UNIVERSITI PUTRA MALAYSIA

DETECTION OF HEAVY METAL IONS IN SOLUTION USING SURFACE PLASMON RESONANCE OPTICAL SENSOR

YAP WING FEN

FS 2012 1

DETECTION OF HEAVY METAL IONS IN SOLUTION USING SURFACE PLASMON RESONANCE OPTICAL SENSOR

By

YAP WING FEN

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

January 2012

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

DETECTION OF HEAVY METAL IONS IN SOLUTION USING SURFACE PLASMON RESONANCE OPTICAL SENSOR

By

YAP WING FEN

January 2012

Chairman : Professor W. Mahmood Mat Yunus, PhD

Faculty : Science

The sensitive, selective and cost-effective method for detection of heavy metal ions in solution is very important in environmental application. Therefore in this study, surface plasmon resonance (SPR) optical sensor has been proposed as an alternative for detection of heavy metal ions (Hg^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Mn^{2+}) in solution by developing a chitosan based active layer.

The optical properties of heavy metal ions were studied using Kretchmann SPR technique, where gold thin film was used as the interface. Both real and imaginary part of refractive index of the heavy metal ions solution increased with the concentration. This result reveals the basic idea such that SPR can be used to detect heavy metal ions in solution.

In order to enhance the sensitivity for SPR in sensing these heavy metal ions, a thin chitosan based active layer is introduced. The chitosan solution was synthesized by homogeneous reaction of medium molecular weight chitosan in aqueous acetic acid solution with glutaraldehyde as crosslinking agent. It was deposited on the gold layer by spin coating. The optical properties of the chitosan active layer before and after contacting with different concentration of heavy metal ions ranging 0.5 to 100 ppm were studied by fitting the experimental results to theoretical data. The results also show that the shift of resonance angle is directly proportional to the concentration of all heavy metal ions solution. The sensitivity of this heavy metal ions optical sensor is in the range of 10^{-3} ° ppm^{-1}, which follows the order: $Hg^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Mn^{2+}$. In this case, the gold/chitosan interface in SPR technique is sensitive with detection limit of 0.5 ppm.

The kinetic behaviour of the heavy metal ions on the surface of gold/chitosan was studied by monitoring the self-assembling process in real time. The shift of resonance angle was found to increase exponentially with time, for all concentration of heavy metal ions in the range of 0.5 to 100 ppm, and reach to a saturation value. At low concentration (5 ppm and below), the kinetic reaction is complete in about 100 s. A more complex kinetic profile was observed and complete at approximately 500 s for higher concentration (more than 5 ppm).

It is difficult to detect a specific heavy metal ion optically since all heavy metal ions solution are transparent and have similar refractive index when they are at low concentration. Therefore, the modification of the active layer was investigated so that it can selectively detect a specific heavy metal ion and also increase the sensitivity of

the detection. The immobilization of p-tert-butylcalix[4]arene-tetrakis in the chitosan thin film has been used. In this case, Pb^{2+} can be selectively detected with increased sensitivity of 0.045° ppm^{-1} and detection limit has been improved down to 0.03 ppm. The immobilization of tetrabutyl thiuram disulfide in chitosan as active layer gives the selective detection of Zn^{2+} with sensitivity of 0.032° ppm^{-1} and detection limit of 0.1 ppm.

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

PENGESANAN ION-ION LOGAM BERAT DALAM LARUTAN DENGAN MENGGUNAKAN SENSOR OPTIK RESONAN PLASMON PERMUKAAN

By

YAP WING FEN

Januari 2012

Pengerusi : Profesor W. Mahmood Mat Yunus, PhD

Fakulti : Sains

Kaedah sensitif, selektif dan kos efektif bagi pengesanan ion-ion logam berat dalam larutan adalah sangat penting dalam aplikasi alam sekitar. Oleh yang demikian dalam kajian ini, sensor optik resonan plasmon permukaan (SPR) telah dicadangkan sebagai alternatif untuk mengesan ion-ion logam berat (Hg^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} dan Mn^{2+}) dalam larutan dengan membangunkan satu lapisan aktif yang berasaskan kitosan.

Sifat optik ion-ion logam berat telah dikaji dengan menggunakan teknik SPR Kretchmann, di mana filem nipis emas digunakan sebagai muka perantara. Kedua-dua nilai bahagian nyata dan khayalan indeks biasan larutan ion-ion logam berat meningkat dengan kepekatan. Keputusan ini menunjukkan idea asas bahawa SPR boleh digunakan untuk mengesan ion-ion logam berat di dalam larutan.

Untuk meningkatkan kepekaan SPR dalam pengesanan ion-ion logam berat ini, satu lapisan nipis aktif yang berasaskan kitosan telah diperkenalkan. Larutan kitosan telah disintesis dengan menggunakan tindak balas homogen kitosan berjisim molekul sederhana dalam larutan akueus asid asetik dengan glutaraldehid sebagai ejen penyilang. Ia disalutkan ke atas lapisan nipis emas dengan menggunakan salutan putaran. Ciri-ciri optik lapisan aktif kitosan sebelum dan selepas berhubung dengan ion-ion logam berat berlainan kepekatan yang berjulat 0.5 hingga 100 ppm telah dikaji dengan memuatkan keputusan eksperimen kepada data teori. Keputusan juga menunjukkan bahawa anjakan sudut resonan adalah berkadar terus dengan kepekatan larutan ion-ion logam berat. Kepekaan sensor optik ion-ion logam berat ini adalah dalam julat 10^{-3} ° ppm^{-1}, yang mengikut turutan: $Hg^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Mn^{2+}$. Dalam kes ini, perantara muka emas/kitosan dalam teknik SPR adalah sensitif dengan had pengesanan 0.5 ppm.

Perlakuan kinetik ion-ion logam berat pada permukaan emas/kitosan telah dikaji dengan memantau proses berkumpul sendiri dalam masa nyata. Anjakan sudut resonan didapati meningkat secara eksponen dengan masa, bagi semua kepekatan ion logam berat dalam julat 0.5 hingga 100 ppm, dan mencapai satu nilai ketepuan. Pada kepekatan rendah (5 ppm dan kurang), reaksi kinetik adalah lengkap pada kira-kira 10 s. Profil kinetik yang lebih kompleks diperhatikan dan lengkap pada kira-kira 500 s untuk kepekatan yang lebih tinggi (lebih daripada 5 ppm).

Ia adalah sukar untuk mengesan ion logam berat secara optik kerana semua larutan ion logam berat adalah lutsinar dan mempunyai indeks biasan yang sama apabila mereka berada dalam kepekatan yang rendah. Oleh itu, pengubahsuaian lapisan aktif

dikaji supaya ia dapat mengesan ion logam berat yang khusus secara terpilih dan juga meningkatkan kepekaan pengesanan. Imobilisasi "p-tert-butylcalix[4]arene-tetrakis" dalam filem nipis kitosan telah digunakan. Dalam kes ini, Pb^{2+} boleh dikesan secara terpilih dengan peningkatan kepekaan 0.045° ppm^{-1} dan had pengesanan telah bertambah baik kepada 0.03 ppm. Imobilisasi "tetrabutyl thiuram disulfide" dalam kitosan sebagai lapisan aktif memberikan pengesanan terpilih Zn^{2+} dengan kepekaan 0.032° ppm^{-1} dan had pengesanan 0.1 ppm.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude and thanks to my supervisor, Prof. Dr. W. Mahmood Mat Yunus for his strong support, kind advice, proper guidance and patience throughout this research project. Without the persistent assistance and exceptional generosity, this work would not have been possible.

Next, I wish to convey special thank to Prof. Dr. Mohd Maarof Moksin, Assoc. Prof Dr. Zainal Abidin Talib and Assoc. Prof. Dr. Nor Azah Yusof as my co-supervisors for their concern and assist in my project. Special thanks are extended to all the lecturers and technical staffs in the Department of Physics, Faculty of Science, Universiti Putra Malaysia for their help and cooperation.

I would also like to acknowledge my indebtedness to Ministry of Higher Education for the degree of Doctor of Philosophy scholarship (SLAI). The financial support from the ministry is indeed very important in helping me to accomplish this research project successfully.

Last but not least, grateful thanks to my family members and friends for their continuous moral support and encouragement throughout this research project. I am really appreciated for their never ending support. Thank you.

This thesis was submitted to the Senate of 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:

W. Mahmood Mat Yunus, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Maarof H.A. Moksin, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Zainal Abidin Talib, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Nor Azah Yusof, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

I certify that a Thesis Examination Committee has met on 19 January 2012 to conduct the final examination of Yap Wing Fen on his thesis entitled "Detection of Heavy Metal Ion in Solution Using Surface Plasmon Resonance Optical Sensor" 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.

Members of the Thesis Examination Committee were as follows:

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Elias Saion, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Azmi Zakaria, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Din Ping Tsai, PhD
Professor
Department of Physics
National Taiwan University
Taiwan
(External Examiner)

_____

SIEW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

YAP WING FEN

Date: 19 January 2012

TABLE OF CONTENTS