REAL-TIME ABSORBANCE MONITORING OF LAYER-BY-LAYER COATING PROCESS OF OPTICAL FIBER PH SENSOR

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DEDICATION

This thesis is dedicated to all my family members who are awaiting me to complete my master.

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ABSTRACT

Fiber optical cable was initially used as waveguides to transmit data over long distances. Various sensor applications can be developed using optical fiber by coating it with different coating materials. Layer-by-layer (LbL) technique is utilized in this research in order to introduce coating layers on sensing region. The utilization of this technique enables the production of scalable ultra-thin film using various materials especially polyelectrolyte. Although various studies had been performed using LbL technique, there still a need to monitor the LbL coating process for optimization of the sensor performance. This is because the performance depends on the coating properties including the thickness of the coat. The main objectives of this research were LbL coating system development, determining the optimal number of bilayers coating on the sensing region and evaluation of fabricated fiber sensor performance. The LbL coating system was developed using power supply, Arduino Uno, stepper motors, breadboard, drivers and laser engraver axis. LbL coating process on optical fiber was monitored in real-time using a white light source and a spectrometer. Multiple layers of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were coated to create pH-sensitive coating on the surface of the optical fiber core. Real-time monitoring of the absorbance spectrum during the coating process was conducted from 0 to 50 PAH/PAA bilayers. Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX) were used to verify the existence of the fiber coating. The results of EDX proved that the PAH and PAA were coated on the fiber. The monitoring spectrum showed that the absorbance value was increased with the increment of PAH/PAA bilayers up to 30 bilayers and started to decrease as the bilayers exceed that value. The results showed that 30 bilayers of PAH/PAA coatings is the optimum number of bilayers coating for pH sensing due to its high absorbance of 0.87 Optical Density (OD) at 800 nm. The pH sensing performance of fiber without PAH/PAA coating and with 5, 10, 15, 20, 30 and 40 bilayers of PAH/PAA coating were compared by immersing the fiber in pH buffer solutions. The performance was determined through the sensitivity, linearity and repeatability of the sensor. 10 PAH/PAA bilayers coated fiber sensor was 120 times more sensitive than the fiber without coating. This shows that the PAH/PAA coating is highly sensitive to pH as compared with uncoated fiber. The best performance was achieved by 30 bilayers of PAH/PAA coated fiber with a sensitivity of 0.453 OD/pH, linearity of 0.959 and standard deviation value below 4%. Numerous physical, chemical and biological sensors can be produced by utilizing the developed LbL coating system in future.

ABSTRAK

Gentian kabel optik pada mulanya digunakan sebagai pandu gelombang optik untuk penghantaran data pada jarak jauh. Pelbagai aplikasi sensor dapat dibangunkan menggunakan gentian optik dengan menyalutkannya dengan bahan-bahan salutan yang berlainan. Teknik lapisan-demi-lapisan (LbL) digunakan dalam kajian ini untuk memperkenalkan lapisan salutan pada bahagian pengesanan. Penggunaan teknik ini membolehkan penghasilan filem ultra-nipis berskala menggunakan pelbagai bahan terutama polielektrolit. Walaupun pelbagai kajian telah dilakukan dengan menggunakan teknik LbL, masih ada keperluan untuk memantau proses salutan LbL bagi mengoptimumkan prestasi sensor. Objektif utama penyelidikan ini adalah pembangunan sistem salutan LbL, menentukan bilangan optimum salutan lapisan pada bahagian pengesanan dan penilaian prestasi sensor gentian rekaan. Sistem salutan LbL dibangunkan dengan menggunakan bekalan kuasa, Arduino Uno, motor pelangkah, papan reka, pemacu dan paksi penuris laser. Proses salutan LbL ke atas gentian optik telah dipantau dalam masa-nyata menggunakan sumber cahaya putih dan spektrometer. Lapisan *poly(allylamine hydrochloride)* (PAH) dan *poly(acrylic acid)* (PAA) disalut untuk mewujudkan lapisan yang peka-pH pada permukaan teras gentian optik. Pemantauan masa-nyata spektrum penyerapan semasa proses salutan dijalankan daripada 0 sehingga 50 lapisan PAH/PAA. Mikroskopi electron pengimbasan pancaran medan (FESEM) dan spektrum tenaga serakan sinar-X (EDX) telah dilakukan untuk mengesahkan kewujudan lapisan pada gentian. Hasil EDX membuktikan bahawa PAH dan PAA telah tersalut pada permukaan gentian. Spektrum pemantauan menunjukkan nilai serapan telah meningkat dengan peningkatan dwi-lapisan PAH/PAA sehingga 30 dwi-lapisan PAH/PAA dan mula menurun apabila dwi-lapisan PAH/PAA melebihi nilai tersebut. Hasil kajian menunjukkan bahawa 30 dwi-lapisan PAH/PAA adalah bilangan dwi-lapisan yang optimum oleh kerana nilai penyerapannya yang tinggi iaitu 0.87 *Optical Density* (OD) pada 800 nm. Prestasi sensor pH gentian tanpa salutan PAH/PAA telah dibandingkan dengan gentian bersalut 5, 10, 15, 20, 30 dan 40 dwi-lapisan PAH/PAA dengan merendam gentian dalam larutan-larutan penimbal pH. Prestasi telah ditentukan melalui kepekaan, kelinearan dan kebolehulangan sensor. Sensor gentian dengan 10 dwi-lapisan PAH/PAA adalah 120 kali lebih peka daripada gentian tanpa salutan. Ini menunjukkan bahawa salutan PAH/PAA adalah sangat peka kepada pH berbanding dengan gentian tanpa salutan. Prestasi terbaik telah dicapai oleh gentian bersalut 30 dwi-lapisan PAH/PAA dengan kepekaan 0.453 OD/pH, kelinearan 0.959 dan sisihan piawai bawah 4% . Pelbagai sensor fizikal, kimia dan biologi boleh dihasilkan dengan menggunakan sistem salutan LbL yang telah dibangunkan pada masa hadapan.

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LIST OF ABBREVIATIONS

LbL	-	Layer-by-layer
pH	-	Potential of hydrogen
TOF	-	Tapered Optical Fiber
CROF	-	Cladding Removed Optical Fiber
FBG	-	Fiber Bragg Grating
LPG	-	Long Period Grating
SPR	-	Surface Plasmon Resonance
LMR	-	Lossy Mode Resonance
LSPR	-	Localized Surface Plasmon Resonance
FESEM	-	Field Emission Scanning Electron Microscope
EDX	-	Energy Dispersive X-ray spectroscopy
PAH	-	Poly(allylamine hydrochloride)
PAA	-	Poly (acrylic acid)
SMF	-	Single Mode Fiber
MMF	-	Multimode Fiber
TIR	-	Total Internal Reflection
FOS	-	Fiber Optic Sensor
TM	-	Transverse Magnetic
TE	-	Transverse
T-SMF	-	Tapered Single Mode Fiber
NR	-	Neutral Red
PB	-	Prussian blue
BY	-	Brilliant Yellow
UTM	-	Universiti Teknologi Malaysia
TECS	-	Technology enhanced cladding silica
IDE	-	Integrated development environment
RI	-	Refractive index

LIST OF SYMBOLS

n	-	Refractive index
θ_I	-	Incidence angle
θ_R	-	Refraction angle
E	-	Evanescence wave
x	-	Distance
d_p	-	Penetration depth
λ	-	Wavelength
n_{co}	-	Refractive index of core
n_{cl}	-	Refractive index of cladding
θ	-	Angle
I	-	Intensity
$\Delta\phi$	-	Phase difference
n_{eff}	-	Effective refractive index
L	-	Length
A	-	Absorbance
α	-	Absorption coefficient
η	-	Fraction of light in evanescence field
ε	-	Molar absorption
C	-	Concentration of surrounding medium
S	-	Sensitivity
%	-	Percentage
nm	-	Nanometre
μm	-	Micrometer
M_w	-	Molecular weight
mM	-	Millimolar
K	-	Kelvin
W	-	Watt
h	-	Hours
ms	-	Microseconds
sec	-	Seconds
g/mol	-	Gram per mole
$Brix$	-	Sugar content of an aqueous solution

V	-	Volt
mm	-	Millimetre
mL	-	Millilitre
g	-	Gram
A	-	Ampere
M	-	Molarity
OD	-	Optical Density
R^2	-	Linearity
σ	-	Standard deviation
C	-	Carbon
H	-	Hydrogen
O	-	Oxygen
Si	-	Silica
Au	--	Gold
Cl	-	Chlorine
$w.t$	-	Weight

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The optical fiber sensors revolutions become more sophisticated over the years. Numerous optical fiber sensors have been created almost 40 years to track various physical factors, such as refractive index, temperature, pressure strain, biosensor and chemical sensor [1]. This is because optical fiber has unique features including electromagnetic immunity, low attenuation and miniature in size [2]. These properties make the optical fiber can perform in harsh environment, such as high voltage locations and oceans. Various approaches had been done by researcher on the development of optical fiber sensors, such as in optical fibers configuration, sensing mechanism and applications. Tapered optical fiber (TOF), cladding removed optical fiber (CROF), D-shape, fiber bragg gratings (FBG) and long-period gratings (LPG) are the example of optical configurations [3-6]. There are also several sensing mechanism had been discovered by previous researchers. The mechanisms are evanescent wave, fluorescence, surface plasmon resonance (SPR), localized surface plasmon resonance (LSPR) and lossy mode resonance (LMR) [7-9].

Another approach has been implemented to produce new optical fiber sensors by combining of optical configuration with coating materials as sensitive layers [10]. The sensitive layer is normally coated on optical fiber and the coated region is known as sensing region. At the sensing region, sensor reacts with the surrounding medium. The common types of materials used as sensing region are metal nanoparticles, metal oxide nanoparticles, dyes and polymers [11-17].

Several techniques had been used for coating deposition on optical fiber that are drop cast, sputtering deposition and layer-by-layer (LbL) [18-20]. Recently, the LbL technique becomes popular due to its versatility, convenience, scalability and flexibility which allow precision of controlling the coating composition and thickness. The LbL coating process involves the sequential and ordered by using an immersion technique. The main capability of this technique is that wide range materials can be utilized as the coating materials, such as polyelectrolytes, metal or metal oxide nanoparticles, hybrid particles, luminescence materials, dyes and bio-molecules [21-20]. Polyelectrolytes are polymers with ionisable functional groups that form positive charge (polycation) or negative charge (polyanion). For pH sensing application, the common polyelectrolyte pairs used are poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) [23]. It is also known as “weak polyelectrolyte” with pH-dependent ionization degrees [11].

Recently, the work using LbL method has been done on generating optical fiber sensor [24]. As reported by Zamarenno et. al., the studied has been done by fabricated optical fiber pH sensor utilizing LMR absorption band that was based on wavelength shift. The wavelength can be tune by alternating the thickness of the coating. From the work, they gain an average sensitivity of 0.027 pH units/nm, accuracy of ±0.001 pH units within pH range from 3.0 to 6.0. However, the research was lack of monitoring results on LbL coating process performance. LbL coating process is not focused by previous researchers because they are more focused on sensing working principle during utilizing LbL coating.

1.2 Problem Statement

Various techniques to coat the optical fiber with sensing materials have been used, such as drop cast and sputter deposition. Although drop cast is simple technique, the disadvantages of this technique is non-uniformity coating and uncontrollable coating thickness [25]. Sputtering technique requires complex system and it is an expensive deposition method. The use of LbL technique for deposition of sensing layer on optical fiber shows promising sensing performance [24]. The simple, convenient and highly scalable fabrication technique for good through put without using sophisticated equipment is advantage of utilizing the LbL deposition method [11]. It also has possibility of designing and fabricating coating in nanometer scale [1]. It also offered additional advantages since it is possible to control the composition and morphological characteristic of the film independently. Therefore, a good control of film can be used to produce ultra-thin film. The capabilities of this technique had attracted researchers to use LbL technique to fabricated new optical fiber sensors with new sensing coating materials.

Although numerous studies had been done using LbL technique, there still lacks of monitoring result of LbL coating process. The monitoring on the LbL coating process is crucial for optimization of sensing performance of optical fiber sensor. Thus, in this research, a low cost and convenient LbL coating system with real-time coating monitoring feature was developed.

1.3 Objectives of Study

The objectives of this study were:

1. To develop an LbL coating system with capability to monitor the coating process in real-time.
2. To determine the composition of bilayers coating of coated fiber using FESEM and EDX.
3. To determine the optimum number of bilayers coatings on an optical fiber for sensing applications.
4. To determine the pH sensing sensitivity, linearity and repeatability of fabricated optical fiber with various number of bilayer coatings.

1.4 Scope of Study

The research covered the development of LbL coating system with coating monitoring capability. The material used for coating were poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). The optical fiber used was multimode fiber (FT200EMT) with 225 µm of cladding and 200 µm of core. The integration time and the number of scan were set according to the time needed for 50 bilayers of PAH/PAA. The coating process for 50 bilayers of PAH/PAA was monitored to analyse which coating bilayers give highest value of absorbance. The fabricated fiber was characterized using optical microscope, field emission scanning electron microscope (FESEM) and energy x-ray dispersive (EDX) analysis. The range of number of bilayers coated in this study was 5, 10, 15, 20, 30 and 40 bilayers. In this research, the optical fiber was fabricated for pH sensing application in acidified region from pH 3 to pH 7. This is because the PAH/PAA coating is more sensitive in acidic pH range. The performance of fabricated fiber sensors also was analyzed in terms of the sensitivity, linearity and repeatability.

1.5 Significant of Study

The LbL technique is considered as an eco-friendly since it is based on water soluble without any volatile organic compound. The LbL system developed is a low-cost system because it is highly reproducible technique without using sophisticated instrument or equipment. The optimization of coating bilayer can produce various physical, chemical and biological sensors by varying the coating materials. Thus, the optimization of LbL coating process is crucial to fabricate the optical fiber sensor with better performances. Thereby, this research will provide the real-time absorbance monitoring of LbL coating process for each coating bilayers and the performances of fabricated fiber for 5, 10, 15, 20, 30 and 40 bilayers were studied as pH sensing application. As the consequence, the develop LbL coating system is easy to handle and time conserve because it capable to monitor the coating process in real-time and directly optimized the number of bilayers coating for sensing application.

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LIST OF PUBLICATIONS

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Yatim, K. M., Johari, A. R., Krishnan, G., Bakhtiar, H., Daud, S., Aziz, M. S. A., & Harun, S.W. (2020, July). Optimization of Coating Thickness on Optical Fiber via Layer-by-Layer Technique for pH Sensing Application. In *International Journal of Microwave and Optical Technology (IJMOT)* 15 (4), pp. 399-406.

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