UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

DIRECT GROWTH OF VERTICALLY ALIGNED CARBON NANOTUBE (VACNT) ON DIFFERENT CONDUCTING SUBSTRATES FOR ELECTROCHEMICAL CAPACITOR (EC)

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Master of Science in Manufacturing Engineering

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A thesis submitted
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DECLARATION

I declare that this thesis entitle “Direct Growth of Vertically Aligned Carbon Nanotube (VACNT) on Different Conducting Substrates for Electrochemical Capacitor (EC)” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : …...

Name : ....

Date : ....

APPROVAL

I hereby declare that I have read this thesis and my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering (Advanced Materials).

Signature	:	....
Supervisor Name	:	....
Date	:	....

DEDICATION

To my beloved family and friends.

ABSTRACT

Electrochemical capacitor (EC) is highly promising energy device due to its electrical charge storage performance and significant lifecycle ability. Construction of the EC cell especially its electrode fabrication is critical to ensure great application performance. The purpose of this research is to introduce direct growth of vertically aligned carbon nanotube (VACNT) on conducting substrates, namely SUS 310S, Inconel 600, and YEF 50 and their usage as symmetric VACNT electrode in EC. The substrates were deposited by alumina and cobalt catalyst thin films, and then the growth was done by using alcohol catalytic chemical vapour deposition. By this, VACNT was successfully grown and their structures (dimension, walls) have been confirmed by means of electron microscopies. The thickness of the VACNT is typically about 31.68 μm (SUS 310S) and 10.58 μm (Inconel 600), respectively which indicate that no particular agglomerated metals were observed on the exposed surface of the substrate. In contrast, the field emission scanning electron microscopy (FESEM) image obtained shows that most of the entire areas, a thicker carbon products forest/agglomerated was formed on the top surface of YEF 50 substrate. Meanwhile, the transmission electron microscopy (TEM) image reveals that the VACNT on Co/Al_2O_3/SUS 310S are multi-walled CNTs (MWCNTs) with the inner and outer diameter of CNTs are approximately 4.89 nm and 16.43 nm, respectively. The Raman spectra results indicate that the CNT was typical of MWCNTs, which is in agreement with the TEM observation. Regardless of the difference in current collectors being used, cyclic voltammetry (CV) analysis from the EC depicted a relatively good specific gravimetric capacitance (C_{sp}) and rate capability performance. A nearly rectangular-shaped CV curve was observed even at a scan rate of 1000 mV s^{-1}. The C_{sp} measured at 1 mV s^{-1} was 33.35 F g^{-1} (SUS 310S), 16.73 F g^{-1} (Inconel 600), and 24.82 F g^{-1} (YEF 50), respectively. Besides, from the charge-discharge measurement, the symmetrical triangular curves reveal that there is no IR drops or voltage drops because of low internal resistance in the electrode for SUS 310S, Inconel 600, and YEF 50 substrates. Also, the VACNT electrode shows excellent discharge behaviour and good capacitance retention of up to 1,000 cycles. Thus, this binder free and aligned CNT structure may provide excellent rate capabilities, high capacitance, and long lifecycle energy device. This is very promising for the development of high energy and high power density of device for multi-scale applications or industries.

ABSTRAK

Kapasitor elektrokimia merupakan alat tenaga yang bagus kerana ia mempunyai prestasi yang baik dalam penyimpanan cas elektrik dan keupayaan kitaran hidup yang menarik. Pemasangan sel kapasitor elektrokimia terutamanya dalam fabrikasi elektrod sangat kritikal untuk prestasi aplikasi yang mantap. Tujuan penyelidikan ini adalah untuk memperkenalkan pertumbuhan secara langsung karbon nanotiub yang menegak sejajar di atas substrat yang boleh mengalirkan arus elektrik dinamakan sebagai SUS 310S, Inconel 600, dan YEF 50 dan juga kegunaannya sebagai elektrod yang simetri dalam kapasitor elektrokimia. Semua substrat telah menjalani proses pemendapan menggunakan filem nipis alumina dan kobalt, kemudian pertumbuhan karbon nanotiub telah dilakukan menggunakan alkohol pemangkin wap kimia pemendapan. Dengan ini, karbon nanotiub yang menegak sejajar telah berjaya tumbuh dan strukturnya (dimensi, dinding) telah disahkan menggunakan mikroskopi elektron. Ketebalan karbon nanotiub yang menegak sejajar ialah 31.68 µm (SUS 310S) dan 10.58 µm (Inconel 600) menunjukkan tiada kewujudan pengumpulan logam di atas permukaan pada kedua-dua substrat. Sebaliknya, imej FESEM yang diperolehi menunjukkan karbon yang tebal terbentuk di atas permukaan substrat YEF 50 di kebanyakan kawasan,. Sementara itu, imej TEM mendedahkan bahawa karbon nanotiub yang tumbuh di atas Co/Al_2O_3/SUS 310S adalah karbon nanotiub yang mempunyai dinding yang banyak dengan diameter luaran dan dalaman karbon nanotiub 4.98 nm dan 16.43 nm. Keputusan raman spektrum menandakan bahawa karbon nanotiub yang terhasil mempunyai dinding yang banyak, yang mana bertepatan dengan pemerhatian menggunakan TEM. Tidak kira perbezaan pengumpulan arus yang digunakan, analisis menggunakan kitaran voltammetri dari kapasitor elektrokimia menunjukkan spesifik gravimetrik kapasitan dan kadar prestasi keupayaan yang sangat baik. Hasil pemerhatian mendapati lengkuk menyerupai bentuk segi empat tepat kitaran voltammetri yang terbentuk bertahan sehingga kadar imbasan pada 1000 mV s^{-1}. Nilai spesifik gravimetrik kapasitan diukur pada kadar 1 mV s^{-1} ialah 33 35 F g^{-1} (SUS 310S), 16.73 F g^{-1} (Inconel 600), dan 24.82 F g^{-1} (YEF 50). Tambahan juga, daripada pengukuran kadar alir-pembebasan, lengkuk segi tiga yang simetri menunjukkan tiada penurunan IR atau penurunan voltan disebabkan rintangan dalaman yang rendah dalam elektrod untuk ketiga-tiga substrat. Elektrod karbon nanotiub yang menegak sejajar juga mempunyai tingkah laku pelepasan cas yang agak cemerlang dan pengekalan kapasitan yang sangat baik sehingga mencecah 1,000 kitaran. Oleh itu, struktur karbon nanotiub yang menegak akan menghasilkan kadar keupayaan yang sangat cemerlang, kapasitan yang tinggi, dan kitaran hayat yang panjang bagi alat tenaga. Ini menjanjikan penghasilan ketumpatan tenaga yang tinggi dan kuasa yang tinggi bagi alat untuk digunakan dalam aplikasi skala yang pelbagai dalam industri.

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LIST OF ABBREVIATIONS

ACCVD	Alcohol Catalytic Chemical Vapour Deposition
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
EBPVD	Electron Beam Physical Vapour Deposition
EC	Electrochemical Capacitor
EDLC	Electrochemical Double Layer Capacitor
FESEM	Field Emission Scanning Electron Microscopy
IL	Ionic Liquid
KOH	Potassium Hydroxide
MWCNT	Multi-Walled Carbon Nanotube
SWCNT	Single-Walled Carbon Nanotube
TEM	Transmission Electron Microscopy
VACNT	Vertically Aligned Carbon Nanotube
XPS	X-ray Photoelectron Spectroscopy

LIST OF SYMBOLS

Al_2O_3	-	Alumina
Co	-	Cobalt
C_{sp}	-	Specific gravimetric capacitance
F g^{-1}	-	Farad per gram
g	-	Gram
k	-	Kilo
mA	-	Miliampere
min	-	Minute
mm	-	Milimeter
mV s^{-1}	-	MiliVolts per second
M	-	Molar
μm	-	Micrometer
nm	-	Nanometer
Pa	-	Pascal
s	-	Second
W kg^{-1}	-	Watts per kilogram
Wh kg^{-1}	-	Watts hour per kilogram
°C	-	Degree celcius

LIST OF PUBLICATIONS

(i) Peer reviewed journals

Seman, R. N. A. R., Azam, M. A. and M. A. Mohamed, Vertically Aligned Carbon Nanotube Directly Grown on Stainless Steel and Inconel Foils for Supercapacitor Electrode. Journal of Nanoscience and Nanotechnolgy. (accepted for publication).

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(ii) Conference presentation

Vertically Aligned Carbon Nanotube Directly Grown on Different Metal Alloy Substrates for Supercapacitor Electrode, Energy Materials Nanotechnology, Holiday Inn Resort Phuket Thailand, 4-7 May 2015 (Oral)

Cyclic Voltammetry Analysis of Carbon Based Electrochemical Capacitor in Aqueous Electrolytes, 3rd International Conference on Design & Concurrent Engineering 2014 - iDECON2014, Avilion Legacy Hotel Melaka Malaysia, 22-23 September 2014 (Oral)

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Electrochemical Performance of Activated Carbon and Graphene based Supercapacitor, International Symposium on Advanced Functional Materials-ISAFM 2014, Monash University Kuala Lumpur Malaysia, 1-2 August 2014 (Oral)

CHAPTER 1

INTRODUCTION

1.1 Background

Since the discovery of electricity, there has been the sought of effective methods to store the energy for the used in demand. Energy storage devices offer a powerful technological approach to manage power supply in order to produce more resilient energy framework and bring cost effective to societies. Also, the existing of advanced technology in modern economy and society demands the execution and design of cheap, good efficiency, and various infrastructures for energy storage systems (Pint et al., 2011).

There is some of the different technologies are predicted to provide the country with renewable energy in the long term period such as hydroelectric systems, biomass, wind power, solar thermal and geothermal systems. In particular, fuel cells, batteries, electrochemical capacitors (ECs), and conventional capacitors are being used as energy storage devices due to their excellent in enhancing the energy or power densities and becoming more critical to supply energy within a relatively short or long period of time. However, by increasing the energy and power densities of the devices is highly desirable seems their performance are measured by these characteristic (Kim et al., 2012).

Among the energy storage devices, ECs have appeared as the most promising for the upcoming energy challenge (Simon and Gogotsi, 2008; Yang et al., 2011). Moreover, some potentially electrode materials with high specific area like single-walled carbon nanotubes (SWCNTs) are being used in EC application especially in electrochemical double-layer capacitors (EDLCs) (Sharma and Bhatti, 2010). The present of available electrodes in the energy storage devices such as low electrolyte accessibility with narrow electrochemical window, flammability, toxicity, thermal instability and low capacitance have restricted the performance of the devices. With these limited properties, there is a need to overcome this problem in order to develop high performance EC with high rate performance, and long lifecycle (Lu et al., 2009).

Carbon nanotube is being used as electrode materials in EC application because they possess high conductivity, continuous conductive paths, low mass density, regular pore structures, high mechanical strength and high chemical stability (Zhang et al., 2009; Merkoci et al., 2005; Kim et al., 2005; Kim et al. 2002). Moreover, it is possible to synthesize the CNTs directly on current collector substrates without using binder agents. There has been extensively study about the growth of vertically aligned carbon nanotubes (VACNTs) due to it produce high yield and uniformity as well as homogeneous distribution of nanotube growth (Vinten et al., 2011).

1.2 Problem Statement

Recent work on aligned CNT has drawn increasing attention since aligned CNT have shown good characteristic in various applications (Bistamam and Azam, 2014) such as nanoscale electronic devices (Murakami et al., 2000), ECs (Chen et al., 2004), and sensors (Arab et al., 2006). Previously, quartz and silicon wafer have been used as non-conducting substrates to synthesis VACNT. In spite of that, these non-conducting substrates have been replaced with conducting substrates to be used in EC application to directly grow VACNT. This is because it provides excellent electrical contact among the substrate and VACNT and thus will increase the conductivity of electrode materials.

Therefore, the process to assemble the electrode materials make easier because there is no need to have additional materials to prepare the electrode materials including conductive additive and binders (Zhang et al., 2007). There are various method to grow VACNTs on conducting substrates including liquid dip-coating method (Parthangal et al., 2007), bias-enhanced microwave plasma chemical vapour deposition (CVD) (Lin et al., 2004), and vapour-phase catalyst delivery method (Katayama et al., 2001).

In contrast, physical transfer techniques such as flip-over (Kim et al., 2006), lift-off (Chai et al., 2007), and contact transfer techniques (Kumar et al., 2006) have been introduced to transfer VACNT on conducting substrates. Although this technique was reliable, it will result in poor electrical contact between substrate and CNT electrode and known as complicated processes which can affect electrochemical properties of the VACNT. In addition, conventional coating was used in preparing the slurry to fabricate the electrode material for EC. This method needed a binder material as insulating material which directly can affect the electrochemical performance of electrode. Meanwhile transfer technique was introduced to minimize the internal resistance of the electrode. CNT was grow on Silicon wafer substrate by CVD process, then CNT with catalyst thin films were cutting by using razor blade and pasted on conducting substrate for EC application. This method will increase the number process steps.

In order to enhance the electrode performance in various applications especially in ECs, aligned CNT that shows excellent performance are required because its possess good properties including high mechanical strength and good electrical conductivity. Many efforts have been made by researchers to optimize and improve the properties of aligned CNT structure. The direct growth of CNT on conducting substrate is highly desirable in EC application to minimize the contact resistance between substrate and CNT. This technique was develop particularly by using low cost ethanol vapour gas and metal catalyst thin film in order to optimize the high precision of CNT growth for electronic device application. By developing the direct growth technique, binder free and additional process step in device fabrication can be avoided which might introduce internal resistance at once affecting charge storage performance of EC (Lu and Dai, 2010).

From the above justification and explanation, the direct growth technique was choosing in this research. By using direct growth technique it will produce superb electrical contact between substrate and CNT compared to physical transfer technique which can increase the conductivity of electrode materials. Also, this is simple technique because there is no need the binder and conductive additives material which will influence the performance of device fabrication.

1.3 Objectives

The objectives of this research are as follows:

1) To synthesis vertically aligned carbon nanotube (VACNT) on conducting substrates by using ethanol based growth technique.
2) To characterize as-grown VACNTs by using morphological and analytical techniques.
3) To assess electrochemical performance of VACNT electrode by using cyclic voltammetry and charge-discharge.

1.4 Scopes

The scope of this research is to grow the VACNT on various conducting substrates by using ethanol based growth technique. The substrates or foils are SUS 310S, Inconel 600, and YEF 50, and the main focus is to determine the VACNT growth performance as well as the electrochemical performance VACNT electrode in EC. In order to directly grow VACNT, there is a need to prepare the catalyst and catalyst-support thin films. The electron beam physical vapour deposition (EBPVD) system was used to prepare the thin films. In specific, cobalt (2-6 nm) and alumina (20-30 nm) were used as catalyst and catalyst-support, respectively. The CVD temperature and processing time for CNT growth were fixed to 700 °C and 10 min, respectively.

The as-grown VACNTs on the substrates were characterized by using electron microscopies; FESEM, TEM, and Raman spectroscopy. For the confirmation of VACNT morphology and dimension (thickness), FESEM and TEM were used. The structural information of VACNT was characterized by using Raman spectroscopy. Further, VACNT electrodes were prepared to evaluate the electrochemical performances by using cyclic voltammetry (CV), and charge-discharge. Various scan rates including 1, 5, 10, 50, 100, 250, 500, and 1000 mV s^{-1} were used to evaluate the charge storage ability of all electrode materials. Meanwhile, charge-discharge was tested up to 1,000 cycles to investigate the charge-discharge characteristic from the electrode materials. For the fabrication of EC, aqueous electrolyte, 6 molar potassium hydroxide (6 M KOH) was used as the electrolyte, and polypropylene (PP) as the separator.