UNIVERSITI PUTRA MALAYSIA

FABRICATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)-GRAPHENE QUANTUM DOT-COBALT OXIDE/POLY(3,4-ETHYLENEDIOXYTHIOPHENE) FOR HIGH-PERFORMANCE SUPERCAPACITOR

SHARIFFAH NUR JANNAH SYED ZAINOL ABIDIN

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By

SHARIFFAH NUR JANNAH SYED ZAINOL ABIDIN

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

December 2017

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DEDICATION

To my beloved parents

Mr Syed Zainol Abidin Syed Sheikh & Mrs Masiah Abdul Rahim….

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

FABRICATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)-GRAPHENE QUANTUM DOT-COBALT OXIDE/POLY(3,4-ETHYLENEDIOXYTHIOPHENE) FOR HIGH-PERFORMANCE SUPERCAPACITOR

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December 2017

Chairman : Associate Professor Yusran Sulaiman, PhD
Faculty : Science

Fabrication of highly conductive nanofiber by coating polyvinyl alcohol-graphene quantum dot-cobalt oxide (PVA-GQD-Co_3O_4) nanofiber composites with a conductive material, poly(3,4-ethylenedioxythiophene) (PEDOT) for symmetrical supercapacitor was prepared via two-step technique i.e. electrospinning and electropolymerization. The prepared electrode materials were characterized using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray diffraction (XRD) analysis to confirm the structure of the electrospun nanofiber composites. The presence of cauliflower-like structure studied by field emission scanning electron microscopy (FESEM) revealed that PEDOT was uniformly coated on PVA-GQD-Co_3O_4 electrospun nanofibers. The limited cycling stability of PEDOT, poor capacitance of GQDs and low conductivity of Co_3O_4, were overcome by forming the nanofiber composite. The electrochemical performance were investigated and evaluated by sandwiching a filter paper immersed in a sulphuric acid solution between two indium tin oxide (ITO) glass coated with the nanofiber composite. Owing to large surface area and better spacing of nanofiber network structures, PVA-GQD-Co_3O_4/PEDOT nanofiber composites exhibited the highest specific capacitance of 361.97 F/g compared to PEDOT (161.48 F/g), PVA/PEDOT (220.73 F/g) and PVA-GQD/PEDOT (291.86 F/g) nanofiber composites. PVA-GQD-Co_3O_4/PEDOT nanofiber composite also demonstrated a high specific energy and excellent specific power ranged from 16.51 to 19.98 Wh/kg and 496.10 to 2396.99 W/kg, as the current density increased from 1.0 to 5.0 A/g. In addition, the equivalent series resistance (ESR) for PVA-GQD-Co_3O_4/PEDOT (15.6 Ω) nanofiber composite exhibited the lowest value as compared to PEDOT (53.7 Ω), PVA/PEDOT (45.0 Ω) and PVA-GQD/PEDOT (41.9 Ω). Moreover, PVA-GQD-Co_3O_4/PEDOT nanofiber composite also showed an excellent stability with retention of 96% of its specific capacitance after 1000 cycles. Therefore,

PVA-GQD-Co_3O_4/PEDOT nanofiber composite can be considered as a promising electrode material for application in supercapacitors.

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

PENYEDIAAN DAN PENCIRIAN NANOFIBER KOMPOSIT POLI(VINIL ALKOHOL)-TITIK KUANTUM GRAFIN-KOBALT OKSIDA/ POLI(3,4-ETILENADIOKSITIOFENA) UNTUK PRESTASI TINGGI SUPERKAPASITOR

Oleh

SHARIFFAH NUR JANNAH SYED ZAINOL ABIDIN

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Penyediaan nanofiber yang sangat konduktif dengan menyalut komposit nanofiber poli(vinil alkohol)-grafin titik kuantum-kobalt oksida (PVA-GQD-Co_3O_4) dengan bahan konduktif, poli(3,4-etilenadioksitiofena) (PEDOT) untuk superkapasitor berjaya disiapkan melalui gabungan dua teknik iaitu elektroputaran dan elektroenapan. Bahan elektrod yang disediakan dicirikan menggunakan analisis spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi Raman dan belauan sinar-x (XRD) untuk mengesahkan struktur komposit nanofiber yang telah dielektroputarankan. Kehadiran struktur seperti bunga kubis yang dikaji dengan mikroskopi imbasan elektron (FESEM) menunjukkan bahawa PEDOT bersalut dengan seragam pada PVA-GQD-Co_3O_4. Kitaran yang terhad bagi PEDOT, kapasitansi yang lemah untuk GQD dan kekonduksian yang rendah bagi Co_3O_4 telah diatasi dengan penghasilan komposit nanofiber. Prestasi elektrokimia diselidiki dan dinilai dengan mengepitkan kertas turas yang direndam dalam larutan asid sulfurik di antara dua kaca indium timah oksida (ITO) yang disalut dengan komposit nanofiber. Oleh kerana luas permukaan yang besar dan jarak rangkaian struktur nanofiber yang lebih baik, komposit nanofiber PVA-GQD-Co_3O_4/PEDOT menunjukkan kapasiti khusus tertinggi 361.97 F/g berbanding komposit nanofiber PVA-GQD/PEDOT (291.86 F/g) dan PVA/PEDOT (220.73 F/g). Komposit nanofiber PVA-GQD-Co_3O_4/PEDOT juga menunjukkan tenaga spesifik yang tinggi dan kuasa spesifik yang sangat baik antara 16.51 hingga 19.98 Wh/kg dan 496.10 hingga 2396.99 W/kg, semasa peningkatan ketumpatan arus daripada 1.0 hingga 5.0 A/g. Di samping itu, rintangan siri bersamaan (ESR) bagi komposit nanofiber PVA-GQD-Co_3O_4/PEDOT (15.6 Ω) menunjukkan nilai terendah berbanding PVA-GQD/PEDOT (41.9 Ω) dan PVA/PEDOT (45.0 Ω). Selain itu, komposit nanofiber PVA-GQD-Co_3O_4/PEDOT juga menunjukkan kestabilan yang sangat baik dengan

mengekalkan 96% nilai kapasitan spesifik selepas 1000 kitaran. Oleh itu, komposit nanofiber PVA-GQD-Co_3O_4/PEDOT boleh dianggap sebagai bahan elektrod yang sesuai digunakan untuk aplikasi dalam superkapasitor.

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First of all, in a humble way I wish to give all the praise to Allah, the Almighty God for His mercy has given me the strength, blessing and time through this journey. Say: "*Surely my prayer, my sacrifice, my life and my death are all for God, the Lord of all creation*".

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I certify that a Thesis Examination Committee has met on 27 December 2017 to conduct the final examination of Shariffah Nur Jannah binti Syed Zainol Abidin on her thesis entitled "Fabrication and Characterization of Poly(Vinyl Alcohol)-Graphene Quantum Dot-Cobalt Oxide/Poly(3,4-Ethylenedioxythiophene) for High-Performance Supercapacitor" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF SYMBOLS

Symbol		Unit
C_{sp}	specific capacitance	F/g
m	mass of the active material	g
ΔV	potential difference	v
v	scan rate	V/s
E	specific energy	Wh/kg
P	specific power	W/kg
ΔV	potential difference at discharge process	V
I	current applied	A
ESR	equivalent series resistance	Ω
R_{ct}	charge transfer resistance	Ω
W	Warburg element	-
χ^2	chi-square	-
CPE	constant phase element	F
C_{dl}	double-layer capacitor	-

LIST OF ABBREVIATIONS

CB	Conduction Band
CP	Conducting Polymers
C_{sp}	Specific Capacitance
CPE	Constant Phase Element
CV	Cyclic Voltammetry
DSCs	Dye-Sensitized Solar Cells
EC	Eletcrochemical Capacitor
EDLC	Electrochemical Double Layer Capacitor
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
F/g	Farad per gram
GCD	Galvanostatic Charge Discharge
HOMO	Highest Occupied Molecular Orbital
ICP	Intrinsically Conducting Polymers
LUMO	Lowest Unoccupied Molecular Orbital
LEDs	Light-Emitting Diodes
PPV	Poly(P-Phenylenevinylene)
PPP	Poly(P-Phenylene)
PET	Poly(Ethylene Tere- Phthalate)
PEO	Poly(Ethylene Oxide)
PLA	Polylactide
PCL	Poly(*E*-Caprolactone)
PEDOT	Poly(3,4-Ethylenedioxythiophene)
PVA-GQD	Polyvinyl alcohol-graphene quantum dot
PVA-GQD-Co_3O_4	Polyvinyl alcohol-graphene quantum dot-cobalt oxide
PVA-GQD/PEDOT	Polyvinyl alcohol-graphene quantum dot/ poly(3,4-ethylenedioxythiophene)
PVA-GQD-Co_3O_4/PEDOT	Polyvinyl alcohol-graphene quantum dot-cobalt oxide/ poly(3,4-ethylenedioxythiophene)
VB	Valence Band
0 D	Zero- Dimension
1D	One-Dimensional
2D	Two-Dimensional
+½	Spinless Positive Charge
½	Radical

CHAPTER 1

INTRODUCTION

1.1 Background

Energy production and consumption that depend on the combustion of fossil fuels is estimated to have severe impact on the world environment. Besides, the reducing availability and environmental pollution from fossil fuels have become an intense interest for researchers to design a more environmentally friendly and more sustainable energy. Therefore, the development of energy storage such as capacitor, batteries, and supercapacitor has been considered as a new alternative to overcome this problem. Among all these energy storage devices, supercapacitors have been widely investigated owing to their greater specific power than batteries and higher specific energy than capacitors (Yao *et al.*, 2017). Moreover, it is worth mentioning that supercapacitor with a symmetrical electrode configuration (both electrodes consist of the same material) have been extensively studied recently for next-generation power devices.

The emergence of nanotechnology consequently affects the fabrication of electrode materials for supercapacitor. Nanotechnology is referring to the particles or assemblies whose dimensions range in size from a few nanometers up to around 100 nm (Lines, 2008). The development is covering a wide variety of materials including carbon-based nanomaterials, quantum dots, nanofibers, nanoparticles and nanocomposites (Schwirn *et al.*, 2014). Recently, nanofibers have attracted a great deal of attention in the area of technology due to their superior characteristics such as a high surface area to volume ratio, low specific mass and high porosity. Specifically, the development of research on nano-scale fiber is being conducted to fulfill the demands for many applications including energy storage devices. Additionally, electrically conducting polymers have drawn increasing attention since the early 1970s (Shirakawa *et al.*, 1977) due to their outstanding properties such as excellent conductivity, low ionization potential and large electron affinity (Unsworth *et al.*, 1992) as compared to the polymer. However, the preparation of nanofiber using conducting polymer has become a great challenge which may lead to the detriment of the electronic properties (Laforgue and Robitaille, 2010). Therefore, in order to increase the electrical properties of the electrospun nanofiber, in this work, a facile method has been developed by depositing a conducting polymer onto the PVA nanofiber containing graphene quantum dot and cobalt oxides. The introduction of cobalt oxides and carbon-based materials into the electrospun nanofiber enhance the supercapacitive performance of the electrode material due to its theoretically high specific capacitance of cobalt oxide and abundance active sides of graphene quantum dot. Hence, the incorporation of these materials is believed to play a vital role in improving the electrochemical performance of supercapacitor applications.

1.2 Problem Statement

The development of energy storage devices such as supercapacitors has been explored to meet the growing energy needs. Therefore, the growth of promising electrode materials is essential in order to improve the overall electrochemical performance of symmetrical supercapacitors. Conducting polymers have poor long-term stability due to its weak and brittle mechanical strength (Azman *et al.*, 2016, Sonia *et al.*, 2013). While carbon materials have a drawback of low capacitance (Choudhury *et al.*, 2016, Jiang *et al.*, 2012) and metal oxides exhibit poor conductivity. As a consequence, there has been a trend towards the production of composites nanofiber with a combination of EDLC and pseudocapacitor materials as a promising approach to improve the performance of supercapacitors.

Poly(3,4-ethylenedioxythiophene) (PEDOT) possesses high conductivity however it has a drawback of structure damage during cycling stability which restricts its application for supercapacitor. To overcome this drawback, PEDOT is incorporated with nanomaterial such as nanofibers that have a high surface area to volume ratio and high mechanical strength which can serve as a template for deposition of PEDOT. In addition, to further enhance the supercapacitive performance in terms of specific capacitance, cobalt oxide which displays high theoretical specific capacitance and graphene quantum dot (GQDs) will also be incorporated in the nanocomposite. In this work, PVA nanofibers which have high surface area and high mechanical strength was incorporated with the high theoretical specific capacitance of cobalt oxide and abundance active sides and accessible edges of graphene quantum dot. Thus, the coating of PEDOT onto PVA-GQD-Co_3O_4 nanofiber composite is believed to provide a synergistic effect that can enhance the supercapacitor applications.

1.3 Research Objectives

The goal of this research is to study the unique properties of electrically conductive PVA-GQD-Co_3O_4/PEDOT nanofiber composite for symmetrical supercapacitor. This study embarks on the following objectives:

1. To prepare PVA-GQD/PEDOT and PVA-GQD-Co_3O_4/PEDOT nanofibers via a combination of electrospinning and electropolymerization techniques.

2. To evaluate the supercapacitive performance of the PVA-GQD/PEDOT and PV-GQD-Co_3O_4/PEDOT nanofibers for supercapacitor application.

3. To compare the electrochemical properties of PVA-GQD/PEDOT and PVA-GQD-Co_3O_4/PEDOT.

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