



DEVELOPMENT OF A CHEMIREISTOR SENSOR  
BASED ON POLYANILINE (PANI) NANOFIBERS FOR  
DETECTION OF AMMONIA

by

**Zulhairi Bin Zakaria**  
**(1240410785)**

A thesis submitted  
in fulfillment of the requirements for the degree of  
Doctor of Philosophy in Material Engineering

**School of Materials Engineering**  
**UNIVERSITI MALAYSIA PERLIS**

2016

# UNIVERSITI MALAYSIA PERLIS

## DECLARATION OF THESIS

Author's full name : ZULKHAIRI BIN ZAKARIA  
Date of birth : 04 JANUARY 1985  
Title : DEVELOPMENT OF A CHEMIREISTOR SENSOR BASED ON  
POLYANILINE (PANI) NANOFIBERS FOR DETECTION OF AMMONIA

Academic Session : 2012-2016

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**

\_\_\_\_\_  
**SIGNATURE OF SUPERVISOR**

\_\_\_\_\_  
**(NEW IC NO. / PASSPORT NO.)**

\_\_\_\_\_  
**NAME OF SUPERVISOR**

Date:

Date:

## ACKNOWLEDGEMENT

In the name of Allah The Most Gracious and The Most Merciful

Thanks to Allah Azza wa Jalla for his love, blessings and enlightenment that allowed for the successful completion of this thesis as part of my Doctor of Philosophy (Material Engineering) at University Malaysia Perlis. I wish to express sincere gratitude to my supervisor, Prof. Dr. Mohd Noor Ahmad through whom that I have learned a lot and for his unfailing patience and guidance with regards to this doctoral research. I am also extremely thankful my co-supervisor Prof. Dr. Uda Hashim and Assoc. Prof. Dr. Yufridin Wahab for giving a lot of advice and encouragements for my academic and research efforts. Besides, I would like to thank Prof. Ali Yeon Md. Shakaff for his support, and sharing of his immense knowledge.

It would have been impossible for me to complete my doctoral without the help from Center of Excellent for Advanced Sensor Technology (CEASTech), Institute of Nanoelectronic Engineering (INEE), School of Materials Engineering, School of Microelectronic Engineering, School of Bioprocess Engineering, and School of Manufacturing Engineering staff who have continuously aided in the successful completion of this research.

I would also like to thank to all my postgraduate friends especially Iqmal Tahir, Nurul Farhanah, Nur Hazwani, Noorhidayah, Azalina, Nurhidayah Aziz, Siti Fatimah, Mohd Izhar, Mubaraq, Nur Zawatil Isqi, Zatul Iffah, Muhammad Kashif, Azman and Zaki.

Lastly, a very big thank you to my parents Zakaria Yaacob and Zainab Ahmad, my brothers Zazali, Zafandi, Zaesham and Zahafiz, my sisters Zarina and Zahera Adnin, my beloved wife Nor Hafizah Che Harun, my sons Abdullah and Abdurrahman, and my parents-in-law Che Harun Che Hasan and Noraini Yusoff for their support, love and constant encouragement the have bestowed upon me. Without their support, I would never have gotten so far.

## TABLE OF CONTENTS

<b>THESIS DECLARATION</b>	i
<b>ACKNOWLEDGEMENT</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF TABLES</b>	vii
<b>LIST OF FIGURES</b>	ix
<b>LIST OF ABBREVIATIONS</b>	xiii
<b>LIST OF SYMBOLS</b>	xv
<b>ABSTRAK</b>	xvi
<b>ABSTRACT</b>	xvii
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Overview	1
1.2 Problem statements	4
1.3 Objective of studies	5
1.4 Scope of works	6
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Introduction	8
2.2 Conducting polymers	8
2.3 Polyaniline (PANI)	12
2.3.1 Mechanism of PANI polymerization	14
2.4 Synthesis of nanostructured polyaniline	16
2.4.1 Interfacial polymerization	17
2.4.2 Rapid mixing polymerization	19

2.5 Chemiresistor sensors	22
2.5.1 Chemiresistor	22
2.5.2 Gas sensor	24
2.5.3 Conducting polymers (PANI) as chemiresistor sensor	27
2.5.4 Mechanism of detection	31

## CHAPTER 3 METHODOLOGY

3.1 Introduction	34
3.2 Materials, instrumentations and software	36
3.3 Synthesis of polyaniline (PANI) nanofibers	37
3.3.1 Interfacial polymerization method (IP)	38
3.3.2 Rapid mixing polymerization method (RP)	40
3.3.3 Effect of HCl concentration synthesized by RP	42
3.3.4 Effect of APS/ANI molar ratio synthesized by RP	43
3.4 Characterization of PANI nanofibers	44
3.4.1 Time of polymerization	44
3.4.2 Fourier transform infrared spectroscopy (FTIR) analysis	44
3.4.3 UV-Vis spectrometry analysis	44
3.4.4 Morphology analysis	45
3.4.5 Electrical conductivity measurement	45
3.5 Development of chemiresistor sensor	49
3.5.1 Fabrication of interdigitated electrodes (IDE)	49
3.5.2 Deposit of PANI nanofibers on IDE pattern	51
3.5.3 Fabrication of airtight gas chamber	52
3.5.4 Preparation of analyte (ammonia)	52

3.5.5 Experimental setup system for gas response	54
3.6 Characteristics of ammonia chemiresistor sensor	55
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>	
4.1 Introduction	56
4.2 Characterization of polyaniline (PANI) nanofibers	57
4.2.1 Effect of different synthesis methods on PANI nanofibers	57
4.2.2 Effect of HCl concentration on PANI nanofibers	63
4.2.3 Effect of APS/ANI molar ratio on PANI nanofibers	72
4.3 Detection of Ammonia	78
4.3.1 Effect of HCl concentration of chemiresistor sensor for ammonia	78
4.3.2 Effect of APS/ANI molar ratio of chemiresistor sensor for ammonia	82
4.4 Characteristics of Chemiresistor sensor for ammonia	84
4.4.1 Repeatability	84
4.4.2 Reproducibility	86
4.4.3 Sensitivity	89
4.4.4 Selectivity	91
4.4.5 Shelf life of chemiresistor sensor	94
<b>CHAPTER 5 CONCLUSION</b>	
5.1 Conclusions	98
5.2 Recommendations for future study	100
<b>REFERENCES</b>	102

**LIST OF PUBLICATIONS**

112

**APPENDIX A**

113

©This item is protected by original copyright

## LIST OF TABLES

NO.		PAGE
3.1	Injection of ammonia liquid corresponding to ammonia (ppm)	53
4.1	Polymerization time of PANI nanofibers obtained with different synthesis methods	59
4.2	FTIR spectra of PANI nanofibers obtained with different synthesis Methods	60
4.3	The electrical conductivity of of PANI nanofibers obtained with different synthesis methods	63
4.4	Polymerization time of PANI nanofibers obtained at different HCl concentrations	64
4.5	FTIR spectra of PANI nanofibers obtained with different HCl concentrations	66
4.6	UV-Vis spectra of the third absorption band of PANI nanofibers obtained with different HCl concentrations	69
4.7	The electrical conductivity of PANI nanofibers obtained with different HCl concentrations	71
4.8	Polymerization time of PANI nanofibers obtained with different APS/ANI molar ratios	73
4.9	FTIR spectra of PANI nanofibers obtained with different APS/ANI molar ratios	74
4.10	UV-Vis position of the third absorption band of PANI nanofibers obtained with different APS/ANI molar ratios	76
4.11	The electrical conductivity of PANI nanofibers with different APS/ANI molar ratios	77
4.12	Output resistance of chemiresistor sensor with different HCl concentrations, upon exposure to 355 ppm ammonia	80
4.13	Response time ( $t_1$ ), and recovery time ( $t_2$ ) of chemiresistor sensor with different HCl concentrations, upon exposure to 355 ppm ammonia	81
4.14	Output resistance of chemiresistor sensor with different APS/ANI molar ratios, upon exposure to 355 ppm ammonia	83



4.15	Response time ( $t_1$ ), and recovery time ( $t_2$ ) of chemiresistor sensor with different APS/ANI molar ratios, upon exposure to 355 ppm ammonia	84
4.16	Repeatability of the chemiresistor sensor, upon exposure to 355 ppm ammonia	86
4.17	Reproducibility of chemiresistor sensor upon exposure to 355 ppm Ammonia	88
4.18	Dynamic response of chemiresistor sensor, upon exposure 35 to 355 ppm ammonia	91
4.19	Selectivity of chemiresistor sensor, upon exposure to 355 ppm of ammonia, methanol, ethanol, and acetone analytes	93
4.20	Shelf life of chemiresistor sensor, upon exposure to 355 ppm ammonia	96

©This item is protected by original copyright

## LIST OF FIGURES

NO.		PAGE
2.1	Some common conducting polymers (Nguyen & Yoon, 2016)	9
2.2	Electrical conductivity of some metals, semiconductor and doped conducting polymers (MacDiarmid, 2002; Kaur et al., 2015)	11
2.3	Basic structures of PANI, (a) base structure, (b) leucoemeraldine, (c) pernigraniline, and (d) emeraldine base (Baraton, 2009)	14
2.4	Mechanism for the polymerization of aniline to PANI in the doped-ES state, where (A <sup>-</sup> ) represents a charge balancing counter-ion (Geniès et al., 1990)	15
2.5	Redox transitions in PANI are showed in the vertical reaction sequence: (a) pernigraniline (PB), (b) emeraldine base (EB), and (c) Leucoemeraldine (LB). The horizontal reaction reflects proton doping of EB to (d) emeraldine salt (ES), where (A <sup>-</sup> ) represents charge-balancing counter-ions (Tarver et al., 2009)	16
2.6	Interfacial polymerization methods for producing: (a) polyamide (Nylon) and (b) PANI nanofiber	18
2.7	SEM images of PANI nanofibers in different aqueous acidic solution: (a) HCl, (b) H <sub>2</sub> SO <sub>4</sub> , (c) HNO <sub>3</sub> , and (d) HClO <sub>4</sub> (Huang & Kaner, 2004a)	19
2.8	SEM images of PANI at (a) slowly-mixed reaction, and (b) rapidly-mixed reaction (Huang & Kaner, 2004b)	20
2.9	Schematic of PANI nanofibers synthesized in sequence from (a), (b) to (c) by rapid mixing polymerization	21
2.10	SEM images of PANI nanofiber at different HCl concentrations (a) 0.5 M and (b) 1.0 M (Rezaei et al., 2014)	22
2.11	Configuration of a chemiresistor (Shaik et al., 2016)	23
2.12	Schematic layout of a gas sensor	24
2.13	Variation of resistance versus time on the exposure of ammonia vapour (Liu et al., 2009)	28
2.14	Variation of resistance versus time of PANI nanofibers sensor on the exposure of ammonia vapour (Bandgar et al., 2015)	29

2.15	Changes in resistance versus time of the CSA-doped PA6/PANI composite nanofibers on the exposure of ammonia vapour (Pang et al., 2014)	30
2.16	Response of the CSA-doped PA6/PANI composite nanofibers (Pang et al., 2014)	30
2.17	PANI undergoes dedoping by deprotonation when expose to ammonia gas (Bai & Shi, 2007)	32
2.18	Reaction of nanocomposite of Pd/PANI toward methanol vapour (Athawale et al., 2006)	32
3.1	Overall flow chart of the research	35
3.2	Flow chart synthesis of PANI nanofibers	37
3.3	PANI nanofibers solution (green colour) after synthesized by interfacial polymerization method	38
3.4	Flowchart synthesis of PANI nanofibers by interfacial polymerization method	39
3.5	PANI nanofibers solution (green colour) after synthesized by rapid mixing polymerization method	40
3.6	Flow chart synthesis of PANI nanofibers by rapid mixing polymerization method	41
3.7	PANI nanofibers solution (green colour) after synthesized by rapid mixing polymerization method at different HCl concentrations: (a) 0.5 M, (b) 1.0 M, (c) 1.5 M, (d) 2.0 M, (e) 2.5 M, and (f) 3.0 M	42
3.8	PANI nanofibers solution (green colour) after synthesized by rapid mixing polymerization method at different APS/ANI molar ratio: (a) 1/4, (b) 1/1, and (c) 4/1	43
3.9	A set of tool steel die that has been used for compacting the PANI nanofibers samples	46
3.10	The flow of the compaction process	47
3.11	Four point probe method	48
3.12	Fabrication of interdigitated electrodes (IDE): (a) stainless steel mask plate, (b) IDE pattern on PET substrate, and (c) configuration of the IDE design	50
3.13	Dropping of PANI nanofiber solution on IDE pattern PET substrate by drop-cast technique	51

3.14	Snapshot of a chemiresistor sensor after deposited with nanofibers	51
3.15	An in-house built airtight test gas chamber	52
3.16	Experimental setup for chemiresistor sensor response	54
4.1	Photo showing the interfacial polymerization of PANI nanofibers at room temperature. The reaction times are (a) 15 s, (b) 60 s, (c) 240 s, (d) 300 s, (e) 390 s, (f) 480 s, and (g) 540 s. The top layer is aniline dissolved in the organic solvent (toluene); the bottom layer is an aqueous solution of 1.0 M HCl and APS	58
4.2	Photo showing the rapid mixing polymerization of PANI nanofibers at room temperature. The reaction times are (a) 15 s, (b) 60 s, (c) 180 s, (d) 240 s, (e) 300 s, (f) 420 s, and (g) 480 s. Both of aniline and APS dissolved in the aqueous solution of 1.0 M HCl	58
4.3	FTIR spectra of PANI nanofibers obtained with different synthesis methods	59
4.4	Chemical structures of PANI nanofibers doped with HCl	60
4.5	UV-Vis spectra of PANI nanofibers obtained with different synthesis methods	61
4.6	FESEM images of (a) interfacial polymerization, and (b) rapid maxing polymerization methods of PANI nanofibers synthesized at room temperature (100,000x)	62
4.7	FTIR spectra of PANI nanofibers obtained with different HCl concentrations	65
4.8	UV-Vis spectra of PANI nanofibers obtained with different HCl concentrations	67
4.9	SEM images of the PANI Nanofibers prepared with different HCl Concentrations: (a) 0.5 M, (b) 1.0 M, (c) 1.5 M, (d) 2.0 M, (e) 2.5 M, and (f) 3.0 M	70
4.10	FTIR spectra of PANI nanofibers obtained with different APS/ANI molar ratios	73
4.11	UV-Vis spectra of PANI nanofibers obtained with different APS/ANI molar ratios	75
4.12	SEM images of PANI nanofibers obtained with different APS/ANI molar ratios: (a) 1/1, and (b) 4/1	76
4.13	Effect of HCl concentration of chemiresistor sensor, upon exposure to 355 ppm ammonia at exposure time of 180 s	79

4.14	Effect of APS/ANI molar ratio of chemiresistor sensor upon exposure to 355 ppm ammonia at exposure time of 180 s	82
4.15	Repeatability of chemiresistor sensor, upon exposure to 355 ppm ammonia at exposure time of 180 s	85
4.16	Reproducibility of chemiresistor sensor, upon exposure to 355 ppm ammonia at exposure time of 180 s	87
4.17	Dynamic response of chemiresistor sensor, upon exposure to six different concentrations of ammonia at exposure time of 180 s	89
4.18	Sensitivity curve of chemiresistor sensor, upon exposure to six different concentrations of ammonia	90
4.19	Selectivity of chemiresistor sensor, upon exposure to 355 ppm ammonia at exposure time of 180 s	92
4.20	Suggested mechanism of the interaction of ammonia with PANI (ES)	94
4.21	Shelf life of chemiresistor sensor, upon exposure to 355 ppm ammonia at exposure time of 180 s until 30th days	95
4.22	Shelf life curve of chemiresistor sensor, upon exposure to 355 ppm ammonia until 30th days	96

## LIST OF ABBREVIATIONS

ACGIH	American Conference of Industrial Hygienists
ANI	Aniline
APS	Ammonium peroxydisulfate
CHEMFET	Chemical field effect transistor
CNT	Carbon nanotubes
CP	Conducting polymer
CSA	Camphorsulfonic acid
CV	Coefficient of variability
DBSA	Dodecylbenzenesulfonic acid
DMM	Digital multimeter
EB	Emeraldine base
ES	Emeraldine salt
FESEM	Field effect scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
ICP	Intrinsically conducting polymer
IDE	Interdigitated electrode
IP	Interfacial polymerization
IP-PANI	Polyaniline nanofiber synthesise through interfacial polymerization method
LB	Leucoemeraldine
MOS	Metal oxide semi-conductor
MW	Molecular weight
OSHA	Occupational Safety and Health Administration

PANI	Polyaniline
PB	Pernigraniline
Pd	Palladium
PEDOT	Poly (3,4-ethylene-dioxythiophene)
PEL	Permissible exposure limit
PET	Polyethylene terephthalate
ppb	Parts per billion
PPE	Poly (phenylene ethynylene)
ppm	Parts per million
PPV	Poly (phenyl vinlene)
PPY	Polypyrrole
PTH	Polythiophene
QCM	Quartz crystal microbalance
RP	Rapid mixing polymerization
RP-PANI	Polyaniline nanofiber synthesize through rapid mixing polymerization method
RSD	Relative standard deviation
SAW	Surface acoustic wave
SEM	Scanning electron microscopy
TLV-STEL	Threshold limit value - short-term exposure limit time weighted average
TLV-TWA	Threshold limit value - time weighted average
TWA	Time weighted average
UV-Vis	Ultraviolet-visible
VOC	Volatile organic compound
WHO	World Health Organization

## LIST OF SYMBOLS

$A^-$	Charge balancing counter-ion
$C_{\text{ppm}}$	Vapour concentration
$H^+$	Proton
$I$	Current
$I-V$	Current-voltage
$M$	Molar
$NH_3$	Ammonia
$NH_4^+$	Ammonium
$-NH-$	Amine
$-N=$	Imine
$PA6$	Nylon 6
$R_{\text{air}}$	Electrical resistance when exposed to air
$R_{\text{gas}}$	Electrical resistance when exposed to ammonia
$r-GO$	Reduced graphene oxide
$S \%$	Sensitivity of sensor
$S \cdot \text{cm}^{-1}$	Siemens per centimeter
$t_1$	Response time
$t_2$	Recovery time
$\sigma$	Conductivity of the pellet (in S/cm)



## **Pembangunan Sensor Perintang-Kimia berasaskan Serat-Nano Polianilina (PANI) untuk Pengesanan Amonia**

### **ABSTRAK**

Polimer pengalir berstruktur nano telah menerima banyak perhatian disebabkan oleh sifat yang unik dan kebolehan aplikasinya dalam bahan nano dan teknologi nano. Antara polimer pengalir yang ada, nanostruktur polianilina (PANI) telah dikaji secara meluas disebabkan ia mudah disediakan, kekonduksian yang baik, kestabilan persekitaran, struktur permukaan yang luas dan sifat redoks berbalik yang tinggi. Dalam kajian ini, pembangunan sensor perintang-kimia berasaskan serat-nano PANI untuk pengesanan ammonia telah dikaji. Kajian ini dibahagi kepada dua bahagian iaitu penyediaan serat-nano polianilina dalam pelbagai parameter dan pembangunan sensor perintang-kimia untuk mengesan gas ammonia. Masa pemolimeran, struktur kimia, morfologi permukaan dan sifat-sifat elektrik bagi serat-nano polianilina telah dicirikan dengan menggunakan masing-masing jam digital, FTIR, UV-Vis, FESEM, SEM dan pengesanan 4-titik. Melalui penyediaan PANI oleh antara-muka (IP-PANI) dan pemolimeran pencampuran pantas (RP-PANI), tiada perubahan ketara yang dapat diperhatikan kecuali masa pemolimeran. Masa pemolimeran bagi IP-PANI dan RP-PANI adalah masing-masing pada 390 dan 300 saat. Analisis FTIR adalah selaras dengan ciri-ciri PANI dengan kewujudan puncak-puncaknya pada 3286, 1580, 1490, 1218, 1146 dan 620  $\text{cm}^{-1}$ , berkaitan dengan masing-masing fungsi kumpulan N-H, C=C, C-N, satah-dalam C-H, dan satah-luar C-H. Analisis UV-Vis bagi serat-nano PANI menunjukkan bahawa tiga peralihan jalur telah muncul iaitu pada 340, 420, dan 814 nm yang merujuk kepada  $\pi$ - $\pi^*$ , polaron- $\pi^*$ , dan jalur polaron setempat, manakala purata saiz diameter serat-nano untuk kedua-dua kaedah adalah  $\sim 70$  nm. Kesan kepekatan asid hidroklorik (HCl) dan nisbah molar ammonium persulfat/anilina (APS/ANI) pada serat-nano PANI yang disintesis melalui kaedah pencampuran pemolimeran pantas turut dikaji. Didapati, masa pemolimeran serat-nano PANI telah menurun dengan peningkatan kepekatan HCl dan nisbah molar APS/ANI masing-masing daripada 0.5 M kepada 3.0 M dan daripada 1/4 kepada 4/1. Analisis FTIR dan UV-Vis menunjukkan jalur serapan serat-nano PANI telah beralih kepada frekuensi yang lebih rendah dan lebih tinggi disebabkan oleh perubahan kekonduksian elektrik. Saiz diameter PANI telah meningkat daripada  $\sim 60$  kepada  $\sim 190$  nm dengan peningkatan kepekatan HCl disebabkan peningkatan gumpalan serat-nano manakala tiada perubahan diperhatikan dengan nisbah molar APS/ANI. Untuk mengesan gas ammonia, sistem sensor telah dibangunkan terdiri daripada sensor perintang-kimia, kebuk gas dan pengukuran respon gas. Adalah didapati bahawa 0.5 M HCl telah menghasilkan sensor yang optimum dengan respon yang terpanjang disebabkan saiz diameter serat-nano yang sangat kecil. Kebolehulangan yang baik diperhatikan dengan respon sensor yang tetap manakala kebolehasil menunjukkan perubahan yang kecil disebabkan oleh teknik pengendapan serat-nano PANI. Analisis kepekaan membuktikan bahawa rintangan sensor telah berkurangan dengan kepekatan gas ammonia manakala ujikaji kepilihan dan jangka hayat sensor yang baik telah diperolehi.

## Development of a Chemiresistor Sensor based on Polyaniline (PANI) Nanofibers for Detection of Ammonia

### ABSTRACT

Nanostructured conducting polymers have received great attention due to their unique properties and promising applications in nanomaterials and nanotechnology. Among them, nanostructured polyaniline (PANI) has been extensively studied due to its ease of synthesis, excellent conductivity, environmental stability, large surface area, and highly reversible redox properties. This study reports a development of a chemiresistor sensor based on PANI nanofibers for ammonia detection. The studies are divided into two parts, which are the preparation of PANI nanofibers at various parameters and the development of chemiresistor sensor for the detection of ammonia. The polymerization time, chemical structure, surface morphology, and electrical properties of the synthesized PANI nanofibers were characterized using digital watch, FTIR, UV-Vis, FESEM, SEM, and 4-point probe, respectively. The preparation of PANI through interfacial (IP-PANI) and rapid mixing polymerization (RP-PANI) give not significant difference except the polymerization time which was 390 and 300s, respectively. FTIR spectra analysis was corresponded to well-doped PANI with the existence of peaks at 3286, 1580, 1490, 1218, 1146 and 620  $\text{cm}^{-1}$ , respectively, which are related to N-H, C=C, C-N, in-plane C-H, and out-plane C-H functional group. UV-Vis spectra of the PANI nanofibers showed that three band transitions were appeared at 340, 420, and 814 nm, respectively, which referred to  $\pi$ - $\pi^*$ , polaron- $\pi^*$ , and localized polaron band while the average diameter size of PANI nanofibers for both methods was  $\sim 70\text{nm}$ . The effect of hydrochloric acid (HCl) concentration and ammonium persulfate/aniline (APS/ANI) molar ratio on PANI nanofibers synthesized by rapid mixing polymerization were also studied. It was found that, the polymerization time of PANI nanofibers was decreased with increasing HCl concentration and APS/ANI molar ratio from 0.5 M to 3.0 M and 1/4 to 4/1, respectively. FTIR and UV-Vis spectra showed the absorption bands of PANI nanofibers were shifted to lower and higher frequencies region due to changing of electrical conductivity. The diameter size of PANI was increased from  $\sim 60$  to 190 nm with the increasing of HCl concentration due to agglomeration of nanofibers, while no effect was observed with APS/ANI molar ratio. For the detection of ammonia, a sensor system was developed consists of a chemiresistor sensor, airtight test gas chamber and sensor response measurement. It was recorded that the 0.5 M HCl has resulted an optimum sensor with the fastest response time due to smallest diameter size. Good repeatability was observed by constant response while reproducibility exhibited a small change of response that may result from the deposition technique. Sensitivity analysis proved that the resistance of the sensor was decreasing with the concentration of ammonia. Good selectivity and a long shelf life of the sensor were also observed.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Overview

Ammonia is an inorganic compound containing the element nitrogen and hydrogen with the formula  $\text{NH}_3$ . It is a colourless gas with a characteristic highly flavored smell and is lighter than air. This smell is well-known among people because it is widely used in salts, household, and industrial cleaners. Ammonia can be dissolved in water to form liquid, aqueous or solution of ammonia. As we know, in water, ammonia changes to ammonium ions,  $\text{NH}_4^+$ , but when it exposed to surrounding air, this liquid immediately changes into a gas or vapour. Ammonia is an essential compound for sustaining life such as plant and animal as well as human life. Commonly, ammonia comes from water, soil, and air. It is also an important source of nitrogen for plants and animals. Naturally, ammonia exists in the air at levels between 1 - 5 ppb (parts per billion) and commonly found in rainwater. It is also found in rivers and bays at levels less than 6 ppm (parts per million). While in the soil, ammonia contains at levels between 1 - 5 ppm. Most of the ammonia in the natural world comes from the natural breakdown of manure, animals and dead plants. Basically at this level, ammonia is not dangerous to human life.

Today, ammonia is one of the most commonly produced chemicals in the world due to its widespread application. Globally, nearly 90 % of ammonia production is used

as fertilizers in plantation or soil (Jewell, 2016). Ammonia is also used in water purification, as a removing agent in microbial contamination, cotton treatment, and production of plastics, dyes, fabrics, pesticides, cosmetics, pharmaceuticals, paper and petrochemicals. In addition, it is utilized in large scale industrial manufacturing of coolant, refrigeration, and power plant (Kannan & Saraswathi, 2014). An extensive use of ammonia will facilitate its exposure to humans either consciously or otherwise.

Due to its many uses and widespread presence surroundings us, questions often arise about its impact on human health. An exposure to high concentrations of ammonia is very dangerous. It can cause burning of the nose, skin, throat and respiratory tract. These burns might be serious enough to cause permanent blindness, lung disease, or death. The American Conference of Industrial Hygienists (ACGIH) recommends that the exposure limit value of ammonia is 25 ppm at threshold limit value - time weighted average (TLV-TWA) (the average exposure over a 8 hour) and 35 ppm on a threshold limit value - short-term exposure limit time weighted average (TLV-STEL) (the average exposure over a 15 minutes) to prevent any throat, eyes and nose irritation. According to the Occupational Safety and Health Administration (OSHA), the permissible exposure limit (PEL) as a time weighted average (TWA), the least amount of ammonia which is found to be irritating to the eyes, nose and throat of the most sensitive individuals is 50 ppm. While, the World Health Organization (WHO) state that, continuous exposure to 25 ppm of ammonia in the air does not result in a significant increase in blood levels of ammonia in the body (Ryer-Powder, 1991).

A detection and analysis system should be developed to detect ammonia due its high levels of toxicity and adverse effects on humans. A gas sensor is an effective tool to detect toxic substances and has a great potential for development. Gas sensor can be

defined as a small device in which, when exposed to a gaseous elements, it will change their physical or chemical properties that can be measured (Joshi & Singh, 2010). Actually gas sensors, chemiresistor sensor, chemical gas sensors, or biosensors can be classified depending on its operating principle for and each type of sensor has different characteristics. Gas sensors usually utilize an electrical or optical response by adsorption of gas molecules on surface of sensing material. This makes them commonly used for industrial, commercial and residential applications.

Nanostructured conducting polymer (CP) based gas sensors have received many interest in recent years because of their sensing ability, high sensitivities, short response times, easily fabrication and operation at room temperature (Bai et al., 2007). Trojanowicz (2003) described CP as polymers with spatially extended  $\pi$ -bonding systems obtained by electrochemical polymerization or chemical oxidation of their monomer. The simple characteristic of CP materials is the existence of a conjugated  $\pi$ -electron system which extends on the polymer chain. Wilson & Baietto (2009) said that the operation of CP gas sensors is based on an alteration of its electrical resistance response caused by chemical reaction or adsorption of gases onto the sensor surface and it's commonly known as a chemiresistor gas sensor. Chemiresistor is a simple, cheap and small gas sensor. It consist of a substrate, such as silicon, glossy paper (Arena et al., 2010) or polyethylene terephthalate (PET) (Su et al., 2009; Surwade et al., 2009; Khan et al., 2014), a pair of gold-plated electrodes (interdigitated electrode, IDE or sometimes called as chemiresistor) (Wang et al., 2009) and a coating of conducting organic polymer as the sensing material (sensing elements or active sensing layers) (Jiménez-Cadena et al., 2007; Peres et al., 2012).

There are several CP used as the sensing materials of gas sensor such as Polyaniline (PANI), Polypyrrole (PPY), Polythiophene (PTH), Poly(3,4-ethylene-dioxythiophene) (PEDOT) and Poly(phenyl vinylene) (PPV) (Bai & Shi, 2007; Li et al., 2013b; Kaushik et al., 2015). Among the available CP, PANI is the most commonly used in gas sensors because of its good stability and outstanding properties compared to other CP (Bhadra et al., 2009). It is one of the “doped polymers”, in which its electrical conductivity results from partial oxidation or reduction process. By now, various methods have been used to synthesis PANI, especially in nanostructures form, including hard template such as porous membrane or zeolite, electrochemical polymerization, electrospinning, self-assembly (soft template) such as surfactant, organic dopant or polyelectrolytes, and free template polymerization such as interfacial and rapid-mixed reaction. Among the variety of methods, interfacial and rapid mixing polymerizations are the simple and effective chemical method to synthesize PANI in a large scale. Therefore, in this research, both of these methods were used to synthesize PANI into nanofiber form and their physical and chemical properties on different synthesis parameters were studied to get the best performance towards gas sensing application.

## **1.2 Problem Statements**

Ammonia is one of the most commonly produced chemical in the world due to widespread applications such as industrial process, fertilizer, food technology, clinical diagnosis, farms, and household cleaning agents (Du et al., 2011; Kannan & Saraswathi, 2014). An exposure to high concentration of ammonia could be extremely dangerous to human health and life. Therefore, detection should be developing to detect its presents.

Currently, most available gas sensors are based on metal oxide semiconductor (MOS) and they usually operate at higher temperature and thus very costly to allow best performance. Besides, its production is expensive. To overcome this issue, chemiresistor sensor based on nanostructured PANI has been developed. The main advantage of this type of sensor is that it can be operated at room temperature. It is a simple and cost effective gas sensor technology assembled with nanostructured PANI that gives a huge impact in sensing technology and performance.

### **1.3 Objective of Studies**

The aim of this research is to synthesize and characterize PANI nanofibers using free template route for detection of ammonia. The research is accomplished using the following specific objectives.

- i. To compare the physical and chemical properties of IP-PANI and RP-PANI.
- ii. To determine the effect of HCl concentration and APS/ANI molar ratio on the physical and chemical properties of PANI nanofibers.
- iii. To investigate the effect of HCl concentration and APS/ANI molar ratio of PANI nanofibers on the sensing performance of the chemiresistor sensor.
- iv. To investigate sensing properties PANI nanofibers towards ammonia using chemiresistor sensor.

## 1.4 Scope of Works

This research was focused on the study of synthesis and characterization of PANI nanofibers for detection of ammonia. The study can be divided into two parts, which are the synthesis of PANI nanofibers at various parameters and the development of chemiresistor sensor for the detection of ammonia. In the first part, PANI nanofibers are synthesized by chemical oxidative polymerization corresponding monomers (aniline) as sensing material. Hydrochloric acid (HCl) is used as a dopant material, and ammonium persulfate (APS) as an oxidant material. Three parameters have been used in the preparation of PANI nanofibers that are different synthesis method (interfacial and rapid-mixed reaction), effect of HCl concentration, and effect of APS/ANI molar ratio. All the reactions were carried out at room temperature. While in the second part, chemiresistor sensor was fabricated by thermal vacuum evaporation. Aluminum (Al) was used as an electrode material. The sensing substrates upon which the PANI nanofibers films were deposited consisted of Al electrodes 0.30 mm wide with 0.50 mm gap each 14 mm long on a polyethylene terephthalate (PET) substrate. Then, PANI nanofibers was deposited by drop-cast technique onto the Al tracks of the sensing substrate.

The polymerization time of PANI nanofibers was recorded by digital watch, while its electrical conductivity was measured by four-point probe. Ultraviolet-visible (UV-Vis) spectra analysis of the synthesized PANI nanofibers was analyzed by UV-Vis spectroscopy. Field Effect Scanning Electron Microscopy (FESEM) and Scanning Electron Microscopy (SEM) were used to investigate the morphology of PANI nanofibers thin film. Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out for identifying chemicals compounds that are either organic or inorganic.