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Effect of the Deposited Layer, Withdrawal Speed and Coated Length on Immobilised Bromothymol Blue in Polyaniline Sol Gel towards pH Sensing Sensitivity

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ABSTRACT

In this work, sensors were prepared by depositing the pH sensitive indicator (bromothymol blue) entrapped in polyaniline sol-gel onto the un-cladded middle potion of optical fiber. Polyaniline is sensitive to pH. However, it is important to study ways to increase sensitivity of the indicator by improving a combination of the materials used and pH sensor fabrication method. The fabrication and characterisation of optical fiber pH sensor on absorption intensity in arbitrary unit (a.u) were evaluated and optimised. The better sensitivity of the optical pH sensor was used to identify the optimum setting for number of layers deposited, coated length, and withdrawal rate. Thickness of the membrane film depends on the number of deposited layers and withdrawal speed which mainly affects sensitivity. The sensitivity of the optical pH sensor represents the slope (a.u/pH) of the absorbance intensities in pH 4, 5, 7, 9 and 10. Results obtained herein suggest that the optimised setting for bromothymol blue sol-gel coated optical fiber with thickness of 285.4 nm is 4 deposited layers, 20mm/s withdrawal rate and 0.5 cm coated length.

Keywords: Bromothymol blue, plastic optical fiber, pH sensor, sol-gel

INTRODUCTION

Indicator is important in optical pH sensing due to its capability to detect changes in absorbance intensity in the presence of hydrogen ion activity. Hydrogen ion is an important element because of its presence in almost all chemicals. It is very useful for medical applications, such as in monitoring the acidity and alkalinity of human blood which could change as little as 0.03 pH unit or less. Even small changes in pH can adversely

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affect the human body functionality. Moreover, animals and plants are also dependent on changes in the pH of their habitat (Korostynska, Arshak, Gill, & Arshak, 2008; Rovati et al., 2012; Zauner et al., 1995). Therefore, it is crucial to investigate and develop pH sensor that is able to act fast, accurate, sensitive, and stable (Hussain, 2014).

Polyaniline has been found to be the most suitable organic material to act as a matrix in aqueous medium and it is widely used in the development of pH sensor (Ayad et al., 2010; Cheng-Hsin et al., 2011; Florea et al., 2011; Patil et al., 2015; Sotomayor et al., 2001; Song & Choi, 2014; Vieira et al., 2011; Jin, Su, & Duan, 2000). Furthermore, polyaniline requires simple preparation, stable under ambient conditions and possesses high conductivity and sensitivity to detect chemical properties. This versatility makes polyaniline to be frequently used in numerous applications due its capability to act as sol-gel matrix to support pH indicator. Moreover, it has a high permeability for water and ions. The entrapment of bromothymol blue in polyaniline sol-gel films is a very important technique.

In this work, the fiber optic pH sensor was prepared with varying numbers of layers, withdrawal speeds and coated lengths of the fibers using the dip coating technique.

METHOD

The experimental process is divided into two sections; preparation of the sensor; and instrumentation. A brief explanation on this is given below.

Preparation of the Optical Fiber pH Sensor

The sensor membrane film is fabricated by sol-gel method. Polyaniline acts as a matrix to entrap pH indicator which was dissolved in N, N-Dimethylformamide (DMF). The mixture was magnetically stirred for 24 hours at room temperature to obtain an optimum dissolved sol-gel. 3.2 mM of bromothymol blue was mixed into 20 ml polyaniline solution and magnetically stirred under ambient temperature for 1 hour.

1000 μm diameter optical fiber (CF01493-15) was used to fabricate the sensor. Using a knife, plastic jacket buffer at a middle portion of the fiber with 0.5 cm lengths was removed, as shown in Figure 1. These portions of fiber optic were immersed into hydrofluoric acid to remove 17.5 μm of the cladding diameter. Prior to this, the un-cladded portion was exposed to sol-gel and the samples were then treated with Nitric Acid (HNO_3). Finally, the un-clad portion was coated with sol-gel by a controlled dip-coating rig for 4 deposited layers and withdrawal speed was 10 mm/s. These optical fibers were kept for heat treatment at 100°C for 24 hours. The samples had to be immersed for 15 minutes in distilled water so as to allow the unbound dye to leach out prior to testing. The fabrication process was done by varying the number of deposited layers (i.e., 1, 2, 3 and 4 layers) with fixed withdrawal speed and deposited length setting of 10 mm/s and 0.5 cm, respectively. Then, the fabrication process was continued by using the optimised deposited layer but varying the withdrawal speeds at 10, 15, 20 and 25 mm/s and fixing the deposited length setting at 0.5 cm. Finally, another set of the samples was

fabricated by varying the deposited lengths to 0.5, 1.5, 2.5 and 3.5 cm against the optimised parameters for number of deposited layers and withdrawal speed. These samples were ready to be characterised.

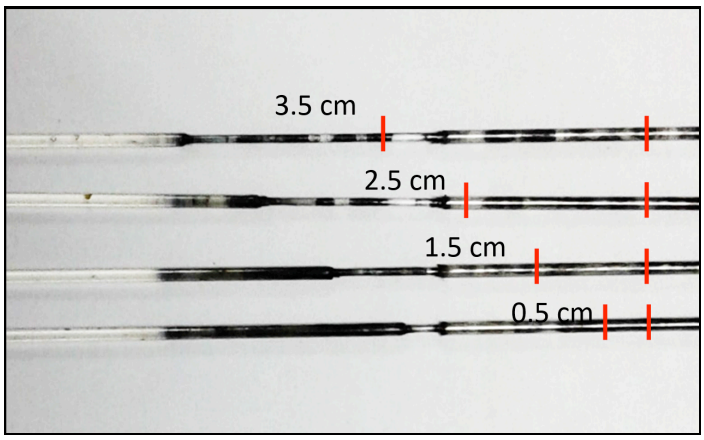


Figure 1. Plastic optical fiber with bromothymol blue sol-gel for differences re-clad region length

Instrumentation

A schematic view of the experimental setup shown in Figure 2 was used to measure the pH sensor performance using spectroscopy of the absorption peak at 460 nm for bromothymol blue LED as the light source. A portion of re-cladded optical fiber was placed in the container filled with pH buffer solution. The optical absorption of the bromothymol blue was captured in computer with the spectrometer. Details of the pH test setup are illustrated by the flowchart in Figure 3.

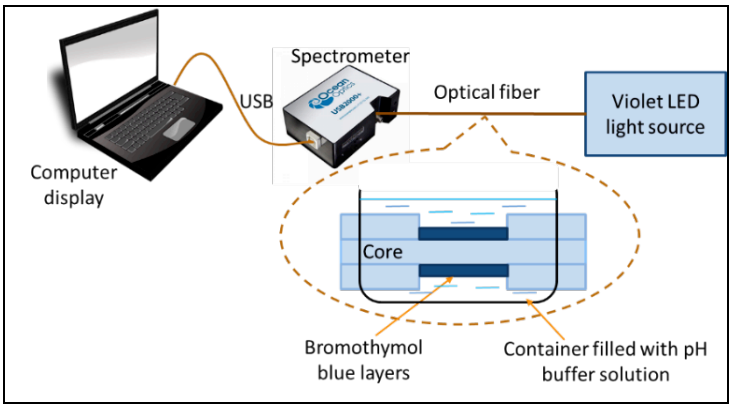


Figure 2. The experimental setup to measure the spectral response of the fiber optic pH sensor

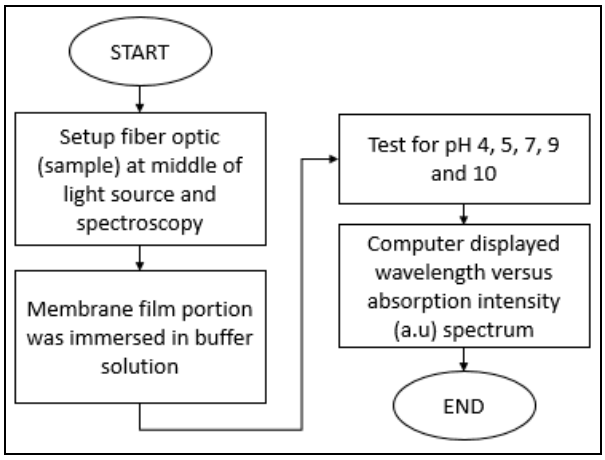


Figure 3. A flowchart of the pH test setup

RESULTS AND DISCUSSION

Optical Properties of Bromothymol Blue Entrapped in Polyaniline Sol-Gel

Figure 4 shows that the excitation peak for bromothymol blue in solution is strong at the wavelengths of 433 nm and 616 nm, while bromothymol blue on thin film is 430 nm. Two absorption bands were observed at 433 nm and 616 nm for the free bromothymol blue in the solution and only one absorption band was observed at 430 nm for the immobilised bromothymol blue film. This finding implies that the chemical bond between bromothymol blue and polyaniline molecules is responsible for the peak wavelength (Culshaw & Kersey, 2008; Korostynska, Arshak, Gill, & Arshak, 2007; Shastry, Abdi, & Nnanna, 2008). This shifting phenomenon of the maximum peak of wavelength could be explained as the large change in the polarity of the surrounding molecules while going from solution to film and the type of intermolecular interactions. Therefore, the blue light LED (460 nm) was selected as an appropriate wavelength for pH monitoring.

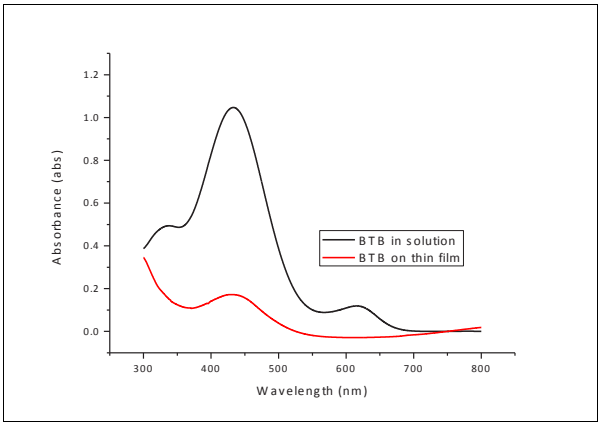
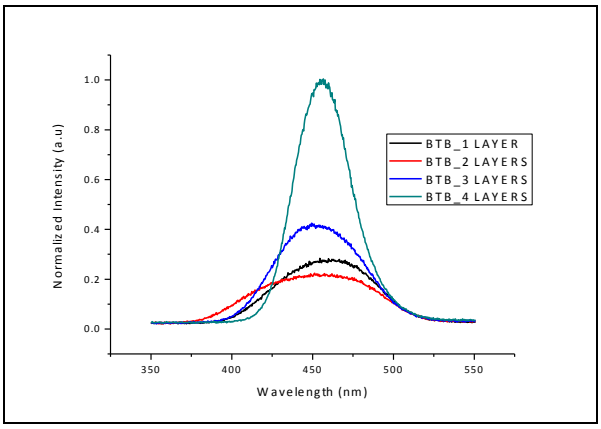


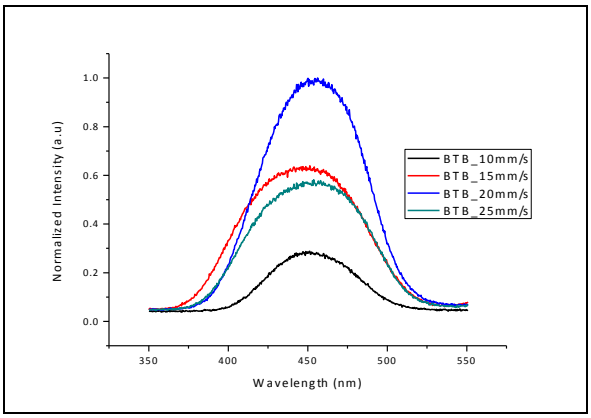
Figure 4. AUV-Vis absorption spectrum of free bromothymol blue (BTB) in DMF solvent and entrapped bromothymol blue (BTB) on the glass slide

Sensing Analysis

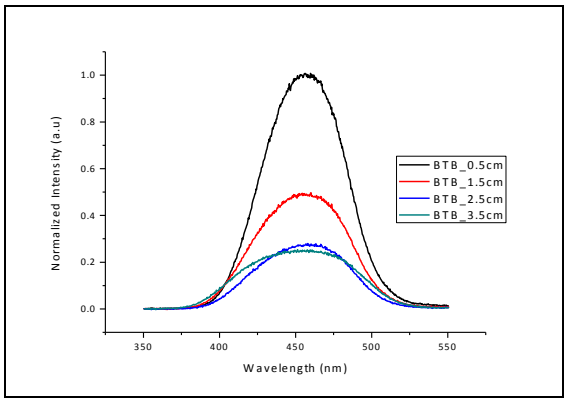
Figure 5 represents the normalised absorbance intensities of light for different number of deposited layers, withdrawal speed and coated length. Figure 5 (a) shows the normalised absorbance intensity dependence for the different multilayers deposition process that was varied for 1, 2, 3 and 4 layers. The thickness for 1, 2, 3 and 4 layers is 264.1, 268.43, 293.4 and 284.2 nm, respectively. By considering the film thickness, it is obvious that absorbance measurement increases directly proportional to the increasing number of layers (El Nahhal et al., 2012). Figure 5(b) shows the normalised absorbance intensity of the fiber optic pH sensor using immobilised bromothymol blue dye in polyaniline film deposited with different withdrawal speeds. The absorbance intensity at the maximum band increases with the increase in the withdrawal speed. However, the absorbance intensity of the optical properties decreases when the withdrawal speeds at 25 mm/s. The thickness of the samples prepared at 10, 15, 20 and 25 mm/s was 284.89, 288.52, 296.3 and 311.3 nm, respectively. It was observed that, besides the thickness, the deposited membrane film on difference un-cladded length of fiber optic is one of the important steps to produce a good sensing membrane. It is crucial to deposit the selected materials in suitable concentration, thickness of film, dried duration, and deposited length during the deposition process. Figure 5(c) shows four different deposited lengths (namely, 0.5, 1.5, 2.5 and 3.5 cm) used to investigate absorbance intensity. This measurement was to study the influence of deposited length of membrane film on the response of the optical membrane. The highest absorbance intensity of light travel in fiber optic exhibited at excitation peak of 460 nm, and the deposited length of 0.5 cm. From the graph, the output intensity of light slightly decreased when the deposited length increased from 0.5, 1.5, 2.5 and to 3.5 cm with the thickness of 285.4, 282.7, 278.4 and 279.8 nm, respectively. Initial results indicated that the highest spectral intensity of light was achieved with 4 deposited layers at 20 mm/s withdrawal rate and 0.5 cm coated length.



(a)



(b)



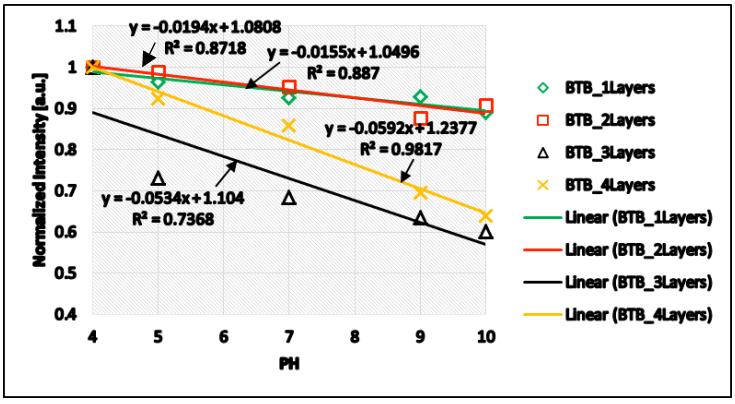
(c)

Figure 5. Entrapped bromothymol blue film normalised intensity of light spectrum for different: (a) number of deposition layers (i.e., 1, 2, 3, and 4); (b) withdrawal speeds (i.e., 10, 15, 20 and 25 mm/s); and (c) coated lengths (0.5, 1.5, 2.5 and 3.5 cm)

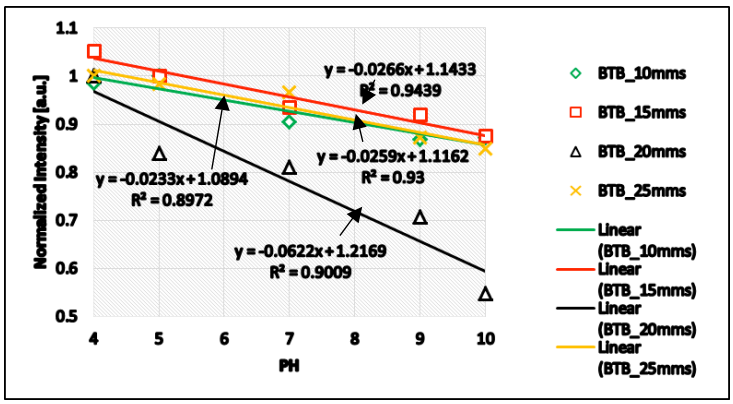
However, each parameter needs to be tested for its sensitivity to pH and to reconfirm that they are indeed optimised parameters. Hence, the sample was tested in various pH buffer solutions and the sensitivity was analysed from the slope of a linear regression line (trendline) against the calibration curve of the optical fiber pH sensor. This calibration curve was evaluated from the normalised absorbance intensity plots of light against various pH values at 460 nm. Hence, the slope and standard deviation of linear line were obtained. The slope and standard deviation of linear line represented the sensitivity and linearity of the membrane film, respectively. The sensitivity and linearity values are shown in Figure 6. Besides, the highest absorbance intensity of lights was observed at pH 4, which continued to decline as it was approaching to pH 5, 7, 9 and 10. This character shows that the highest absorbance was absorbed in the membrane film when it was treated in pH 4. Meanwhile, when the sensor exposed in the buffer solution, the hydrogen ions interacted with the molecules of pH indicators, the refractive index of sensing membrane would change, and as a result, it affected the input light absorption ability

and influenced the rate of light intensity travelling on it. The swelling and shrinkage of the polymer when pH changes are also caused by their refractive index (Chen et al., 2012; Florea, Diamond, & Benito-Lopez, 2013; Pandey & Ramontja, 2016). Thus, the optical output will be determined by the density of the hydrogen ions in the pH solution.

Figures 6(a), (b) and (c) show the calibration curve for the samples with different number of layers, withdrawal speeds and different coated lengths, respectively. The samples were also treated in various pH solutions, namely, pH 4, 5, 7, 9 and 10. Figure 6(a) shows that the number of deposited layers increased proportionally with the measured thickness. Membrane film thickness of the 4 deposited layers is 284.2 nm has the highest sensitivity 0.0592 a.u/pH and its linearity is 0.9817. This phenomenon is in agreement with the previous investigation by El Nahhal et al. (2012), which revealed that the presence of more polymer networks increased its surface area. In Figure 6(b), withdrawal speed continued to 20 mm/s and produced 296.3 nm thickness. This membrane film gave the highest sensitivity value of 0.0622 a.u/pH. Unfortunately, the linearity value dropped to 0.9009. According to Wu and Jun (2002), the influence of withdrawal speed depends on the thickness, porosity and refractive index of films. The researchers found that the increase in withdrawal speed would increase the thickness and refractive index of the film, as a result of the increasing number of crystalline particles per unit area and therefore decreased the porosity. This result is in agreement to the case study by Figus (2015), in which the film thickness was monitored as a function of withdrawal speed. Figus (2015) highlighted that it is important to optimise the relevant parameters at suitable withdrawal speed in order to produce good homogenous and crack-free membrane films. Figure 6(c) shows that a comparison was made between the various deposited lengths fabricated membrane sensing film; the deposited length of 0.5 cm with 285.4 nm deposited thickness exhibited the highest sensitivity toward hydrogen ions that contained in pH buffer solution, which is 0.0818 a.u/pH. This result is also supported with the linearity value of 0.9259, which is the highest compared to other deposited lengths.



(a)



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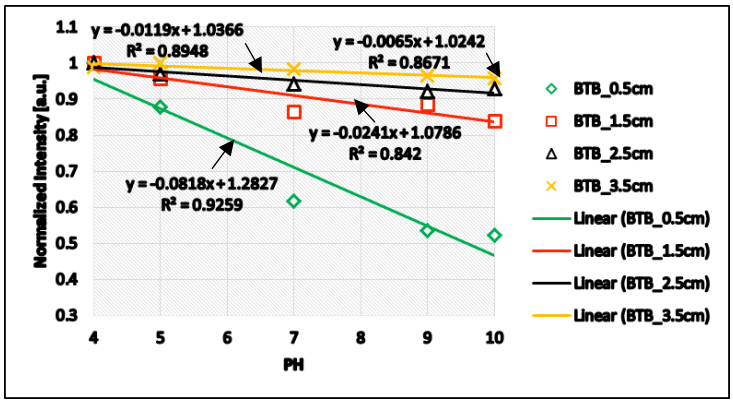

(c)

Figure 6. Calibration curve plot for different: (a) coated number of layers; (b) withdrawal rate; and (c) coated length at 460 nm

Theoretically, a good sensitivity of sensor device should have a high slope (Zolkapli et al., 2016). Based on the results obtained, the highest sensitivity was achieved using 4 deposited layers, withdrawal speed of 20 mm/s, and coated length of 0.5 cm. The proposed sensor shows the sensitivity (slope) and linearity (standard deviation, R^2) of 0.0818 a.u/pH and 0.9259 over a pH range of 4 to 10, respectively, as shown by the green line in Figure 6(c). Linearity describes how closely the straight line fits the data when R^2 is nearly approaching 1 (El Nahhal et al., 2012). This linearity measurement is important to ensure the sample is reliable to be used as a sensor device.

Figure 7 shows the spectral response of bromothymol blue entrapped in polyaniline sol-gel in various pH buffer solutions. As shown in the graphs, the light intensity peak decreases as pH increases. The changes of light intensities are a measurement of how strongly a substance absorbs light. This result is in agreement with the works done by El Nahhal et al. (2012), and Shastry, Abdi and Nnanna (2008).

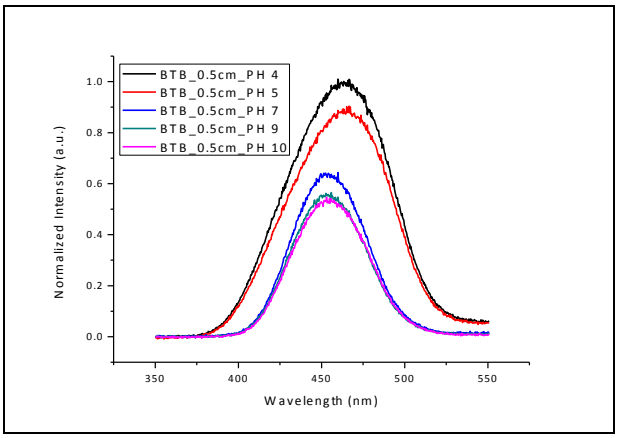

Figure 7. The normalised intensity of light spectra of optical fiber pH sensor at deposited layers is 4 layers, withdrawal speed of 20 mm/s and deposited length of 0.5 cm

CONCLUSION

In summary, we have investigated the effects of the number deposited layers, withdrawal speed and coated length of the bromothymol blue entrapped in polyaniline sol-gel film in optical pH response. The optimised combination of parameters was found to produce the highest sensitivity with 4 deposited layers, withdrawal speed of 20 mm/s and coated length of 0.5 cm. These results will be the basis for the development of fiber optic pH sensor.

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