UNIVERSITI PUTRA MALAYSIA

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Faculty : Science

Surface plasmon resonance (SPR) spectroscopy is a surface-sensitive technique that has been used to characterize the thickness and index of refraction of dielectric medium at noble metal interface. Nowadays surface plasmon resonance technique has emerged as a powerful technique for a variety of chemical and biological sensor applications.

In this study, gold and silver with purity of 99.99% were used to fabricate thin metal films. The thin film was deposited onto a glass cover slip and attached onto the surface of a 60° prism using index matching oil. Liquid samples, such as chlorine, saccharide, swimming pool water, pesticide, virus and DNA were studied using Kretschmann Surface Plasmon Resonance technique. All the measurements were carried out at room temperature. The experiment was carried out by measuring the intensity of the optical reflectivity as a function of incident angle.

It found that the shift of resonance angle ($\Delta\theta$) increased linearly with the sample concentration. The detection limit of the sensor was estimated better than 0.01 pM for the sample of DNA (Oligo2-Bio). Larger sensor sensitivity of 9.42°/(mol/L) is obtained for the sucrose sample.

The kinetic behaviour of the system was also examined to monitor the self-assembling process on the metal surface in real time. The shift in resonance angle increased greatly with time during the increment of the molecules deposited on the gold surface. In contrast it was found decrease with time during self-assembling process.

This work also studied the molecule-dielectric interaction for a thin Fatty Hydroxamic Acid (FHA) film (extract from crude palm oil), which the FHA layer was coated using spin coating on the top of metal film. When the medium outside the surface of Au film was changed from air to FHA layer, the resonance angle shifted to the higher value. The shift of resonance angle increased linearly with the increasing concentration FHA layer. When the metal ion was attached to the FHA film, the resonance angle was changed to the maximum value.

The experimental results reveal that the technique that based on surface plasmon resonance phenomenon can be used to determine the optical properties and the kinetic behaviour. It also suitable to study the molecule-dielectric interaction for the polymer film. This technique can become an effective chemical optical sensor. Saccharide, pesticide and chlorine concentration in water can be detected using this sensor. Furthermore it also can be used to detect DNA and viruses solution.

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

SIFAT OPTIK DAN PERLAKUAN KINETIK TERHADAP BEBERAPA SPESIS KIMIA DAN BIOLOGI MENGGUNAKAN SENSOR OPTIK RESONANS PLASMON PERMUKAAN

Oleh

WAN YUSMAWATI BINTI WAN YUSOFF

Julai 2005

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Spektroskopi Resonans Plasmon Permukaan (SPR) ialah satu teknik sensitif-permukaan yang digunakan untuk mengenalpasti ketebalan dan indeks biasan medium dielektrik pada antaramuka logam. Kini, teknik resonans plasmon permukaan telah muncul sebagai teknik yang berguna dalam pelbagai penggunaan pengesan kimia dan biologi.

Dalam kajian ini, emas dan perak dengan ketulenan 99.99% digunakan untuk membuat filem tipis logam. Filem tipis logam tersebut telah disaputkan kepada slip kaca dan dilekatkan kepada satu permukaan prisma 60° dengan menggunakan minyak indeks sepadan. Sampel cecair seperti klorin, sakarida, air kolam renang, pestisid, virus dan DNA dikaji dengan menggunakan teknik Plasmon Resonans Permukaan Kretschmann. Semua pengukuran telah dilakukan pada suhu bilik. Eksperimen telah dilakukan dengan mengukur keamatan keterpantulan optik sebagai satu fungsi kepada sudut tuju.

Keputusan menunjukkan anjakan sudut resonans ($\Delta\theta$) meningkat secara linear dengan kepekatan larutan sampel. Had pengesanan bagi pengesan dianggarkan lebih baik daripada 0.01 pM untuk sampel DNA (Oligo2-Bio) dan kepekaan pengesan tertinggi ialah 9.42°/(mol/L) untuk sampel sukrosa.

Perlakuan kinetik sistem juga telah diperiksa untuk memerhati proses berkumpul-sendiri pada permukaan logam dalam masa nyata. Anjakan sudut resonans bertambah secara mendadak dengan masa ketika peningkatan endapan molekul pada permukaan emas. Anjakan ini didapati menurun dengan masa ketika proses perhimpunan-sendiri.

Kajian ini juga mengkaji interaksi antara molekul-dielektrik untuk filem tipis Fatty Hydroxamic Acid, FHA (ekstrak dari minyak kelapa sawit mentah), dengan lapisan FHA telah disaput menggunakan 'spin coating' atas filem logam. Apabila medium permukaan luar filem tipis logam ditukarkan daripada udara kepada filem polimer FHA, sudut resonans berganjak kepada nilai yang lebih tinggi. Anjakan sudut resonans telah meningkat secara linear dengan kepekatan lapisan FHA. Apabila ion logam dilekatkan pada lapisan FHA, sudut resonans telah berubah kepada nilai maksimum.

Keputusan eksperimen menunjukkan teknik yang berdasarkan fenomena resonans plasmon permukaan boleh digunakan untuk menentukan sifat-sifat optik dan kelakuan kinetik. Ia juga sesuai untuk mengkaji interaksi molekul-dielektrik bagi filem polimer. Teknik ini boleh menjadi pengesan pengesan optik kimia yang berkesan. Sakarida, pestisid dan kepekatan klorin dalam air boleh dikesan menggunakan teknik ini. Malahan pengesan ini boleh juga digunakan untuk mengesan DNA dan virus dalam larutan.

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May Allah Ta'ala bless you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERM

$\Delta\theta_0$	The initial shift of resonance angle respect to distilled water
ε_r	Real part of dielectric constant
ε_i	Imaginary part of dielectric constant
ε_0	Dielectric constant of medium prism
θ	Incidence angle
θ_r	Resonant angle of incidence
θ_i	External angle
θ_{SP}	Surface plasmon resonance angle
$\Delta\theta$	The shift of resonance angle
α	Internal angle of prism
μ	Magnetic permeability
k_x	Wavevector component along surface electromagnetic wave propagation
k_{SP}	Wavevector of a plasmon
κ_1	Wavevector media 1
κ_2	Wavevector media 2
λ	Wavelength
n_p	Refractive index of prism
n_m	Refractive index of metal
n_o	Refractive index of dielectric
ε_1	Dielectric constant of medium metal film
ε_2	Dielectric constant of medium dielectric
DNA	Oligodeoxyribonucleic acid
RNA	Ribonucleid Acid
PC	Personal Computer
FHA	Fatty Hydroxamic Acid
HCl	Hydrochloric Acid
EDTA	Ethylene Diamine Tetra Aceticacid
UV	Ultra Violet
XRD	X-ray Diffractometer
MIP	Molecular Imprinted Polymer

BaP	benzo[a]pyrene
DOP	dioctyl phthalate
ssDNA	single-stranded oligonucleotides
HDT	hexanedithiol
TM	Transverse Magnetic Field
TE	Transverse Electric Field
M	Concentration solution
V	Volume of concentration
MWR	Molecular weight relative
LFS	Low Square Fitting
SPR	Surface Plasmon Resonance
ATR	Attenuated total reflection
SP	Surface Plasmon
R	Reflection coefficient
R_{min}	Reflectance minimum
R_P	Reflectance as a function of incidence angle
R_T	Actual optical reflectance that loss factor has been considered
t^2	Loss factor
A	Angle of prism
I_0	Incidence light
I_r	Reflected light
d	Thickness
β	'stretching coefficient'
τ	Time constant
c	Concentration
k	Adsorption constant
K	Kinetic constant
T	Absolute temperature
Au	Gold
Ag	Silver
G70	Calcium Hypochlorite
G90	Trichloroisocyanuric Acid
Cu (II)	Copper (II)

Fe (III)	Ferum (III)
V (V)	Vanadium (V)
wt/wt	Weight per weight
ppm	Part per million
pM	PicoMolar
rpm	Round per minutes

CHAPTER 1

INTRODUCTION

1.1 Surface Plasmon Resonance

Surface plasmon resonance (SPR) is well known as a powerful and expensive optical method for the study of interface phenomena. SPR is an optical phenomenon arising in thin metal films under condition of total internal reflection. This phenomenon produces a sharp dip in the intensity of the reflected light at a specific angle (called the resonant angle). This resonant angle depends on several factors, including the refractive index of the medium (refractive index is directly correlated to the concentration of dissolved material in the medium) close to the non-illuminated side of the metal film. By keeping other factors constant, SPR is used to measure the change in the concentration of molecules in the surface layer of solution in contact with the sensor surface.

Surface plasmon resonance is a collective oscillation of the free electron charges, at a metal-dielectric boundary, which propagates along interface. These charge fluctuations are accompanied by an electromagnetic field having a maximum at the metal-dielectric interface and decaying exponentially with distance from either side of it [Sadowski et al., 1991; Kitajima et al., 1981]. The resonance excitation of the surface plasmon resonance occurs at a characteristic angle of incidence, which depends on the thickness as well as on the dielectric permittivity of the layers and of adjacent medium. Since the permittivity depend on the frequency of the exciting laser light, so does too the resonance angle. When the frequency is fixed, SPR permits the measurement of changes in the refractive index in the medium adjacent to the metal film as well as changes in the absorption layer on the metal surface. The plasmon wave can be excited at the interface between a thin metal film and air or other non-metal medium with a positive dielectric sign. The wave can be thought of as having a section inside the thin film and a section outside of the film in the air / metal interface, much like an ocean wave has part of the wave unseen inside the ocean, while another part of the wave is seen in the ocean / horizon interface. Under normal circumstances, a laser light source incident upon a thin film is reflected or scattered, and there would be an insignificant surface plasmon wave, which would absorb very little of the incident energy [Kolomenskii et al., 1997].

Surface plasmon resonance occurs when the energy from incident light is of just the right frequency and angle of incidence to couple its energy with the surface plasmon, so that no light is reflected from a normally reflective surface. Thickness of a thin film can be determined through surface plasmon resonance due to the fact that as the thickness of the thin film increases, less of the surface plasmon is in the air / metal interface and more of it is contained within the metal itself. We can use the characteristic peak and shape of the resonance curve to characterize different thin film thickness of different materials.

Typically, SPR technique employs the principle of attenuated total reflection (ATR) using either Kretschmann or Otto geometries. Surface plasmon are collective oscillations of free charge of metal, which under appropriate conditions, may be coupled to by incident optical radiation resulting in the absorption of light. Coupling is accomplished in two ways either angular or spectral. In the former, the incident