UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

PREPARATION OF GRAPHENE/MOLYBDENUM DISULFIDE BASED ELECTRODES AND ITS ELECTROCHEMICAL PERFORMANCE IN SUPERCAPACITORS

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A thesis submitted
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DECLARATION

I declare that this thesis entitled "Preparation of Graphene/Molybdenum Disulfide Based Electrodes and Its Electrochemical Performance in Supercapacitors" 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.

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Date	:	7/11/2019

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Doctor of Philosophy.

Signature : ....

Supervisor Name : Assoc. Prof. Ir. Dr. Mohd Asyadi 'Azam bin Mohd Abid

Date : 7 NOV. 2019..........

DEDICATION

To my beloved family.

ABSTRACT

Supercapacitor is highly promising energy device due to its electrical charge storage performance and significant lifecycle ability. Construction of the supercapacitor cell especially its electrode fabrication is critical to ensure great application performance. The purpose of this research is to fabricate the molybdenum disulfide (MoS_2), graphene and G/MoS_2 hybrid electrode and their usage as symmetric and asymmetric supercapacitors. The electrode was prepared by using a simple and facile slurry technique. By this, XRD was used to analyze the crystal phase and structure of the as-prepared graphene, MoS_2, and G/ MoS_2 hybrid. The peaks at 14.3°, 33.8°, and 57.5° are attributed to the (002), (100), and (110) plane of MoS_2 crystal. From Raman spectroscopy shows the characteristic peaks of graphene (D, G and 2D) and MoS_2 (E^1_{2g} band at 377 cm^{-1} and A_{1g} band at 403 cm^{-1}) are retained in the Raman spectra of G/MoS_2 which can confirm the fact that the hybrid of G/MoS_2 is composed of MoS_2 and graphene. Next, the XPS analysis was carried out to deduce the exact elemental composition of the G/MoS_2. The full scan of the G/MoS_2 gives the characteristic peaks for Mo 3d, S 2p, C 1s and O 1s with their corresponding binding energies. The morphologies and microstructures of the MoS_2, graphene and G/MoS_2 are systematically characterized by FESEM observation. The high resolution of FESEM image further reveals that the MoS_2 structures are constructed with layers of nanosheets. Meanwhile, FESEM image of graphene sheets illustrating the uniformly distributed of graphene into the Ni foam. Also, the inclusion of MoS_2 nanosheets resulted in a rough surface, logically due to co-stacking of MoS_2 nanosheets over the graphene nanosheets. Further, the morphology of the G/MoS_2 was examined by TEM and reveals the crystal lattice structure of MoS_2 and graphene in G/MoS_2. The interlayer spacing of MoS_2 in the hybrid were estimated to be ~0.63 nm, which can be indexed to their (002) lattice planes of hexagonal phase of MoS_2. Regardless of the difference in electrode being used, cyclic voltammetry (CV) analysis from the supercapacitor depicted a relatively good specific gravimetric capacitance (C_{sp}) and rate capability performance. A nearly rectangular-shaped CV curve was observed even at high scan rate. 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 electrodes. Also, the electrode shows excellent discharge behavior and good capacitance retention of up to 10,000 cycles. Thus, this 2D heterostructures 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

Superkapasitor adalah peranti tenaga yang sangat menarik kerana prestasi penyimpanan cas elektrik dan keupayaan kitaran hayat yang penting. Pembinaan sel superkapasitor terutamanya fabrikasi elektrod adalah penting untuk memastikan prestasi aplikasi yang hebat. Tujuan penyelidikan ini adalah untuk menyediakan elektrod molibdenum disulfida (MoS_2), grafin dan hybrid G/MoS_2 dan penggunaannya sebagai superkapasitor simetri dan asimetrik. Elektrod telah disediakan dengan menggunakan teknik campuran separa cair yang mudah dan senang. Dengan ini, XRD digunakan untuk menganalisis fasa kristal dan struktur grafin yang disediakan, MoS_2, dan hibrid G/MoS_2. Puncak pada 14.3°, 33.8° dan 57.5° dikaitkan dengan kristal MoS_2 (002), (100), dan (110). Dari spektroskopi Raman menunjukkan puncak ciri-ciri grafin (D, G dan 2D) dan MoS_2 (band E^1_{2g} pada 377 cm^{-1} dan A1g pada 403 cm^{-1}) dikekalkan dalam spektrum Raman hybrid G/MoS_2 yang dapat mengesahkan fakta bahawa hibrid G/MoS_2 terdiri daripada MoS_2 dan grafin. Seterusnya, analisis XPS dijalankan untuk menyimpulkan komposisi elemen sebenar hibrid G/MoS_2. Siaran penuh hibrid G/MoS_2 memberikan puncak ciri untuk Mo 3d, S 2p, C 1s dan O 1s dengan tenaga mengikat yang sama. Morfologi dan mikrostruktur MoS_2, grafin dan hibrid G/MoS_2 secara sistematik dicirikan oleh pemerhatian FESEM. Resolusi tinggi imej FESEM dengan lebih lanjut mendedahkan bahawa struktur MoS_2 dibina dengan lapisan nano. Sementara itu, imej FESEM lembaran grafin yang menggambarkan gambarajah secara seragam ke dalam Ni. Juga, kemasukan lapisan nano MoS_2 menyebabkan permukaan yang kasar, secara logiknya disebabkan oleh penyambungan lapisan nano MoS_2 ke atas lapisan nano grafin. Tambahan lagi, morfologi hibrid G/MoS_2 diperiksa oleh TEM dan mendedahkan struktur kristal MoS_2 dan grafin dalam hibrid G/MoS_2. Jarak lapisan dalam MoS_2 di dalam hibrid adalah dianggarkan ~ 0.63 nm, yang boleh diindeks ke permukaan (002) fasa heksagon MoS_2. Tanpa mengira perbezaan elektrod yang digunakan, analisa voltammetri siklik (CV) dari superkapasitor menggambarkan kapasitan gravimetrik spesifik (C_{sp}) dan prestasi kadar keupayaan yang agak baik. CV berbentuk persegi panjang hampir diperhatikan walaupun pada kadar imbasan tinggi. Di samping itu, dari pengukuran caj pelepasan, lengkung segitiga simetri mendedahkan bahawa tiada kejatuhan IR atau penurunan voltan kerana rintangan dalaman yang rendah dalam elektrod. Juga, elektrod menunjukkan tingkah laku pelepasan yang sangat baik dan pengekalan kapasiti yang baik sehingga 10,000 pusingan. Jadi, heterostruktur 2D ini boleh memberikan keupayaan kadar yang sangat baik, kapasitan yang tinggi, dan peranti tenaga kitaran hayat yang panjang. Ini sangat menjanjikan untuk pembangunan tenaga tinggi dan ketumpatan kuasa tinggi untuk aplikasi pelbagai skala atau industri.

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LIST OF ABBREVIATIONS

AC	-	Activated Carbon
ASC	-	Asymmetric Supercapacitor
CNT	-	Carbon Nanotube
CP	-	Conducting Polymer
C_{sp}	-	Specific Gravimetric Capacitance
CV	-	Cyclic Voltammetry
CVD	-	Chemical Vapor Deposition
ED	-	Energy Density
EDLC	-	Electrochemical Double Layer Capacitor
EIS	-	Electrochemical Impedance Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
G	-	Graphene
GCD	-	Galvanostatic Charge-Discharge
H_2SO_4	-	Sulfuric Acid
KOH	-	Potassium Hydroxide
LIB	-	Lithium Ion Battery
MoS_2	-	Molybdenum Disulfide
Na_2SO_4	-	Sodium Sulfate
NMP	-	N-Methyl-2-pyrrolidone
PTFE	-	Polytetrafluoroethylene
TEM	-	Transmission Electron Microscopy
TMD	-	Transition Metal Dichalcogenide
XRD	-	X-Ray Powder Diffraction
XPS	-	X-Ray Photoelectron Spectroscopy
2D	-	Two Dimensional

LIST OF SYMBOLS

$F\ g^{-1}$	-	Farad per gram
g	-	Gram
k	-	Kilo
m	-	Meter
e	-	Electron
mA	-	MiliAmpere
$mV\ s^{-1}$	-	MiliVolts per second
μm	-	Micrometer
nm	-	Nanometer
Pa	-	Pascal
s	-	Second
$W\ kg^{-1}$	-	Watts per kilogram
$Wh\ kg^{-1}$	-	Watts hour per kilogram
°C	-	Degree celcius
V	-	Voltage
W	-	Watt
CV	-	Cyclic voltammetry
Ψ0	-	Electrode potential
Ψ	-	Potential

LIST OF PUBLICATIONS

(i) Peer reviewed journals

1. Seman, R.N.A.R., Azam, M.A. and Ani, M.H., 2018. Graphene/transition Metal Dichalcogenides Hybrid Supercapacitor Electrode: Status, Challenges, and Perspectives. *Nanotechnology*, 29(50), pp. 502001–502025.

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5. Azam, M.A., Seman, R.N.A.R., Zulkifli, M.F., Mohamed, M.A. and Ani M.H., 2018. Carbon Nanomaterials Derived from Malaysia's Highway Road Asphalt Waste as Electrode for Supercapacitor. *Journal of Materials and Environmental Sciences*, 9 (7), pp. 2164–2168.

6. Azam, M.A., Seman, R.N.A.R. and Effendi S.M., 2017. Preparation of Hydrous Ruthenium Oxide/Activated Carbon Electrode and Its Supercapacitive Performance in 6M KOH. *Journal of Advanced Manufacturing Technology (JAMT)*, 11(2), pp. 1–8.

7. Azam, M.A., Alias, F.M., Tack, L.W., Seman, R.N.A.R. and Taib, M.F.M., 2017. Electronic Properties and Gas Adsorption Behaviour of Pristine, Silicon-, and Boron-Doped (8, 0) Single-Walled Carbon Nanotube: A First Principles Study. *Journal of Molecular Graphics and Modelling*, 75, pp. 85–93.

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11. Seman, R.N.A.R., Azam, M.A. and Mohamed M.A., 2016. Highly Efficient Growth of Vertically Aligned Carbon Nanotubes on Fe–Ni Based Metal Alloy Foils for Supercapacitors. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 7(4), pp. 045016–045024.

(ii) Conference presentation

1. Electrochemical performance of molybdenum disulfide Supercapacitor Electrode in potassium hydroxide and sodium sulfate electrolytes, 5th International Conference and Exhibition on Sustainable Energy and Advanced Materials Holiday Inn Melaka, 16–19 October 2017 (Oral presentation).

2. Effects of PTFE binder ratio on the performance of graphene supercapacitor, ISoRIS'17, Ramada Hotel, Melaka, 18 & 19 July 2017 (Oral presentation).

LIST OF AWARDS

1. 29th International Invention, Innovation & Technology Exhibition 2018

   Place: KLCC Convention Centre Kuala Lumpur

   Date: 10–12 May 2018

   ITEX 2018 Silver medal

2. UTeM Research and Innovation Expo (UTeMEX)

   Date: 17 November 2017

   Place: FTK Universiti Teknikal Malaysia Melaka

   Jury Special award & Gold award

3. Seoul International Invention Fair (SIIF 2016)

   Date: 1–2 December 2016, Korea

   Place: Seoul, Korea

   Silver Medal

4. Malaysia Technology Expo 2016 (MTE 2016)

   Date: 18–20 February 2016

   Place: PWTC Kuala Lumpur

   Special Award & Gold Award

CHAPTER 1

INTRODUCTION

1.1 Background

Currently new electrode materials are under intense study to be used in supercapacitor applications, including transition metal oxides, metal hydroxides, and conducting polymers. Compared with other electrode materials such as carbon based materials, these electrode materials give high capacitance. Despite having high capacitance, these electrode materials possess low electrical conductivity, leading to inferior cycling stability as well as lower energy and power densities.

Graphene, composed of carbon atoms arranged in a honeycomb lattice, has been shown to possess unique properties. Additionally, the transition metal chalcogenide molybdenum disulfide (MoS_2) (Figure 1.1) shows prospects for various applications, including supercapacitors, because of the unique atomic structure analogues with graphene (Cao et al., 2013; Hu et al., 2013; Shi et al., 2013; He and Que, 2016).

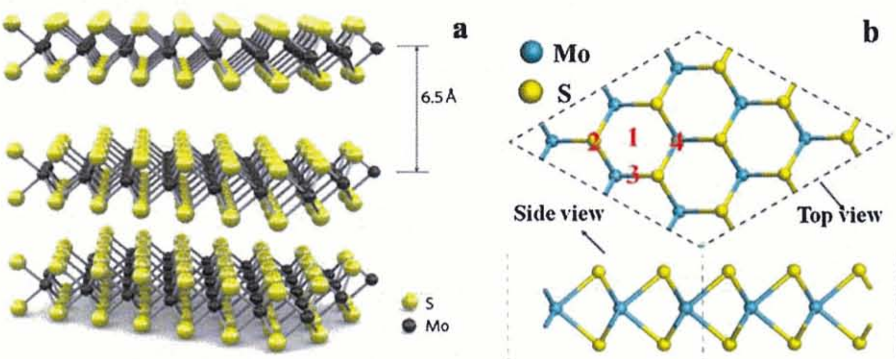

Figure 1.1: Molybdenum disulfide atomic structure (He and Que, 2016)

Research into green and renewable energy materials is expanding, as well as the market for low cost and light-weight electrochemical energy storage systems. Among energy storage devices, supercapacitors are one of the most popular energy storage devices contrasted with batteries because of their long life stabilities, fast charge-discharge processes, and high power density (Lu et al., 2013a).

Fabrication of superior electrode materials with well design structures is a crucial factor to increase high electrochemical performance of the energy storage devices such as high energy density an

d high power density (Cakici et al., 2017; Chen et al., 2017). Layered MoS_2 is analogous to the two-dimensional (2D) structure of graphene. The intercalation of electrolyte ions is permitted from the usage of MoS_2 as an electrode material in supercapacitors.

Thus, the key factor that determines the storage mechanism of supercapacitor is the diameter of electrolyte ion as well as matching of the interlayer spacing (Zhou et al., 2017). The construction of 2D hybrid heterostructures of graphene and MoS_2 (G/MoS_2) is believed to allow strongly coupled nanohybrid materials with optimized functionalities for supercapacitor application.

In addition, chemical vapor deposition (CVD), reduction-induced in situ self-assembly, chemical assembly, and the hydrothermal method (Figure 1.2) are simple methods which provide a unique approach for the synthesis of G/MoS_2 for energy storage applications (Yang et al., 2017). These novel materials and the fabrication of symmetric and asymmetric supercapacitors are important in meeting energy and power demands.

Asymmetric supercapacitors (ASCs) are composed of two dissimilar electrodes such as carbon and pseudocapacitive materials based electrodes (Wu et al., 2014; Sun et al., 2015). Commonly, the negative electrode in ASC is composed of carbon based materials including graphene, carbon nanotube, and activated carbon. Meanwhile, metal oxides and conducting polymers are the example of the positive electrode in ASC.