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Plastic Optical Fiber pH Sensor based on Sol-Gel Film

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Abstract

A plastic optical fiber (POF) pH sensor is developed based on a sol-gel film. A sol-gel film was prepared by mixing tetramethyl orthosilicate (TMOS), trimethoxymethylsilane (MTMS), ethanol, distilled water and Neutral Red (NR) powder. Then, plastic optical fiber is coated by manually depositing the sol-gel film onto the tip of the POF. The sensing probe is dissolved into analytes with different pH levels, such as Coca-Cola (pH 3), tomato sauce (pH 4), black coffee (pH 5), tea (pH 6), distilled water (pH 7), soap (pH 8), baking soda (pH 9) and Clorox bleach(pH 10). The Refractive index will increase when the analytes are more acidic or more alkaline because they are concentrated with hydrogen and hydroxide ions at pH 3 and pH 10. The output power is varied based on the chemical reaction with the pH sol-gel film in the fiber-optic sensing probe. From the experimental results, it is concluded that the sensitivity of coated POF sensor, which is 0.0566 a.u/RIU, is higher than the sensitivity of the uncoated POF, which is 0.0429 a.u/RIU.

Keywords fiber-optic sensor, pH sensor, sol-gel, plastic optical fiber

1.0 INTRODUCTION

The measurement of pH is widely required in biochemistry, clinical chemistry and environmental science. Generally, there are three methods of pH sensing, which are pH paper, electrode and optical sensing or optode (Kulkarni & Shaw, 2016). The use of pH paper is a simple method that determines pH visually. This method uses pH-responsive molecules, also known as indicator dyes, to change color according to the solutions' pH value. Glass electrodes filled with a buffered chloride solution in which silver wire is immersed and coated with silver chloride are the most commonly utilized pH electrodes. Nowadays, pH sensors based on optical fiber have attracted remarkable attention due to their compact size and flexibility in harsh environments. Plastic Optical Fiber (POF) has plentiful advantages such as simple manipulation, low cost, resistance to electromagnetic interferences, and can endure a tinier radiant emission than a glass fiber (Cennamo et al., 2011; Zhang et al., 2010). In addition, it gives more advantages of ease of joining, capable of negative thermos-optic coefficient, smaller density and larger elastic distortion limits (Bilro et al., 2012). In the case of fiber-optic sensors, the reaction between the coated materials with surroundings will change the propagation of lights inside the fibers and can be used as a sensor. These changes depend on the variation of the refractive index when reacting with the analyte (Rashid et al., 2017; Rashid et al., 2019).

The sol-gel method was suggested as the best technique because this method only required simple equipment that could be used to prepare either fine powder or film. Sol-gel films have high homogeneity and transparency (Jeon et al., 2013). The sol-gel method offers a high homogeneity, transparency film and harder films. Besides, sol-gel is a simple method and a low-cost thin film deposition process, but it needs soluble materials (Shaari et al., 2013). Precursors will mix well with the solvent and reagent, which are usually stirred for a few hours to obtain a homogenous solution. It can be obtained by hydrolysis or polymerization reactions and deposited on the substrate as a thin film using spin coating or dip coating technique. Because of these advantages, the sol-gel process is suitable for material preparation and can coat the fiber probe (Islam et al., 2016). In this study, a pH sensor based on POF fiber coated with a sol-gel film immobilized with a pH indicator is developed. The output power readings will vary based on the intensity of light reflected from the fiber probe, which depends on the analytes of different pH values.

2.0 MATERIALS AND METHOD

A film was fabricated through a sol-gel process and coated at the end of the fiber probe by using the dip-coating method. To fabricate a pH sol-gel film, 24 ml of tetramethyl orthosilicate (TMOS), 6 ml trimethoxymethylsilane (MTMS), 60 ml of ethanol, 7.0 of distilled water and 0.28 g of neutral red were mixed together. TMOS act as a silica precursor for the synthesis of a colloid. MTMS is used in order to prevent crack formation and improve the chemical bonding between silica and the polymer (Jean et al., 2013). Meanwhile, ethanol as a solvent to uniformly mix the sol-gel materials, distilled water to promote hydrolysis, and neutral red powder as a pH indicator. Mix the solutions using a magnetic stirrer at 80ºC for 2 hours in order to approach the gel point and obtain the appropriate mechanical properties (Islam et al., 2016). The sol-gel film was then characterized using FTIR to detect the presence of silica. Next, the jacket of the fiber optic was removed for about 3.5 cm. Then, it was etched with acetone to remove its cladding.

The pH sensing probe was developed by manually depositing the sol-gel film onto the tip of the fiber optic. Then, the fiber probe was dried under atmospheric pressure and ambient room temperature for 24 hours to increase the extent of the sol-gel reaction and to induce strong interfacial connectivity between the sensing matrix and the POF. The final appearance of the sensing probe is recorded in **Figure 1**.

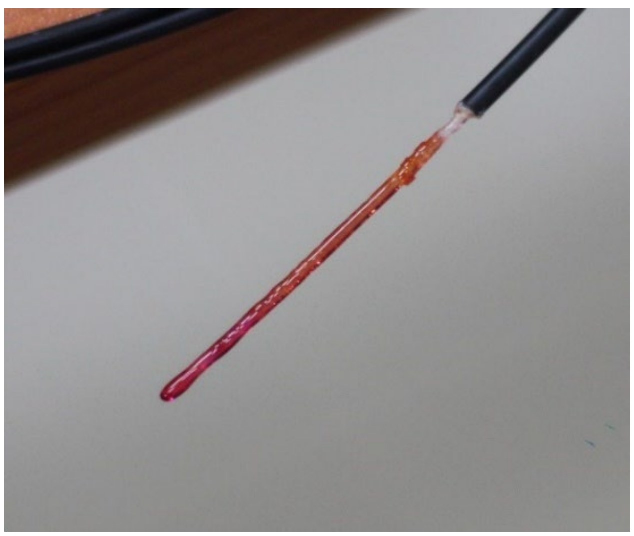

Figure 1 pH sensing probe coated with a sol-gel film.

For the experimental setup, a reflection-type fiber-optic pH sensor system consisting of a pH-sensing probe, a POF (Mitsubishi Rayon GH-4001), and a fiber-optic Y-coupler with a splitting ratio of 50:50 was used, as shown in **Figure 2**. In addition, an optical light source (Advance Power Solution OS417-5MD) at a wavelength of 650 nm and optical power meter (Advanced Fiber Solutions OM120A) is used. The POF fiber without a jacket has a diameter of 1.0 mm. The materials of the core and cladding are PMMA resin and fluorinated polymer, with refractive indices of 1.49 and 1.402, respectively, while the jacket is made of black PE.

The experiment was carried out by dissolving the sensing probe into analytes with different pH levels and refractive indices, such as Coca-Cola, tomato sauce, black coffee, tea, distilled water, soap, baking soda and Clorox bleach. The pH values were recorded using a digital pH meter, while their refractive indices were recorded using a digital refractometer. There were five tests that had been carried out in order to determine the repeatability of the pH sensor. The first test was done two days before the other four tests to ensure the sensor recovered to its original state. Meanwhile, the time interval for the next four tests is 5 minutes each. The difference in the time interval is important to study its effect on the sensing probe and its performance or sensitivity.

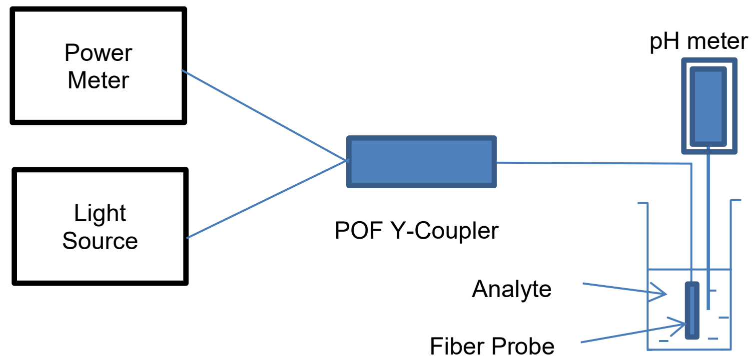

Figure 2 Experimental Setup for coated fiber probe sensor.

3.0 RESULT AND DISCUSSION

3.1 Sol-Gel Film Characterization

The main purpose of the characterization of FTIR is to detect the presence of silica in pH sol-gel film, as shown in **Figure 3**. At the wavenumber of 3889 cm^{-1}, isolated silanol vibrations exist. Water contribution (-OH) is shown by the broadband. The peak at 3577 cm^{-1} shows the mutually H-bonded Si-OH hydroxyl surface stretching and Si-OH silanol stretching. Vibrations of hydroxyl groups were superimposed on the surface of silica, such as SiO – H stretching of surface H-bonded silanols to molecular water between the range of 3510 to 3360 cm^{-1}. At higher frequencies, the peak at 1044 cm^{-1} was appointed to the Si – O stretching area. The band is assigned to the O – H bending mode of hydrogen-bonded in the region of 782 cm^{-1} (Khan et al., 2017).

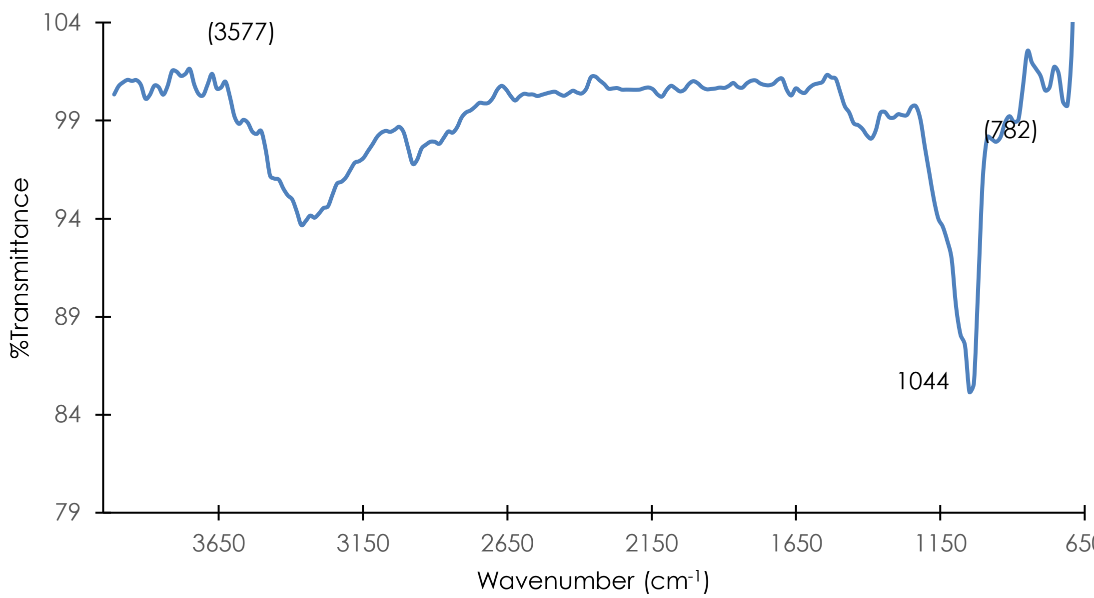

Figure 1 FTIR spectrum of sol-gel film.

3.2 pH and Refractive Index Measurements

The pH level and refractive index of the selected analytes are shown in **Table 1**. The refractive index decreases when the pH value is approaching 7 or neutral. The highest refractive index, which is 1.352, belongs to Coca-Cola, with a pH value of around 3. Meanwhile, Clorox bleach, with a pH value of around 10, also has a high refractive index which is 1.3487. This shows that the refractive index increases when the analytes are more acidic or alkaline. Refractive Index is a dimensionless number that defines the speed of when light travels through a material. The higher the refractive index of a material, the slower the light movement is through them (Singh, 2002). Acidic materials have high concentrations of hydrogen (H^+) in them, while Alkaline materials have high concentrations of hydroxide (OH^-). The acidity of Coca-Cola drinks is due to phosphoric acid, while sodium hypochlorite increases the basicity of Clorox. These materials with a high concentration of hydrogen and hydroxide, such as Coca-Cola and Clorox bleach, make the movement of light slower in them compared to when light travels through distilled water because it is the least concentrated material and has the lowest refractive index compared to other analytes.

Table 1 Types of analytes with their pH levels and refractive index values.

Analytes	pH levels	Refractive Index
Coca-Cola	3	±1.352
Tomato Sauce/Ketchup	4	±1.345
Black Coffee	5	±1.3374
Tea	6	±1.3336
Distilled Water	7	±1.3318
Soap	8	±1.337
Baking Soda	9	±1.3399
Clorox	10	±1.3487

3.3 Coated Plastic Optical Fiber Probe Performance Assessment

The sol-gel film-coated POF is tested with selected analytes. There were five tests performed to assess the pH sensor's repeatability. **Figure 4** shows the graph of output power against sol-gel film-coated POF. Test 1 was carried out two days before Test 2, as shown in **Figure 4(a)**. Test 2 shows that the power output could be reversibly modulated and recover to the value near the original state compared to 5 minutes duration. It can be observed that when the pH is approaching 7 (neutral), the output power increases. This is because an analyte with pH 7 has the lowest refractive index, and the tendency for the light to propagate outside the fiber is reduced compared higher refractive index. Besides that, the light will travel faster in a lower refractive index, and the signal loss is small. Thus, the power meter can detect more light from the pH sensing probe. Contradict to analytes with pH 3 (acidic) and pH 10 (alkali) that have a high refractive index. The power output decreases with an increment of the refractive index because the light tends to propagate outside the fiber. At a higher refractive index, light travels slower, and the signal loss is greater. The more acidic or alkali an analyte is, the smaller the amount of output power that can be detected by a power meter. In a more alkaline medium, the intensity is found to be reduced due to the leaching of the dye molecules, which may be related to the weak interaction between analytes and sol-gel film. **Figure 4(b)** shows the repeatability of coated POF that was tested three times with 5 minutes of duration for each test. The pattern of the response is still the same, but it needs longer recovery times in order to recover back to the initial response referring to Test 2 pattern.

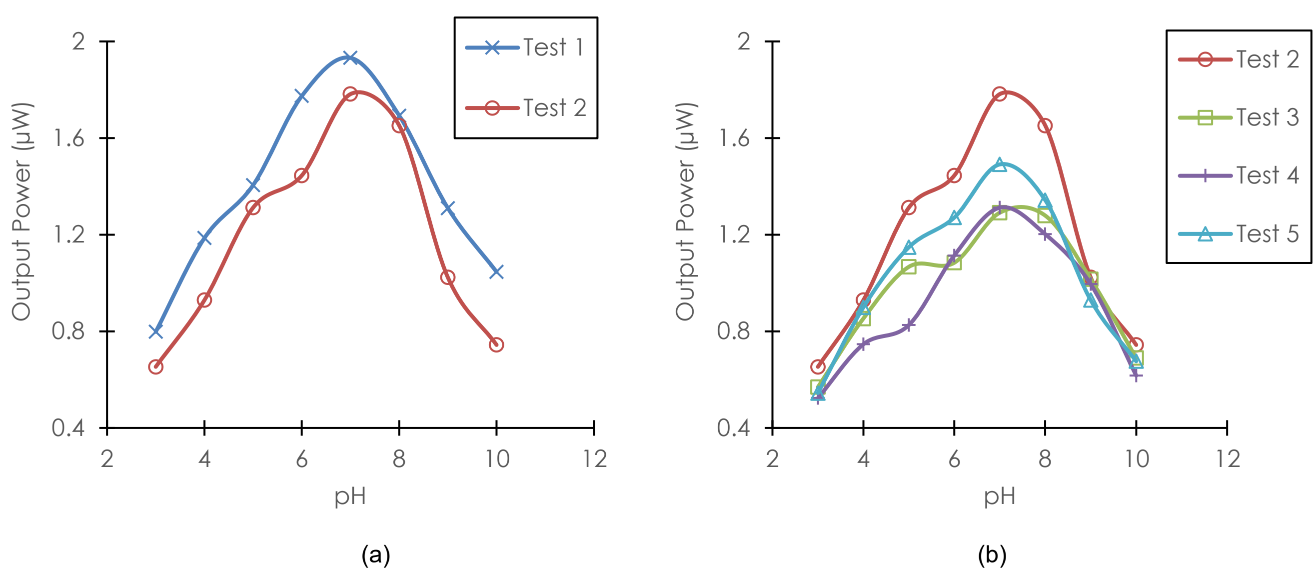

Figure 4 Output power of coated POF against pH level for (a) 2 days and (b) 5 min durations.

Figure 5 shows the power output ratio against the refractive index for coated POF. The sensitivity of coated POF is 0.0566 a.u/RIU and 0.0429 a.u/RIU for uncoated POF. It can be observed that the higher the refractive index, the higher the power output ratio. Penetration depth value will be reduced when the refractive index value of coated fiber decreases. As a result, evanescent absorbance becomes weak, and then the light propagation increases. The lowest power output ratio belongs to pH 7, which is distilled water, while the highest power output ratio belongs to pH 3, which is Coca-Cola. The propagation of light decreases after coating resulting in the good interaction of the beam with the sol-gel film. The small changes in the surrounding medium affect the transmitted optical power due to the interaction of the evanescent field.

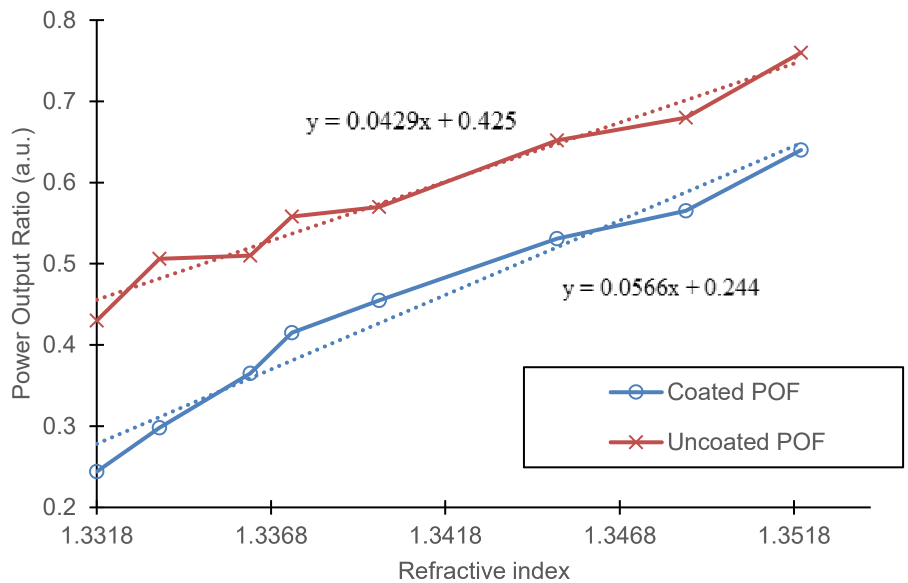

Figure 5 Sensitivity of pH sensing probe.

An evanescent field is produced between the cladding and core interface, and it has an exponential decay shape as they become smaller from the core to the cladding, as shown in **Figure 6**. The evanescent field is described in **Equation (1)** (Pollock, 1995), in which z is the distance from the fiber core, E is the magnitude of the field, and d_p represents penetration depth. Generally, penetration depth d_p is the measurement of how deep the penetration of light or any electromagnetic radiation is into a material (Chauhan et al., 2016).

$$E(z) = E_0 \exp(-z / d_p) \quad (1)$$

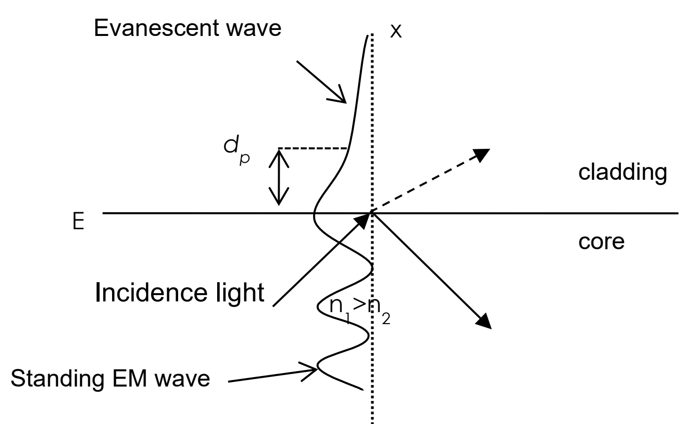

Figure 6 Evanescent wave at an interface of different medium.

Penetration depth, d_p can be calculated using **Equation (2)**, where λ, n_{silica} = 1.318 and $n_{surrounding}$ represent wavelength, the refractive index of silica and surrounding.

$$d_p = \frac{\lambda}{2\pi\left({n_{silica}}^2 sin^2\theta - {n_{surrounding}}^2\right)^{1/2}} \tag{2}$$

Let the incident ray more than 45°. Thus, the penetration depth can be calculated as the critical angle are varied from 46°, 47°, 48°, 49° and 50°. **Figure 7** depicts the relation between different incident angles and penetration depth. It can be observed that the penetration depth decreases when the angle of an incident increases at medium where light incident at silica and air interface.

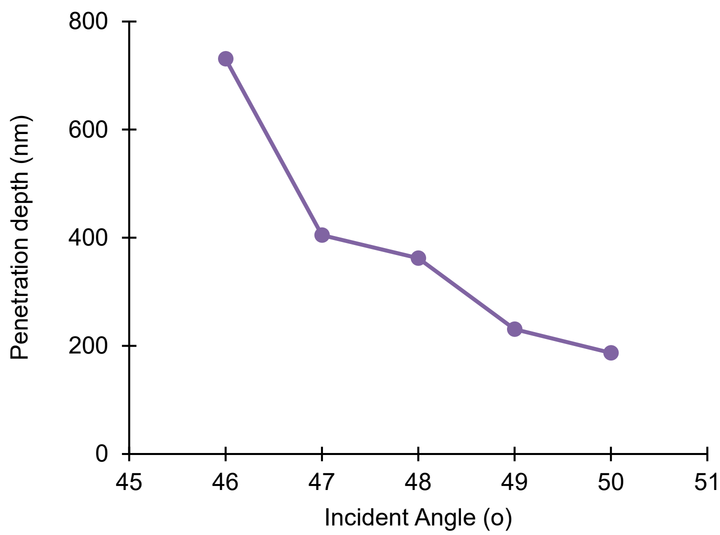

Figure 7 Penetration depth against incident angles.

4.0 CONCLUSION

Coated POF has a sensitivity of 0.0566 a.u/RIU, which is higher than uncoated POF, which has a sensitivity of 0.0429 a.u/RIU. The penetration depth of the fiber is around 731 nm at an incident angle of 46°. The small changes in the surrounding medium of coated fiber affect the transmitted optical power due to the interaction of the evanescent field. For research recommendations, nanocomposite metal and metal oxide-coated fiber optics can be used for pH detection by examining surface plasmon resonance mechanisms.

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