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Wavelength Dependent pH Optical Sensor Using the Layer-by-Layer Technique

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Abstract

In this work, the design and characteristics of a wavelength-dependent pH optical sensor have been studied. To create the sensor itself, brilliant yellow (BY) as a pH indicator and poly (allylamine hydrochloride) [PAH] as a cross-linker have been deposited on the end of a bare silica core of an optical fibre by use of a 'layer-by-layer' technique. In the experiments carried out to characterize the sensor, it was observed that the value of pK_a (the dissociation constant) of the thin film is dependent both on the outer layer and the number of bilayers. A heat treatment process was applied to the sensor to reduce the effect on the deposited layers during the testing of the probe. As a result of these series of experiments, it could be concluded that the probe design on which were deposited structured layers comprising six double layers of (PAH/BY) showed the best sensitivity for a pH range from 6.80 to 9.00 (with an accuracy of ± 0.20) and showing an average wavelength shift of 4.65 nm per 0.2 pH units, while the concentration of the BY and the PAH solutions was maintained as 0.25mM and 2.5mM respectively.

Key words: Brilliant yellow, pH sensor, optical sensor, Layer-by-Layer (LbL)

1. Introduction

The 'Layer-by-Layer' (LbL) deposition technique is one of the most frequently utilized methods for preparing multilayered thin films on different substrates e.g. glass, ceramics, metals, wood, plastics and so on [1-4] of any size and topology [5, 6]. In essence, the process is based on the electrostatic attraction of opposite charges and can be used with various reagents such as polymers [7], nanoparticles [8, 9], metals [10], dyes [11, 12], quantum dots [13], nanotubes [14], biomolecules like enzymes [15], proteins [16], etc. The technique is based simply on the alternate dipping of a charged substrate into cationic and anionic solutions. The electrostatic attraction that exists between the opposite charged molecules in every monolayer is the driving force in forming the layers and hence in creating an increasing coating thickness. However, in order to use these coated substrates for optical sensing, it is important to maintain an optically homogeneous surface. Furthermore, several important optical properties can be controlled through the layer thickness, the numbers of layers and their composition. Additionally, the layer thickness depends on the temperature, the pH and the concentration of the polyion solutions, as well as the dipping time.

One of the applications of the electrostatic self-assembly (ESA) technique is in its use to functionalize an optical fibre for optical recognition purposes [17]. However, active indicators must be used as sensitive films. To immobilize some active indicators like azo dyes (for colorimetric sensing purposes) on optical fibres, the use of a polymeric matrix has been recommended [18]. Poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) are the most popular polycation and polyanion, respectively [19-22]. Changing the optical properties of sensitive films with changing analyte concentration is based on the recognition measurement. For instance, the variation in the

refractive index is the basis for a humidity or a gas sensor when chemicals such as PDDA, PSS, poly S119, silica nanoparticles, aluminium oxide, poly-R and prussian blue were applied for humidity measurement or gas recognizing [9, 20, 23-26]. However, optical pH sensors have been considered more widely than other types of sensors due to the importance of pH measurement in both scientific research and industrial applications e.g. oil and gas industry, pharmaceutical, manufacturing and food production processes. To date, a limited numbers of pH indicators such as neutral red, methylene blue and Prussian blue have been deposited onto optical fibres to create pH sensors [7, 11, 12, 27-29]. In the present study, brilliant yellow is applied as an indicator because of better wavelength shift with pH change compared to the use of other indicators. The wavelength shift and the sensitivity of the probes prepared in this work are considered indicating the novelty of this approach and the achievable sensitivity. In addition, the characteristics of the probes created with differing numbers of bilayers (and in particular the contribution of the last deposited layer on the probe) are evaluated and their performance reviewed.

2. Material and Methods

2.1 Dye and Reagent

In this work, in order to create an effective optical pH sensor, brilliant yellow (BY) was selected as a pH indicator. BY was chosen as it has considerable wavelength shift compared to other indicators. Its chemical structure is shown in Fig. 1(a) and its absorbance spectra are shown in Fig.2. This molecule is negatively charged due to the presence of two sulfonate groups. In addition two phenolic hydroxyl groups are able to be dissociated at high pH and make a stronger negatively charged molecule. Its colour changes from yellow in pH 6.4 to red-orange in pH 8.0 while pK_a is 7.2 and shows a peak in 497nm in UV-visible spectroscopy. This molecule is strongly water soluble.

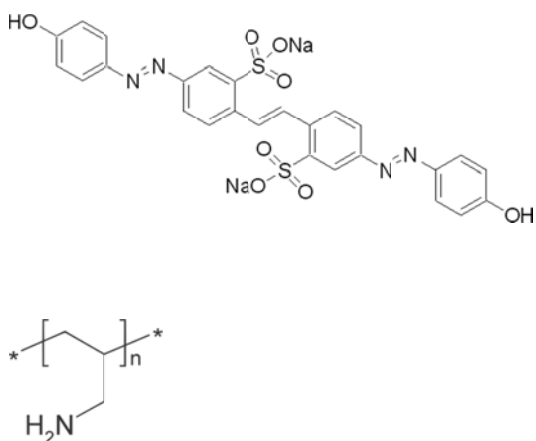


Fig. 1 The chemical structure of (above) brilliant yellow (BY) and (below) Poly(allylamine hydrochloride)

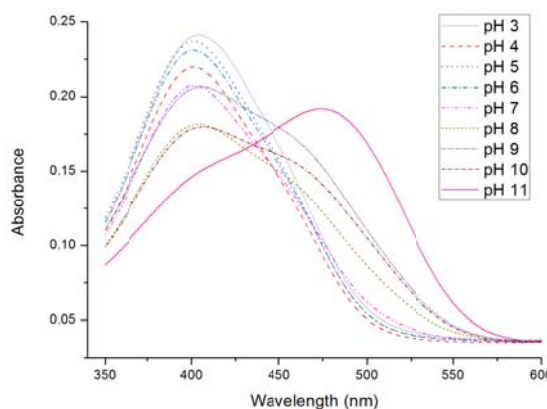


Fig. 2 Absorbance spectra of brilliant yellow in different pH buffer solutions.

2.2 Polymer

It is generally accepted that macromolecule materials are more suitable for use for building up the requisite layers in Electrostatic Self-Assembly (ESA) [1]. Hence, the larger molecular weight chains simply spread out and occupy more surface area without increasing the thickness of the adsorbed layer [30]. It is common for both negative and positive charged layers to be selected as polymers; moreover, using the polymers for either a positive or a negative layer has been reported [3, 5, 31]. In

the present work PAH is used as a polycation and Fig. 1(b) shows its chemical structure where the amine group in PAH provides the positive charge.

2.3 Types of chemicals and solutions

The indicator and chemicals used and applied to develop the optical sensors were brilliant yellow dye (content 70%, Poly(allylamine hydrochloride) and average molecular weight (MW) $\sim 15,000$) and H_2SO_4 .

The probes used, having a variety of compositions were prepared by use of the Layer-by-Layer technique and were tested in pH buffer solutions. In order to prepare the wide range of pH buffer solutions from acidic to alkaline, the mixture of 2.5 mM NaH_2PO_4 and 2.5 mM citric acid monohydrate in distilled water was used and aqueous NaOH was applied to adjust the desired pH.

In order to create a mirror at the distal end of the fibre, 2 ml of 0.1M AgNO_3 was placed in a vial and NH_3 solution then added drop by drop until the brown sediment dissolved. 1.4 ml of 0.8 M KOH was added to the vial, and if brown precipitate re-formed NH_3 was used dropwise to create a clear solution – the solution being Tollen's reagent. The cleaned fibre core was rinsed with 0.2% SnCl_2 solution, followed by distilled water and was then dipped into the vial containing the Tollen's reagent. By adding 0.4ml of 0.25M dextrose to the vial silver starts to cover the surface and the mirror was ready in approximately 1 minute.

2.4 Sensor probe preparation

To create the sensor probe, a silica multimode fibre with a core diameter of 600 μm was used. The fibre has a low optical attenuation (low OH) which exhibits transmission over the spectral range from the visible to the NIR (400 to 2200nm) e.g. 4dB/km at 800nm, with a numerical aperture (NA) of 0.37 [32], and with the fibre supplied by Thorlabs. To create an evanescent sensor a part of the fibre was stripped from the jacket and polished with 5 μm , 3 μm , 1 μm and 0.3 μm stone-papers respectively. As the cladding is acetone soluble, it was easily removed. The distal end of the fibre was treated with piranha solution (30:70 (v/v) mixture of H_2O_2 (30%) and concentrated H_2SO_4) for 60 minutes to produce the negatively charged surface and was then rinsed in distilled water followed by drying with compressed nitrogen. To reflect the radiated light back and guide it to the other end of the fibre, a mirror was placed at the tip of the fibre allowing it to be ready to be coated with positively charged molecules.

The layer-by-layer technique is based on the successive deposition of oppositely charged molecules onto the solid surface; the negatively charged fibre was dipped into the polycation solution for 5 minutes. As a result, a thin layer of the positive molecules is adsorbed onto the surface. The fibre was then dipped into the distilled water for 5 minutes to remove unbonded molecules from its surface; the substrate was alternately placed into the polyanion solution for a further 5 minutes and unbonded molecules were again washed out using distilled water. This procedure was repeated to build up a multilayer coating. Each pair of negatively and positively charged layers is called a bilayer and the number of bilayers is shown by the subscript e.g. (PAH/BY)₉ means 9 bilayers of PAH and BY were coated on the fibre.

2.5 Experimental setup

To measure the absorbance spectrum of the coated optical fibre, the Ocean Optics USB2000 spectrometer was used as shown in Fig. 3. In this setup, the output from a white light source was passed through a multimode UV/Visible fibre which is connected to the fabricated sensor probe. The distal end of the fibre, which is coated with a pH indicator, is dipped into a buffer solution at a specific pH. Due to the interaction with the pH solution, the indicator changes colour and as a result a

portion of the total light is absorbed at a specific wavelength by the sensing layer with the remaining light emitted through the other end of the fibre coupler and is guided to the spectrometer. The output from the spectrometer was then displayed using the spectroscopy application software. The probe was designed using a coated optical fibre (polycation/polyanion)_n and was successively dipped into buffer solutions with increasing pH.

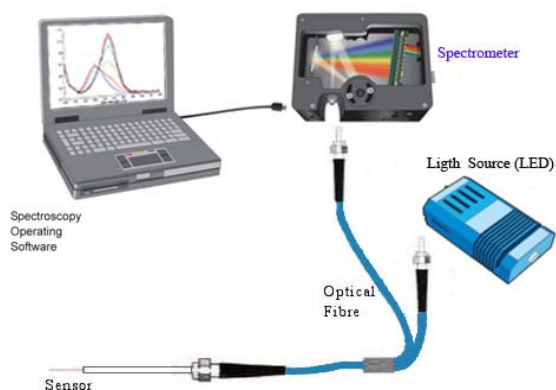


Fig. 3 The experimental setup applied to measure the optical performance of the fabricated optical sensor (All component images have been extracted from <http://www.oceanoptics.com>)

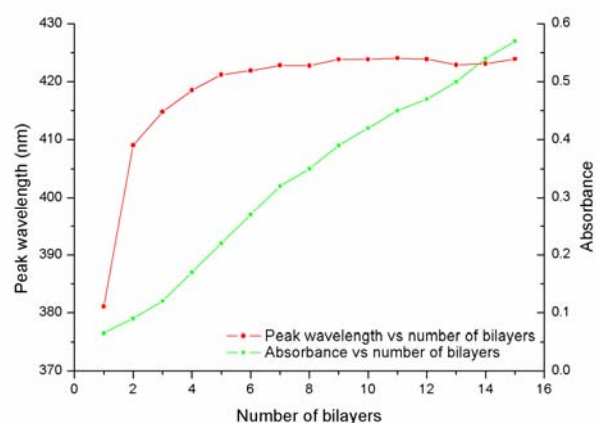


Fig. 4 The wavelength shift and absorbance change when increasing numbers of bilayers are added to the surface. The concentration of PAH and BY in saline solution were 1.5 and 0.25 mM respectively.

Destruction of bilayers happens when the coated surface is immersed in the pH buffer solution. However, a thermal treatment was used in which the coated substrate was cured at 120°C for 2 hours and then at 100°C for a further 2 hours. The thickness of the film increases as further numbers of bilayers are added onto the surface and thus to monitor the effect, the change in the absorbance and the wavelength at which this occurs is recorded. The peak wavelength shifts to higher values with lower number of bilayers used in the probe while with adding a further number of bilayers, the peak wavelength remains constant. Absorbance, in contrast, increases continuously with the number of bilayers. Fig. 4 displays the peak wavelength and absorbance as a function of the number of bilayers for brilliant yellow deposited on a glass slide. As this graph shows, the peak wavelength remains the same level after 6 bilayers are coated. Further it shows that this zone is suitable as the basis of the performance of the sensor.

3. Results and Discussion

3.1 Experiments on optical fibre

To study the characteristics of the sensors which had been prepared by building up the pH indicator on the distal end of the optical fibre, a suitable experimental setup was developed.

Measuring the absorbed light at different wavelengths using a spectrophotometer, when the probe is inserted in different pH buffer solutions, results in a series of spectra. From these, each wavelength corresponding to the maximum of each graph was plotted with respect to pH and the graphs thus generated were seen essentially to obey Dose-Response relationships curve fitting (using a sigmoidal curve fitting) which is displayed in Fig. 5, and using the following formula:

$$y = A_1 + \frac{A_2 - A_1}{1 + 10^{(x_0 - x)p}} \quad (1)$$

where A_1 and A_2 are minimum and maximum values of y respectively, p is the slope factor and x_0 is the Dose value when the response is halfway between A_1 and A_2 . The more sensitive probe shows a dramatic wavelength shift from A_1 to A_2 while the steeper area introduces the range of pH in which the sensor has a good performance in comparison with other pHs.

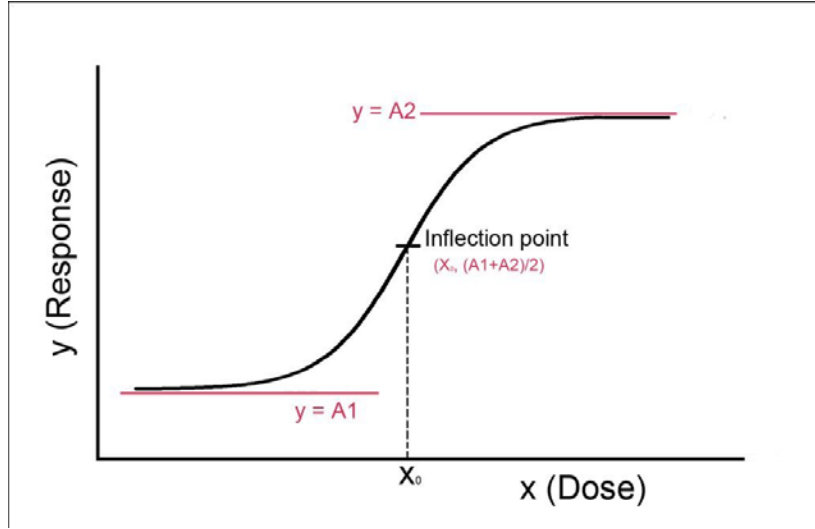


Fig. 5 Dose-Response curve sample

The first derivative of Equation (1) shows an inflection point which reveals the average slope of the curve in the steeper region which can be written as:

$$y^{(1)} = p \cdot \ln(10) \cdot (A_2 - A_1) = 2.3p(A_2 - A_1) \quad (2)$$

The inflection point in this graph has a $(x_0, (A_1+A_2)/2)$ coordinate and it demonstrates the pK_a of the thin film which is a function of the degree of ionization, revealing the pH at which 50% of the thin film functional groups are ionized[33]. The pK_a is given by $-\log_{10}K_a$, where K_a is the acid dissociation constant which is the equilibrium constant of the dissociation reaction in the context of the acid-base reaction in which an acid is ionized reversibly into its conjugate base and the hydrogen ion. As Choi et.al. have discussed in the literature [33], the effective pK_a of a polyelectrolyte substantially differs from that in the solution state value when incorporated into a multilayer film. On the other hand, the degree of ionization affects the thickness of the bilayer [33]; likewise adding a copolymer such as salt to the polyelectrolyte solution increases the film thickness and the degree of ionization [31].

Furthermore, the pH of the polyelectrolyte solution is an important parameter that can change the degree of ionization and it can then allow for a thicker or thinner multilayer film [30]. Therefore, every thin film has its own pK_a (dissociation constant) which depends on specific factors such as utilizing a copolymer, the pH of the polyelectrolyte solution and the degree of ionization of the deposited material.

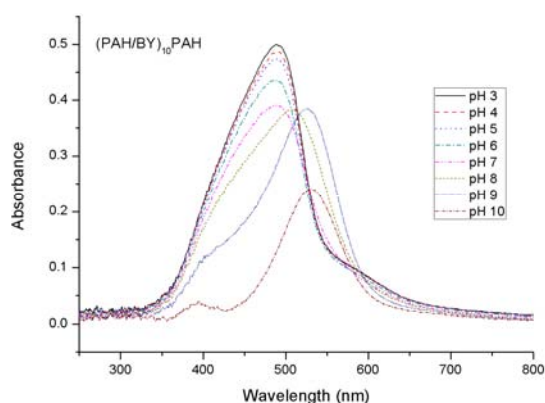


Fig. 6 Absorbance spectra for the optical fibre coated with 10 double layers of (PAH/BY) and one further PAH layer in different pH buffer solutions.

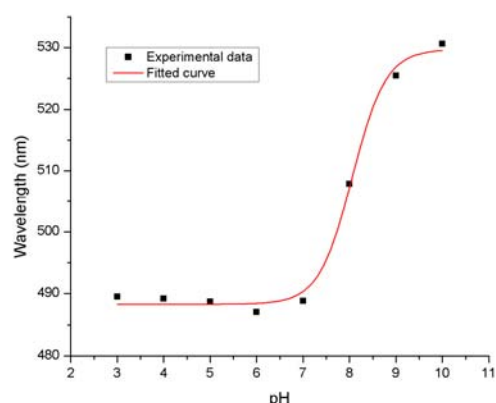


Fig. 7 The peak wavelength for each spectrum with respect to pH for Probe coated by (PAH/BY)₁₀PAH.

3.2 Fabrication of the sensor with brilliant yellow (BY)

The concentrations of the PAH and BY solutions (in 150mM saline solution) respectively were identical at 2.5mM and 0.25 mM for all samples. The dipping time for all the stages of the coating was 5 minutes for each stage without drying. To enhance the stability of the bilayers, heat treatment was used after the deposition, where the fibre was cured at 120°C for 2 hours and at 100°C for 2 further hours. To study the behaviour of the fibre coated with BY in the presence of different pH solutions, an initial experiment was carried out on a range of pH from pH 3 to pH 10. To create the initial probe ten bilayers were coated on the end of the fibre and the deposition was terminated by a PAH layer which has a positive charge. Fig. 6 shows the graphs that were produced from the spectrometer. To study the probe performance, the wavelength at the maximum absorbance for each spectrum, as a function of pH, was plotted. The result is shown in Fig. 7 which shows a good fit ($R^2=0.99$) to the Dose-Response curve. Furthermore, it was observed that this probe is more sensitive in the pH range 6.5 to 9.5. In order to study the detection accuracy of the fibre probe, a subsequent experiment was done using a narrower increment where the pH range was varied between 6.2 and 9.4.

The layers of PAH and BY were built up on the optical fibre using a range of different bilayers (numbered from 3.5 to 9.5 where a whole number represents a series of full double (bi-)layers is used and a fraction e.g. 3.5 indicates 3 full bilayers and one single layer (represented by the 0.5 added)). Thus probes with whole numbers of layers e.g. 4.0 end with BY whereas those that end with PAH are represented by a decimal 0.5 added to the whole number e.g. 4.5. In all the probes the mirror length was 3mm and sensor length was 22mm. The prepared probes were evaluated in pH buffer solutions using the method presented in Section 2.5 and the absorbance spectra for each probe were recorded. Figures 8 to 10 demonstrate the results obtained from the spectrometer for probes with 5.5, 8.0 and 9.5 bilayers. These figures show that the absorbance intensity increases with the addition of layers, as shown in Fig. 4, while the peak wavelength shift decreases when further layers are added. The graph of peak wavelength versus pH, extracted from the spectrometer spectra, was plotted for each probe and these scattered data were fitted by a Dose-Response graph at the end. The performance of the first four probes is compared in Fig. 11 and that of last four probes in Fig. 12. Fig. 13 and Fig. 14 further show the probe performance for even numbers of layers and odd numbers of layers respectively.

The properties of the respective Dose-Response graph for every probe are summarized in Table 1.

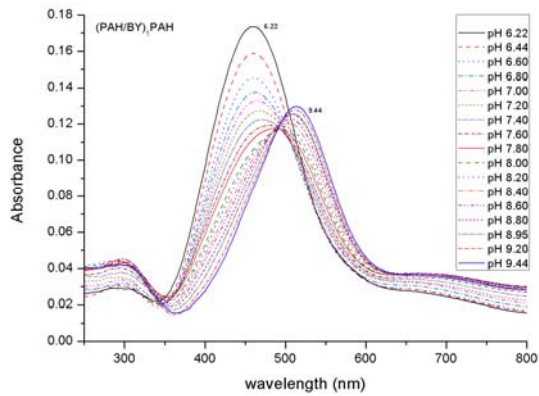


Fig. 8 Absorbance spectra for the optical fibre coated using 5 double layers of (PAH/BY) and one further PAH layer in different pH buffer solutions.

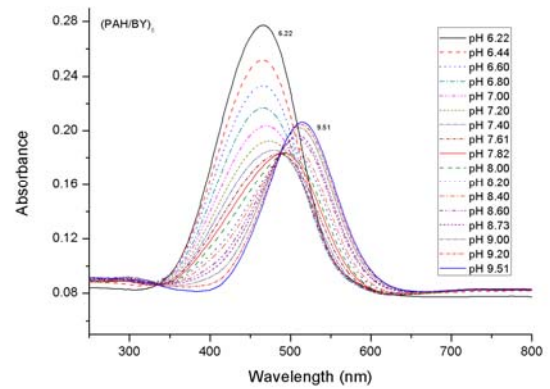


Fig. 9 Absorbance spectra for the optical fibre coated using 8 double layers of (PAH/BY) in different pH buffer solutions

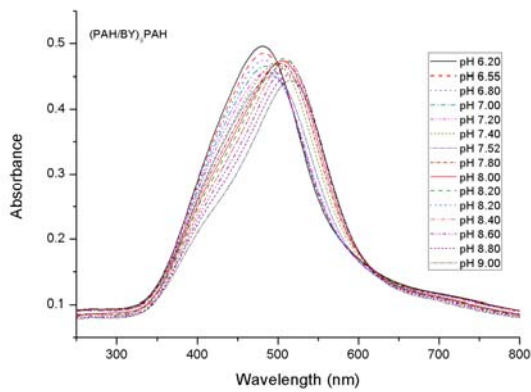


Fig. 10 Absorbance spectra for the optical fibre coated using 9 double layers of (PAH/BY) and one further PAH layer in different pH buffer solutions

3.3 Discussion

The purpose of this study has been to create wavelength dependent pH sensors which will yield high resolution measurements where the wavelength shift gives a measure of the sensitivity. The wavelength shift can be demonstrated by the slope of Dose-Response graph at the inflection point, which is shown in the last column of Table 1. The series of the experiments undertaken started with a probe with 3.5 bilayers for which its slope at the inflection point is 119.8 nm/pH unit. The second probe with 4 bilayers shows a greater sensitivity, since its slope increases to 128.2 nm/pH unit. The slope further increases to 177.6 nm/pH unit for a probe with 5.5 bilayers. However, the probe with 6 bilayers shows a sensitivity that begins to decrease with a slope of 148.7nm/pH unit. The slope for all the probes beyond this number of bilayers shows a downward trend, as shown in Fig. 15, while the slope reduction for the last three probes is somewhat less than for the other probes. Referring to Fig. 4, which shows the wavelength peak at which the graph reaches a plateau for a higher number of bilayers, the coated probe with ~ 5 bilayers shows the most interesting and useful performance. Although it is expected that the sensitivity of the probe could be improved with the addition of more

bilayers [20, 34] this series of experiments shows that a different behaviour is evident. The sensitivity of a pH sensor is, of course, a measure of the degree of change in the sensor output with change in the solution pH. In optical sensors this transduction effect (that can then be related to the measurand) typically can be absorbance [12, 35, 36], reflected optical power [20, 34], transmitted power [37] or the wavelength at maximum absorbance [22], for example, and indeed other effects can be used. Therefore, the sensitivity of the device will depend on the optimum choice of this transduction mechanism – where for example, a cross-comparison of Fig. 8, Fig. 9 and Fig. 10 shows a significant change in absorbance from pH 6.22 to 7.20 for the probe coated with eight bilayers and the least change for the probe with 9.5 bilayers. Hence, an eight bilayer-deposited fibre creates a more sensitive device for use over the pH range 6.2 to 7.2 than it does with either a 5.5 or 9.5 bilayer coated fibre. Reviewing its response to wavelength, the sensitivity of these probes is limited over the range considered but for the higher pH range the wavelength shift is clearly measurable, especially for the probe coated with 5.5 to 6.5 bilayers which shows the highest slope and thus device sensitivity. This means that the sensitivity is significant over the pH values from pH 7 to pH 9 for all probes coated with BY. Looking at this more closely, as shown in Table 1, the average peak wavelength shift, seen for a sample 0.2 pH units, varies from 2.58 nm for P9.5 to 4.65 nm for P6 (designating a probe with 6 bilayers where, in general, P_n represents a probe with n bilayers) and the best sensitivity (measured per nm shift) is 0.043 pH units for P6, with the least sensitivity seen being 0.078 pH units for P9.5. The conclusion of this is that increasing the number of bilayers does not necessarily increase the sensitivity and, in addition, the sensitivity can even decrease when the number of bilayers on the fibre is increased. Fig. 15 confirms a continuous reduction of sensitivity for the probes ranging from P6.5 to P9.5 and there is a dramatic decline in sensitivity for the probes from P8 to P9.5, although, the probes with fewer than 5 bilayers are not as sensitive as P5.5, P6 and P6.5. This may arise due to lower stability of the layers as the thin film may not be sufficiently stable in the cases of both very high and very low bilayer thickness values [20, 34].

Probe Code	Number of bilayers (n)	A1	A2	X ₀ (pKa)	Adj. R-Square	Y ⁽¹⁾ (gradient in the inflection point)	wavelength at pH 7	wavelength at pH 9	Wavelength shift/0.2 pH units	pH units/nm
P3.5	3.5	454.146	497.923	7.962	0.9983	119.868	457.284	494.777	3.7493	0.0533
P4	4	455.982	500.800	7.686	0.9970	128.224	461.663	499.709	3.8046	0.0525
P5	5	447.000	505.937	7.649	0.9961	150.724	457.307	497.145	3.9838	0.0502
P5.5	5.5	458.361	512.042	7.743	0.9943	177.610	462.964	504.788	4.1824	0.0478
P6	6	447.810	508.024	7.565	0.9961	148.703	459.446	505.983	4.6537	0.0429
P6.5	6.5	464.504	514.417	7.813	0.9981	155.845	467.875	512.642	4.4767	0.0446
P7.5	7.5	466.988	516.218	7.831	0.9991	127.530	471.787	513.819	4.2032	0.0475
P8	8	465.311	513.571	7.708	0.9964	126.514	471.848	511.323	3.9475	0.0506
P8.5	8.5	479.139	516.303	7.842	0.9963	89.201	482.971	514.097	3.1126	0.0642
P9	9	481.625	516.993	7.722	0.9980	85.397	487.284	515.204	2.792	0.0716
P9.5	9.5	489.176	518.990	7.872	0.9991	82.238	491.61	517.367	2.5747	0.0776

Table 1 Does-Response curve properties for the prepared probes

Considering the data shown in Fig. 12, Fig. 13 and Fig. 14, the probes coated with more than 6 bilayers demonstrate a slightly different behaviour in comparison to those probes with fewer than 6 bilayers. With the higher number of bilayers (n>6), each probe with more coated layers (than 6) has a

peak which tends to move up to a higher wavelength. The onset point for each graph as a (function of the number of bilayers) varies both up and down as a probe with more deposited layers starts from the greater peak wavelength at lower pH region by contrast all the graphs approach convergence in the higher pH regions.

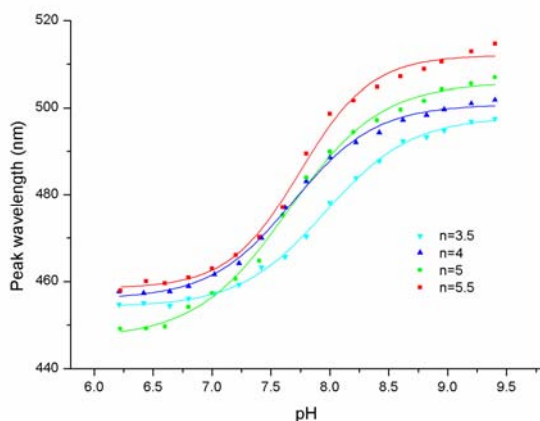


Fig. 11 The peak wavelength for each spectrum with respect to pH for probes with 3.5, 4, 5 and 5.5 bilayers.

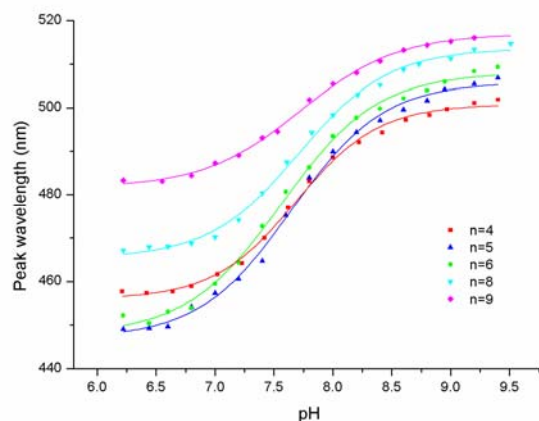


Fig. 13 The peak wavelength for each spectrum with respect to pH for probes with 4, 5, 6, 8, and 9 bilayers.

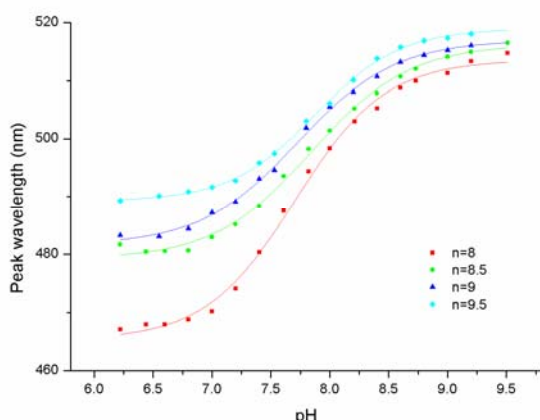


Fig. 12 The peak wavelength for each spectrum with respect to pH for probes with 8, 8.5, 9 and 9.5 bilayers.

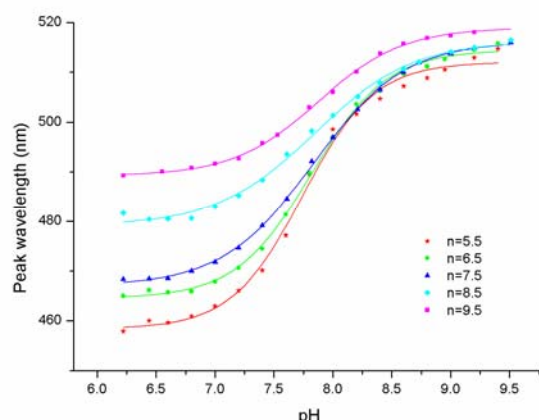


Fig. 14 The peak wavelength for each spectrum with respect to pH for probes with 5.5, 6.5, 7.5, 8.5 and 9.5 bilayers.

In spite of the fact that all the probes considered demonstrate their peak sensitivity in the pH range 7 to 9, they do not have the same inflection point and, as a result, the same pK_a . With reference to Table 1, the value of pK_a varies from one probe to another. The outer layer in the thin film directly effects on the pK_a ; overall, a thin film terminated with a PAH shows a higher pK_a compared to a probe terminated with BY, as shown in Fig. 16. The PAH film is individually applied as a pH indicator [12, 22, 33] for which the value of pK_a is reported to be between 8.0 to 8.8 [33, 38-41], where the pK_a value for BY is 7.2 [42]. It seems clear that they substantially influence each other and the pK_a of the multilayer built up with a combination of such coatings shows pK_a values between those of the PAH and BY films. The values obtained from this series of experiments (represented in Table 1) confirm this claim. The average pK_a value for an odd number of layers (where the PAH is the outer layer) is 7.84 whilst for an even number of layers (where the BY is outer layer) is 7.66. However, it can be

observed that the pK_a value for both the odd and even number of layers decreases with an increase in the thickness of the thin film from 5.5 to 6 bilayers, whilst beyond this the pK_a value starts to go up with an increasing number of bilayers. This means that the peak sensitivity of the probes slightly shifts for the alkaline region when more layers are deposited onto the fibre. In addition, when the PAH is applied as the outer layer, the pK_a of the multilayer film rises to reach a higher level; in other words, when there is one more layer of PAH than BY, the probe shows greater sensitivity in the alkaline region because of higher association constant of the PAH compared to the BY.

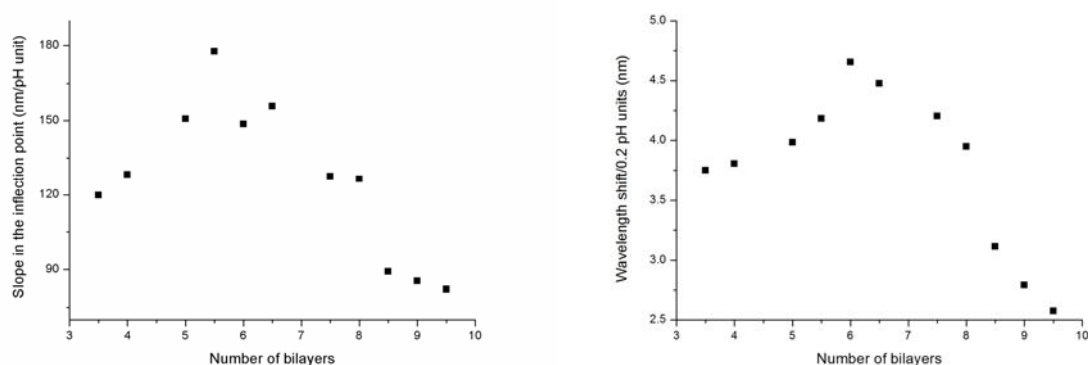


Fig. 15 Left: The graph gradient in the inflection point for each probe. Right: The average wavelength shift at each measurement from pH 7 to pH 9

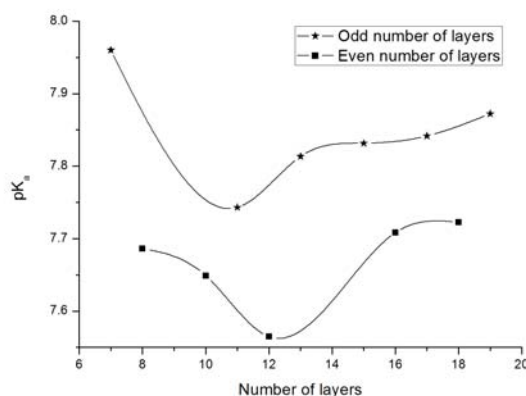


Fig. 16 The amount of pK_a related to number of layers and outer layer deposited which is PAH for the upper graph and BY for lower one.

4. Conclusions

In this study a wavelength- dependent optical sensor with high resolution sensitivity is proposed. To achieve this aim over the pH range of 7 to 9, brilliant yellow (BY) was applied as the pH indicator. A variety of probes with different deposited layers was prepared using PAH and BY and their performance characteristics compared. The concentration of PAH considered in the work were 2.5 mM and that of BY was 0.25 mM, with different concentrations showing different results and performance of the probes constructed using these layers. The Dose-Response graph was created and studied for each probe and a major conclusion was that those probes with 5 to 6 bilayers demonstrated the optimum sensitivity. It has also been observed that the sensitivity of the probes improves with an increasing the number of bilayers (typically about 5 to 6 bilayers) and beyond this a reduction of sensitivity occurs with an increasing number of bilayers. For a pH range from 6.80 to 9.00 (with an

accuracy of ± 0.20) the probe coated by 6 bilayers displayed 4.65nm peak wavelength shift per 0.2 units showing the maximum sensitivity. Additionally, the pK_a slowly rises with an increasing number of layers, with the contrary behaviour seen for a smaller number of layers and the outer layer of thin film also clearly influences the pK_a value. In conclusion, it has been shown that increasing the number of layers increases the sensitivity towards a higher pH and alkaline area; although higher alkalinity is seen in sensors deposited with PAH as the outer layer due to pK_a of PAH itself.

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