ETCHING AND COATING MECHANISMS EVALUATION OF GOLD NANOPARTICLES-COATED SURFACE PLASMON RESONANCE SENSORS IN PROTIC SOLVENTS

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DEDICATION

This thesis is dedicated to many educators, family members, events, and guardians who keep us in their prayers by encouraging the knowledge spirit to spring.

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ABSTRACT

In recent years, the demand for high-quality sensors for various industrial, medical and environmental applications has been exponentially growing. Based on these facts, four gold nanoparticles (AuNPs)-coated surface plasmon resonance sensors were fabricated through etching and coating processes in the protic solvents. The performance of the designed localized surface plasmon resonance (LSPR)-based sensors were optimized in terms of their repeatability, selectivity, sensitivity, and linearity parameters. The Weibull etching and coating mechanisms in the protic solvents were evaluated using the fabricated sensors. The AuNPs size and optical fibre diameter dependent organic solvents parameters (SP) enable to achieve a high-performance sensing useful for varied applications. The etching and coating mechanisms were shown to play a significant role in the obtained sensors performance. These sensors' sensitivity, selectivity, repeatability, and linearity were determined using varied laser-ablated energies (LAE) of 240, 250, 260, and 270 mJ. Protic solvents such as ethanol, methanol, 1-propanol, and 1-butanol were used for the measurements. Three mechanisms for etching and coating were proposed wherein the first one before the solvent inclusion, second one after dipping the LSPR-sensor in the protic solvent, and the last one after withdrawing the solvent from the LSPR-sensor. A comparative evaluation of the sensing performance was made using the Weibull analysis and survival analysis test. The Weibull analysis demonstrated the best outcomes for the diameter and thickness measurements, indicating that more than one measurement can produce better comparability of sensitivity (up to 72 for 260 mJ LAE-sensor) and selectivity (in methanol). Among all four solvents, methanol revealed the most significant influence on the sensing performance, ascribed to the formation of Au-OH and Au-CH bonds surrounding the plasmonic AuNPs. Besides, the solvent's highest polarity factors, dielectric constant, hydrogen-bond donor, lowest refractive index, and molarity played a vital role. The Weibull method was shown to be most suitable for analysing the sensor's sensitivity, performance and certainty, thus paving the way for designing susceptible devices.

ABSTRAK

Sejak beberapa tahun kebelakangan ini, permintaan untuk sensor berkualiti tinggi untuk kegunaan pelbagai aplikasi industri, perubatan dan alam sekitar telah berkembang dengan pesat. Berdasarkan fakta ini, empat sensor resonans plasmon permukaan bersalut nanopartikel emas (AuNPs) telah dibuat melalui proses punaran dan salutan dalam pelarut protik. Prestasi sensor berasaskan resonans plasmon permukaan setempat (LSPR) yang direka bentuk telah dioptimumkan dari segi kebolehulangan, kepilihan, kepekaan dan ciri-ciri kelinearan. Mekanisma punaran dan salutan Weibull dalam pelarut protik dinilai menggunakan sensor yang direka. Pergantungan parameter pelarut organik (SP) pada saiz AuNPs dan diameter gentian optik boleh mencapai penderiaan yang berprestasi tinggi untuk pelbagai aplikasi. Mekanisme punaran dan salutan ini telah menunjukkan peranan yang penting dalam prestasi sensor yang diperolehi. Kepekaan, kepilihan, keterulangan dan kelinearan sensor ini ditentukan menggunakan tenaga laser ablasi (LAE) yang pelbagai iaitu 240, 250, 260, dan 270 mJ. Pelarut protik seperti etanol, metanol, 1-propanol, dan 1-butanol digunakan untuk pengukuran. Tiga mekanisma punaran dan salutan Weibull telah dicadangkan, di mana yang pertama adalah sebelum penambahan pelarut, yang kedua adalah selepas mencelupkan sensor LSPR dalam pelarut protik, dan yang terakhir selepas mengeluarkan pelarut daripada sensor LSPR. Penilaian perbandingan prestasi sensor dibuat menggunakan analisis Weibull dan ujian analisi daya tahan. Analisis Weibull menunjukkan hasil terbaik untuk ukuran diameter dan ketebalan di mana terdapat lebih daripada satu ukuran boleh menghasilkan kebolehbandingan kepekaan (sehingga 72 untuk 260 mJ LAE-sensor) dan kepilihan (dalam metanol) yang lebih baik. Di antara keempat-empat pelarut, metanol menunjukkan pengaruh yang paling ketara terhadap prestasi penderiaan, yang disebabkan oleh pembentukan ikatan Au-OH dan Au-CH yang mengelilingi AuNPs plasmonik. Selain itu, faktor kekutuban tertinggi pelarut, pemalar dielektrik, penderma ikatan hidrogen, indeks biasan terendah, dan kemolaran juga memainkan peranan penting. Kaedah Weibull telah terbukti paling sesuai untuk menganalisis kepekaan, prestasi dan kepastian sensor, dan telah membuka jalan untuk mereka bentuk peranti yang lebih rentan.

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LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
AuNPs	-	Gold nanoparticles
AuNPs	-	Gold nanoparticles
AgNPs	-	Silver nanoparticles
AWS	-	After withdrawing solvent
BDS	-	Before dipping solvent
COD	-	Coefficient of determination
Cr	-	Chromium
DDS	-	During dipping solvent
EDX	-	Energy-dispersive X-ray spectroscopy
EPA	-	Electron-pair acceptor
EPD	-	Electron-pair donor
FFT	-	Fast Fourier transform
FOM	-	Figure of merit
FOM*	-	A modified figure of merit
FTIR	-	Fourier transform infrared spectroscopy
HBA	-	Hydrogen-bond acceptor
HBD	-	Hydrogen-bond donor
HBD	-	Hydrogen-bond donor
HBA	-	Hydrogen-bond acceptor
EPD	-	Electron-pair donor
EPA	-	Electron-pair acceptor
HR-TEM	-	High-resolution transmission electron microscopy
IR	-	Refractive index
LAE	-	Laser ablated energy
LSPR	-	Localized surface plasmon resonance
LT	-	Low Tension
MFC	-	Microfiber coupler
NA	-	Numerical aperture

OSA	-	Optical spectrum analyzer
PL	-	Photoluminescence
PLAL	-	Pulse laser-ablated in liquid
P-V	-	Maximum-profile valley depth
Ra	-	Roughness average
Rz	-	Maximum height of the profile
SAED	-	Selected area (electron) diffraction
SEM	-	Scanning electron microscopy
SI	-	Resonance peak sensitivity
SN1	-	Substitution reaction
SNR	-	Signal-to-noise ratio
SP	-	Solvent polarity
SPR	-	Surface plasmon resonance
$S\lambda$	-	Wavelength sensitivity
TDLI	-	Tailoring Decorations by Laser Irradiation
TiO_2	-	Titania
TSCSMF	-	Tapered small core single-mode fibre
UTF	-	U-type fibre sensors
UV-Vis	-	UV-Visible spectroscopy.
VOCs	-	Volatile organic compounds
XRD	-	X-ray diffraction
Γ	-	Line width

LIST OF SYMBOLS

μ_E - Excited-state
μ - Permenant dipole moment
π^* - Polarity measures
α - Solvent index HBD
β - Solvent index HBA
m_1 - Weibull parameter (diameter measurement)
m_2 - Weibull parameter (thickness measurement)
σ - Characteristics of strength calculations
$\ln\sigma$ - Intensity at failure
$F(\sigma)$ - Cumulative probability of failure
$h\gamma$ - Incident radiation photon energy
k - Band independent invariant
Eg - Optical band gap energy
β_T - Total broadening or the tip width (FWHM)
β_D - Broadening due to crystallite size
β_ϵ - Broadening due to micro-strain
K - Scherrer constant
$\boldsymbol{\delta}$ - Dislocation density
$E_T^{(30)}$ - Electronic transition energies parameter
E_T^{N} - The relative polarity of transition energy
σ_{01} - Etching strength
σ_{02} - Coating strength

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In association with the nanoparticles, metallic nanoparticles are of great interest for sensing applications. The metallic nanoparticles have strong absorption bands in the visible and near-infrared regions employing localized surface plasmon resonances (LSPR or SPR) optical properties (Rivero, Goicoechea & Arregui, 2017). LSPR is non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field. Indeed, these modes emerge from the scattering problem of a minor, sub-wavelength conductive nanoparticle in an oscillating electromagnetic field. The curved particle surface snippet an effective restoring force on the driven electrons so that resonance perhaps arises, leading to field amplification inside the particle and in the near-field zone outside of it either (Maier, 2007). The conjugation of specific modes of the incident light to the conduction electrons collective oscillation of the metallic nanoparticles (NPs) construct these optical resonances. The LSPR extinction bands are susceptible to refractive index variations of the surrounding medium of the nanoparticles, which would motivate sensing applications with outstanding properties such as high sensitivity and optical self-reference. LSPR is highly reliant on the composition, size, geometry, dielectric environment, and particle-particle separation distance of NPs (Petryayeva & Krull, 2011).

The quantum size regime of metallic NPs such as Ag and Au is due to the energy levels of d–d transitions that exhibited LSPR in the visible range of the spectrum (Liz-Marzan, 2006). Although Ag display the strongest and sharpest bands among all metals, Au is preferred for biological and chemical applications. Though the sensitive coatings devices are designed, gold nanoparticles have been incorporated into these devices. Additionally, AuNPs have magnificent chemical stability and high corrosion resistance. The diversity of technological applications pave the way to predict and manipulate LSPR of metal nanoparticle systems. The following are some applications for LSPR, such as nanoparticle manipulation by optical bistability (Neuendorf, Quinten, & Kreibig, 1996; Haus et al., 1989) and optical tweezers (Novotny, Bian, & Xie, 1997). Additionally, LSPR applications have a wide range in ultrafast optical switching (Feldstein et al., 1997; Fukumi et al., 1994; Haglund et al., 1993), optical trapping (Gu & Ke, 1999; Svoboda & Block, 1994), and optical filters (Dirix et al., 1999; Kroschwitz, & Howe-Grant, 1994). Concerning chemical and biological sensing (Elghanian et al., 1997; Bauer, Pittner, & Schalkhammer, 1999) persists the aperture of sufficient solvents' influences on LSPR sensors. Moreover, lightweight devices, electromagnetic immunity, biocompatibility, and remote sensing (Rivero, Goicoechea, & Arregui, 2017) are LSPR applications for sensitivity measures. The intense and localized electromagnetic (EM) fields induce by LSPR made NPs highly sensitive convertors of small changes in the local refractive index. These changes exhibit in spectral shifts of extinction (absorption plus elastic light-scattering) and scattering spectra. Luo et al. 2021 reported in their article that the resonance frequency and absorption of fibre optic LSPR are affected by the local environment of the AuNPs. LSPR perhaps provide a platform for multiplexed analysis, which is crucial for clinical diagnostics and proteomics. Even though the refractive index sensitivity is significantly greater for SPR, the decay length and sensing volume are smaller for LSPR. The polydispersity of NPs, particularly with wet synthesis methods, give rise to broad absorption spectra hindering spectral resolution.

Other researchers have drawn significant attention to the LSPR application-based optical fibre probes as refraction index (RI) sensors in sucrose and alcohol solutions (Spasopoulos et al., 2017). The fundamental optical sensors observe the minute changes in the optical signal (absorbance, reflectivity, refractivity) and detect the sample characteristics or the target measurement changes (Lee et al., 2021). There are various reported series of experimental studies in the literature related to similar fields of LSPR-optical fibre, but in this study, we delineate magnificent findings. The high-energy lasers expansion assessed the optical component's mechanical strength of fused silica or quartz SiO_2. The strength of this material is known to be highly dependent on the stressed area (sensing region) and the surface finish (coating) but have not yet been adequately characterized in the published literature. The investigated parameters in the literature were dedicated to the refractive index for ethanol and methanol concerning sensitivity measurements. Indeed, the study tend to magnify the consideration by blending six parameters of four alcohols. The protic solvents (alcohols) parameters are polarity factors, dielectric constants, dipolar, hydrogen-bond donor (HBD), refractive index, and molarity. According to their environmental health and safety assessment, we have chosen the alcohols in our investigation, as reported by Jessop and et al., 2012. The parameters play an essential role in the interfacial epitaxial growth mechanism for studying gold nanoparticles.

The stamp of the study is the blending of optical fibre, gold nanoparticles, and four protic solvents. From the perspective of literature aperture, the study persist the entire effort to investigate the ethanol, methanol, 1-propanol, and 1- butanol parameters' influence on etching (diameter) mechanism and coating (thickness) measurements concerning sensitivity enhancement and significant solvent selectivity. The optical fibre sensor coated gold nanoparticles is the platform in which the solvents' parameters influence examined. Previously, the research focused on only one numerical diameter and thickness measurements throughout the experiment. Our study has approved the possibility of having three different thickness and diameter values; one before the addition of the solvent commenced, then dipping the LSPR-sensor in solvents, and the last one after withdrawing the solvents from LSPR-sensors. Our study applied new analytical methods to analyze the results as a first-opportunity application in a comparable field. Other researchers have not yet utilized the Weibull statistics and survival analysis test to determine the two measurements variations, which enhanced the current study to establish a robust platform for future analysis.

1.2 Problem Statement

Earlier researchers till date only involved one core diameter with one material thickness when dealing with surface plasmon resonance sensors - surrounding parameters. The deviation in the standard previous studies requires further understanding and investigation. The perceived gap in others researchers work suggest the study could determine and optimize the possibility of having more than one thicknesses and core diameters values to optimize the performance of LSPR, especially in term of the LSPR sensor sensitivity. The one value for diameter and thickness would not be sufficient and precise to measure the sensitivity and selectivity analyses.

The proof of such phenomenon was not a simple and fluent undertaking; thus, the analysis surpasses the ultimate experimental calculations to render the evidence. Because of the evidence investigations, the study proposes Weibull statistics to clarify probability dependence, considering the stressed area (a sensing region in terms of diameter) and the surface finish (coating thickness). Previously, the research applied to calculate the linearity measurements (R^2) employing the Weibull parameters. On the contrary, the current study has a holistic estimation utilizing the Weibull statistics with comparing the survival analysis test, and the latter was limited in terms of parameters. The survival analysis test estimated the thickness measurements but failed to provide the diameter measurements.

Previously, the surface plasmon resonance sensors were compared in terms of two analyses. It gained its purpose of comparison but limited the quality of analyses. The comparison and validation of the study LAE-sensors performance has enlarged the analyses span to repeatability, selectivity, and linearity along with sensitivity. Accordingly, the Weibull statistics evaluated the assessment of the solvents' parameters influence on gold nanoparticles' growth and the diameter measurements. The evaluation of the sensors stimulated the comparisons between the four LAE-sensors by determining the optimal selected sensor and solvent for further applications. Employing the Weibull statistics, the study succeeded in establishing the solutions for both fabrication and coating challenges.

The study strength is leveraged when the sensor has a higher Weibull modulus, maximizing the sensors' sensitivity. Despite utilizing the Weibull statistics method, its limitation persisted for brittle materials (e.g., optical fibre) that could not be applied for solid and gas materials. However, it is the best option to analyze the sensitivity and selectivity measurements. Furthermore, the survival analysis test process was limited for comparison-wise in terms of refining the two methods. The optical fibre as a brittle material was handled gently and prudently; however, it fractured more than once during the experimental setup. The identified constraints were behind the consumption of the framed time of the study, exerted effort, and resources, but the problem was resolved.

1.3 Research Objectives

The following objectives have sustained what was approved over a series of experimental analyses:

(a) To characterize the gold nanoparticles-coated surface plasmon resonance sensors (LAE-sensors) for achieving optimum sensing traits.

(b) To determine the etching and coating mechanisms for the LAE-sensors integration in various protic solvents.

(c) To evaluate the performance of the proposed sensors in terms of repeatability, selectivity, sensitivity, and linearity parameters.

1.4 Research Scope

The study is focused on evaluating and optimizing the mechanisms and the function of the gold nanoparticles-coated surface plasmon resonance sensors. The protic solvents parameters such as refractive index, dielectric constant, dipolar, molarity, HBD (hydrogen-bond donors), and polarity factors are the subject of the study investigations. The timeframe to conduct the study is about five years at Unversity Technologhy Malaysia in the Laser centre allocated in faculty of science. For the alcohol sensing (protic solvents), the study will utilize pure liquid samples of ethanol, methanol, 1-butanol, and 1-propanol. The study will be accomplished quantitatively through experimental procedures. The analyses obtain from the bunch of repeated data (about 3648 data) that requires a particular program mode, such as survival analysis test and Weibull statistics. The findings revealed that the polarity factors and refractive index are the significant parameters in AuNPs' thickness growth and core diameter variations.

1.5 Significance of the Study and Original Contributions

This section of the study contains the beneficiaries of the research. The potential contribution of a study to entities is to evaluate the material quality through Weibull analysis. The stated evaluation can be applied through determining the factors of sensor flaws in fabrication and coating mechanisms. Thus, researchers that depend on brittle materials will be able to diagnosis the fault of their setup. The new approach of the study will benefit the student by conducting bundle of data to achieve the accuracy of the analysis. Qualitative and quantitative methods' analyzed data filtrate the sensors considering their cons and pros for future recommendation. The study signifies and supported its significance by comparing two program modes to ensure the fabrication and surface finish confidence. The remarkable achievement of the study is its diverge from other conventional measures that emphasize the distinction between the Weibull or other distributions and find out which model is more effective.

1.6 Thesis Outline

Chapter two has shown the aperture of other researchers' regions and how the study developed the shortage to develop divergent and successful outcomes. Concerning developing the research protocol, chapter two would state the inclusion and exclusion studies' criteria and assess the articles' quality based on well-defined benchmarks, data extraction, synthesis, and analysis. Chapter three sequentially has detailed the fabrication of sensors, characterization of the utilized material and sensors optimization of sensing, and solvent preparation. Nevertheless, it has explored the immersion of sensors procedures, Weibull estimation, and the research architecture flowchart. When the minute of chapter four, the intensive investigations has applied to optimizing the surface plasmon resonance sensors. The etching and coating mechanisms assessment on protic solvents has discussed in chapter four. The study has concluded in chapter five by eliminating the research objectives, achievements, and recommendation.

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