UNIVERSITI PUTRA MALAYSIA

SIDE-POLISHED PLASTIC OPTICAL FIBER COATED WITH NANOMATERIALS FOR CHEMICAL SENSING APPLICATIONS

AHMED LATEEF KHALAF

FK 2018 38

SIDE-POLISHED PLASTIC OPTICAL FIBER COATED WITH NANOMATERIALS FOR CHEMICAL SENSING APPLICATIONS

By

AHMED LATEEF KHALAF

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

November 2017

DEDICATIONS

To

The Memory of My Late Father for His Love and Endless Support,

My Mother, Number One for Me

My lovely wife, My Soul Mate, for her patience and encouragement,

My beloved sons (Alkaram & Lateef), The Reasons to Get Through Another Day,

My beloved brother (Husham), The Shoulder to Lean On,

Sisters, My Day and Night,

My Supervisor,

All my Supervisory Committee,

All of My Friends,

My beloved first and second country Iraq and Malaysia

Without Your Support and Encouragement, My Success Wouldn't Have Been Possible.

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

SIDE-POLISHED PLASTIC OPTICAL FIBER COATED WITH NANOMATERIALS FOR CHEMICAL SENSING APPLICATIONS

By

AHMED LATEEF KHALAF

November 2017

Chairman : **Mohd Hanif Yaacob, PhD**
Faculty : **Engineering**

Gaseous and liquid pollutants such as ammonia (NH_3) gas and ethanol liquid, are ubiquitous in daily human activities and have been extensively studied because of their high toxicity and wide use in many fields. Common NH_3 gas and ethanol liquid detectors are electrical based. Although these electrical or conductometric sensors attain high sensitivity, they suffer from drawbacks that include poor selectivity, high operating temperature, and being prone to electromagnetic interference, which can be addressed by optical sensor. Optical fiber sensors present advantages in certain aspects as compared with electrical sensor, such as their compact size, capability to work in harsh environment, and capacity for remote and distributed sensing. However, chemical sensing using optical fiber has not been fully explored.

Presently, nanotechnology enabled chemical sensors have been increasingly used to enhance the sensing performance as compared with the conventional sensors toward target analytes owing to their high surface area. The sensing layer based on nanostructures has been identified to work at low temperature with high sensitivity. Therefore, this research project aims to design and comprehensively analyze optical fiber based NH_3 gas and ethanol liquid sensors with the incorporation of different nanostructure coatings as sensing layers. Plastic optical fiber (POF) was selected as the transducing platform for the sensor because of its low cost, ease in fabrication, and suitability for remote sensing applications. The sensitivity of POF based sensors can be improved by simply polishing part of the fiber to form side-polished optical fiber (SPPOF) using simple mechanical polishing technique. Thus, the light interaction upon coating with the sensing layer will significantly improve and great absorbance response will be achieved upon exposure to different target chemical concentrations. The influence of nanostructures morphology and roughness on the sensing performance was also studied in this PhD research.

The nanostructures under investigation were tungsten oxide (WO_3), graphene oxide (GO), and carbon nanotubes (CNTs). Chemically synthesized aluminum oxide (Al_2O_3)/polyaniline (PANI) and graphene/PANI nanocomposites were also considered as sensing layers. The different nanostructured sensing layers were integrated with the polished area of the POF via radio frequency sputtering and drop-casting deposition techniques. Micro-nano characterization techniques such as SEM, EDX, AFM, Raman spectroscopy and XRD were utilized to obtain detailed structural properties of these nanostructures to fundamentally understand their functionalities with respect to the optical sensor performance.

The response of the sensors towards target chemicals at different concentrations was measured using absorbance change within the wavelength range of 400 – 800 nm at room temperature. The sensing performance was evaluated in terms of response time, recovery time, sensitivity, and repeatability. The chemical sensing performance of the developed SPPOF sensors was compared with the performance of another modified fiber, which is uncladded POF (UCPOF), using absorbance measurement. The optical sensing mechanisms of the analyte molecules and nanostructured sensing layer coated onto the polished fiber region towards NH_3 and ethanol with concentrations of 0.125% – 1% and 20% – 100%, respectively, at room temperature were explained.

For the first time, according to the author's knowledge, an SPPOF NH_3 sensor coated with sputtered gold (Au)/WO_3 nanostructure thin films was successfully developed. The obtained sensitivity, response time and recovery time were 29.26/vol%, 1.2 min, and 7.3 min, respectively. Novel NH_3 sensor based on SPPOF coated with graphene/PANI nanocomposite demonstrated significant sensitivity of 55.47/vol%. The remote sensing performance of the developed SPPOF sensors was also investigated by connecting them to 1.1 km multimode silica optical fiber. The SPPOF remote sensors coated with graphene/PANI and CNT exhibited excellent sensitivities of 16.63/vol% and 0.23/vol% toward different concentrations of NH_3 and ethanol, respectively, at room temperature with high selectivity and long shelf life. The developed chemical sensors using SPPOF coated with nanomaterials showed superior performance as compared with the electrical based sensors. The excellent sensing performance of the optical fiber sensors via low cost and simple techniques indicates its high efficiency for remote chemical sensing in various industrial and environmental applications.

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

TEKNIK PENGILAPAN SEBAHAGIAN PERMUKAAN GENTIAN OPTIK PLASTIK DENGAN UNSUR NANO DALAM APLIKASI SENSOR KIMIA

Oleh

AHMED LATEEF KHALAF

November 2017

Pengerusi : **Mohd Hanif bin Yaacob, PhD**
Fakulti : **Kejuruteraan**

Gas dan cecair berbahaya seperti gas ammonia (NH_3) dan cecair etanol, terdapat dalam aktiviti manusia seharian dan kajian meluas telah dijalankan kerana tahap keracunan yang tinggi dan penggunaannya yang meluas dalam pelbagai bidang. Biasanya, medium pengesanan gas NH_3 dan pengesan cecair etanol adalah berasaskan elektrik. Walaupun sensor elektrik atau konduktor metrik ini mencapai sensitiviti yang tinggi, ia mempunyai kelemahan termasuk pemilihan yang terhad, suhu operasi yang tinggi, dan terdedah kepada gangguan elektromagnetik, dimana ini boleh diatasi menggunakan sensor optik. Kelebihan sensor optik dalam aspek tertentu berbanding dengan sensor elektrik, seperti saiz yang kompak, keupayaan untuk bekerja dalam persekitaran yang mencabar, dan boleh beroperasi dalam kawalan jarak jauh dan serta pengesanan secara berkelompok. Walau bagaimanapun, sensor kimia yang menggunakan gentian kaca optik masih belum diterokai sepenuhnya.

Pada masa ini, nanoteknologi membolehkan sensor kimia semakin digunakan untuk meningkatkan prestasi pengesanan berbanding dengan sensor konvensional ke arah kejituan pada kawasan permukaannya yang luas. Lapisan penginderaan berdasarkan struktur nano telah dikenal pasti untuk beroperasi pada suhu yang rendah dengan kepekaan yang tinggi. Oleh itu, projek penyelidikan ini bertujuan untuk membuat analisis dan menganalisis sensor cecair gas NH_3 dan etanol cecair etanol secara terperinci dengan memasukkan lapisan struktur nano yang berbeza sebagai lapisan penginderaan. Gentian optik plastik (POF) dipilih sebagai platform pengantara untuk sensor kerana kosnya yang lebih rendah, kemudahan dalam fabrikasi, dan kesesuaian untuk aplikasi pengesanan jarak jauh. Sensitiviti sensor berasaskan POF boleh ditingkatkan dengan menggilap sebahagian daripada gentian fiber untuk membentuk medan optik berpilingan sisi (SPPOF) menggunakan teknik penggilap mekanikal mudah. Oleh itu, interaksi cahaya apabila salutan dengan lapisan penginderaan akan

memberi kesan yang lebih tepat serta tindak balas penyerapan yang baik boleh dicapai apabila terdedah kepada kepekatan kimia yang berlainan. Pengaruh morfologi struktur nano dan status prestasi penderiaan juga dikaji dalam penyelidikan PhD ini.

Bahan-bahan nano yang digunakan adalah tungsten oxide (WO_3), graphene oxide (GO), dan nanotube karbon (CNTs). Aluminium oksida sintetik (Al_2O_3)/polyaniline (PANI) dan graphene/PANI komposit nano juga digunakan sebagai lapisan penginderaan. Lapisan penginderaan struktur nano yang berbeza telah diintegrasikan dengan kawasan yang digilap oleh POF menerusi teknik pendepositan frekuensi dan spekteran frekuensi radio. Teknik pengekstrakan mikro-nano seperti SEM, EDX, AFM, spektroskopi Raman dan XRD digunakan untuk mendapatkan maklumat terperinci tentang struktur nano bagi memahami fungsinya dengan prestasi sensor optik.

Tindak balas sensor terhadap bahan kimia pilihan pada kepekatan yang berbeza diukur dengan memanupulasi penyerapan dalam jarak panjang 400 – 800 nm pada suhu bilik. Prestasi penginderaan dinilai dari segi masa tindak balas, masa pemulihan, kepekaan, dan kebolehulangan. Prestasi penginderaan kimia sensor SPPOF dibandingkan dengan prestasi gentian optik yang lain, seperti POF (UCPOF), dengan menggunakan teknik pengukuran penyerapan. Mekanisme penderiaan optik molekul analitik dan lapisan penderiaan struktur nano yang yang telah digilap ke dalam NH_3 dan etanol dengan kepekatan 0.125% – 1% dan 20% – 100%, pada suhu bilik dijelaskan.

Untuk pertama kali, sensor SPPOF NH_3 yang dilapisi dengan emas (Au)/ WO_3 struktur nano nipis berjaya dibangunkan. Sensitiviti, masa tindak balas dan masa pemulihan yang diperolehi masing-masing adalah 29.26/vol%, 1.2 min, dan 7.3 min. Sensor Novel NH_3 berdasarkan SPPOF yang disalut dengan graphene / PANI nano composite menunjukkan kepekaan yang signifikan 55.47/vol%. Prestasi penderiaan jauh dari sensor SPPOF yang maju juga dikaji dengan menyambungkannya ke gentian optik multimode silika sepanjang 1.1 km. Sensor penderiaan jauh SPPOF yang disalut dengan graphene/PANI dan CNT mempamerkan sensitiviti yang sangat baik dari 16.63/vol% dan 0.23/vol% dalam kepekatan NH_3 dan etanol yang berbeza, masing-masing pada suhu bilik dengan selektiviti tinggi dan jangka hayat yang panjang. Sensor kimia yang dibangunkan menggunakan SPPOF yang disalut dengan kemasan nano menunjukkan prestasi yang unggul berbanding dengan sensor berasaskan elektrik. Prestasi penderiaan optik yang sangat baik dengan kos yang rendah dan teknik mudah menunjukkan kecekapan tinggi untuk penginderaan kimia jarak jauh dalam pelbagai aplikasi perindustrian dan persekitaran.

ACKNOWLEDGEMENTS

Alhamdulillah, all thanks and praise is due to the most gracious Allah s.w.t for granting me the required good health guidance, spiritual comfort and steadfastness throughout my research journey.

First and foremost, I would like to express my special gratitude and appreciation to my main supervisor Dr. Mohd Hanif Yaacob for his invaluable support, guidance, encouragement throughout my PhD study at University of Putra Malaysia. His broad knowledge, interest and intuition in our research area will affect the way I do my research throughout my life. He is a role model in research, teaching and generally as a kind person.

Special heartfelt thanks are to the pure soul of my late father (Mr. Lateef), may Allah s.w.t bless him. I also would like to take this opportunity to express my sincerest love to my lovely mother; Mrs. Bahira Fakhri for her unconditional love, pray, support and patience. No words can express my gratitude to my dear wife, Ghufran Mohammed, for all of the support she has given through all of these years of PhD work. Her understanding, pray, patience, and endless encouragement was in the end what made this work possible. My big gratitude to my brother Husham and my sisters for their continuous inspiration and trust. Many more thanks to my parents in law, Mr. and Mrs. Mohammed Sahib, for their continuous support, asking and praying.

A special gratitude as well to my supervisory committee members, Prof. Dr. Mohd Adzir Mahdi, Prof. Dr. Nor Azah Yusof, Assoc. Prof. Dr. Janet Lim Hong Ngee, and Dr. Suriati Paiman 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. My special thanks also goes to Prof. Dr. Hayder A. Bari, Dr. Norizah Abdul Rahman and Dr. Mutaz Shunasi for their great assistance, support, friendship and encouragement. I am also indebted to all my friends and colleagues: Dr. Punithavathi Thirunavakkarasu, Mr. Ali Ahmed, Dr. Arafat A. Shabaneh, Mr. Luqman Saleh (from Photonic Lab and WIPNET), Ms. Aliffah Mustaffa (from Physics department, UPM) and last but not least Ms. Wafa'a Abd (from Chemistry department, UMP) for sharing their pearls of wisdom with me and their continuous support during this research journey. I would like to thank my dearest friend Mr. Ahmed Salah for his support may our friendship last forever. I would like to thank the Universiti Putra Malaysia especially the staffs of the Department of Computer and Communication Systems Engineering for their continuing support.

AHMED LATEEF KHALAF

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 Hanif Yaacob, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

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

Nor Azah Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Janet Lim Hong Ngee, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Suriati Paiman, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

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

Date:

Declaration by Members of Supervisory Committee

This is to confirm that:
- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ______________________
Name of Chairman
of Supervisory
Committee: Dr. Mohd Hanif Yaacob

Signature: ______________________
Name of Member
of Supervisory
Committee: Prof. Dr. Mohd Adzir Mahdi

Signature: ______________________
Name of Member
of Supervisory
Committee: Prof. Dr. Nor Azah Yusof

Signature: ______________________
Name of Member
of Supervisory
Committee: Assoc. Prof. Dr. Janet Lim Hong Ngee

Signature: ______________________
Name of Member
of Supervisory
Committee: Dr. Suriati Paiman

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
Al_2O_3	Aluminum oxide
APS	Ammonium peroxydisulfate
Ar	Argon
Au	Gold
BCB	Bromocresol purple
C	Carbon
C_2H_5OH	Ethanol
CH_4	Methane
CNT	Carbon nanotube
CO_2	Carbon dioxide
COOH	Carbolic acid groups
CSA	Camphorsulfonic acid
Cu	Copper
CuO	Copper oxide
DC	Direct current
EDX	Energy Dispersive X-Ray Spectroscopy
EMI	Electromagnetic interference
GO	Graphene oxide
H_2	Hydrogen
HCl	Hydrochloric acid
HF	Hydrofluoric acid
ITO	Indium tin oxide
MWCNT	Multi walled carbon nanotube
NA	Numerical aperture
NAP	Nano-Analytical Platform
NH_3	Ammonia
NIR	Near Infrared
O	Oxygen
OSHA	Occupational safety and health administration
PANI	Polyaniline
Pd	Palladium
PLD	Pulsed laser deposition
PMMA	Polymethyl methacrylate
POF	Plastic optical fiber
Pt	Platinum
RF	Radio frequency
RI	Refractive index
SEM	Scanning Electron Microscopy
SiO_2	Silicon dioxide
SnO_2	Tin oxide
SOF	Silica optical fiber
SPPOF	Side-polished plastic optical fiber
SWCNT	Single walled carbon nanotube

TiO_2	Titanium dioxide
TIR	Total internal reflection
UCPOF	Uncladded plastic optical fiber
UMP	Universiti Malaysia Pahang
V_2O_5	Vanadium(V) oxide
V_7O_{16}	Vanadium(V) oxide
VOC	Volatile organic compound
W	Tungsten
WO_3	Tungsten trioxide
XRD	X-Ray Diffraction
YSZ	Yttria-stabilized zirconia
ZnO	Zinc oxide

CHAPTER 1

INTRODUCTION

This chapter presents an overview on the research conducted by the author. Section 1.1 presents a background on optical fibers, with a focus on the importance of their use in chemical sensing applications. The motivation behind the research is discussed in the same section, which explains how the problem statements are formed as a result of the limitations found in conventional chemical sensors. Section 1.2 reviews the advances in optical sensors integrated with nanostructured coatings. Section 1.3 presents the problem statements. Section 1.4 discusses the research objectives and research questions. Finally, Sections 1.5 and 1.6 present the research scope and thesis organization, respectively.

1.1 Research Background and Motivations

Air and liquid pollutants are ubiquitous in daily human activities, such as agriculture, food processing, industrial coolants, and household detergents. Two important chemicals for industrial applications are ammonia (NH_3) and ethanol. Advanced NH_3 gas and ethanol liquid real-time sensing methods have been continuously developed over the past few decades because of their high toxicity and wide use in many fields. Thus, it is critical to develop highly sensitive and reliable sensors to measure these chemicals in their applications and to prevent safety hazards.

NH_3 is a natural gas that exists in the earth atmosphere. This natural gas is colorless flammable gas with strong odor and is commonly produced from various sources, such as chemical plants, livestock farming, and motor vehicles [1]. The world market production of NH_3 is estimated to grow at an average rate of 3.5% in 2017, with a global capacity of approximately 198 million tons, which leads to revenues of approximately one hundred billion US dollar [2, 3].

NH_3 is an irritant gas, and its permissible exposure limit is 35 ppm according to occupational safety and health administration (OSHA) [4]. The inhalation of large quantities of NH_3 can cause harmful effects on human health, such as eye irritation, pulmonary edema, and respiratory arrest [5]. Recently, in India, five people were killed and over 140 others complained of breathing problems and eye irritation after they inhaled large amounts of NH_3 gas that leaked from an NH_3 gas tanker. The leakage of gas also can lead to the death of plants and animals within 4 km radius [6]. Therefore, NH_3 concentrations should be monitored using reliable and low cost sensors that can be operated at room temperature to prevent environmental pollution risks and comply with the safety regulations.

Ethanol is a volatile organic compound (VOC) that is commonly used in the food, beverage, fuel and pharmaceutical industries [7, 8]. The ethanol production has risen substantially over the past decade as a result of the rise in demand for ethanol blend fuels. A report indicated that 14.7 billion gallons of ethanol was transported in the United States of America (USA) either by rail or barges from production facilities in 2015 [9]. Ethanol is currently considered one of the largest volume hazardous materials shipped by rail in the USA aside from crude oil and chlorine [10, 11]. Figure 1.1 shows the increase in production volume of ethanol in the USA from 2000 to 2012. One of the major concerns is ethanol leakage or spills during transportation or storage. Liquid ethanol is flammable, with a lower explosive limit to an upper explosive limit range of 3.3% – 19% [12]. In addition, ethanol is colorless and is completely miscible in water. Eleven major spills were reported in the USA from 2006 to 2010, which mostly resulted in water contamination [12]. Exposure to high concentrations of ethanol may cause irritation to the skin and inflammation of the nasal mucous membrane. Therefore, ethanol detection in a liquid medium is crucial for the quality control of food, beverages and medicines [13, 14].

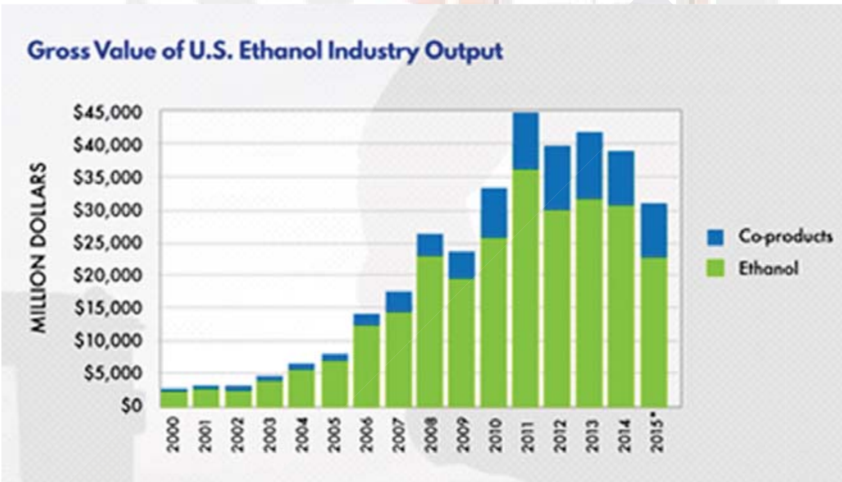

Figure 1.1: Ethanol production from 2000 to 2015 [12].

A wide range of real-time approaches have been developed for sensing applications, such as liquid chromatography and mass spectrometry, to meet such an ever-increasing demand [15]. However, despite their good selectivity, these approaches suffer from limitations that include high cost and bulky size. Meanwhile, low cost conductometric and electrochemical sensors attain high sensitivity in chemical sensing applications [16, 17]. However, these sensors are limited by several drawbacks, such as poor selectivity, high power consumption, and susceptibility to electromagnetic interference (EMI), which restrict their use in practical application. In addition, all the aforementioned sensors require an elevated working temperature (> 300 °C) and several mechanical moving elements, thereby leading to implementation difficulties for remote sensing applications. Thus, to overcome these drawbacks, optical fibers have been explored as an alternative to the conventional chemical sensors owing to their numerous advantages. Optical fiber sensors are easily integrated into optical networks and telecommunications systems with the added capability of distributed and remote sensing. The introduction of chemical based optical fiber sensors in the last few decades has gained great attention because of their micro-sized, immunity to EMI, and their capability to work in harsh environments [18]. Since then, optical fiber based chemical sensors have been adopted in various applications and enormous efforts have been made to enhance their performance.

1.2 Optical Fiber Sensor with Nanostructured Sensing Enhancements

Optical fiber sensors have gained much popularity and market acceptance in recent years due to the number of advantages compared with their electrical counterparts. These advantages include miniaturization, flexibility, and immunity to EMI in addition to their capability to operate in hostile environments, such as high temperature or chemically reactive surroundings [19]. Optical fibers are also inert, passive, and electrically nonconductive. As a result, optical fiber is safe to be used near flammable or explosive materials, such as in the oil and gas industries [20].

The recent advances in optical sensing with nanostructured material enhancements are making a significant impact on the direction of future sensor technology. The rapid progress in nanofabrication methods and nanoparticle synthesis is leading to the development of various new nanostructured materials with unique physical and chemical properties. Nanostructures are materials that have at least one dimension in nanoscale range, which is less than 100 nm [21]. These materials are particularly suitable for chemical and biological sensing applications owing to the fact that many of the reactions occur in nanoscale [22].

When materials are reduced to nanoscale dimensions, they reveal new and unique properties such high surface-to-volume ratio, high heat capacity, mechanical strength, and changes in magnetic behavior. Distinctive changes in optical properties include reflectivity, absorbance, and luminescence [23].

Optical sensors with nanostructured enhancements are new and an interesting path for developing chemical sensors. Integration of nanostructured material thin films on optical transducing platforms has demonstrated improvements in sensing performance. The optical techniques generally employed to measure response in chemical sensing applications are based on reflectance, absorbance, fluorescence, surface plasmon resonance, and luminescence changes, which are caused by the interaction between the nanostructured coatings and diverse chemical molecules [24].

1.3 Problem Statement

Most of chemical sensors are electrical based. The main reason electrical sensors are widely used is due to their high sensitivity and low cost. Nonetheless, these sensors suffer from poor selectivity and limited deployment in a volatile environment, especially where high risk of explosion or proneness to EMI is expected. Dangerous chemicals, such as NH_3 gas and ethanol liquid, are highly toxic and flammable. The limitations of electrical sensors to detect these chemicals can be addressed with the use of optical transducers, such as optical fiber.

Common optical fiber sensors are based on glass or silicon dioxide (SiO_2) material. Glass sensor is highly deployed in optical communications because of its high temperature and low cost. Nevertheless, its high fragility owing to small waist diameter ($<$100 µm) and the complexity in its modification can restrict the platform deployment in sensing applications.

Plastic optical fiber (POF) offers numerous advantages, including low cost, ease of manipulation, and high degree of flexibility [25]. In optical fiber chemical sensors, strong interaction between the sensing layer and light propagates in the fiber core is highly required to improve their sensitivity. This can be achieved by modifying the POF through removing part of the fiber structure via a simple mechanical polishing technique and coating it with an active sensing layer. Changes in the optical, physical, and chemical properties may occur as a result of the interaction between the analyte molecules and the sensing layer coated on the exposed area of the optical fiber.

Most of the sensing layers deployed in chemical detection during the last decades are dominantly based on thick films (approximately more than 10 µm). Nevertheless, the advancement of nanotechnology provides opportunity to integrate sensing materials at nanoscale with transducing platforms. Nanostructured materials have numerous advantages that include large surface-to-volume ratio, high specific surface area, and several surface active sites [26, 27]. Recent studies have identified that the use of nanostructured material as active sensing layer can improve the chemical sensing performance with regard to sensitivity, selectivity, and response time in comparison with thick film sensing layers [28].

Remote sensing using optical fibers has attracted great attention in many applications in recent years because of the distinctive features of these optical fibers that make them efficient candidate for applications in harsh and combustible environments [29]. Moreover, the telemetry channel based on optical fiber is immune to EMI in addition to its capability to avoid reflections from natural and artificial obstacles and bad weather interruptions [30]. Generally, the main concept of optical fiber remote sensing is to continuously observe a structure from a central station located away from the sensor critical site without the need for electrical power feeds in the remote locations. Thus, optical fiber remote sensor allows instant hazard detection as compared with the currently used electrical remote sensor that suffers from complexity and slow response times [31]. Apart from that, the use of optical fiber remote sensing for chemical sensing applications remains in its infancy stage.

1.4 Research Objectives and Questions

The aim of this research is to design and fabricate SPPOF for chemicals detection by integrating nanostructured materials as sensing layer. The objectives to achieve this include:

1. To fabricate and characterize side-polished POF (SPPOF) for NH_3 and ethanol sensing.
2. To synthesis and deposit the nanomaterial onto the polished sensing area.
3. To investigate and relate the micro-nano characteristics of the nanomaterials and their influence on the optical sensor's performance.
4. To analyze and evaluate the optical sensing performance of the developed in-situ and remote SPPOF sensors towards NH_3 and ethanol at room temperature.
5. To propose and explain the chemical sensing mechanism of all the developed novel optical fiber sensors.

To achieve these objectives, the following research questions are outlined:

1. What sensing layers are suitable to be used in order to obtain a response to NH_3 and ethanol?
2. What are the suitable synthesis and deposition methods accessible to coat nanomaterials onto optical fibers?
3. What are the optimized dimensions of the SPPOF as chemical sensor?
4. How different are the sensing performances of side-polished optical fiber sensors coated with various nanostructured sensing layers?
5. How to understand the nature of interaction between the target chemical and the sensing layer?

Based on the research questions, the research project focused on developing SPPOF as a chemical sensor and investigating suitable nanostructured materials that would enhance the performance of the optical sensor toward NH_3 gas and ethanol liquid detection. The author developed an SPPOF-assisted chemical sensor coated with nanostructured sensing layers of gold (Au)/tungsten oxide (WO_3), graphene oxide (GO) and carbon nanotubes (CNT) in addition to aluminum oxide (Al_2O_3)/polyaniline (PANI) and graphene/PANI nanocomposites. The nanostructured materials were deposited on the proposed optical fibers by use of drop-casting and radio frequency (RF)-sputtering techniques to analyze their sensing performance.

1.5 Research Scope

This research project covers the development of opto-chemical sensor starting from materials leading to optical devices. The scope of the project can be best explained with the tree diagram in Figure 1.2. The solid lines represent the direction followed in this thesis to achieve the goal and objectives of the work, while the dotted lines refer to other research areas that are out of the scope of this work. The highlighted boxes represent the elements deployed to achieve the research objectives proposed for the development of optical fiber chemical sensor.

1.6 Thesis Organization

This thesis is divided into six chapters. Chapter 1 presents an overview of the research area, focusing on the problems that motivated this work. In addition, this chapter demonstrates the problem statements, aim and objectives of the research. Chapter 2 indicates a comprehensive review on the optical fiber types and properties and the principles of optical measurement. A critical review on optical fiber sensors used for chemical applications is also discussed in this chapter. The nanostructured materials utilized in this PhD work are included, and their properties and applications are discussed. The reported research, most relevant to this project, is critically reviewed, showing the trade off in the performance of these works. Chapter 3 gives the full description for the fabrication and design of SPPOF and uncladded POF (UCPOF) sensors. The nanostructured material synthesis and deposition are also presented and discussed, followed by the testing setup for the developed optical fiber sensors. Chapter 4 provides the characterization results of the nanostructures deposited on SPPOF and UCPOF. Chapter 5 discusses the sensing results obtained from the SPPOF and UCPOF sensors performance integrated with nanostructured materials toward NH_3 and ethanol. The effect of the morphology of the nanostructured materials on the sensor responses toward different concentrations of NH_3 and ethanol is elucidated. The performance of the remote sensing of SPPOF is discussed and configured for different nanomaterial coatings. This chapter also discusses the sensor performance in terms of sensitivity, selectivity, repeatability, and response and recovery times. The optical sensing mechanisms for NH_3 gas and ethanol liquid interaction with different nanomaterials are explained. Chapter 6 concludes the thesis and presents a list of contributions of this work. Potential ideas to be pursued as future works are also suggested.

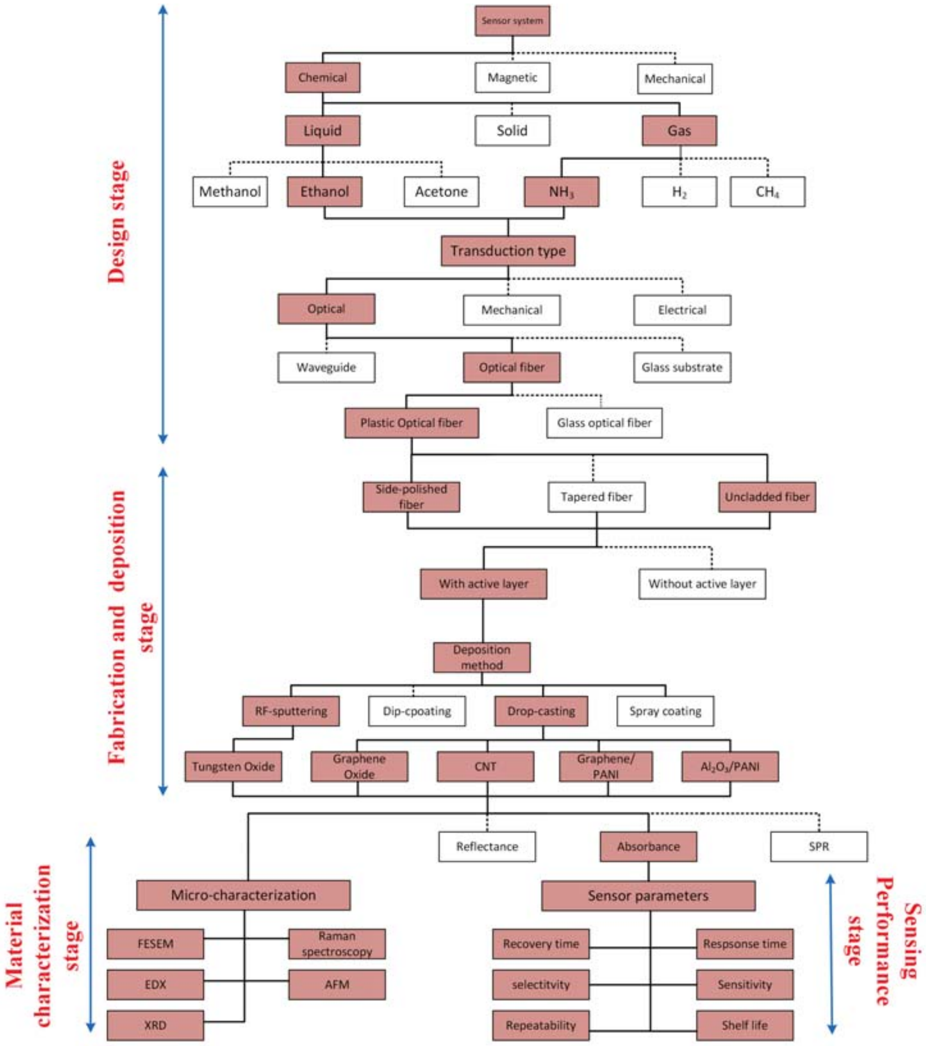

Figure 1.2: Study scope.

REFERENCES

[1] D.-Q. Wu, L.-L. Wu, H.-C. Cui, H.-N. Zhang, and J.-Y. Yu, “A rapid ammonia sensor based on lysine nanogel-sensitized PANI/PAN nanofibers,” *Journal of Materials Chemistry B*, vol. 4, no. 8, pp. 1520–1527, 2016.

[2] “Ammonia: 2017 world market outlook and forecast up to 2021.” [Online]. Available: https://mcgroup.co.uk/researches/ammonia, (accessed 18 Feb 2017).

[3] “Market study: Ammonia.” [Online]. Available: http://www.ceresana.com/en/market-studies/chemicals/ammonia/, (accessed 17 Feb 2017).

[4] A. J. Kulandaisamy, J. R. Reddy, P. Srinivasan, K. J. Babu, G. K. Mani, P. Shankar, and J. B. B. Rayappan, “Room temperature ammonia sensing properties of ZnO thin films grown by spray pyrolysis: Effect of Mg doping,” *Journal of Alloys and Compounds*, vol. 688, pp. 422–429, 2016.

[5] A. Pathak, S. K. Mishra, and B. D. Gupta, “Fiber-optic ammonia sensor using Ag/SnO_2 thin films: optimization of thickness of SnO_2 film using electric field distribution and reaction factor,” *Applied Optics*, vol. 54, no. 29, pp. 8712–8721, 2015.

[6] “Five dead, 100 injured in punjab ammonia gas tanker leak.” [Online]. Available: http://timesofindia.indiatimes.com/india/Five-dead-100-injured-in-Punjab-ammonia-gas-tanker-leak/articleshow/47651388.cms, (accessed 11 Nov 2016).

[7] P. Hu, G. Du, W. Zhou, J. Cui, J. Lin, H. Liu, D. Liu, J. Wang, and S. Chen, “Enhancement of ethanol vapor sensing of TiO_2 nanobelts by surface engineering,” *ACS Applied Materials & Interfaces*, vol. 2, no. 11, pp. 3263–3269, 2010.

[8] C. Elosua, I. R. Matias, C. Bariain, and F. J. Arregui, “Volatile organic compound optical fiber sensors: A review,” *Sensors*, vol. 6, no. 11, pp. 1440–1465, 2006. sensors-06-01440[PII] Sensors (Basel).

[9] “2016 ethanol industry outlook,” tech. rep., Renewable Fuels Foundation, 2016.

[10] “Safe rail transport of crude oil,” tech. rep., California Senate Committee on Energy, Utilities and Communications, 2014.

[11] “Hazardous materials rail shipments,” tech. rep., United States Government Accountability Offic, 2016.

[12] “Large volume ethanol spills- environmental impacts and response options,” tech. rep., Shaws Infrastructure and Environmental Group, 2011.

[13] S. B. Khan, M. M. Rahman, K. Akhtar, A. M. Asiri, J. Seo, H. Han, and K. Alamry, “Novel and sensitive ethanol chemi-sensor based on nanohybrid materials,” *Int J Electrochem. Sc*, vol. 7, pp. 4030–4038, 2012.

[14] Alpat and A. Telefoncu, “Development of an alcohol dehydrogenase biosensor for ethanol determination with toluidine blue O covalently attached to a cellulose acetate modified electrode,” *Sensors*, vol. 10, no. 1, p. 748, 2010.

[15] T. Buttler, L. Gorton, H. Jarskog, G. MarkoVarga, B. HahnHäGerdal, N. Meinander, and L. Olsson, “Monitoring of ethanol during fermentation of a lignocellulose hydrolysate by on–line microdialysis sampling, column liquid chromatography, and an alcohol biosensor,” *Biotechnology and bioengineering*, vol. 44, no. 3, pp. 322–328, 1994.

[16] B. Tao, J. Zhang, S. Hui, and L. Wan, “An amperometric ethanol sensor based on a Pd–Ni/SiNWs electrode,” *Sensors and Actuators B: Chemical*, vol. 142, no. 1, pp. 298–303, 2009.

[17] G. Neri, A. Bonavita, G. Micali, N. Donato, F. Deorsola, P. Mossino, I. Amato, and B. De Benedetti, “Ethanol sensors based on Pt-doped tin oxide nanopowders synthesised by gel-combustion,” *Sensors and Actuators B: Chemical*, vol. 117, no. 1, pp. 196–204, 2006.

[18] C. R. Zamarreno, I. R. Matias, and F. J. Arregui, “Nanofabrication techniques applied to the development of novel optical fiber sensors based on nanostructured coatings,” *IEEE Sensors Journal*, vol. 12, no. 8, pp. 2699–2710, 2012.

[19] J. BelBruno, “Nanomaterials in sensors,” *Nanomaterials*, vol. 3, no. 4, p. 572, 2013.

[20] B. D. Gupta and R. K. Verma, “Surface plasmon resonance-based fiber optic sensors: principle, probe designs, and some applications,” *Journal of sensors*, vol. 2009, 2009.

[21] D. R. Boverhof, C. M. Bramante, J. H. Butala, S. F. Clancy, M. Lafranconi, J. West, and S. C. Gordon, “Comparative assessment of nanomaterial definitions and safety evaluation considerations,” *Regulatory Toxicology and Pharmacology*, vol. 73, no. 1, pp. 137–150, 2015.

[22] S. Chaturvedi, P. N. Dave, and N. K. Shah, “Applications of nano-catalyst in new era,” *Journal of Saudi Chemical Society*, vol. 16, no. 3, pp. 307–325, 2012.

[23] K. Kalantar-zadeh and B. Fry, *Nanotechnology-enabled sensors*. Springer Science & Business Media, 2007.

[24] B. Gupta, A. Shrivastav, and S. Usha, “Surface plasmon resonance-based fiber optic sensors utilizing molecular imprinting,” *Sensors*, vol. 16, no. 9, p. 1381, 2016.

[25] L. Bilro, N. Alberto, J. L. Pinto, and R. Nogueira, “Optical sensors based on plastic fibers,” *Sensors*, vol. 12, no. 9, p. 12184, 2012.

[26] M. R. Alenezi, S. J. Henley, N. G. Emerson, and S. R. P. Silva, “From 1D and 2D ZnO nanostructures to 3D hierarchical structures with enhanced gas sensing properties,” *Nanoscale*, vol. 6, no. 1, pp. 235–247, 2014.

[27] X. Liu, J. Zhang, S. Wu, D. Yang, P. Liu, H. Zhang, S. Wang, X. Yao, G. Zhu, and H. Zhao, "Single crystal -Fe_2O_3 with exposed 104 facets for high performance gas sensor applications," *RSC Advances*, vol. 2, no. 15, pp. 6178–6184, 2012.

[28] J. Zhang, X. Liu, G. Neri, and N. Pinna, "Nanostructured materials for room–temperature gas sensors," *Advanced Materials*, vol. 28, no. 5, pp. 795–831, 2016.

[29] G. Rajan, *Optical fiber sensors: advanced techniques and applications*, vol. 36. CRC press, 2015.

[30] M. Fernandez-Vallejo and M. Lopez-Amo, "Optical fiber networks for remote fiber optic sensors," *Sensors*, vol. 12, no. 4, pp. 3929–3951, 2012.

[31] C.-l. Wei, C.-c. Lai, S.-y. Liu, W. Chung, T. K. Ho, H.-y. Tam, S. Ho, A. McCusker, J. Kam, and K. Lee, "A fiber bragg grating sensor system for train axle counting," *IEEE Sensors Journal*, vol. 10, no. 12, pp. 1905–1912, 2010.

[32] C. Liu, H. Tai, P. Zhang, Z. Ye, Y. Su, and Y. Jiang, "Enhanced ammonia-sensing properties of PANI-TiO_2-Au ternary self-assembly nanocomposite thin film at room temperature," *Sensors and Actuators B: Chemical*, vol. 246, pp. 85 – 95, 2017.

[33] "Ammonia." [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/compound/222 (accessed July 17, 2017).

[34] A. Kumar, A. Sanger, A. Kumar, and R. Chandra, "Fast response ammonia sensors based on TiO_2 and NiO nanostructured bilayer thin films," *RSC Adv.*, vol. 6, pp. 77636–77643, 2016.

[35] J. Huotari, J. Lappalainen, J. Eriksson, R. Bjorklund, E. Heinonen, I. Miinalainen, J. Puustinen, and A. L. Spetz, "Synthesis of nanostructured solid-state phases of V_7O_{16} and V_2O_5 compounds for ppb-level detection of ammonia," *Journal of Alloys and Compounds*, vol. 675, pp. 433 – 440, 2016.

[36] C. Wang, X. Li, F. Xia, H. Zhang, and J. Xiao, "Effect of V_2O_5-content on electrode catalytic layer morphology and mixed potential ammonia sensor performance," *Sensors and Actuators B: Chemical*, vol. 223, pp. 658 – 663, 2016.

[37] Z. Zhu, C.-T. Kao, and R.-J. Wu, "A highly sensitive ethanol sensor based on Ag@ TiO_2 nanoparticles at room temperature," *Applied Surface Science*, vol. 320, pp. 348–355, 2014.

[38] A. S. Zoolfakar, M. Z. Ahmad, R. A. Rani, J. Z. Ou, S. Balendhran, S. Zhuiykov, K. Latham, W. Wlodarski, and K. Kalantar-zadeh, "Nanostructured copper oxides as ethanol vapour sensors," *Sensors and Actuators B: Chemical*, vol. 185, pp. 620 – 627, 2013.

[39] D. T. Dimitrov, N. K. Nikolaev, K. I. Papazova, L. K. Krasteva, I. A. Pronin, I. A. Averin, A. S. Bojinova, A. T. Georgieva, N. D. Yakushova, T. V. Peshkova, A. A. Karmanov, N. V. Kaneva, and V. A. Moshnikov, "Investigation of the electrical and ethanol-vapour sensing properties of the junctions based on ZnO nanostructured

thin film doped with copper," *Applied Surface Science*, vol. 392, pp. 95 – 108, 2017.

[40] K. C. Kao and G. A. Hockham, "Dielectric-fibre surface waveguides for optical frequencies," *Electrical Engineers, Proceedings of the Institution of*, vol. 113, no. 7, pp. 1151–1158, 1966.

[41] C. DeCusatis and C. J. S. DeCusatis, *Fiber optic essentials*. Academic Press, 2010.

[42] K. T. V. Grattan and T. Sun, "Fiber optic sensor technology: an overview," *Sensors and Actuators A: Physical*, vol. 82, no. 1–3, pp. 40–61, 2000.

[43] Y. Jin and A. Granville, "Polymer fiber optic sensors—a mini review of their synthesis and applications," *J. Biosens. Bioelectron*, vol. 7, p. 194, 2016.

[44] N. Cennamo, D. Massarotti, R. Galatus, L. Conte, and L. Zeni, "Performance comparison of two sensors based on surface plasmon resonance in a plastic optical fiber," *Sensors*, vol. 13, no. 1, pp. 721–735, 2013.

[45] J. Zubia and J. Arrue, "Plastic optical fibers: An introduction to their technological processes and applications," *Optical Fiber Technology*, vol. 7, no. 2, pp. 101–140, 2001.

[46] N. Zhong, Q. Liao, X. Zhu, M. Zhao, Y. Huang, and R. Chen, "Temperature-independent polymer optical fiber evanescent wave sensor," *Scientific Reports*, vol. 5, p. 11508, 2015.

[47] M. Pospíšilová, G. Kuncová, and J. Trögl, "Fiber-optic chemical sensors and fiber-optic bio-sensors," *Sensors*, vol. 15, no. 10, p. 25208, 2015.

[48] A. Apelsmeier, B. Schmauss, and M. Shamonin, "Compensation of parasitic losses in an extrinsic fiber-optic temperature sensor based on intensity measurement," *Sensors and Actuators A: Physical*, vol. 173, no. 1, pp. 49–54, 2012.

[49] S. Poeggel, D. Tosi, G. Leen, and E. Lewis, "Low-cost miniature fiber optic extrinsic Fabry-Perot interferometric sensor for cardiovascular pressure measurement," in *Lasers and Electro-Optics Europe (CLEO EUROPE/IQEC), 2013 Conference on and International Quantum Electronics Conference*, pp. 1–1.

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

[51] S. Chong, A. Aziz, and S. Harun, "Fibre optic sensors for selected wastewater characteristics," *Sensors*, vol. 13, no. 7, p. 8640, 2013.

[52] P. C. A. Jerónimo, A. N. Araújo, and M. Conceição B.S.M. Montenegro, "Optical sensors and biosensors based on sol–gel films," *Talanta*, vol. 72, no. 1, pp. 13–27, 2007.

[53] K. Lim, L. Wong, W. K. Chiu, and J. Kodikara, "Distributed fiber optic sensors for monitoring pressure and stiffness changes in out-of-round pipes," *Structural Control and Health Monitoring*, vol. 23, no. 2, pp. 303–314, 2016.

[54] G. Liu, M. Han, and W. Hou, "High-resolution and fast-response fiber-optic temperature sensor using silicon Fabry-Pérot cavity," *Optics Express*, vol. 23, no. 6, pp. 7237–7247, 2015.

[55] E. Schena, D. Tosi, P. Saccomandi, E. Lewis, and T. Kim, "Fiber optic sensors for temperature monitoring during thermal treatments: An overview," *Sensors*, vol. 16, no. 7, p. 1144, 2016.

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

[57] X.-d. Wang and O. S. Wolfbeis, "Fiber-optic chemical sensors and biosensors (2013–2015)," *Analytical Chemistry*, vol. 88, no. 1, pp. 203–227, 2016.

[58] A. B. Forouzan, *Data communications & networking (sie)*. Tata McGraw-Hill Education, 2006.

[59] Z. Qiang, L. Junyang, Y. Yanling, G. Libo, and X. Chenyang, "Micro double tapered optical fiber sensors based on the evanescent field-effect and surface modification," *Optik - International Journal for Light and Electron Optics*, vol. 125, no. 17, pp. 4614–4617, 2014.

[60] A. Leung, P. M. Shankar, and R. Mutharasan, "A review of fiber-optic biosensors," *Sensors and Actuators B: Chemical*, vol. 125, no. 2, pp. 688–703, 2007.

[61] H. Saad, M. T. Ali, and M. K. Abd-Rahman, "High sensitivity optical POF sensor for detecting low ethanol concentration in water," *Advanced Materials Research*, vol. 1107, 2015.

[62] F. B. Xiong, W. Z. Zhu, X. G. Meng, H. F. Lin, X. H. Huang, and Y. Q. Huang, "Monitor light water concentration in deuterium oxide by evanescent absorption sensor," *Optik - International Journal for Light and Electron Optics*, vol. 124, no. 15, pp. 2008–2012, 2013.

[63] S. K. Mishra, S. Bhardwaj, and B. D. Gupta, "Surface plasmon resonance-based fiber optic sensor for the detection of low concentrations of ammonia gas," *IEEE Sensors Journal*, vol. 15, no. 2, pp. 1235–1239, 2015.

[64] H. Zhang, A. Kulkarni, H. Kim, D. Woo, Y.-J. Kim, B. H. Hong, J.-B. Choi, and T. Kim, "Detection of acetone vapor using graphene on polymer optical fiber," *Journal of nanoscience and nanotechnology*, vol. 11, no. 7, pp. 5939–5943, 2011.

[65] A. Bueno, D. Lahem, C. Caucheteur, and M. Debliquy, "Reversible NO_2 optical fiber chemical sensor based on $LuPc_2$ using simultaneous transmission of UV and visible light," *Sensors*, vol. 15, no. 5, pp. 9870–9881, 2015.

[66] J. Ou, M. Yaacob, J. Campbell, M. Breedon, K. Kalantar-Zadeh, and W. Wlodarski, “H_2 sensing performance of optical fiber coated with nano-platelet WO_3 film,” *Sensors and Actuators B: Chemical*, vol. 166, pp. 1–6, 2012.

[67] Z. Yanaz, H. Filik, and R. Apak, “Development of an optical fibre reflectance sensor for lead detection based on immobilised arsenazo iii,” *Sensors and Actuators B: Chemical*, vol. 147, no. 1, pp. 15–22, 2010.

[68] E. Maciak, P. Sufa, and A. Stolarczyk, “A low temperature operated NO_2 gas POF sensor based on conducting graft polymer,” *Photonics Letters of Poland*, vol. 6, no. 4, pp. pp. 124–126, 2014.

[69] J. Dai, M. Yang, X. Yu, K. Cao, and J. Liao, “Greatly etched fiber Bragg grating hydrogen sensor with Pd/Ni composite film as sensing material,” *Sensors and Actuators B: Chemical*, vol. 174, pp. 253 – 257, 2012.

[70] S. Sridevi, K. Vasu, N. Bhat, S. Asokan, and A. Sood, “Ultra sensitive NO_2 gas detection using the reduced graphene oxide coated etched fiber Bragg gratings,” *Sensors and Actuators B: Chemical*, vol. 223, pp. 481–486, 2016.

[71] P. Arasu, A. Noor, A. Khalaf, and M. Yaacob, “Highly sensitive plastic optical fiber with palladium sensing layer for detection of hydrogen gas,” in *2016 IEEE Region 10 Symposium (TENSYMP)*, pp. 390–393, IEEE.

[72] A. Khalaf, P. Arasu, H. Lim, S. Paiman, N. Yusof, M. A. Mahdi, and M. H. Yaacob, “Modified plastic optical fiber with CNT and graphene oxide nanostructured coatings for ethanol liquid sensing,” *Opt. Express*, vol. 25, pp. 5509–5520, Mar 2017.

[73] Y. Xu, P. Lu, L. Chen, and X. Bao, “Recent developments in micro-structured fiber optic sensors,” *Fibers*, vol. 5, no. 1, p. 3, 2017.

[74] E. Angelini, S. Grassini, D. Mombello, A. Neri, M. Parvis, and G. Perrone, “Plasma modified POF sensors for in situ environmental monitoring of museum indoor environments,” *Applied Physics A*, vol. 100, no. 3, pp. 975–980, 2010.

[75] R. Cartotto, *Chemical Burns*, pp. 201–210. Cham: Springer International Publishing, 2016.

[76] S. H. Girei, A. A. Shabaneh, H. M. Lim, N. H. Huang, M. A. Mahdi, and M. H. Yaacob, “Absorbance response of graphene oxide coated on tapered multimode optical fiber towards liquid ethanol,” *Journal of the European Optical Society-Rapid publications*, vol. 10, 2015.

[77] A. Aziz, H. Lim, S. Girei, M. Yaacob, M. Mahdi, N. Huang, and A. Pandikumar, “Silver/graphene nanocomposite-modified optical fiber sensor platform for ethanol detection in water medium,” *Sensors and Actuators B: Chemical*, vol. 206, pp. 119–125, 2015.

[78] S. Guo and S. Albin, “Transmission property and evanescent wave absorption of cladded multimode fiber tapers,” *Optics Express*, vol. 11, no. 3, pp. 215–223, 2003.

[79] W. Jin, H. Ho, Y. Cao, J. Ju, and L. Qi, "Gas detection with micro-and nano-engineered optical fibers," *Optical Fiber Technology*, vol. 19, no. 6, pp. 741–759, 2013.

[80] M. Yasin, S. W. Harun, and H. Arof, "Recent progress in optical fiber research," 2011.

[81] M. R. R. Khan and S.-W. Kang, "A high sensitivity and wide dynamic range fiber-optic sensor for low-concentration VOC gas detection," *Sensors*, vol. 14, no. 12, pp. 23321–23336, 2014.

[82] Y. Wu, B. Yao, X. Cao, Z. Wang, Y. Rao, Y. Chen, and K. S. Chiang, "Highly sensitive chemical gas sensor based on graphene deposited D-shaped-fiber," in *Lasers and Electro-Optics (CLEO), 2015 Conference on*, pp. 1–2, IEEE.

[83] A. Patnaik, K. Senthilnathan, and R. Jha, "Graphene-based conducting metal oxide coated D-shaped optical fiber SPR sensor," *IEEE Photonics Technology Letters*, vol. 27, no. 23, pp. 2437–2440, 2015.

[84] T. Chen, C. Liao, D. Wang, and Y. Wang, "Passively mode-locked fiber laser by using monolayer chemical vapor deposition of graphene on D-shaped fiber," *Applied optics*, vol. 53, no. 13, pp. 2828–2832, 2014.

[85] B. Lee and T. Chung, *Overview of Micro-and Nano-Structured Surface Plasmon Resonance Fiber Sensors*, pp. 335–354. Springer, 2015.

[86] G. Liu and D. Feng, "Evanescent wave analysis and experimental realization of refractive index sensor based on D-shaped plastic optical fiber," *Optik - International Journal for Light and Electron Optics*, vol. 127, no. 2, pp. 690–693, 2016.

[87] Z. L. Poole, P. R. Ohodnicki, A. Yan, Y. Lin, and K. P. Chen, "The potential to detect hydrogen concentration gradients with palladium infused mesoporous-titania on D-shaped optical fiber," *ACS Sensors*, 2016.

[88] N. Cennamo, G. D'Agostino, A. Donà, G. Dacarro, P. Pallavicini, M. Pesavento, and L. Zeni, "Localized surface plasmon resonance with five-branched gold nanostars in a plastic optical fiber for bio-chemical sensor implementation," *Sensors*, vol. 13, no. 11, pp. 14676–14686, 2013.

[89] C.-L. Tien, H.-W. Chen, W.-F. Liu, S.-S. Jyu, S.-W. Lin, and Y.-S. Lin, "Hydrogen sensor based on side-polished fiber Bragg gratings coated with thin palladium film," *Thin Solid Films*, vol. 516, no. 16, pp. 5360–5363, 2008.

[90] H. Gan, H. Gan, J. Zhang, Z. Chen, J. Tang, Y. Luo, J. Yu, Z. Zang, and H. Lu, "High sensitivity side-polished multimode fiber based refractometer," in *OFS2014 23rd International Conference on Optical Fiber Sensors*, pp. 91571W–91571W, International Society for Optics and Photonics, 2014.

[91] F. Sequeira, L. Bilro, A. Rudnitskaya, M. Pesavento, L. Zeni, and N. Cennamo, "Optimization of an evanescent field sensor based on D-shaped plastic optical fiber for chemical and biochemical sensing," *Procedia Engineering*, vol. 168, pp. 810 – 813, 2016. Proceedings of the 30th anniversary Eurosensors Conference – Eurosensors 2016, 4-7. Sepember 2016, Budapest, Hungary.

[92] Y. Ying, G.-y. Si, F.-j. Luan, K. Xu, Y.-w. Qi, and H.-n. Li, "Recent research progress of optical fiber sensors based on D-shaped structure," *Optics & Laser Technology*, vol. 90, pp. 149–157, 2017.

[93] P. K. Jain, X. Huang, I. H. El-Sayed, and M. A. El-Sayed, "Noble metals on the nanoscale: optical and photothermal properties and some applications in imaging, sensing, biology, and medicine," *Accounts of chemical research*, vol. 41, no. 12, pp. 1578–1586, 2008.

[94] Y. Seekaew, D. Phokharatkul, A. Wisitsoraat, and C. Wongchoosuk, "Highly sensitive and selective room-temperature NO_2 gas sensor based on bilayer transferred chemical vapor deposited graphene," *Applied Surface Science*, vol. 404, pp. 357 – 363, 2017.

[95] V. Semwal, A. M. Shrivastav, R. Verma, and B. D. Gupta, "Surface plasmon resonance based fiber optic ethanol sensor using layers of silver/silicon/hydrogel entrapped with ADH/NAD," *Sensors and Actuators B: Chemical*, vol. 230, pp. 485 – 492, 2016.

[96] S. Noimark, R. J. Colchester, B. J. Blackburn, E. Z. Zhang, E. J. Alles, S. Ourselin, P. C. Beard, I. Papakonstantinou, I. P. Parkin, and A. E. Desjardins, "Carbon-nanotube–PDMS composite coatings on optical fibers for all-optical ultrasound imaging," *Advanced Functional Materials*, vol. 26, no. 46, pp. 8390–8396, 2016.

[97] P. Arasu, A. Noor, A. Shabaneh, M. Yaacob, H. Lim, and M. Mahdi, "Fiber Bragg grating assisted surface plasmon resonance sensor with graphene oxide sensing layer," *Optics Communications*, vol. 380, pp. 260 – 266, 2016.

[98] M. H. Yaacob, M. Z. Ahmad, A. Z. Sadek, J. Z. Ou, J. Campbell, K. Kalantar-zadeh, and W. Wlodarski, "Optical response of WO_3 nanostructured thin films sputtered on different transparent substrates towards hydrogen of low concentration," *Sensors and Actuators B: Chemical*, vol. 177, pp. 981 – 988, 2013.

[99] D. Liu, W. Han, A. K. Mallik, J. Yuan, C. Yu, G. Farrell, Y. Semenova, and Q. Wu, "High sensitivity sol-gel silica coated optical fiber sensor for detection of ammonia in water," *Optics express*, vol. 24, no. 21, pp. 24179–24187, 2016.

[100] M. Yang, Z. Yang, J. Dai, and D. Zhang, "Fiber optic hydrogen sensors with sol–gel WO_3 coatings," *Sensors and Actuators B: Chemical*, vol. 166, pp. 632–636, 2012.

[101] Y. Liu, X. Zhao, B. Cai, T. Pei, Y. Tong, Q. Tang, and Y. Liu, "Controllable fabrication of oriented micro/nanowire arrays of dibenzo-tetrathiafulvalene by a multiple drop-casting method," *Nanoscale*, vol. 6, pp. 1323–1328, 2014.

[102] S. Cong, F. Geng, and Z. Zhao, "Tungsten oxide materials for optoelectronic applications," *Advanced Materials*, vol. 28, no. 47, pp. 10518–10528, 2016.

[103] K. Huang, Q. Pan, F. Yang, S. Ni, X. Wei, and D. He, "Controllable synthesis of hexagonal WO_3 nanostructures and their application in lithium batteries," *Journal of Physics D: Applied Physics*, vol. 41, no. 15, p. 155417, 2008.

[104] C. H. Chen, T. Y. Tseng, and C. J. Hung, "Fabrication of flexible electrochromic devices based on tungsten trioxide nanobundles," in *2016 2nd International Conference on Intelligent Green Building and Smart Grid (IGBSG)*, pp. 1–6, June 2016.

[105] S. Fardindoost, F. Rahimi, R. Ghasempour, *et al.*, "Pd doped WO_3 films prepared by sol–gel process for hydrogen sensing," *International Journal of Hydrogen Energy*, vol. 35, no. 2, pp. 854–860, 2010.

[106] V. Kruefu, A. Wisitsoraat, A. Tuantranont, and S. Phanichphant, "Ultra-sensitive H_2S sensors based on hydrothermal/impregnation-made Ru-functionalized WO_3 nanorods," *Sensors and Actuators B: Chemical*, vol. 215, pp. 630–636, 2015.

[107] C.-H. Lin, S.-J. Chang, and T.-J. Hsueh, "A WO_3 nanoparticles NO gas sensor prepared by the hot-wire CVD," *IEEE Electron Device Letters*, 2017.

[108] M. U. Qadri, F. E. Annanouch, M. Aguiló, F. Díaz, J. F. Borull, M. C. Pujol, and E. Llobet, "Metal decorated WO_3 nanoneedles fabricated by aerosol assisted chemical vapor deposition for optical gas sensing," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 9, pp. 10125–10132, 2016.

[109] J. Chu, J. Lan, D. Lu, J. Ma, X. Wang, B. Wu, M. Gong, R. Zhang, and S. Xiong, "Facile fabrication of WO_3 crystalline nanoplate on FTO glass and their application in electrochromism," *Micro & Nano Letters*, vol. 11, no. 11, pp. 749–752, 2016.

[110] M. Qiu, P. Sun, L. Shen, K. Wang, S. Song, X. Yu, S. Tan, C. Zhao, and W. Mai, "WO_3 nanoflowers with excellent pseudo-capacitive performance and the capacitance contribution analysis," *Journal of Materials Chemistry A*, vol. 4, no. 19, pp. 7266–7273, 2016.

[111] Y. L. Wang, X. L. Wang, Y. H. Li, L. J. Fang, J. J. Zhao, X. L. Du, A. P. Chen, and H. Yang, "Controllable synthesis of hexagonal WO_3 nanoplates for efficient visible-light-driven photocatalytic oxygen production," *Chemistry–An Asian Journal*, 2016.

[112] A. Palla-Papavlu, M. Filipescu, C. W. Schneider, S. Antohe, P. M. Ossi, G. Radnóczi, M. Dinescu, A. Wokaun, and T. Lippert, "Direct laser deposition of nanostructured tungsten oxide for sensing applications," *Journal of Physics D: Applied Physics*, vol. 49, no. 20, p. 205101, 2016.

[113] M. Z. Ahmad, J. Kang, A. S. Zoolfakar, A. Z. Sadek, and W. Wlodarski, "Gas sensing studies of pulsed laser deposition deposited WO_3 nanorod based thin films," *Journal of nanoscience and nanotechnology*, vol. 13, no. 12, pp. 8315–8319, 2013.

[114] F. Amano, D. Li, and B. Ohtani, "Fabrication and photoelectrochemical property of tungsten (VI) oxide films with a flake-wall structure," *Chemical Communications*, vol. 46, no. 16, pp. 2769–2771, 2010.

[115] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, "Metal oxide gas sensors: sensitivity and influencing factors," *Sensors*, vol. 10, no. 3, pp. 2088–2106, 2010.

[116] K. Ito and T. Ohgami, "Hydrogen detection based on coloration of anodic tungsten oxide film," *Applied physics letters*, vol. 60, no. 8, pp. 938–940, 1992.

[117] Z. Li, M. Yang, J. Dai, G. Wang, C. Huang, J. Tang, W. Hu, H. Song, and P. Huang, "Optical fiber hydrogen sensor based on evaporated Pt/WO_3 film," *Sensors and Actuators B: Chemical*, vol. 206, pp. 564–569, 2015.

[118] Y. Okamoto and W. Brenner, *Organic semiconductors*. Reinhold Pub. Corp., 1964.

[119] G. Ćirić-Marjanović, "Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications," *Synthetic Metals*, vol. 177, pp. 1–47, 2013.

[120] P. Kunzo, P. Lobotka, M. Micusik, and E. Kovacova, "Palladium-free hydrogen sensor based on oxygen-plasma-treated polyaniline thin film," *Sensors and Actuators B: Chemical*, vol. 171, pp. 838–845, 2012.

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

[122] D. Verma and V. Dutta, "Role of novel microstructure of polyaniline-csa thin film in ammonia sensing at room temperature," *Sensors and Actuators B: Chemical*, vol. 134, no. 2, pp. 373–376, 2008.

[123] U. Patil, N. S. Ramgir, N. Karmakar, A. Bhogale, A. Debnath, D. Aswal, S. Gupta, and D. Kothari, "Room temperature ammonia sensor based on copper nanoparticle intercalated polyaniline nanocomposite thin films," *Applied Surface Science*, vol. 339, pp. 69–74, 2015.

[124] H. Bai and G. Shi, "Gas sensors based on conducting polymers," *Sensors*, vol. 7, no. 3, pp. 267–307, 2007.

[125] H. Tai, Y. Jiang, G. Xie, J. Yu, and X. Chen, "Fabrication and gas sensitivity of polyaniline–titanium dioxide nanocomposite thin film," *Sensors and Actuators B: Chemical*, vol. 125, no. 2, pp. 644–650, 2007.

[126] V. Kumar, V. Patil, A. Apte, N. Harale, P. Patil, and S. Kulkarni, "Ultrasensitive gold nanostar–polyaniline composite for ammonia gas sensing," *Langmuir*, vol. 31, no. 48, pp. 13247–13256, 2015.

[127] L. Zhihua, Z. Xucheng, S. Jiyong, Z. Xiaobo, H. Xiaowei, H. E. Tahir, and M. Holmes, "Fast response ammonia sensor based on porous thin film of polyaniline/sulfonated nickel phthalocyanine composites," *Sensors and Actuators B: Chemical*, vol. 226, pp. 553–562, 2016.

[128] N. P. S. Chauhan, M. Mozafari, N. S. Chundawat, K. Meghwal, R. Ameta, and S. C. Ameta, “High-performance supercapacitors based on polyaniline–graphene nanocomposites: Some approaches, challenges and opportunities,” *Journal of Industrial and Engineering Chemistry*, vol. 36, pp. 13–29, 2016.

[129] M. M. Rana, M. M. Rana, D. S. Ibrahim, D. S. Ibrahim, M. Mohd Asyraf, M. Mohd Asyraf, S. Jarin, S. Jarin, A. Tomal, and A. Tomal, “A review on recent advances of cnts as gas sensors,” *Sensor Review*, vol. 37, no. 2, pp. 127–136, 2017.

[130] L. Xue, W. Wang, Y. Guo, G. Liu, and P. Wan, “Flexible polyaniline/carbon nanotube nanocomposite film-based electronic gas sensors,” *Sensors and Actuators B: Chemical*, vol. 244, pp. 47–53, 2017.

[131] S. K. Pradhan, P. J. Reucroft, and Y. Ko, “Crystallinity of Al_2O_3 films deposited by metalorganic chemical vapor deposition,” *Surface and Coatings Technology*, vol. 176, no. 3, pp. 382–384, 2004.

[132] G. Balakrishnan, P. Kuppusami, S. T. Sundari, R. Thirumurugesan, V. Ganesan, E. Mohandas, and D. Sastikumar, “Structural and optical properties of -alumina thin films prepared by pulsed laser deposition,” *Thin Solid Films*, vol. 518, no. 14, pp. 3898 – 3902, 2010.

[133] E. Ienei, L. Isac, and A. Duţ, “Synthesis of alumina thin films by spray pyrolysis,” *Revue Roumaine de Chimie*, vol. 55, no. 3, pp. 161–165, 2010. cited By 10.

[134] A. B. Khatibani and S. Rozati, “Synthesis and characterization of amorphous aluminum oxide thin films prepared by spray pyrolysis: Effects of substrate temperature,” *Journal of Non-Crystalline Solids*, vol. 363, pp. 121 – 133, 2013.

[135] K. Shamala, L. Murthy, M. Radhakrishna, and K. N. Rao, “Characterization of Al_2O_3 thin films prepared by spray pyrolysis method for humidity sensor,” *Sensors and Actuators A: Physical*, vol. 135, no. 2, pp. 552 – 557, 2007.

[136] P. Katiyar, C. Jin, and R. Narayan, “Electrical properties of amorphous aluminum oxide thin films,” *Acta Materialia*, vol. 53, no. 9, pp. 2617 – 2622, 2005.

[137] L. Juhász and J. Mizsei, “Humidity sensor structures with thin film porous alumina for on-chip integration,” *Thin Solid Films*, vol. 517, no. 22, pp. 6198 – 6201, 2009. Proceedings of {VI} International Workshop on Semiconductor Gas Sensors - {SGS} 2008.

[138] B. Hu, M. Yao, R. Xiao, J. Chen, and X. Yao, “Optical properties of amorphous Al_2O_3 thin films prepared by a sol–gel process,” *Ceramics International*, vol. 40, no. 9, Part A, pp. 14133 – 14139, 2014.

[139] E. C. Dickey, O. K. Varghese, K. G. Ong, D. Gong, M. Paulose, and C. A. Grimes, “Room temperature ammonia and humidity sensing using highly ordered nanoporous alumina films,” *Sensors*, vol. 2, no. 3, pp. 91–110, 2002.

[140] G. Eranna, B. Joshi, D. Runthala, and R. Gupta, “Oxide materials for development of integrated gas sensors—a comprehensive review,” *Critical Reviews in Solid State and Materials Sciences*, vol. 29, no. 3-4, pp. 111–188, 2004.

[141] B. Renganathan, D. Sastikumar, R. Srinivasan, A. C. Bose, and A. Ganesan, "Nanocrystalline aluminum oxide coating fiber optic vapour sensors," *Asian Journal of Chemistry*, vol. 25, no. Supplementary Issue, p. S373, 2013.

[142] G. N. Chaudhari, D. R. Bambole, A. B. Bodade, and P. R. Padole, "Characterization of nanosized TiO_2 based H_2S gas sensor," *Journal of Materials Science*, vol. 41, no. 15, pp. 4860–4864, 2006.

[143] V. K. Anand, S. Sood, G. Virdi, *et al.*, "Fabrication and characterization of zinc oxide based thick and thin film ethanol sensors doped with aluminium oxide," *International Journal of Applied Science and Engineering Research*, vol. 5, no. 1, pp. 81–89, 2016.

[144] J. Zhu, S. Wei, L. Zhang, Y. Mao, J. Ryu, N. Haldolaarachchige, D. P. Young, and Z. Guo, "Electrical and dielectric properties of polyaniline–Al_2O_3 nanocomposites derived from various Al_2O_3 nanostructures," *Journal of Materials Chemistry*, vol. 21, no. 11, pp. 3952–3959, 2011.

[145] A. Tripathi, K. P. Misra, and R. Shukla, "Enhancement in ammonia sensitivity with fast response by doping Al_2O_3 in polyaniline," *Journal of Applied Polymer Science*, vol. 130, no. 3, pp. 1941–1948, 2013.

[146] M. H. Lissarrague, M. E. Lamanna, N. B. D'Accorso, and S. Goyanes, "Effects of different nucleating particles on aniline polymerization," *Synthetic Metals*, vol. 162, no. 11, pp. 1052–1058, 2012.

[147] S. Cui, Z. Wen, E. C. Mattson, S. Mao, J. Chang, M. Weinert, C. J. Hirschmugl, M. Gajdardziska-Josifovska, and J. Chen, "Indium-doped SnO_2 nanoparticle–graphene nanohybrids: simple one-pot synthesis and their selective detection of NO_2," *Journal of Materials Chemistry A*, vol. 1, no. 14, pp. 4462–4467, 2013.

[148] T. Wang, D. Huang, Z. Yang, S. Xu, G. He, X. Li, N. Hu, G. Yin, D. He, and L. Zhang, "A review on graphene-based gas/vapor sensors with unique properties and potential applications," *Nano-Micro Letters*, vol. 8, no. 2, pp. 95–119, 2016.

[149] M. Hernaez, C. R. Zamarreño, S. Melendi-Espina, L. R. Bird, A. G. Mayes, and F. J. Arregui, "Optical fibre sensors using graphene-based materials: A review," *Sensors*, vol. 17, no. 1, p. 155, 2017.

[150] S. Dhibar and C. K. Das, "Electrochemical performances of silver nanoparticles decorated polyaniline/graphene nanocomposite in different electrolytes," *Journal of Alloys and Compounds*, vol. 653, pp. 486–497, 2015.

[151] 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 and Actuators B: Chemical*, vol. 178, pp. 485–493, 2013.

[152] Z. Wu, X. Chen, S. Zhu, Z. Zhou, Y. Yao, W. Quan, and B. Liu, "Room temperature methane sensor based on graphene nanosheets/polyaniline nanocomposite thin film," *IEEE Sensors Journal*, vol. 13, no. 2, pp. 777–782, 2013.

[153] K. Sheng, H. Bai, Y. Sun, C. Li, and G. Shi, "Layer-by-layer assembly of graphene/polyaniline multilayer films and their application for electrochromic devices," *Polymer*, vol. 52, no. 24, pp. 5567–5572, 2011.

[154] H. Liu, Y. Wang, X. Gou, T. Qi, J. Yang, and Y. Ding, "Three-dimensional graphene/polyaniline composite material for high-performance supercapacitor applications," *Materials Science and Engineering: B*, vol. 178, no. 5, pp. 293–298, 2013.

[155] A. V. Murugan, T. Muraliganth, and A. Manthiram, "Rapid, facile microwave-solvothermal synthesis of graphene nanosheets and their polyaniline nanocomposites for energy strorage," *Chemistry of Materials*, vol. 21, no. 21, pp. 5004–5006, 2009.

[156] K. Toda, R. Furue, and S. Hayami, "Recent progress in applications of graphene oxide for gas sensing: A review," *Analytica chimica acta*, vol. 878, pp. 43–53, 2015.

[157] V. Georgakilas, J. N. Tiwari, K. C. Kemp, J. A. Perman, A. B. Bourlinos, K. S. Kim, and R. Zboril, "Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications," *Chemical reviews*, vol. 116, no. 9, pp. 5464–5519, 2016.

[158] F. A. Chowdhury, T. Morisaki, J. Otsuki, and M. S. Alam, "Annealing effect on the optoelectronic properties of graphene oxide thin films," *Applied Nanoscience*, vol. 3, no. 6, pp. 477–483, 2013.

[159] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, and S. Seal, "Graphene based materials: past, present and future," *Progress in materials science*, vol. 56, no. 8, pp. 1178–1271, 2011.

[160] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, "Graphene and graphene oxide: synthesis, properties, and applications," *Advanced materials*, vol. 22, no. 35, pp. 3906–3924, 2010.

[161] S. H. Girei, A. A. Shabaneh, H. Ngee-Lim, M. N. Hamidon, M. A. Mahdi, and M. H. Yaacob, "Tapered optical fiber coated with graphene based nanomaterials for measurement of ethanol concentrations in water," *Optical Review*, vol. 22, no. 3, pp. 385–392, 2015.

[162] S. S. Varghese, S. Lonkar, K. Singh, S. Swaminathan, and A. Abdala, "Recent advances in graphene based gas sensors," *Sensors and Actuators B: Chemical*, vol. 218, pp. 160–183, 2015.

[163] S. Basu and P. Bhattacharyya, "Recent developments on graphene and graphene oxide based solid state gas sensors," *Sensors and Actuators B: Chemical*, vol. 173, pp. 1–21, 2012.

[164] S. Some, Y. Xu, Y. Kim, Y. Yoon, H. Qin, A. Kulkarni, T. Kim, and H. Lee, "Highly sensitive and selective gas sensor using hydrophilic and hydrophobic graphenes," *Scientific reports*, vol. 3, p. 1868, 2013.

[165] R. Nair, H. Wu, P. Jayaram, I. Grigorieva, and A. Geim, "Unimpeded permeation of water through helium-leak–tight graphene-based membranes," *Science*, vol. 335, no. 6067, pp. 442–444, 2012.

[166] S. L. Rebelo, A. Guedes, M. E. Szefczyk, A. M. Pereira, J. P. Araújo, and C. Freire, "Progress in the raman spectra analysis of covalently functionalized multiwalled carbon nanotubes: unraveling disorder in graphitic materials," *Physical Chemistry Chemical Physics*, vol. 18, no. 18, pp. 12784–12796, 2016.

[167] C. Herrero-Latorre, J. Álvarez-Méndez, J. Barciela-García, S. García-Martín, and R. Peña-Crecente, "Characterization of carbon nanotubes and analytical methods for their determination in environmental and biological samples: A review," *Analytica chimica acta*, vol. 853, pp. 77–94, 2015.

[168] H. Elhaes, A. Fakhry, and M. Ibrahim, "Carbon nano materials as gas sensors," *Materials Today: Proceedings*, vol. 3, no. 6, pp. 2483 – 2492, 2016. Recent Advances In Nano Science And Technology 2015.

[169] R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, "Carbon nanotubes–the route toward applications," *science*, vol. 297, no. 5582, pp. 787–792, 2002.

[170] M. Holzinger, A. Le Goff, and S. Cosnier, "Carbon nanotube/enzyme biofuel cells," *Electrochimica Acta*, vol. 82, pp. 179–190, 2012.

[171] S. Manivannan, A. Saranya, B. Renganathan, D. Sastikumar, G. Gobi, and K. C. Park, "Single-walled carbon nanotubes wrapped poly-methyl methacrylate fiber optic sensor for ammonia, ethanol and methanol vapors at room temperature," *Sensors and Actuators B: Chemical*, vol. 171, pp. 634–638, 2012.

[172] A. Shabaneh, S. Girei, P. Arasu, M. Mahdi, S. Rashid, S. Paiman, and M. Yaacob, "Dynamic response of tapered optical multimode fiber coated with carbon nanotubes for ethanol sensing application," *Sensors*, vol. 15, no. 5, pp. 10452–10464, 2015.

[173] H.-Z. Yang, X.-G. Qiao, M. M. Ali, M. R. Islam, and K.-S. Lim, "Optimized tapered optical fiber for ethanol (C_2H_5OH) concentration sensing," *Journal of Lightwave Technology*, vol. 32, no. 9, pp. 1777–1783, 2014.

[174] A. Shabaneh, S. H. Girei, P. Arasu, S. Rashid, Z. Yunusa, M. A. Mahdi, S. Paiman, M. Z. Ahmad, and M. Yaacob, "Reflectance response of optical fiber coated with carbon nanotubes for aqueous ethanol sensing," *IEEE Photonics Journal*, vol. 6, no. 6, pp. 1–10, 2014.

[175] L. R. Shobin, B. Renganathan, D. Sastikumar, K. C. Park, and S. Manivannan, "Pure and iso-butyl methyl ketone treated multi-walled carbon nanotubes for ethanol and methanol vapor sensing," *IEEE Sensors Journal*, vol. 14, no. 4, pp. 1238–1243, 2014.

[176] S. Ippolito, S. Kandasamy, K. Kalantar-Zadeh, and W. Wlodarski, "Hydrogen sensing characteristics of WO_3 thin film conductometric sensors activated by Pt and Au catalysts," *Sensors and Actuators B: Chemical*, vol. 108, no. 1, pp. 154–158, 2005.

[177] J. Cheng, J. Wang, Q. Li, H. Liu, and Y. Li, “A review of recent developments in tin dioxide composites for gas sensing application,” *Journal of Industrial and Engineering Chemistry*, vol. 44, pp. 1–22, 2016.

[178] E. Dilonardo, M. Penza, M. Alvisi, R. Rossi, G. Cassano, C. Di Franco, F. Palmisano, L. Torsi, and N. Cioffi, “Gas sensing properties of MWCNT layers electrochemically decorated with Au and Pd nanoparticles,” *Beilstein Journal of Nanotechnology*, vol. 8, p. 592, 2017.

[179] A. Cusano, M. Consales, A. Crescitelli, and A. Ricciardi, *Lab-on-fiber technology*, vol. 56. Springer, 2015.

[180] M. Ando, R. Chabicovsky, and M. Haruta, “Optical hydrogen sensitivity of noble metal–tungsten oxide composite films prepared by sputtering deposition,” *Sensors and Actuators B: Chemical*, vol. 76, no. 1, pp. 13–17, 2001.

[181] D. Buso, M. Guglielmi, A. Martucci, G. Mattei, P. Mazzoldi, C. Sada, and M. L. Post, “Growth of cookie-like Au/NiO nanoparticles in SiO_2 sol–gel films and their optical gas sensing properties,” *Crystal Growth and Design*, vol. 8, no. 2, pp. 744–749, 2008.

[182] L. K. Randeniya, P. J. Martin, A. Bendavid, and J. McDonnell, “Ammonia sensing characteristics of carbon-nanotube yarns decorated with nanocrystalline gold,” *Carbon*, vol. 49, no. 15, pp. 5265–5270, 2011.

[183] Z.-D. Lin, S.-J. Young, and S.-J. Chang, “Carbon nanotube thin films functionalized via loading of Au nanoclusters for flexible gas sensors devices,” *IEEE Transactions on Electron Devices*, vol. 63, no. 1, pp. 476–480, 2016.

[184] M. Gautam and A. H. Jayatissa, “Ammonia gas sensing behavior of graphene surface decorated with gold nanoparticles,” *Solid-State Electronics*, vol. 78, pp. 159–165, 2012.

[185] A. R. Tao, S. Habas, and P. Yang, “Shape control of colloidal metal nanocrystals,” *small*, vol. 4, no. 3, pp. 310–325, 2008.

[186] C. Rao, G. Kulkarni, P. J. Thomas, and P. P. Edwards, “Size-dependent chemistry: properties of nanocrystals,” *Chemistry–A European Journal*, vol. 8, no. 1, pp. 28–35, 2002.

[187] L. Bilro, N. J. Alberto, L. M. Sa, J. de Lemos Pinto, and R. Nogueira, “Analytical analysis of side-polished plastic optical fiber as curvature and refractive index sensor,” *Journal of Lightwave Technology*, vol. 29, no. 6, pp. 864–870, 2011.

[188] C. Teng, F. Yu, N. Jing, Y. Ding, Z. Si, and J. Zheng, “Investigation of refractive index sensors based on side-polished plastic optical fibers,” *Optical Fiber Technology*, vol. 36, pp. 1 – 5, 2017.

[189] F. Sequeira, D. Duarte, L. Bilro, A. Rudnitskaya, M. Pesavento, L. Zeni, and N. Cennamo, “Refractive index sensing with D-shaped plastic optical fibers for chemical and biochemical applications,” *Sensors*, vol. 16, no. 12, p. 2119, 2016.

[190] B. Ghanbarzadeh, S. A. Oleyaei, and H. Almasi, “Nanostructured materials utilized in biopolymer-based plastics for food packaging applications,” *Critical reviews in food science and nutrition*, vol. 55, no. 12, pp. 1699–1723, 2015.

[191] Z. H. Khan, A. Kumar, S. Husain, and M. Husain, *Introduction to Nanomaterials*, pp. 1–23. New Delhi: Springer India, 2016.

[192] F. R. Baptista, S. Belhout, S. Giordani, and S. Quinn, “Recent developments in carbon nanomaterial sensors,” *Chemical Society Reviews*, vol. 44, no. 13, pp. 4433–4453, 2015.

[193] U. Tisch and H. Haick, “Nanomaterials for cross-reactive sensor arrays,” *MRS bulletin*, vol. 35, no. 10, pp. 797–803, 2010.

[194] M. U. Qadri, A. F. D. Diaz, M. Cittadini, A. Martucci, M. C. Pujol, J. Ferré-Borrull, E. Llobet, M. Aguiló, and F. Díaz, “Effect of Pt nanoparticles on the optical gas sensing properties of WO_3 thin films,” *Sensors*, vol. 14, no. 7, pp. 11427–11443, 2014.

[195] M. Al-Kuhaili, A. Al-Aswad, S. Durrani, and I. Bakhtiari, “Transparent heat mirrors based on tungsten oxide–silver multilayer structures,” *Solar Energy*, vol. 83, no. 9, pp. 1571–1577, 2009.

[196] T. Polcar, N. Parreira, and A. Cavaleiro, “Tungsten oxide with different oxygen contents: Sliding properties,” *Vacuum*, vol. 81, no. 11, pp. 1426–1429, 2007.

[197] S. Balaji, Y. Djaoued, A.-S. Albert, R. Brüning, N. Beaudoin, and J. Robichaud, “Porous orthorhombic tungsten oxide thin films: synthesis, characterization, and application in electrochromic and photochromic devices,” *Journal of Materials Chemistry*, vol. 21, no. 11, pp. 3940–3948, 2011.

[198] C. A. Triana, C.-G. Granqvist, and G. A. Niklasson, “Electrochromism and small-polaron hopping in oxygen deficient and lithium intercalated amorphous tungsten oxide films,” *Journal of Applied Physics*, vol. 118, no. 2, p. 024901, 2015.

[199] S. Sharma, S. Vyas, C. Periasamy, and P. Chakrabarti, “Structural and optical characterization of ZnO thin films for optoelectronic device applications by RF sputtering technique,” *Superlattices and Microstructures*, vol. 75, pp. 378 – 389, 2014.

[200] V. R. Buch, A. K. Chawla, and S. K. Rawal, “Review on electrochromic property for WO_3 thin films using different deposition techniques,” *Materials Today: Proceedings*, vol. 3, no. 6, pp. 1429 – 1437, 2016. Recent Advances In Nano Science And Technology 2015.

[201] M. M. Aqil, M. A. Azam, M. F. Aziz, and R. Latif, “Deposition and characterization of molybdenum thin film using direct current magnetron and atomic force microscopy,” *Journal of Nanotechnology*, vol. 2017, p. 10, 2017.

[202] X. Yang, V. Salles, Y. V. Kaneti, M. Liu, M. Maillard, C. Journet, X. Jiang, and A. Brioude, "Fabrication of highly sensitive gas sensor based on Au functionalized WO_3 composite nanofibers by electrospinning," *Sensors and Actuators B: Chemical*, vol. 220, pp. 1112–1119, 2015.

[203] Y. Wang, B. Zhang, J. Liu, Q. Yang, X. Cui, Y. Gao, X. Chuai, F. Liu, P. Sun, X. Liang, *et al.*, "Au-loaded mesoporous WO_3: Preparation and n-butanol sensing performances," *Sensors and Actuators B: Chemical*, vol. 236, pp. 67–76, 2016.

[204] U. Nakate, R. Bulakhe, C. Lokhande, and S. Kale, "Au sensitized ZnO nanorods for enhanced liquefied petroleum gas sensing properties," *Applied Surface Science*, vol. 371, pp. 224–230, 2016.

[205] L. Rajan, C. Periasamy, and V. Sahula, "Comprehensive study on electrical and hydrogen gas sensing characteristics of Pt/ZnO nanocrystalline thin film-based schottky diodes grown on n-Si substrate using RF sputtering," *IEEE Transactions on Nanotechnology*, vol. 15, no. 2, pp. 201–208, 2016.

[206] N. M. Hieu, H. Kim, C. Kim, S.-K. Hong, and D. Kim, "A hydrogen sulfide gas sensor based on Pd-decorated ZnO nanorods," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 10, pp. 10351–10355, 2016.

[207] A. Sadek, W. Wlodarski, K. Shin, R. B. Kaner, and K. Kalantar-Zadeh, "A layered surface acoustic wave gas sensor based on a polyaniline/In_2O_3 nanofibre composite," *Nanotechnology*, vol. 17, no. 17, p. 4488, 2006.

[208] X. Yao, X. Kou, and J. Qiu, "Nano-Al_2O_3/PANI composites with high negative permittivity," *Organic Electronics*, vol. 39, pp. 133–137, 2016.

[209] H. Lim, N. Huang, S. Lim, I. Harrison, and C. Chia, "Fabrication and characterization of graphene hydrogel via hydrothermal approach as a scaffold for preliminary study of cell growth," *Int J Nanomedicine*, vol. 6, pp. 1817–1823, 2011.

[210] M. Faisal, S. B. Khan, M. M. Rahman, A. Jamal, and A. Umar, "Ethanol chemi-sensor: Evaluation of structural, optical and sensing properties of CuO nanosheets," *Materials Letters*, vol. 65, no. 9, pp. 1400–1403, 2011.

[211] W. Lim, Y. Yap, W. Chong, C. Pua, N. Huang, R. De La Rue, and H. Ahmad, "Graphene oxide-based waveguide polariser: From thin film to quasi-bulk," *Optics express*, vol. 22, no. 9, pp. 11090–11098, 2014.

[212] A. Harlin, H. Myllymaki, and K. Grahn, "Polymeric optical fibres and future prospects in textile integration," *Autex Res. J*, vol. 2, no. 1, 2002.

[213] Z. Yunusa, M. N. Hamidon, and S. A. Rashid, "Growth of multi-walled carbon nanotubes on platinum," in *Micro and Nanoelectronics (RSM), 2013 IEEE Regional Symposium on*, pp. 363–366, IEEE, 2013.

[214] A. Malarvizhi *et al.*, "Bonding of cholesterol oxides to functionalised multiwalled carbon nanotubes for in-vitro biosensor application," *Biomedical Research*, vol. 23, no. 4, 2012.

[215] Ocean Optics, Inc., *Spectrometer Operating Software, Installation and Operation Manual*, 2009.

[216] S. Ammu, V. Dua, S. R. Agnihotra, S. P. Surwade, A. Phulgirkar, S. Patel, and S. K. Manohar, "Flexible, all-organic chemiresistor for detecting chemically aggressive vapors," *Journal of the American Chemical Society*, vol. 134, no. 10, pp. 4553–4556, 2012.

[217] V. Kazmiruk, ed., *Scanning Electron Microscopy*. InTech, 2012.

[218] M. H. Yaacob, *Investigation of metal oxide nanostructured thin films based optical hydrogen sensors*. PhD thesis, RMIT University Melbourne, Australia, 2012.

[219] S. Hong, J. Yeom, I. T. Song, S. M. Kang, H. Lee, and H. Lee, "Pyrogallol 2-aminoethane: A plant flavonoid-inspired molecule for material-independent surface chemistry," *Advanced Materials Interfaces*, vol. 1, no. 4, 2014.

[220] G. Binnig, C. F. Quate, and C. Gerber, "Atomic force microscope," *Physical review letters*, vol. 56, no. 9, p. 930, 1986.

[221] F. Marinello, *Atomic Force Microscopy*, pp. 1–5. Berlin, Heidelberg: Springer Berlin Heidelberg, 2016.

[222] P. Eaton and P. West, *Atomic force microscopy*. Oxford University Press, 2010.

[223] R. A. Halvorson and P. J. Vikesland, "Surface-enhanced Raman spectroscopy (SERS) for environmental analyses," 2010.

[224] C. S. Kumar, *Raman spectroscopy for nanomaterials characterization*. Springer Science & Business Media, 2012.

[225] Q. Tu and C. Chang, "Diagnostic applications of Raman spectroscopy," *Nanomedicine: Nanotechnology, Biology and Medicine*, vol. 8, no. 5, pp. 545–558, 2012.

[226] J. R. Ferraro, *Introductory raman spectroscopy*. Academic press, 2003.

[227] R. Chang, *Surface enhanced Raman scattering*. Springer Science & Business Media, 2013.

[228] K. Kneipp, "Surface-enhanced raman scattering," *Physics Today*, vol. 60, no. 11, pp. 40–46, 2007.

[229] M. Z. Ahmad, *Investigation of nanostructured metal oxide based H_2, NO_x & C_2H_5OH conductometric and optical sensors*. PhD thesis, RMIT University Melbourne, Australia, 2013.

[230] I. De Wolf, C. Jian, and W. M. van Spengen, "The investigation of microsystems using Raman spectroscopy," *Optics and Lasers in Engineering*, vol. 36, no. 2, pp. 213–223, 2001.

[231] C. Giannini, M. Ladisa, D. Altamura, D. Siliqi, T. Sibillano, and L. De Caro, "X-ray diffraction: a powerful technique for the multiple-length-scale structural analysis of nanomaterials," *Crystals*, vol. 6, no. 8, p. 87, 2016.

[232] R. J. Bose, V. Kavitha, C. Sudarsanakumar, and V. M. Pillai, "Phase modification and surface plasmon resonance of Au/WO_3 system," *Applied Surface Science*, vol. 379, pp. 505–515, 2016.

[233] F. Gennari, C. Neyertz, G. Meyer, P. Fornasiero, and M. Graziani, "Kinetics of hydrogen chemisorption on high surface area Pd/$Ce_{0.8}Zr_{0.2}O_2$," *Journal of alloys and compounds*, vol. 404, pp. 317–322, 2005.

[234] B. Liu, L. Wen, H. Zhang, and X. Zhao, "TiO_2/WO_3 layered film with dual-function of anti-UV light and high photoelectrocatalytic activity: Facile preparation and characterization," *Journal of the American Ceramic Society*, vol. 95, no. 10, pp. 3346–3351, 2012.

[235] M. Yaacob, M. Breedon, K. Kalantar-Zadeh, and W. Wlodarski, "Absorption spectral response of nanotextured WO_3 thin films with Pt catalyst towards H_2," *Sensors and Actuators B: Chemical*, vol. 137, no. 1, pp. 115–120, 2009.

[236] P. Zhao, Y. Tang, J. Mao, Y. Chen, H. Song, J. Wang, Y. Song, Y. Liang, and X. Zhang, "One-dimensional MoS_2-decorated TiO_2 nanotube gas sensors for efficient alcohol sensing," *Journal of Alloys and Compounds*, vol. 674, pp. 252 – 258, 2016.

[237] T.-A. Nguyen, S. Park, J. B. Kim, T. K. Kim, G. H. Seong, J. Choo, and Y. S. Kim, "Polycrystalline tungsten oxide nanofibers for gas-sensing applications," *Sensors and Actuators B: Chemical*, vol. 160, no. 1, pp. 549–554, 2011.

[238] L. Fu, W. Cai, A. Wang, and Y. Zheng, "Photocatalytic hydrogenation of nitrobenzene to aniline over tungsten oxide-silver nanowires," *Materials Letters*, vol. 142, pp. 201–203, 2015.

[239] R. J. Bose, N. Illyaskutty, K. Tan, R. Rawat, M. V. Matham, H. Kohler, and V. M. Pillai, "Hydrogen sensors based on Pt-loaded WO_3 sensing layers," *EPL (Europhysics Letters)*, vol. 114, no. 6, p. 66002, 2016.

[240] S. Ghosh, S. S. Acharyya, S. Adak, L. S. Konathala, T. Sasaki, and R. Bal, "Selective oxidation of cyclohexene to adipic acid over silver supported tungsten oxide nanostructured catalysts," *Green Chemistry*, vol. 16, no. 5, pp. 2826–2834, 2014.

[241] H.-C. Chen, D.-J. Jan, Y.-S. Luo, and K.-T. Huang, "Electrochromic and optical properties of tungsten oxide films deposited with DC sputtering by introducing hydrogen," *Applied optics*, vol. 53, no. 4, pp. A321–A329, 2014.

[242] M. Penza, M. Tagliente, L. Mirenghi, C. Gerardi, C. Martucci, and G. Cassano, "Tungsten trioxide (WO_3) sputtered thin films for a NO_x gas sensor," *Sensors and Actuators B: Chemical*, vol. 50, no. 1, pp. 9 – 18, 1998.

[243] M. Dou, M. Hou, H. Zhang, G. Li, W. Lu, Z. Wei, Z. Shao, and B. Yi, "A highly stable anode, carbon-free, catalyst support based on tungsten trioxide nanoclusters for proton-exchange membrane fuel cells," *ChemSusChem*, vol. 5, no. 5, pp. 945–951, 2012.

[244] A. Tripathi, S. K. Mishra, I. Bahadur, and R. Shukla, "Optical properties of regiorandom polythiophene/Al_2O_3 nanocomposites and their application to ammonia gas sensing," *Journal of Materials Science: Materials in Electronics*, vol. 26, no. 10, pp. 7421–7430, 2015.

[245] S. Sugumaran, C. S. Bellan, and M. Nadimuthu, "Characterization of composite PVA–Al_2O_3 thin films prepared by dip coating method," *Iranian Polymer Journal*, vol. 24, no. 1, pp. 63–74, 2015.

[246] J. Yang, Y. Liu, S. Liu, L. Li, C. Zhang, and T. Liu, "Conducting polymer composites: material synthesis and applications in electrochemical capacitive energy storage," *Materials Chemistry Frontiers*, 2017.

[247] F. Kanwal, A. Batool, M. Adnan, and S. Naseem, "The effect of molecular structure, band gap energy and morphology on the dc electrical conductivity of polyaniline/aluminium oxide composites," *Materials Research Innovations*, vol. 19, no. sup8, pp. S8–354, 2015.

[248] L. T. Duy, T. Q. Trung, V. Q. Dang, B.-U. Hwang, S. Siddiqui, I.-Y. Son, S. K. Yoon, D. J. Chung, and N.-E. Lee, "Flexible transparent reduced graphene oxide sensor coupled with organic dye molecules for rapid dual-mode ammonia gas detection," *Advanced Functional Materials*, vol. 26, no. 24, pp. 4329–4338, 2016.

[249] R. Singh and R. Choudhary, "Optical absorbance and ohmic behavior of PANI and PANI/ZnO nanocomposites for solar cell application," *Optik - International Journal for Light and Electron Optics*, vol. 127, no. 23, pp. 11398 – 11405, 2016.

[250] G. M. Do Nascimento, M. Temperini, *et al.*, "Studies on the resonance Raman spectra of polyaniline obtained with near-IR excitation," *Journal of Raman Spectroscopy*, vol. 39, no. 7, pp. 772–778, 2008.

[251] R. Tucceri, P. M. Arnal, and A. N. Scian, "Spectroscopic characterization of poly (ortho-aminophenol) film electrodes: a review article," *Journal of Spectroscopy*, vol. 2013, 2012.

[252] M. Boyer, S. Quillard, M. Cochet, G. Louarn, and S. Lefrant, "RRS characterization of selected oligomers of polyaniline in situ spectroelectrochemical study," *Electrochimica acta*, vol. 44, no. 12, pp. 1981–1987, 1999.

[253] S. N. Rasool, L. R. Moorthy, and C. Jayasankar, "Spectroscopic investigation of Sm 3+ doped phosphate based glasses for reddish-orange emission," *Optics Communications*, vol. 311, pp. 156 – 162, 2013.

[254] A. K. Yadav and P. Singh, "A review of the structures of oxide glasses by Raman spectroscopy," *RSC Advances*, vol. 5, no. 83, pp. 67583–67609, 2015.

[255] M. Cochet, G. Louarn, S. Quillard, J. Buisson, and S. Lefrant, “Theoretical and experimental vibrational study of emeraldine in salt form. part ii,” *Journal of Raman Spectroscopy*, vol. 31, no. 12, pp. 1041–1049, 2000.

[256] A. Petrovski, P. Paunović, R. Avolio, M. E. Errico, M. Cocca, G. Gentile, A. Grozdanov, M. Avella, J. Barton, and A. Dimitrov, “Synthesis and characterization of nanocomposites based on PANI and carbon nanostructures prepared by electropolymerization,” *Materials Chemistry and Physics*, vol. 185, pp. 83 – 90, 2017.

[257] L. Li, Z. Lou, W. Han, D. Chen, K. Jiang, and G. Shen, “Highly stretchable micro-supercapacitor arrays with hybrid MWCNT/PANI electrodes,” *Advanced Materials Technologies*, vol. 2, no. 3, 2017.

[258] J. Xiang and L. T. Drzal, “Templated growth of polyaniline on exfoliated graphene nanoplatelets (GNP) and its thermoelectric properties,” *Polymer*, vol. 53, no. 19, pp. 4202–4210, 2012.

[259] M. Trchová, Z. Morávková, M. Bláha, and J. Stejskal, “Raman spectroscopy of polyaniline and oligoaniline thin films,” *Electrochimica Acta*, vol. 122, pp. 28–38, 2014.

[260] L. Al-Mashat, K. Shin, K. Kalantar-zadeh, J. D. Plessis, S. H. Han, R. W. Kojima, R. B. Kaner, D. Li, X. Gou, S. J. Ippolito, *et al.*, “Graphene/polyaniline nanocomposite for hydrogen sensing,” *The Journal of Physical Chemistry C*, vol. 114, no. 39, pp. 16168–16173, 2010.

[261] F. D. Amado and S. Krishnamurthy, “Synthesis and characterisation of polyaniline (PAni) membranes for fuel cell,” *Advanced Materials Letters*, vol. 7, no. 9, pp. 719–722, 2016.

[262] A. N. Papathanassiou, O. Mykhailiv, L. Echegoyen, I. Sakellis, and M. E. Plonska-Brzezinska, “Electric properties of carbon nano-onion/polyaniline composites: a combined electric modulus and ac conductivity study,” *Journal of Physics D: Applied Physics*, vol. 49, no. 28, p. 285305, 2016.

[263] S. Benykhlef, A. Bekhoukh, R. Berenguer, A. Benyoucef, and E. Morallon, “PANI-derived polymer/Al_2O_3 nanocomposites: synthesis, characterization, and electrochemical studies,” *Colloid and Polymer Science*, vol. 294, no. 12, pp. 1877–1885, 2016.

[264] J. N. Ansari, S. Khasim, A. Parveen, O. A. Al-Hartomy, Z. Khattari, N. Badi, A. Roy, *et al.*, “Synthesis, characterization, dielectric and rectification properties of PANI/Nd_2O_3: Al_2O_3 nanocomposites,” *Polymers for Advanced Technologies*, 2016.

[265] E. A. Sanches, A. d. S. Carolino, A. L. d. Santos, E. G. Fernandes, D. M. Trichês, and Y. P. Mascarenhas, “The use of le bail method to analyze the semicrystalline pattern of a nanocomposite based on polyaniline emeraldine-salt form and α-Al_2O_3,” *Advances in Materials Science and Engineering*, vol. 2015, 2015.

[266] J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang, and F. Wei, "Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance," *Carbon*, vol. 48, no. 2, pp. 487–493, 2010.

[267] V. K. Shukla, P. Yadav, R. S. Yadav, P. Mishra, and A. C. Pandey, "A new class of PANI–Ag core–shell nanorods with sensing dimensions," *Nanoscale*, vol. 4, no. 13, pp. 3886–3893, 2012.

[268] H. Yu, T. Wang, B. Wen, M. Lu, Z. Xu, C. Zhu, Y. Chen, X. Xue, C. Sun, and M. Cao, "Graphene/polyaniline nanorod arrays: synthesis and excellent electromagnetic absorption properties," *Journal of Materials Chemistry*, vol. 22, no. 40, pp. 21679–21685, 2012.

[269] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical review B*, vol. 61, no. 20, p. 14095, 2000.

[270] H.-P. Cong, X.-C. Ren, P. Wang, and S.-H. Yu, "Flexible graphene–polyaniline composite paper for high-performance supercapacitor," *Energy & Environmental Science*, vol. 6, no. 4, pp. 1185–1191, 2013.

[271] P. Sambyal, A. P. Singh, M. Verma, M. Farukh, B. P. Singh, and S. Dhawan, "Tailored polyaniline/barium strontium titanate/expanded graphite multiphase composite for efficient radar absorption," *RSC Advances*, vol. 4, no. 24, pp. 12614–12624, 2014.

[272] Y. Guo, T. Wang, F. Chen, X. Sun, X. Li, Z. Yu, P. Wan, and X. Chen, "Hierarchical graphene–polyaniline nanocomposite films for high-performance flexible electronic gas sensors," *Nanoscale*, vol. 8, no. 23, pp. 12073–12080, 2016.

[273] Z. Zhang, M. Wan, and Y. Wei, "Highly crystalline polyaniline nanostructures doped with dicarboxylic acids," *Advanced Functional Materials*, vol. 16, no. 8, pp. 1100–1104, 2006.

[274] K. Zhang, L. L. Zhang, X. S. Zhao, and J. Wu, "Graphene/polyaniline nanofiber composites as supercapacitor electrodes," *Chemistry of Materials*, vol. 22, no. 4, pp. 1392–1401, 2010.

[275] S. Park, S. He, J. Wang, A. Stein, and C. W. Macosko, "Graphene-polyethylene nanocomposites: Effect of graphene functionalization," *Polymer*, vol. 104, pp. 1 – 9, 2016. Rheology.

[276] E. M. Elnaggar, K. I. Kabel, A. A. Farag, and A. G. Al-Gamal, "Comparative study on doping of polyaniline with graphene and multi-walled carbon nanotubes," *Journal of Nanostructure in Chemistry*, vol. 7, no. 1, pp. 75–83, 2017.

[277] A. Riaz, A. Usman, M. Faheem, Z. Hussain, A. N. Khan, and S. Soomro, "Effect of polymerization of aniline on thermal stability, electrical conductivity and band gap of graphene oxide/polyanilinenanocomposites," *Int. J. Electrochem. Sci*, vol. 12, pp. 1785–1796, 2017.

[278] B. Paulchamy, G. Arthi, and B. Lignesh, "A simple approach to stepwise synthesis of graphene oxide nanomaterial," *Journal of Nanomedicine & Nanotechnology*, vol. 6, no. 1, p. 1, 2015.

[279] J. Chen, D. Zhao, X. Jin, C. Wang, D. Wang, and H. Ge, "Modifying glass fibers with graphene oxide: towards high-performance polymer composites," *Composites Science and Technology*, vol. 97, pp. 41–45, 2014.

[280] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *carbon*, vol. 45, no. 7, pp. 1558–1565, 2007.

[281] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, and Y. Chen, "Evaluation of solution-processed reduced graphene oxide films as transparent conductors," *ACS nano*, vol. 2, no. 3, pp. 463–470, 2008.

[282] R. Gao, N. Hu, Z. Yang, Q. Zhu, J. Chai, Y. Su, L. Zhang, and Y. Zhang, "Paper-like graphene-Ag composite films with enhanced mechanical and electrical properties," *Nanoscale research letters*, vol. 8, no. 1, p. 32, 2013.

[283] A. Ambrosi and M. Pumera, "Electrochemically exfoliated graphene and graphene oxide for energy storage and electrochemistry applications," *Chemistry–A European Journal*, vol. 22, no. 1, pp. 153–159, 2016.

[284] X. Wang, Q. Fan, S. Yu, Z. Chen, Y. Ai, Y. Sun, A. Hobiny, A. Alsaedi, and X. Wang, "High sorption of U (VI) on graphene oxides studied by batch experimental and theoretical calculations," *Chemical Engineering Journal*, vol. 287, pp. 448–455, 2016.

[285] S. Y. Toh, K. S. Loh, S. K. Kamarudin, and W. R. W. Daud, "Graphene production via electrochemical reduction of graphene oxide: synthesis and characterisation," *Chemical Engineering Journal*, vol. 251, pp. 422–434, 2014.

[286] S.-S. Du, F. Li, H.-M. Xiao, Y.-Q. Li, N. Hu, and S.-Y. Fu, "Tensile and flexural properties of graphene oxide coated-short glass fiber reinforced polyethersulfone composites," *Composites Part B: Engineering*, vol. 99, pp. 407–415, 2016.

[287] X. Wang, Z. Chen, and S. Yang, "Application of graphene oxides for the removal of Pb (II) ions from aqueous solutions: Experimental and DFT calculation," *Journal of Molecular Liquids*, vol. 211, pp. 957–964, 2015.

[288] S. N. Alam, N. Sharma, and L. Kumar, "Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO)," *Graphene*, vol. 6, no. 01, p. 1, 2017.

[289] L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek, and I. Bieloshapka, "Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 195, pp. 145 – 154, 2014.

[290] K. Kardimi, T. Tsoufis, A. Tomou, B. J. Kooi, M. I. Prodromidis, and D. Gournis, "Synthesis and characterization of carbon nanotubes decorated with Pt and PtRu nanoparticles and assessment of their electrocatalytic performance," *international journal of hydrogen energy*, vol. 37, no. 2, pp. 1243–1253, 2012.

[291] Y.-H. Nien, *The Application of Carbon Nanotube to Bone Cement*. INTECH Open Access Publisher, 2011.

[292] P. Majzlíková, J. Sedláček, J. Prášek, J. Pekárek, V. Svatoš, A. G. Bannov, O. Jašek, P. Synek, M. Eliáš, L. Zajíčková, *et al.*, "Sensing properties of multiwalled carbon nanotubes grown in MW plasma torch: electronic and electrochemical behavior, gas sensing, field emission, IR absorption," *Sensors*, vol. 15, no. 2, pp. 2644–2661, 2015.

[293] N. Andrade, T. Vasconcelos, C. Gouvea, B. Archanjo, C. Achete, Y. Kim, M. Endo, C. Fantini, M. Dresselhaus, and A. Souza Filho, "Linear carbon chains encapsulated in multiwall carbon nanotubes: Resonance Raman spectroscopy and transmission electron microscopy studies," *Carbon*, vol. 90, pp. 172–180, 2015.

[294] S. Chaunchaiyakul, T. Yano, K. Khoklang, P. Krukowski, M. Akai-Kasaya, A. Saito, and Y. Kuwahara, "Nanoscale analysis of multiwalled carbon nanotube by tip-enhanced Raman spectroscopy," *Carbon*, vol. 99, pp. 642–648, 2016.

[295] H. Hu, H. Cheng, G. Li, J. Liu, and Y. Yu, "Design of SnO_2/C hybrid triple-layer nanospheres as Li-ion battery anodes with high stability and rate capability," *Journal of Materials Chemistry A*, vol. 3, no. 6, pp. 2748–2755, 2015.

[296] R. A. DiLeo, B. J. Landi, and R. P. Raffaelle, "Purity assessment of multiwalled carbon nanotubes by Raman spectroscopy," *Journal of applied physics*, vol. 101, no. 6, p. 064307, 2007.

[297] S. K. Pillai, S. S. Ray, and M. Moodley, "Purification of multi-walled carbon nanotubes," *Journal of nanoscience and nanotechnology*, vol. 8, no. 12, pp. 6187–6207, 2008.

[298] L. Bokobza and J. Zhang, "Raman spectroscopic characterization of multiwall carbon nanotubes and of composites," *Express Polym. Lett*, vol. 6, no. 7, pp. 601–608, 2012.

[299] M. Karthikeyan, A. G. Kannan, and S. Um, "Sub-zero temperature thermo-electrochemical energy harvesting system using a self-heating negative temperature coefficient CNT-vanadium oxide cathode," *Journal of Applied Electrochemistry*, vol. 47, no. 1, pp. 125–132, 2017.

[300] C. Altavilla, M. Sarno, P. Ciambelli, A. Senatore, and V. Petrone, "New 'chimie douce' approach to the synthesis of hybrid nanosheets of MoS_2 on CNT and their anti-friction and anti-wear properties," *Nanotechnology*, vol. 24, no. 12, p. 125601, 2013.

[301] I. Jiménez, J. Arbiol, G. Dezanneau, A. Cornet, and J. Morante, "Crystalline structure, defects and gas sensor response to NO_2 and H_2S of tungsten trioxide nanopowders," *Sensors and Actuators B: Chemical*, vol. 93, no. 1–3, pp. 475 – 485, 2003. Proceedings of the Ninth International Meeting on Chemical Sensors.

[302] A. Sanger, A. Kumar, A. Kumar, and R. Chandra, "Highly sensitive and selective hydrogen gas sensor using sputtered grown Pd decorated MnO_2 nanowalls," *Sensors and Actuators B: Chemical*, vol. 234, pp. 8–14, 2016.

[303] M. Z. Ahmad, A. Z. Sadek, M. Yaacob, D. P. Anderson, G. Matthews, V. B. Golovko, and W. Wlodarski, "Optical characterisation of nanostructured Au/WO_3 thin films for sensing hydrogen at low concentrations," *Sensors and Actuators B: Chemical*, vol. 179, pp. 125 – 130, 2013. A Special Issue in Honour of Professor A. D'Amico.

[304] M. Yang, Y. Sun, D. Zhang, and D. Jiang, "Using Pd/WO_3 composite thin films as sensing materials for optical fiber hydrogen sensors," *Sensors and Actuators B: Chemical*, vol. 143, no. 2, pp. 750 – 753, 2010.

[305] Y. Zhou, X. Lin, Y. Wang, G. Liu, X. Zhu, Y. Huang, Y. Guo, C. Gao, and M. Zhou, "Study on gas sensing of reduced graphene oxide/ZnO thin film at room temperature," *Sensors and Actuators B: Chemical*, vol. 240, pp. 870 – 880, 2017.

[306] K. Lee, V. Scardaci, H.-Y. Kim, T. Hallam, H. Nolan, B. E. Bolf, G. S. Maltbie, J. E. Abbott, and G. S. Duesberg, "Highly sensitive, transparent, and flexible gas sensors based on gold nanoparticle decorated carbon nanotubes," *Sensors and Actuators B: Chemical*, vol. 188, pp. 571 – 575, 2013.

[307] D. D. Nguyen, D. V. Dang, and D. C. Nguyen, "Hydrothermal synthesis and NH_3 gas sensing property of WO_3 nanorods at low temperature," *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, vol. 6, no. 3, p. 035006, 2015.

[308] M. D'Arienzo, L. Armelao, C. M. Mari, S. Polizzi, R. Ruffo, R. Scotti, and F. Morazzoni, "Macroporous WO_3 thin films active in NH_3 sensing: role of the hosted Cr isolated centers and Pt nanoclusters," *J. Am. Chem. Soc.*, vol. 133, no. 14, pp. 5296–5304, 2011.

[309] M. Urbańczyk, E. Maciak, K. Gut, T. Pustelny, and W. Jakubik, "Layered thin film nanostructures of Pd/$WO_{3\text{-}x}$ as resistance gas sensors," *Bull. Pol. Acad. Sci.-Tech. Sci.*, vol. 59, no. 4, pp. 401–407, 2011.

[310] D. Manno, G. Micocci, A. Serra, and A. Tepore, "Thermal deposition and characterization of Se-Sn mixed oxide thin films for NO gas sensing applications," *J. Appl. Phys.*, vol. 83, no. 7, pp. 3541–3546, 1998.

[311] D. Fu, C. Zhu, X. Zhang, C. Li, and Y. Chen, "Two-dimensional net-like SnO_2/ZnO heteronanostructures for high-performance H_2S gas sensor," *Journal of Materials Chemistry A*, vol. 4, no. 4, pp. 1390–1398, 2016.

[312] L. Kumar, I. Rawal, A. Kaur, and S. Annapoorni, "Flexible room temperature ammonia sensor based on polyaniline," *Sensors and Actuators B: Chemical*, vol. 240, pp. 408 – 416, 2017.

[313] N. M. Vuong, D. Kim, and H. Kim, "Porous Au-embedded WO_3 nanowire structure for efficient detection of CH_4 and H_2S," *Scientific reports*, vol. 5, p. 11040, 2015.

[314] H.-H. Cheng, F. Chen, J. Yu, and Z.-X. Guo, "Gold-nanoparticle-decorated thermoplastic polyurethane electrospun fibers prepared through a chitosan linkage for catalytic applications," *Journal of Applied Polymer Science*, vol. 134, no. 1, 2017.

[315] K.-P. Yoo, K.-H. Kwon, N.-K. Min, M. J. Lee, and C. J. Lee, "Effects of O_2 plasma treatment on NH_3 sensing characteristics of multiwall carbon nanotube/polyaniline composite films," *Sensors and Actuators B: Chemical*, vol. 143, no. 1, pp. 333–340, 2009.

[316] P. V. Tong, N. D. Hoa, N. V. Duy, D. T. T. Le, and N. V. Hieu, "Enhancement of gas-sensing characteristics of hydrothermally synthesized WO_3 nanorods by surface decoration with Pd nanoparticles," *Sensors and Actuators B: Chemical*, vol. 223, pp. 453 – 460, 2016.

[317] S. Ibrahim, N. Rahman, M. A. Bakar, S. Girei, M. Yaacob, H. Ahmad, and M. Mahdi, "Room temperature ammonia sensing using tapered multimode fiber coated with polyaniline nanofibers," *Optics express*, vol. 23, no. 3, pp. 2837–2845, 2015.

[318] L. Shobin, D. Sastikumar, and S. Manivannan, "Glycerol mediated synthesis of silver nanowires for room temperature ammonia vapor sensing," *Sensors and Actuators A: Physical*, vol. 214, pp. 74–80, 2014.

[319] D. R. Raj, S. Prasanth, T. Vineeshkumar, and C. Sudarsanakumar, "Ammonia sensing properties of tapered plastic optical fiber coated with silver nanoparticles/PVP/PVA hybrid," *Optics Communications*, vol. 340, pp. 86–92, 2015.

[320] M. Dang, L. Yongyao, G. Kecheng, Z. Guiping, and Y. Renkuan, "Ellipsometric spectra and refractive index of polyaniline," *Chinese Physics Letters*, vol. 10, no. 6, p. 374, 1993.

[321] N.-R. Chiou and A. J. Epstein, "Polyaniline nanofibers prepared by dilute polymerization," *Advanced Materials*, vol. 17, no. 13, pp. 1679–1683, 2005.

[322] S. Bai, J. Ye, R. Luo, A. Chen, and D. Li, "Hierarchical polyaniline microspheres loading on flexible PET films for NH_3 sensing at room temperature," *RSC Advances*, vol. 6, no. 9, pp. 6939–6945, 2016.

[323] N. F. Attia and K. E. Geckeler, "Polyaniline as a material for hydrogen storage applications," *Macromolecular rapid communications*, vol. 34, no. 13, pp. 1043–1055, 2013.

[324] Q. Nie, Z. Pang, H. Lu, Y. Cai, and Q. Wei, "Ammonia gas sensors based on In_2O_3/PANI hetero-nanofibers operating at room temperature," *Beilstein Journal of Nanotechnology*, vol. 7, no. 1, pp. 1312–1321, 2016.

[325] Y.-C. Chang, H. Bai, S.-N. Li, and C.-N. Kuo, "Bromocresol green/mesoporous silica adsorbent for ammonia gas sensing via an optical sensing instrument," *Sensors*, vol. 11, no. 4, pp. 4060–4072, 2011.

[326] H. Qiu, S. Xu, S. Jiang, Z. Li, P. Chen, S. Gao, C. Zhang, and D. Feng, "A novel graphene-based tapered optical fiber sensor for glucose detection," *Applied Surface Science*, vol. 329, pp. 390–395, 2015.

[327] M. L. Y. Sin, G. C. T. Chow, G. M. K. Wong, W. J. Li, P. H. W. Leong, and K. W. Wong, "Ultralow-power alcohol vapor sensors using chemically functionalized multiwalled carbon nanotubes," *IEEE Transactions on Nanotechnology*, vol. 6, no. 5, pp. 571–577, 2007.

[328] W. Xue and P. Li, "Dielectrophoretic deposition and alignment of carbon nanotubes," in *Carbon Nanotubes-Synthesis, Characterization, Applications*, InTech, 2011.

[329] B. Philip, J. K. Abraham, A. Chandrasekhar, and V. K. Varadan, "Carbon nanotube/PMMA composite thin films for gas-sensing applications," *Smart materials and structures*, vol. 12, no. 6, p. 935, 2003.