The Influence of Exfoliated Graphite on Sensing Properties of Chitosan/PVA Based Ammonia Sensors

by

Nur Zuraihan Bt Abd Wahab
(1530411626)

A thesis submitted in fulfillment of the requirements for the degree of
Master of Science in Materials Engineering

School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

2017

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name : NUR ZURAIHAN BT ABD WAHAB

Date of birth : 18 JULY 1990

Title : THE INFLUENCE OF EXFOLIATED GRAPHITE ON SENSING PROPERTIES OF CHITOSAN/PVA BASED AMMONIA SENSORS

Academic Session : 2015/2016

I hereby declare that the thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)*

☐ **RESTRICTED** (Contains restricted information as specified by the organization where research was done)*

☑ **OPEN ACCESS** I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of ____ years, if so requested above).

Certified by:

_____ **SIGNATURE**

900718-02-5498 **(NEW IC NO. / PASSPORT NO.)**

Date : _____

_____ **SIGNATURE OF SUPERVISOR**

_____ **NAME OF SUPERVISOR**

Date : _____

NOTES : * If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentially or restriction.

APPROVAL AND DECLARATION SHEET

This thesis titled study on The Influence of Exfoliated Graphite in Sensing Properties of Chitosan/PVA based Ammonia Sensors was prepared and submitted by Nur Zuraihan Bt Abd Wahab (Matrix no : 1530411626) and has been founds satisfactory in term of scope, quality and presentation as fulfillment of the requirement of Master in Science (Materials Engineering) in University Malaysia Perlis (UniMAP).

Checked and approved by:

_____

(DR. IRWANA NAINGGOLAN)

Supervisor

Date: _____

_____

(ASSOC. PROF. DR. MOHD NAZREE DERMAN)

Co-Supervisor

Date: _____

School of Materials Engineering

University Malaysia Perlis

(2017)

ACKNOWLEDGEMENT

Firstly, I would like to praise the Al – Mighty Allah for His blessing in finishing my project and write this thesis with limited time. I also would like to express my appreciation to Dr. Irwana Nainggolan as my supervisor for her views, advice and recommendations as well as for cooperation given during my lab work as well as in writing this thesis. Not forgotten, my co-supervisor Assoc. Prof. Dr. Mohd Nazree Derman for the advices and support given until the end of this journey. Besides that, I would like to place a special thanks to my parent Abd Wahab Bin Abd Rahman, Saolah Bt Ahmad and my siblings Nurlaili and Hilmy Noor for supporting me mentally, physically and as my backbone to go through this journey. Lastly, I love to thanks all my clique, Dr. Devi Shantini, Dr. Roshidah Mustaffa, Ahmed Masud, Mdm Norizah Karim, Ms. Najwa Alyani, Nur Amirah, my fellow friends and UniMAP staffs for their support and helps all the way in finishing this postgraduate world.

Thank you.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

VOCs	Volatile Organic Compound
PVA	Polyvinyl alcohol
KOH	Potassium hydroxide
EG	Exfoliated Graphite
SnO_2	Tin oxide
Cr_2O_3	Chromium (III) oxide
TiO_2	Titanium dioxide
CNTs	Carbon nanotubes
NH_3	Ammonia
CO_2	Carbon dioxide
NO_x	Nitrogen oxide
RFID	Radio-frequency identification
O_2	Oxygen
NO	Nitric oxide
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric analysis
FESEM	Field Emission Scanning Electron Microscope
AgNPs	Silver nanoparticles
SPR	Surface plasmon resonance
HRTEM	*High-resolution transmission electron microscopy*
AA	*Acrylic acid*

AN	*Aniline*
PANI	Polyaniline
PPy	Polypyrrole
MFC	Mass flow controller
GIC	Graphite intercalated compound
EMI	Electromagnetic shielding
N_2	Nitrogen
xGNP	Exfoliated graphite nanoplatelet
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
PCB	Printed circuit board
CS	Chitosan
ATR	Attenuated total reflection
KBR	Potassium bromide
eV	Electron volt
A	Absorbance
m	meter
S	Siemen
S	Sensor response
V	Volts
R^2	Correlation coefficient
ppm	Part per million

LIST OF SYMBOLS

π	pi
σ	sigma
Ω	Ohm
°C	Celcius
ε	Strain
d_o	Strain free inter-planar spacing

Pengaruh Grafit Terkelupas pada Sifat-Sifat Pengesan Ammonia yang Didasarkan pada Kitosan/PVA

ABSTRAK

Kitosan telah digunakan sebagai bahan pengesan untuk aplikasi pengesanan gas. Untuk mengukuhkan sifat-sifat kitosan sebagai bahan pengesan, kitosan (CS) telah diadun dengan polivinil alcohol (PVA) dan ditambahkan grafit terkelupas (EG). Kitosan filem, CS/PVA filem dan CS/PVA/EG filem telah dikaji untuk tujuan pencirian kesan EG ke atas microstruktur dan sifat elektrik daripada gabungan filem tersebut. Filem komposit disediakan dengan kaedah penuangan untuk tujuan pencirian. Ujikaji pencirian telah dibuat menggunakan alatan Spektrofotometer Ultra Lembayung-Nampak (UV-VIS), Probe Empat Titik (Ujian Kekonduksian), Pembelauan X-Ray (XRD), Mikroskop Elektron Pengimbas (FESEM) and Spektroskopi Infra-Merah (FTIR). Kitosan dengan kepekatan 1.75 (w/v) % telah diadun dengan polivinil alkohol (PVA) dengan kepekatan 5.00 (v/v) % dan dicampur dengan nisbah 95:5 ml dan ditambah dengan grafit terkelupas (EG). Keputusan menunjukkan penambahan EG dengan kepekatan 0.8 (w/v) % memberikan kekonduksian yang tertinggi dalam CS/PVA/EG filem.Filem CS/PVA/EG filem pengesan telah menjalani pembentukan di atas elektrod bersalut emas dengan menggunakan teknik pemendapan elektokimia untuk membentuk bahan pengesan untuk mengesan kehadiran gas. Kesimpulan telah dibuat bahawa masa pemendapan elektrokimia 6 minit dan voltan pemendapan elektrokimia 2.5 voltan adalah parameter terbaik untuk membentuk filem pengesan. Tahap terbaik ciri-ciri pengesan telah dapat dikenalpasti bahawa kitosan dengan kepekatan 1.75 (w/v) %, CS/PVA bernisbah 95:5 ml dengan kepekatan PVA (5.00 (v/v) %) dan EG dengan kepekatan 0.8 (w/v)% dengan mendedahkan filem pengesan ke atas udara basah. Parameter ini telah digunakan untuk membentuk filem pengesan untuk diujikaji dengan mendedahkan filem pengesan ke atas gas ammonia. Kitosan filem pengesan dan CS/PVA/EG filem pengesan telah didedahkan kepada gas ammonia dengan kepekatan yang berlainan seperti 10 ppm, 20 ppm, 30 ppm, 40 ppm dan 50 ppm untuk mengenalpasti tahap tindak balas daripada Kitosan filem pengesan dan CS/PVA/EG filem pengesan. Keputusan ujikaji elektrik telah menunjukkan bahawa Kitosan filem pengesan dan CS/PVA/EG filem pengesan teleh memberi tindak balas yang meningkat selaras dengan meningkatnya kepekatan gas ammonia. Kedua-dua filem pengesan telah menunjukkan ciri-ciri yang baik, stabil, kebolehupayaan untuk menghasilkan tindak balas yang sekata dan kebolehupayaan untuk kembali kepada tindak balas yang terendah, sensitive. CS/PVA/EG filem pengesan telah memberikan nilai tindak balas yang tinggi berbanding dengan kitosan filem pengesan sepanjang terdedahnya filem pengesan ke atas gas ammonia. Selain itu, CS/PVA/EG filem pengesan telah menunjukkan kebolehupayaan untuk membezakan nilai tindak balas sepanjang didedahkan dengan gas lain seperti gas hexanal.

The Influence of Exfoliated Graphite on Sensing Properties of Chitosan/PVA Based Ammonia Sensor

ABSTRACT

Chitosan was used as a sensing material for gas sensing applications. In order to nurture the chitosan properties as a sensing material, chitosan (CS) was blended with polyvinyl alcohol (PVA) and filled with exfoliated graphite (EG). The chitosan films, CS/PVA films and CS/PVA/EG films were characterized to study the effect of EG on microstructure and electrical properties of the composites films. The films casting method has been used to characterize the composite films. The characterization analysis was done using Ultra Violet-Visible (UV-VIS), Four Point Probe (Conductivity testing), X-Ray Diffraction (XRD), Fourier Electron Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR). Chitosan with concentration 1.75 (w/v) % was blended with polyvinyl alcohol (PVA) with concentration 5.00 (v/v) % of ratio 95:5 ml and filled with exfoliated graphite (EG). The results showed that the addition of EG with concentration of 0.8 (w/v) % gives the highest conductivity value of CS/PVA/EG films. The CS/PVA/EG films sensor was deposited on the gold pattern electrode by using electrochemical deposition technique to fabricate the sensor for the ammonia detection. The best electrochemical deposition time and deposition voltage in this study were 6 minutes and 2.5 voltage to fabricate the films sensor. The optimum sensing properties were obtained with CS concentration of 1.75 (w/v) %, CS/PVA ratio of 95:5 ml with PVA concentration of 5.00 (v/v) % and EG concentration of 0.8 (w/v) % upon exposure to wet air. This parameter of CS films sensor and CS/PVA/EG films sensor was used to fabricate the films sensor to test upon exposure of ammonia gas. The CS film sensor and CS/PVA/EG film sensors were exposed to ammonia with different concentration i.e. 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm to examine the sensing properties of the CS film sensor and CS/PVA/EG film sensors. The electrical results showed that the CS film sensor and CS/PVA/EG film sensors showed the increasing response value as the concentration of ammonia increases. Both sensors exhibit good response, stability, repeatability, recovery, sensitivity and selectivity during exposure to ammonia. CS/PVA/EG films sensor yield highest response compared to CS films sensors towards exposure of ammonia gas. In addition, CS/PVA/EG films sensor was selective towards exposure of different analyte such as hexanal.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The detection of volatile compounds and pollutants gases is important to ensure the safety of mankind. The emission of volatile compounds and pollutant gases need to be controlled in order to concern by the harmful effects to health of humans. This harmful gas was mainly produced by industrial processes, engines combustion, transportations, manufacturing of fertilizers and etc (Wales et al., 2016). Volatile compounds and pollutants gases are categorized as toxic gases and have potential to cause cancer to human and give harm to environments (Celebioglu et al., 2016).

Ammonia (NH_3) in one of the toxic gases that exists in our surrounding environment include in air, soil and water. Exposure to high concentration of ammonia (>5000 ppm) lead to severely affects human health and contribute to death. Low exposure of low concentration (25-150 ppm) of ammonia cause the irritation of human skin, eyes and respiratory tract (Basova et al. 2016). Therefore, it is necessary to monitor the presence of ammonia in potential sites and fields of having the probability presence of ammonia such as agriculture, chemical industries, pharmaceutical, hydrogen fuels, defense and food processing industries. Therefore, the development of fast and real time detection of ammonia in atmosphere at room temperature (Mani et al. 2013).