UNIVERSITI PUTRA MALAYSIA

DETECTION OF LARD VIA FLUORESCENT FIBER PROBE SENSOR UTILIZING GRAPHENE QUANTUM DOTS

CHE NUR HAMIZAH BINTI CHE LAH

FK 2018 175

DETECTION OF LARD VIA FLUORESCENT FIBER PROBE SENSOR UTILIZING GRAPHENE QUANTUM DOTS

By

CHE NUR HAMIZAH BINTI CHE LAH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

June 2018

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

DETECTION OF LARD VIA FLUORESCENT FIBER PROBE SENSOR UTILIZING GRAPHENE QUANTUM DOTS

By

CHE NUR HAMIZAH BINTI CHE LAH

June 2018

Chairman : Associate Professor Ahmad Shukri Bin Muhammad Noor, PhD
Faculty : Engineering

Graphene quantum dots (GQDs) recently emerge as a superior and universal fluorophores because of their unique combination of a number of key merits, including small in size, excellent photostability, biocompatibility, and highly tunable photoluminescence properties. These glowing carbon nanocrystals provide unprecedented opportunities for bioimaging and optical sensing. In this research, the usage of optical fiber which is tapered multimode fiber (TMMF) is used for detection of lard. Prior to this, several methods that have been introduced include electronic nose (zNose), Fourier-transform infrared spectroscopy, high performance liquid chromatography/tandem mass spectroscopy (HPC-MS/MS) and polymerase chain reaction (PCR). However, all of these techniques require large detector and are time consuming. In this research, detection of lard was done using optical fiber characterization of GQDs and GQDs coated with gold nanoparticles (Au-GQDs), more reliable and environmentally friendly fluorescence fiber probe sensor. TMMF with 20nm diameter was chosen and then coated with GQDs or Au-GQDs using drop casting method. The main interest of the investigation was to identify the effect of combining TMMF with GQDs and Au-GQDs as the nanoparticles. The characterization of annealing effects at different temperature of the GQDs and Au-GQDs shows that at 70ºC and 100ºC respectively gives the highest sensitivity. Three types of TMMF probe sensors were then used to detect lard with different concentrations, ranging from 20% to 100%. The fluorescence responses of the sensor were investigated for uncoated TMMF and TMMF coated with GQD and Au-GQDs.

The result from this study shows that TMMF coated with GQDs and annealed in 70ºC gives better and strong fluorescence emission peak at 652nm. However, the sensitivity of lard detection achieved is 0.034/a.u.%. By introducing Au NPs to GQD creating Au-GQDs TMMF probe sensor, the peak shifted to 680nm and give the highest

sensitivity and linearity of detection which are 0.042/a.u.% and 85% respectively at 100ºC. The difference in the annealing temperature resulted in different carbon-carbon bond formation between the carbons of fats bound with the carbon from GQDs. Then, the mixture of carbon-carbon bond became excited and the energy was emitted as fluorescence. Throughout this research work, an in-depth understanding on GQDs and Au-GQDs as fluorescent sensing platform in detection of lard concentration via fluorescence fiber probe sensor was studied. As well as an investigation on the binding process between GQDs and Au-GQDs with the lard to perform fluorescence emission. Ultimately, this research work achieved its goals to develop a method to detect lard concentration via fluorescence fiber probe sensor.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

MENGESAN LEMAK BABI MELALUI PENGESAN PENDARFLUOR GENTIAN MENGGUNAKAN BINTIK KUANTUM GRAFENA

Oleh

CHE NUR HAMIZAH BINTI CHE LAH

Jun 2018

Pengerusi : Profesor Madya Ahmad Shukri Bin Muhammad Noor, PhD
Fakulti : Kejuruteraan

Bintik kuantum grafena (GQDs) baru-baru ini muncul sebagai flororora yang unggul dan universal kerana kombinasi unik mereka dari beberapa merit utama, termasuk saiz kecil, kepelbagaian kestabilan foto, keserasian bio, dan sifat pendarcahaya foto yang sangat mudah berubah. Kristal nano karbon yang menyerlah memberikan peluang yang belum pernah terjadi sebelumnya untuk pengimejan bio dan penderiaan optik. Dalam kajian ini, penggunaan gentian optik multimod yang ditiruskan (TMMF) digunakan untuk pengesanan lemak babi. Sebelum ini, beberapa kaedah yang telah diperkenalkan termasuk Hidung Elektronik (zNose), Spektroskopi Inframerah Transformasi Fourier Spectroscopy, Kromatografi cecair Prestasi Tinggi / Spekroskopi jisim Tandem (HPC-MS / MS) dan Reaksi Rantai Polimerase (PCR). Walau bagaimanapun, semua teknik ini memerlukan pengesan bersaiz besar dan memakan masa. Dalam penyelidikan ini, pengesanan lemak babi dilakukan dengan menggunakan pencirian gentian optik GQD dan GQD yang disalut dengan nanopartikel emas (Au-GQDs), sensor pendarfluor gentian penderiaan yang lebih dipercayai dan mesra alam. TMMF dengan diameter 20nm dipilih dan kemudian dilapisi dengan GQD atau Au-GQD menggunakan kaedah menitik. Kepentingan utama penyiasatan adalah untuk mengenal pasti kesan penggabungan TMMF dengan GQD dan Au-GQD sebagai partikel nano. Pencirian kesan penyepuhlindapan pada suhu yang berbeza dari GQDs dan Au-GQDs menunjukkan bahawa pada 70˚C dan 100˚C masing-masing memberikan kepekaan tertinggi. Tiga jenis alat pengesan TMMF kemudiannya digunakan untuk mengesan lemak babi dengan kepekatan yang berbeza, antara 20% hingga 100%. Tindak balas pengesan pendarfluor telah disiasat untuk TMMF dan TMMF yang tidak bersalut bersalut dengan GQD dan Au-GQDs. Hasil daripada kajian ini menunjukkan bahawa TMMF bersalut dengan GQD dan anil di 70˚C memberikan puncak pelepasan pendarfluor tertinggi dan kuat pada 652nm. Walau bagaimanapun, kepekaan pengesanan lemak babi yang dicapai adalah 0.034 / a.u.%. Dengan memperkenalkan Au NPs kepada GQD yang mencipta alat pengesan

Au-GQD TMMF, puncaknya beralih kepada 680nm dan memberikan sensitiviti dan kelinearan tertinggi pengesanan masing-masing sebanyak 0.042 / a.u.% dan 85% pada 100˚C. Perbezaan suhu penyepuhlindapan menghasilkan pembentukan ikatan karbon karbon yang berbeza di antara karbohidrat lemak yang terikat dengan karbon dari GQDs. Kemudian, campuran ikatan karbon-karbon menjadi teruja dan tenaga dipancarkan sebagai pendarfluor. Sepanjang kajian ini, pemahaman mendalam tentang GQDs dan Au-GQDs sebagai platform penderiaan pendarfluor dalam pengesanan kepekatan lemak melalui penderia pengesan gentian pendarfluor telah dikaji. Serta penyiasatan mengenai proses mengikat antara GQD dan Au-GQD dengan lemak babi untuk melakukan pelepasan pendarfluor. Akhirnya, kerja penyelidikan ini mencapai matlamatnya untuk membangunkan satu kaedah untuk mengesan kepekatan bakteria melalui pengesan pendarfluor gentian pendarfluor.

ACKNOWLEDGEMENTS

Ahamdulillah, I am very grateful to Allah, this thesis has been carried out up to the final stage of my research. I would like to express my special appreciation and million thanks to my supervisor Associate Prof. Dr. Ahmad Shukri Bin Muhammad Noor because of his dedication to help me with his advices and guidance throughout the entire project. His patience to explain many times without complaining is the best experience I have ever had and the knowledge I received is priceless. Without his supervision and constant help this dissertation would not have been possible.

I would also to express my gratitude to my co-supervisor, Associate Prof. Dr. Suraya Binti Abdul Rashid and Dr. Fakhrul Zaman Bin Rokhani for their guidance, support and knowedge throughout my study. Thank you also to Mr. Mohd Anwarul Arif, a former Master student for his helps in this project even though he already busy with his project.

Also special thanks to my family. Words cannot express how grateful I am to my beloved parents Che Lah Bin Che Ibrahim and Rosmayati Binti Sidek for all the sacrifices that they had made and also because of their understanding and tolerating towards my study. Besides, I am deeply thanks to my sibling Che Nor Hazwani and Che Muhd Luqman for supporting me and always be a good listener to me. A big thanks to all my colleagues and friends at the Alnair Lab, Kak Akmar, Kak Nurul, Maisarah, Kak Nad, Atiq, Piji, Kak Min, Nadiya, Kak Intan, Ng, Lau and other that I do not mention for all the cheers and happiness that we share in the laboratory. Thank you for give me moral support when I distress and also for creating memorable moment in my life. I always appreciate the time we had spent together such as playing table tennis, having lunch at fancy places, trip to Japan for attending symposium and others.

I would also like to thank Universiti Putra Malaysia for giving me the opportunity and financial assistance in completing this master. Last but not least thank you very much to all the people who are involved directly or indirectly in the completion of this project. Without them this project cannot be completed. Thank you.

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

Ahmad Shukri Bin Muhammad Noor, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Suraya Binti Abdul Rashid, PhD
Associate Professor
Institute Teknologi Maju
Universiti Putra Malaysia
(Member)

Fakhrul Zaman Bin Rokhani, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

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

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature: ________________________ Date: ___________________

Name and Matric No.: Che Nur Hamizah Binti Che Lah, GS45807

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) were adhered to.

Signature: ______________________________

Name of Chairman of Supervisory Committee: Associate Professor Dr. Ahmad Shukri Bin Muhammad Noor

Signature: ______________________________

Name of Member of Supervisory Committee: Associate Professor Dr. Suraya Binti Abdul Rashid

Signature: ______________________________

Name of Member of Supervisory Committee: Dr. Fakhrul Zaman Bin Rokhani

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATONS

GQDs	Graphene Quantum Dots
GO	Graphene Oxide
Au-GQDs	Graphene Quantum Dots functionalize Gold Nanoparticles
Au NPs	Gold Nanoparticlles
NPs	Nanoparticles
zNOSE	Electronic Nose (zNose)
PRC	Polymerase Chain Reaction
FAME	Fatty Acid Methyl Esters
TG	Gas Chromatography and Triglyceride
PVC	Polyvinyl Chloride
TIR	Total Internal Reflection
TIRF	Total Internal Reflection Fluorescence
MMF	Multi-mode Fiber
TMMF	Tapered Multi-mode Fiber
UV	Ultraviolet
Vis	Visible
SPR	Surface Plasmon Resonance
FSR	Free Spectral Range
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
Na_2SO_4	Sodium Sulfate
Zn	Zinc
H	Hydrogen
O	Oxygen
C	Carbon
N	Nitrogen

CHAPTER 1

INTRODUCTION

1.1 Overview

Optical fiber based biosensors recently receive a lot of attention as diagnostic tools for different applications. Judging by their light weight, small size, low cost, and immunity to electromagnetic interference, optical fibers offer a perfect platform for the development of sensing probe. Optical fiber probes sensor is also a compact and convenient answer for many measurements of fluorescence [1], absorbance [2], and reflection [3] in a wide variety of biosensor sample.

Optical fiber biosensors dependency on total internal reflection fluorescence (TIRF) have given an excessive potential in providing viable solutions to these challenges [4]. The basic principle of total internal reflection is applied in optical fiber transmissions of light, the evanescent wave penetrates fundamentally into the surrounding cladding of lower refractive index. Then, the light exponentially decays with distance. The evanescent wave can excite fluorescence mainly from the fluorescent labelled analyte complexes bound to the surface through bond identification interactions [5].

Graphene, a zero-bandgap semiconductor, has attracted huge attention because of its impressive properties in electronic, mechanical and thermal. Besides, graphene also has good chemical stability for many potential applications in scientific and technological fields [6]. However, due to the lack of bandgap in graphene, the possibility of observing luminescence seems highly improbable, which limits its application in electronic and opto-electronic [7]. Therefore, many studies have been conducted to create a bandgap in graphene to induce photoluminescence (PL) by controlling the size and surface chemistry of graphene [8–10].

In recent research, ultrafine graphene quantum dots (GQDs) as a part of the graphene group act as a fluorescent graphene material due to their strong quantum confinement and edge effects [11]. Analyte such as GQDs have recently emerge as superior and universal fluorophores because of their unique properties, including excellent photostability, small size, biocompatibility, and highly tunable photoluminescence property. In particular, GQDs are a zero dimensional (0D) material and nanometer-sized GQDs provide large surface areas which enhanced the dispersibility in the development of strategies for the design of new imaging probes and biosensors.

GQDs special structure and configuration inherit the characteristics of graphene oxide (GO), such as outstanding water solubility, low cytotoxicity, high surface area and good surface grafting property. With that, GQDs contain oxygen groups and functional groups on the surface. Consequently, the fluorescence mechanism of GQD is similar to the fluorescence outcome of graphene oxide. The shapes of most GQD are either circular or elliptical, but in some research, it was stated that the shapes of GQDs are in the form of triangular, quadrate and hexagonal dots. Additional improvement towards GQDs is its strong capability to adsorb biomolecules with its carbon based atomic ring structure. According to literature reference present in bio molecules study, there is interaction between its hexagonal cells and the carbon-based ring structures due to its stacking. These advantages have led to many applications such as photovoltaic cells [12], light emitting diode [13], diode lasers [14], bioimaging [15], biosensing [16] and catalysts [17]. These properties led researches and scientists to develop sensors. Gold is preferred in this research due to its characteristic which is low oxidation and high sensitivity. Gold nanoparticles (Au NPs) have been widely employed for sensor development including optical fiber sensors especially surface plasmon resonance (SPR). The Au NPs, also known as gold colloids, have attracted a growing attention due to their special properties in multi-disciplinary research fields [18–20]. The Au NPs in 1-100 nm size range have been considered by researchers to fabricate an effective sensing devices in biosensor as diagnostic tools. It has also been recognized that hybridizing Au NPs with graphene oxide sheets can enhance the detection [21].

Most of the Au NPs studies show improvement in selectivity and sensitivity toward biological and chemical sample, that cause changes in Raman signals, fluorescence or absorbance. Their sensing performance relies on the Au NPs changes in the size, morphology or the distance between nanoparticles. Furthermore, fluorescent Au NPs are initiated through photo reduction and chemical reduction of Au^{3+} in the existence of ligands that have strong binding of ions. Thus, the fluorescence of Au NPs is practically related to their charge, surface ligand, size and structure [22]. It is considered that the fluorescence of Au NPs is generated from the relation between metal center electron transition and ligand–metal/metal–metal charge transfer [23]. Therefore, fluorescent Au NPs show greater biocompatibility and quantum yields.

Lard is known as fat rendered from pig abdomen fat, which of consists high proportion of adipose tissues. Moreover, the usage of fats in food manufacturing is very common from the beginning of the 20^{th} century as they are very economical and accessible. Currently, in food production, lard is still a primary element in the preparation of certain food products, especially instant products. For example, in the cuisine world, lard is a highly used ingredient for raw material in mass production of bakery products and also acts as frying oil. This kind of fat are considered as marketable product throughout the world. The fact that pigs are easily adaptable animals, where they can survive almost everywhere, makes it very popular.

Foods adulteration has become a common issue in Malaysia nowadays. Especially in some food manufacturers, they prefer to mix vegetable oils with lard. It is because lard is much more aff ordable than coconut oil, olive oil and other healthy fats, and it can be sustainably accessed in food industries. However, lard in food is a serious matter in the view of religion, biological problem and health. For Islam, Judaism and Hinduism followers, they are prohibited to consume food containing porcine ingredients and its derivatives. Figure 1.1 shows the pie chart of world consumption for major fats and oil in 2015 from IHS Markit Ltd. company [24].

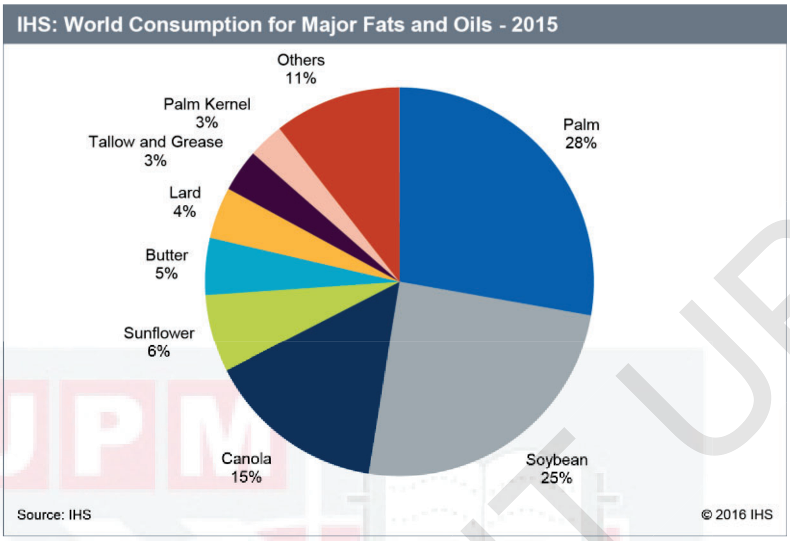

Figure 1.1 : Pie chart of world consumption for major fats and oil in 2015

Related to this constraint, it is crucial to create reliable approaches to sense the existence of lard in food to protect consumers from intended or non-intended food deception. Consequently, a number of analytical techniques either physical or chemical-based have been studied to detect lard.

Several methods that have been introduced to detect lard include electronic nose (zNose) [25], Fourier transform infrared spectroscopy, high performance liquid chromatography/tandem mass spectroscopy (HPC-MS/MS) and polymerase chain reaction (PCR) [26]. However, these methods are time consuming and have to be conducted in the laboratory. Thus, their disadvantages result in the formation of the problem statement and motivation to perform this research. Therefore, it is essential to develop a rapid and reliable method for determining lard concentration.

1.2 Problem Statement

Recently, there have been some issues regarding the adulteration of products in Malaysia. It is common in Malaysia that fats and oils are used in both food manufacturing and industrial uses. They are consumed in food, as well as, personal care products, greases, paints, lubricants, and biodiesel. Lard is widely used in food production industry to greatly reduce the product cost due to its vast availability and cost effectiveness. Therefore, it is important to develop an effective method to detect the presence of lard in food manufacturing for Halal purpose.

However, most of the sensors used to detect lard concentration are electrical based. They have several weaknesses, for example, large in size and the sample has to be sent to a lab. Therefore, it is necessary to have a low-cost, portable and non-destructive sensors that provide information of Halal authentication for consumers and authorities on Halal standard certification.

1.3 Objectives

The purpose of this project is to study new quantum dots coated on TMMF to detect the concentration of lard. Investigation and analysis on the differences between types of coating material and condition of coating process are also achievable. To ensure this project run efficiently, a few objectives have been formed, which are:

- To introduce graphene quantum dots as a fluorescence marker for lard detection sensor for Halal application.
- To study the differences on fluorescence changes of quantum dots in different concentration of lard.
- To improvise and enhance the detection of lard by introducing graphene quantum dots coated with gold nanoparticles.

1.4 Research Scope of Study

The scope of study in this research is summarized in Figure 1.2. Mainly, this research look into designing and fabricating a sensitive lard sensor based on TMMF coated with various quantum dots. The TMMF itsef were not varied. This is due to previous research by [27] that provide high sensitivity. In this work, quantum dots from graphene such as GQDs and Au-GQDs were chosen. Commonly, an analysis of lard detection on electrical methods, for this work an optica method was chosen. The optical changes due to the reaction between quantum dots and fats were detected by using the TMMF. This research was focus on fluorescence detection. GQDs and Au-GQDs were chosen as sensing element.

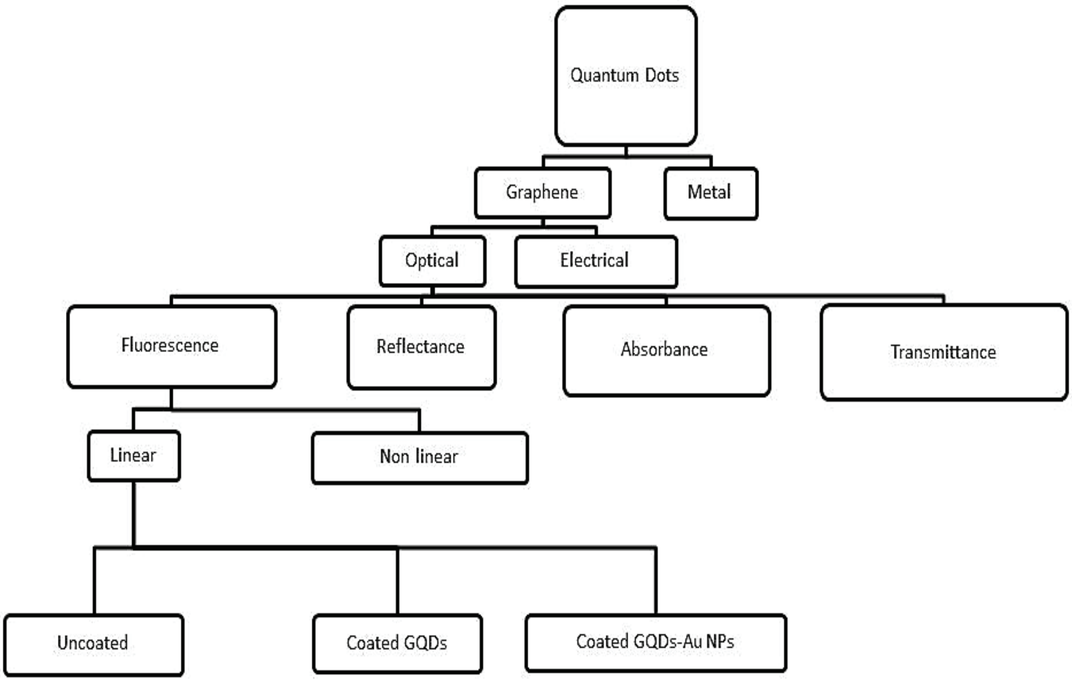

Figure 1.2 : Flow chart scope of study

1.5 Limitation

The aim of this research is to design and fabricate tapered optical sensors for lard concentration detection. Therefore, there is limitation that should be considered which is other types of fat are not discussed in this research. In order to focus on the detection of different concentration of lard and the different sensing element used. The visibility of this work was focus on quantum dots coated on TMMF to detect the concentration of lard.

1.6 Summary

This thesis consists of five different chapters. The thesis presentation is outlined as follows:

I. Chapter 1: This chapter introduces the project, outlines the research objectives, problem statement and summary of the contributions to the body of knowledge.
II. Chapter 2: In this chapter the discussion on the background of the project and other related works will be studied and reviewed. The justification behind the research and literature reviews supporting the application of optical sensors using quantum dots.

III. Chapter 3: In this chapter the design of tapered multimode fiber will be discussed. The chemical synthesis and deposition of the quantum dots as the optical sensing element are discussed in detail. The project methods and equipment that will be used in this project are explained.

IV. Chapter 4: This chapter will highlight and discuss the experimental results obtained from the tapered multimode fiber sensors performance towards lard via UV-Vis spectroscopy. The characterization of the quantum dots employed as the optical sensing layer on TMMF was also performed and reviewed.

Chapter 5: The project will be concluded and the contributions in the area of fiber probe sensors are discussed. Recommendations for future works in this optical fiber probe sensor are also presented.

REFERENCES

[1] M. Haidekker, W. J. Akers, D. Fischer, and E. Theodorakis, "Optical fiber-based fluorescent viscosity sensor.," Optics letters **31**(17), 2529–2531 (2006).

[2] P. Arasu, A. Noor, and A. Shabaneh, "Absorbance properties of gold coated fiber Bragg grating sensor for aqueous ethanol," Journal of the European Optical Society **9**, 14018 (2014).

[3] A. A. Shabaneh, S. H. Girei, P. T. Arasu, S. A. Rashid, Z. Yunusa, M. A. Mahdi, S. Paiman, M. Z. Ahmad, and M. H. Yaacob, "Reflectance Response of Optical Fiber Coated With Carbon Nanotubes for Aqueous Ethanol Sensing," IEEE Photonics Journal **6**(6), (2014).

[4] A. P. Abel, M. G. Weller, G. L. Duveneck, M. Ehrat, and H. M. Widmer, "Fiber-optic evanescent wave biosensor for the detection of oligonucleotides," Analytical Chemistry **68**(17), 2905–2912 (1996).

[5] F. Long, S. Wu, M. He, T. Tong, and H. Shi, "Ultrasensitive quantum dots-based DNA detection and hybridization kinetics analysis with evanescent wave biosensing platform," Biosensors and Bioelectronics **26**(5), 2390–2395 (2011).

[6] G. Eda, Y. Y. Lin, C. Mattevi, H. Yamaguchi, H. A. Chen, I. S. Chen, C. W. Chen, and M. Chhowalla, "Blue photoluminescence from chemically derived graphene oxide," Advanced Materials **22**(4), 505–509 (2010).

[7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films," Science **306**(5696), 666–669 (2004).

[8] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao, and J.-J. Zhu, "Focusing on luminescent graphene quantum dots: current status and future perspectives," Nanoscale **5**(10), 4015 (2013).

[9] S. Abdul Rashid, S. A. Mohd Zobir, S. Krishnan, M. M. Hassan, and H. N. Lim, "One-pot synthesis of graphene oxide sheets and graphene oxide quantum dots from graphite nanofibers," Journal of Nanoparticle Research **17**(5), 1–11 (2015).

[10] F. Wang, Z. Gu, W. Lei, W. Wang, X. Xia, and Q. Hao, "Graphene quantum dots as a fluorescent sensing platform for highly efficient detection of copper(II) ions," Sensors and Actuators, B: Chemical **190**, 516–522 (2014).

[11] F. Wang, Z. Gu, W. Lei, W. Wang, X. Xia, and Q. Hao, "Graphene quantum dots as a fluorescent sensing platform for highly efficient detection of copper(II) ions," Sensors and Actuators, B: Chemical **190**, 516–522 (2014).

[12] Z. Zeng, S. Chen, T. T. Y. Tan, and F. X. Xiao, "Graphene quantum dots (GQDs) and its derivatives for multifarious photocatalysis and photoelectrocatalysis," Catalysis Today (December 2017), 0–1 (2018).

[13] Y. Kang, B. Yuan, D. Zhang, T. Ma, X. Huang, Z. Chu, and K. Lai, "Green synthetic strategy of BCNO nanostructure and phosphor-based light – Emitting diodes," Journal of Luminescence **179**, 501–510 (2016).

[14] V. Saikiran, M. H. Dar, and D. N. Rao, "Femtosecond laser induced nanostructuring of graphite for the fabrication of quasi-periodic nanogratings and novel carbon nanostructures," Applied Surface Science **428**, 177–185 (2018).

[15] Z. Luo, D. Yang, C. Yang, X. Wu, Y. Hu, Y. Zhang, L. Yuwen, E. K. L. Yeow, L. Weng, W. Huang, and L. Wang, "Graphene quantum dots modified with adenine for efficient two-photon bioimaging and white light-activated antibacteria," Applied Surface Science **434**, 155–162 (2018).

[16] J. Shi, J. Lyu, F. Tian, and M. Yang, "A fluorescence turn-on biosensor based on graphene quantum dots (GQDs) and molybdenum disulfide (MoS2) nanosheets for epithelial cell adhesion molecule (EpCAM) detection," Biosensors and Bioelectronics **93**, 182–188 (2017).

[17] X. Fei, Z. Liu, Y. Li, G. Yang, C. Su, H. Zhong, Z. Zhuang, and Z. Guo, "One-pot green synthesis of flower-liked Au NP@GQDs nanocomposites for surface-enhanced Raman scattering," Journal of Alloys and Compounds **725**, 1084–1090 (2017).

[18] Y. Zhang, W. Chu, A. D. Foroushani, H. Wang, D. Li, J. Liu, C. J. Barrow, X. Wang, and W. Yang, "New gold nanostructures for sensor applications: A review," Materials **7**(7), 5169–5201 (2014).

[19] K. M. A. El-Nour, E. T. A. Salam, H. M. Soliman, and A. S. Orabi, "Gold Nanoparticles as a Direct and Rapid Sensor for Sensitive Analytical Detection of Biogenic Amines," Nanoscale Research Letters **12**(1), (2017).

[20] H. N. Verma, P. Singh, and R. M. Chavan, "Gold nanoparticle: Synthesis and characterization," Veterinary World **7**(2), 72–77 (2014).

[21] J. Qian, L. Jiang, X. Yang, Y. Yan, H. Mao, and K. Wang, "Highly sensitive impedimetric aptasensor based on covalent binding of gold nanoparticles on reduced graphene oxide with good dispersity and high density.," The Analyst **00**, 1–7 (2014).

[22] Z. Yuan, M. Peng, L. Shi, Y. Du, N. Cai, Y. He, H.-T. Chang, and E. S. Yeung, "Disassembly mediated fluorescence recovery of gold nanodots for selective sulfide sensing," Nanoscale **5**(11), 4683 (2013).

[23] J. Zheng, C. Zhou, M. Yu, and J. Liu, "Different sized luminescent gold nanoparticles," Nanoscale **4**(14), 4073 (2012).

[24] "Despite FDA Phase-out of Partially Hydrogenated Oils, Global Outlook for Fats and Oils Remains Positive as Use Essential to Food and Nonfood Production, IHS Says," .

[25] Y. B. C. Man, H. L. Gan, I. NorAini, S. A. H. Nazimah, and C. P. Tan, "Detection of lard adulteration in RBD palm olein using an electronic nose," Food Chemistry **90**(4), 829–835 (2005).

[26] P. Hashim and D. Mat Hashim, "A review of cosmetic and personal care products: Halal perspective and detection of ingredient," Pertanika Journal of Science and Technology **21**(2), 281–292 (2013).

[27] Y. Zhao, Z. Q. Deng, and Q. Wang, "Fiber optic SPR sensor for liquid concentration measurement," Sensors and Actuators, B: Chemical **192**, 229–233 (2014).

[28] Y. Tian, W. Wang, N. Wu, X. Zou, and X. Wang, "Tapered optical fiber sensor for label-free detection of biomolecules," Sensors **11**(4), 3780–3790 (2011).

[29] J. An, T. Liu, and Y. Jin, "Fiber Optic Vibration Sensor Based on the Tilted Fiber Bragg Grating," Advances in Materials Science and Engineering **2013**, 1–4 (2013).

[30] I. de Lourenço, G. R. C. Possetti, M. Muller, and J. L. Fabris, "Fiber Bragg grating sensor to monitor stress kinetics in drying process of commercial latex paints.," Sensors (Basel, Switzerland) **10**(5), 4761–76 (2010).

[31] I. R. Matias, F. J. Arregui, J. M. Corres, and J. Bravo, "Evanescent field fiber-optic sensors for humidity monitoring based on nanocoatings," IEEE Sensors Journal **7**(1), 89–95 (2007).

[32] S. Sridevi, K. S. Vasu, N. Jayaraman, S. Asokan, and a. K. Sood, "Optical bio-sensing devices based on etched fiber Bragg gratings coated with carbon nanotubes and graphene oxide along with a specific dendrimer," Sensors and Actuators, B: Chemical **195**, 150–155 (2014).

[33] A. Qureshi, W. P. Kang, J. L. Davidson, and Y. Gurbuz, "Review on carbon-derived, solid-state, micro and nano sensors for electrochemical sensing applications," Diamond and Related Materials **18**(12), 1401–1420 (2009).

[34] nanoComposix, "Gold Nanoparticles in Solution," .

[35] S. Tips, F. O. Cables, F. O. Cable, F. Optic, F. O. Patch, F. O. Splicing, F. O. Test, F. O. Tools, F. O. Training, F. O. Network, F. O. Cabling, O. Fiber, S. M. S. M. Fiber, M. Fiber, C. C. Tutorial, T. Tutorial, F. O. Testing, I. Tutorial, I. Profile, D. Between, and G. M. Fiber, "Multimode Fiber and Multimode Fiber Optic Cable Tutorial Multimode Fiber and Multimode Fiber Optic Cable Tutorial," .

[36] J. R. Lakowicz, "Total Internal Reflection," .

[37] 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 (Switzerland) **15**(5), 10452–10464 (2015).

[38] S. Guo and S. Albin, "Transmission property and evanescent wave absorption of cladded multimode fiber tapers," Optics express **11**(3), 215–223 (2003).

[39] C. Lutzler, "Fabrication of Optical Microfibers," (September), (2012).

[40] J. Lu, Z. Chen, F. Pang, and T. Wang, "Theoretical Analysis of Fiber-Optic Evanescent Wave Sensors," 2008 China-Japan Joint Microwave Conference 583–587 (2008).

[41] "Sensors _ Free Full-Text _ Tapered Optical Fiber Sensor for Label-Free Detection of Biomolecules _ HTML," (n.d.).

[42] H. Qiu, S. Gao, P. Chen, Z. Li, X. Liu, C. Zhang, Y. Xu, S. Jiang, C. Yang, Y. Huo, and W. Yue, "Evanescent wave absorption sensor based on tapered multimode fiber coated with monolayer graphene film," Optics Communications **366**, 275–281 (2016).

[43] D. Bischof, F. Kehl, and M. Michler, "Design method for a distributed Bragg resonator based evanescent field sensor," Optics Communications **380**, 273–279 (2016).

[44] X. Wang and O. S. Wolfbeis, "Optical methods for sensing and imaging oxygen: materials, spectroscopies and applications," Chemical Society Reviews Soc. Rev. **43**(10), 3666–3761 (2014).

[45] G. P. Anderson, J. P. Golden, L. K. Cao, D. Wijesuriya, L. C. Shriver-Lake, and F. S. Ligler, "Development of an Evanescent Wave Fiber Optic Biosensor," IEEE Engineering in Medicine and Biology Magazine **13**(3), 358–363 (1994).

[46] C. R. Taitt, G. P. Anderson, and F. S. Ligler, "Evanescent wave fluorescence biosensors: Advances of the last decade," Biosensors and Bioelectronics **76**, 103–112 (2016).

[47] A. P. Demchenko, *Introduction to Fluorescence Sensing* (2009).

[48] F. Instrumentation, "Tutorial on Fluorescence and Fluorescent Instrumentation," 1–12 (2011).

[49] J. X. Zhang, "Introduction to Fluorescence and Confocal Microscopy," (2003).

[50] A. Kuzmanoski and C. Feldmann, "Fluorescent Nanoparticles," Optical Molecular Imaging 33–51 (2014).

[51] M. J. Ruedas-Rama, J. D. Walters, A. Orte, and E. A. H. Hall, "Fluorescent nanoparticles for intracellular sensing: A review," Analytica Chimica Acta **751**, 1–23 (2012).

[52] J. M. Chem, "One-step and high yield simultaneous preparation of single- and multi-layer," 8764–8766 (2012).

[53] D. Pan, J. Zhang, Z. Li, and M. Wu, "Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots," Advanced Materials **22**(6), 734–738 (2010).

[54] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, "Chemically Derived Ultramooth Graphene Nanoribbon Semiconductors," Science Magazine **319**(5867), 1229–1232 (2008).

[55] L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, and K. Geim, "Chaotic Dirac billiard in graphene quantum dots," Science **320**(5874), 356–358 (2008).

[56] Y. Yang, A. M. Asiri, Z. Tang, D. Du, and Y. Lin, "Graphene based materials for biomedical applications," Materials Today **16**(10), 365–373 (2013).

[57] S. Zhu, S. Tang, J. Zhang, and B. Yang, "Control the size and surface chemistry of graphene for the rising fluorescent materials," Chemical Communications **48**(38), 4527 (2012).

[58] H. Zhao, Y. Chang, M. Liu, S. Gao, H. Yu, and X. Quan, "A universal immunosensing strategy based on regulation of the interaction between graphene and graphene quantum dots," Chemical Communications (207890), 234–237 (2012).

[59] M. Grzelczak, J. Pérez-Juste, P. Mulvaney, and L. M. Liz-Marzán, "Shape control in gold nanoparticle synthesis," Chemical Society Reviews **37**(9), 1783 (2008).

[60] Y. Liu, W. Q. Loh, A. Ananthanarayanan, C. Yang, P. Chen, and C. Xu, "Fluorescence quenching between unbonded graphene quantum dots and gold nanoparticles upon simple mixing," RSC Adv. **4**(67), 35673–35677 (2014).

[61] X. Ran, H. Sun, F. Pu, J. Ren, and X. Qu, "Ag nanoparticle-decorated graphene quantum dots for label-free, rapid and sensitive detection of Ag+ and biothiols.," Chemical communications (Cambridge, England) **49**(11), 1079–81 (2013).

[62] Z. Zhang, L. Xu, H. Li, and J. Kong, "Wavelength-tunable luminescent gold nanoparticles generated by cooperation ligand exchange and their potential application in cellular imaging," RSC Adv. **3**(1), 59–63 (2013).

[63] S. Luong, S. Jing, A. Ananthanarayanan, K. Chew, and P. Chen, "Electrochimica Acta Graphene quantum dots functionalized gold nanoparticles for sensitive electrochemical detection of heavy metal ions," Electrochimica Acta **172**, 7–11 (2015).

[64] W. Hong, H. Bai, Y. Xu, Z. Yao, Z. Gu, and G. Shi, "Preparation of gold nanoparticle/graphene composites with controlled weight contents and their application in biosensors," Journal of Physical Chemistry C **114**(4), 1822–1826 (2010).

[65] J. Li, J. Qu, R. Yang, L. Qu, and P. de B. Harrington, "A Sensitive and Selective Electrochemical Sensor Based on Graphene Quantum Dot/Gold Nanoparticle Nanocomposite Modified Electrode for the Determination of Quercetin in Biological Samples," Electroanalysis **28**(6), 1322–1330 (2016).

[66] X. Hai, X. Lin, X. Chen, and J. Wang, "Highly selective and sensitive detection of cysteine with a graphene quantum dots-gold nanoparticles based core-shell nanosensor," Sensors and Actuators, B: Chemical **257**, 228–236 (2018).

[67] Y. Zhu, S. Lu, A. Gowri Manohari, X. Dong, F. Chen, W. Xu, Z. Shi, and C. Xu, "Polydopamine interconnected graphene quantum dots and gold nanoparticles for enzymeless H2O2detection," Journal of Electroanalytical Chemistry **796**(April), 75–81 (2017).

[68] R. H. Franco, R. and Pereira, E. in ; Kretsinger, "Interactions of gold nanoparticles with proteins," .

[69] M. E. Ali, U. Hashim, M. Kashif, S. Mustafa, Y. B. Che Man, and S. B. Abd Hamid, "Development of swine-specific DNA markers for biosensor-based halal authentication," Genetics and Molecular Research **11**(2), 1762–1772 (2012).

[70] A. Rohman, K. Triyana, Sismindari, and Y. Erwanto, "Differentiation of lard and other animal fats based on triacylglycerols composition and principal component analysis," International Food Research Journal **19**(2), 475–479 (2012).

[71] F. Gunstone, "Fatty Acid and Lipid Chemistry," Fatty Acid and Lipid Chemistry 2–3 (1996).

[72] F. Wikipedia, "Chemical structure," 1–5 (2008).

[73] F. Gunstone, "Fatty acids and lipids chemistry," 252 (1996).

[74] N. A. M. Yanty, J. M. N. Marikkar, and M. S. Miskandar, "Comparing the thermo-physical characteristics of lard and selected plant fats.," Grasas y Aceites **63**(3), 328–334 (2012).

[75] K. Bonne and W. Verbeke, "Muslim consumer trust in halal meat status and control in Belgium," Meat Science **79**(1), 113–123 (2008).

[76] N. I. M. Johan, K. N. Khamil, and K. S. Leong, "An analysis of impedance sensing in lard detection," Proceedings - 6th IEEE International Conference on Control System, Computing and Engineering, ICCSCE 2016 (November), 262–267 (2017).

[77] M. A. Sairin, N. N. A. Nizar, S. A. Aziz, D. M. Hashim, and F. Z. Rokhani, "Potential of dielectric spectroscopy measurement for lard detection," Proceedings of the International Conference on Sensing Technology, ICST **2016–March**, 722–727 (2016).

[78] S. Sensors, *Sensors for Everyday Life* (2017), **23**.

[79] M. A. Sairin, N. Hamilia, A. Latiff, S. A. Aziz, F. Z. Rokhani, and S. Systems, "Distinguishing edible oil using dielectric spectroscopy at microwave frequencies of 8 . 2-12 . 1 GHz," 630–633 (2016).

[80] Sucipto, Irzaman, T. Tedja Irawadi, and A. Miftah Fauzi, "Potential of conductance measurement for lard detection," International Journal of Basic & Applied Sciences IJBAS-IJENS **11**(October), 5–26 (2011).

[81] A. A. Shabaneh, S. H. Girei, P. T. Arasu, W. B. W. A. Rahman, A. A. A. Bakar, A. Z. Sadek, H. N. Lim, N. M. Huang, and M. H. Yaacob, "Reflectance response of tapered optical fiber coated with graphene oxide nanostructured thin film for aqueous ethanol sensing," Optics Communications **331**, 320–324 (2014).

[82] M. A. A. Rosli, "Investigation Forms Of Graphene Oxide Layer On Tapered Optical Fiber Sensor For Aqueous Ethanol," Universiti Putra Malaysia

(2016).

[83] N. Jamaludin, "Biochar as a green source to synthesize photoluminescent materials," University Putra Malaysia (2016).

[84] 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 **65**(9), 1400–1403 (2011).

[85] D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field, C. A. Ventrice, and R. S. Ruoff, "Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy," Carbon **47**(1), 145–152 (2009).

[86] C. Lim, HN Huang, NM Lim, SS Harrison, I Chia, "From the SelectedWorks of Huang Nay Ming Fabrication and characterization of graphene hydrogel via hydrothermal approach as a scaffold for preliminary study of cell growth Fabrication and characterization of graphene hydrogel via hydrothermal approach as," International Journal of Nanomedicine **6**, 1817–1823 (2011).

[87] F. Mohamad, M. A. Sairin, N. N. A. Nizar, S. A. Aziz, D. M. Hashim, S. Misbahulmunir, and F. Z. Rokhani, "Investigation on interdigitated electrode design for impedance spectroscopy technique targeting lard detection application," Proceedings of the International Conference on Sensing Technology, ICST **2016–March**, 739–744 (2016).

[88] O. Instructions, "LS-1 Series Tungsten Halogen Light Sources Installation and Operation Instructions LS-1 Tungsten Halogen Light Source," 1–12 (2000).

[89] OceanOptics, "USB4000 Data Sheet," 1–44 (2017).

[90] A. Shabaneh, "Development Of Chemical Sensors Based On Tapered Optical Fiber Tip Coated With Nanostructured Thin Films," Universiti Putra Malaysia (2015).

[91] P. Wang, G. Brambilla, M. Ding, Y. Semenova, Q. Wu, and G. Farrell, "Investigation of single-mode – multimode – single-mode fiber structures and their application for refractive index sensing," Josab **28**(5), 1180–1186 (2011).

[92] Y. M. Kamil, M. A. Mustapa, M. H. A. Baka, B. Musa, A. Syahir, M. H. Yaacob, and M. A. Mahdi, "Refractive index sensor with asymmetrical tapered fiber based on evanescent field sensing," IBP 2015 - 2015 IEEE International Broadband and Photonics Conference (April), 35–39 (2015).

[93] C. Li and Y. Yue, "Fluorescence spectroscopy of graphene quantum dots: Temperature effect at different excitation wavelengths," Nanotechnology **25**(43), (2014).

[94] M. Tortello, S. Colonna, M. Bernal, J. Gomez, M. Pavese, C. Novara, F. Giorgis, M. Maggio, G. Guerra, G. Saracco, R. S. Gonnelli, and A. Fina, "Effect of thermal annealing on the heat transfer properties of reduced graphite oxide fl akes : A nanoscale characterization via scanning thermal microscopy," **109**, 390–401 (2016).

[95] R. Andrews, D. Jacques, D. Qian, and E. C. Dickey, "Purification and structural annealing of multiwalled carbon nanotubes at graphitization temperatures," Carbon **39**(11), 1681–1687 (2001).

[96] M. Alyobi, C. Barnett, and R. Cobley, "Effects of Thermal Annealing on the Properties of Mechanically Exfoliated Suspended and On-Substrate Few-Layer Graphene," Crystals **7**(11), 349 (2017).

[97] C. M. Chen, J. Q. Huang, Q. Zhang, W. Z. Gong, Q. H. Yang, M. Z. Wang, and Y. G. Yang, "Annealing a graphene oxide film to produce a free standing high conductive graphene film," Carbon **50**(2), 659–667 (2012).

[98] B. Herman, J. R. Lakowicz, and D. B. Murphy, "Fluorescence Excitation and Emission Fundamentals," Unknown (2009).

[99] J. L. Robeson and R. D. Tilton, "Effect of concentration quenching on fluorescence recovery after photobleaching measurements," Biophysical Journal **68**(5), 2145–2155 (1995).

[100] M. Tortello, S. Colonna, M. Bernal, J. Gomez, M. Pavese, C. Novara, F. Giorgis, M. Maggio, G. Guerra, G. Saracco, R. S. Gonnelli, and A. Fina, "Effect of thermal annealing on the heat transfer properties of reduced graphite oxide flakes: a nanoscale characterization via scanning thermal microscopy," (2016).

[101] B. Quantum, "An Introduction to Fluorescence Spectroscopy," Chem 312 (2007).

[102] S. Huang, L. Wang, C. Huang, B. Hu, W. Su, and Q. Xiao, "Graphene quantum dot coupled with gold nanoparticle based “off-on” fluorescent probe for sensitive and selective detection of L-cysteine," Microchimica Acta **183**(6), 1855–1864 (2016).

[103] J. Hou, F. Zhang, X. Yan, L. Wang, J. Yan, H. Ding, and L. Ding, "Sensitive detection of biothiols and histidine based on the recovered fluorescence of the carbon quantum dots-Hg(II) system," Analytica Chimica Acta **859**, 72–78 (2015).

[104] F. M. Fartas, J. Abdullah, N. A. Yusof, Y. Sulaiman, and M. I. Saiman, "Biosensor based on tyrosinase immobilized on graphene-decorated gold nanoparticle/chitosan for phenolic detection in aqueous," Sensors (Switzerland) **17**(5), (2017).

[105] X. Fei, Z. Liu, Y. Li, G. Yang, C. Su, H. Zhong, Z. Zhuang, and Z. Guo, "One-pot green synthesis of flower-liked Au NP@GQDs nanocomposites for surface-enhanced Raman scattering," Journal of Alloys and Compounds **725**, 1084–1090 (2017).

[106] S. L. Ting, S. J. Ee, A. Ananthanarayanan, K. C. Leong, and P. Chen, "Graphene quantum dots functionalized gold nanoparticles for sensitive electrochemical detection of heavy metal ions," Electrochimica Acta **172**, 7–11 (2015).

BIODATA OF STUDENT

Che Nur Hamizah binti Che Lah was born on February 11, 1992. Her hometown in Kuala Terengganu, Terengganu. After completing Sijil Pelajaran Malaysia (SPM) in 2009 at an ordinary school 'Sekolah Menengah Tengku Mizan Zainal Abidin', she went to Pahang Matriculation Collage. After finished one year pre-university preparatory programme she was accepted into Universiti Putra Malaysia (UPM) under program Bachelor of Science (Honours) in Instrumentation Science. After 4 years, she was graduated in August 2015. At September 2015 she was accepted to become a Research Assistant to Dr. Fakhrul Zaman Rokhani under project 'Impedance characteristic of Lard'. This experience ignited her passion to pursue a career in scientific research. Then, she further her Master study in February 2016. She was an active student member of the Optical Society of America (OSA). Currently she was further her PhD study in Shizuoka University, Japan under The Ministry of Education, Culture, Sports, Science and Technology (MEXT) scholarships.

UNIVERSITI PUTRA MALAYSIA

STATUS CONFIRMATION FOR THESIS / PROJECT REPORT AND COPYRIGHT

ACADEMIC SESSION : ____________________

TITLE OF THESIS / PROJECT REPORT :

DETECTION OF LARD VIA FLUORESCENT FIBER PROBE SENSOR UTILIZING GRAPHENE QUANTUM DOTS

NAME OF STUDENT: CHE NUR HAMIZAH BINTI CHE LAH

I acknowledge that the copyright and other intellectual property in the thesis/project report belonged to Universiti Putra Malaysia and I agree to allow this thesis/project report to be placed at the library under the following terms:

1. This thesis/project report is the property of Universiti Putra Malaysia.
2. The library of Universiti Putra Malaysia has the right to make copies for educational purposes only.
3. The library of Universiti Putra Malaysia is allowed to make copies of this thesis for academic exchange.

I declare that this thesis is classified as :

*Please tick (V)

☐	CONFIDENTIAL	(Contain confidential information under Official Secret Act 1972).
☐	RESTRICTED	(Contains restricted information as specified by the organization/institution where research was done).
☐	OPEN ACCESS	I agree that my thesis/project report to be published as hard copy or online open access.

This thesis is submitted for :

☐	PATENT	Embargo from ____________ until ____________ (date) (date)

Approved by:

(Signature of Student)	(Signature of Chairman of Supervisory Committee)
New IC No/ Passport No.:	Name:
Date :	Date :

[Note : If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization/institution with period and reasons for confidentially or restricted.]