



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

by

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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_{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_{air}	Electrical resistance when exposed to air
R_{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
σ	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 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 π - π^* , polaron- π^* , dan jalur polaron setempat, manakala purata saiz diameter serat-nano untuk kedua-dua kaedah adalah ~ 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 ~ 60 kepada ~ 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 kepilahan 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 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 π - π^* , polaron- π^* , 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 ~ 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 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, 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 π -bonding systems obtained by electrochemical polymerization or chemical oxidation of their monomer. The simple characteristic of CP materials is the existence of a conjugated π -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.

Chemiresistor sensor for ammonia was analyzed to determine the effect of HCl concentration and APS/ANI molar ratio, response time, recovery time, repeatability, reproducibility, sensitivity, selectivity, and shelf life (lifetime) of sensor as gas sensor characteristics.

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