UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBE/GRAPHITE NANOFIBER AND CARBON NANOTUBE/GRAPHITE NANOFIBER/METAL OXIDE (METAL = Zn AND Fe) NANOCOMPOSITES FOR SUPERCAPACITOR APPLICATION

NURUL INFAZA TALALAH BINTI RAMLI

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By

NURUL INFAZA TALALAH BINTI RAMLI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

June 2016

DEDICATION

Dedicated to my late father, Ramli bin Arifin,
Mother Jeanne abie binti Kornelius, and my siblings,
Without their understanding and support, I would never completed this project.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBE/GRAPHITE NANOFIBER AND CARBON NANOTUBE/GRAPHITE NANOFIBER/METAL OXIDE (METAL = Zn AND Fe) NANOCOMPOSITES FOR SUPERCAPACITOR APPLICATION

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June 2016

Chairman : Suraya binti Abdul Rashid, PhD

Faculty : Institute of Advanced Technology

The ever-increasing demand for energy storage devices have stimulated intensive efforts to search for better energy storage materials. The impetus of this work was to synthesis a new material for supercapacitor electrodes that can bridge the storage gap between battery and conventional capacitor. In this research work, the physicochemical and electrochemical properties of CNT/GNF nanocomposite for supercapacitor application were studied. The CNT/GNF hybrid nanocomposites with varying weight percentage (5-40 wt %) of CNTs addition were prepared by simple mixing technique that involves stirring and sonicating technique. The performance of the optimum sample of CNT/GNF hybrid nanocomposite was further tested by investigating its effect upon addition of metal oxides (MO) including zinc oxide (ZnO) and iron oxide (Fe_2O_3). Varying amount of MO ranging from 5-40 wt % was impregnated into the CNT/GNF nanocomposite, to form CNT/GNF/MO ternary composites via hydrothermal method. Field emission scanning electron microscopy and transmission electron microscopy shows the random entanglement of CNTs on the GNFs surfaces, and the random attachment of MO on the sidewalls of CNT/GNF hybrid. Raman spectroscopy analysis depict the enhanced I_D/I_G ratios, which attributed to disorder and defects. CNT/GNF sample was found to be thermally stable as much as its individual components, and the thermal stability were increased with the addition of ZnO and Fe_2O_3. In terms of electrochemical analysis, the combination of CNTs and GNFs was proved to be better compared to its individual component. Through cyclic voltammetry analysis, the specific capacitances (C_s) of CNT/GNF hybrid nanocomposites was found to be as high as 173 Fg^{-1} with 20% of CNT addition shows the optimum performance. For CNT/GNF/ZnO sample, it was found that

the increased weight percentage of ZnO addition enhanced the supercapacitive performance. 40 wt % ZnO addition was determined to produce the best C_s value, 298 Fg^{-1}. On the other hand, CNT/GNF/Fe_2O_3 revealed a comparable C_s value at 30 wt % Fe_2O_3, which found to be 290 Fg^{-1}. In brief, this research has demonstrated that the synergistic effect between novel CNT/GNF hybrid nanocomposites and metal oxides (ZnO and Fe_2O_3) possess a great potential in energy storage applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

PENYEDIAAN DAN PENCIRIAN TIUB NANO KARBON/GRAFIT SERAT NANO DAN TIUB NANO KARBON/GRAFIT SERAT NANO/LOGAM OKSIDA (LOGAM= Zn DAN Fe) NANOKOMPOSIT UNTUK KEGUNAAN SUPERKAPASITOR

Oleh

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Permintaan terhadap alat penyimpanan tenaga yang sentiasa meningkat telah merangsang usaha-usaha intensif untuk mencari bahan bagi penyimpanan tenaga yang lebih baik. Dorongan utama kajian ini adalah untuk mensintesis bahan baru untuk kegunaan elektrod superkapasitor yang mampu merapatkan jurang penyimpanan tenaga antara bateri dan kapasitor konvensional. Dalam kajian ini, sifat fizikokimia dan elektrokimia bagi hibrid CNT/GNF nanokomposit telah dikaji. Hibrid CNT/GNF nanokomposit dengan peratusan berat penambahan CNT yang meningkat (5-40 wt %) telah disintesis dengan menggunakan kaedah pencampuran mudah yang melibatkan teknik mengacau dan sonikasi. Sampel hibrid CNT/GNF nanokomposit yang mempunyai pencapaian optimum diuji dengan lebih lanjut dengan melihat kepada kesan penambahan oksida logam (MO) seperti zink oksida (ZnO) dan besi oksida (Fe_2O_3). Jumlah MO yang berbeza-beza dari 5-40 peratusan berat telah dimasukkan ke dalam CNT/GNF nanokomposit untuk membentuk CNT/GNF/MO komposit pertigaan dengan menggunakan kaedah hidroterma. Analisis mikroskop pengimbas elektron dan mikroskop penghantaran elektron menunjukkan CNT tersebar secara rawak pada permukaan GNF, dan MO melekat secara rawak pada sisi dinding hibrid CNT/GNF. Seterusnya, analisis spektroskopi Raman menunjukkan peningkatan pada nisbah I_D/I_G yang boleh dikaitkan dengan gangguan dan kecacatan pada struktur karbon. Sampel CNT/GNF juga mempunyai kestabilan haba yang sama seperti komponen individunya, dan kestabilan haba didapati meningkat dengan tambahan ZnO dan Fe_2O_3. Dari segi analisis elektrokimia pula, kombinasi CNT dan GNF disahkan mempunyai pencapaian yang lebih baik berbanding dengan komponen yang tidak bergabung. Melalui analisis voltammetri berkitar, kapasitans tertentu (C_s) bagi hibrid CNT/GNF nanokomposit adalah 173 Fg^{-1} dengan 20 % penambahan CNT menunjukkan prestasi paling optimum. Untuk sampel CNT/GNF/ZnO, peningkatan peratusan penambahan ZnO turut meningkatkan prestasi superkapasitor. Penambahan sebanyak 40 % berat ZnO telah menghasilkan nilai C_s terbaik iaitu 298 Fg^{-1}. Manakala, CNT/GNF/Fe_2O_3 mendedahkan nilai C_s sebanyak 290 Fg^{-1} bagi 30 % penambahan Fe_2O_3.

Ringkasnya, kajian ini telah menunjukkan bahawa kesan sinergi antara hibrid CNT/GNF nanokomposit yang baru dan oksida logam (ZnO dan Fe_2O_3) mempunyai potensi yang besar dalam aplikasi penyimpanan tenaga.

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

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LIST OF SYMBOLS AND ABBREVIATIONS

FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
CV	Cyclic Voltammetry
GCD	Galvanostatic charge-discharge cycle
CNT	Carbon nanotube
GNF	Graphitic nanofiber
MWCNT	Multiwall carbon nanotube
SWCNT	Single wall carbon nanotube
EDLC	Electrochemical double layer capacitor
ECP	Electrically conducting polymer
SSCNT	Super short carbon nanotube
PANI	Polyaniline
3DHBGP	Three dimensional hollow balls of graphene
CVD	Chemical vapor deposition
GCE	Glassy carbon electrode
LIB	Lithium ion battery
MO	Metal oxides
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared spectroscopy
EDX	Energy dispersive
ESR	Equivalent series resistance
a.u	Arbitrary unit
FWHM	Full width half maximum
C_s	Specific capacitance
E	Energy density
P	Power density
V	Voltage
ΔV	Voltage range
v	Scan rates

Δt	Time taken
Θ_B	Bragg angle
R_{ct}	Charge transfer resistance
Z	Impedance
λ	X-ray wavelength
B	Line broadening

CHAPTER 1

INTRODUCTION

1.1. Research background

Nanoparticle and nanocomposite research is currently an area of intense research due to its variety of potential applications. The most recent applications that involves nanosize material are energy generation and storage devices, biomedical, semiconductor, and many more. Nanoparticles can be associated as particulate dispersions or solid particles with a size in the range of 10-100 nm (Mohanraj, Chen, & Chen, 2006). Nano scale material shows a very interesting trend where the surface area of the particles increases dramatically as the size decreases. This is the most desired feature that is needed in order to upgrade the performance of the existing energy storage device.

Nearly every aspect of human lives relies on using energy. Due to this, the demand for better energy storage device has been on the increase. There is a great need for electrical energy storage, not only for mobile electronic devices, but also for automotive and aerospace applications. One of the most distinctive properties of the energy storage device is the amount of electricity or energy that can be stored over short periods of time. Supercapacitors and batteries are by far the most common form of energy storage devices. Supercapacitor is labeled as efficient storage devices that produce output energy typically exceeding 90% of its input energy (Whittingham, 2008). Supercapacitors are also called as ultracapacitors in certain books and journals. Recently, supercapacitor has appeared to be a promising energy storage system due to its pulse power supply, long cyclic life (more than 100,000 cycles), simple operational mechanism, and high dynamics of charge propagation (Li *et al*., 2015). It is an electrochemical energy storage device that combine the high-energy storage capability of a conventional battery and the fast-charging process of conventional capacitors (Chen & Dai, 2013).

The advantages of nano scale materials and the urge to improve the performance of existing energy storage devices is the theme of this work. In order to achieve higher energy density, which is a desirable characteristic for energy storage device, porous materials with larger surface area and thinner distance between electrodes should be used. Carbon nanomaterials are by far the best porous materials that have been studied extensively because of its superlative properties (Zhi *et al*., 2013). To date, carbon nanomaterials especially carbon nanotubes (CNTs) and graphitic nanofibers (GNFs) have already made their contribution to various applications including fuel cells, solar cells, sensors, supercapacitors and lithium ion batteries (LIB) (Andersen *et al*., 2013; Li *et al*.,2012). GNF, an extremely unique material are reported to have an interesting physicochemical properties including large surface area, good electronic conductivity, and chemically stable at wide temperature range (An *et al*., 2015). As for CNTs, it is known because of its remarkable physical properties. Nanotubes are suitable as electron field emitters because of their nanosize, structural perfection, high electrical conductivity, and also chemical stability. The combination of both, forming a hybrid could be expected to establish a highly effective charge transportation network (Zeng *et al*., 2014).

1.2 Problem statement

Energy storage devices that are being used to power the gadgets nowadays greatly depends on LIB and capacitor. The mediocre performance of low power density LIB and low energy density capacitor that has been commercialized so far has triggered many group of researchers to produce better and upgraded version of energy storage devices, to satisfy the current demands.

Although many important fundamental results concerning the outstanding properties of carbon nanotubes and its family have been reported in previous work, the properties of its hybrid forms have not yet been studied extensively. It is known that CNTs and GNFs works extraordinarily well for energy storage applications because of its extra-large surface area that enables the ion insertions to occur(An *et al*., 2015). Then, the addition of metal oxides such as zinc oxide (ZnO) and iron oxide (Fe_2O_3) onto the carbon matrices enhances the specific capacitance (C_s) and energy density value (Aravinda *et al*, 2013 ; Lorkit *et al*., 2014).

Currently, no studies have been reported on hybrid nanostructures that combine CNTs, GNFs and metal oxides for supercapacitor applications. Most of the research have focused on LIB applications as it has higher energy density (150-200 $Whkg^{-1}$). However, supercapacitors can provide much higher power density (10 $kWkg^{-1}$), long cycle life (exceeding 100000 cycles) and fast discharge processes. Thus, the impetus of this work was to synthesis a new material for supercapacitor electrodes that can possess both supercapacitor and battery properties.

1.3 Objectives

This thesis reports a comprehensive study on the synthesis of a new hybrid structure which combines GNFs, CNTs and metal oxide (MO) that can function better as supercapacitor electrodes. The specific objectives of this work are:

i. To prepare and characterize CNT/GNF hybrid nanocomposites.
ii. To evaluate the effect of ZnO and Fe_2O_3 addition on the supercapacitive performance of CNT/GNF hybrid nanocomposites.
iii.

1.4 Scope of work

The scope of work for the first objective has been directed towards the determination of the electrochemical and physicochemical properties of CNT/GNF hybrid nanocomposites. The preparation of CNT/GNF hybrid nanocomposites involves a very simple method which includes sonicating and stirring. The electrochemical properties of the hybrid were studied by employing three characterization methods, namely cyclic voltammetry, galvanostatic charge-discharge cycles, and electrochemical impedance spectroscopy. Both cyclic voltammetry and galvanostatic charge-discharge cycles will be used to determine the value of specific capacitance and the charge-discharge profile of the material for supercapacitor applications. On the other hand, the electrochemical impedance spectroscopy (EIS) is responsible in providing the resistance and impedance information. Various other characterizations were also performed in order to determine the physicochemical properties of the hybrid nanocomposites. The samples were characterized in terms of the graphitization (Raman spectroscopy), particle size and morphology (field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM)), crystallinity (X-ray diffraction (XRD)), thermal behavior (thermogravimetric analysis (TGA)), and functional group study (Fourier transform infrared spectroscopy (FTIR)).

The scope of work for the second objective includes the same characterization methods as the first objective. The second objective was focused towards the investigation of the metal oxides addition on the properties of GNFs/CNTs hybrid nanocomposites. The effect of ZnO and Fe_2O_3 addition were examined in terms of its electrochemical properties (via cyclic voltammetry, galvanostatic charge discharge cycles, and electrochemical impedance spectroscopy) and physicochemical properties (via Raman spectroscopy, XRD, TGA, FESEM, TEM, EDX, and FTIR).

1.5 Thesis outline

Chapter 2 provides the background of CNTs and GNFs, followed by the introduction of metal oxides such as ZnO and Fe_2O_3 on carbon structures. Energy storage aspects, especially supercapacitor properties and overview of its related research are also included in chapter 2. The preparation and characterization methods are described in chapter 3. Chapter 4 explains the findings based on two objectives. The first part explained about the effect of CNTs loading on the physicochemical and electrochemical behavior of CNT/GNF nanocomposites. The second part is focusing towards the effect of transition metal oxides loading on the properties of CNT/GNF hybrid nanocomposites. Finally, chapter 5 give drawn conclusion of the result in chapter 4 and contains suggestions for future works.

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