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The pH sensor based optical fiber coated with PAH/PAA

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The pH sensor based optical fiber coated with PAH/PAA

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Abstract. pH-sensitive optical fiber sensors were fabricated with layer-by-layer (LbL) method. Multiple layers of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) bilayers were coated on an unclad fiber to create the pH-sensitive region. The coating process was done using a coating system developed in this work. 10 to 40 bilayers of PAH/PAA were coated on the fiber core to evaluate its performance as pH sensor. The existences of coating on the fiber were verified with field emission scanning electron microscopy (FESEM) and energy-dispersive x-ray spectroscopy (EDX) analysis. It was shown that the fabricated sensor is pH sensitive and independent of variation in the refractive index of the surrounding. The best performance was obtained with 30 bilayers fiber sensor. The sensitivity and resolution of the sensor were 0.453 a.u/pH and 0.0022 pH units respectively. With the developed coating system, various physical and chemical sensors can be realized by varying the coating materials.

1. Introduction

Optical fiber sensor has undergone tremendous development in the past decades. Its advancement has attracted the attention of researchers due to its capabilities as a sensor and becomes an active research area due to its electromagnetic immunity, isolation to electrical parameter variation, ruggedness and remote sensing [1]. Physical and chemical parameters also could be detected using fiber sensors where it propagates the light from a remote source to a detector.

The development of optical fiber as pH sensors based on the immobilization of thin films and other waveguide materials has become an increasingly active area of research. One of the methods used for deposition of thin-film is layer-by-layer (LbL) due to the good uniformity and convenient. This method is based on the electrostatic attraction of the sequential adsorption of oppositely charged molecules [2]. For pH sensing, poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) layers were coated on an unclad fiber via LbL method in the previous study [1]. At the sensing region, an evanescent wave (attenuated total internal reflection) spectrum of PAH/PAA was used to monitor the effect of pH [1]. Most of the investigation focused on optical fiber sensor based on fluorescence and UV-Visible spectroscopy [1-4]. However, the recent publication reported the use of an infrared region for sensing and it shows a promising performance [5]. The work based on the generation of lossy mode resonance (LMR) using PAH/PAA polymeric pH-sensitive showing an average sensitivity of 0.027 pH units/nm with resolution varied from 0.00054 pH and 0.2268 pH units [5]. LbL technique was used to fabricate the sensors, yet the coating system was not discussed in detailed [5]. Therefore, in the current paper, the development of an automated coating system and the performance of the fabricated pH sensors are discussed.

2. Materials and methods

2.1. Materials
The polymers poly(allylamine hydrochloride) (PAH) (Mw ~ 19000) was obtained from Huichem and poly(acrylic acid) (PAA) (Mw ~ 1800) was obtained from Sigma Aldrich and used without further purification. Aqueous solutions of the polymers (10 mM) were prepared using distilled water and adjusted at pH 4.4. Potassium hydroxide (KOH) 1M and pH 3, 4, 5, 6 and 7 buffer solutions were obtained from Quirec. The pH solutions were verified using pH-meter by Hanna Instruments and a few drops of NaOH or HCl was added to adjust the pH solution. Optical fiber with 200/225 µm core/cladding diameter (FT200EMT) produce by Thorlabs was used.

2.2. Development of Coating System
The coating system was set up using Arduino driver, 3 stepper motor with a driver, power supply, breadboard and 3D printer axis as shown in figure 1. 2 stepper motor were set to control the vertical movement of a platform containing the coating materials and the stepper motors were placed parallel to each other. Another stepper motor was set to control the horizontal movement of the platform and the stepper motor was placed perpendicular to 2 stepper motors. All stepper motors were connected to its respective stepper motor drivers and the drivers were connected to a DC power supply as shown in figure 1. The power supply supplied a voltage of 4.2 V and a current of 0.84 A to the motors. An Arduino Uno microcontroller board was used to control the movement of the stepper motors. The movements were coded with Arduino IDE software according to the dipping time required during the coating process.

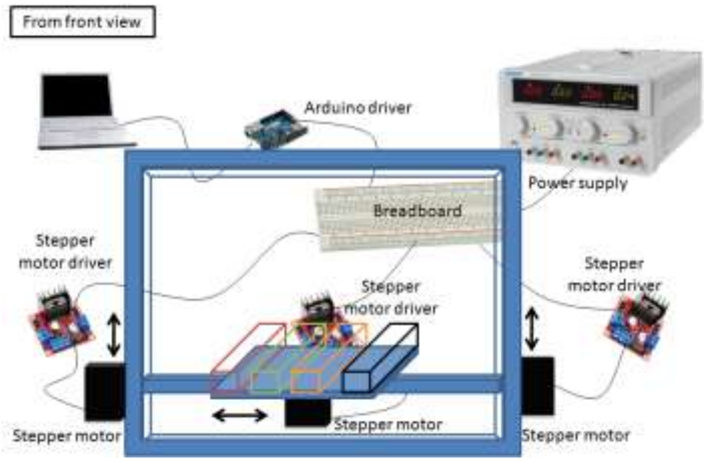

Figure 1. The schematic setup for the coating system.

2.3. Coating Process
The 4 cm long cladding was removed by heating the fiber and then followed by wiping and cleaning the remaining optical fiber with acetone. The optical fiber was attached to a holder as represented in figure 2.

The PAH/PAA coating was coated on the fiber core via LbL technique and the coating process was carried out using the developed coating system. Firstly, the unclad region was immersed in 1M of KOH solution for 10 minutes. This was to acquire the negative charge on the surface of fiber core and then was cleaned up in distilled water for 1 minute. Next, the unclad region was immersed into the 10 mM of PAH solution for 2 minutes to absorb the positive charged. This step was followed by rinsing in distilled water for 1 minute to remove the excess of the material adsorbed and dried for 30 seconds. Then, the unclad region was immersed into10mM of PAA solution for 2 minutes to absorb the negative charged material and was rinsed again in distilled water for 1 minute and dried for 30 seconds. As a result, a single bilayer of [PAH/PAA] coating had been coated on the core. This process was repeated until the desired number of bilayers coated on the core. Fiber sensors with 10 to 40 bilayers were fabricated in this work to evaluate its performance as a pH sensor.

2.4. Device Characterization
Figure 2 shows the setup for pH sensing using the fabricated fiber sensors system. One end of the optical fiber was connected to white halogen lamp (Avalight) in order to couple light into the optical fiber. The light propagates through the sensitive region located in the transmission path and the other end of the fiber was connected to a spectrometer (USB4000 Ocean Optics). The sensing region was attached to a holder as shown in figure 2. The absorbance response was recorded during the immersion of the sensing region into the pH buffer solution. The measurements were performed at room temperature (25°C).

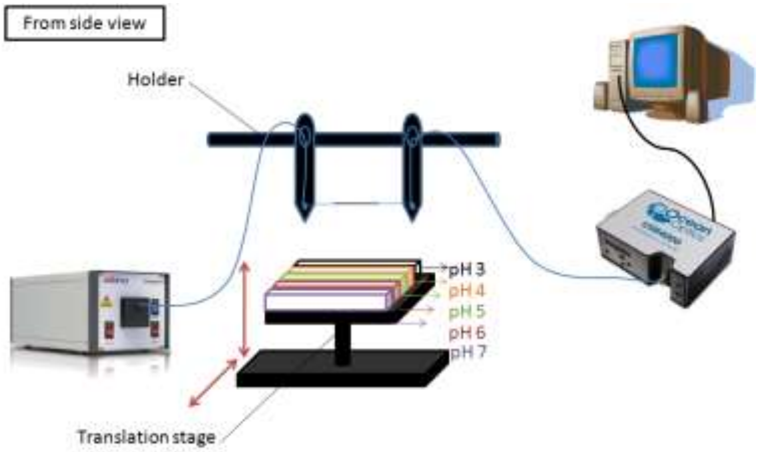

Figure 2. Schematic image of the experimental setup for device characterization.

3. Results and Discussion

3.1. Coating Characterization
Figure 3 shows the field emission scanning electron microscopy (FESEM) and energy-dispersive x-ray spectroscopy (EDX) results of the cross-section of the coated fiber. The result shows that PAH/ PAA layer was successfully coated on optical fiber core as shown in figure 3. From figure 3, it can be seen the core of fiber was 200.4 µm. Also, a layer of coating was seen on the circumference of the core. The thickness coating ranges between 201.0 nm and 240.1 nm for 25 bilayers. The thickness of the coating obtained in this study is comparable to the one obtained by Zamarenno et al. for 25 bilayers [5].

The EDX results display all the elements exist on the surface of the coated fiber. The highest percentage is gold (Au). This is due to the sputtered gold element, which is to avoid charging effect during image scanned. Other than that, there is no impurity element exist. The carbon (C) and oxygen (O) are the constituents of PAH/PAA with the molecular formula for PAH is (C_3H_8Cl)n and PAA is ($C_3H_4O_2$)n. On the other hand, Si is an element in the fiber core which is glass made from silica.

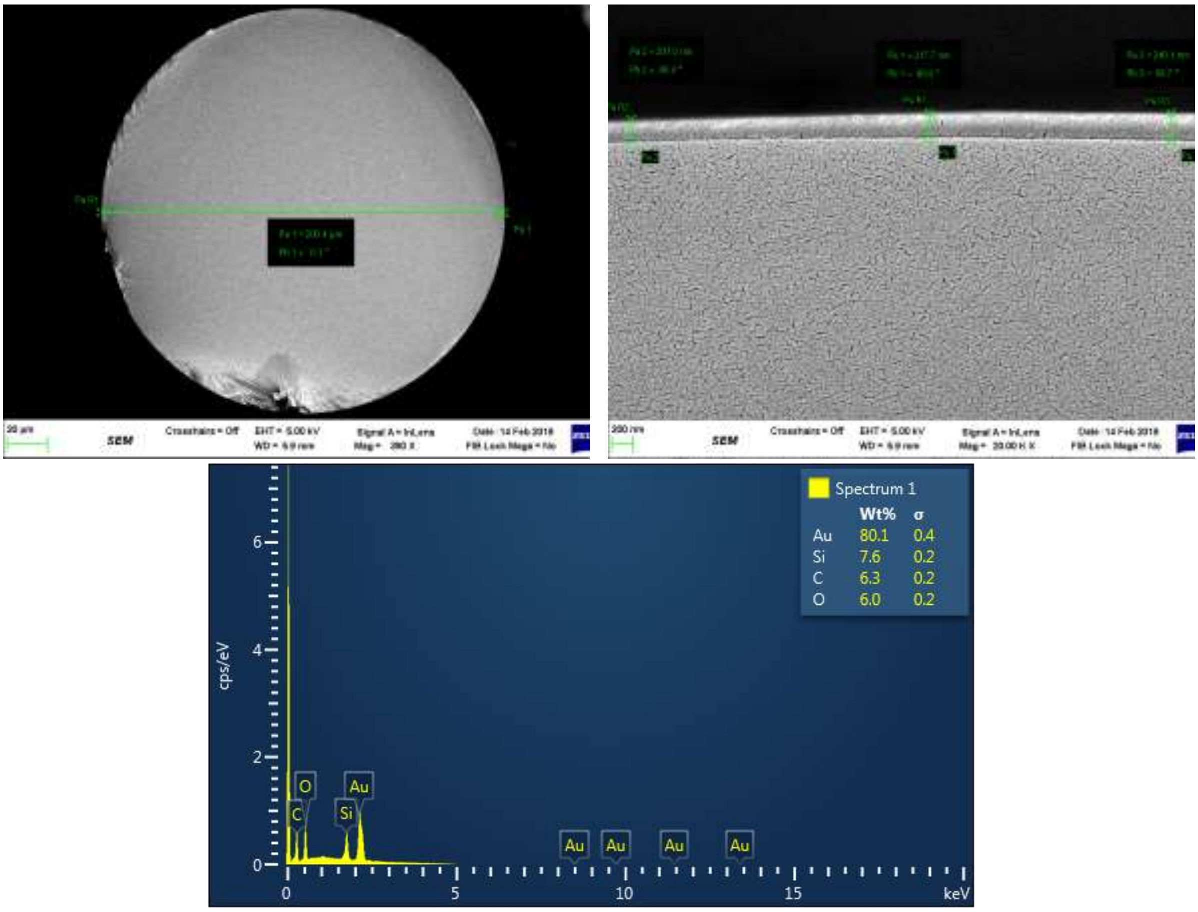

Figure 3. Cross-section and EDX analysis of optical fiber coated with 25 bilayers of PAH/PAA .

3.2. Device Fabrication Response

The fabricated device showed a spectral response when immersed in different pH buffer. Figure 4 shows the absorbance spectrum for 10 bilayers and 0 bilayer (uncoated fiber). It could be observed that for 0 bilayer the changes in absorbance value is negligible compared to 10 bilayers. For the 0 bilayer fiber, the change in absorbance is 0.001 a.u/pH was shown in figure 5. This change may cause by the variation in the refractive index of pH buffer solution and not due to the change in pH. The change in absorbance for 10 bilayers is 0.120 a.u/pH was showed in figure 5. It shows that the PAH/PAA coating layer on optical fiber core is pH sensitive and it is not an influence of the surrounding refractive index. The utilization of PAH/PAA as polyelectrolyte materials pair is one due to its intrinsic swelling pH behaviour of the resultant films. The structural changes in the bilayer form from PAH/PAA can be induced by changes in pH [6]. The changing in absorbance intensity is due to the swelling/deswelling behaviour of the coating that contributes to the thickness alteration during the immersion of fabricated fiber into different pH buffer.

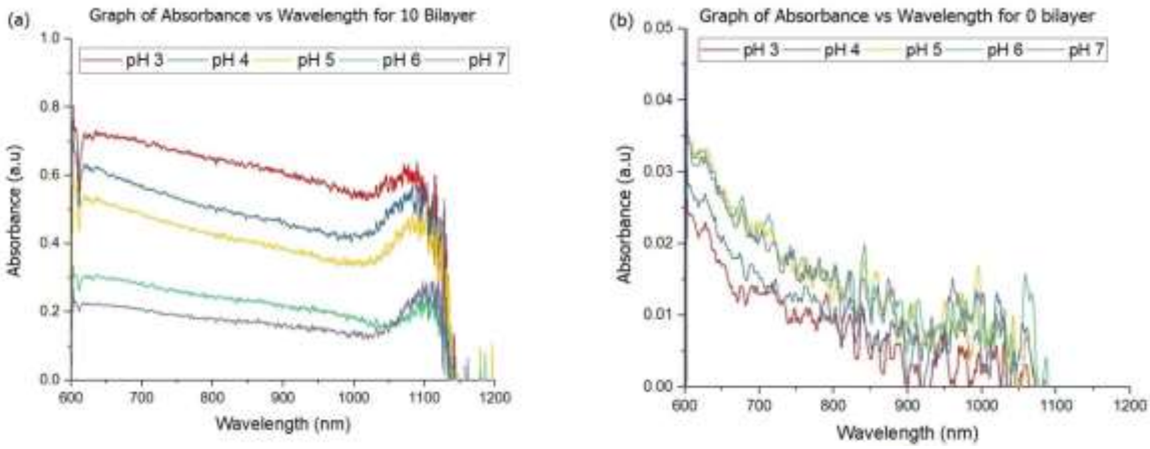

Figure 4. Absorbance spectrum of fabricated fiber (a) 10 bilayer and (b) 0 bilayer during immersed in different pH buffer respectively.

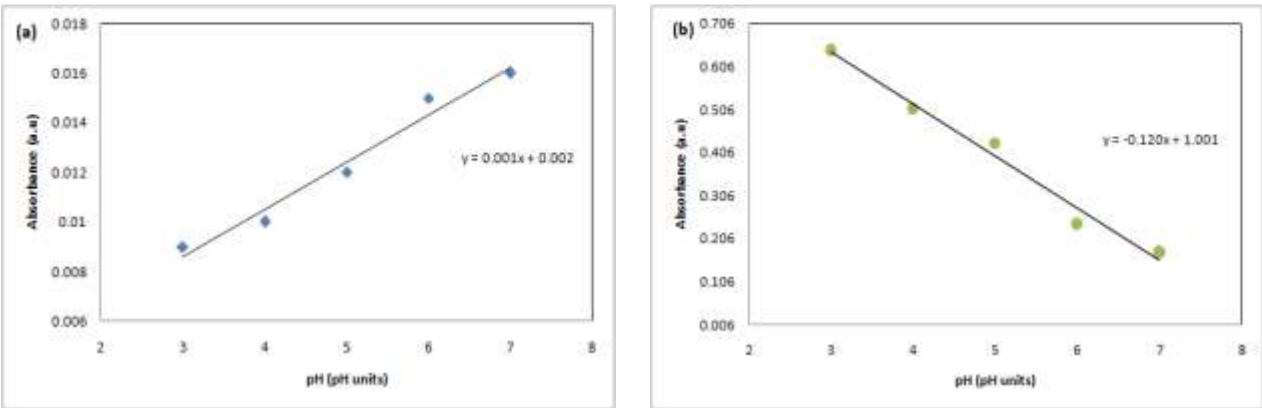

Figure 5. Absorbance value at 800 nm of (a) 0 bilayer and (b) 10 bilayers fiber in various pH buffer solutions.

The comparison of performance fiber sensor coated with different bilayers is listed in table 1. From the table, the best sensitivity and resolution of the fabricated device is showed by 30 bilayers of PAH/PAA coating with 0.453 a.u/pH for sensitivity and 0.0022 pH units for resolution. From 0 to 30 bilayers, the sensitivity value is increasing, however, the sensitivity value is decreased for 40 bilayers which is 0.058 a.u/pH. This result shows that the performance of sensors is coating thickness dependent and there exists an optimum coating thickness. The linearity of sensors is decreasing with the increase in the number of bilayers due to nonlinear swelling behaviour of the coating with pH.

Table 1. The list of performance comparison for each bilayer for pH sensor.

Bilayer	Linearity, (R^2)	Sensitivity, (a.u/pH)	Resolution, (pH units)
0	0.970	0.001	1
10	0.981	0.120	0.0083
20	0.968	0.241	0.0042
30	0.959	0.453	0.0022
40	0.953	0.058	0.0172

4. Conclusion
pH sensors based optical fiber were successfully fabricated with the developed coating system. In term of the number of bilayers, 30 bilayers have better sensitivity and resolution compared with other numbers of bilayers. The linearity of 30 bilayers can be improved in future study and other sensor performance parameters such as repeatability will be reported. With the development of this coating system, various physical and chemical sensors can be realized by varying the coating materials.

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