UNIVERSITI PUTRA MALAYSIA

SURFACE PLASMON RESONANCE SENSORS USING REDUCED GRAPHENE OXIDE-MAGHEMITE COMPOSITE MATERIAL FOR PLUMBUM ION DETECTION

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By

ALI ABDULKHALEQ ABDULHADI ALWAHIB

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

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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February 2017

Chairman : Professor Mohd Adzir Mahdi, PhD
Faculty : Engineering

As industries rapidly expand to meet the demands of massive dynamic development around the globe, plumbum contamination persists to be among the unsettled environmental issues we have today. The exposure to plumbum is known to cause severe systemic disease even at very low concentrations. The fears from close of Pb^{2+} sources such as plumbing components to clinical applications and healthy environment are the motivating for developing sensors. Over the past few years, researchers have shown enormous interest in surface plasmon resonance (SPR) based sensors due to its sensitivity and fast response for chemical, biological and environmental sensing applications. The attached nanocomposite-sensing layer to a plasmonic material has created vast integration for sensitivity and selectivity enhancement in detection of heavy metals. This research work focuses on plumbum (Pb^{2+}) ion detection using SPR sensor have a new nanocomposite called reduced graphene-maghemite (rGO/γ-Fe_2O_3) as a sensing layer. The main aspects of the study are the sensing potentiality of rGO/γ-Fe_2O_3 in prism based SPR sensor technique, protect the rGO/γ-Fe_2O_3 from degradation in water environment and finally detect plumbum in water using rGO/γ-Fe_2O_3 at sub ppb detection limits. Preliminary studies of the sensing layer when tested with hydrocarbon vapor show that it is sensitive towards acetone as compared to ethanol, propanol and methanol, which highlights the first demonstration of rGO/γ-Fe_2O_3 nanomaterial in optical sensing applications. For heavy metal ion detection, its main challenge is the erosion of graphene-based nanomaterial when the layer interacts with aqueous analyte. Therefore, a special material matrix is required to enhance the adhesiveness of rGO/γ-Fe_2O_3 to the gold (Au) layer on SPR and the combination of Au-rGO/γ-Fe_2O_3 sensing layer and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide/ N-Hydroxysuccinimide/ (EDC/NHS) as a protection layer is used in the sensor structure. The optimized thicknesses of Au, rGO/γ-Fe_2O_3 and EDC/NHS are 41, 8.75 and 4 nm, respectively and its limit of detection for Pb^{2+} ions is 0.001 ppm in static water conditions. The limit of detection is further enhanced to 0.3 ppb by adopting the water circulation method. Selectivity of Pb^{2+} ions is greatly enhanced, by replacing EDC/NHS with polyvinylchloride (PVC).

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This work highlights the advantages of rGO/γ-Fe_2O_3 nanocomposite as the sensing layer on an SPR based sensor for the detection of Pb^{2+} ions in water. Its sensing performance has shown great potential in matching the need for a robust, cheap, sensitive and selective sensing method to detect heavy metals and help curb the environmental problem. The quantitative research findings are 1.1-degree angle shift in 10% concentration vapor acetone, EDC/NHS enhanced the sensing layer to work under water circulation for 50 experiments and detection of plumbum ions in water at concentration 0.3 ppb .

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

SENSOR PENGESANAN PLUMBUM DENGAN MENGGUNAKAN RESONANS PLASMON PERMUKAAN DISELAPUTI GRAPHENE OKSIDA-MAGHEMITE

Oleh

ALI ABDULKHALEQ ABDULHADI ALWAHIB

Februari 2017

Pengerusi : Profesor Mohd Adzir Mahdi, PhD
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Dalam era perkembangan industri pesat untuk memenuhi pembangunan dinamik antarabangsa, pencemaran logam berat merupakan antara isu alam sekitar yang belum diselesaikan sehingga hari ini. Pendedahan terhadap logam berat merosotkan kesihatan sistemik meskipun pada kepekatan yang rendah. Oleh itu, pemantauan konsisten terhadap logam berat menjadi amat penting. Walau bagaimanapun, kaedah untuk mengesan bahan cemar secara konvensional sangat rumit dan mahal. Kebelakangan ini, penyelidik telah menunjukkan minat yang tinggi dalam teknologi Permukaan Plasmon Resonans (SPR) yang menunjukkan sensitiviti tinggi dan tindak balas yang cepat terhadap bahan kimia, biologi dan aplikasi melibatkan alam sekitar. Kawasan penderiaan terhadap konfigurasi SPR untuk menguji sampel telah memberi peluang untuk melibatkan integrasi dengan bahan lain demi kepekaan dan mempelbagaikan pemilihan. Kerja penyelidikan ini memberi tumpuan kepada pengesanan ion plumbum (Pb^{2+}) menggunakan kaedah SPR dengan integrasi komposit nano baru iaitu *reduced graphene-maghemite* (rGO/γ-Fe_2O_3) sebagai lapisan penderiaan. Aspek-aspek utama dalam kajian ini menglibatkan penilaian rGO/γ-Fe_2O_3 sebagai lapisan aktif pengesanan dlm SPR berdasarkan prisma, cara untuk melindungi lapisan rGO/γ-Fe_2O_3 dari penghakisan, serta kebolehan SPR dengan integrase lapisan rGO/γ-Fe_2O_3 untuk pengesanan plumbum. Kajian awal lapisan penderiaan tehadap wap hidrokarbon membuktikan bahawa rGO/γ-Fe_2O_3 lebih sensitif terhadap aseton, berbanding dengan etanol, propanol dan metanol. Di samping itu, penemuan ini menonjolkan kajian pertama yang melibatkan rGO/γ-Fe_2O_3 dalam aplikasi penderiaan optik. Cabaran utama dalam mengesan ion logam berat merupakan masalah hakisan bahan nano berunsur graphene ketika bahan ini berinteraksi dengan analit dalam keadaan akueus. Sehubungan itu, matriks bahan khas amat diperlukan untuk melekatkan lapisan penderiaan rGO/γ-Fe_2O_3 terhadap lapisan emas (Au). Penyelidikan ini telah membuktikan bahawa N-Hidrooksisuccinimide/1-etil-3-(3-dimethylaminopropyl) carbodiimide (EDC/NHS) boleh bertindak sebagai lapisan perlindungan yang berkesan dalam struktur penderiaan. Ketebalan optimum lapisan Au, rGO/γ-Fe_2O_3 dan EDC/NHS ialah 41, 8.75 dan 4 nm masing-masing dan had

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pengesanan lapisan penderiaannya terhadap ion Pb^{2+} menunjukkan kepekatan 0.001 ppm dalam eksperimen air statik. Walau bagaimanapun, had pengesanan ini dapat dipertingkat dengan menggunakan kepekatan 0.3 ppb dengan kaedah peredaran air. Pemilihan terhadap ion Pb^{2+} boleh ditingkatkan dengan menggantikan EDC/NHS dengan polyvinylchloride (PVC). Kerja ini menonjolkan kelebihan komposit nano rGO/γ-Fe_2O_3 sebagai lapisan penderiaan dalam penderia berasaskan SPR bagi mengesan ion Pb^{2+} dalam air. Prestasi penderiaannya menunjukkan potensi besar dalam teknik penderiaan yang teguh, murah, sensitif dan memilih terhadap pengesanan logam berat, di samping memainkan peranan dalam mengatasi masalah alam sekitar.

Keputusan kajian kuantitatif menunjukkan peredaran sudut pada 1.1 darjah dalam wap aseton berkepekatan 10 %, EDC/NHS mempertingkat lapisan penderiaan untuk berfungsi di bawah peredaran air untuk 50 eksperimen dan pengesanan ion plumbum dalam air pada kepekatan 0.3 ppb.

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I certify that a Thesis Examination Committee has met on 1 February 2017 to conduct the final examination of Ali Abdulkhaleq Abdulhadi on his thesis entitled "Surface Plasmon Resonance Sensors using Reduced Graphene Oxide-Maghemite Composite Material for Plumbum Ion Detection" 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 Doctor of Philosophy.

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Declaration by graduate student

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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
Ar	Arsenic
ASV	Anodic stripping voltammetry
Au	Gold
BCAT	P-Tert-butycalix[4]arene-textrakis
$CdCl_2$	Cadmium chloride
CNT	Carbon nano tube
cp	Centipoise
$CuSo_4$	Copper sulfide
CVD	Chemical Vapor Deposition
DI	Deionized
EDC	1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide
E_i	Incident electric filed
E_r	Reflected electric filed
FESEM	Field Emission Scanning Electron Microscope
G	Graphene
GO	Graphene Oxide
$HgCl_2$	Mercuric chloride
ICPMS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis

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ITO	Indium tin oxide
l/min	liter/minute
MOS	Mercury Specific Oligonucleotide
NHS	N-hydroxysuccinimide
Pb	Plumbum element
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
PPy-ChI	Polypyrrole chitosan
PVC	Polyvinyl chloride
rGO	Reduced Graphene
RI	Refractive index
sc	chitosan
SEM	Scanning Electron Microscope
SPR	Surface Plasmon Resonance
TEM	Transmission electron microscopy
TIR	Total internal reflection
TM	Transverse magnetically
UTHSCSA	UT Health Science Center San Antonio
XRF	X-ray fluorescence spectrometry
δ	Phase shift
ε_d	Dielectric of medium
ε_m	Dielectric constant of metal
θ_{res}	resonance angle

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CHAPTER 1

INTRODUCTION

The first chapter of this thesis outlines the work carried out in this PhD research project. This includes the research motivation, objectives, the author's achievements as well as the organization of this thesis.

1.1 Background

Heavy metal contamination around the world is becoming an alarming issue, as it continues to challenge the environmental sustainability today. The Department of Environment Malaysia has reported that out of 1,705,308.14 metric tons of waste generated in 2009, 4.9 % of the contents alone was heavy metal sludge [1]. A more pressing issue is the uncontrolled accessibility of these contaminants to migrate into drinking water sources as reported in India, Thailand, Nepal, Bangladesh, and China [2].

Heavy metals are metallic elements which density exceeds 5 g/cm^3 [3]. It is due to their heaviness that they are known to cause severe toxicity, even at minimal concentrations. The presence of heavy metals in the environment can be from both natural processes and industrial activities. Among the heavy metals that have been threatening human health include Plumbum (Pb^{2+}), Cadmium (Cd^{2+}), Mercury (Hg^{2+}), and Arsenic (As^{3+}).

Case studies reported damage of the central nervous system, lungs, liver, endocrine glands, kidneys and bones due to acute intoxication of the aforementioned heavy metals [4].Chronic exposure towards the elements, on the other hand, implicated high risk of cancer and degenerative diseases[5], [6].

There are a number of powerful conventional methods available for the determination of heavy metals. Among the procedures include atomic absorption spectroscopy (AAS), total reflection X-Ray fluorimetry (TXRF), inductively coupled plasma mass spectrometry (ICP-MS) and anodic stripping voltammetry (ASV) [7]. Yet, despite the wide linear ranges and good limit of detection these methods offer, the procedures are laborious and require sophisticated facilities that are expensive. With the escalating number of cases related to heavy metal pollution, it has become a necessity to find an excellent continuous monitoring system that can be a useful tool in managing the issue.

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1.2 Problem Statement

Contamination of Pb^{2+} in water sources is among the severe threats to human health associated with heavy metals. Published studies have documented that young children are most vulnerable towards Pb^{2+} toxicity and may suffer adverse effects like growth retardation and neurological development [8].

Common sources of Pb^{2+} contamination may come from old structures built using plumbing alloys and also the continuation usage of plumbum components such as water valves and water meters [9] [10]. Reviews reported a geometric mean of plumbum levels in drinking water to be less than 10 parts per billion (ppb) [11]. Therefore, the optimal way of monitoring plumbum traces in water sources is with a sensing setup that has a very low limit of detection. However, no portable sensors have the ability to work within the ppb region efficiently and continuously.

Surface plasmon resonance (SPR) based sensors have shown reliable performance in various sensing applications [12]. The fundamental concept relies on the effect of refractive index change within the external surrounding towards the optical properties of the plasmonic waves created on the sensing region of the SPR, which would produce a measurable shift in the output spectrum. Prism based SPR has reported a detection limit of 1 ppb for the detection of Pb^{2+} using a combined differential SPR and anodic stripping voltammetry approach [13]. To the best of our knowledge, this method has achieved the lowest limit of detection for the sensing of Pb^{2+}. However, the sensing mechanism of the sensor is complicated as compared to the conventional SPR technique.

Over the decade, extensive investigations of additional sensing layers onto SPR have diversified in terms of not only application, but also performance of the sensor. The exposed sensing region of the SPR creates a platform of integration with other materials for the enhancement of both sensitivity and selectivity of the sensor. Ni (II) ion detection by using nanoparticle enhanced SPR managed to obtain good selectivity with a limit of detection as low as 0.05 ppb[14]. We have yet to find any thorough reports on nanoparticle enhanced SPR for the detection of Pb^{2+} with comparable performance.

1.3 Research Objective

The main objective of this research is to propose new SPR sensors, which has low detection limit and selectivity to Pb^{2+} ions. The following specific research objectives are to be fulfilled in this research work;

a) To investigate the feasibility of reduced graphene-maghemite (rGO/γ-Fe_2O_3) nanomaterial as a sensing layer in prism-based SPR sensors using hydrocarbon vapors as test sample.

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b) To study *N*-(3-dimethylaminopropyl)-*N*ethylcarbodiimide hydrochloride/ hydroxysuccinimide (EDC/NHS) as a protection layer against the adverse effects of water towards the rGO/γ-Fe_2O_3 nanomaterial-sensing layer.
c) To develop SPR prism-based sensors with the integration of rGO/γ-Fe_2O_3 and EDC/NHS that aims to detect Pb^{2+} ions in concentration of less than 1 part per billion.

1.4 Research Hypothesis

The present study was performed under the hypothesis that the ability of SPR technique to have excellent detection limits in range of sub part per billion for Pb^{2+}. This task will be accomplished by using rGO/γ-Fe_2O_3 new sensing layer, Au layer as plasmonic material, EDC/NHS as protection layer and finally PVC to enhance the selectivity to Pb^{2+}.

Reduced Graphene oxide and nanomaterial each of them has their own properties however at same time contradict between them. The ability of using one material in two different processes under SPR theory can create a big challenge due to varying in modulation method. In sensor application, the low detection limit and selectivity are depending directly on the sensing material and the detection process. Therefore, that composite material can play a vital role in detection because composite materials have properties which is found most difficult in one material.

1.5 Scope of Research

In this research study, the focus is to investigate an SPR based optical sensor for the detection of Pb^{2+}, as depicted in Figure 1.1. A prism-based SPR is chosen as the main sensor platform.

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Figure 1.1 : Scope of research diagram

The work introduces an investigation on the integration of a new nanocomposite material known as reduced graphene oxide (rGO) and maghemite (γ-Fe_2O_3) to the SPR setup. Up until today, rGO/γ-Fe_2O_3 nanocomposite has yet to be utilized for any sensing applications. The rGO/γ-Fe_2O_3 integrated SPR setup will be introduced to samples of two different phases: gas phase and liquid phase. For gas phase, the feasibility of graphene nanocomposite material for detection hydrocarbon vapors will be investigated and tested. Then, this nanocomposite will be used to detect the presence of Pb^{2+} in both static water and water circulation, which the core of the work.

For all experimental works, the thickness optimization of gold and sensing layers will be performed using a theoretical model. Limit of detection and selectivity of the sensor will be analyzed.

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1.6 Thesis Layout

This thesis is consists of six chapters and is outlined as follows:

a) Chapter 1 discusses on the introduction, overview of the undertaking research in SPR-based heavy metals sensors.
b) Chapter 2 focuses on the literature review that describes the rationale behind the research work. This includes a thorough discussion on the fundamental concept of SPR as a sensor. Prism based SPR techniques and the performance in heavy metal detection is reviewed, followed by a comparison on different type of active sensing layers.
c) Chapter 3 shows the design and fabrication process of the prism based SPR sensor for the detection of hydrocarbon vapors. This includes the preparation and deposition of the transparent substrates used in this research.
d) Chapter 4 shows the design and fabrication process of the prism based SPR sensor for the detection of Pb^{2+} ions. This includes the preparation and deposition of transparent substrates used in this research. Results and discussion of prism based SPR are presented and analyzed according to three different experiments. The thickness analysis of the gold layer, the sensing layer and the protection layer are discussed and fitting are made between experimental results and Fresnel equations model.
e) Chapter 5 concludes the work with a brief summary of the research findings made during the study and its contribution, as well as recommendations, for future work.

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