UNIVERSITI PUTRA MALAYSIA

OPTICAL AND STRUCTURAL STUDIES OF GRAPHENE-POLYVINYL ALCOHOL BASED THIN FILM FOR POTENTIAL SENSING OF CARBARYL USING SURFACE PLASMON RESONANCE SPECTROSCOPY

NURUL 'ILLYA BINTI MUHAMAD FAUZI

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By

NURUL 'ILLYA BINTI MUHAMAD FAUZI

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

September 2022

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

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September 2022

Chair : Yap Wing Fen, PhD
Institute : Nanoscience and Nanotechnology

Pesticides are commonly employed in modern agriculture to improve crop yield, and these could potentially to pollute the environment and endanger human life. Hence, developing a highly sensitive sensing element for pesticide detection is important for food safety and environmental protection. The development of polymer nanomaterials-based optical sensor for monitoring pesticides has attracted great attention in recent years. Aside from the novelty of material, the effectiveness and efficiency of materials as sensing layers also should be highlighted. Therefore, the aim of this research is to incorporate graphene nanomaterials and synthetic polymer materials in enhancing the detection properties towards carbaryl based surface plasmon resonance sensor. Herein two different sensing layers based thin film presented, i.e., graphene oxide-polyvinyl alcohol (GO-PVA) and graphene quantum dots-polyvinyl alcohol (GQDs-PVA). The structural properties of both thin films were characterized by Fourier transform infrared (FTIR) spectroscopy had confirmed the presence of functional groups in the composites such as hydroxyl, carbonyl, carboxyl, epoxy and alkoxy. Then, the atomic force microscopy (AFM) shows that the roughness of thin films increased for GO-PVA and GQDs-PVA thin films compared to single element, which shows that the surface morphology influenced by the presence of graphene and PVA. Meanwhile, the optical properties of synthesized thin films were investigated using Ultraviolet-visible (UV-vis) spectroscopy and surface plasmon resonance (SPR) spectroscopy. Based on the UV-vis analysis, the absorbance peaks for the thin films can be observed at the wavelength around 200–500 nm and the band gap obtained for both thin films are 4.086 eV and 4.114 eV for GO-PVA and GQDs-PVA thin films, respectively. Then, the proposed thin films have been incorporated with SPR sensor to evaluate the effectiveness and efficiency for carbaryl detection. From that experimental result, GO-PVA thin film exhibited an excellent SPR sensor's performance with sensitivity at 14.174° ppb^{-1} with correlation coefficient of 0.999, while the

sensitivity of the GQDs-PVA thin film was 8.636° ppb^{-1} with a correlation coefficient of 0.995. The sensitivity for both these thin films was achieved at a carbaryl concentration of 0.001 ppb, indicating the best concentration limit obtained so far. As conclusion, this study successfully demonstrated an effective new sensing layer that potentially can detect carbaryl pesticide and proved that GO-PVA thin film has a better sensing property compared to GQDs-PVA thin film. This is due to the GO-PVA sensing performance, which is able to identify 0.001 carbaryl with full width at half maximum (FWHM) of 2.878° and high detection accuracy (DA) with single noise to ratio (SNR) values of 0.347 $degree^{-1}$ and 0.194, respectively.

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

OPTIK DAN STRUKTUR FILEM NIPIS BERASASKAN GRAFIN-POLIVINIL ALKOHOL UNTUK POTENSI PENGESANAN KARBARIL MENGGUNAKAN RESONANS PLASMON PERMUKAAN SPEKTROSKOPI

Oleh

NURUL ʻILLYA BINTI MUHAMAD FAUZI

September 2022

Pengerusi : Yap Wing Fen, PhD
Institut : Nanosains dan Nanoteknologi

Racun perosak biasanya digunakan dalam pertanian moden untuk meningkatkan hasil tanaman, dan ini berpotensi untuk mencemarkan alam sekitar dan membahayakan nyawa manusia. Oleh itu, membangunkan elemen penderiaan yang sangat sensitif untuk pengesanan racun perosak adalah penting untuk keselamatan makanan dan perlindungan alam sekitar. Pembangunan sensor optik berasaskan bahan nano polimer untuk memantau racun perosak telah menarik perhatian besar dalam beberapa tahun kebelakangan ini. Selain daripada kebaharuan bahan, keberkesanan dan kecekapan bahan sebagai lapisan penderiaan juga harus diserlahkan. Oleh itu, matlamat penyelidikan ini adalah untuk menggabungkan bahan nano grafin dan bahan polimer sintetik dalam meningkatkan sifat pengesanan terhadap karbaril berasaskan sensor resonans plasmon permukaan. Di sini dua lapisan penderiaan berbeza berdasarkan filem nipis dibentangkan, iaitu grafin oksida-polivinil alkohol (GO-PVA) dan titik kuantum grafin-polivinil alkohol (GQDs-PVA). Ciri-ciri struktur kedua-dua filem nipis dicirikan oleh spektroskopi inframerah transformasi Fourier (FTIR) untuk mengesahkan kehadiran kumpulan berfungsi dalam komposit seperti hidroksil, karbonil, karboksil, epoksi dan alkoksi. Kemudian, mikroskopi daya atom (AFM) menunjukkan bahawa kekasaran filem nipis meningkat untuk filem nipis GO-PVA dan GQDs-PVA berbanding unsur tunggal, yang menunjukkan bahawa morfologi permukaan dipengaruhi oleh kehadiran grafin dan PVA. Sementara itu, sifat optik filem nipis yang disintesis telah disiasat menggunakan spektroskopi Ultraviolet-visible (UV-vis) dan spektroskopi resonans plasmon permukaan (SPR). Berdasarkan analisis UV-vis, puncak serapan bagi filem nipis boleh diperhatikan pada panjang gelombang sekitar 200–500 nm dan jurang jalur yang diperolehi bagi kedua-dua filem nipis ialah 4.086 eV dan 4.114 eV untuk GO-PVA dan GQDs-PVA nipis filem, masing-masing. Kemudian, filem nipis yang dicadangkan telah digabungkan dengan sensor SPR untuk menilai keberkesanan dan kecekapan untuk pengesanan karbaril. Daripada keputusan eksperimen itu, filem nipis GO-PVA mempamerkan

prestasi sensor SPR yang sangat baik dengan kepekaan pada 14.174° ppb^{-1} dengan pekali korelasi 0.999, manakala kepekaan filem nipis GQDs-PVA ialah 8.636° ppb^{-1} dengan pekali korelasi 0.995. Kepekaan untuk kedua-dua filem nipis ini telah dicapai pada kepekatan karbaril 0.001 ppb, menunjukkan had kepekatan terbaik yang diperoleh setakat ini. Sebagai kesimpulan, kerja ini telah berjaya membangunkan lapisan penderiaan baharu yang berkesan yang berpotensi dapat mengesan racun perosak karbaril dan membuktikan bahawa filem nipis GO-PVA mempunyai sifat penderiaan yang lebih baik berbanding filem nipis GQDs-PVA. Ini disebabkan oleh prestasi penderiaan GO-PVA yang unggul, yang mampu mengenal pasti 0.001 karbaril dengan lebar penuh pada separuh maksimum (FWHM) pada 2.878° dan ketepatan pengesanan tinggi (DA) dengan nilai nisbah hingar tunggal (SNR) pada 0.347 $degree^{-1}$ dan 0.194, masing-masing.

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This thesis was submitted to the Senate of 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:

Yap Wing Fen, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Jaafar bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mazliana binti Ahmad Kamarudin, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

____
ZALILAH MOHD SHARIFF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Name and Matric No.: Nurul 'Illya Binti Muhamad Fauzi, GS55644

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Signature: ______________________
Name of Chairman of Supervisory Committee: Assoc. Prof. Dr. Yap Wing Fen

Signature: ______________________
Name of Member of Supervisory Committee: Assoc. Prof. Dr. Jaafar bin Abdullah

Signature: ______________________
Name of Member of Supervisory Committee: Dr. Mazliana binti Ahmad Kamarudin

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LIST OF ABBREVIATIONS

Symbol	Description
A	Absorbance
A	Absorption coefficient
AFM	Atomic Force Microscopy
Cs	Chitosan
DA	Detection accuracy
E_g	Energy band gap
FTIR	Fourier Transform Infrared
FWHM	Full width at half maximum
GO	Graphene oxide
GQDs	Graphene quantum dots
Hv	Photon energy
I_o	Intensities of incident light
I_t	Intensities of transmitted light
K	Plank's constant
Ppb	Parts per billion
PVA	Polyvinyl alcohol
Rms	Root-mean-square
Rpm	Revolution per minute
SNR	Signal-to-noise-ratio
SPR	Surface Plasmon Resonance
T	Transmittance
T	Thickness
UV-Vis	Ultraviolet-visible

CHAPTER 1

INTRODUCTION

1.1 Graphene Nanomaterials

The development of nanoscience and nanotechnology is one of the most significant revolutions in modern science and technology. During the last decade, nanoscience and nanotechnology have been emerged exponentially in many scientific disciplines due to their excellent and unique optical and mechanical properties. In this context, graphene one of the most promising carbon nanomaterials has received extensive research attention in the last decades owing to their fascinating properties such as large surface area, outstanding mechanical properties, exceptional thermal or electrical conductivity and optical property (Baez et al., 2021). It has an atomic layered sheet with sp2-bonded carbon atoms that can be prepared using either a top-down or bottom-up approaches (Huang et al., 2021). Since graphene was discovered, its exotic properties and potential applications have been intensively explored and studied. Nevertheless, researchers have realized several shortcomings of graphene, such as low absorptivity and zero bandgap (Bafekry et al., 2021). To alleviate such problems, the modification of structural properties for graphene was explored further. Therefore, the family members of graphene nanomaterials including graphene oxide (GO) and graphene quantum dots (GQDs) were fabricated. Each member exhibits different chemical and physical features which open new opportunities for a various number of applications due to their special features.

GO is a single monomolecular layer that is artificially created by treating graphite with strong oxidizes (Boroujerdi et al., 2020). This compound is made up of carbon, hydrogen and oxygen. It is relatively easy to produce and in contrast to conductive graphene, GO is an electrical insulator (Fadil et al., 2022). It is simple to treat since it is hydrophilic and highly dissolves in water and various organic solvents. This is an important benefit of GO that makes it as an excellent platform for use in various applications. Additionally, GO can easily be modified with different polymers and other materials, to reinforce its physical, chemical and electrochemical properties. Aside from GO, GQDs have received much attention in recent years because of their unique structure-related features, including optical, electrical and optoelectrical functionality (Tian et al., 2018). GQDs are considered a new kind of quantum dots (QDs), as they are chemically and physically stable because of its intrinsic inert carbon property, have a large surface to mass ratio and can be dispersed in water easily due to functional groups at the edges (Yan et al., 2019). It is consisting of one or more layers of graphene and is smaller than 100 nm in size (Bianco et al., 2013). Based on the interdisciplinary properties of GO and GQDs, they have a wide range of applications such as energy storage (Olabi et al., 2021), catalyst (Feng et al., 2021), biomedical application (Reina et al., 2017) and environmental monitoring (Shamik and Balasubramanian, 2014).

In this project, GO and GQDs were used to fabricate as composite thin film-based surface plasmon resonance (SPR) sensor to detect pesticide. The purpose of chemical sensors is to detect just one molecule of a potentially harmful material. This is aligned with the properties of GO and GQDs, which have a large specific surface area and an abundance of functional groups on the molecular surface. Due to these properties, they may detect changes in their surroundings when exposed to the environment. To enhance the sensitivity and lower the detection limit for the detection of pesticide, some modification to the GO and GQDs based SPR method has been further explored.

1.2 Polymeric Synthetic Materials

Polymeric synthetic materials are human-made polymers that consist of thousands repeating units called macromolecules (Gu, 2003). It can be produced by addition and condensation polymerization reaction (Johnson et al., 2020). Synthetic polymers that can be utilized for surface modification include polyvinyl alcohol, polyethylene-co-vinyl acetate, polyethylene glycol, and polyvinylpyrrolidone (Khulbe et al., 2009). Among them, polyvinyl alcohol (PVA) has gained wide considerable attention in terms of theoretical interest and practical uses.

PVA is a type of vinyl polymer made from carbon-carbon bonds (Yang et al., 2013). Due to the high density of hydroxyl groups on its side chains, it is capable of self-cross-linking. The linkage is the same as that of plastic products like polypropylene, polystyrene, polyethylene, polyacrylamide and polyacrylic acid (Caló and Vitaliy, 2014). The degree of hydrolysis of PVA is around 98.5 %, allowing it to dissolve in water at a temperature of more than 70 °C (Mansur and Costa, 2008). PVA is the only vinyl polymer that completely can be mineralized by microorganisms among those made industrially (Chiellini et al., 2003). As a result, it is used to generate water-soluble and biodegradable carriers, which may be beneficial in the production of chemical delivery systems such as fertilizers and pesticides.

Indeed, PVA offers desired properties that are useful in the use of sensor technologies. For example, it is a great matrix for homogenous dispersion and good adsorption of nanoparticles, as well as an environmentally friendly polymer with outstanding film-forming properties (Gautam et al., 2021). It is also low-cost material, can be functionalized on different substrates and synthesized with various nanoparticles as a reducing and capping agent (He et al., 2009). Furthermore, PVA has good optical properties and a great load storage capacity, but low conductivity values (Mohamed and Kader, 2019).

The poor conductivity properties can be overcome by altering with another material. PVA is an insulating polymer that can be turned conductive by combining it with other materials to widen its applications, especially in sensor devices (Lu et al., 2011). Previous research also has demonstrated that PVA-based nanomaterials can be used in electrical and optical devices (Aslam, et al., 2018). Focusing on sensor devices, prior studies reported that PVA-based materials can improve the recognition of target molecules by changing their physical and chemical properties. Thus, they can detect the target molecules with better sensor performance. PVA-based materials also can enhance their biocompatibility, resistance, reactivity to degradation and flexibility. In this context, the PVA polymer integrated with graphene is expected to improve the properties of the composite materials while also producing a better high-sensitivity sensing material for pesticides detection.

1.3 Surface Plasmon Resonance

Surface plasmon resonance (SPR) sensor has witnessed an explosive growth during the past decade. The main advantages of using SPR sensor are no need for labelling, real-time detection, simple, economical and quick analysis (Hashim et al., 2021) It has drawn tremendous attention in the field of chemical sensors and biosensors applications since the phenomenon was first noticed by Wood in 1902 and first applied by Liedberg in 1983. Over 3000 articles have been published that cover a wide range application of SPR sensor technology (Karlsson 2004). The applications included environmental monitoring, medical diagnostic, food safety, pharmaceutical development, security and biotechnology (Mitchell, 2010; Wittenberg et al., 2014; Nguyen et al., 2015).

In SPR biosensors technology, several approaches have been used such as optical prism couplers, optical waveguides, optical fibers and grating couplers. The most frequent approach in SPR application is by prism coupler and attenuated total reflection method that demonstrated by Kretschmann configuration. The Kretchmann configuration is popular because it eliminates the need for a narrow air gap allying the prism base and the metal film. The SPR technique based on the Kretschmann configuration involves the detection of the resonance oscillations at the interfaces between a metal thin film and the analyte (Galvez et al., 2012). Gold, silver, aluminum and copper are among the types of metals that hold a large number of free electrons. However, gold is highly sensitive and stable, so it is very suitable to fabricate as a metal film and this metal is positioned at two dielectric media interfaces (Rosddi et al., 2021).

Thereafter, SPR can occur when p-polarized light hits the gold that coated on the thin film that attached on the prism under complete conditions of internal reflection. Then the reflected beam will be identified for data processing. Different thin films will have different refractive indices, which will influence the resonance intensity (Fen and Yunus, 2009). Basically, in the Kretschmann-configuration, the light is totally reflected at the prism-metal interface by generating an evanescent wave when it intends to pass through the prism (Eddin et al., 2021). To prevent the refractive of the incidence laser in the surface of the prism, the incidence or reflected laser is principally vertical to the prism surface (Omar et al., 2020a). The Kretschmann prism is used to measure the response and reactions on a sensor chip affixed to the prism. The apparatus consists of a light source (laser), a sensor chip (sample), a prism (Kretschmann Prism) and a light detector. The schematic of the Kretschmann configuration of prism coupler is shown in Figure 1.1.

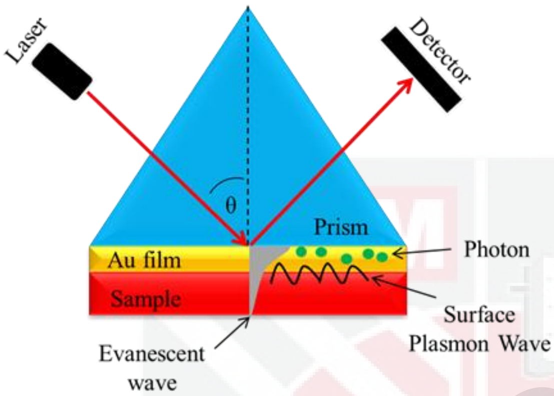

Figure 1.1: Schematic of Kretschmann configuration of prism coupler.

The notion of SPR sensor has shown a quite progressive milestone among other sensing platforms due to its salient features such as high sensitivity (Prabowo et al., 2018). To improve the SPR sensitivity, considerable efforts have been invested by researchers to immobilize various types of recognition elements and nanomaterials. Recognition elements, also known as target receptors are important elements of chemical sensors and biosensors since they are in charge of recognizing target analytes of interest (Justino et al., 2015). Specific recognition elements significantly can enhance the sensitivity SPR sensor by increasing the analyte refractive index in the analyte–nanoparticle conjugates. It also has been proven that the nanomaterial plays a crucial effect in affecting SPR sensitivity. It can enhance the sensitivity of SPR by increasing the plasmonic modes (Szunerits et al., 2014; Mohammadzadeh-asl et al., 2018). The development of nanomaterials as recognition elements also has led to a renewed interest in SPR sensor for various applications.

1.4 Problem Statement

Recently, the various in-situ characterization techniques of graphene have revealed that this material possesses excellent mechanical, electrical, thermal, optical and chemical properties. This has sparked research interest in graphene and its new applications in a variety of fields including high-performance transistors, biomedical systems, sensors and solar cells (Diez-Pascual, 2021). In previous studies, graphene has been successfully synthesized to GO and GQDs through various methods to enhance the properties of the materials.

Compared with graphene composite itself, GO and GQDs are proven to be promising candidates in biosensor and bio-imaging, polymeric composite materials, sorbent and protective coating due to their good dispersibility and low toxicity (Kuilla et al., 2010).

Even though GO and GQDs have many advantages, they still have limitations in optical sensor applications to detect pesticides. Firstly, GO and GQDs are not sensitive enough to detect pesticides and secondly, the material is easy to degrade with the high concentration of pesticides. Therefore, this study intends to prepare PVA polymer to develop GO-PVA and GQDs-PVA solutions in order to overcome the challenges. It must be pointed out that PVA is hydrophilic, has chemical stability, resistant to oil, grease and solvents, and contain high density of reactive functional groups (Lo’ay et al., 2017; Yang et al., 2018). In addition, it has high tensile strength and flexibility as well as high oxygen and aroma barrier properties which can interact strongly with GO and GQDs (Wang et al., 2014). Thus, PVA is excellent in enhancing the sensing properties of GO and GQDs in the detection of pesticides without compromising their biocompatibility (Mo et al., 2015; Zhang et al., 2019). Moreover, GO-PVA and GQDs-PVA have remained much less explored. Therefore, the structural, morphology, optical and sensing properties of the composite materials are investigated; since it is believed that the properties of composite materials will be improved compared to the independent material in detecting pesticides.

Pesticides released into the ecosystem through various industries are generally not appropriately managed, resulting in hazardous pesticide residues that harm humans and the environment. In this study the focus of pesticide is carbaryl (1-naphthyl methylcarbamate). It is because this pesticide very harmful to humans and cause respiratory depression and anxiety, headaches, confusion, stinging eyes, difficulty breathing, dizziness, vomiting, diarrhea, loss of consciousness and appetite (Damalas and Eleftherohorinos, 2011). The optical methods used widely to detect carbaryl are colorimetric, fluorescence, chemiluminescence, High Fundamental Frequency Quartz Crystal Microbalance (HFF-QCM) and electrochemical. Although these approaches are successfully used, they suffer from several disadvantages, such as high instrument operating cost, tedious pre-treatment procedures and long initiation times (Fauzi et al., 2021). Therefore, enormous efforts devoted in developing sensors to overcome the limitation with high sensitivity are plenty needed nowadays.

Corresponding to the SPR method, this sensor provided an affordable, label-free detection, ease of operation, quick detection and great sensitivity toward chemicals (Omar et al., 2020b). As far as we know, there is no report about detection of carbaryl by SPR via graphene-based polymer including GO-PVA and GQDs-PVA. For this purpose, the optical sensor for carbaryl detection will be created by the synergetic interactivity between GO-PVA and GQDs-PVA on the metallic chips by using SPR spectroscopy.

1.5 Research Objectives

From the problem statement stated above, the objectives of this study are:

1. To identify the optical and structural properties of GO-PVA and GQDs-PVA thin films.

2. To determine the potential of GO-PVA and GQDs-PVA thin films in sensing carbaryl using surface plasmon resonance spectroscopy.

1.6 Outlines of Thesis

This thesis is divided into five chapters: introduction, literature review, method, results and discussion, and conclusion. The introduction presented in detail for each major element in this work, which are graphene nanomaterials and synthetic polymer used. Furthermore, in this section, surface plasmon resonance has been described as an efficient instrument for evaluating the potential sensitivity of the sensor layer in pesticide detection. This chapter also discusses and states the problem statements that lead to the objectives of this study. Chapter 2 then focuses on some of the prior research on the optical and structural properties of graphene-based polymers. This chapter also covers past research on graphene and polymer-based materials for pesticide detection. Aside from that, previous research on SPR based various materials in pesticide detection has been emphasized. Moving on to Chapter 3, the methodology of this study is presented, including the synthesis of chemicals, the fabrication of thin films, the characterization techniques and ends with the sensing properties via the surface plasmon resonance sensor. In Chapter 4, the experimental results obtained through characterization have been evaluated. By the results obtained, this chapter provides comprehensive explanations and comparison of the structural, optical properties and sensing potential of the thin films in detecting carbaryl solution. Finally, Chapter 5 concludes and summarizes the research findings based on the structural, optical and performance of the sensing layer. Some recommendations and suggestions for future work are also included in this chapter.

REFERENCES

Abdulla, H. S., & Abbo, A. I. (2012). Optical and electrical properties of thin films of polyaniline and polypyrrole. International Journal of Electrochemical Science, 7:10666–78.

Argawai, S., Giri, P., Prajapati, Y. K., & Chakrabarti, Parthasarathi, Chakrabarti. (2016). Effect of surface roughness on the performance of optical spr sensor for sucrose detection: fabrication, characterization, and simulation study. IEEE Sensors Journal, 16:8865–8873.

Aksornneam, L., Kanatharana, P., Thavarungkui, P., & Thammakhet, C. (2016). 5-Aminofluorescein doped polyvinyl alcohol film for the detection of formaldehyde in vegetables and seafood. Analytical Methods, 8:1249–56.

Almeda, L. K. S. D., Chigome, S., Torto, N., Frost, C. L., & Pletschke, B. I. (2015). A novel colorimetric sensor strip for the detection of glyphosate in water. Sensors & Actuators: B. Chemical, 206:357–63.

Anas, N. A. A., Fen, Y. W., Yusof, N. A., Omar, N. A. S., Ramdzan, N. S. M., & Daniyal, W. M. E. M. M. (2020). Investigating the properties of cetyltrimethylammonium bromide/hydroxylated graphene quantum dots thin film for potential optical detection of heavy metal ions. Materials, 13:2591.

Anas, N. A. A., Fen, Y. W., Yusof, N. A., Omar, N. A. S., Ramdzan, N. S. M., Daniyal, W. M. E. M. M., Saleviter, S., & Zainudin, A. A. (2019). Optical properties of chitosan/hydroxyl-functionalized graphene quantum dots thin film for potential optical detection of ferric (III) ion. Optics and Laser Technology, 120:105724.

Aslam, M., Mazhar A. K., & Zulfiqar A. R. (2018). Polyvinyl alcohol: a review of research status and use of polyvinyl alcohol based nanocomposites. Polymer Engineering and Science, 58:1–14.

Baez, D. F., Brito, T. P., Espinoza, L. C., Mendez-Torres, A. M., Sierpe, R., Siera-Rosales, P., Venegas, C. J., Yanez, C., & Bollo, S. (2021). Graphene-based sensors for small molecule determination in real samples. Microchemical Journal, 167:106303.

Bafekry, A., Gogova, D., Fadlallah, M., Chuong, N. V., Ghergherehchi, M., Faraji, M., Feghhi, S. A. H., & Oskoeian, M. (2021). Electronic and optical properties of two-dimensional heterostructures and heterojunctions between doped-graphene and c- and n-containing materials†. Physical Chemistry Chemical Physical, 23:4865–73.

Bhatnagar, D., Sukhbir S., Sriniwas Y., Ashok K., & Inderpreet, K. (2017). Experimental and theoretical investigation of relative optical band gaps in graphene generations. Materials Research Express, 4:15101.

Bianco, A., Cheng, H. M., Enoki, T., Gogotsi, Y., Hurt, R. H. Koratkar, N. Kyotani, T., Monthioux, M., Park, C. R., Tascon, J. M. D., & Zhang, J. (2013). All in the graphene family- a recommended nomenclature for two-dimensional carbon materials. Carbon, 65:1–6.

Boroujerdi, R., Amr, A., & Paul R. (2020). State of the art in alcohol sensing with 2D materials. Nano-Micro Letters, 33:1–33.

Çakır, O., & Zübeyde, B. (2019). Pesticide analysis with molecularly imprinted nanofilms using surface plasmon resonance sensor and LC-MS/MS: comparative study for environmental water samples. Sensors & Actuators B: Chemical, 297:126–764.

Cakir, O., Monireh, B., Ligim, G., Fatma, Y., & Zubeyde, B. (2021). Sensitive and selective detection of amitrole based on molecularly imprinted nanosensor. Journal of Molecular Recognition, 34:1–10.

Caló, E., & Vitaliy, V. K. (2014). Biomedical applications of hydrogels : a review of patents and commercial products. European Polymer Journal, 65:252–67.

Cao, J., He, G., Ning, X., Chen, X., Fan, L., Yang, M., Yin, Y., & Cai, W. (2022). Preparation and properties of o-chitosan quaternary ammonium salt/ polyvinyl alcohol/graphene oxide dual self-healing hydrogel. Carbohydrate Polymers, 287:119318.

Cao, L., Fei, Z., Qiugen, W., & Xiaofeng, W. (2017). Fabrication of chitosan/graphene oxide polymer nanofiber and its biocompatibility for cartilage tissue engineering. Materials Science & Engineering C, 79:697–701.

Cervera-chiner, L., Carmen, M., & Antonio, A. (2020). Detection of DDT and carbaryl pesticides in honey by means of immunosensors based on high fundamental frequency quartz crystal microbalance (HFF-QCM). Journal of the Science of Food and Agriculture, 100:2468–2472. .

Chamuah, N., Bhuyan, N., Das, P. P., Ojah, N., Choudhary, A. J., Medhi, T., & Nath, P. (2018). Gold-coated electrospun pva nano fibers as sers substrate for detection of pesticides. Sensors & Actuators: B. ChemicaL, 273:710–17.

Chen, J., Liu, Z., Fang, J., Wang, Y., Cao, Y., Xu, W., Ma, Y., Meng, X., & Wang, B. (2022). A turn-on fluorescence biosensor for sensitive detection of carbaryl using flavourzyme-stabilized gold nanoclusters. Lebensmittel-Wissenschaft & Technologie, 157:113099.

Chen, X., Pan, M., & Jiang, K. (2010). Sensitivity enhancement of spr biosensor by improving surface quality of glass slides. Microelectronic Engineering, 87:790–792.

Chen, Y., Qin, X., Yuan, C., Shi, R., & Wang, Y. (2020). Double responsive analysis of carbaryl pesticide based on carbon quantum dots and Au nanoparticles. Dyes and Pigments, 181:108529.

Chen, Y., Wang, Y., Shi X., Jin, M., Cheng, W., Ren, L., & Wang, Y. (2017). Hierarchical and reversible assembly of graphene oxide/polyvinyl alcohol hybrid stabilized pickering emulsions and their templating for macroporous composite hydrogels. Carbon, 111:38–47.

Chiellini, E., Andrea, C., Salvatore D. A., & Roberto, S. (2003). Biodegradation of poly (vinyl alcohol) based materials. Progress in Polymer Science, 28:963–1014.

Chiu, N., Tu, Y., & Huang, T. (2014). Enhanced sensitivity of anti-symmetrically structured surface plasmon resonance sensors with zinc oxide intermediate layers. Sensors, 14:170–87.

Dai, H., Huang, Y., & Huang, H. (2018). Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue. Carbohydrate Polymers, 185:1–11.

Damalas, C. A., &. Eleftherohorinos, I. G. (2011). Pesticide exposure, safety issues, and risk assessment indicators. International Journal of Environmental Research, 8:1402–19.

Daniyal, W. M. E. M. M., Fen. Y. W., Anas, N. A. A., Omar, N. A. S. Ramdzan, N. A. S., Nakajima, H., & Mahdi, M. A. (2019). Enhancing the sensitivity of a surface plasmon resonance-based optical sensor for zinc ion detection by the modification of a gold thin film. RSC Advances, 9:41729–36.

Daniyal, W. M. E. M. M., Fen. Y. W., Abdullah, J., Sadrolhosseini, A. R., Saleviter, S., & Omar, N. A. S. (2018). Label-free optical spectroscopy for characterizing binding properties of highly sensitive nanocrystalline cellulose-graphene oxide based nanocomposite towards nickel ion. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 212:25–31.

Deshmukh, K., Ahamed, M. B., Deshmukh, R. R., Pasha, S. K. K., Chidambaram, K., & Sadasivuni, K. K. (2016). Eco-friendly synthesis of graphene oxide reinforced hydroxypropyl methylcellulose (HPMC)/polyvinyl alcohol (PVA) blend nanocomposites filled with zinc oxide (ZnO) nanoparticles for high-K capacitor applications. Polymer-Plastics Technology and Engineering, 55:2559.

Deshmukh, K., Ahamed, M. B., Sadasivuni, K. K., Ponnamma, D., Deshmukh, R. R., Pasha, S. K. K., Al-Maadeed, A. A., & Chidambaram, K. (2016). Graphene oxide reinforced polyvinyl alcohol/polyethylene glycol blend composites as high-performance dielectric material. Journal of Polymer Research, 23:159.

Deshmukh, K., Ahamed, M. B., Pasha, S. K. K., Deshmukh, R. R., & and Bhagat, P. R. (2015). Highly dispersible graphene oxide reinforced polypyrrole/polyvinyl alcohol blend nanocomposites with high dielectric constant and low dielectric loss. RSC Advances, 5:61933–45.

Diez-Pascual, A. M. (2021). Development of graphene-based polymeric nanocomposites : a brief overview. Polymers, 13:2978.

Dolgonos., A. Mason, T. O., & Poeppelmeier, K. R. (2016). Direct optical band gap measurement in polycrystalline semiconductors : a critical look at the tauc method. Journal of Solid State Chemistry, 240:43–48.

Dong, H., Zou, F., Hu, X., Zhu, H., Koh, K., & Chen, H. (2018). Analyte induced aunps aggregation enhanced surface plasmon resonance for sensitive detection of paraquat. Biosensors and Bioelectronics, 117:605–12.

Dong, J., Gao, N., Peng, Y., Guo, C., Lv, Z., Wang, Y., Zhou, C., Ning, B., Liu, M., & Gao, Z. (2012). Surface plasmon resonance sensor for profenofos detection using molecularly imprinted thin film as recognition element. Food Control, 25:543–49.

Dong, J., Zhao, X., Cao, E., Han, Q., Liu, L., Zhang, W., Sun, M. (2019). Flexible and transparent AuNP/G/AuNP 'sandwich' substrate for surface-enhanced Raman scattering. Materials Today Nano, 9:100067.

Eddin, F. B. K., Fen, Y. W., Omar, N. A. S., Liew, J. Y. C., & Daniyal, W. M. E. M. M. (2021). Femtomolar detection of dopamine using surface plasmon resonance sensor based on chitosan/graphene quantum dots thin film. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 263:120202.

El-Gohary, S. H., Eom, S., Lee, S. Y., & Byun, K. M. (2016). Dispersion curve-based sensitivity engineering for enhanced surface plasmon resonance detection. Optics Communications, 370:299–305.

Fadil, Y., Thickett, S. C., Agarwal, V., & Zetterlund, P. B. (2022). Synthesis of graphene-based polymeric nanocomposites using emulsion techniques. Progress in Polymer Science, 125:101476.

Faix, O. (1988). Practical uses of FTIR spectroscopy in wood science and technology. Microchimica Acta, 94:21–25.

Fauzi, N. I. M., Fen, Y. W., Omar, N. A. S., & Hashim, H. S. (2021). Recent advances on detection of insecticides using optical sensors. Sensors, 21:3856.

Felipe, B. H. S., Cabral, R. L. B., Ladchumananandasivam, R., Zille, A., Kim, S., Fechine, P. B. A., Nascimento, J. H. O. (2022). Nanocoating on cotton fabric with nitrogen-doped graphene quantum dots/titanium dioxide/PVA: An erythemal UV protection and photoluminescent finishin. Journal of Materials Research and Technology, 18:2435–50.

Fen, Y. W., & Yunus, W. M. M. (2009). Surface plasmon resonance spectroscopy as an alternative for sensing heavy metal ions: a review. Sensor Review, 33:305–14.

Fen, Y. W., Yunus, W. M. M., & Yusof, N. A. (2011). Detection of mercury and copper ions using surface plasmon resonance optical sensor. Sensors and Materials, 23:325–34.

Fen, Y. W., Yunus, W. M. M., Moksin, M. M., Talib, Z. A., & Yusof, N. A. (2011). Surface plasmon resonance optical sensor for mercury ion detection by crosslinked chitosan thin film. Journal of Optoelectronics and Advanced Materials, 13:279–85.

Fen, Y. W., Yunus, W. M. M., & Yusof, N. A. (2012). Surface plasmon resonance optical sensor for detection of Pb^{2+} based on immobilized P-Tert-butylcalix[4]arene-Tetrakis in chitosan thin film as an active layer. Sensors and Actuators, B: Chemical, 171–172:287–93.

Feng, Y., Li, W., An, J., Zhao, Q., Wang, X., Liu, J., Hei, W., & Li, N. (2021). Science of the total environment graphene family for hydrogen peroxide production in electrochemical system. Science of the Total Environment, 769:144491.

Fornaro, T., Burini, D., Biczysko, M., & Barone, V. (2015). Hydrogen-bonding effects on infrared spectra from anharmonic computations: uracil-water complexes and uracil dimers. Journal of Physical Chemistry A, 119:4224.

Galvez, F., Monton, C., Serrano, A., Valmianski, I., Venta, J., Schuller, I. K., & Garcia, M. A. (2012). Effect of photodiode angular response on surface plasmon resonance measurements in the kretschmann-raether configuration effect of photodiode angular response on surface plasmon resonance measurements in the kretschmann-raether configuration. Review of Scientific Instruments, 83:2–5.

Gautam, S., Sharma, S., Sharma, B., & Jain, P. (2021). Antibacterial efficacy of poly (vinyl alcohol) nanocomposites reinforced with graphene oxide and silver nanoparticles for packaging applications. Polymer Composites, 42:2829–37.

Gaveria, M. I., Barrientos, K., Arango, J. B., Cano, J. B., &. Peñuela, G. A. (2022). Highly sensitive fluorescent biosensor based on acetylcholinesterase and carbon dots – graphene oxide quenching test for analytical and commercial organophosphate pesticide detection. Frontiers in Environmental Science, 10:1–13.

Geisse, N. A. (2009). AFM and combined optical techniques. Materials Today, 12:40–45.

Gnutzmann, U., & Clausecker, K. (1974). Theory of direct optical transitions in an optical indirect semiconductor with a superlattice structure. Applied Physics, 14:9–14.

Gu, J. (2003). Microbiological deterioration and degradation of synthetic polymeric materials : recent research advances. International Biodeterioration & Biodegradation, 52:69–91.

Hashim, H. S., Fen, Y. W., Omar, N. A. S., Fauzi, N. I. M., & Daniyal, W. M. E.

M. (2021). Recent advances of priority phenolic compounds detection using phenol oxidases-based electrochemical and optical sensors. Measurement, 184:109855.

He, D., Hu, B., Yao, Q. F., Wang, K., & Yu, S. (2009). Large-scale synthesis of flexible free- sensitivity: electrospun PVA nanofibers of silver nanoparticles. ACS Nano, 3:3993–4002.

He, Y., Xu, B., Li, W., & Yu, H. (2015). Silver nanoparticle-based chemiluminescent sensor array for pesticide discrimination. Journal of Agricultural and Food Chemistry, 63:2930–34.

He, Y., Hong, S., Wang, M., Wang, J., El-Aty, A. M. A., Wang, J., Hacimuftuoglu, , A., Khan, M., & She, Y. (2020). Development of a fluorescent lateral flow strips based on electrospinning molecular imprinting membrane for detection of triazophos residues in tap water. New Journal of Chemistry, 44:6026–36.

Hossain, S. M. Z., Luckham, R. E., McFadden, M. J., & Brennan, J. D. (2009). Reagentless bidirectional lateral flow bioactive paper sensors for detection of pesticides in beverage and food samples. Analytical Chemistry, 81:9055–64.

Huang, H. D., Ren, P. G., Chen, J., Zhang, W. Q., Ji, X., & Li, Z. M. (2012). High barrier graphene oxide nanosheet/poly(vinyl alcohol) nanocomposite films. Journal of Membrane Science, 410:156–63.

Huang, J. J., Liu, J., Liu, J. X., & Wang, J. P. (2020). A microtitre chemiluminescence sensor for detection of pyrethroids based on dual-dummy-template molecularly imprinted polymer and computational simulation. The Journal of Biological and Chemical Luminiscence, 35:120–28.

Huang, T, Tang, X., Luo, K., Wu, Y., Hou, X., & Tang, S. (2021). An overview of graphene-based nanoadsorbent materials for environmental contaminants detection. Trends in Analytical Chemistry, 139:116255.

Islam, M. R., Pias, S. M. N. S., Alam, R. B., & Khondaker, S. I. (2020). Enhanced electrochemical performance of solution-processed single-wall carbon nanotube reinforced polyvinyl alcohol nanocomposite synthesized via solution-cast method. Nano Express, 1:30013.

Islam, M. R., & Mollik, S. I. (2020). Enhanced electrochemical performance of flexible and eco-friendly starch/graphene oxide nanocomposite. Heliyon, 6:e05292.

Jiang, S. D., Bai, Z. M., Tang, G., Hu, Y., & Song, L. (2014). Fabrication and characterization of graphene oxide-reinforced poly (vinyl alcohol)-based hybrid composites by the sol–gel method. Composites Science and Technology, 102:51–58.

Johnson, A. N., Barlow, D . E., Kelly, A. L., Varaljay, V. A., Goodson, W. J. C., Biffinger, J. C. (2020). Current progress toward understanding the biodegradation of synthetic condensation polymers with active hydrolases. Polymer International, 70:977–83.

Justino, C. L. I., , Freitas, A. C., Pereira, R., Duarte, A. C., & Santos. T. A. P. R. (2015). Recent developments in recognition elements for chemical sensors and biosensors. Trends in Analytical Chemistry, 68:2–17.

Kant, R. (2020). Surface plasmon resonance based fiber–optic nanosensor for the pesticide fenitrothion utilizing Ta_2O_5 nanostructures sequestered onto a reduced graphene oxide matrix. Microchimica Acta, 187:2–11.

Karlsson, R. (2004). SPR for molecular interaction analysis: a review of emerging application areas. Journal of Molecular Recognition, 17:151–61.

Kazemifard, N., Ensafi, A. A., & Rezaei, B. (2020). Green synthesized carbon dots embedded in silica molecularly imprinted polymers, characterization and application as a rapid and selective fluorimetric sensor for determination of thiabendazole in juices. Food Chemistry, 310:125812.

Khan, S.A., Khan, S.B., Khan, L.U., Farooq, A., Akhtar, K., & Asiri, A.M. (2018). Fourier transform infrared spectroscopy: fundamentals and application in functional groups and nanomaterials characterization. In: Sharma, S. (eds) Handbook of Materials Characterization. Springer, Cham. https://doi.org/10.1007/978-3-319-92955-2_9

Khulbe, K. C., Feng, C., & Matsuura, T. (2009). The art of surface modification of synthetic polymeric membranes. journal of applied polymer science, 115:855–95.

Kong, L., Huang, M., Chen, J., & Lin, M. (2020). In situ detection of thiram in fruits and vegetables by colorimetry/surface- in situ detection of thiram in fruits and vegetables by colorimetry/surface-enhanced Raman spectroscopy. Laser Physics, 30:65602.

Kuilla, T., Bhadra, S., Yao, D., Kim, N. H., Bose, S., Lee, J. H. (2010). Recent advances in graphene based polymer composites. Progress in Polymer Science, 35:1350–75.

Kwon, Y., & Leckie, J. O. (2006). Hypochlorite degradation of crosslinked polyamide membranes ii. changes in hydrogen bonding behavior and performance. Journal of Mebrane Science, 282:456–64.

Lee, D., & Kim, D. Y. (2019). Hydrophobic paper-based SERS sensor using gold nanoparticles arranged on graphene oxide flakes. Sensors, 19:5471.

Li, H., Li, Y., & Cheng, J. (2010). Molecularly imprinted silica nanospheres embedded cdse quantum dots for highly selective and sensitive optosensing of pyrethroids. Chemistry of Materials, 22:2451–57.

Li, H., Wang, Y., Li, Y., Zhang, J., Qiao, Y., Wang, Q., & Che, G. (2020). Fabrication of pollutant-resistance SERS imprinted sensors based on

SiO_2@TiO_2@Ag composites for selective detection of pyrethroids in water. Journal of Physics and Chemistry of Solids, 138:109254.

Li, Y., Umer, R., Samad, Y. A., Zheng, L., & Liao, K. (2013). the effect of the ultrasonication pre-treatment of graphene oxide (GO) on the mechanical properties of GO/polyvinyl alcohol composites. Carbon, 55:321–27.

Li, Q., Dou, X., Zhao, X., Zhang, L., Luo, J., Xing, X., & Yang, M. (2019). A gold/Fe_3O_4 nanocomposite for use in a surface plasmon resonance immunosensor for carbendazim. Microchimica Acta, 186:2–8.

Liedberg, B. O. (1983). Surface plasmon resonance for gas detection and biosensing*. Sensors and Actuators, 4:299–304.

Lina, Z., Yujuan, C., Bixia, L., Shuhua, S., Ying, Y., & Lingling, S. (2017). In-situ visual and ultrasensitive detection of phosmet using a fluorescent immunoassay probe. Sensors & Actuators: B. Chemical, 241:915–22.

Lingamdinne, L. P., Koduru, J. R., Chang, Y., Naushad, M., & Yang, J. K. (2021). Polyvinyl alcohol polymer functionalized graphene oxide decorated with gadolinium oxide for sequestration of radionuclides from aqueous medium : characterization, mechanism, and environmental feasibility studies. Polymers, 13:3835.

Liu, X., Yang, Y., Mao, L., Li, Z., Zhou, C., Liu, X., Zheng, S., & Hu, Y. (2015). SPR quantitative analysis of direct detection of atrazine traces on au-nanoparticles: nanoparticles size effect. Sensors and Actuators B: Chemical, 218:1–7.

Liu, Y., Cao, N., Gui, W., & Ma, Q. (2018). Nitrogen-doped graphene quantum dots-based fluorescence molecularly imprinted sensor for thiacloprid detection. Talanta, 183:339–44.

Liu, Z., Wang, Y., Deng, R., Yang, L., Yu, S., Xu, S., & Xu, W. (2016). Fe_3O_4@graphene oxide@Ag particles for surface magnet solid-phase extraction surface-enhanced Raman scattering (SMSPE-SERS): From sample pretreatment to detection all-in-one. ACS Applied Materials and Interfaces, 8:14160–68.

Lo'ay, A. A., & Dawood, H. D. (2017). Active chitosan/PVA with ascorbic acid and berry quality of 'superior seedless' grapes. Scientia Horticulturae, 224:286–292.

Lu, X., Zhang, W., Wang, C., Wen, T., & Wei, Y. (2011). One-dimensional conducting polymer nanocomposites : synthesis, properties and applications. Progress in Polymer Science, 36:671–712.

Maharana, P. K., Padhy, P., & Jha, R. (2013). On the field enhancement and performance of an ultra-stable spr biosensor based on graphene. IEEE Photonics Technology Letters, 25:2156–59.

Maharana, P. K., & Srivastava, T. (2014). On the performance of highly sensitive and accurate graphene-on-aluminum and silicon-based spr biosensor for visible and near infrared. Plasmonics, 9:1113–20.

Mansur, H. S., & Costa, H. S. (2008). Nanostructured poly(vinyl alcohol)/bioactive glass and poly(vinyl alcohol)/chitosan/bioactive glass hybrid scaffolds for biomedical applications. Chemical Engineering Journal, 137: 72–83.

Martinez, G. (2009). Polymeric modification of graphene through esterification of graphite oxide and poly(vinyl alcohol). Macromolecules, 42:6331–34.

Mauriz, E., Calle, A., Lechuga, L. M., Quintana, J., Montoya, A., & Manclus, J. J. (2006). Real-time detection of chlorpyrifos at part per trillion levels in ground, surface and drinking water samples by a portable surface plasmon resonance immunosensor. Analytica Chimica Acta, 561:40–47.

Mauriz, E., Calle, A., Manclus, J. J., Montoya, A., Escuela, A. M., Sendra, J. A., Lechuga, L. M. (2006). Single and multi-analyte surface plasmon resonance assays for simultaneous detection of cholinesterase inhibiting pesticides. Sensors and Actuators B, 118:399–407.

Mihalache, et al., Radoi, A., Munteanu, C., Kusko, M., & Kusko, C. (2014). Charge storage and memory effect in graphene quantum dots – peg600 hybrid nanocomposite. Organonic Electronics, 15, 216–225.

Minha, P. H., Hoang, V. T., Dinh, N. X., Hoang, O. V., Cuong, N. V., Hop, D. T. B., Tuan, T. Q., Khi, N. T., Huy, T. Q., & Le, A. T. (2020). Reduced graphene oxide-wrapped silver nanoparticles for applications to ultrasensitive colorimetric detection of Cr (VI) ions and carbaryl pesticide. New Journal of Chemistry, 44:7611–20.

Mitchell, J. (2010). Small molecule immunosensing using surface plasmon resonance. Sensors, 10:7323–46.

Mo, S., Peng, L., Yuan, C., Zhao, C., Tang, W., Ma. C., Shen. J., Yang. Y., Min, Y., & Epstein, A. J. (2015). Enhanced properties of poly(vinyl) alcohol composite films with functionalized graphene, RSC Advances, 5:97738–97745.

Mohamed, M. B., & Kader, M. H. A. (2019). Effect of excess oxygen content within different nano-oxide additives on the structural and optical properties of PVA/PEG blend. Applied Physics A, 125:1–11.

Mohammadzadeh-asl, S., Keshtkar, A., Dolatabadi, J. E. N., & Guardia, M. D. (2018). Nanomaterials and phase sensitive based signal enhancment in surface plasmon resonance. Biosensors and Bioelectronic, 110:118–31.

Mohebbi, A., Farajzadeh, M. A., Mahmoudzadeh, A., & Etemady, A. (2019). Combination of poly (ε–caprolactone) grafted graphene quantum dots–based dispersive solid phase extraction followed by dispersive liquid–liquid microextraction for extraction of some pesticides from fruit juices prior to their quantification by gas chromatography. Microchemical Journal, 153:104328.

Morimune, S., Nishino, T., & Goto, T. (2012). Poly(vinyl Alcohol)/graphene Oxide nanocomposites prepared by a simple eco-process. Polymer Journal, 44:1056–63.

Nair, R. V., Thomas, R. T., Mohamed, A. P., & Pillai, S. (2020). Fluorescent turn-off sensor based on sulphur-doped graphene quantum dots in colloidal and film forms for the ultrasensitive detection of carbamate pesticides. Microchemical Journal, 157:104971.

Nemati, F., Hosseini, M., Zare-Dorabei, R., & Ganjali, M. R. (2018). Sensitive recognition of ethion in food samples using turn-on fluorescence n and s co-doped graphene quantum dots. Royal Society of Chemistry, 10:1760–66.

Nguyen, H. H., Park, J., Kang, S., & Kim. M. (2015). Surface plasmon resonance: a versatile technique for biosensor applications. Sensors,15:10481–510.

Nguyen, T. H. D., Zhang, Z., Mustapha, A., Li, H., & Lin, M. (2014). Use of graphene and gold nanorods as substrates for the detection of pesticides by surface enhanced raman spectroscopy. Journal of Agricultural and Food Chemistry, 62:10445–51.

Ng, Z. C., Lau, W. J., & Ismail, A. F. (2020). GO-PVA-integrated TFN RO membrane: exploring the effect of orientation switching between PA and GO/PVA and evaluanting the GO loading impact. Desalination, 496: 114538.

Olabi, A. G., Abdelkareem, M. A., Wilberforce, T., & Sayed, E. T. (2021). Application of graphene in energy storage device – a review. Renewable and Sustainable Energy Reviews, 135:110026.

Omar, N. A. S., Fen, Y. W., Saleviter, S., Kamil, Y. M., Daniyal, W. M. E. M. M., Abdullah, J., & Mahdi, M. A. (2020). Experimental evaluation on surface plasmon resonance sensor performance based on sensitive hyperbranched polymer nanocomposite thin films. Sensors & Actuators A: Physical, 303:111830.

Omar, N. A. S., Fen, Y. W., Saleviter, S., Kamil, Y. M., Daniyal, W. M. E. M. M., Abdullah, J., & Mahdi, M. A. (2020). Quantitative and selective surface plasmon resonance response based on a reduced graphene oxide – polyamidoamine nanocomposite for detection of dengue virus E-Proteins. Nanomaterials, 10:1–14.

Omar, N. A. S., Fen, Y. W., Ramli, I., Sadrolhosseini, A. R., Abdullah, J., Yusof, N. A., Kamil, Y. M., & Mahdi, M. A. (2021). An optical sensor for dengue envelope proteins using polyamidoamine dendrimer biopolymer-based nanocomposite thin film: enhanced sensitivity, selectivity, and recovery studies. Polymers, 13:762.

Omar, N. A. S., Irmawati, R., Fen, Y. W., Abdullah, J., Daud, N. F. M., Daniyal,

M. E. M. M., & Mahdi, M. A. (2021). A sensing approach for manganase ion detection by carbon dots nanocomposite thin film-based surface plasmon resonance sensor. Optik, 243: 167435.

Omar, N. A. S., Irmawati, R., Fen, Y. W., Muhamad, E. N., Eddin, F. B. K., Anas N. A. A., Ramdzan, N. A. S., Fauzi, N. I. M., & Mahdi, M. A. (2022). Surface refractive index sensor based on titanium dioxide composite thin film for detection of cadmium ions. Measurement, 187:110287.

Pandele, A. M., Ionita, M., Crica, L., Dinescu, S., Costache, M., & Lovu, H. (2014). Synthesis, characterization, and in vitro studies of graphene oxide/chitosan–polyvinyl alcohol films. Carbohydrate Polymers, 102:813–20.

Passos, M. L. C., Lúcia, M., & Saraiva, M. F. S. (2019). Detection in UV-Visible spectrophotometry : detectors, detection systems, and detection strategies. Measurement, 135:896–904.

Philip, A., & Kumar, A. R. (2022). The performance enhancement of surface plasmon resonance optical sensors using nanomaterials: a review. Coordination Chemistry Reviews, 458:214424.

Prabowo, B. A., Purwidyantri, A., & Liu, K. C. (2018). Surface plasmon resonance optical sensor : a review on light source technology. Biosensors, 80:1–27.

Qi, X., Yao, X., Deng, S., Zhou, T., & Fu, Q. (2014). Water-induced shape memory effect of graphene oxide reinforced polyvinyl alcohol nanocomposites†. Journal of Materials Chemistry A, 2:2240–49.

Qi, X., Zhou, T., Deng S., Zong, G., Yao, X., & Fu, Q. (2014). Size-specified hraphene oxide sheets: ultrasonication assisted preparation and characterization. Journal of Materials Science, 49:1785–1793.

Qi, Y. Y., Tai, Z. X., Sun, D. F., Chen, J. T., Ma, H. B., Yan, X. B., Liu, B., & Xue, Q. J. (2012). Fabrication and characterization of poly (vinyl alcohol)/graphene oxide nanofibrous biocomposite scaffolds. Journal of Applied Polymer science, 127:1–10.

Rahman, M. S., Rikta, K. A., Faisal, L., & Anower, M. S. (2020). Enhanced performance of SnSe-Graphene hybrid photonic surface plasmon refractive sensor for biosensing applications. Photonics and Nanostructures - Fundamentals and Applications, 39:100779.

Rajender, G., & Giri, P. K. (2016). Formation mechanism of graphene quantum dots and their edge state conversion probed by photoluminescence and raman spectroscopy. Journal of Materials Chemistry C, 4:10852–10865.

Ramdzan, N. S. M., Y. W. Fen, Omar, N. A. S., Saleviter, S., & Zainudin, A. A. (2019). Optical and surface plasmon resonance sensing properties for chitosan/carboxyl-functionalized graphene quantum dots thin film. Optik, 178:802–12.

Ramdzan, N. S. M., Fen, Y. W., Omar, N. A. S., Anas, N. A. A., Liew, J. Y. C., Daniyal, W. M. E. M. M., & Hashim, H. S. (2021). Detection of mercury ion using surface plasmon resonance spectroscopy based on nanocrystalline cellulose/poly (3,4-Ethylenedioxythiophene) thin film. Measurement, 182:109728.

Rapisarda, M., Piero, G., Fierro, M., & Meo, M. (2021). Ultralight graphene oxide/polyvinyl alcohol aerogel for broadband and tuneable acoustic properties. Scientific Reports, 11:10572.

Reina, G., Dominguez, J. M. G., Criado, A., Vazquez, E., Bianco, A., & Prato, M. (2017). Promises, facts and challenges for graphene in biomedical applications. Chemical Society Reviews, 46:4400–4416.

Ren, X., & Chen, L. (2015). Quantum dots coated with molecularly imprinted polymer as fluorescence probe for detection of cyphenothrin. Biosensors and Bioelectronic, 64:182–88.

Ridout, M. J., A. P. Gunning, M. L. Parker, R. H. Wilson, and V. J. Morris. (2002). Using AFM to image the internal structure of starch granules. Carbohydrate Polymers, 50:123–32.

Rosddi, N. M. M., Fen, Y. W., Anas, N. A. A., Omar, N. A. S., Ramdzan, N. S. M., & Daniyal, W. M. E. M. M. (2020). Cationically modified nanocrystalline cellulose/carboxyl-functionalized graphene quantum dots nanocomposite thin film: characterization and potential sensing application. Crystals, 10:875.

Rosddi, N. M. M., Fen, Y. W., Anas, N. A. A., Omar, N. A. S., Ramdzan., Fauzi, N. I. M., Anuar, M. F., & Daniyal, W. M. E. M. M. (2021). Glucose detection by gold modified carboxyl-functionalized graphene quantum dots-based surface plasmon resonance. Optik, 239:166779.

Roshidi, M. D. A., Fen, Y. W., Omar, N. A. S., Saleviter, S., & Daniyal, W. M. E. M. M. (2019). Optical studies of graphene oxide/poly(amidoamine) dendrimer composite thin film and its potential for sensing Hg^{2+} using surface plasmon resonance spectroscopy. Sensors and Materials, 31:1147–56.

Ruggeri, F. S., Sneideris, T., Vendruscolo, M., & Knowles, T. P. J. (2019). Atomic force microscopy for single molecule characterisation of protein aggregation. Archives of Biochemistry and Biophysics, 664: 134–48.

Ruiz, S., Tamayo, J. A., Ospina, J. A., Porras, D. P. N., Zapata, M. E. V., Hernandez, J. H. M., Valencia, C. H., Zuluaga, F., & Tovar, C. D. G. (2019). Antimicrobial films based on nanocomposites of chitosan/poly(vinyl alcohol)/graphene oxide for biomedical applications. Biomolecules, 9:109.

Saleviter, S., Fen, Y. W., Omar, N. A. S., & Zainudin, A. A. (2018). Optical and structural characterization of immobilized 4-(2-Pyridylazo) resorcinol in chitosan-graphene oxide composite thin film and its potential for Co^{2+} sensing using surface plasmon resonance technique. Results in Physics, 11:118–22.

Saleviter, S., Fen, Y. W., Omar, N. A. S., Daniyal, W. M. E. M. M. (2018). Structural and optical studies of cadmium sulfide quantum dot- graphene oxide-chitosan nanocomposite thin film as a novel spr spectroscopy active layer. Journal of Nanomaterials, 2018:1–8.

Sanchez-Ballester, S. C., Soria, V., Rydzek, G., Ariga, K., & Ribes-Greus, A. (2020). Synthesis and characterization of bisulfonated poly(vinyl alcohol)/graphene oxide composite membranes with improved proton exchange capabilities. Polymer Testing, 91:106752.

Sangiorgi, N., Aversa, L., Tatti, R., Verucchi, R., & Sanson, A. (2017). Spectrophotometric method for optical band gap and electronic transitions determination of semiconductor materials. Optical Materials, 64:18–25.

Sarkar, N., Sahoo, G., & Swain, S. K. (2020). Graphene quantum dots decorated magnetic graphene oxide filled polyvinyl alcohol hybrid hydrogel for removal of dye pollutants. Journal of Molecular Liquids, 302:112591.

Saylan, Y., Akgnollu, S., Cimen, D., Derazshamshir, A., Bereli, N., Yilmaz, F., & Denizli, A. (2017). Development of surface plasmon resonance sensors based on molecularly imprinted nanofilms for sensitive and selective detection of pesticides. Sensors and Actuators B: Chemical, 241:446–54.

Shahdost-fard, F., Fahimi-Kashani, N., & Hormozi-nezhad, M. (2020). A ratiometric fluorescence nanoprobe using CdTe QDs for fast detection of carbaryl insecticide in apple. Talanta, 221:121467.

Shamik, C., & Balasubramanian, R. (2014). Recent advances in the use of graphene-family nanoadsorbents for removal of toxic pollutants from wastewater. Advances in Colloid and Interface Science, 204:35–56.

Sharma, A. K., & Gupta, B. D. (2005). On the sensitivity and signal to noise ratio of a step-index fiber optic surface plasmon resonance sensor with bimetallic layers. Optics Communications, 245:159–69.

Sharma, S., Usha, S. P., Shrivastav, A. M., & Gupta, B. D. (2017). A novel method of SPR based SnO_2: GNP nano-hybrid decorated optical fiber platform for hexachlorobenzene sensing. Sensors & Actuators B: Chemical, 246:927–36.

Shrivastav, A. M., Usha, S. P., & Gupta. B. D. (2016). Fiber optic profenofos sensor based on surface plasmon resonance technique and molecular imprinting. Biosensors and Bioelectronics, 79:150–57.

Soriano, M. L., Jimenez-Sanchez, A., & Cardenas, S. Passivated graphene quantum dots for carbaryl determination in juices. (2021), Journal of Separation Science, 44:1652–1661.

Swinehart, D. F. (1962). The Beer-Lambert law. Journal of Chemical Education, 39:333–35.

Szunerits, S., Spadavecchia, J., & Boukherroub R. (2014). Surface plasmon resonance : signal amplification using colloidal gold nanoparticles for enhanced sensitivity. Reviews in Analytical Chemistry, 33:153–64.

Tan, Y., Ahmad, I., & Wei, T. (2015). Detection of parathion methyl using a surface plasmon resonance sensor combined with molecularly imprinted films. Chinese Chemical Letters, 26:797–800.

Tan, P., JHu, Y. W., & Tan, X. (2017). Adsorption of Cu^{2+} and Cd^{2+} from aqueous solution by novel electrospun poly(vinyl alcohol)/graphene oxide nanofibers. RSC Advances, 6:79641–50.

Thepudom, T., Lertvachirapaiboon, C., Shinbo, K., Kato, K., Kaneko, F., Kerdcharoen, T., & Baba, A. (2018). Surface plasmon resonance-enhanced photoelectrochemical sensor for detection of an organophosphate pesticide chlorpyrifos. MRS Communications, 8:1–6.

Thi, H. N., Nguyen, D. H., Vu, M. T., Tran, H. N., Tran, L. P. P., Thi, N. T. N., Le, N. T. T., & Tri, N. L. M. (2020). Fabrication process and characterization of AgNPs/PVA/ cellulose as a SERS platform for in-situ detection of residual pesticides in fruit. Materials Research Express, 7:35019.

Tian, P., Tang, L., Teng, K. S., & Lau, S. P. (2018). Graphene quantum dots from chemistry to applications. Materials Today Chemistry, 10:221–58.

Tsagkaris, A. S., Uttl, L., Pulkrabova, J., & Hajslova, J. (2020). Screening of carbamate and organophosphate pesticides in food matrices using an affordable and simple spectrophotometric acetylcholinesterase assay. Applied Sciences, 10:565.

Vahabi, S., Salman, B. N., & Javanmard, A. (2013). Atomic force microscopy application in biological research : a review study. Iranian Journal of Medical Sciences, 38:76–83.

Wang, B., Chen, Z., Zhang, J., Cao, J., Wang, S., Tian, Q., Gao, M., & Xu, Q. (2014). Fabrication of PVA/graphene oxide/TiO_2 composite nanofibers through electrospinning and interface solgel reaction: Effect of graphene oxide on PVA nanofibers and growth of TiO_2. Colloids and Surfaces A, 457:318-325.

Wang, K., Wang, Y., Li, Q., Liu, Z., & Liu, S. (2022). A fluorescence and localized surface plasmon resonance dual-readout sensing strategy for detection of acetamiprid and organophosphorus pesticides. Sensors and Actuators: B. Chemical, 351:130977.

Wang, L., Zheng, J., Yang, S., Wu, C., Liu, C., Xiao, Y., Li, Y., Qing, Z., & Yang, R. (2015). Two-photon sensing and imaging of endogenous biological cyanide in plant tissues using graphene quantum dot/gold nanoparticle conjugate two-photon sensing and imaging of endogenous biological cyanide in plant tissues using graphene quantum dot/gold nanoparticles. ACS Applied Materials and Interfaces, 7:19509–15.

Wang, L., Zang, X., Chang, Q., Zhang, G., Wang, C., & Wang, Z. (2014). Determination of triazole fungicides in vegetable samples by magnetic solid-phase extraction with graphene-coated magnetic nanocomposite as adsorbent followed by gas chromatography–mass spectrometry detection. Food Analytical Methods, 7:318–25.

Wei, J., Wang, R., Pan, F., & Fu, Z (2022). Polyvinyl alcohol/graphene oxide conductive hydrogels via the synergy of freezing and salting out for strain sensors. Sensors, 22:3015.

Wittenberg, N. J., Wootla, B., Jordan, L. R., Denic, A., Warrington, A. E., & Oh, S. H., Rodriguez, M. (2014). Applications of SPR for the characterization of molecules important in the pathogenesis and treatment of neurodegenerative diseases. Expert Review of Neurotherapeutics, 14:449–63.

Wood, R. W. (1902). On a remarkable case of uneven distribution of light in a diffraction grating spectrum. Philosophical Magazine, 64:396–402.

Wu, T., & Chen, B. (2017). Facile fabrication of porous conductive thermoplastic polyurethane nanocomposite films via solution casting. Scientific Reports, 17470:1–11.

Wu, Z., Huang, Y., Xiao, L., Lin, D., Yang, Y., W ang, H., Yang, Y., Wu, D., Chen, H., Zhang, Q., Qin, W., & Pu, S. (2019). Physical properties and structural characterization of starch/ polyvinyl alcohol/graphene oxide composite films. International Journal of Biological Macromolecules, 123:569–75.

Xiao, T., Shi, X. Z., Jiao, H. F., Sun, A. L., Ding, H., Zhang, R. R., Pan, D. D., Li, D. X., & Chen, J. (2016). Selective and sensitive determination of cypermethrin in fish via enzymelinked immunosorbent assay-like method based on molecularly imprinted artificial antibody-quantum dot optosensing materials. Biosensors and Bioelectronic, 75:34–40.

Xu, Y., Hong, W., Bai, H., Li, C., & Shi, G. (2009). Strong and ductile poly(vinyl alcohol)/graphene oxide composite films with a layered structure. Carbon, 47:3538–43.

Xu, S., Zou, Y., & Zhang, H. (2020). Well-defined hydrophilic ‘turn-on’-type ratiometric fluorescent molecularly imprinted polymer microspheres for direct and highly selective herbicide optosensing in the undiluted pure milks. Talanta, 211:120711.

Yahia, I. S. & Mohammed, M. I. (2018). Facile synthesis of graphene oxide/pva nanocomposites for laser optical limiting: band gap analysis and dielectric constants. journal of materials science: Materials in Electronics, 29:8555–63.

Yan, X., Song Y., Zhu, C., Song, J., Du, D., Su, X., & Lin, Y. (2016). A sensitive fluorescence ‘turn off-on’ nanosensor for glutathione detection and intracellular imaging graphene quantum dot-MnO_2 nanosheet-based optical sensing platform. ACS Applied Materials & Interfaces, 34:21990–96.

Yan, X., Li, H., Wang, X., & Su, X. (2015). A novel fluorescence probing strategy for the determination of parathion-methyl. Talanta, 131:88–94.

Yan, Y., Gong, J., Chen, J., Zeng, Z., Huang, W., Pu, K., Liu, J., & Chen, P. (2019). Recent advances on graphene quantum dots : From chemistry and physics to applications. Advanced Materials, 31:1808283.

Yang, H., Xu, S., Jiang, L., & Dan, Y. (2013). Thermal decomposition behavior of poly (vinyl alcohol) with different hydroxyl content thermal decomposition behavior of poly (vinyl alcohol) with different hydroxyl content. Journal of Macromolecular Science, Part B: Physics, 51:464–80.

Yang, J. M., Fan, C. S., Wang, N. C., & Chang, Y. H. (2018). Evaluation of membrane preparation method on the performance of alkaline polymer electrolyte: Comparison between poly(vinyl) alcohol)/chitosan blended membrane and poly(vinyl) alcohol/chitosan electrospun nanofiber composite membranes. Electrochimica Acta, 266:332–340.

Yang, S., Lei, P., Shan, Y., & Zhang. D. (2018). Preparation and characterization of antibacterial electrospun chitosan/poly (vinyl alcohol)/graphene oxide composite nanofibrous membrane. Applied Surface Science, 435:832–40.

Yao, G., Liang, R., Huang, C., Wang, Y., & Qiu, J. (2013). Surface plasmon resonance sensor based on magnetic molecularly imprinted polymers amplification for pesticide recognition. Analytical Chemistry 85:11944–51.

Yi, Y., Zhu, G., Liu, C., Huang, Y., Zhang, Y., Li, H., Zhao, J., & Yao, S. (2013). A label-free silicon quantum dots-based photoluminescence sensor for ultrasensitive detection of pesticides. Analytical Chemistry 85:11464–70.

Yilmaz, F., Saylan, Y., Akgonullu, S., Cimen, D., Derazshamshir, A., Bereli, N., & Denizli A. (2017). Surface plasmon resonance based nanosensors for detection of triazinic pesticides in agricultural foods. New Pesticides and Soil Sensors, 679–718.

Zainudin,A. A., Fen, Y. W., Yusof, N. A., & Omar, N. A.S. (2017). Structural, optical and sensing properties of ionophore doped graphene based bionanocomposite thin film. Optik, 144:308–15.

Zhang, C., Cui, H., Cai, J., Duan, Y., & Liu, Y. (2015). Development of fluorescence sensing material based on CdSe/ZnS quantum dots and molecularly imprinted polymer for the detection of carbaryl in rice and chinese cabbage. Journal of Agricultural and Food Chemistry, 63:5–11.

Zhang, C., Lin, B., Cao, Y., Guo, M., & Yu, Y. (2017). Fluorescence determination of omethoate based on dual-strategy for improving sensitivity. Journal of Agricultural and Food Chemistry, 65:3065–73.

Zhang, D., Dai, F., Zhang P., An, Z., Zhao, Y., & Chen, L. (2019). The photodegradation of methylene blue in water with PVDF/GO/ZnO composite membrane. Materials Science and Engineering: C, 96:684–692.

Zhang, R., Wang, Y., Ma, D., Ahmed, S., Qin, W., & Liu, Y. (2019). Effects of ultrasonication duration and graphene oxide and nano-zinc oxide contents on the properties of polyvinyl alcohol nanocomposites. Ultrasonics - Sonochemistry, 59: 104731.

Zhang, Y., Gao, L., Ma, S., & Hu, T. (2022). Porous MB@Cd-MOF obtained by post-modification: self-calibrated fluorescent turn-on sensor for highly sensitive detection of carbaryl. Crystal Growth & Design, 22:2662–2669.

Zhao, N., Chen, C., & Zhou, J. (2012). Surface plasmon resonance detection of ametryn using a molecularly imprinted sensing film prepared by surface-initiated atom transfer radical polymerization. Sensors & Actuators: B. Chemical, 166–167:473–79.

Zhao, X., Zhang, Q., Hao, Y., Li Y., Fang, Y., Chen, D. (2010). Alternate multilayer films of poly(vinyl alcohol) and exfoliated graphene oxide fabricated via a facial layer-by-layer assembly. Macromolecules Article, 43:9411–16.

Zhao, Y., Tong, R., Chen, M., & Xia, F. (2019). Relative humidity sensor based on hollow core fiber filled with GQDs-PVA. Sensors & Actuators: B. Chemical, 284:96–102.

Zhu, S., Song, Y., Wang, J., Wan, H., Zhang, Y., Ning, Y., & Yang, B. (2017). Photoluminescence mechanism in graphene quantum dots: quantum confinement effect and surface/edge State. Nano Today, 13:10–14.

Zidan, H. M. (2003). Electron spin resonance and ultraviolet spectral analysis of UV-irradiated PVA Films filled with $MnCl_2$ and CrF_3. Journal of Applied Polymer Science, 88:104–111.

Zor, E., Narvaez, E. M., Galvez, A. Z., Bingol, H., Ersoz, M., & Merkoci, A. (2015). Graphene quantum dots-based photoluminescent sensor : A multifunctional composite for pesticide detection. ACS Applied Materials & Interfaces, 36:20272–79.