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FEASIBILITY STUDIES OF POLYANILINE NANOSTRUCTURES COATED ON TAPERED OPTICAL FIBER FOR AMMONIA SENSING

SITI AZLIDA BINTI IBRAHIM @ GHAZALI

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By

SITI AZLIDA BINTI IBRAHIM @ GHAZALI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Chairman : Mohd. Adzir Mahdi, PhD
Faculty : Engineering

Polyaniline (PANI) has been used for ammonia (NH_3) sensing for several decades, mostly in electrical based sensors due to its variation in conductivity during the interaction. Optical sensors are known to have advantages in certain aspects as compared to electrical sensors, but this area of research has not been fully explored. Therefore, this research project aims to explore optical based NH_3 sensor with the incorporation of PANI nanostructure. Tapered multimode fiber (MMF) was chosen as the transducing platform for the sensor because of ease in fabrication, high sensitivity and its suitability for remote sensing applications. The sensitivity of tapered fiber based sensors can be improved by reducing the waist diameter. The influence of PANI nanostructure morphology, thickness and dopants on the sensing performance was also studied in this thesis.

In this project, PANI nanostructures were synthesized and deposited on tapered MMF using two methods. The first method was in-situ deposition method, where poly(methyl vinyl ether-*alt*-maleic acid)(PMVEA)-doped PANI (PANI-PMVEA) nanogranules and nanofibers were grown on tapered MMF surface during polymerization process. For the second method, camphorsulfonic acid (CSA)-doped PANI (PANI-CSA) nanofibers were spray coated on the tapered MMF. Three processes were involved in the preparation of PANI-CSA, namely the synthesis of hydrochloric acid-doped PANI (PANI-HCl), the dedoping of PANI-HCl to obtain emeraldine base PANI (PANI-EB) powder and the redoping of PANI-EB with CSA to obtain PANI-CSA nanostructures. The thickness and morphology of PANI nanostructures were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The formation of PANI nanostructures in emeraldine salt form was confirmed from molecular vibrational analysis using Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). The response of the sensors towards NH_3 at different concentration was measured using cumulative absorbance change within the wavelength range of 500 – 800 nm. The sensing

performance was evaluated in terms of response time, recovery time, sensitivity and repeatability.

PANI-PMVEA coating thickness and morphology was varied by varying the deposition duration and PMVEA/aniline ratio. The highest sensitivity was achieved by the most uniformly-distributed nanogranules PANI-PMVEA coating with thickness of approximately 913 nm. The achieved sensitivity, response and recovery time was 2.19/vol%, 2.82 minutes and 11.52 minutes, respectively. PANI-CSA nanofibers were coated on tapered MMF with different waist diameters. The highest sensitivity of 2.44/vol% was attained by the smallest diameter (20 μm) sensor with PANI-CSA coating of approximately 700 – 850 nm. The response and recovery time are 1.73 minutes and 12 minutes, respectively. The sensor using PANI-CSA nanofibers have higher sensitivity and faster response than the sensor using PANI-PMVEA nanostructures at 1% NH_3.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KAJIAN KELAYAKAN POLYANILINE BERSTRUKTUR NANO DI SALUT PADA FIBER OPTIK TIRUS SEBAGAI PENDERIA AMMONIA

Oleh

SITI AZLIDA BINTI IBRAHIM @ GHAZALI

Januari 2017

Pengerusi : Mohd. Adzir Mahdi, PhD
Fakulti : Kejuruteraan

Polianilina (PANI) telah digunakan untuk penderiaan ammonia (NH_3) selama beberapa dekad, kebanyakannya dalam penderia berasaskan elektrik disebabkan oleh konduktivitinya yang berubah-ubah ketika bertindak balas dengan gas NH_3. Penderia optik diketahui mempunyai kelebihan dalam aspek tertentu berbanding dengan penderia elektrik tetapi masih belum diterokai secara meluas. Oleh itu, projek penyelidikan ini bertujuan untuk meneroka penderia NH_3 berasaskan optik dengan menggabungkan nano struktur PANI. Gentian berbilang mod (MMF) tirus dipilih sebagai platform transduksi untuk penderia kerana mudah direka, kepekaan yang tinggi dan sesuai untuk penggunaan penderiaan jauh. Kepekaan penderia berasaskan gentian tirus boleh ditingkatkan dengan mengecilkan diameter tengah. Pengaruh morfologi, ketebalan dan bahan dop nano struktur PANI terhadap prestasi penderiaan juga dikaji dalam tesis ini.

Dalam projek ini, nano struktur disintesiskan dan terendap pada MMF tirus menggunakan dua kaedah. Kaedah pertama ialah kaedah pengendapan in-situ iaitu poli(metil vinil eter-alt-asid maleik) (PMVEA) terdop granul nano dan gentian nano PANI (PANI-PMVEA) terhasil pada permukaan tirus MMF semasa proses pempolimeran. Bagi kaedah kedua, asid kamforsulfonik (CSA) terdop gentian nano PANI (PANI-CSA) disembur menyaluti MMF tirus. Tiga proses yang terlibat dalam penyediaan PANI-CSA, iaitu sintesis asid hidroklorik terdop PANI (PANI-HCl), pengedopan PANI-HCl untuk mendapatkan serbuk PANI-EB dan pengedopan semula PANI-EB dengan CSA untuk mendapatkan struktur nano PANI-CSA. Ketebalan dan morfologi nano struktur PANI dicirikan menggunakan imbasan mikroskop elektron dan mikroskop daya atom. Pembentukan struktur nano PANI dalam bentuk garam yang berwarna hijau zamrud disahkan melalui analisis getaran molekul menggunakan Spektroskopi Raman dan Spektroskopi Inframerah Transformasi Fourier. Tindak balas penderia terhadap NH_3 pada kepekatan berbeza diukur menggunakan perubahan

keserapan kumulatif dalam julat jarak gelombang 500-800 nm. Prestasi penderiaan dinilai dari segi masa tindak balas, masa pemulihan, kepekaan dan keterulangan.

Ketebalan dan morfologi salutan PANI-PMVEA dipelbagaikan dengan mempelbagaikan masa pengendapan dan nisbah PMVEA\anilina. Kepekaan tertinggi dicapai dengan taburan granul nano salutan PANI-PMVEA paling sekata dengan ketebalan kira-kira 913 nm. Kepekaan, tindak balas dan masa pemulihan yang dicapai adalah masing-masing 2.19/vol%, 2.82 minit dan 11.52 minit. Gentian nano PANI-CSA disalutkan pada MMF tirus dengan diameter tengah yang berbeza. Kepekaan tertinggi ialah 2.44/vol% dicapai dengan penderia diameter terkecil (20 μm) dengan salutan PANI-CSA kira-kira 700 – 850 nm. Masa tindak balas dan pemulihan adalah masing-masing 1.73 minit dan 12 minit. Penderia yang menggunakan gentian nano PANI-CSA mempunyai kepekaan lebih tinggi dan tindak balas lebih cepat berbanding dengan penderia yang menggunakan nano struktur PANI-MVEA pada 1% NH_3.

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I certify that a Thesis Examination Committee has met on 31 January 2017 to conduct the final examination of Siti Azlida binti Ibrahim @ Ghazali on her thesis entitled "Feasibility Studies of Polyaniline Nanostructures Coated on Tapered Optical Fiber for Ammonia Sensing" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Y.M. Raja Syamsul Azmir bin Raja Abdullah, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Ahmad Shukri bin Muhammad Noor, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Mohd Nizar bin Hamidon, PhD
Associate Professor
Institute of Advance Technology
Universiti Putra Malaysia
(Internal Examiner)

Yongxiang Li, PhD
Professor
Royal Melbourne Institute of Technology University
Australia
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 April 2017

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mohd Adzir Mahdi, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Mohd Hanif Yaacob, PhD
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Norizah Abdul Rahman, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Muhammad Hafiz Abu Bakar, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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I hereby confirm that:

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Name and Matric No.: Siti Azlida binti Ibrahim @ Ghazali, GS33902

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This is to confirm that:

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Signature: ______________________________
Name of Chairman of Supervisory Committee: Prof. Dr. Mohd Adzir Mahdi

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Mohd. Hanif Yaacob

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Norizah Abdul Rahman

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Muhammad Hafiz Abu Bakar

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
APS	Ammonium persulfate
Au	Gold
BTB	Bromothymol blue
BTC	benzene-1,3,5-tricarboxylate
BTEX	Benzene, toluene, ethylbenzene, and xylene
CSA	Camphorsulfonic acid
CH_4	Methane
CO	Carbon monoxide
CPR	chlorophenol red
DBSA	Dodecylbenzenesulfonate
DiOHP	bis(2-ethylhexyl) hydrogen phosphate
EB	Emeraldine base
ES	Emeraldine salt
FBG	Fiber Bragg Grating
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
FTO	Fluorine-doped tin oxide
GO	Graphene oxide
He-Ne	Helium-neon
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HF	Hydrofluoric acid
Hydrazine	N_2H_4
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
IR	Infrared
ITO	Indium tin oxide
I_2	Iodine
LEB	Leucoemeraldine base
Mid-IR	Mid-Infrared
MMF	Multimode Fiber
NH_3	Ammonia

NH_4Cl	Ammonium chloride
NIR	Near Infra-red
NO_x	Nitric oxides
O_3	Ozone
PANI	Polyaniline
PANI-CSA	Camphorsulfonic acid-doped polyaniline
PANI-EB	Emeraldine base polyaniline
PANI-ES	Emeraldine salt polyaniline
PANI-HCl	Hydrochloric acid-doped polyaniline
PANI-PMVEA	Poly(methyl vinyl ether-*alt*-maleic acid)-doped polyaniline
PEB	Pernigraniline base
PMMA	polymethyl methacrylate
PMVEA	Poly(methyl vinyl ether-*alt*-maleic acid)
PA6	polyamide 6
PPy	Polypyrrole
PTh	Polythiophene
P4PV	Poly(4-vinylpyridine)
SMF	Single mode fiber
SnO_2	Tin oxide
SO_2	Sulfur dioxide
SPR	Surface plasmon resonance
TiO_2	Titanium dioxide
UV-Vis	Ultraviolet-visible
VOC	Volatile organic compound
WO_3	Tungsten trioxide

CHAPTER 1

INTRODUCTION

1.1 Overview

Silica optical fiber is well-known as a medium for data transmission in the telecommunication industry, which enables high speed data communications. In the past three decades, optical fiber has been studied; not only for communication but also for many other applications. One of the most interesting areas is for sensing applications. Even though electrical-based sensor is a well-established technology, there are some limitations that these electrical sensors face, which can be overcomed by using optical fiber sensors. Electrical sensors are not suitable to be used in harsh environments such as in high voltage machinery or in chemical interaction medium. Optical fiber can stand those harsh conditions because it is a dielectric medium that does not conduct electrical signal. It is immunes to electromagnetic interference or any electrical signal disturbance and it can stands high temperature up to 1200ºC before it start to soften [1]. In addition, the fiber is inexpensive, small size and not susceptible to corrosion.

Fiber optic sensors can be designed either to replace existing sensors or to be applied in new applications. In order for optical fiber sensors to be able to replace conventional sensors, they have to show a significant improvement in terms of performance, accuracy, reliability, safety and cost. Optical fiber gyroscopes is one of the important example of a sensor that has been successfully replaced the conventional sensor. This sensor are used in automobile navigation system, inertial measurement system for aircraft, and backup guidance system for Boeing 777 [2]. Applications of fiber optic sensors are very broad. It ranges from supporting process control in manufacturing system, medical applications, building and structures monitoring system, remote monitoring in harsh environment, natural hazard emergency response system, marine system monitoring, oil exploration and many more that are impossible to be covered here [3]. The number of applications keep increasing because of the rapid research and development in this area, and decreasing in the cost factor. The broad range of applications is also due to the various configurations and parameters that can be measured including pressure, acoustic waves, vibration, position, strain, liquid level, flow, velocity, acceleration, rotation rate, temperature, electrical current, magnetic field, electromagnetic field, chemical process, and the surrounding refractive index [4].

The sensors can be classified based on the working principle such as interferometric sensor. This class of sensor obtained the information from the interference between two optical signals. Well-known sensors under this category are Mach-Zehnder and Michelsen interferometer [2]. Besides that, fiber sensor can be designed based on microbending [5], grating [6], or evanescent wave [7][8]. Evanescent wave sensor can be fabricated by removing some part of the cladding or by tapering the conventional optical fiber. Recently, research on sensors based on the tapered optical fiber has attracted great attention due to various advantages in terms of compactness, robustness, strong evanescent field, and simple fabrication method. Tapered optical fiber has been studied to measure physical parameters such as temperature [9], humidity [10], strain [11], refractive index [12], to detect chemicals species [13] and also for biosensors [14]. Great potentials of tapered fiber sensors are now recognized by the research community.

Detection of chemical species using fiber sensors has been studied since 1970s. There are two main approaches to sense chemical using fiber sensor [15]. One of the approaches is by measuring the intrinsic optical properties of the analyte such as its refractive index, emission or absorption. The other one is done by monitoring the change in optical properties of the immobilized indicator, or sensing layer that is deposited on the fiber. The second approach usually incorporates some materials as sensing layer that can react with the target analyte. Materials for sensing layer are typically a material that has the switching capability such as conducting polymers (organic), semiconductor metal oxides (inorganic), and composite materials.

Conducting polymer is an organic material that has semiconductor or metal-like conductivity. Its synthesis method and processing is easier than metals, making it very attractive as sensing layer. It has served as sensing layer in electronic gas sensors since 1980s. The sensors were reported to have high sensitivities, short response time, and the most attractive feature is good response at room temperature [16]. Conducting polymers that have been investigated as sensing layer are polyaniline (PANI), polypyrrole (PPy), and polythiophine (PTh). Among these polymers, PANI has been widely studied because of its simple synthesis, low cost, high conductivity and high environmental stability [17]. It has been used to sense nitrogen dioxide (NO_2), hydrogen sulphide (H_2S), sulfur dioxide (SO_2), and most widely for ammonia (NH_3). Recent development on the nanostructure PANI has increase the interest to incorporate PANI as sensing layer, since nanostructure materials have shown much higher sensitivity compared to bulk material.

Applying optical fiber sensors for gas sensing applications has open up new possibilities of in-situ monitoring on various types of gases at remote or hard-to-reach areas. Real-time and continuous monitoring of certain gas species is in huge demand in process control, automotive, medical, agricultural and many more. Combining the advantages of optical fiber sensors with sensitive nanomaterials for gas sensing application is an interesting research direction to be explored.

1.2 Problem Statement

NH_3 is a natural gas that exists in our atmosphere. The main sources include decomposition of manure in agricultural and wildlife, chemical plants (fertilizer & refrigerator manufacturing industries), natural bacterial nitrification activities, and motor vehicles. In industries that use pure NH_3 such as fertilizer and refrigerator industries, leakage in the system may lead to life threatening situations. Exposure to high NH_3 concentrations is hazardous to human health; at concentration of 500 ppm, the person exposed will experience breathing difficulties, and irritation to the nose, eyes and throats. At concentration higher than 1000 ppm can cause pulmonary oedema, long term lung disorder and can be fatal. Exposure to extremely high concentration (5000 – 10,000 ppm) is deadly within 5 – 10 minutes [18]. More worrying, the gas is flammable at 50ºC at very high concentration (150,000 ppm) [19]. In history, one of the worst disasters related to NH_3 happened in April 1947, when a ship that carried solid fertilizers exploded while it was docking in Texas City [20] The incident had damaged more than 1,500 buildings and killed almost 600 people. Therefore, it is extremely important to develop an NH_3 gas monitoring system with good sensors to avoid such safety hazards.

Research on electrical-based NH_3 sensors employing PANI is well established. The sensing mechanism is based on measuring changes in conductance (conductometry) or resistance (chemresistors) as PANI chemically reacts towards NH_3. However, as mentioned earlier, electrical-based sensors are not suitable to be deployed in certain environment especially when there is risk of explosion. PANI has also been used in optical-based sensors by measuring changes in light absorbance, reflectance or transmittance. The sensors were realized by depositing thin PANI film on waveguides [21], glass substrate [22][23][24], and optical fibers [25][26][27]. The use of waveguide as the transducing platform in [21] requires the use of optical bench setup, which is quite bulky and sensitive to misalignment problem. The technique which uses glass substrate in [22] and [24] is more suitable for remote monitoring application because it is less bulky than the waveguide bench setup. However, misalignment of the two fibers that carry light to and from the sensing glass surface is a big challenge that needs to be addressed. The use of optical fibers as the transducing platform overcome the misalignment problem, and enables the sensor to be used for remote monitoring applications.

Evanescent-based fiber sensor is very attractive due to its simple and cheap fabrication methods. It can be realized using side-polished, D-shaped, removed-clad or tapered fibers [28]. Tapered fiber was shown to be more sensitive than side-polished and D-shape fiber [29]. This is due to the presence of evanescent wave surrounding the taper waist region, while D-shape or side polished fiber only has evanescent at one side of the fiber. Usually, to fabricate removed-clad fiber, the cladding of silica optical fibers were removed using chemical etching method [30]. The major drawback with chemical etching method is that it is difficult to control; hence cause low reproducibility. With the advanced in fiber tapering technology, a more reproducible and controllable process to produce evanescent fiber sensors is realized. Tapering does not involve the removal of the fiber cladding, but it reduces the fiber diameter by heating while pulling the fiber. Since the transition between the original fiber and the tapered fiber waist is smooth, it is less fragile than remove-clad fiber. Due to various advantages of tapered fiber compared to other types of evanescent fiber, it was chosen to be used in this thesis. To the best of author's knowledge, there is no work reported on NH_3 sensor developed by using PANI on tapered optical fiber. Therefore, in this thesis, a new NH_3 sensor deploying PANI as sensitive layer, coated on tapered MMF was developed.

Currently, research on gas sensors using nanostructure materials is a hot topic due to the impressive sensitivity improvement. High surface to volume ratio increases the adsorption and fusion rate of gas molecules into the nanostructures, which leads to faster response and higher sensitivity. Deployment of PANI nanostructures (nanogranules, nanofibers, nanotubes, etc) in electrical-based sensors has been widely studied [31] [32], [33]. On the other hand, study on optical sensor characteristics that employ PANI nanostructure is still at the infancy stage. Only few optical sensing research works are found in literature that deposited PANI nanostructure on glass substrate and observed the absorbance response towards NH_3 [34][23]. Since the sensor in [34] used the most similar measurement setup and unit, it can be used as the benchmark for this work. Their sensor has achieved the sensitivity of 0.1018/vol%. From the author's thorough literature survey, there is no work reported so far regarding the study on the NH_3 optical fiber sensor by employing PANI nanostructures as sensitive sensing layer.

Factors that influence the PANI sensing performance includes its morphology and type of dopants. For tapered fiber sensor, the tapered fiber dimension such as its waist diameter determines the penetration depth and the strength of evanescent field surrounding it; hence influence the sensor's sensitivity. In addition, PANI deposition methods will determine its morphology and thickness, which also affects the sensor's performance. In this thesis, detail investigation on the influence of these parameters on the sensor's absorbance response is carried out systematically.

1.3 Objectives

The aim of this thesis is to develop optical fiber NH_3 sensors by integrating PANI nanostructures with tapered optical fibers. The specific objectives are listed as follows:

- To synthesis and deposit PANI nanostructure on tapered optical fiber.
- To characterize the PANI nanostructure material properties and analyse its relation with the sensing performance in terms of sensitivity, response time, recovery time and repeatability.

- To analyse the influence of tapered fiber geometrical properties on the sensing performance.
- To understand and explain the optical sensing mechanism to sense the interaction between PANI nanostructures and NH_3 gas molecules.

In order to achieve these objectives, the following research questions are outlined:

- What are the suitable synthesis and deposition methods to coat PANI nanostructures on tapered optical fiber?
- How do the synthesis and deposition methods affect the sensing layer's morphology and thickness?
- How different are the sensing performances of PANI nanostructures with different morphologies and thickness?
- How different are the sensing performances of tapered fiber sensors with different waist diameters?

1.4 Scope and limitation

This thesis is focusing on evanescence-based optical fiber sensor using tapered multimode fiber. Two types of PANI nanostructures were used as the sensing layer, which are PANI-CSA nanofibers and PANI-PMVEA nanogranules. The sensing mechanism is based on evanescent wave absorption. The sensors were tested at room temperature (26°C) to sense NH_3 at four different concentrations (0.125%, 0.25%, 0.5% and 1%). The sensors were not tested for different temperature because it is purposely designed for room temperature applications. PANI, a type of conducting polymer, was chosen as the sensing layer because it is known to have good response at room temperature. Besides, the polymer is not suitable to be used at high temperature because it will decompose at temperature of more than 100°C.

The tapered fiber used in this thesis was fabricated from conventional graded index multimode fiber with core/cladding ratio of 62.5 μm/125 μm. The tapered fiber has fixed down taper and up taper length of 2mm, and fixed waist length of 10 mm. In the method that uses PANI-CSA as sensing layer, the waist diameter was varied between 20 μm to 50 μm. The diameter was not reduced below 20 μm because the fiber becomes very fragile and difficult to handle. A preliminary work using tapered fiber with waist diameter of 15μm was done, but it was not continued because the fiber was broken. So, it was decided not to use the fiber with diameter of less than 20 μm. Meanwhile, the sensor with 50 μm showed a very low sensitivity due to very small evanescent penetration depth. Therefore, it is useless to further increase the diameter. For sensor with PANI-PMVEA coating, the diameter was not varied because the focus of that chapter is to study the effect of sensing layer morphology and thickness.

This thesis also does not focus on the doping level of the CSA and PMVEA into PANI. In Chapter 3, PMVEA was only varied by 5%, which does not really affect the doping level, because the amount of polymer coated on the fiber is very small relative to the total amount of polymer produced in 100 ml of solution. Meanwhile, in Chapter 4, the amount of CSA was not varied.

1.5 Thesis Organisation

This research work is reported in a thesis that consists of 5 chapters. Chapter 1 provides a brief overview of the tapered fiber sensor fields followed by the problem statements and objectives. Theoretical background and review on the previous reported research findings related to this work are presented in Chapter 2. In Chapter 3, the sensor fabrication process that involves in-situ deposition of PANI-PMVEA nanogranules on tapered fiber is elaborated in details. The analyses on the PANI coating properties together with the sensing results are included in the same chapter. Chapter 4 discusses the sensor fabrication method that involves synthesis and spray coating of PANI-CSA nanofibers together with the PANI coating properties and sensing performance. Finally, research findings and outlines of future recommendations for this research are concluded in Chapter 5.

REFERENCES

[1] K. L. Loewenstein, *The Manufacturing Technology of Continuous Glass Fibres*, 3rd ed. Elsevier, 1993.

[2] E. Udd, *Fiber Optic Sensors*, Second. New York: CRC Press, 2008.

[3] G. D. Pitt, P. Extance, R. C. Neat, D. N. Batchelder, R. E. Jones, J. A. Barnett, and R. H. Pratt, "Optical-fibre sensors," *Optoelectron. IEE Proc. J*, vol. 132, pp. 214–248, 1985.

[4] Y. Shi-Kay and C. Asawa, "Fiber Optical Intensity Sensors," *Sel. Areas Commun. IEEE J.*, vol. 1, pp. 562–575, 1983.

[5] J. W. Berthold, "Optical Fiber Sensor Technology: Applications and Systems," K. T. V Grattan and B. T. Meggitt, Eds. Boston, MA: Springer US, 1999, pp. 225–240.

[6] Y. J. Rao, "Recent progress in applications of in-fibre Bragg grating sensors," *Opt. Lasers Eng.*, vol. 31, pp. 297–324, 1999.

[7] P. Wang, G. Brambilla, M. Ding, Y. Semenova, Q. Wu, and G. Farrell, "High-sensitivity, evanescent field refractometric sensor based on a tapered, multimode fiber interference.," *Opt. Lett.*, vol. 36, no. 12, pp. 2233–5, Jun. 2011.

[8] A. G. Mignani, R. Falciai, and L. Ciaccheri, "Evanescent Wave Absorption Spectroscopy by Means of Bi-tapered Multimode Optical Fibers SPECTROSCOPY USING A MULTIMODE," *Appl. Spectrosc.*, vol. 52, no. 4, pp. 546–551, 1998.

[9] M. Barbu, K. Jovanovich, R. Trahan, and P. Chirlian, "The Use of Tapered Fibers in an Intensity Based Single Mode Temperature Sensor," pp. 47–50, 2000.

[10] L. Zhang, F. Gu, J. Lou, X. Yin, and L. Tong, "Fast detection of humidity with a subwavelength-diameter fiber taper coated with gelatin film.," *Opt. Express*, vol. 16, no. 17, pp. 13349–53, Aug. 2008.

[11] S. Mas, J. Mart, and J. Palac, "Biconical tapered fibers manipulation for refractive index and strain sensing applications," *IEEE Sens. J.*, vol. 15, no. 3, pp. 1331–1335, 2015.

[12] W. Bin Ji, H. H. Liu, S. C. Tjin, K. K. Chow, and A. Lim, "Ultrahigh Sensitivity Refractive Index Sensor Based on Optical Microfiber," *IEEE Photonics Technol. Lett.*, vol. 24, no. 20, pp. 1872–1874, Oct. 2012.

[13] J. Villatoro, D. Luna-Moreno, and D. Monzón-Hernández, "Optical fiber hydrogen sensor for concentrations below the lower explosive limit," *Sensors Actuators B Chem.*, vol. 110, no. 1, pp. 23–27, Sep. 2005.

[14] A. Leung, K. Rijal, P. M. Shankar, and R. Mutharasan, "Effects of geometry on transmission and sensing potential of tapered fiber sensors.," *Biosens. Bioelectron.*, vol. 21, no. 12, pp. 2202–9, Jun. 2006.

[15] O. S. Wolfbeis, "Fibre-optic chemical sensors and biosensors," *Anal. Chem.*, vol. 78, no. 12, pp. 3859–74, 2006.

[16] H. Bai and G. Shi, "Gas Sensors Based on Conducting Polymers," *Sensors*, vol. 7, no. 3, pp. 267–307, Mar. 2007.

[17] G. Ciric-Marjanovic, "Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications," *Synth. Met.*, vol. 177, no. 3, pp. 1–47, 2013.

[18] B. Timmer, W. Olthuis, and A. Van Den Berg, "Ammonia sensors and their applications—a review," *Sensors Actuators B Chem.*, vol. 107, no. 2, pp. 666–677, Jun. 2005.

[19] Praxair, "Ammonia , anhydrous Ammonia , anhydrous Safety Data Sheet P-4562," pp. 1–9, 2015.

[20] "1947 Texas City Disaster," *Moore Memorial Public Library*. [Online]. Available: http://www.texascity-library.org/disaster/fire.php.

[21] A. Airoudj, D. Debarnot, B. Bêche, and F. Poncin-Epaillard, "A new evanescent wave ammonia sensor based on polyaniline composite.," *Talanta*, vol. 76, no. 2, pp. 314–9, Jul. 2008.

[22] S. Christie, E. Scorsone, K. Persaud, and F. Kvasnik, "Remote detection of gaseous ammonia using the near infrared transmission properties of polyaniline," *Sensors Actuators B Chem.*, vol. 90, no. 1–3, pp. 163–169, 2003.

[23] P. Stamenov, R. Madathil, and J. M. D. Coey, "Dynamic response of ammonia sensors constructed from polyaniline nanofibre films with varying morphology," *Sensors Actuators B Chem.*, vol. 161, no. 1, pp. 989–999, Jan. 2012.

[24] J. Castrellon-Uribe, M. E. Nicho, and G. Reyes-Merino, "Remote optical detection of low concentrations of aqueous ammonia employing conductive polymers of polyaniline," *Sensors Actuators B Chem.*, vol. 141, no. 1, pp. 40–44, Aug. 2009.

[25] M. El-Sherif, "Fiber Optic Sensors For Detection of Toxic and Biological Threats," vol. 7, no. 12, pp. 3100–3118, Dec. 2007.

[26] L. Ai, J. C. Mau, W. F. Liu, T. C. Chen, and W. K. Su, "A volatile-solvent gas fiber sensor based on polyaniline film coated on superstructure fiber Bragg gratings," *Meas. Sci. Technol.*, vol. 19, no. 1, p. 17002, Jan. 2008.

[27] S. K. Mishra, D. Kumari, and B. D. Gupta, "Surface plasmon resonance based fiber optic ammonia gas sensor using ITO and polyaniline," *Sensors Actuators B Chem.*, vol. 171–172, pp. 976–983, Aug. 2012.

[28] W. Jin, H. L. Ho, Y. C. Cao, J. Ju, and L. F. Qi, "Gas detection with micro- and nano-engineered optical fibers," *Opt. Fiber Technol.*, vol. 19, no. 6 PART B, pp. 741–759, 2013.

[29] W. Henry, "Evanescent field devices: a comparison between tapered optical fibres and polished or D-fibres," *Opt. Quantum Electron.*, vol. 26, no. 3, pp. 261–272, 1994.

[30] M. El-Sherif, "Fiber-optic chemical sensor using polyaniline as modified cladding material," *IEEE Sens. J.*, vol. 3, no. 1, pp. 5–12, Feb. 2003.

[31] I. Fratoddi, I. Venditti, C. Cametti, and M. V. Russo, "Chemiresistive polyaniline-based gas sensors: A mini review," *Sensors Actuators, B Chem.*, vol. 220, pp. 534–548, 2015.

[32] A. L. Sharma, K. Kumar, and A. Deep, "Nanostructured polyaniline films on silicon for sensitive sensing of ammonia," *Sensors Actuators A Phys.*, vol. 198, pp. 107–112, Aug. 2013.

[33] V. Talwar, O. Singh, and R. C. Singh, "ZnO assisted polyaniline nanofibers and its application as ammonia gas sensor," *Sensors Actuators B Chem.*, vol. 191, pp. 276–282, Feb. 2014.

[34] H. Kebiche, D. Debarnot, A. Merzouki, F. Poncin-Epaillard, and N. Haddaoui, "Relationship between ammonia sensing properties of polyaniline nanostructures and their deposition and synthesis methods," *Anal. Chim. Acta*, vol. 737, pp. 64–71, 2012.

[35] J. Hodgkinson and R. P. Tatam, "Optical gas sensing: a review," *Meas. Sci. Technol.*, vol. 24, no. 1, p. 12004, Jan. 2013.

[36] O. S. Wolfbeis, "Fiber-optic chemical sensors and biosensors," *Analytical Chemistry*, vol. 80, no. 12. pp. 4269–4283, 2008.

[37] M. H. Yaacob, M. Breedon, K. Kalantar-zadeh, and W. Wlodarski, "Absorption spectral response of nanotextured WO3 thin films with Pt catalyst towards H2," *Sensors Actuators B Chem.*, vol. 137, no. 1, pp. 115–120, Mar. 2009.

[38] A. Airoudj, D. Debarnot, B. Bêche, and F. Poncin-Epaillard, "Development of an optical ammonia sensor based on polyaniline/epoxy resin (SU-8) composite.," *Talanta*, vol. 77, no. 5, pp. 1590–6, Mar. 2009.

[39] Y. Zhao, X. Li, X. Zhou, and Y. Zhang, "Review on the graphene based optical fiber chemical and biological sensors," *Sensors Actuators B Chem.*, vol. 231, pp. 324–340, 2016.

[40] M. H. Yaacob, M. Z. Ahmad, A. Z. Sadek, J. Z. Ou, J. Campbell, K. Kalantar-Zadeh, and W. Wlodarski, "Optical response of WO3 nanostructured thin films sputtered on different transparent substrates towards hydrogen of low concentration," *Sensors Actuators, B Chem.*, vol. 177, pp. 981–988, 2013.

[41] A. Y. Mironenko, A. A. Sergeev, A. E. Nazirov, E. B. Modin, S. S. Voznesenskiy, and S. Y. Bratskaya, "H2S optical waveguide gas sensors based on chitosan/Au and chitosan/Ag nanocomposites," *Sensors Actuators, B Chem.*, vol. 225, pp. 348–353, 2016.

[42] A. Yimit, K. Itoh, and M. Murabayashi, "Detection of ammonia in the ppt range based on a composite optical waveguide pH sensor," *Sensors Actuators, B Chem.*, vol. 88, no. 3, pp. 239–245, 2003.

[43] M.-K. Bae, J. A. Lim, S. Kim, and Y.-W. Song, "Ultra-highly sensitive optical gas sensors based on chemomechanical polymer-incorporated fiber interferometer.," *Opt. Express*, vol. 21, no. 2, pp. 2018–23, Jan. 2013.

[44] J. Homola, "Present and future of surface plasmon resonance biosensors.," *Anal. Bioanal. Chem.*, vol. 377, no. 3, pp. 528–39, Oct. 2003.

[45] A. K. Sharma, R. Jha, and B. D. Gupta, "Fiber-Optic Sensors Based on Surface Plasmon Resonance: A Comprehensive Review," *IEEE Sens. J.*, vol. 7, no. 8, pp. 1118–1129, Aug. 2007.

[46] R. Kashyap and G. Nemova, "Surface Plasmon Resonance-Based Fiber and Planar Waveguide Sensors," *J. Sensors*, vol. 2009, pp. 1–9, 2009.

[47] B. Lee, S. Roh, and J. Park, "Current status of micro- and nano-structured optical fiber sensors," *Opt. Fiber Technol.*, vol. 15, no. 3, pp. 209–221, 2009.

[48] C. J. Gouveia, J. M. Baptista, and P. S. Jorge, "Refractometric Optical Fiber Platforms for Label Free Sensing," *Curr. Dev. Opt. Fiber Technol.*, no. May 2016, pp. 345–373, 2013.

[49] Z. L. Poole, P. Ohodnicki, R. Chen, Y. Lin, and K. P. Chen, "Engineering metal oxide nanostructures for the fiber optic sensor platform," vol. 22, no. 3, pp. 2009–2013, 2014.

[50] X. Chong, K. J. Kim, P. R. Ohodnicki, E. Li, C. H. Chang, and A. X. Wang, "Ultrashort Near-Infrared Fiber-Optic Sensors for Carbon Dioxide Detection," *IEEE Sens. J.*, vol. 15, no. 9, pp. 5327–5332, 2015.

[51] G. Brambilla, V. Finazzi, and D. J. Richardson, "Ultra-low-loss optical fiber nanotapers," *Opt. Express*, vol. 12, pp. 2258–2263, 2004.

[52] L. S. Grattan and B. T. Meggit, *Optical Fiber Sensor Technology*. Springer US, 1999.

[53] H. Tai, H. Tanaka, and T. Yoshino, "Fiber-optic evanescent-wave methane-gas sensor using optical absorption for the 3.392-Mm line of a He-Ne laser," vol. 12, no. 6, pp. 437–439, 1987.
[54] J. Villatoro and D. Monzón-Hernández, "Fast detection of hydrogen with nano fiber tapers coated with ultra thin palladium layers.," *Opt. Express*, vol. 13, no. 13, pp. 5087–92, Jun. 2005.
[55] R. Jarzebinska, S. Korposh, S. James, W. Batty, R. Tatam, and S.-W. Lee, "Optical Gas Sensor Fabrication Based on Porphyrin-Anchored Electrostatic Self-Assembly onto Tapered Optical Fibers," *Anal. Lett.*, vol. 45, no. 10, pp. 1297–1309, Jul. 2012.
[56] S. O. Korposh, N. Takahara, J. J. Ramsden, S.-W. Lee, and T. Kunitake, "Nano-assembled thin film gas sensors. I. Ammonia detection by a porphyrin-based multilayer film," *J. Biol. Phys. Chem.*, vol. 6, no. August, pp. 125–132, 2006.
[57] S. Korposh, S. Kodaira, W. Batty, S. W. James, and S. W. Lee, "Nanoassembled Thin-Film Gas Sensor II. An Intrinsic Highly Sensitive Fibre Optic Sensor for Ammonia Detection," *Sensors Mater.*, vol. 21, no. 4, pp. 179–189, 2009.
[58] L. I. Espada, M. Shadaram, J. Robillard, and K. H. Pannell, "Ferrocenylenesilylene Polymers as Coatings for Tapered Optical-Fiber Gas Sensors," *J. Inorg. Organomet. Polym.*, vol. 10, no. 4, pp. 169–176, 2000.
[59] G. B. Bredas, J. L. and Street, "Polarons, Bipolarons, Solitons in Conducting Polymers," *Acc. Chem. Res.*, vol. 18, pp. 309–315, 1985.
[60] N. Abdul Rahman, "Electrospun Conducting Polymer Nanofibers for Biomedical Applications," The University of Auckland, New Zealand, 2012.
[61] P. R. T. Gordon G. Wallace, Geoffrey M. Spinks, Leon A. P. Kane-Maguire, *Conductive Electroactive Polymers: Intelligent Polymer Systems*, 3rd ed. CRC Press, 2009.
[62] J. Stubb, H., Punkka, E., Paloheimo, "Electronic and optical properties of conducting polymer thin films," *Mater. Sci. Eng.*, vol. 10, pp. 85–140, 1993.
[63] A. Partridge, M. Jansen, and W. Arnold, "Conducting polymer-based sensors," *Mater. Sci. Eng. C*, vol. 12, no. 1–2, pp. 37–42, Aug. 2000.
[64] U. Lange, N. V Roznyatovskaya, and V. M. Mirsky, "Conducting polymers in chemical sensors and arrays.," *Anal. Chim. Acta*, vol. 614, no. 1, pp. 1–26, Apr. 2008.
[65] S. L. Patil, M. a. Chougule, S. Sen, and V. B. Patil, "Measurements on room temperature gas sensing properties of CSA doped polyaniline–ZnO nanocomposites," *Measurement*, vol. 45, no. 3, pp. 243–249, Apr. 2012.
[66] D. Nicolas-Debarnot and F. Poncin-Epaillard, "Polyaniline as a new sensitive layer for gas sensors," *Anal. Chim. Acta*, vol. 475, no. 1–2, pp. 1–15, Jan. 2003.
[67] W. Prissanaroon, L. Ruangchuay, A. Sirivat, and J. Schwank, "Electrical conductivity response of dodecylbenzene sulfonic acid-doped polypyrrole films to SO2–N2 mixtures," *Synth. Met.*, vol. 114, no. 1, pp. 65–72, Jul. 2000.
[68] L.-X. Wang, X.-G. Li, and Y.-L. Yang, "Preparation, properties and applications of polypyrroles," *React. Funct. Polym.*, vol. 47, no. 2, pp. 125–139, Mar. 2001.
[69] L. Al-Mashat, H. D. Tran, W. Wlodarski, R. B. Kaner, and K. Kalantar-Zadeh, "Conductometric Hydrogen Gas Sensor Based on Polypyrrole Nanofibers," *IEEE Sens. J.*, vol. 8, no. 4, pp. 365–370, Apr. 2008.
[70] D. Verma and V. Dutta, "Role of novel microstructure of polyaniline-CSA thin

film in ammonia sensing at room temperature," *Sensors Actuators B Chem.*, vol. 134, no. 2, pp. 373–376, Sep. 2008.

[71] V. C. Gonçalves and D. T. Balogh, "Optical chemical sensors using polythiophene derivatives as active layer for detection of volatile organic compounds," *Sensors Actuators B Chem.*, vol. 162, no. 1, pp. 307–312, Feb. 2012.

[72] B. Li, S. Santhanam, L. Schultz, M. Jeffries-EL, M. C. Iovu, G. Sauvé, J. Cooper, R. Zhang, J. C. Revelli, A. G. Kusne, J. L. Snyder, T. Kowalewski, L. E. Weiss, R. D. McCullough, G. K. Fedder, and D. N. Lambeth, "Inkjet printed chemical sensor array based on polythiophene conductive polymers," *Sensors Actuators B Chem.*, vol. 123, no. 2, pp. 651–660, May 2007.

[73] J. Cerón Solís, E. De la Rosa, and E. Peña Cabrera, "Absorption and refractive index changes of poly (3-octylthiophene) under NO2 gas exposure," *Opt. Mater. (Amst).*, vol. 29, no. 2–3, pp. 167–172, Nov. 2006.

[74] X. Guo, Y. Kang, T. Yang, and S. Wang, "Low-temperature NO2 sensors based on polythiophene/WO3 organic-inorganic hybrids," *Trans. Nonferrous Met. Soc. China*, vol. 22, no. 2, pp. 380–385, Feb. 2012.

[75] S. Virji, J. Huang, R. B. Kaner, and B. H. Weiller, "Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms," *Nano Lett.*, vol. 4, no. 3, pp. 491–496, Mar. 2004.

[76] A. Airoudj, D. Debarnot, B. Bêche, and F. Poncin-Epaillard, "Design and sensing properties of an integrated optical gas sensor based on a multilayer structure.," *Anal. Chem.*, vol. 80, no. 23, pp. 9188–94, Dec. 2008.

[77] S. Sinha, S. Bhadra, and D. Khastgir, "Effect of Dopant Type on the Properties of Polyaniline," *Appl. Polym. Sci.*, vol. 112, pp. 3135–3140, 2009.

[78] Y.-Z. Long, M.-M. Li, C. Gu, M. Wan, J.-L. Duvail, Z. Liu, and Z. Fan, "Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers," *Prog. Polym. Sci.*, vol. 36, no. 10, pp. 1415–1442, 2011.

[79] A. H. Navarchian, Z. Hasanzadeh, and M. Joulazadeh, "Effect of Polymerization Conditions on Reaction Yield, Conductivity, and Ammonia Sensing of Polyaniline," *Adv. Polym. Technol.*, vol. 32, no. 3, p. n/a-n/a, 2013.

[80] V. V. Chabukswar, S. Pethkar, and A. A. Athawale, "Acrylic acid doped polyaniline as an ammonia sensor," *Sensors Actuators, B Chem.*, vol. 77, no. 3, pp. 657–663, 2001.

[81] M. Matsuguchi and T. Asahi, "Properties and stability of polyaniline nanofiber ammonia sensors fabricated by novel on-substrate method," *Sensors Actuators, B Chem.*, vol. 160, no. 1, pp. 999–1004, 2011.

[82] Z. Pang, J. Fu, P. Lv, F. Huang, and Q. Wei, "Effect of CSA Concentration on the Ammonia Sensing Properties of CSA-Doped PA6/PANI Composite Nanofibers," *Sensors*, vol. 14, no. 11, pp. 21453–21465, 2014.

[83] T. Mérian, N. Redon, Z. Zujovic, D. Stanisavljev, J. L. Wojkiewicz, and M. Gizdavic-Nikolaidis, "Ultra sensitive ammonia sensors based on microwave synthesized nanofibrillar polyanilines," *Sensors Actuators B Chem.*, vol. 203, pp. 626–634, Nov. 2014.

[84] K. Crowley, a Morrin, a Hernandez, E. Omalley, P. Whitten, G. Wallace, M. Smyth, and a Killard, "Fabrication of an ammonia gas sensor using inkjet-printed polyaniline nanoparticles," *Talanta*, vol. 77, no. 2, pp. 710–717, Dec. 2008.

[85] Y. Huang, L. Wieck, and S. Tao, "Development and evaluation of optical fiber

NH3 sensors for application in air quality monitoring," *Atmos. Environ.*, vol. 66, pp. 1–7, 2013.

[86] Y. Leng, "Scanning Electron Microscopy," in *Materials Characterization*, John Wiley & Sons (Asia) Pte Ltd, 2008, pp. 121–144.

[87] Y. Leng, "Vibrational Spectroscopy for Molecular Analysis," in *Materials Characterization*, John Wiley & Sons (Asia) Pte Ltd, 2008, pp. 253–300.

[88] Y. Leng, "Scanning Probe Microscopy," in *Materials Characterization*, John Wiley & Sons (Asia) Pte Ltd, 2008, pp. 145–170.

[89] L. Zhang, H. Peng, C. F. Hsu, P. a Kilmartin, and J. Travas-Sejdic, "Self-assembled polyaniline nanotubes grown from a polymeric acid solution," *Nanotechnology*, vol. 18, no. 11, p. 115607, Mar. 2007.

[90] C. Koo, B. Jeon, and I. Chung, "The Effect of Poly(methyl vinyl ether-alt-maleic acid) Stabilizer on the Stability of Polyaniline-Poly(methyl vinyl ether-alt-maleic acid) Dispersions.," *J. Colloid Interface Sci.*, vol. 227, no. 2, pp. 316–321, 2000.

[91] M. Ahmad and L. L. Hench, "Effect of taper geometries and launch angle on evanescent wave penetration depth in optical fibers.," *Biosens. Bioelectron.*, vol. 20, no. 7, pp. 1312–9, Jan. 2005.

[92] C. Liu, J. Zhang, G. Shi, and F. Chen, "Doping level change of polyaniline film during its electrochemical growth process," *J. Appl. Polym. Sci.*, vol. 92, no. 1, pp. 171–177, 2004.

[93] H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen, and Z. Ying, "Influence of polymerization temperature on NH3 response of PANI/TiO2 thin film gas sensor," *Sensors Actuators, B Chem.*, vol. 129, no. 1, pp. 319–326, 2008.

[94] H. Tai, Y. Jiang, G. Xie, and J. Yu, "Preparation, Characterization and Comparative NH3-sensing Characteristic Studies of PANI/inorganic Oxides Nanocomposite Thin Films," *J. Mater. Sci. Technol.*, vol. 26, no. 7, pp. 605–613, 2010.

[95] N. Abdul Rahman, M. Gizdavic-Nikolaidis, S. Ray, A. J. Easteal, and J. Travas-Sejdic, "Functional electrospun nanofibres of poly(lactic acid) blends with polyaniline or poly(aniline-co-benzoic acid)," *Synth. Met.*, vol. 160, no. 17–18, pp. 2015–2022, Sep. 2010.

[96] Z. Wu, X. Chen, S. Zhu, Z. Zhou, Y. Yao, W. Quan, and B. Liu, "Enhanced sensitivity of ammonia sensor using graphene/polyaniline nanocomposite," *Sensors Actuators B Chem.*, vol. 178, pp. 485–493, Mar. 2013.

[97] V. J. Babu, S. Vempati, and S. Ramakrishna, "Conducting Polyaniline-Electrical Charge Transportation," *Mater. Sci. Appl.*, vol. 4, no. 1, pp. 1–10, 2013.

[98] B. Min, "SnO2 thin film gas sensor fabricated by ion beam deposition," *Sensors Actuators B Chem.*, vol. 98, no. 2–3, pp. 239–246, Mar. 2004.

[99] J. Chen, B. Winther-Jensen, Y. Pornputtkul, K. West, L. Kane-Maquire, and G. G. Wallace, "Synthesis of Chiral Polyaniline Films via Chemical Vapor Phase Polymerization," *Electrochem. Solid-State Lett.*, vol. 9, no. 1, p. C9, 2006.

[100] M. C. Bernard and A. Hugot-Le Goff, "Quantitative characterization of polyaniline films using Raman spectroscopy," *Electrochim. Acta*, vol. 52, no. 2, pp. 595–603, Oct. 2006.

[101] Sudha, D. Kumar, and M. Iwamoto, "Investigation of the chiroptical behavior of optically active polyaniline synthesized from naturally occurring amino

acids," *Polymer (Guildf).*, vol. 45, no. 2, pp. 160–165, 2013.
[102] A. B. Socorro, I. Del Villar, J. M. Corres, I. R. Matias, and F. J. Arregui, "Lossy mode resonances dependence on the geometry of a tapered monomode optical fiber," *Sensors Actuators A Phys.*, vol. 180, pp. 25–31, Jun. 2012.
[103] N. G. Deshpande, Y. G. Gudage, R. Sharma, J. C. Vyas, J. B. Kim, and Y. P. Lee, "Studies on tin oxide-intercalated polyaniline nanocomposite for ammonia gas sensing applications," *Sensors Actuators, B Chem.*, vol. 138, no. 1, pp. 76–84, 2009.
[104] P. Kilmartin, "Polymeric Acid Doped Polyaniline Nanotubes for Oligonucleotide Sensors," *Electroanalysis*, 2007.