UNIVERSITI PUTRA MALAYSIA

HYDROUS FERRIC OXIDE COMPOSITE-INTEGRATED SURFACE PLASMON RESONANCE SENSOR FOR ARSENIC ION DETECTION

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By

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Heavy metal contamination is undoubtedly a major global threat that has sparked ecological and public health concerns. High exposure to heavy metals may cause chronic degenerative diseases that can cause permanent damage to the organ systems and leads to death. Heavy metals that are mostly found as contaminants in the environment would be arsenic (As) and plumbum (Pb). In response to this dire situation, detection and monitoring of these dangerous elements have become a vital necessity. Surface plasmon resonance (SPR) spectroscopy is a sensing technique that has gained exponential research interest especially in biological and chemical diagnostics. The technique is known for its high sensitivity in characterizing thickness and refractive index of a dielectric medium by analysing the resultant angular shift of the SPR output curve. What is more intriguing is the design of SPR and the proximity of the sensing region with the sample which would allow the incorporation of nanomaterials for sensing performance enhancement to detect lower than 0.6 ppb concentration of As in drinking water. This research work demonstrated the development of prism-based SPR sensor integrated with nanocomposites for the detection of As ions utilizing gold (Au) layer. Nanocomposites that were tested include hydrous ferric oxide ($Fe_2H_2O_4$), hydrous ferric oxide-multi-walled carbon nanotube ($Fe_2H_2O_4$-MWCNT) and hydrous ferric oxide-maghemite–reduced graphene oxide ($Fe_2H_2O_4$-Fe_3O_4-rGO). Sensing performance of each nanocomposite layer was analyzed by introducing different concentrations of As(III) and As(V) within the range of 0.1 – 1.0 ppb. The sensitivity values for Au/$Fe_2H_2O_4$ when tested with As(III) and As(V) were 1.640 °ppb^{-1} and 1.363 °ppb^{-1}, respectively, with a detection limit of 0.6 ppb for both ions. The research work was continued with analysing the sensing performance of Au/$Fe_2H_2O_4$-MWCNT nanocomposite. Based on the experimental results, sensitivity values for As(III) and As(V) were achieved at

1.756 $^{o}ppb^{-1}$ and 0.575 $^{o}ppb^{-1}$, respectively, with an enhanced limit of detection value at 0.2 ppb. The final nanocomposite sensing layer, Au/$Fe_2H_2O_4$-Fe_3O_4-rGO, was conducted and the sensitivity values of 2.155 $^{o}ppb^{-1}$ and 1.190 $^{o}ppb^{-1}$ were obtained for As(III) and As(V), respectively. It is worth to note that the sensing performance from this nanocomposite managed to achieve the lowest detection limit for both As ions at 0.1 ppb. Based on these findings, the SPR technique incorporating nanomaterials have shown reliable performance as an As sensor. It is anticipated that this work may contribute greatly towards better As detection methods.

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

SISTEM PENDERIAAN RESONANS PLASMON PERMUKAAN DENGAN PENGGABUNGAN KOMPOSIT HIDROUS FERRIK OKSIDA UNTUK PENGESANAN ION ARSENIK

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Sejak kebelakangan ini, tidak dapat dinafikan bahawa pencemaran logam telah menjadi antara ancaman dunia yang mencetuskan masalah kesihatan ekologi dan kesihatan awam. Pendedahan yang berlebihan terhadap logam berat boleh mengakibatkan penyakit degeneratif kronik dan kerosakan kekal kepada sistem organ manusia. Logam berat yang kerap ditemui menjadi pencemar alam utama ialah arsenik (As) dan plumbum (Pb). Oleh itu, kajian meliputi pengesanan dan pemantauan elemen-elemen ini adalah penting terutamanya dalam keadaan yang semakin diperlukan ini. Spektroskopi resonans plasmon permukaan (SPR) merupakan teknik penderiaan yang menarik tumpuan penyelidikan terutamanya dalam bahagian diagnostik biologi dan kimia. Teknik ini dikenali dengan tahap sensitiviti tinggi terhadap pengukuran ketebalan dan indeks biasan pada medium dielektrik dengan mengkaji peralihan sudut daripada keluaran lengkung SPR. Apa yang lebih menarik adalah reka bentuk SPR dan penderiaan setempat dengan sampel yang boleh digabungkan bersama bahan nano untuk mengesan prestasi penderiaan terutama dengan kepekatan lebih rendah 0.6 ppb seperti yang ada dalam air minuman. Kerja penyelidikan ini menunjukkan perkembangan penderia SPR berasaskan prisma yang berintegrasikan komposit bersaiz nano untuk pengesanan ion As menggunakan lapisan emas (Au). Komposit nano yang diuji dalam eksperimen merangkumi *hydrous ferric oxide* ($Fe_2H_2O_4$), *hydrous ferric oxide-multi-walled carbon nanotube* ($Fe_2H_2O_4$-MWCNT) dan *hydrous ferric oxide-maghemite–reduced graphene oxide* ($Fe_2H_2O_4$-Fe_3O_4-rGO). Prestasi penderiaan setiap lapisan penderia dianalisa dengan kepekatan As(III) dan As(V) dalam julat 0.1 - 1.0 ppb. Nilai sensitiviti untuk Au/$Fe_2H_2O_4$ semasa diuji dengan As(III) dan As(V) adalah 1.640 °ppb^{-1} dan 1.363 °ppb^{-1} masing-masing dengan pencapaian had pengesanan pada

0.6 ppb bagi kedua-dua ion. Kerja penyelidikan diteruskan dengan manganalisa prestasi penderiaan komposit nano $Au/Fe_2H_2O_4$-MWCNT. Berdasarkan kepada keputusan eksperimen, nilai sensitiviti untuk As(III) dan As(V) yang dicapai adalah 1.756 $°ppb^{-1}$ and 0.575 $°ppb^{-1}$ dengan penambahbaikan had pengesanan pada 0.2 ppb. Lapisan penderia berasaskan komposit nano yang terakhir iaitu $Au/Fe_2H_2O_4$-Fe_3O_4-rGO telah dijalankan dan nilai sensitiviti pada 2.155 $°ppb^{-1}$ and 1.190 $°ppb^{-1}$ telah dicapai untuk As(III) dan As(V), masing-masing. Adalah penting untuk diberitahu bahawa prestasi penderiaan daripada komposit nano ini telah berjaya mencapai had pengesanan yang terendah iaitu 0.1 ppb. Berdasarkan penemuan kerja penyelidikan ini, teknik SPR yang menggabungkan komposit bersaiz nano telah menunjukkan potensi yang boleh dipercayai sebagai penderia terhadap As. Adalah dijangkan bahawa kerja penyelidikan ini boleh menyumbang ke arah kaedah pengesanan As yang lebih baik.

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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 Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

θ_R	Resonance angle
a.u.	An arbitrary unit
AAS	Atomic absorption spectroscopy
ATR	Attenuated total reflection
AFM	Atomic-force microscopy
As	Arsenic
ASV	Anodic stripping voltammetry
Au	Gold
WHO	World Health Organization
ETAAS	Electro-thermal atomic absorption spectrometric
CNT	Carbon nano tube
As3+	Arsnite
AsV+	Arsnate
HMs	Heavy metals
CVD	Chemical Vapor Deposition
DI	Deionized
AFS	Atomic fluorescence Spectrometry
E_i	Incident electric filed
E_r	Reflected electric filed
FESEM	Field Emission Scanning Electron Microscope
G	Graphene
GO	Graphene Oxide
ASV	Anodic stripping voltammetry

ICPMS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
ITO	Indium tin oxide
l/min	liter/minute
LOD	Limit of detection
SPW	Surface Plasma Wave
Pb	Plumbum element
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
PPy-Chl	Polypyrrole chitosan
GSH	Glutathione
RI	Refractive index
SEM	Scanning Electron Microscope
TEM	Transmission electron microscopy
TM	Transverse magnetically
XRF	X-ray fluorescence spectrometry
ε_d	Dielectric of medium
ε_m	Dielectric constant of metal
θ_{res}	Resonance angle
$Fe_5HO_8.4H_2O$	Ferrihydrite
α-FeOOH	Goethite

α-Fe_2O_3	Hematite
γ-Fe_2O_3	Maghemite
Fe_3O_4	Magnetite
DTT	Dithiothreitol
DTGluc	N (dithiocarboxy) - N-methyl-D-glucamine
rGO	Reduced Graphene
sc	Chitosan
SPR	Surface Plasmon Resonance
TIR	Total internal reflection
ESPR	Electrochemical Surface plasmon Resonance
MMA	Monomethylarsonate
GNEE	Nano-electrode ensemble
SWASV	Square wave anodic stripping voltammetry
GCE	Glassy carbon electrode
HFO	Hydrated iron (lll) oxide
SNR	Signal-to-noise ratio
FWHM	Full width at half maximum
pH_{PZC}	Point of zero charge

CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metals are highly toxic chemical compounds with an atomic weight ranging from 63.5 to 200.6 g mol^{-1} and a specific gravity greater than 5 g cm^3 [1, 2]. They are non-biodegradable, ubiquitously distributed [3] and impose fatal implications to human health. Among the heavy metals which are harmful, include cadmium (Cd), lead (Pb), mercury (Hg) and Arsenic (As). As contamination has been reported by the World Health Organization to have caused the largest poisoning in history [4, 5]. Due to its abundance and toxicity, monitoring As in water, soil and various food stuffs used for human consumption is becoming important.

A number of techniques have been developed for this purpose within the last five decades which showed reliable sensing performance for extremely low concentrations of As. Detecting As at such level is a challenge in the development of portable and economic high sensitivity detection systems. Previously, As detection was done using several established methods in the field of analytical chemistry such as atomic absorption spectrometric (AAS) methods which include ultraviolet spectrometry, hydride generation AAS[6], electro-thermal AAS in graphite furnace (ETAAS) [7], atomic fluorescence spectrometry (AFS) [8], atomic emission spectrometry (AES) [9], inductively coupled plasma (ICP) [10], inductively coupled plasma-mass spectrometry (ICPMS) [11], and X-ray spectrometry [12]. Most of these methods are reliable and can be used for the measurement of extremely low concentrations of As. Despite the known advantages, these methods suffer from some major disadvantages like heavy and expensive instrumentation, field applicability, requirement of highly skilled technical persons, chemical processing of sample, etc. It has become a necessity to find an excellent continuous monitoring system that can be a useful tool in managing the issue. Surface plasmon resonance (SPR) is one of reliable techniques for heavy metal detections at exceptionally low detection limit [13] . In this technique, plasmonic waves are created between metal layer and dielectric medium. This technique is very sensitive to any changes occur in the dielectric medium. By functionalizing the dielectric medium with nanomaterials-based active layer, the limit of detection towards a specific heavy metal ion can be enhanced. For As ion detection in SPR, the lowest concentration of 0.6 ppb has been reported in [14]. This value sets the benchmark for other researchers to achieve lower detection limit. With the advancement of new nanomaterials, this creates research opportunities to contribute new findings.

1.2 Problem Statement

Contamination of As ions in natural water and wastewater have considered to be a serious issue by many government bodies and international organizations. Toxicity caused by the heavy metal may lead to fatal chronic diseases such as cancer. As a preventive measure, WHO, as well as other regulatory entities, have set the maximum allowable level of As ions as low as 10 ppb in drinking water[15]. Common analytical chemistry techniques today are known to detect As ions at low concentrations. However, the procedures to these techniques are laborious, bulky and very expensive. This creates a crucial demand for a low-cost and chemically stable alternative that can deliver better, if not the same, sensing performance as compared to the available techniques. Over the recent decades, many research groups have ventured onto developing new techniques for As detection and SPR has emerged as the preferred technique owing to its efficient sensitivity. The study which has reported the lowest detection limit, thus far, implemented a carbon nanotube filter to enhance the absorption of As ions. The detection limit was obtained at 0.6 ppb [14]. Aside from that, iron oxides have been gaining attention from researchers that are particularly interested in As detection, as well. They are known to have high sorption capacity specifically towards As ions which makes them enticing as sensing layers in As sensors [16]. This unique capability of iron oxides can be explained by its inner sphere surface complexation which makes it favorable for interactions with As ions [17]. A recent study reported the incorporation of iron(III) oxide composite to an SPR based sensor which yielded a detection limit of 1 ppb [18]. A more effective iron oxide when it comes to As ion absorption is known as hydrous ferric oxides ($Fe_2H_2O_4$). This is attributed to its high specific surface area and iso-electric point [19]. Also, the presence of hydroxyl groups on $Fe_2H_2O_4$ improves its adsorption properties as they enhance the ion exchange between the compound and As ions [19]. However, the integration of $Fe_2H_2O_4$ in SPR based sensor systems have yet to be reported. Hence, the motivation of this work is to develop an alternative sensing technique for As ions using an SPR based sensor with the integration of hydrous ferric oxide nanocomposites as its sensing layer. It is to believe that the sensing layer combined with the exceptional sensing performance of an SPR based sensor will attain a detection method with enhanced sensitivity at a lower cost.

1.3 Objectives Of Study

In this work, SPR optical sensor is promoted as sensitive, selective and cost effective method which can be simultaneously detect As ion. The main objective of this research is to propose new SPR sensors, which have low detection limit and selectivity to As ions. The following specific research objectives are to be fulfilled in this research work;

1. To investigate and analyze the sensing performance of Hydrous ferric oxide ($Fe_2H_2O_4$) as a sensing layer for SPR sensor in detection of As ions.
2. To enhance the sensing performance of SPR sensor by improving its sensitivity, specificity and standard limit of detection.
3. To investigate the feasibility of $Fe_2H_2O_4$–multi-walled carbon nanotubes (MWCNT) as a sensing layer for SPR sensor in detection As ions.
4. To investigate the feasibility of $Fe_2H_2O_4$– iron oxide – reduced graphene oxide (Fe_3O_4-rGO) as a sensing layer for SPR sensor in detecting As ions.

1.4 Research Scope

In the recent years, SPR has emerged as an intriguing diagnostic technology especially in areas like biological, chemical and medical sciences. This is mainly attributed to its non-invasive, real-time and label-free nature which makes it a good alternative as a sensor. Here, an investigation of nanocomposite integrated SPR sensors is introduced with aims to detect As ions at very low concentration. The nanocomposites which will be used as sensing layers are $Fe_2H_2O_4$, $Fe_2H_2O_4$–MWCNT and Fe_2H_2O4–Fe_3O_4-rGO Figure 1.1. These nanocomposites are chosen due to its carbon and ferum based properties which have been reported as good adsorbents of As ions and that they have been used in applications involving the removal of As ions from water sources. The mechanics of the sensor relies on the SPR angle shift as a response to refractive index change at the interface of the sensor's surface. The research scope of the work is summarized in**Figure 1.2**.

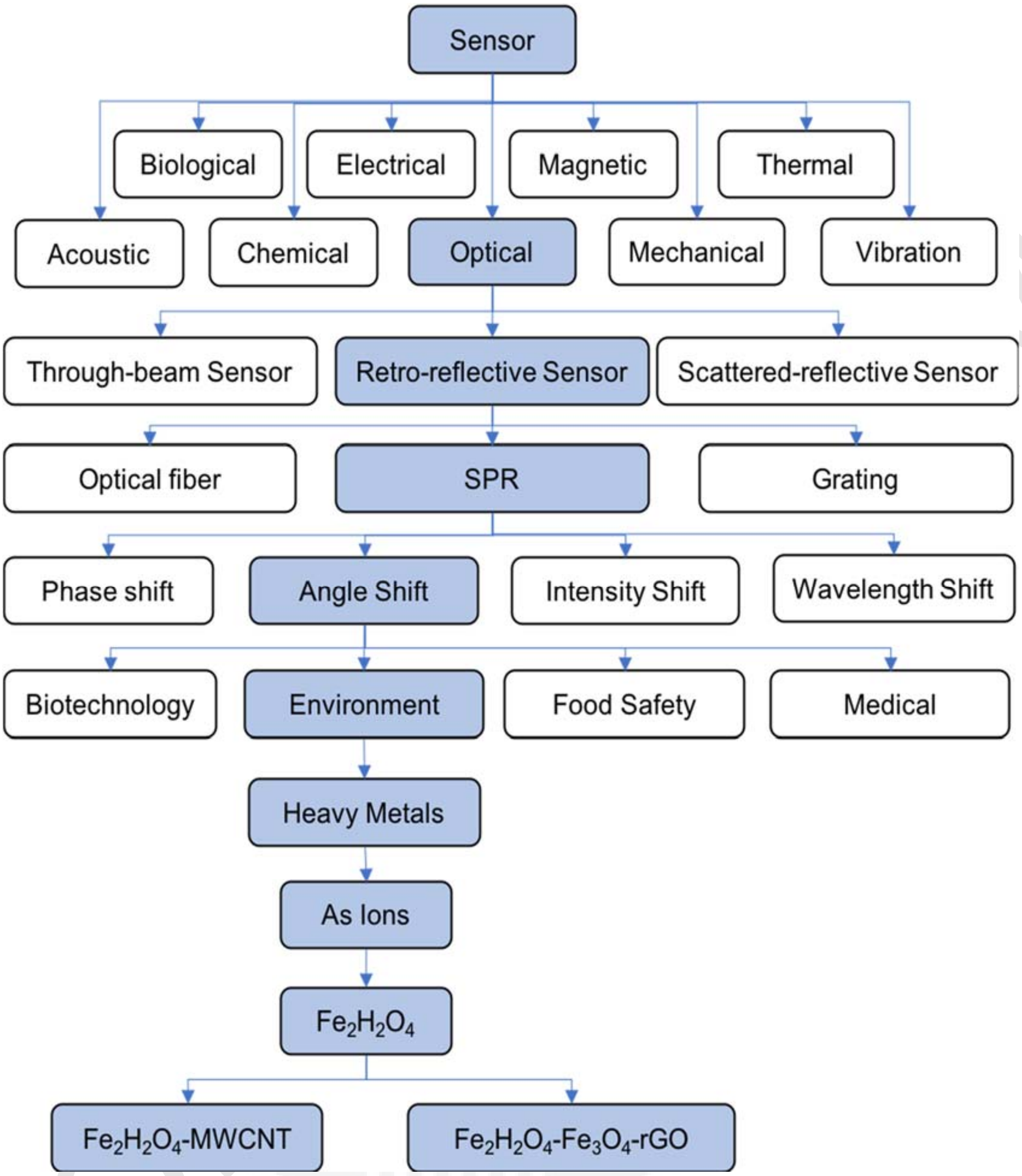

Figure 1.1 : Research scope of As ion detection using SPR technique

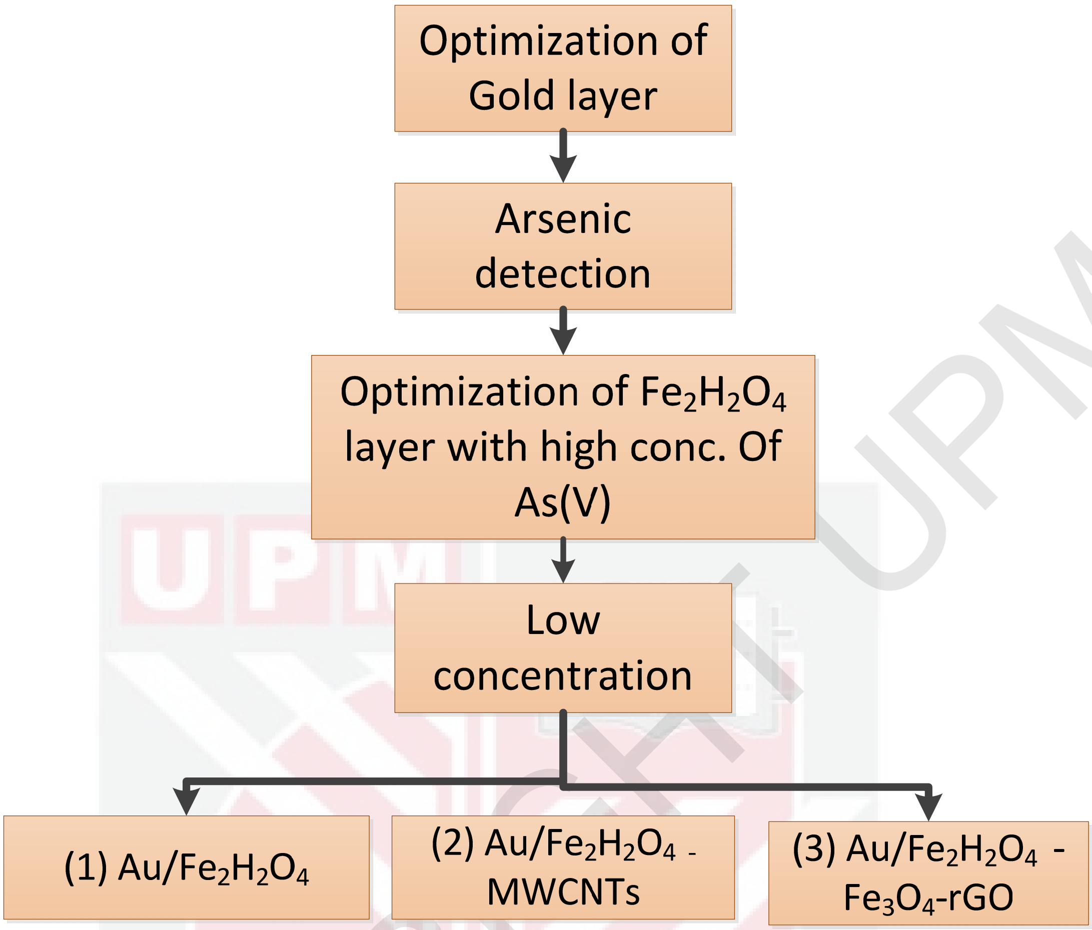

Figure 1.2 : Research work flow chart

1.5 Thesis Outline

This research consists of six chapters including:

Chapter 1 presents a brief background about the main issues in heavy metal detection and the motivations in conducting the research.

Chapter 2 elaborates the conventional methods of As detection, the fundamental concept of SPR as a sensor, and the theory of heavy metal ion binding onto sensing layers.

Chapter 3 describes the experimental setup and methods used to achieve the objectives in this research work. This includes the thickness characterization of the implemented sensitive layers and the sensitivity analysis of the SPR using gold-silver and gold-PANI when tested with high-concentrations of As.

Chapter 4 and 5 present the results and findings of experimental work explained in Chapter 3 where As (II) and As (V) were detected using Chapter 6 concludes the research work by summarizing the key points and introducing suggestions to further the study.

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