

UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYVINYL ALCOHOL-GRAPHENE OXIDE/POLY(3,4-ETHYLENEDIOXYTHIOPHENE) COMPOSITE NANOFIBER

NUR AFIFAH BINTI ZUBAIR

FS 2016 39



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NUR AFIFAH BINTI ZUBAIR

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

August 2016

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DEDICATION

To my beloved parents Mr Zubair Ahmad & Mrs Radziah Abdul Ghani

For always believing in me, encouraging me, and loving me unconditionally...



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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 POLYVINYL ALCOHOL-GRAPHENE OXIDE/POLY(3,4-ETHYLENEDIOXYTHIOPHENE) COMPOSITE NANOFIBER

By

NUR AFIFAH BINTI ZUBAIR

August 2016

Chairman : Yusran Sulaiman, PhD Faculty : Science

Electrically conductive nanofibers are nanostructured materials which attracted extensive interest for their superior properties. These materials are being studied in various research fields include, electrochemistry, material science and electronic applications. In this work, conducting nanofibers composed of polyvinyl alcohol (PVA), graphene oxide (GO) and poly(3,4-ethylenedioxythiophene) (PEDOT) were fabricated via a combined method using electrospinning and electropolymerization techniques. During electrospinning, the concentration of PVA or PVA-GO solution, and the applied voltage were deliberately altered in order to determine the optimized electrospinning conditions. The optimized parameters with 0.1 mg/mL of GO and 10 w/v% of PVA concentration with electrospinning voltage of 15 kV were obtained. The electrospun PVA and PVA-GO nanofiber mats were further modified by coating with the conjugated polymer, PEDOT using electropolymerization techniques which is a facile approach for coating the nanofibers. SEM images of the obtained nanofibers revealed that PEDOT grew well on the surface of the electrospun nanofibers during the potentiostatic mode of the electropolymerization process. The presence of GO and PEDOT in nanofiber was confirmed by FTIR and Raman spectroscopy analyses. The optimum electropolymerization of PEDOT was at potential of 1.2 V in 5 mins. The electrochemical measurements demonstrated that the PVA-GO/PEDOT composite nanofiber could enhance the current response and reduce the charge transfer resistance of the nanofiber. The equivalent circuit models were used to fit the impedance spectra of PEDOT, PVA/PEDOT and PVA-GO/PEDOT nanofibers where the spectra were fitted well.

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

PENYEDIAAN DAN PENCIRIAN NANOFIBER KOMPOSIT POLIVINIL ALKOHOL-GRAFIN OKSIDA/ POLI(3,4-ETILENADIOKSITIOFENA)

Oleh

NUR AFIFAH BINTI ZUBAIR

Ogos 2016

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Nanofiber pengalir elektrik adalah bahan berstruktur nano yang telah menarik perhatian luas kerana sifat-sifat unggul yang dimilikinya. Bahan ini telah dikaji dalam pelbagai bidang penyelidikan termasuk elektrokimia, sains bahan dan aplikasi elektronik. Dalam kajian ini, nanofiber konduktor yang terdiri daripada polivinil alkohol (PVA), grafin oksida (GO) dan poli(3,4-etilenadioksitiofina) (PEDOT) telah dihasilkan melalui kaedah gabungan menggunakan teknik elektroputaran dan elektroenapan. Semasa proses elektroputaran, kepekatan larutan PVA atau PVA-GO, dan voltan yang digunakan diubah untuk menentukan keadaan elektroputaran yang optimum. Parameter optimum dengan kepekatan 0.1 mg/mL GO, 10 w/v% PVA dan 15 kV voltan elektroputaran telah diperolehi. Nanofiber PVA dan PVA-GO yang telah dielektroputar diubahsuai selanjutnya dengan menyadurinya menggunakan polimer konjugat, PEDOT melalui teknik pengelektroenapan yang merupakan pendekatan ringkas untuk menyalut nanofiber. Imej SEM daripada nanofiber yang diperolehi mendedahkan bahawa PEDOT berkembang dengan baik pada permukaan nanofiber yang telah dielektroputaran semasa proses pengelektroenapan melalui mod potentiostatik. Kehadiran GO dan PEDOT dalam nanofiber telah disahkan oleh analisis spektroskopi FTIR dan Raman. Keadaan optimum pengelektroenapan PEDOT adalah pada keupayaan 1.2 V dalam masa 5 minit. Pengukuran elektrokimia menunjukkan bahawa nanofiber komposit PVA-GO/PEDOT boleh meningkatkan tindak balas arus dan mengurangkan rintangan pemindahan cas pada nanofiber itu. Padanan model litar telah digunakan untuk disesuaikan dengan spektrum impedans PEDOT, PVA/PEDOT dan PVA-GO/PEDOT yang mana menunjukkan kesemua spektrum itu telah disesuaikan dengan baik.

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LIST OF SYMBOLS

Symbol Unit cm² electrode area А $\frac{mol\ cm^{-3}}{cm^2\ s^{-1}}$ C* concentration of redox species diffusion coefficient D V ΔE peak potential anodic peak current $i_{\rm pa}$ A cathodic peak current А $i_{\rm pc}$ $\hat{R}_{\rm ct}$ resistance of charge transfer Ω R_s resistance of solution Ω V s⁻¹ v scan rate $\begin{array}{c} \gamma \\ T \\ W \\ \chi^2 \end{array}$ diffusion element Ω warburg impedance Ω chi squared

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LIST OF ABBREVIATIONS

ACN	acetonitrile
AFM	Atomic force microscopy
ATR	attenuated total reflectance
BET	Brunauer-Emmett-Teller
CE	counter electrode
CPE	constant phase element
CS	chitosan
CV	cyclic voltammetry
DI	deionized
EIS	electrochemical impedance spectroscopy
$[Fe(CN)_6]^{3-/4-}$	ferricyanide and ferrocyanide ion
FESEM	field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GO	graphene oxide
ICPs	intrinsically conducting polymers
ITO	indium tin oxide
kV	kilovolt
mA	milliampere
min	minute
mM	millimolar
mPa.s	millipascal-second
mV	millivolt
nm	nanometer
OCP	open circuit potential
PANI	polyaniline
PEDOT	poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
PLGA	poly(lactide-co-glycolide)
PPy	polypyrrole
PVA	polyvinyl alcohol
PVA-GO	polyvinyl alcohol-graphene oxide
PVA/PEDOT	polyvinyl alcohol/poly(3,4-ethylenedioxythiophene)
PVA-GO/PEDOT	polyvinyl alcohol-graphene oxide/ poly(3,4-
	ethylenedioxythiophene)
RE	reference electrode
rGO	reduced graphene oxide
SEM	scanning electron microscopy
TBAPF ₆	tetra(n-butyl) ammonia hexafluorophosphate
WE	working electrode

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nanotechnology has become a prominent area of research in future with immense potential in terms of various applications. According to the National Science Foundation (NSF) and science related literature, nanotechnology deals with matter in the length scale of approximately 1 - 100 nanometer range (Lines, 2008, Roco, 2007) at atomic, molecular or macromolecular levels where having novel properties and functions due to the arrangement of their atoms in nanoscales. In the advancements of nanotechnology, a diverse range of nanomaterials are being explored include carbon nanotubes, graphene-based materials, nanofibers, nanocomposites, nanoparticles, nanowires, quantum dots, nanorods, nanofilms, and nanopores (Schwirn *et al.*, 2014). Recently, nanofibers have been broadly investigated as high-performance materials due to their unique and remarkable properties which exhibit tremendous advantages. Nanofibers have attracted a great deal of attention because of their excellent characteristics including a high surface area to volume ratio, low specific mass and extensive porosity (Greiner and Wendorff, 2007) which make them appropriate for a diverse range of applications.

Additionally, the interest in electrically conductive nanofibers has increased markedly. This can be seen by a large number of publications and a broad spectrum of the application was studied. These nanofibers have been utilized extensively as electrochromic devices, chemical sensors (Ding *et al.*, 2009), drug delivery (Nima Khadem *et al.*, 2013), wound dressings (Catherine *et al.*, 2014) and photovoltaic devices (Katsuhiro *et al.*, 2006). In conjunction with increased throughput, the fabrication of nanofibers with various adjustments is preferable. There are several techniques to produce nanofibers namely electrospinning, phase separation, self-assembly and template synthesis (Khajavi and Abbasipour, 2012). Electrospinning has been found to be the most versatile process for producing nanoscale fibers with relatively low cost, scalability, high productivity and ability to produce long continuous fibers. At present, various attempts were made in the modification of electrospun nanofibers to improve their properties for specific applications (Hong, 2005, Zhang *et al.*, 2010b).

1.2 Problem Statement

Recently, conductive polymer nanofibers have emerged as excellent supporting materials in the production of nanostructures with narrow diameter distribution. However, it is difficult to use intrinsically conducting polymers (ICPs) in the electrospinning process for nanofiber production due to its intrinsic high crystallinity (Park *et al.*, 2013) low solubility in general solvents (Xu *et al.*, 2009) and too stiff to be electrospun by themselves (Laforgue and Robitaille, 2010). Therefore, a combination

of ICPs with another electrospinnable polymer is effectively considered to fabricate nanofibers but this may lead to the detriment of the electronics properties. Hence, despite declining its special characteristics, a facile method was studied to fabricate highly conductive nanofiber by coating electrospun nanofibers with conductive materials. This method is adjustable and essentially enhances the electrical properties of the electrospun nanofiber. Additionally, introducing conducting polymer onto the polymer nanofiber has a potential for producing electroactive nanomaterials. Current studies reported upon the deposition of conducting polymers on electrospun nanofiber structures, the template could potentially produce a promising class of nanomaterials with highly porous structure, large surface area to volume ratio, (Zhang et al., 2006b) and an ultrathin conducting layer (Greiner and Wendorff, 2007), thus make such materials attractive for various applications. The modification of the electrospun polymer nanofiber could enhance the properties of the electrically conductive nanofiber mats in order to achieve some requirement for spesific uses. As reported in the literature, PEDOT coated TiO₂ nanofibers were shown to have increased in electrical conductivity and high sensitivity for sensing applications (Wang et al., 2009b). PEDOT as one of the conductive polymer from polythiophene derivatives has been widely explored due to its excellent environmental and thermal stability, highspeed electron transfer, good mechanical strength and relatively high optical transparency when in its electrically conductive state (Jin et al., 2013).

Another important approach in producing polymer-based composites is the incorporation of carbon-based materials such as carbon nanotubes (CNT) and graphene derivatives into the nanofibers. The complete dispersion of nanofiller represents another challenge that can be countered by specific material, in order to increase their affinity for the polymer matrix in an appropriate solvent. This issue can be overcome by selecting a kind of effective nanofiller to be encapsulated into an electrospun nanofiber matrix. Graphene oxide (GO) is appointed as the best candidate for nanofillers to be reinforced with a hydrophilic polymer such as polyvinyl alcohol (PVA) due to its abundance of hydrophilic groups on its surface. Additionally, PVA is considered as a commonly used electrospinnable polymer due to its processibility, good biodegradability, non-toxicity and good mechanical properties (Cai *et al.*, 2015). Therefore, the high dispersibility of GO in water makes it the best material as nanofiller to be incorporated with PVA matrices. Moreover, GO as one of the most important graphene derivatives has attracted tremendous interest because of their unique properties which are high surface area and good electrical conductivity.

As reported by Rose *et al.*, (2015), polymers will exhibit excellent properties after being reinforced with nanofillers, which contribute to the high performances of materials. The incorporation of nanofillers into electrospun nanofibers improves their properties to a certain extent. Hence, the special criteria of nanofibers which make them commercially important are their role in enhancing the electroactive nature, high surface area and high flexibility in surface functionalities. Consequently, in order to generate conductive nanofibers, significant efforts are being deployed to develop nanofibrous materials for applications. The unique combination of PEDOT as conducting polymers and GO as nanofiller to produce highly conductive materials has sparked an interest in the development of electrospun nanofibers.

1.3 Objectives

The primary aim of this research is to study the unique properties of electrically conductive PVA-GO/PEDOT composite nanofibers produced by a combination of two controllable techniques, electrospinning and electropolymerization. The fabrication of this conductive polymer nanofiber is beneficial as its applicability in various potential applications.

To that aim, this research work has three specific objectives:

- 1. To prepare PVA/PEDOT and PVA-GO/PEDOT nanofibers by a combination of electrospinning and electropolymerization techniques.
- 2. To characterize the physical properties of the prepared nanofibers using scanning electron microscope (SEM), Fourier transform infrared spectrometer (FTIR) and Raman spectrometer.
- 3. To study the electrochemical behavior of PVA/PEDOT and PVA-GO/PEDOT nanofibers by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

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