UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF CHEMICAL SENSORS BASED ON TAPERED OPTICAL FIBER TIP COATED WITH NANOSTRUCTURED THIN FILMS

ARAFAT ABDALLAH ABDELWADOD SHABANEH

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By

ARAFAT ABDALLAH ABDELWADOD SHABANEH

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

May 2015

DEDICATION

قال تعالى:

((وَوَصَّيْنَا الإِنسَانَ بِوَالِدَيْهِ حَمَلَتْهُ أُمُّهُ وَهْناً عَلَى وَهْنٍ وَفِصَالُهُ فِي عَامَيْنِ أَنْ اشْكُرْ لِي وَلِوَالِدَيْكَ إِلَيَّ الْمَصِيرُ))

لقمان 14

This thesis is dedicated to:

My mum (Layla) for her love and endless support, and to the soul of my dad (Abdallah),

My loving brother (Abbas) for his love and encouragement throughout all my study period,

My beloved sisters and their husbands,

Special thanks to my supervisor,

All of my friends,

My beloved first and second country Palestine and Malaysia

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

DEVELOPMENT OF CHEMICAL SENSORS BASED ON TAPERED OPTICAL FIBER TIP COATED WITH NANOSTRUCTURED THIN FILMS

By

ARAFAT ABDALLAH ABDELWADOD SHABANEH

May 2015

Chairman: Mohd Hanif Yaacob, PhD

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In this PhD research, novel chemical sensors based on nanomaterial thin films on tapered optical fiber tips were developed and investigated. Nanotechnology enabled chemical sensors have been reported to show better sensing performance as compared to the conventional sensors towards target analytes due to their high surface area. Nevertheless, the previous developments were mostly concentrated on the thick films and electrical based sensors rather than optical based sensors. Therefore, this PhD research project is to explore the sensing potential of the tapered optical sensor and comprehensively study various kinds of nanomaterial thin films as the chemical sensing layers. This was undertaken with the aspirations of enhancing the performance of the nanomaterial thin films based tapered optical fiber sensors as compared to the conventional based sensors.

Two of the chemicals frequently utilized in biomedical, chemical and food industries are ammonia (NH_3) and ethanol. NH_3 is used in the food industries although it is a colorless gas with a strong offensive odor. Some sources of this gas are power plants, chemical industries and fertilizer manufacturing. It can be extremely hazardous to humans if inhaled. On the other hand, ethanol sensors are also widely deployed for health applications such as breath analyzer. Therefore it is important to have a sensing system that can detect the presence and concentration of these chemicals in the environment. In this project, the developed sensor system is tested towards NH_3 gas and aqueous ethanol.

One of the most suitable optical transducing platforms for sensing applications is tapered optical fiber. In this PhD work, tapered optical fibers were fabricated using Vytran glass processing workstation to achieve tapers with different tip diameters. The tips were coated with different nanomaterials thin films known to be sensitive towards NH_3 and ethanol. The nanomaterials under investigation are zinc oxide (ZnO), polyaniline (PANI), graphene oxide (GO) and carbon nanotubes (CNTs). These

materials are known to have optical, mechanical and excellent physiochemical properties. However, their potential in optical based chemical sensing applications has yet to be fully explored especially in their nanostructure forms. Optical sensors require a thin catalytic metal layer such as palladium (Pd) or gold (Au) to dissociate the gas molecules into the nanomaterials thin films. The deposition of these catalysts and nanomaterials were done via different deposition techniques such as DC-sputtering, dip coating as well as drop casting. Micro-nano characterization techniques such as FESEM, XRD, EDX, AFM, Raman and UV-vis-NIR spectroscopies were employed to obtain detailed structural properties of these nanomaterials in order to fundamentally understand their functionalities with respect to the optical sensors' performance.

The investigations of the chemical sensing performance of the developed tapered optical sensors were carried out. The nanomaterial thin films were deposited onto the tapered optical fiber tip and tested towards the chemicals using reflectance measurement in a customized chamber. The optical fiber tip was connected to a spectrophotometer system (Ocean Optics) to measure the optical signal. The chamber was connected to mass flow controllers (MFC-Aalborg). The optical sensing mechanism of the molecules and sensing layer interaction of the nanomaterials coated onto the optical fiber tip towards NH_3 and ethanol were explained. Furthermore, the NH_3 sensing performance was also compared for ZnO and PANI nanostructured thin films with different catalysts (Au and Pd). The sensing performances of these nanomaterials were investigated towards NH_3 and ethanol with concentrations 0.25% - 1% and 5% - 80%, respectively.

For the first time, tapered optical fiber sensors based on Pd/ZnO and Au/PANI nanostructure thin films which are sensitive towards NH_3 with low concentrations 0.25% at room temperature were successfully developed. Au and Pd were proven to be highly efficient in improving the optical response as compared to coated sensors without catalyst. Furthermore, the superior optical response exhibited by the Au/ZnO and Pd/PANI nanostructure thin films towards NH_3 has never been reported before and thus, can be considered as a significant contribution to the body of knowledge. This was proven with high sensitivity and fast response of the tapered optical fiber tip 25 µm in diameter. The response and recovery times were 38 s and 55 s for Au/ZnO and 58 s and 80 s for Pd/PANI nanostructured thin films coated fiber tip, respectively. The sensitivity of Au/ZnO coated tapered optical fiber sensor is 70.4/vol% NH_3 concentration and has slope linearity of more than 99%. The sensitivity of the Pd/PANI coated tapered optical fiber is shown to be 45.8/vol% NH_3 concentration and linearity of 95%.

The tapered optical fiber tip sensor with a 50 µm diameter which coated with GO exhibited fast sensing performance by having both response and recovery time of less than 25 s at room temperature. The tapered optical fiber tip (50 µm) coated with CNT nanostructured thin films showed an excellent dynamic performance with both response and recovery time. The response and recovery time are less than 1 minute in the visible spectrum range at room temperature.

Finally, this PhD work also included the remote sensing of the developed tapered optical fiber sensors for NH_3 and ethanol with a distance of 3 km. the results of the remote sensing experiments are stable and repeatable with low reflectance spectrum as compared to the normal sensor. As a result of this PhD research project, several novel tapered optical fiber tip sensors for NH_3 and ethanol sensors based on the nanomaterials thin films were developed and investigated.

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

PEMBANGUNAN SENSOR KIMIA BERDASARKAN HUJUNG GENTIAN OPTIK TIRUS BERSALUT FILEM NIPIS BERNANOSTRUKTUR

Oleh

ARAFAT ABDALLAH ABDELWADOD SHABANEH

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Dalam kajian PhD ini, buat pertama kalinya sensor kimia berasaskan filem nipis nanobahan yang disalut ke atas hujung gentian optik yang ditiruskan telah dikaji dan dibangunkan dengan lebih mendalam. Telah dilaporkan bahawa nanoteknologi membolehkan sensor kimia berfungsi dengan lebih baik dari segi pengesanan/penderiaan berbanding dengan sensor konvensional terhadap analit sasaran kerana kawasan permukaan yang lebih luas. Walau bagaimanapun, perkembangan sebelumnya lebih tertumpu kepada filem-filem tebal dan sensor berasaskan elektrik dan bukannya berasaskan sensor gentian optik. Oleh itu, projek penyelidikan PhD ini adalah untuk menerokai potensi penderiaan sensor gentian optik yang tirus dan kajian komprehensif ke atas pelbagai jenis nanobahan filem nipis sebagai lapisan yang digunakan untuk mengesan secara kimia. Kajian ini telah dijalankan dengan aspirasi secara meningkatkan prestasi nanobahan filem nipis berasaskan sensor optik tirus berbanding dengan sensor berasaskan konvensional.

Dua daripada bahan kimia yang sering digunakan dalam industri seperti bioperubatan, kimia dan makanan adalah ammonia (NH_3) dan etanol. NH_3 sering kali digunakan dalam industri makanan walaupun ia adalah gas tidak berwarna beserta bau busuk yang kuat. Sesetengah sumber gas ini adalah daripada loji kuasa, industri kimia, pembuatan baja dan pembakaran di dalam kenderaan bermotor. Ia boleh menjadi amat berbahaya kepada manusia jika dihidu. Sebaliknya, sensor etanol juga digunakan secara meluas bagi aplikasi kesihatan seperti penganalisa nafas. Oleh yang demikian, adalah penting untuk mempunyai sistem penderiaan yang boleh mengesan kehadiran dan kepekatan bahan kimia ini yang berada di persekitaran. Dalam projek ini sistem sensor yang dibangunkan akan diuji terhadap gas NH_3 dan cecair etanol. Salah satu platform transducing optik yang paling sesuai untuk aplikasi penderiaan adalah gentian optik tirus. Dalam projek ini, gentian optik tirus telah direka dan dihasilkan dengan menggunakan Vytran pemprosesan kaca untuk mencapai diameter yg berbeza pada hujung gentian optik tersebut. Hujung gentian optik tirus kemudiannya disalut dengan pelbagai nanobahan yang dikatakan peka dalam penderiaan terhadap NH_3 dan etanol. Nanobahan yang telah kaji adalah Graphene Oksida (GO), Carbon Nanotube (CNTs),

Zink Oksida (ZnO) dan Polyaniline (PANI). Bahan-bahan ini diketahui mempunyai sifat fizikal, kimia dan mekanik yang terbaik. Walau bagaimanapun, potensi mereka dalam aplikasi penderiaan kimia berasaskan optik masih belum diterokai sepenuhnya terutama sekali dari segi struktur berskala nano. Sensor optik juga memerlukan lapisan nipis pemangkin logam seperti palladium (Pd) atau emas (Au) untuk memisahkan molekul gas ke dalam nanobahan filem nipis. Salutan pemangkin dan nanobahan telah dilakukan melalui teknik salutan yang berbeza seperti sputtering, dip coating dan juga drop casting. Teknik mikro-pencirian nano seperti SEM, XRD, EDX, AFM, Raman dan spektroskopi UV-vis-NIR telah digunakan untuk mendapatkan sifat-sifat struktur yang terperinci bagi nanobahan ini untuk memahami fungsi asas mereka terhadapat prestasi gentian optik sebagai sensor.

Kajian mengenai prestasi penderiaan kimia daripada sensor gentian optik tirus telah dijalankan. Nanobahan filem nipis disalut ke atas hujung gentian optik yang telah ditirus dan kemudiannya diuji terhadap bahan kimia yang mana system ini diukur dengan menggunakan pantulan cahaya dalam kebuk yang disediakan. Gentian optik tersebut disambungkan kepada sistem spektrofotometer (Model Ocean Optics) untuk mengukur isyarat optik dan kebuk disambungkan kepada mass flow system (Model Aalborg). Mekanisma penggunaan penderiaan optik yang mana interaksi antara molekul dan lapisan penderiaan yang bersalut nanobahan di hujung gentian optik terhadap NH_3 dan etanol telah dijelaskan. Tambahan pula, prestasi penderiaan NH_3 juga telah dibandingkan bagi nanobahan ZnO filem nipis dengan pemangkin yang berbeza (dan Au Pd). Prestasi penderiaan daripada nanobahan ini telah disiasat terhadap NH_3 dan etanol dengan setiap satu kepekatan berbeza dari 0.25% - 1% dan 5% - 80%.

Buat pertama kalinya, satu sensor optik tirus berdasarkan Au/ZnO dan Au/Pani berstruktur nano filem nipis yang sensitif terhadap NH3 dengan kepekatan serendah 0.25% pada suhu bilik berjaya dibangunkan. Pd telah terbukti sangat berkesan dalam menambah baik respon optik berbanding Au. Tambahan pula, respon optik yang unggul dipamerkan oleh Au/Pani dan Pd/Pani berstruktur nano filem nipis ke arah NH_3 tidak pernah dilaporkan sebelum ini dan dengan itu, boleh dianggap sebagai sumbangan terbesar dalam pengajian ini.

Tirus optik sensor dihujung gentian dengan diameter sebesar 50 µm disalut dengan GO telah menunjukkan prestasi penderiaan pantas di mana kedua-dua masa tindak balas dan pemulihan adalah kurang daripada 25 s pada suhu bilik. Malahan sensor CNT yang mempunyai prestasi dinamik yang sangat baik dengan kedua-dua masa tindak balas dan pemulihan kurang daripada 1 minit dalam julat spectrum visible pada suhu bilik.

Akhir kata, kajian PhD ini juga meliputi penderiaan jauh ke atas tirus sensor gentian optik untuk NH_3 dan etanol. Jarak penderiaan jauh adalah sebanyak 3 km. Bedasarkan keputusan eksperimen penderiaan jauh, hasilnya adalah stabil dan boleh berulang dengan spektrum pantulan agak rendah jika dibandingkan dengan sensor yang dibangunkan sebelum ini. Hasil daripada projek penyelidikan PhD ini, beberapa novel tirus optik NH_3 dan etanol sensor berdasarkan nanobahan filem nipis telah dibangunkan dan disiasat dengan mendalam.

ACKNOWLEDGEMENTS

First and foremost, Alhamdulillah, all thanks and praise is due to the most gracious Allah for granting me the required good health guidance, spiritual comfort and steadfastness throughout my research journey. A big thank you to my senior supervisor Dr. Mohd Hanif Yaacob for his invaluable support, guidance, encouragement, intellectual input and friendship towards me in conducting this research to its success.

Special heartfelt thanks are to the pure soul of my father (Abdalla), may God bless and wach him by his mercy. I also would like to take this opportunity to express my sincerest love to my family and my lovely mother; Mrs. Layla Nairoukh for her unconditional love, support and patience. I thank my beloved brother, Mr. Abbas, his wife Mrs. Sahar Al-Qawasmi and their daughter Sidra and son Abdallah for their continuous support and encouragement. Special thank you to my sisters, their husbands (Reyad, Musa, Asaad, Ayman, Lutfi, Jafar and Majdi) as well as their children for their endless encouragement, pray and support especially to Anan, Ola, Anadel, Asma, Raghda, Rida and Ayah.

A special gratitude as well to Prof. Dr. Mohd Adzir Mahdi and Dr. Suriati Paiman as my co-supervisors for making my PhD program a truly fruitful experience. Their helpful suggestions and advices on various aspects of my research work have certainly been very constructive.

I wish to thank to my colleagues Mr. Saad H. Girei, Mrs. Punithavathi Thirunavakkarasu, Mrs. Nor Akmar, Ahmed Lateef and Mr. Wan Baihaqi Wan Ab Rahman for their help, good humour and providing a friendly and inspiring environment for conducting research. May the friendship lasts forever.

I would also like to pass my special thanks to Dr. Suraya Abdul Rashid, Dr. Norizah Abdul Rahman, Dr. Ahmad Ashrif A. Bakar, Dr. Muhammad Z. Ahmad, Prof. Nor Kamariah bt. Noordin, Dr. Aduwati bt. Sali, Dr. Huang Nay Ming and Dr. Janet Lim Hong Ngee for their support, friendship and encouragement.

My special sincere thanks also to Mr. Alhareth Zyoud, Mr. Belal Salhab, Mr. Haytham Shabaneh, Mr. Mohammed Alarja, Mr. Ameer Sider, Mr. Fuad Erman, Mr. Fadel Huseen, Mr. Khalel Badran, Mr. Baha Alqawasmi, Mr. Osaid Qasim, Mr. Ahmed Sameer, Mr. Taiwo Hambali, Mr. yahaya Idriss and Mr. Hamam Al-Ghali for their excellent help, timely suggestions, guidance and active support.

I thank the Palestine Polytechnic University (PPU), International Islamic University Malaysia (IIUM) and Universiti Putra Malaysia especially the staffs of the Department of Computer and Communication Systems Engineering for their continuing support. Finally, I want to dedicate this work to Palestine the holy land. May peace be with you….

ARAFAT ABDALLAH ABDELWADOD SHABANEH

I certify that a Thesis Examination Committee has met on (21th May 2015) to conduct the final examination of **(Arafat Abdallah Abdelwadod Shabaneh)** on his thesis entitled **(Highly Sensitive Chemical Sensors Based On Tapered Optical Fiber Tip Coated With Nanostructured Thin Films)** 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)**.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
APS	Ammonium Peroxydisulfate
Au	Gold
CCD	Charge-Coupled Device
CH_3CH_2OH	Ethanol
CH_4N_2O	Urea
CNT	Carbon Nanotube
CO_2	Carbon Dioxide
EDX	Energy-Dispersive X-ray Spectroscopy
ESD	Electrostatic Discharge
FESEM	Field Emission Scanning Electron Microscopy
FHB	Fiber Holding Block
GO	Graphene Oxide
GPX	Glass Processing System
HNO_3	Nitric Acid
ICDD	International Centre of Diffraction Data
ICP	International Conference on Photonics
IIUM	International Islamic University Malaysia
IR	Infrared
ITMA	Institut Teknologi Maju
LANs	Local Area Networks
LED	Light Emitting Diode
MEMS	Microelectromechanical systems
MFC	Mass Flow Controllers
MMF	Multi-Mode Fiber
MoO_3	Molybdenum Trioxide
MWCNTs	Multi-Walled Carbon Nanotubes
NH_3	Ammonia
NO_2	Nitrogen Dioxide
OSA	Optical Society of America
PANI	Polyaniline
PC	Personal Computer
Pd	Palladium
PdHx	Palladium Hydride
ppb	Parts Per-Billion

PPU	Palestine Polytechnic University
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
Si	Silicon
SiO_2	Silica
SPR	Surface Plasmon Resonance
SVR	Surface-to-Volume Ratio
SWCNTs	Single-Walled Carbon Nanotubes
TIR	Total Internal Reflection
TOFs	Tapered Optical Fibers
UITM	Universiti Teknologi MARA
UM	Universiti Malaysia
UPM	Universiti Putra Malaysia
UV	Ultra-Violet
Vis	Visual
VOCs	Volatile Organic Compounds
WO_3	Tungsten Trioxide
XRD	X-Ray Diffraction
ZnO	Zinc Oxide
$(Zn(NO_3)_2.6H_2O)$	Zinc Nitrate Hexahydrate

CHAPTER 1

INTRODUCTION

The first chapter of this thesis presents the work carried out in this PhD research project. It comprises of motivations, problem statement, objectives, achievements and the thesis organization.

1.1 Background and Motivations

There has been an increasing interest in research on chemical sensing as wider applications of chemicals are deployed in the industries. Chemical sensor measurement plays an important role in controlling the inputs of many production processes. Chemicals are utilized in different industries as raw materials for production; they can also be harmful to the environment [1]. Some of the important chemicals for industrial applications are ammonia (NH_3) and ethanol. In addition, they can be toxic, flammable and volatile. Therefore, it is extremely significant to develop highly sensitive and reliable NH_3 and ethanol sensors to detect or monitor the chemicals as well as to prevent safety hazards.

NH_3 or azane is formed from chemical composition of hydrogen and NH_3 having pungent smells. NH_3 plays important rule in terrestrial organisms' nutrition which is a precursor for food and fertilizer. It is a colorless gas that is frequently used in pharmaceuticals product and in some cleaning industries. It is also chemical that is hazardous and caustic [2].

As manufacturing technology improved the applications that uses NH_3 continue grow and reach the community. Worldwide production of NH_3 was estimated to be 198 million tonnes in 2012 [3]. This figure is 35% increments over the evaluated worldwide production in 2006 [4].

Fifteen homes were evacuated after a leak was discovered in an anhydrous ammonia tank in Clarks Grove as shown in Figure 1.1.

Figure 1.1: Leakage in an anhydrous ammonia tank in Clarks Grove [5]

Anhydrous ammonia billows past grain bins at the Clarks Grove grain elevator after a leak was discovered in the tank. Part of Clarks Grove was evacuated as the gas can be harmful and potentially lethal if breathed in.

Despite the benefits of NH_3, there is need for major safety owing to its properties. The auto-ignition temperature property of 651˚C is higher than those of other fuels. Leaking from NH_3 is hazardous due to usual electrostatic discharge (ESD) which is sufficient to cause ignition. The ignition temperature of NH_3-air mixture is commonly higher than the temperature of the flame. The flammability of NH_3 in the air is around 16–25% [6]. Due to small ignition energy with huge flame propagation velocity, the risks posed by NH_3 leak are obvious. Therefore, it is greatly significant to design effective sensors for monitoring and detecting ammonia with high reliability to prevent safety hazards related to the gas.

The lowest concentration of NH_3 detectable by smell is 5 ppm. 7 ppm concentration is needed to be detectable which is hazard to human health. 6 - 20 ppm and above causes eye irritation and respiratory problems and 40 - 200 ppm causes headache, nausea, reduced appetite, irritation to airways, nose and throat.

Apart from that, another chemical widely used in the industries is ethanol. The ethyl alcohol (ethanol) has the following properties; colourless liquid, flammable, less odour and volatile. It is one of famous psychoactive drug which is taken by people especially in rural areas which intoxicate them. Some used it for medicine by combine with herbs. It is best known kind of alcohol from alcoholic beverages; it serves as thermometric liquid, and as a fuel. It is usually called alcohol (spirit) [7].

The city of west Sacramento and a Texas-based gasoline company are battling over whether it is riskier to ship large amounts of ethanol through city streets on trains or on tanker trucks. Figure 1.2 shows how ethanol is being transported by train in cities.

Figure 1.2: Ethanol tanks [8]

In order to resolve the dispute between the city and the chemical company, the ethanol can be transported through pipes where sensors will be deployed to monitor any leakage.

There are many development of chemical sensing technologies for NH_3 and ethanol using different conventional techniques such as thermal conductivity, mass spectrometry, gas chromatography and catalytic bead [9]. All these techniques are utilised in the industry and known to be expensive. These sensing technologies can perform high detection of the chemicals but not suitable for in-situ applications [10].

The fast development in applications of optical components as result of big commercialization in optoelectronic and telecommunication has shifted the focus of researchers and manufacturers to deploy it in sensing applications. Optical sensor is considered new and less endeavoured with regards to electrical sensors. Owing to properties of the optical signal, its benefits are numerous in respect to electrical signal. Part of the significant properties of optical signal are immune to electromagnetic interference, resistance to corrosive, flammable environments and reactive give rise to application of optical sensor in chemical sensing [11]. When optical sensors are integrated with available optical fibre networks, it permits remote and distributed sensing. From author point of view, the scope of utilizing optical sensors for volatile environments can be a strong alternative in reducing the risks due to the leakage of the chemicals especially in factories. Therefore, there is need to detect and monitor aqueous ethanol with the aid of adequate sensors that are reliable in prevent safety hazards.

1.2 Nanotechnology Enabled Optical Chemical Sensors

Currently, the development in the nanotechnology field paved the way for designing, fabricating and deploying nanomaterials, such as sensors in chemical industries. Nanomaterials are defined as the materials that contain at least one dimension in nanoscale range (<100 nm) [12]. Based on this range, the characteristic of nanomaterials are significantly unique from bulk materials in terms of chemical, electronic, physical, optical, biological and mechanical properties [12].

The use of nanomaterials in chemical sensors is expected to enhance the sensing performance. Nanomaterials have high surface area compared to bulk materials thus, the interaction of the chemicals with the sensory device is stronger for the sensor integrated with nanomaterials [12]. The maximum response can be achieved by improving the interaction between the chemicals with the nanostructured sensing layer. The characteristics such as higher sensitivity and lower operating temperature are peculiar to nanomaterials based sensors compared to traditional sensors towards chemicals. Additionally, the time taken for molecules diffusion of the films in and out is reduced due to nanomaterials properties, therefore the response and recovery time of the sensor is significantly improved. Other characteristics that are peculiar to nanomaterial based sensors are high sensitivity and lower operating temperature as compared to the traditional sensors [12]. Utilizing the nanomaterials with optical transducer such as optical fiber can be produce new sensors for chemicals detection.

Integration of the nanomaterials thin film with optical sensors yields better performance. In optical sensor with an applied thin films, these nanostructured materials are added with different type of transducing platforms, like optical fiber/waveguide (planar and channel) and transparent substrates. The optical techniques employed to measure response in chemical sensing applications are mounted on reflectance, absorbance, refractive index, surface plasmon resonance (SPR) and the luminescence change induced due to interaction between the nanostructured films and different chemical molecules.

Many researchers working on combining nanomaterials with optical transducers. Lazcano- Hernández et al. [13] analyzed the optical response of tungsten trioxide (WO_3) using sputtered thin films to NH_3 gas, sensing via transmittance changes. Due to sputtering, films that have a combination of monoclinic and triclinic crystalline structure were achieved. They had integrated optical NH_3 sensor using glass waveguide coated with WO_3 thin film. In their publication, NH_3 gas molecules adsorbed on the metal surface and separated into H ions and electrons [14]. The ions would diffuse into the metal oxide layer and as a result, optical properties of the layer changed. Increase in NH_3 concentrations was found to increase the absorbance of the film. In their work, Lazcano- Hernández et al. observed the response for optical wavelength to be around 1550 nm [13].

In another study, Mutschall et al. [15] stated that, electrical conductivity measures with various tests, gases confirm the suitability of molybdenum trioxide (MoO_3) layers for NH_3 detection in operating temperatures between 400 and 450°C. The reactive sputtering was used to deposit thin films of MoO_3 for gas sensing applications with molybdenum target. The response time at an operating temperature of 400°C is less than 30 s.

Illyaskutty et al. [16] model a novel zinc oxide (ZnO) incorporated MoO_3 nanostructured thin film system that shows high level of sensitivity and selectivity for ethanol. The MoO_3 and ZnO nanostructures showed improved ethanol sensing performance in non-humid and humid atmospheres. The sensors utilized have characteristics of high sensitivity, maximum stability and fast response/recovery time for ethanol out of five different gases according to their study.

The advancement in the nanomaterial fabrication creates big opportunity for the researchers to develop high sensitivity sensors. However, there are plenty room of improvement in integrating the nanomaterials with optical sensors. There are also many issues related to the sensor development which will be discussed in the next subsections.

1.3 Problem Statement

Recently, most of the chemical sensors were developed using electrical based transducers. Electrical sensors are well established and highly sensitive, but it has limitations on its deployment in the environment especially where there is high risk of explosion. Also it cannot be employed in the environment that is prone to electromagnetic interference. Hence, the development of simple, fast and safe sensors for monitoring NH_3 and ethanol concentrations in volatile environment is demanded.

Furthermore, nanomaterials based sensors have been developed and gained popularity as practical and highly sensitive devices towards chemicals with low concentrations. However, new nanomaterials developed such as ZnO, polyaniline (PANI), graphene oxide (GO) and carbon nanotubes (CNT) are yet to be fully explored as a sensing layer towards NH_3 and ethanol.

Currently, optical fiber sensors based on tapered optical fiber has received more attention in the field of optical sensing than the conventional optical fiber sensors. This is because optical fiber sensors based on tapered optical fiber is more sensitive to the surrounding environment [17]. It is expected that highly sensitive and fast response sensors will be realized by employing tapered optical fiber sensor in a volatile environment for NH_3 and aqueous ethanol sensing. Consequently, reducing the risk associated with leakage of NH_3 and ethanol. However, the fabrication technology in optical fiber such as tapering process is also not fully explored for sensing purposes.

1.4 Objectives and Research Questions

The aim of this research is to design and fabricate tapered optical sensors for chemicals by integrating nanomaterial thin films. The objectives to achieve this include:

1. to investigate on the nanomaterials that are sensitive towards NH_3 and ethanol in terms of morphology and roughness.
2. to design of untapered and tapered optical fiber as the transducing platforms.
3. to synthesis and deposit the nanomaterial onto appropriate optical fiber transducers.
4. to investigate the optical sensing properties of the developed sensors towards NH_3 and ethanol with low concentrations.
5. to investigate in details on the micro-nanocharacteristics of the nanomaterials and their relation with clarifying the optical sensor's performance.
6. to analyse and understand the chemical molecules-sensing layer interaction mechanism of these optical sensors specifically the tapered fiber tips.

In order to attain the stated objectives, the author highlighted the following research questions:

- What are the nanomaterials that alter their optical properties when in contact with chemicals especially NH_3 and ethanol?
- What are the deposition techniques or synthesis methods accessible to fabricate nanomaterials onto optical fibers?
- What are the optimized dimensions of the tapered optical fiber tips as chemical sensor?
- Which optical measurement techniques will be employed to examine the chemicals response of the developed sensors towards NH_3 and ethanol?

Based on these research questions, the author focused the investigation on a few types of nanomaterials popular for their optical, mechanical and excellent physiochemical properties. It is also proposed that the nanomaterials possess the ability to show excellent chemical details properties. Owing to this hypothesis, a tapered optical fiber sensors tip were modeled based on nanostructured thin films utilizing ZnO, PANI, GO and CNT combined with palladium (Pd) and gold (Au) as the catalysts. The nanostructured thin films were deposited onto various optical transducing platforms to measure their sensing performance through several optical techniques. The fundamental understanding of the chemical response in the optical sensors is achieved by analyzing both the nanomaterials properties and the developed sensors testing results.

1.5 Outcomes and Author's Achievements

This research has provided significant results which add to the existing knowledge in chemical sensors using optical fiber coated with nanomaterial thin films. In this work, the researcher outlines a detailed analysis based on experiments and theories of novel tapered optical fiber sensors exposed to NH_3 and ethanol with low concentrations, at room temperature. The contributions of this study are presented below:

- Tapered optical sensors coated with various catalytic layer/nanomaterial thin films were successfully developed and showed outstanding sensing performance towards NH_3 with low concentration (<1%). The developed sensors achieved strong response at room temperature as compared to the conventional electrical sensors which requires elevated operating temperature (>150 °C).
- The tapered optical sensors with 25 µm diameter coated Pd and Au were found to show superior response towards NH_3 as compared to the sensors coated without catalyst.
- Novel chemical sensors were developed using tapered optical fiber tip coated with Au/ZnO nanocrystalline, Pd/PANI nanostructured thin films, GO nanostructured thin films and CNT nanostructured thin films for NH_3 and ethanol sensing applications. These sensors showed optical response towards NH_3 and ethanol with concentrations as low as 0.25% and 5%, respectively.
- Remote sensing analysis of the tapered optical fiber sensors coated with nanomaterials thin films were performed for fiber distance of 3.050 km. The remote chemical testings are the first of their kind to the best of the author's knowledge using tapered fiber sensors.
- Remote chemical testings has shown that the NH_3 gas and aqueous ethanol interaction mechanisms with the nanomaterials coated optical fiber were studied to understand their sensing properties.

This Phd study successfully achieved its objectives to investigate and develop novel chemical sensors using tapered optical fiber coated with nanomaterial thin films. The findings has been publicated in high impact journals and presented in several international conferences. These consist of 5 main author and 5 co-author publications in: IEEE Photonics Journal, Sensors, Sensors and Actuators B: Chemical, Optics Communication, and Journal of the European Optical Society-Rapid publications. The details of the author's journal publications are as follows:

1. A. Shabaneh, S. Girei, P. Arasu, S. Rashid, Z. Yunusa, M. Mahdi, et al., "Reflectance Response of Optical Fiber Coated with Carbon Nanotubes for Aqueous Ethanol Sensing." *IEEE Photonics Journal*, 2014.
2. Arafat Shabaneh, Saad Girei, Punitha Arasu, Mohd Mahdi, Suraya Rashid, Suriati Paiman and Mohd Yaacob, "Dynamic Response Of Tapered Optical Multimode Fiber Coated With Carbon Nanotubes For Ethanol Sensing Application," Sensors, (Accepted).
3. A. Shabaneh, S. Girei, P. Arasu, W. Rahman, A. Bakar, A. Sadek, et al., "Reflectance response of tapered optical fiber coated with graphene oxide nanostructured thin film for aqueous ethanol sensing," *Optics Communications*, vol. 331, pp. 320-324, 2014.

The author's also successfully published and presented personally, 6 research papers in highly established sensor conferences. Throughout the candidature, the author personally attended the following conferences:

1- Conference on Photonics (ICP), Malacca, Malaysia, October 28-30, 2013.
2- The 7th Asia-Pacific Conference on Transducers and Micro/Nano Technologies, June 29 - July 2, 2014 / EXCO, Daegu, Korea.
3- The 4th Advanced Lasers and Photon Sources (ALPS'15), Yokohama, April 22 - April 24, 2015, Japan.

The author is also writing another research paper titled "Dynamic Response of Zinc Oxide Nanocrystalline Coated on Tapered Optical Fiber for Ammonia Sensing" which will be submitted to Sensors and Actuators B: Chemical. The complete list of the author's publications is shown in the list of publications.

1.6 Thesis Organization

This thesis consists of seven chapters and four appendices. The thesis presentation is outlined as follows:

- Chapter 1 contains the introduction and the author's motivation to embark on this study. This includes tapered optical fiber sensors using for chemical sensing applications. The research objectives and the author's summary of the achievement contributions to the body of knowledge.
- Chapter 2 describes the rationales behind the research and critical review on optical sensors for chemical using various nanostructured thin films. Properties of NH_3 and ethanol (optical) apart from nanostructured materials like ZnO, PANI, GO, CNT, and catalytic metals (Pd, Au) for sensors used in chemical were reviewed. It is also details the principles of optical measurement as well as transducing

platforms on optical fiber tip sensor. The target is the measurement principles applying reflectance. The optical transducing platforms under studied in this chapter are spectrophotometer based and optical fiber. It covers the tapering technique for the optical fiber tip. Also, the NH_3 and ethanol sensing mechanisms for optical sensors involving the nanostructured thin films is also covered.

- Chapter 3 highlights the design and fabrication processes of both untapered and tapered optical transducers. It also explains the synthesis and deposition of the nanomaterials. Several techniques applied for the physical deposition and chemical synthesis to produce different types of nanomaterials thin films serve as the optical sensing layer are explained in details.
- Chapter 4 presents the characterization of the nanomaterials employed as the optical sensing layer. The outcomes of micro-nanocharacterization were achieved through series of characterization techniques, such as FESEM, SEM, XRD, EDX, AFM and Raman spectroscopy.
- Chapter 5 describes various chemical testing setup for the developed optical sensors. This includes setup to integrate reflectance response of the tapered optical fiber tip as well as chemical chamber constructions their testing procedures.
- Chapter 6 outlines the experimental results obtained from the tapered optical fiber sensors performance towards NH_3 and ethanol via UV-Vis-NIR spectroscopy. The effect of nanostructured materials' morphology and different catalytic metals on the sensor responses towards different concentrations of NH_3 and ethanol are described in details. The performance of the remote sensing of the tapered optical fibers are discussed and configured for different nanomaterial coatings. This includes also the selectivity and reproducibility of the developed sensors. The optical sensing mechanisms for NH_3 and ethanol interact with different nanomaterials are explained.
- Chapter 7 concludes the research findings and the author's contributions in the area of optical fiber sensors. Recommendations for the future works in the area are also presented.

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