphene oxide/carbon nanotube/α-Ni(OH)2 composites for high performance electrochemical supercapacitor. J. Power Sources, 243: 555-561.

Cheng, M., Yang, R., Zhang, L., Shi, Z., Yang, W., Wang, D., Xie, G., Shi, D. & Zhang, G. (2012). Restoration of graphene from graphene oxide by defect repair. Carbon, 50: 2581-2587.

Chu, P.K. & Li, L. (2006). Characterization of amorphous and nanocrystalline carbon films. Mater. Chem. Phys., 96: 253-277.

Dang, S., Ren, G., Liu, J., Cai, Y., Zhang, J. & Qiu, J. (2016). Electrochemical and capacitive properties of carbon dots/reduced graphene oxide supercapacitors. Nanomaterials, 6(11): 212.

Dangchao, W., Yuming, Z., Yimen, Z., Tianmin, L., Hui, G., Yuehu, W., Xiaoyan,T., & Hang, W. (2011). Raman analysis of epitaxial graphene on 6H-SiC $(000\bar{1})$ substrates under low pressure environment. J. Semicon., 32(11): 11303-11304.

Das, P., Sudhagar, P., Kang, Y.S. & Choi, W. (2014). graphene synthesis and application for solar cells. J. Mater. Res., 29(3), 299-319.

Deer, C., Sung, R., Beerman, P.G. & Muralidharan, S. (2005). Synthesis of Mn2+-doped PbS Quantum Dots and Their Spectroscopic Properties, Amer. Lab., 37 (3), 17-20.

DeMoraes, A.C.M., Lima, B.A., de Faria, A.F., Brocchi, M. & Alves, O.L. (2015). Graphene oxide-silver nanocomposite as a promising biocidal agent against methicillin-resistant Staphylococcus aureus, Inter. J. Medicine, 10: 6847.

Dhibar, S. & Das, C.K. (2014). Silver nanoparticles decorated polyaniline/ multiwalled carbon nanotubes nanocomposite for high-performance supercapacitor electrode. Ind. Eng. Chem. Res., 53(9): 3495–3508.

Diez-Betriu, X., Alvarez-Garcia, S., Botas, C., Alvarez, P., Sanchez-Marcos, J., Prieto, C., Menendez, R. & Andres, A. (2013). Raman spectroscopy for the study of reduction mechanisms and optimization of conductivity in graphene oxide thin films. J. Mater. Chem. C., 1: 6905-6912.

Dimiev, A. M. & Tour, J.M. (2014). Mechanism of graphene oxide formation. ACS Nano, 8: 3060-3068.

Ding, Y., Cheng, H., Zhou, C., Fan, Y., Zhu, J., Shao, H. & Qu, L. (2012). Functional microspheres of graphene quantum dots. Nanotech., 23(25): 255605.

Dobrota, A.S., Paštia, I.A., Mentusa, S.V., Johansson, B., Natalia, V. & Skorodumovac, N.V. (2017). Functionalized graphene for sodium battery applications: the DFT insights, Electrochim. Acta, 250: 185–195.

Dong, C., Xu, H., Wang, X., Huang, Y., Park, M.B.C., Zhang, H., Wang, L., Huang, W. & Chen P. (2012). 3D graphene–cobalt oxide electrode for high-performance supercapacitor and enzymeless glucose detection. ACS Nano,6(4): 3206–3213.

Dong, L., Xu, C., Yang, Q., Li, Y. & Kang, F. (2015). High-performance compressible supercapacitors based on functionally synergic multiscale carbon composite textiles. J. Mater. Chem. A, 3: 4729-4737.

Dong, Y., Shao, J., Chen, C., Li, H., Wang, R., Chi, Y., Lin, X. & Chen, G. (2012). Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid. Carbon, 50: 4738-4743.

Dresselhaus, M.S., Jorio, A., Hofmann, M., Dresselhaus, G. & Saito, R. (2010). Perspectives on carbon nanotubes and graphene raman spectroscopy. Nano Lett., 10: 751-758.

Drewniak, S., Muzyka, R., Stolarczyk, A., Pustelny, T., Kotyczka-Mora´nska, M. & Setkiewicz, M., (2016). Studies of reduced graphene oxide and graphite oxide in the aspect of their possible application in gas sensors, Sensors, 16: 103

Dubal, D.P., Suarez-Guevara, J., Tonti, D., Enciso, E. & Gomez-Romero, P. (2015). A High voltage solid state symmetric supercapacitor based on graphene–polyoxometalate hybrid electrodes with a hydroquinone doped hybrid gel electrolyte. J. Mater. Chem. A., 3: 23483.

Eckmann, A., Felten, A., Verzhbitskiy, I., Davey, R. & Casiraghi, C. (2013). Raman study on defective graphene: effect of the excitation energy, type, and amount of defects. Phys. Rev. B., 88: 035426.

Ezeigwe, R., Tan, M., Khiew, P.S. & Siong, C.W. (2015). One-step green synthesis of graphene/zno nanocomposites for electrochemical capacitors, Ceram. Int., 41: 715–724.

Fan, Z., Zhao, Q., Li, T., Ren, Y.Y., Wei, T. (2012). Easy synthesis of porous graphene nanosheets and their use in supercapacitors. Carbon, 50(4): 1699-1703.

Faraji, S. & Ani, F.N. (2015). The development supercapacitor from activated carbon by electroless plating- A review. Renew. Sustain. Energy Rev., 42: 823-834.

Ferrari, A.C. (2007). Raman spectroscopy of graphene and graphite: disorder, electron–phonon coupling, doping and nonadiabatic effects. Solid State Comm., 143(1): 47-57.

Ferrari, A.C., Meyer, J.C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K.S., Roth, S. & Geim, A.K. (2006). Raman spectrum of graphene and graphene layers. Phys. Rev. Lett., 97: 187401.

Gadipelli, S. & Guo, Z.X. (2015). Graphene-based materials: Synthesis and gas sorption, storage and separation. Progress Mater. Sci., 69: 1-60.

Gao, X., Liu, J., Chang, D., Wu, F., Xu, L., Zhang, W., Du, W. & Jiang, K. (2017). Graphene incorporated, n doped activated carbon as catalytic electrode in redox active electrolyte mediated supercapacitor. J. Power Sources, 337: 25-35.

Geim, A.K., & Novoselov, K.S. (2007). The rise of graphene. Nature Mater., 6: 183 192.

Golcalves, G., Vila, M., Portoles, M., Vallet-Regi, M., Gracio, J. & Marques, P.A. (2013). Nano-graphene oxide: a potential multifunctional platform for cancer therapy. Adv. Healthcare Mater., 2: 1072-1090.

Gomez, H., Ram, K.M., Alvi, F., Villaba, P., Stefanakos, E.L. & Kumar, A. (2011). Graphene-conducting polymer nanocomposite as novel electrode for supercapacitor. J. Power Sources, 196(8): 4120-4108.

Graf, D., Molitor, F., Ensslin, K., Stampfer, C., Jungen, A., Hierold, C. & Wirth, L. (2007). Spatially resolved raman spectroscopy of single- and few-layer graphene. Nano Lett., 7: 238–242.

Guo, H.L., Wang, X.F., Qian, Q.Y., Wang, F.B. & Xia, X.H. (2009). A green approach to the synthesis of graphene nanosheets. ACS Nano., 3: 2653–2659.

Han, S., Wu, D., Li, S., Zhang, F. & Feng, X. (2014). Porous graphene materials for advanced electrochemical energy storage and conversion devices. Progress Report, 26: 849-864.

Hassan, E., Haque, E., Reddy, K.R., Minett, A.I., Chen, J. & Gomes, V.G. (2014). Edge-enriched graphene quantum dots for enhanced photoluminescence and supercapacitance. Nanoscale, 6: 11988.

Hodkiewicz, J. & Scientific, T.F., (2005). Characterizing carbon materials with Raman spectroscopy. Prog. Mater. Sci., 50: 929–961.

Hsia, B., Kim, M. S., Carraro, C., & Maboudian, R. (2013). Cycling characteristics of high energy density, electrochemically activated porous-carbon supercapacitor electrodes in aqueous electrolytes. J. Mater. Chem. A., 1: 10518–10523 |

Hu, H., Liu, Q., Ke, J. & Wang, J. (2014). Doping on supercapacitor performance of a mesoporous carbon electrode produced by a hydrothermal soft-templating process. J. Mater. Chem. A., 2: 11753-11758.

Huang, Y., Wu, J. & Hwang, K.C. (2006). Thickness of graphene and single-wall carbon nanotubes. Phys. Rev. B., 74: 245413.

Hudak, N.S., Schlichting, A.D. & Eisenbeiser, K. (2017). Structural supercapacitors with enhanced performance using carbon nanotubes and polyaniline. J. Electrochem. Soc., 164(4): A691-A700.

Iijima, S. (1980). Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy. J. Crystal Growth, 50: 675–683.

Jacobberger, R.M., Machhi, R., Wroblewski, J., Taylor, B., Gillian-Daniel, A.L., Arnold, M.S. (2015). Simple graphene synthesis via chemical vapour deposition. J. Chem. Educ., 92(11):1903–1907.

Jacober, R.M., Machhi, R., Wroblewski, J., Taylor, B., Gillian-Daniel, A.L. & Arnold, M.S. (2015). Simple graphene synthesis via chemical vapor deposition. J. Chem. Educ., 92: 1903-1907.

Jiang, B., Tian, C., Wang, L., Sun, L., Chen, C., Nong, X., Qiao, Y. & Fu, H. (2012). Highly concentrated, stable nitrogen-doped graphene for supercapacitors: simultaneous doping and reduction. Appl. Surf. Sci., 258(8): 3438-3443.

Jiang, D.D., Yao, Q., Mc Kinney, M.A. & Wilkie, C.A. (1999). TGA/FTIR studies on the thermal degradation of some polymeric sulfonic and phosphonic acids and their sodium salts. Polym. Degrad. Stab., 63: 423-434.

Jiang, L. & Fan, Z. (2014). Design of advanced porous graphene materials: from graphene nanomesh to 3D architectures. Nanoscale, 6: 1922-1945.

Johnston, D.H. & Shriver, D.F. (1993). Vibrational study of the trifluoromethane-sulfonate anion: unambiguous assignment of the asymmetric stretching modes. Inorg. Chem., 32: 1045-1057.

Kalita, H., Mohapatra, J., Pradhan, L., Mitra, A., Bahadur, D. & Aslam, M. (2016). Efficient synthesis of rice based graphene quantum dots and their fluorescent properties. RSC Adv., 6: 23518-23524.

Kalsoom, U., Rafique, M.S., Shaheen, R. & Fatima, K. (2014). Metal based synthesis of graphene by pulsed laser deposition technique. Inter. J. Sci. Eng. Res., 5, 1200-1204.

Karthika, K., Rajalakshmi, N. & Dhathathreyan, K.S. (2012). Functionalized exfoliated graphene oxide as supercapacitor electrodes. Soft Nanoscience Lett., 2: 59-66.

Kellici, S., Acord, J., Ball, J., Reehal, H.S., Morgan, D. & Saha, B. (2014). A single rapid route for the synthesis of reduced graphene oxide with antibacterial activities. RSC Adv., 4: 14858-14861.

Kim, H., Park, K.Y., Hong, J. & Kang, K. (2014). All-graphene-battery: bridging the gap between supercapacitors and lithium ion batteries. Scientific Report, 4: 5278.

Kim, T.Y., Jung, G., Yoo, S., Suh, K.S. & Ruoff, R.S. (2013). Activated graphene-based carbons as supercapacitor electrodes with macro- and mesopores. ACS Nano, 8: 6899–6905.

Kim, T.Y., Kang, H.Y., Tung, T.T., Lee, J.D., Kim, H., Yang, W.S., Yoon, H.G. & Suh, K.W. (2012). Ionic liquid-assisted microwave reduction of graphite oxide for supercapacitors. RSC Adv., 2: 8808-8812.

Kitamura, H., Sekido, M., Takeuchi, H., Ohno, M. (2011). The method for surface functionalization of single-walled carbon nanotubes with fuming nitric acid, Carbon, 49: 3851-3856.

Kroto, H.W., Heath, J.R., Obrien, S.C., Curl, R.F., Smalley, R.E., & Buckminsterfullerene, R.E.C. (1985). C60 - the third man, Nature, 318: 162–163.

Kuila, T., Mishra, A.K., Khanra, P., Kim, N.H. & Lee, J.H. (2013). Recent advances in the efficient reduction of graphene oxide and its application as energy storage electrode materials. Nanoscale, 5: 52-71.

Kuo, W.S., Hsu, C.L.L., Chen, H.H., Chang, C.Y., Kao, H.F., Chou, L.C.H., Chen, Y.C., Chen, S.J., Chang, W.T., Tseng, S.W., Wang, J.Y. & Pu, Y.C. (2016). Graphene quantum dots conjugated with polymers for two-photon properties under two-photon excitation, Nanoscale, 8: 16874-16880.

Kurzweil, P. & Chwistek, M. (2008). Electrochemical stability of organic electrolytes in supercapacitors: Spectroscopy and gas analysis of decomposition products, J. Power Sources, 176: 555–567.

Lai, L., Wang, L., Yang, H., Sahoo, N.G., Tam, Q.X. & Liu, J. (2012). Tuning graphene surface chemistry to prepare graphene/polypyrrole supercapacitor with improved performance. Nano Energy, 1(5): 723-731.

Lee, C., Wei, X., Kysar, J.W. & Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science, 321, 385-388.

Li, C. & Chou, T. (2003). A structural mechanics approach for the analysis of carbon nanotubes. Inter. J. Solids Struc., 40: 2487-2499.

Li, L., Wu, G., Yang, G., Peng, J., Zhao, X & Zhu, J. (2013). Focusing on luminescent graphene quantum dots: current status and future perspectives. Nanoscale, 5: 4015-4039.

Li, L., Yin, J., Liu, Y. & Zhao, X. (2015). Graphene oxide vs. reduced graphene oxide as core substrate for core/shell-structured dielectric nanoplates with different electro-responsive characteristics, J. Mater. Chem. C, 3: 5098-5108

Li, X., Chen, W., Zhao, J., Xing, W., & Xu, Z (2005). Microwave polyol-synthesis of Pt/CNTs catalysts: Effects of pH on particle size and elelectroctrocatalyticactivity for methanol electrooxidization. Carbon, 43: 2168-2174.

Li, X., Colombo, L., Ruoff, R.S. (2016). Synthesis of graphene films on copper foils by chemical vapour deposition. Adv Mater, 28 (29):6247-52.

Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., Banerjee, S.K., Colombo, L. & Ruoff, R.S. (2009). Large-area synthesis of high-quality and uniform graphene films on copper foils. Science, 324: 1312-1314.

Lin, L., Rong, M., Luo, F., Chen, D., Wang, Y. & Chen, X. (2014). Luminescent graphene quantum dots as new fluorescent materials for environmental and biological applications. Trends in Anal. Chem., 54: 83-102.

Lin, Y., Liao, Y., Chen, Z. & Connell, J.W. (2017). Holey graphene: a unique structural derivative of graphene, Mater. Res. Lett., 5(4): 209–234

Lin, Y.M., Dimitrakopoulos, C., Jenkins, K.A., Farmer, D.B., Chiu, H., Grill, A. & Avouris, P. (2010). 100-GHz transistors from wafer-scale epitaxial graphene. Science, 327: 662.

Lipomi, D.J., Vosgueritchian, M., Tee, B.C., Hellstrom, S.L., Lee, J.A., Fox, C.H. & Bao, Z. (2011). Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes. Nature Nanotech., 6: 788–792.

Lu, J., Li, Y. & Jiang, S.P. (2016). Self-assembled platinum nanoparticles on sulfonic acid-grafted graphene as effective electrocatalysts for methanol oxidation in direct methanol fuel cells. Sci. Reports, 6: 21530.

Lu, X., Dou, H., Yuan, C., Yang, S., Hao, L., Zhang, F., Shen, L., Zhang, L. & Zhang, X. (2012) Polypyrrole/carbon nanotube nanocomposite enhanced the electrochemical capacitance of flexible graphene film for supercapacitors. J. Power Sources, 197: 319-324.

Ma, P.L., Ren, W.C., Dong, Z. Liu., L.Q. & Cheng, H.M. (2012). Progress of graphene growth on copper by chemical vapor deposition: Growth behavior and controlled synthesis, Chinese Sci. Bull., 57: 2995-2999.

Ma, Y., Ma, C., Sheng, J., Zhang, H., Wang, R., Xie, Z. & Shi, J. (2016). Nitrogen-doped hierarchical porous carbon with high surface area derived from graphene oxide/pitch oxide composite for supercapacitors. J. Coll. & Inter. Sci., 461: 96-103.

Makgopa, K., Ejikeme, P.M., Jafta, C.J., Raju, K., Zeiger, M., Presser, V. & Ozoemen, K.I. (2015). A high-rate aqueous symmetric pseudocapacitor based on highly graphitized onion-like carbon/birnessite-type manganese oxide nanohybrids. J. Mater. Chem. A., 3: 3480.

Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L.B., Lu, W. & Tour, J.M. (2010). Improved synthesis of graphene oxide. ACS Nano, 4: 4806-4814.

Martin-Gullon, I., Vera, J., Conesa, J.A., Gonzalez, J.L. & Merino, C. (2006). Differences between carbon nanofibers produced using Fe and Ni catalysts in a floating catalyst reactor. Carbon, 44: 1572-1580.

Mei, Q., Zhang, K., Guan, G., Liu, B., Wang, S. & Zhang, Z. (2010). Highly efficient photoluminescent graphene oxide with tunable surface properties, Chem. Commun., 46: 7319-7321.

Mikhfarai, T., Oh, J., Kozlov, M., Fok, E.C.W., Zhang, M., Fang, S., Baughman, R.H. & Madden, J.D.W. (2007). Electrochemical actuation of carbon nanotubes yarns. Smart Mater. & Struct., 16(2): 1-10.

Moreno Fernandez, G., Ibañez, J., Rojo, J.M., & Kunowsky, M. (2017). Activated carbon fiber monoliths as supercapacitor electrodes. Adv. Mater. Sci. Eng., Art ID 3625414.

Moussa, M., El-Kady, M.F., Zhao, Z., Majewski, P., Ma, J. (2016). Recent progress and performance evaluation for polyaniline/graphene nanocomposites as supercapacitor electrodes. Nanotech., 27:44-50.

Mungse, H.P., Bhakuni, N., Tripathi, D., Sharma, O.P., Sain, B. & Khatri. O.P. (2014). Fractional distribution of graphene oxide and its potential as an efficient and reusable solid catalyst for esterification reactions. J. Phys. Org. Chem., 27: 944–951.

Naebe, M., Wang, J., Amini, A., Khayyam, H., Hameed, N., Hua, L., Chen, L.Y. & Fox, B. (2014). Mechanical property and structure of covalent functionalised graphene/epoxy nanocomposites. Scientific Reports, 4: 4375.

Naik, J.P., Sutradhar, P. & Sah, M. (2017). Molecular scale rapid synthesis of graphene dots. J. Nanostruct. Chem., 7: 85-89.

Nair, R.R., Blake, P., Grigorenko, A.N., Novoselov, K.S., Booth, T.J., Stauber, T., Peres, N.M.R. & Geim, A.K. (2008). Fine structure constant defines visual transparency of graphene. Science, 320: 1308-1309.

Najafabadi, I., Yamada, T., Futaba, D.N., Yudasaka, M., Takagi, H., Hatori, H., Iijima, S., Hata, K. (2011). High-power supercapacitor electrodes from single-walled carbon nanohorn/nanotube composite. ACS Nano, 5(2): 811–819.

Ning, G., Fan, Z., Wang, G., Gao, J., Qian, W. & Wei, F. (2011). Gram-scale synthesis of nanomesh with high surface area and its application in supercapacitor electrodes. Chem. Commun., 47: 5976-5978.

Notarianni, M., Liu, J., Mirri , F., Pasquali, M. & Motta, N. (2014). Graphene-based supercapacitor with carbon nanotube film as highly efficient current collector. IOP Nanotechnol., 25: 435405.

Novoselov, K.S., Jiang, Z., Zhang, Y., Morozov, S.V., Stormer, H.L., Zeitler, U., Maan, J.C., Boebinger, G.S., Kim, P. & Geim, A.K. (2007). Room-temperature quantum hall effect in graphene. Science, 315: 1379-1380.

Ossonoon, B.D. & Belanger, D. (2017). Synthesis and characterization of sulfophenyl-functionalized reduced graphene oxide sheets. RSC Adv., 7: 27224-27234.

Ostovari, F., Hasanpoori, M., Abbasnejad, M. & Salehi, M.A. (2018). DFT calculations of graphene monolayer in presence of Fe dopant and vacancy, Physica B: Condensed Matter. 541: 6–13.

Ouyang, A., Cao, A., Hu, S., Li, Y., Xu, R., Wei, J., Zhu, H. & Wu, D. (2016). Polymer-coated graphene aerogel beads and supercapacitor application. ACS Appl. Mater. Interfaces, 8 (17): 11179–11187.

Pan, Li. J. & Feng, Y.P. (2010). Carbon nanotubes for supercapacitor. Nanoscale Res. Lett., 5: 654-668.

Pandey, D., Reifenberger, R. & Piner, R. (2008). Scanning probe microscopy study of exfoliated oxidized graphene sheets. Surf. Sci., 602: 1607-1613.

Park, M., Yu, J., Kim, K., Jeong, G., Kim, J., Jo, Y., Hwang, U., Kang, S., Woo, T., Kim, Y. (2012). One-step synthesis of a sulfur-impregnated graphene cathode for lithium–sulfur batteries. Phys. Chem. & Chem. Phys., 14:6796-6804.

Park, S., An, J., Potts, J.R., Velamakanni, A., Murali, S. & Ruoff, R.S. (2011). Hydrazine-reduction of graphite- and graphene oxide. Carbon, 49: 3019 – 3023.

Pellenbarg, T., Dimentev, N., Jean-Gilles, R., Bessel, C., Borguet, E., Dollahon, N. & Giuliano, R. (2010). Detecting and quantifying oxygen functional groups on graphite nanofibers by fluoresence labeling of surface species. Carbon, 48: 4256-4267.

Peng, J., Gao, W., Gupta, B.K., Liu, Z., Romero-Aburto, R. & Ge, L.H. (2012). Graphene quantum dots derived from carbon fibers. Nano Lett., 12: 844–849.

Pirnat, K., Bitenc, J., Jerman, I., Dominko, R. & Genorio, B. (2014). Redox-active functionalized graphene nanoribbons as electrode material for Li-ion batteries. Chem. Electro. Chem., 1: 2131 – 2137.

Qian, Z., Ma, J., Shan, X., Shao, L., Zhou, J., Chen, J. & Feng, H. (2013). Surface functionalization of graphene quantum dots with small organic molecules from photoluminescence modulation to bioimaging applications: an experimental and theoretical investigation. RSC Adv., 3: 14571-14579.

Qu, Q., Yang, S. & Feng, X. (2011). 2D sandwich-like sheets of iron oxide grown on graphene as high energy anode material for supercapacitors. Adv. Mater., 23(46): 5574-5580.

Rakhi, R.B., Chen, W., Cha, D. & Alshareef, H.N. (2011). High performance supercapacitors using metal oxideanchored graphene nanosheet electrodes. J. Mater. Chem., 21: 16197-16204.

Ramli, N.I.T., Rashid, S.A., Sulaiman, Y., Mamat, M.S., Zobir, S.A. & Krishnan, S. (2016). Physicochemical and electrochemical properties of carbon nanotube/graphite nanofiberhybrid nanocomposites for supercapacitor. J. Power Sources, 326: 195-202.

Ramli, N.I.T., Rashid, S.A., Sulaiman, Y., Mamat, M.S., Zobir, S.A. & Krishnan, S. (2017). Incorporation of zinc oxide into carbon nanotube/graphite nanofiber as high performance supercapacitor electrode. Electrochim. Acta, 228: 259-267.

Rangeil, C.E. & Magana, F. (2009). Adsorption of carbon dioxide and methane on graphene with a high titanium coverage. Carbon, 47: 2758-2760.

aRashid, A.S., Zobir, S.A.M., Krishnan, S., Hassan, M.M. & Ngee, L.H. (2015). One-pot synthesis of graphene oxide sheets and graphene oxide quantum dots from graphite nanofibers. J. Nanopart. Res., 17(5): 1-11.

bRashid, S.A., Zobir, S.A.M., Krishnan, S., Hassan, M.M. & Ngee, L.H. (2015). One-pot synthesis of graphene oxide sheets and graphene oxide quantum dots from graphite nanofibers. J. Nanopart. Res., 17: 225.

Raymundo-Piñero, B.E., Khomenko, V., Frackowiak, E. & Béguin, F. (2005). Performance of manganese oxide/CNTs composites as electrode materials for electrochemical capacitors. J. Electrochem. Soc., 152: 229-235.

Reina, A., Tia, X., Ho, J., Nezich, D., Son, H., Bulovic, V., Dresselhaus, M.S., & Kong, J. (2009). Large area, few-layer graphene films on arbitrary substrates by chemical vapour deposition. Nano Lett., 9: 30-35.

Rodriguez, N.M. (1993). Review on catalytic grown carbon nanofibers. J. Mater. Res., 8: 3233-3350.

Rodriguez, N.M., Chambers, A. & Baker, R.T.K. (1995). catalytic engineering of carbon nanostructures. Langmuir, 11: 3862-3866.

Rotella, M., Briegel, A., Hull, J., Lagalante, A. & Giuliano, R. (2015). Synthesis and antibacterial activity of antibiotic-functionalized graphite nanofibers. J. Nanomater., 2015: 204961.

Sahoo, S., Chakraborti, C. K., Mishra, S. C., Naik, S. & Nanda, U. N. (2011). FTIR and RAMAN spectroscopy as a tool for analyzing sustained release hydrogel of ciprofloxacin/carbopol polymer, J. Pharma. Sci. Res., 2(2): 268-277.

Sapkota, B., Benabbas, A., Lin, H.G., Liang, W., Champion, P. & Wanunu, M. (2017). Peptide-decorated tunable-fluorescence graphene quantum dots. ACS Appl. Mater. Interfaces, 9: 9378–9387.

Schniepp, H.C., Li, J.L., McAllister, M.J., Sai, H., Herrera-Alonso, M., Adamson, D.H., Prud'Homme, R.K., Car, R., Saville, D.A. & Aksay, I.A. (2006). Functionalized single graphene sheets derived from splitting graphite oxide. J. Phys. Chem. B., 110: 8535–8539.

Seo, D.H., Pineda, S., Fang, J., Gozukara, Y., Yick, S., Bendavid, A. & Lam, S.K.H. (2017). Single-step ambient-air synthesis of graphene from renewable precursors as electrochemical genosensor. Nature Comm., 8: 14217.

Shahriary, I. & Athawale, A.A. (2014). Graphene oxide synthesized by using modified Hummers approach, Inter. J. Renew. Environ. Eng., 2(1): 2348-0157.

Shen, H., Liu, E., Xiang, X., Huang, Z., Tian, Y., Wu, Y., Wu, Z. & Xie, H. (2012). A novel activated carbon for supercapacitors. Mater. Res. Bull., 47: 662-666.

Shin, Y., Park, J., Hyun, D., Yang, Lee, J., Kim, J. & Lee, H. (2015). Acid-free and oxone oxidant-assisted solvothermal synthesis of graphene quantum dots using various natural carbon materials as resources. Nanoscale, 7: 5633-5637.

Shivakumara, S., Kishore, B., Penki, T.R. & Munichandraiah, N. (2015). Symmetric supercapacitor based on reduced graphene oxide in non-aqueous electrolyte. ECS Electrochem. Lett., 4(8): A87-A89.

Simon, P., and Gogotsi, Y. (2008). Materials for electrochemical capacitors. Nat. Mater., 7: 845–854.

Singh, S.K., Dhavale, V.M., Boukherroub, R., Kurungot, S. & Szunerits, S. (2017). N-doped porous reduced graphene oxide as an efficient electrode material for high performance flexible solid-state supercapacitor. Appl. Mater. Today, 8: 141-149.

Siokou, A.S., Ravani, F., Karakalos, S., Kalbac, F.M. & Galiotis, C. (2011). Surface refinement and electronic properties of graphene layers grown on copper substrate: An XPS, UPS and EELS study. Appl. Surf. Sci., 257: 9785-9790.

Smith, B.W., Monthioux, M., & Luzzi, D.E. (1998). Encapsulated C60 in carbon nanotubes. Nature, 396: 323-324.

Su, D., Ren, M., Li, X. & Huang, W. (2013). Synthesis of graphene by chemical vapor deposition: effect of growth conditions. J. Nanosci Nanotechnol., 13: 6471-6484.

Sun, S., Lipka, M., Swartz, C., Williams, D. & Yang, F. (2016). Hemp-derived activated carbons for supercapacitors. Carbon, 103, 181–192.

Sun, T., Zhang, Z., Xiao, J., Chen, C., Xiao, F., Wang, S. & Liu, Y. (2013). Facile and green synthesis of palladium nanoparticles-graphene-carbon nanotube material with high catalytic activity. Sci Rep., 3: 2527.

Sun, X., Liu, Z., Welsher, K., Robinson, J.T., Goodwin, A., Zaric, S. & Dai, H. (2008). Nano-graphene oxide for cellular imaging and drug delivery. Nano Res., 1: 203-212.

Tamilarasan, P. & Ramaprabhu, S. (2014). Ionic liquid-functionalized partially exfoliated multiwalled carbon nanotubes for high-performance supercapacitors. J. Mater. Chem. A., 2: 14054-14063

Tang, L., Ji, R., Cao, X., Lin, J., Jiang, H., Li, X., Teng, K.S., Luk, C., Zeng, M., Hao, S. & Lau, S.P. (2012). Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots. ACS Nano, 6: 5102-5110.

Tian, L., Yang, S., Yang, Y., Li, J., Deng, Y., Tian, S., He, P., Ding, G., Xie, X. & Wang, Z. (2016). Green simple and large scale synthesis of N-doped graphene quantum dots with uniform edge groups by electrochemical bottom-up synthesis. RSC Adv., 6: 82648-82653.

Ujjain S.K., Ahuja P., Bhatia R. & Attri P. (2016). Printable multi-walled carbon nanotubes thin film for high performance all solid state flexible supercapacitors. Mater. Res. Bul., 83: 167-171.

Ujjain, S.K., Bhatia, R., Ahuja, P. & Attri, P. (2014). Highly conductive aromatic functionalized multi-walled carbon nanotube for inkjet printable high performance supercapacitor. J. Mater. Chem. A., 3: 9925-9931

Ujjain, S.K., Bhatia, R., Ahuja, P. & Attri, P. (2015). Highly conductive aromatic functionalized multi-walled carbon nanotube for inkjet printable high performance supercapacitor electrodes. Plos One, 10(7): 0131475.

Wang, H., Holt, C.M.B., Li, Zhi., Tan, X., Amirkhiz, B.S., Xu, Z. & Olsen, B.C. (2012). Graphene-nickel cobaltite nanocomposite asymmetrical supercapacitor with commercial level mass loading. J. Nanores., 5(9): 605-617.

Wang, H., Qingli, H., Yang, H., Lu, L. & Wang, X. (2009). Graphene oxide doped polyaniline for supercapacitor. Electrochem. Comm., 11(6):1158-1161.

Wang, J., Liang, S., Ma, L., Ding, S., Yu, X., Zhou, L. & Wang, Q. (2014). One-pot synthesis of CdS-reduced graphene oxide 3D composites with enhanced photocatalytic properties. Cryst. Eng. Comm., 16: 399-405.

Wang, S., Guo, M., Penchev, I., Ruiz, I., Bozhilov, K. N., Yan, D., Ozkan, M. & Ozkan, C.S. (2013). Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors. Nano Energy, 2(2): 294-303.

Wang, S., Morelos-Gomez, Lei, Z., Terrones, M., Takeuchi, K. & Sugimoto, W. (2016). Correlation in structure and properties of highly-porous graphene monoliths studied with a thermal treatment method. Carbon, 96: 174-183.

Wang, Y. & Hu, A. (2014). Carbon quantum dots: synthesis, properties and applications, J. Mater. Chem. C., 2: 6921-6939.

Wang, Y., Shi, Z., Huang, Y., Ma, Y., Wang, C., Chen, M. & Chen, Y. (2009). Supercapacitor devices based on graphene materials, J. Phys. Chem. C, 113 (30): 13103–13107.

Wei, D., Liu, Y., Wang, Y., Zhang, H., Huang, L. & Yu, G. (2009). Synthesis of N-doped graphene by chemical vapour deposition and its electrical properties. Nano Lett., 9: 1752-1758.

Whitener Jr., K.E. & Sheehan, P.E. (2014). Graphene synthesis. Diamond Related Mater., 46: 25–34.

Wong, C., Jankovsky, O., Sofer, Z. & Pumera, M. (2014). Vacuum-assisted microwave reduction/exfoliation of graphite oxide and the influence of precursor graphite oxide. Carbon 77: 508–517.

Worsley, M.A., Pauzauskie, P.J., Olson, T.Y., Biener, J., Satcher, J.H., & Baumann, T.F. (2010). Synthesis of graphene aerogel with high electrical conductivity. J. Am. Chem. Soc., 132: 14067–14069.

Wu, Q., Xu, Y., Yao, Z., Liu, A. & Shi, G. (2010). Supercapacitors based on flexible graphene/polyaniline nanofiber composite films. ACS Nano, 4 (4): 1963–1970.

Wu, X., Tian, F., Wang, W., Chen, J., Wu, M. & Zhao J.X. (2013). Fabrication of highly fluorescent graphene quantum dots using L-glutamic acid for in vitro/in vivo imaging and sensing, J. Mater. Chem. C Mater Opt. Electron Devices, 1(31): 4676–4684.

Wu, Z., Ren, W., Gao, L., Zhao, J., Chen, Z., Liu, B., Tang, D., Yu, B., Jiang, C. & Cheng, H. (2009). Synthesis of graphene sheets with high electrical conductivity and good thermal stability by hydrogen arc discharge exfoliation. ACS Nano, 3(2): 411–417.

Wu, Z., Zhou, G., Yin, L., Ren, W., Li, F. & Cheng, H. (2012). Graphene/metal oxide composite electrode materials for energy storage. Nano Energy, 1(1): 107-131.

Wu, Z.S., Parvez, K., Feng, X. & Müllen, K. (2013). Graphene-based in-plane micro-supercapacitors with high power and energy densities, Nat. Commun. 4: 2487

Wu, Z.S., Ren, W., Gao, L., Zhao, J., Chen, Z., Liu, B., Tang, D., Yu, B., Jiang, C. & Cheng, H. (2009). Synthesis of graphene sheets with high electrical conductivity by hydrogen arc discharge exfoliation. ACS Nano, 3: 411-417.

Xia, X., Tu, J., Mai, Y. Chen, R. Wang, X., Gu, C.& Zhao, X. (2011). Graphene sheet/porous NiO hybrid film for supercapacitor applications. Chem. Euro. J., 17(39): 10898-10905.

Xu, W., Wei, C., Lv, J., Liu, H., Huang, X., & Liu, T. (2013). Preparation, characterization, and properties of in situ formed graphene oxide/phenol formaldehyde nanocomposites. J. Nanomater., 2013: 319840.

Xu, Y., Li, J. & Huang, W. (2017). porous graphene oxide prepared on nickel foam by electrophoretic deposition and thermal reduction as high-performance supercapacitor electrodes. Mater., 10: 936.

Yan, H., Tian, C., Sun, L., Wang, B., Wang, L., Yin, J., Wu, A. & Fu., H. (2014). Small-sized and high-dispersed WN from [SiO4(W3O9)4]4− clusters loading on GO-derived graphene as promising carriers for methanol electro-oxidation, Energy Environ. Sci., 7: 1939-1949.

Yan, J., Fan, Z., Wei, T., Qian, W., Zhang, M. & Wei, F. (2010). fast and reversible surface redox reaction of graphene-MnO2 composites as supercapacitor electrodes. Carbon, 48(13): 3825-3833.

Yan, Y., Ge, X., Liu, Z., Wang, J., Lee, J. & Wang, X. (2013). Facile synthesis of low crystalline MoS2 nanosheet-coated CNTs for enhanced hydrogen evolution reaction. Nanoscale, 5: 7768-7771.

Yan, Z., Lin, J., Peng, Z., Sun, Z., Zhu, Y., Li, L., Xiang, C., Samuel, E.L., Kittrell., C. & Tour, J.M. (2012). Toward the synthesis of wafer-scale single-crystal graphene on copper foils. ACS Nano, 6: 9110–911.

Yang, J., Fan, Z., Sun, W., Ning, G., Wei, T., Zhang, Q., Zhang, R., Zhi, L., Wei, F. (2012). Advanced asymmetric supercapacitors based on ni(oh)2/graphene and porous graphene electrodes with high energy density. Adv. Func. Mater., 22(12): 2632-2641.

Yang, K., Feng, L. & Liu, Z. (2015). The advancing uses of nano-graphene in drug delivery. Expert Opin. Drug Del., 12: 601-612.

Yang, S., Deng, B., Ge, R., Zhang, L., Wang, H., Zhang, Z. & Wang, G. (2014). Electrodeposition of porous graphene networks on nickel foams as supercapacitor electrodes with high capacitance and remarkable cyclic stability. Nanoscale Res. Lett. 9: 672.

Yang, S.H., Chang, K.H., Tien, H.W., Lee, Y.F., Li, S.M., Wang, Y.S., Wang, J.Y., Ma, C.C., Hu, C.C. (2011). Design and tailoring of a hierarchical graphene—carbon architecture for supercapacitor . J. Mater. Chem., 21: 2374-2380.

Yu, D. & Dai, L. (2009). Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. J. Phys. Chem. Lett., 2010, 1 (2): 467–470.

Yu, D. & Dai, L. (2010). Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. J. Phys. Chem. Lett., 1(2) : 467–470.

Yu, G., Hu, L., Liu, N., Wang, H., Vosgueritchan, M., Yang, Y., Cui Y. & Bao, Z. (2011). Enhancing the supercapacitor performance of graphene/MnO2 nanostructured electrodes by conductive wrapping. Nano Lett., 11(10): 4438-4442.

Yu, Y., J., Zhao, C., Fan, X., Wang, G. & Qiu, J. (2014). Nanohybrids from NiCoAl-LDH coupled with carbon for pseudocapacitors: understanding the role of nano-structured carbon. Nanoscale, 6: 3097-3104.

Zhang, J., Li, H. & Zhao, X.S. (2011). A high-performance asymmetric supercapacitor fabricated with graphene-based electrodes. Energy Environ. Sci., 4: 4009-4015.

Zhang, L., Zhang, F., Yang, X., Long, G., Wu, Y., Zhang, T., Leng, K., Huang, Y., Ma, Y., Yu, A. & Chen, Y. (2013). Porous 3D graphene-based bulk materials with exceptional high surface area and excellent conductivity for supercapacitors. Sci Rep., 3:1408.

Zhang, L.L., Zhao, X., Stoller, M.D., Zhu, Y., Ji, H. & Murali, S. (2012). Highly conductive and porous activated reduced graphene oxide films for high-power supercapacitors. Nano Lett., 12:1806–1812.

Zhang, X., Wang, X. & Chen, Z. (2017). A novel nanocomposite as an efficient adsorbent for the rapid adsorption of ni(ii) from aqueous solution materials, 10: 1124.

Zheng, H., Yang, G., Chen, S. & Jia, Y. (2017). Hydrothermal synthesis of 3D porous structure Bi2WO6/reduced graphene oxide hydrogels for enhancing supercapacitor performance. Chem. Electro. Chem., 4: 577–584.

Zhou, G., Xu, C., Cheng, W., Zhang, Q. & Nie, W. (2015). Effects of oxygen element and oxygen-containing functional groups on surface wettability of coal dust with various metamorphic degrees based on XPS experiment. J. Anal. Mtd. Chem., 10: 467242.

Zhu, Chen, M., He, Q., Shao, L., Wei, S. & Guo, Z. (2013). An overview of the engineered graphene nanostructures and nanocomposites. RSC Adv., 3: 22790.

Zhu, S.J., Zhang, J.H., Qiao, C.Y., Tang, S.J., Li, Y.F., Yuan, W.J., Li, B., Tian, L. Liu, F., Hu, R., Gao, H., Wei, H., Zhang, H., Sun, H. & Yang, B. (2011). Strongly green-photoluminescent graphene quantum dots for bioimaging applications. Chem. Comm., 47: 6858-6860.