UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF IONOPHORE–DOPED GRAPHENE–BASED BIOCOMPOSITE THIN FILM FOR DETECTION OF POTASSIUM ION USING SURFACE PLASMON RESONANCE

AFIQ AZRI BIN ZAINUDIN

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By

AFIQ AZRI BIN ZAINUDIN

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

June 2017

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

CHARACTERIZATION OF IONOPHORE–DOPED GRAPHENE–BASED BIOCOMPOSITE THIN FILM FOR DETECTION OF POTASSIUM ION USING SURFACE PLASMON RESONANCE

By

AFIQ AZRI BIN ZAINUDIN

June 2017

Chairman : Yap Wing Fen, PhD
Faculty : Science

The preparation of ionophore doped graphene based biocomposite using chitosan, graphene oxide and valinomycin has been studied. After the reaction, valinomycin immobilized in chitosan–graphene oxide thin film was prepared using spin coating technique. The obtained thin film was characterized and confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Photoelectron Spectroscopy (XPS). Surface morphology was evaluated by atomic force microscopy (AFM), shows the thin film is smooth and homogenous. Absorption and transmittance of the thin film were evaluated by the ultraviolet-visible (UV-Vis-NIR) spectroscopy. Valinomycin immobilized in chitosan–graphene oxide thin film has been studied as a sensor element for potassium ion by using surface plasmon resonance (SPR). The K^+ can be detected by measuring SPR signal with a thin film C–GO–V deposited on a gold film when the film in contact with the ion in solution. The sensor produces a linear response for K^+ up to 100 ppm with a sensitivity 0.00948° ppm^{-1}. These results indicate that the C–GO–V films shows potential for the detection K^+ in solution.

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PENCIRIAN FILEM NIPIS IONOPHORE–DIDOPKAN GRAPHENE–BERASASKAN BIOKOMPOSIT UNTUK PENDERIAAN POTASIUM ION MENGGUNAKAN SURFACE PLASMON RESONANCE

Oleh

AFIQ AZRI BIN ZAINUDIN

Jun 2017

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Penyediaan ionophore didopkan biokomposit berdasarkan graphene menggunakan chitosan, graphene oksida dan valinomycin telah dikaji. Selepas tindak balas, campuran valinomycin dalam chitosan–graphene oksida filem nipis telah disediakan dengan menggunakan teknik spin salutan. Filem nipis yang diperolehi telah dicirikan dan disahkan oleh Fourier Transform Infrared Spectroscopy (FTIR) dan X-Ray Photoelectron spectroscopy (XPS). Morfologi permukaan dinilai dengan atomic force microscopy (AFM) untuk menunjukkan filem nipis rata dan seragam. Penyerapan dan penembusan filem nipis oleh cahaya telah dinilai oleh ultraviolet-visible (UV-Vis-NIR) spektroskopi. Campuran valinomycin di dalam chitosan–graphene oksida filem nipis telah dikaji sebagai elemen sensor untuk ion potasium dengan menggunakan surface plasmon resonance (SPR). K^+ boleh dikesan dengan mengukur isyarat daripada SPR daripada filem nipis C–GO–V yang telah di depositkan pada filem emas apabila filem itu bertindak balas dengan ion dalam larutan. Sensor ini menghasilkan tindak balas linear untuk K^+ sehingga 100 ppm dengan sensitiviti 0.00948º ppm^{-1}. Keputusan ini menunjukkan bahawa filem nipis C–GO–V berpotensi untuk pengesanan K^+ dalam larutan.

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I certify that a Thesis Examination Committee has met on 6 June 2017 to conduct the final examination of Afiq Azri bin Zainudin on his thesis entitled "Characterization Of Ionophore–Doped Graphene–Based Biocomposite Thin Film For Detection Of Potassium Ion Using Surface Plasmon Resonance" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

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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:

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Name of Member of Supervisory Committee: Nor Azah Yusof

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
FTIR	Fourier Transform Infrared
K^+	Potassium ion
SPR	Surface Plasmon Resonance
XPS	X-Ray Photoelectron Spectroscopy
C	Chitosan
GO	Graphene oxide
C–GO	Chitosan–graphene oxide
C–GO–V	Chitosan–graphene oxide–valinomycin

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

Thin film is the layer of material with its thickness less than about 1 micrometer. It is different from bulk materials and strongly influenced by surface and interface effect which will cause the changes of electrical, magnetic, optical, thermal and mechanical properties. In order to exhibit thin film, the thickness layer of material must be in the range of the wavelength of visible light (about 500 nm). Layers at this scale can have remarkable reflective properties due to light wave interference and the difference in refractive index between the layers, the air, and the substrate. When light passes through two different (or more) material layers, the optical thin film interference phenomena will occur.

The optical properties of material can be specifically defined as its interaction with an electromagnetic radiation in the visible light. Lights can interact with matter in many different ways depending on some condition such as type of material, its crystal-structure or micro-structure, and also the characteristics of incident light. Moreover, the wide ranges of optical properties observed in solid state materials can be sorted into a small number of general phenomena basically involving reflection, propagation and transmission. Nowadays, optical application is widely used in the industry including luminescence, lasers, thermal emission, photoconductivity and optical fibers (Sharma et al., 2014; Shen et al., 2014; Wang et al., 2013). There are a few phenomenon that can occur when a light beam propagates through an optical medium. For instance, refraction can cause a reduction in the velocity of the wave, while absorption causes attenuation. Luminescence can accompany absorption if the excited atoms radiate by spontaneous emission. Besides, scattering lead a redirection of the light into the matter. After all, the diminishing width of the arrow for the processes of absorption and scattering represents the attenuation of the beam. So, in this project, Ultra-Violet Visible spectroscopy (UV-Vis) was used to describe the optical properties.

Potassium, the second lightest metal, is an alkali-metal denoted by the chemical symbol K and atomic number, Z = 19. Sir Humphry Davy discovered in 1807 by deriving it from potassium hydroxide KOH. Being an alkali atom it has only one electron in the outermost shell and the charge of the nucleus is being shielded by the core electrons. This makes the element very chemically reactive due to the relatively low ionization energy of the outermost electron. Potassium has a chemical weight of 39.0983 and appears naturally in three isotopes, ^{39}K, ^{40}K and ^{41}K. Potassium is a mineral necessary and make up

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about 0.4% mass in the human body. It also play an important role as transmitters in cells and in the regulation of membrane potential, nerve stimulation, and hormone secretion The maintenance of appropriate K^+ concentration is important for many physiological activities in living cells such as nerve transmission, enzyme activation, balancing the pH and regulation of blood pressure (Guo et al.,2015). But, unbalancing K^+ may cause several diseases such as high blood pressure and stroke if excessive and hypokalemia if lack in K^+ in our body system. Since the diseases has getting worse, sensitive detection of K^+ has become a very important issue.

Biocomposite is a material formed by a matrix (resin) and a reinforcement of natural fibers (usually derived from plants or cellulose). They often mimic the structures of the living materials involved in the process in addition to the strengthening properties of the matrix that was used but still providing biocompatibility. Chitosan biocomposite is used in this research. Chitosan is a polysaccharide composed of β-(1-4)-linked-2-2-deoxy-2-amino-D-glucopyranose units. Generally, chitosan obtained by the alkaline deacetylation of chitin which is one of the natural polymers in earth. Chitosan is one of the best for the application due to its superior film-forming properties (Azofeifa et al., 2012; El-Nahrawy et al., 2016; Wang et al., 2012). It is also have the ability to bind cationic and anionic form of noble and metal ion. Owing to its good biocompatibility, biodegradability, low immunogenicity, chitosan has been widely used in applications such as controlled drug release, biosensors, biological, catalysts, packaging materials, and membrane separation (Kaushik et al., 2010; Singh et al., 2010; Zhou et al., 2011; Fen et al., 2013a). Moreover, chitosan has been extensively investigated for several decades to prepare high performance chitosan based materials for meeting this wide range of application. In this research, chitosan has been selected as one of the suitable biopolymers for removal of metals ions due to the presence of the amine functionality which confers both polyelectrolyte and chelate properties.

Graphene is a substance made of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. Graphene consists of interconnected hexagons of carbon atoms as in graphite. The carbon-carbon bond length in graphene is about 0.142 nanometers. Graphene sheets stack to form graphite with inter planar spacing of 0.335 nm. Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. Two main fabrication techniques for graphene are micromechanical cleavage from bulk graphite, and epitaxial growth.

As a robust yet flexible membrane, graphene provides essentially infinite possibilities for the modification or functionalization of its carbon backbone. The

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main derivative of graphene is graphene oxide which can be synthesized from the graphite oxide. The structure of graphene oxide is shown in Figure 1.1. Graphene oxide also has their interesting properties. It is amphiphilic with hydrophilic edges that can be act as surfactant (Kim et al., 2010) and ferromagnetic. Graphene oxide disperses in water and several polar solvents, because the structure of graphene oxide normally includes hydroxyl, epoxy, and carboxyl groups on the graphene sheet.

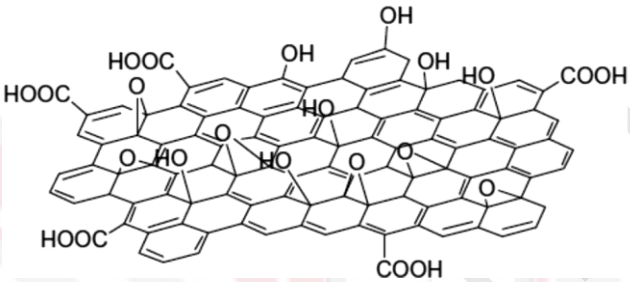

Figure 1.1: Structure of graphene oxide (Nasrollahzadeh et al., 2015).

These graphene oxide derivatives may be useful for luminescent materials and biosensors (Bollella et al., 2017; Yasin et al., 2015). Recently, doping graphene oxide with other elements provides an effective way for achieving goal (Liu et al., 2016; Wang et al., 2014). Thus in this research, good dispersion of graphene oxide in chitosan thin film is expected.

Ionophore, organic and inorganic compounds that bind to ions, ensures the sufficient selectivity of the sensor (Zaitsev et al.,1996). The active sensing components (ionophore and different additives) need to be highly lipophilic and implicity hosted in a hydrophobic polymeric matrix.

Valinomycin one of the ionophores, is a potent antibiotic which acts as a potassium ionophore that brings K^+ conductivity in cell membranes. Valinomycin is a dodecadepsipeptide as shown in Figure 1.2. It is made of twelve alternating amino acids and esters to form a macrocyclic molecule. The twelve carbonyl groups are essential for the binding of metal ions, and also for solvation in polar solvent. The isopropyl and methyl groups are responsible for solvation in nonpolar solvents. The molecule was "locked" into a conformation with the isopropyl groups on the exterior. It is not actually locked into configuration because the size of the molecule makes it highly flexible, but the K^+ gives some degree of coordination to the macromolecule (Berezin, 2015). In this research, the valinomycin doped in the graphene oxide based biocomposite to enhance the sensitivity towards K^+.

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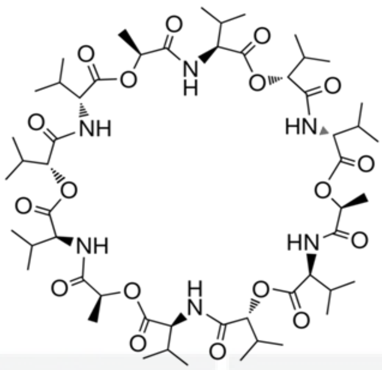

Figure 1.2: **Structure of valinomycin**.

Consequently, the determination of K^+ is very critical in clinical diagnosis, nutritional analysis and also biochemical application. Recently, there are varieties of techniques in order to determine K^+, such as fluorescence spectrum, electrochemistry, calorimetry, flame photometry and so on (Chen et al., 2013; Chen et al., 2014; Radi & O'Sullivan, 2006). However, these method mostly expensive and often take a long time to analysis. Recently, analytical interest has focused on optical sensors that have the advantage of cost-effectiveness, fast measurement capability and no requirement of reference solution (Aragoni et al., 2002; Fen et al., 2012a)

Liedberg et al. (1983) was the earliest to report the application of the surface plasmon resonance (SPR) technique for chemical sensing. SPR offers an economical, showing ease of operation, rapid detection and excellent sensitivity and selectivity toward ion. SPR is a quantum electromagnetic phenomenon arising from the interaction of light with free electrons at a metal-dielectric interface (Pitarke et al., 2007). SPR spectroscopy had emerged a powerful optical sensor based on the sensing of the change in refractive index of a medium adjacent to the metal surface layer.

Basically, when a light passes material higher refractive index (e.g. glass) into material with lower refractive index (e.g. water), light is partially reflected and partially refracted. When the angle at which the light strikes the interface (incident angle) is greater than critical angle, no light is refracted across the interface where total internal reflection is observed. SPR is a phenomenon that based on this basic principle if the interface between the media is coated with a metal thin film and the light is monochromatic and p-polarized.

When the monochromatic light is polarized with its electric field in the plane of incidence, the field causes collective oscillation of the electrons in the metal layer where the energy of the metal surface coincide with the incident photon and the change density wave. The incident light is absorbed and the energy is transferred to the electrons which converted into surface plasmon at the interface. Resonance occurs when the momentum of the incoming light is equivalent to the momentum of the plasmon. Consequently, the intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow called surface plasmon resonance. The momentum of photons and plasmon can be described by a vector function with both magnitude and direction the relative magnitude of the components changes when the angle or wavelength of the incident angle changes. However, plasmons are restricted to the plane of metal film and for SPR it is only the vector component parallel to the surface that matters. Hence, the energy and the angle of incident of light should be right (light is polarized with its electric field in the plane of incidence) to form surface plasmon resonance.

While the incident angle light is totally reflected the electromagnetic field component penetrates a short distance (~300 nm) into a medium of lower refractive index. This field in the lower refractive index medium is called evanescent wave propagates along the interface and decays exponentially with distance normal to the interface. This wave is very sensitive to changes in the refractive index near the metal surface. Such a change may result in a shift in the resonant wavelength of the incident light (Homola et al., 1995) or a change in the resonance angle (Liedberg et al., 1993). SPR-based sensor works based on either of these changes.

1.2 Problem Statement

Numerous studies have focused on the preparation and study the characterization of chitosan/graphene oxide immobilized with various materials (Fan et al., 2016; Yadav & Ahmad, 2015; Kumar & Koh, 2013) and their potential sensing ability. (Kamaruddin et al, 2016; Lokman et al., 2014; Wang et al., 2009). However, there is lack of information on the optical properties of the thin films. Moreover, no work is reported on the properties of chitosan–graphene oxide–valinomycin (C–GO–V) thin film. The physical and optical properties of the C–GO–V thin film have been studied and characterized; and will be discussed in Chapter 4.

The sensing ability of the chitosan–graphene oxide–valinomycin thin film have determined by using surface plasmon resonance (SPR). The use of SPR as a metal ion detection had been widely studied (Li et al., 2016; Liu et al., 2015; Rithesh Raj et al., 2016). However, to the best of our knowledge, SPR is yet applied to K^+ detection in aqueous solution. Thus, the effect of C–GO–V thin film is investigated to detect the K^+ in aqueous solution using SPR method. The

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C–GO–V thin films are envisaged have a high potential sensitive detection of potassium ions.

1.3 Objectives

The objectives of this research are summarized as follows:

1. To study and characterize the physical and optical properties of valinomycin doped chitosan–graphene oxide (C–GO–V) composite thin film.
2. To study the sensing properties of C–GO–V thin film for detection of potassium ion using surface plasmon resonance technique.

1.4 Chapter Organization

This thesis is started with Chapter 1 which is related to the introduction of the chitosan–graphene oxide–valinomycin material and surface plasmon resonance. Previous and current researches by other researcher are reviewed in Chapter 2. Then, the methodology and the instrument used for analysis are well explained in Chapter 3. In Chapter 4, the experimental results and its explanation will be discussed. Finally, the conclusion of the study and recommendation for future work are presented in Chapter 5.

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