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Optical sensor for pH monitoring using a layer-by-layer deposition technique emphasizing enhanced stability and re-usability

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Abstract

Stable and reliable operation of an optical sensor for pH monitoring is important for many industrial applications of these types of devices. The layer-by-layer deposition technique is a simple and versatile method used to deposit a sensitive thin film on such an optical fibre-based device but creating a coating which can often be destroyed in use in highly acid or alkali solutions i.e. with very low or very high pH. It is thus important to create stable and durable sensors to meet the needs of users for operation under these extreme environments. The main aim of this study has been to prepare a number of such sensors and compare the performance of three different stabilization approaches used for the development of an effective wavelength-dependent pH-sensitive optical sensor. Techniques such as employing heat treatment, the deposition of two layers of a PAH/SiO_2 thin film and the deposition of two layers of APTMS/SiO_2 as topping layers have been studied to determine the optimum approach to creating a stable and reliable sensor – one yielding the same value of peak wavelength for a measurement of a known value of pH and to do so repeatibly. An improvement in performance and in shelf-life, stability and re-usability of the sensor has been achieved by the addition of two bilayers of APTMS/SiO_2 (3-Aminopropyl-trimethoxy silane/Silica nanoparticle) in the work carried out and the results of the investigation undertaken are reported.

Key words: Stabilization, stable, Layer-by-layer, sensor, pH optical sensor, re-usability

1. Introduction

In industry today, it is important in many situations to detect a range of chemical and biochemical substances, as well as the measurement of a variety of systems operating parameters. pH is one of the most common analytical measurements needed in both industrial processing and in laboratory research, in which reliable real time sensor data, such as can be obtained from an optical sensor system due to its light weight and non-electrical mode of operation is needed. In order to achieve optical recognition of these parameters using optical fibre-based devices, active indicators such as sensitive films must be immobilized on the distal ends of suitable optical fibres. The layer-by-layer technique is one of the deposition methods widely used to coat such thin films on to optical substrates and optical fibres. The layer-by-layer (LbL)technique is used to build up a sufficient thickness of such material on the fibre and is based on the electrostatic attraction between oppositely charged molecules to create the layers and thereby increase the overall coating thickness [1]. The principal advantage of the use of this technique is the ability to create stable deposited thin films with well-organized structure and controlled nanometer thicknesses on substrates of various shapes and sizes [2-7]. Generally, the thin films created by using the LbL technique are stable [2, 8], and it is difficult to remove them from a solid substrate. There are two main methods to remove LbL deposited films, should this be needed. First, a solution of high pH can be used which will attack the first polycation layer and destroy the ionic bonds that stabilize the films. A second method is to expose the LbL multilayers to a solution with very high ionic strength, such as 3M NaCl, under sonication for approximately 2– 3 hours [9]. Destruction of the layers happens when the coated surface is immersed into the high pH buffer solution. For practical applications, especially those needing continuous monitoring, it is critical to have a pH probe that can give consistent results and survive for as long as possible. However, the destruction of the layers limits the life of the probe and does not make it as suitable for continuous monitoring. A variety of techniques has been proposed to improve the stability of the film and to avoid progressive destruction of the coating. Ionic strength, pH, concentration of the polyion solutions and the presence of a copolymer such as salt affect the LbL assembly, the film thickness and its stability [2, 3]. Heat treatment is also an important process which has been discussed in many works in the literature [10-12] to achieve a higher stability of the thin films and avoid problems with the destruction of the films when they are immersed in buffer solutions of different values of pH [13, 14]. However this sort of treatment affects the sensor performance and decreases its sensitivity [14], as well as allowing for a degradation of the indicator dyes used which happens at high temperatures.

The stability of thin films thus generated does depend on the interaction between the layers, such as through the formation and destruction of hydrogen bonds. Hence, the stabilization of the LbL-assembled films via polyamide bond formation was a further method reported in the literature [15-17]. The amine coupling reaction can easily allow a cross-linkage of an amino group to a cationic polyelectrolytes and a carboxyl group on anionic polyelectrolytes via amide bond formation. There is a further report in the literature [18] which focused on the film stability under chlorine treatment as a means to improve the stability of the LbL-assembled nanofilteration membranes in combined high ionic strength conditions and under chlorine treatment. In another approach, the stabilizing of the thin film is achieved by forming siloxane bonds owing to a silane coupling reaction between oppositely charged polyelectrolytes which leads to the crosslinking between the silane groups [18, 19]. Egawa et al. demonstrated [20] crosslinking between the sulfonate group in the polyanion and the diazonium ion in polycation due to exposure to UV light. The pH sensor reported in their work could be used to measure solutions of high pH.

An alternative approach is to build up several capping layers using different materials such as nanoparticles to enhance the film stability. Prakash et al. [21] discussed applying nanoparticles to achieve an adequate sensitivity and stability with the modification of the sensors (or biosensors) with nanomaterials such as gold and/or silver nanoparticles [6, 22, 23], carbon nanomaterials [24, 25] and silica nanoparticles [26] and these have shown considerable promise. Putzbach et al. reported that the immobilization of enzymes improves stability of the biosensor discussed [27]. In further work reported in the literature [28], a coating of 5 nm layers of Al or 1 nm layers of EuS (Europium (II) sulfide) was applied as a covering layer to stabilize ultrathin tin films and reduce the diffusion of tin atoms. Abdelghani et al. used long chain alkanethiols to protect a silver film from oxidation and thus increase its stability [23]. Ng et al. employed three different drug stabilization approaches in the study presented in literature [29] through changing the architectures of the films. In their work, in the first approach, a solid dispersion film of the drug and polymer was prepared. A second approach involved coating the surface of a freshly prepared drug thin film with a thin polymer film, whereas for the third approach, the solid substrate surface was modified with a polymer coating prior to the laying of the pure drug thin film on top. A cross comparison of these three stabilization approaches was carried out and it was found that the polymer thin film coatings were more effective for the model drugs tested in their study.

The application of silica nanoparticles (SiO_2) has drawn considerable attention for surface modification, due to its uses as an enhancer for the sensitivity, selectivity and strength of the thin films as well as a its use as a pH indicator in many research situations and in industry [30-35]. In the work published by Lee et al. [36], pH-sensitivity of the nanomaterial thin film chemo-resistor and transistors was tuned by depositing a SiO_2 nanoparticles layer on top of a semiconducting nanomaterial multilayer fabricated by using a layer-by-layer self-assembly in which the silica nanoparticles play the role of the charge collector, influencing the conductance of the semiconducting layers of the carbon nanotubes and the indium oxide nanoparticles. Liu et al. also used a silica nanoparticle layer on top of further layers of indium oxide nanoparticles and poly(styrene sulfonate) (PSS) as an insulating layer, in the approach published in [30]. Selectivity for hydrogen gas was obtained by deposition of a thin film of silica nanoparticles on top of the SnO_2±Cu/Pt, in a mixture of the two gases[10].

The use of silica nanoparticles can create a very strong thin film if they are used to cover the indicator multilayers. The work presented in this paper thus takes advantage of this and compares and contrasts three different stabilization approaches with the aim of creating a stable pH sensor which is re-usable and stable under storage. In the course of the investigation and optimization of the sensor system developed, aspects of the fabrication process such as heat treatment, the deposition of two layers of PAH/SiO_2 as thin film 'topping' layers and the deposition of two layers of APTMS/SiO_2 as similar 'topping' layers have been investigated and the resulting sensors characterized to determine the best approach to creating a sensor which is stable and reliable in operation: thus giving the same calibration, in terms of the value of the peak wavelength for a particular value of pH, and doing so in a reproducible way. Further aspects which relate to improved sensor performance, such as longer shelf-life, better stability and sensor re-usability after cleaning for a sensor prepared using the LbL technique in this work are considered and reported, showing the value of the approach taken in this research.

2. Materials and methods

2.1 Chemicals

In order to create an effective optical pH sensor, brilliant yellow (BY) was selected as the pH indicator to be used, as discussed in prior work by the authors [37]. This indicator dye was chosen for its wavelength variation and ease of use and it was cross-linked to poly(allylamine hydrochloride) [PAH] with an average molecular weight (MW) ~15000, supplied by Sigma-Aldrich. PAH is a positively charged molecule and was used as a polycation. 3-Aminopropyl-trimethoxy silane (APTMS) (99%) as a silane coupling agent and SM-30 containing 30 wt% SiO_2 nanoparticles in H_2O as a strength enhancer were used as supplied by Sigma-Aldrich. The structures of these molecules are shown schematically in Figure 1.

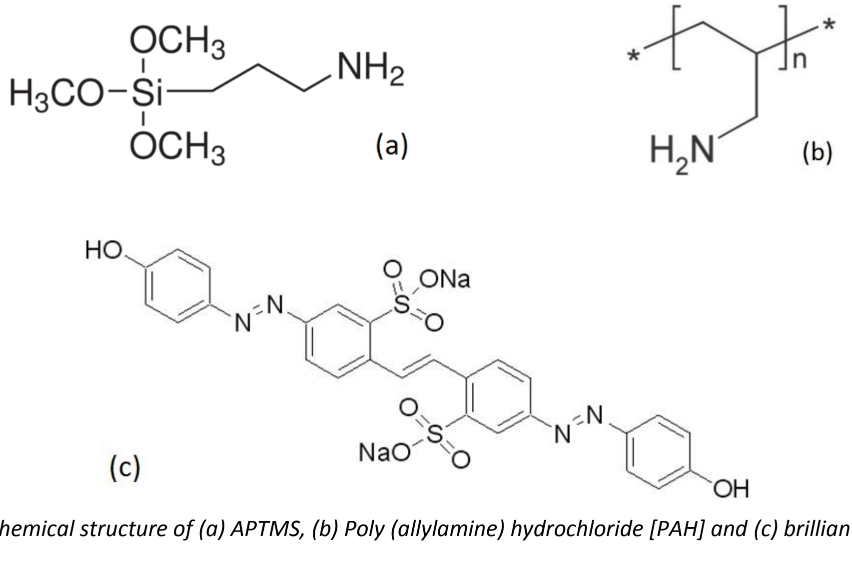

Figure 1 Chemical structure of (a) APTMS, (b) Poly (allylamine) hydrochloride [PAH] and (c) brilliant yellow.

2.2 Procedures

The multilayer coating which was deposited by using a self-assembly, Layer-by-Layer (LbL) technique was carried out using a glass microscope slides of dimensions 76×26 mm, with thickness of 1.0 mm. The glass slide used was treated with Piranha solution (30:70 (v/v) mixture of hydrogen peroxide (H_2O_2) (30%) and concentrated sulfuric acid (H_2SO_4)) for 60 minutes to produce the negatively charged surface and was then rinsed with distilled water, followed by drying with compressed nitrogen. The glass slide was then ready to be coated with positively charged molecules. The Layer-by-Layer technique is based on the successive deposition of oppositely charged molecules onto a solid surface. In this technique, the functionalized surface of a glass slide dipped into PAH solution for 5 minutes to create a polycation layer. The glass slide was then dipped into distilled water for 5 minutes to wash off the un-bonded molecules. This glass slide was then dipped in BY solution for 5 minutes to construct the polyanion layer above the PAH layer. To wash away the un-bonded molecules, the glass slide was then immersed in fresh distilled water for 5 minutes. This operation was then repeated six times to build up six bilayers of (PAH/BY) and thus increase the thickness of the thin film deposited on the glass slide, which then was ready to be used as the active element in the sensor system, tested by being used for measurement of the pH of a buffer solution. The performance of the sensor prepared was examined through the measurement and the evaluation of the change in the peak wavelength of the absorption when the sensor was evaluated by being dipped into buffer solutions of different and varying pH. The process was carried out by dipping the sensor slide into the pH solution for a few minutes, following which the absorbed light versus wavelengths is measured by use of the PerkinElmer spectrophotometer. The glass slide was then taken out of the solution and was immersed in another, fresh buffer solution (of different and known pH), this being following by a measurement of the absorbance spectra. The measurement was carried out several times, using fresh buffer solutions increasing from pH 6 to 9, and then decreasing from pH 9 to 6, this being repeated typically two or three times for a number of such samples. The maximum value of the absorbance was normalized by dividing by the minimum value and the results were plotted as a graph of relative absorbance versus pH. For consistency, the preparation conditions and the concentration of the polyion solutions used were the same in all these experiments. However, it was found that to achieve a sensor performance that is consistent and shows the same values of peak wavelength for an identical pH, especially after -three times of use, further operations on the design and construction of the sensor are needed and this is discussed in the following work.

2.3 Experiments

Following the approach in previous research reported by the authors [37, 38], a glass slide was prepared on which was deposited alternate layers of brilliant yellow (BY) (acting as a pH indicator) and poly (allylamine hydrochloride) [PAH] (acting as a cross-linker of the layers of brilliant yellow), using layer-by-layer coating technique. To determine the stability of thin film, initially neither heat treatment or drying was used in the process of coating of glass slide with a total of 8 bilayers of (PAH/BY); this configuration is denoted by $(PAH/BY)_8$, where the subscript indicates the number of bilayers, in this case 8. As high pH can discharge the first polycation layer and destroy the ionic bonds that stabilize the films, to prevent this action solutions with a pH in the range from 6 to 8 (over the neutral pH range) only were examined. The results of several (three) successive measurements using this sensor approach are shown in Figure 2.

However, it can be seen that the stability of the bilayer system thus prepared could be enhanced and this was achieved by further operations including heat treatment or applying a capping layer, such as a layer of silica nanoparticles. In order to determine the most efficient method of stabilizing the deposited layers, a number of different methods were considered and applied including a) heat treatment b) covering the layers with PAH and silica nanoparticles and c) covering the layers with 3-Aminopropyl-trimethoxysilane (APTMS) and silica nanoparticles. These are discussed below.

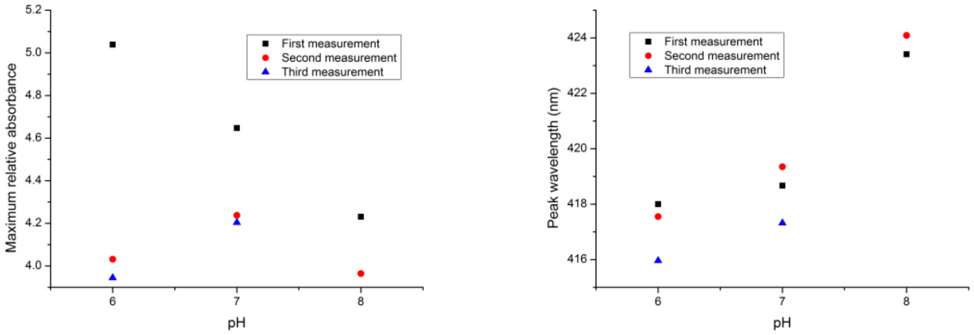

Figure 2 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for (PAH/BY)$_8$ on the glass slide. No heat treatment or drying was used in the process. (The sample is designated GS01)

2.3.1 Heat treatment

In order to make a stable thin film, two glass slides coated as indicated with (PAH/BY)$_{16}$ and (PAH/BY)$_6$ and cured in 120°C for 4 hours were examined. The glass slide coated with (PAH/BY)$_{16}$ was investigated using buffer solutions with pH varying from 6 to 8 and then back from 8 to 6, while the other slide was tested in a similar way with buffer solutions ranging from 6 to 9. The maximum value of the relative absorbance and the peak wavelength versus pH for the consecutive measurements of the pH of the solutions investigated for these two samples are shown in Figure 3 and Figure 4.

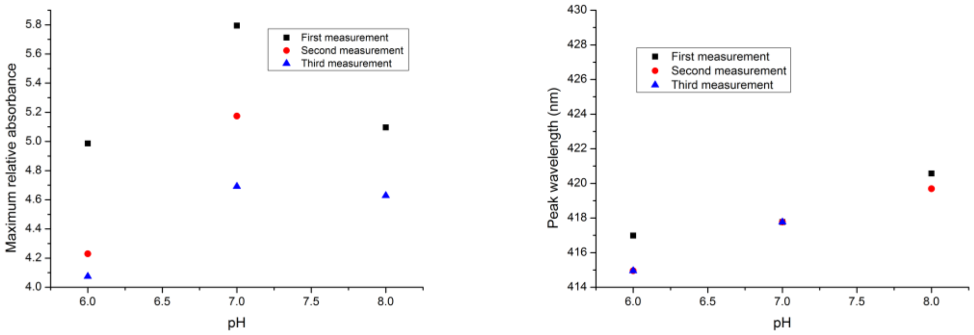

Figure 3 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for (PAH/BY)$_{16}$ on the glass slide. The sample was cured at 120°C for 4 hours. (The sample is designated GS02)

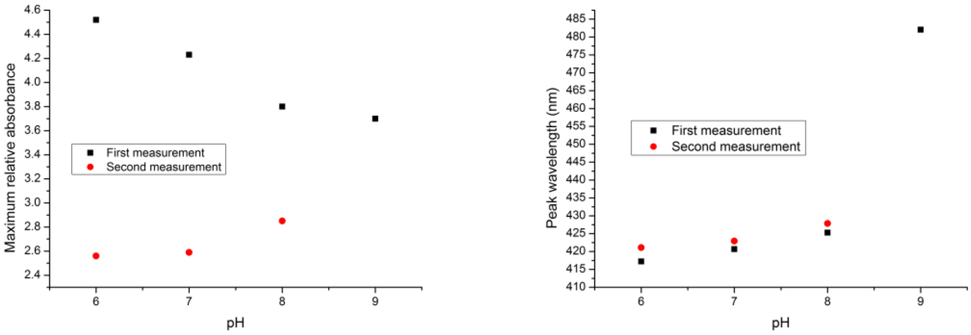

Figure 4 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for (PAH/BY)$_6$ on the glass slide. The sample was cured at 120°C for 4 hours. (The sample is designated GS03)

2.3.2. Using PAH and silica nanoparticle coatings

The use of silica nanoparticles covering the indicator multilayers is designed to enhance the strength of the film. Therefore, a series of experiments was carried out and discussed below in which layers of silica nanoparticles were built up on a glass slide already coated with 6 bilayers of (PAH/BY), i.e (PAH/BY)$_6$. Different methods of curing were examined to find out the most appropriate way to develop the most stable coating. The silica solution used (SiO_2) was prepared at 1 wt.% (1.7mM) concentration. As the SiO_2 solution is strongly alkaline (with pH 10.5), it causes the destruction of the BY layers; hence the pH of the SiO_2 solution was adjusted to pH 7 by adding some drops of HCl to the solution before the deposition of the layers was commenced. The glass slide thus prepared with (PAH/BY)$_6$ was then functionalized by using two bilayers of (PAH/SiO_2) followed by curing at 120°C for four hours (this sample being designated GS04). The results of the measurements taken using this sensor sample, over the range from pH 6 to pH 9 and from 9 back to 6, is shown in Figure 5.

In a further experiment, the temperature used for the annealing of the thin film coating and comprising the following combination – (PAH/BY)$_6$(PAH/SiO_2)$_2$ was heat treated for a longer period, of to 7 hours, at 130°C (with this sample being designated GS05) was and exposed to the buffer solutions. Experiment has shown that higher temperatures cannot be applied successfully because of the degradation caused to the BY material.

In the next experiment, UV irradiation was utilized to provide energy to cause the layers to form a stronger bond, in addition to the electrostatic attraction present. The silica nanoparticle coating is a photosensitive material and the ionic bonds between the SiO_2 and PAH may be converted to covalent bonds by use of this UV irradiation. To do so, the sample was exposed to the UV light (irradiation intensity: 1112 mWcm^{-2} at 365 nm) for 20 minutes, after annealing at 130°C for 7 hours and then the sensor was exposed to the different pH buffer solutions. The results of the spectra recorded for this sample (designated GS06) are shown in Figure 7.

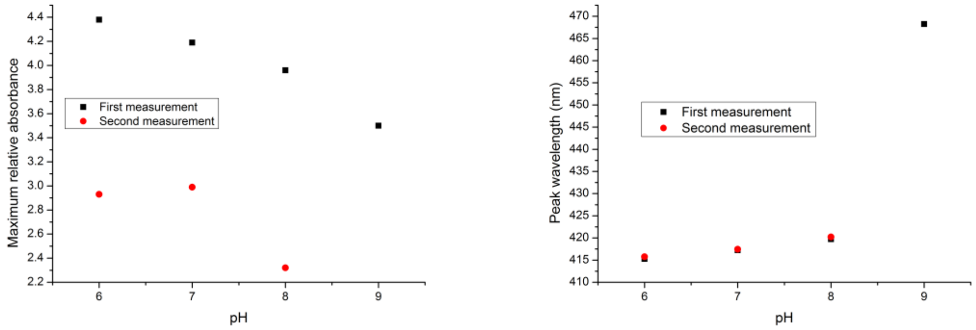

Figure 5 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for $(PAH/BY)_6(PAH/SiO_2)_2$ on the glass slide. (The sample designated as GS04)

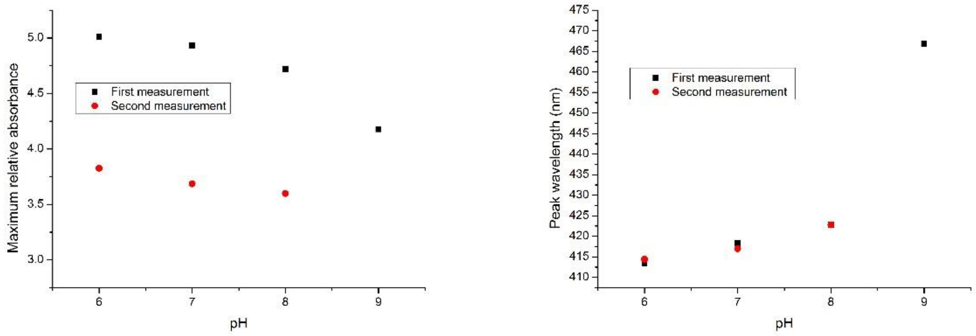

Figure 6 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for $(PAH/BY)_6(PAH/SiO_2)_2$ on the glass slide. The sample was cured at 130°C for 7 hours. (The sample designated as GS05)

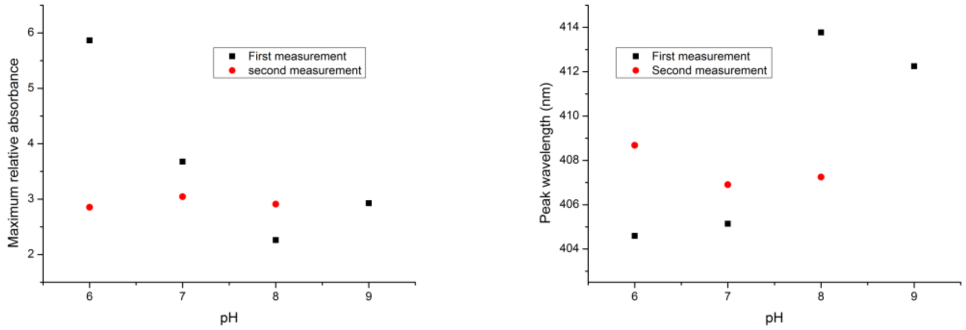

Figure 7 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for $(PAH/BY)_6(PAH/SiO_2)_2$ on the glass slide. The sample was cured at 130°C for 7 hours and exposed to UV light for 20 minutes. (The sample designated as GS06)

The silica nanoparticles act as polyanions in the same way as the BY material. It can be speculated that if the silica molecules are located amongst the molecules of brilliant yellow (BY), then the formation of the molecular bonds between the silica and the PAH molecules would create a bilayer which would surround the BY molecules in each layer. Therefore, a further set of experiments was carried out in which a silica nanoparticle solution was added to a BY solution (1.7 mM SiO_2: 0.25 mM BY) and the pH of the solution was adjusted to pH 6. Having coated the glass slide sensor in this way to create $(PAH/(BY+SiO_2))_6$, then annealing at 120°C for 4 hours, the deposited glass slide (designated GS07) was examined under various buffer solutions of different values of pH. The results of this test and thus the recorded spectra are shown in Figure 8.

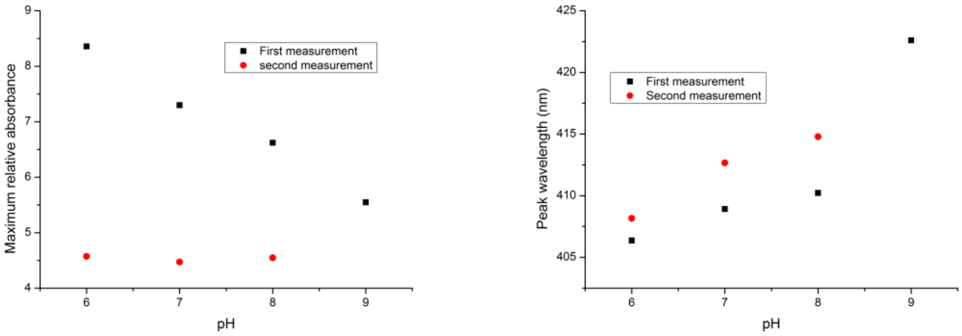

Figure 8 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for $(PAH/(BY+SiO_2))_6$ on the glass slide. The sample was cured at 120°C for 4 hours. (sample designated GS07)

2.3.3 Use of APTMS and silica nanoparticles

Further experimentation was carried out by replacing the polycation; PAH; with 3-Aminopropyl-trimethoxysilane (APTMS) in the capping layers. APTMS is known as a silane coupling agent in which a water based solution is polymerized after hydrolysis, as shown schematically in Figure 9. The surface of the SiO_2 nanoparticle thin film contains hydroxyl groups in the form of SiOH. These groups may donate or accept a proton from the solution, leaving a negatively charged or a positively charged surface group respectively [30]. Therefore, there are two possibilities that the molecules of APTMS bond to the silica nanoparticles; the molecule constitutes of an amine group as a positive charge supplier and hydroxyl groups as negative charges supplier which bond to silicon, as shown in Figure 10. In the experiment, the solution of 1 wt.% APTMS in H_2O (1.4 mM) used was strongly alkaline (with pH 10.8) and should thus be adjusted to the neutral pH that is best suited for use as polyelectrolyte in the LbL technique. Hence several drops of HCl were added to both solutions of the polycation and polyanion to adjust their pH value to pH 6. Two glass slide sensor samples coated with $(PAH/BY)_6(APTMS/SiO_2)_2$ were prepared; one of them was examined the same day of preparation (the sample designated GS08) and the second (the sample designated GS09) was evaluated a week later. The results of the tests carried out are shown in Figure 11 and Figure 12 respectively.

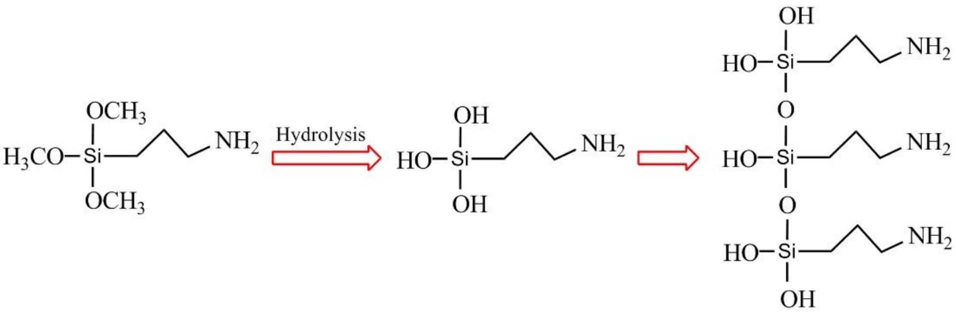

Figure 9 APTMS is polymerized in aqueous solution after hydrolysis.

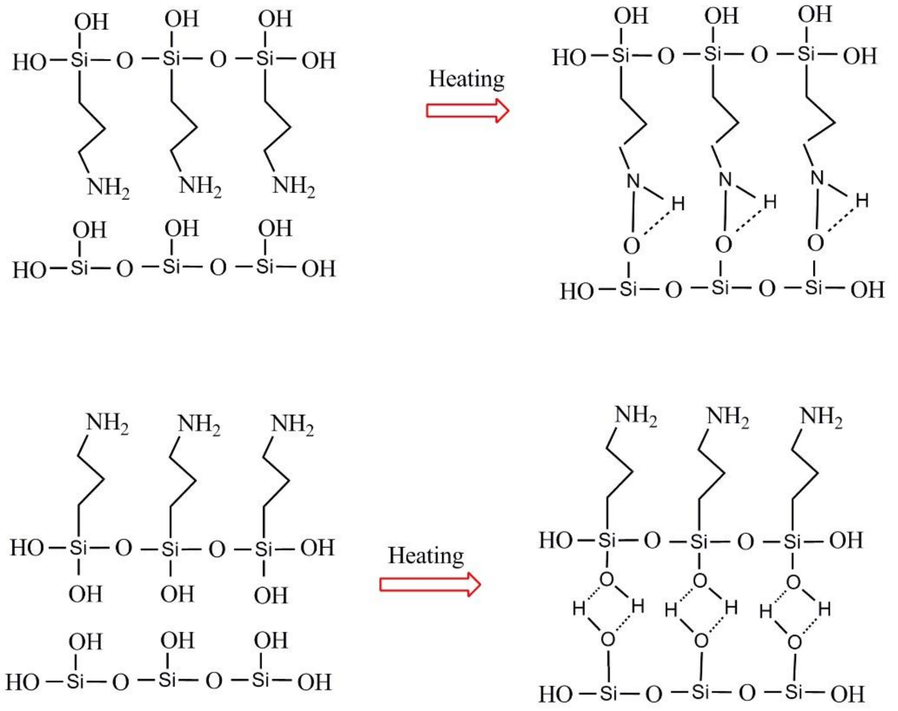

Figure 10 Two possibilities reaction between molecules of APTMS and silica nanoparticles.

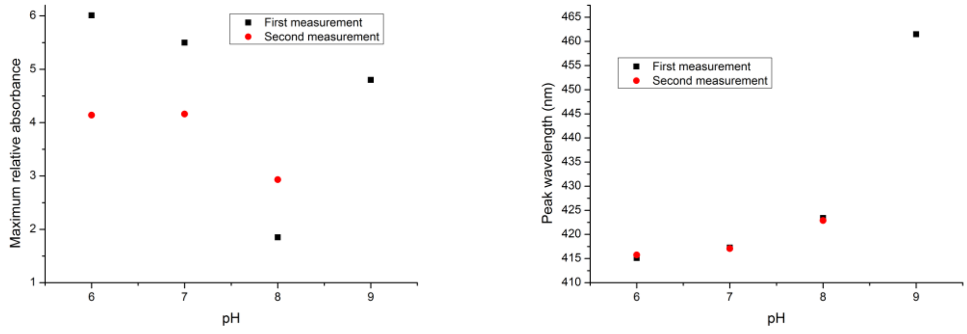

Figure 11 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for (PAH/BY)$_6$(APTMS/SiO$_2$)$_2$ on the glass slide. The sample was cured at 120°C for 4 hours. (The sample designated GS08)

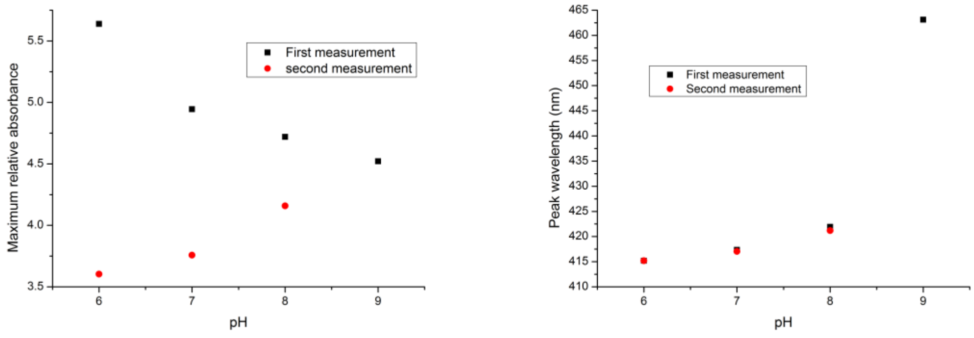

Figure 12 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for (PAH/BY)$_6$(APTMS/SiO$_2$)$_2$ on the glass slide. The sample was cured at 120°C for 4 hours and examined after a week. (The sample designated GS09)

To investigate the effect of the use of APTMS alone, a thin film comprising 6 bilayers of (PAH/BY), dipped in APTMS solution for 30 minutes, followed by dipping in distilled water for 5 minutes, then cured at 120°C for 4 hours was examined. The results of this experiment is shown in Figure 13.

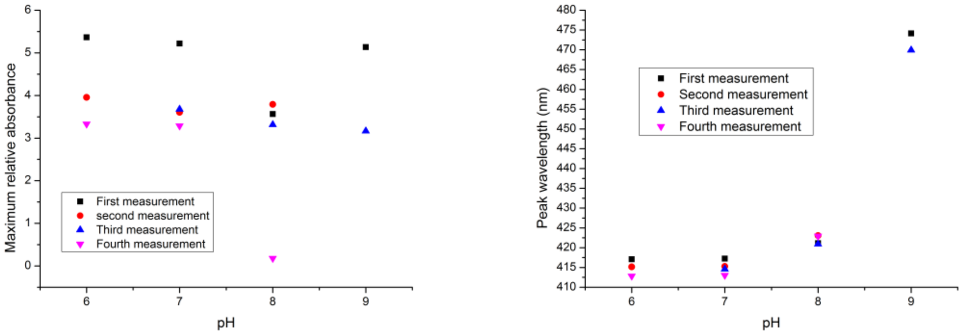

Figure 13 The maximum value of the relative absorbance (left) and the peak wavelength (right) versus pH for the consecutive measurements of the pH solutions for $(PAH/BY)_6$APTMS on the glass slide. The sample was cured at 120°C for 4 hours. (The sample designated GS10)

2.3.4. Re-usability and aging

To investigate the effect on sensor stability of the storage of the glass slides, different coated glass slides of different types were examined. Thus in this investigation, initially the glass slide with a coating was dipped into a fresh buffer solution with constant pH for 60 minutes and after this time the absorbance spectra was recorded as a reference. After that the glass slide was removed from that solution and then was immersed into another solution (with the same pH) for a further 60 minutes and a second absorbance spectra was recorded. This operation was repeated a third time. Several different slides with different films were recorded: the stability and thus the re-usability of the multilayer thin film slides using two different samples with different structures, these being $(PAH/BY)_6$ and $(PAH/BY)_6(APTMS/SiO_2)_2$ were examined at two different values of pH; pH 6 and 8, separately.

The results of this test are shown in Figure 14 and Figure 15 and the positive results obtained imply the stability of these two sensor samples under exposure to these solutions for the times indicated.

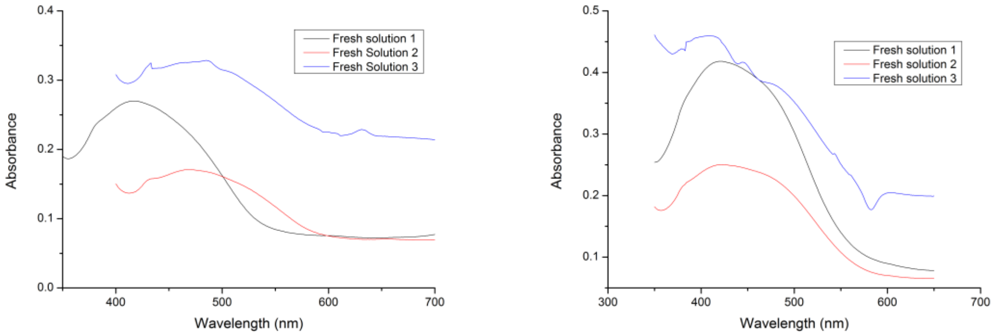

Figure 14 The spectra for the coated glass slides with $(PAH/BY)_6$ dipped into the fresh buffer solution for three times and each time for 60 minutes. Left: pH 6 (The sample designated GS11), Right: pH 8 (The sample is designated GS12). The samples were cured at 120°C for 4 hours.

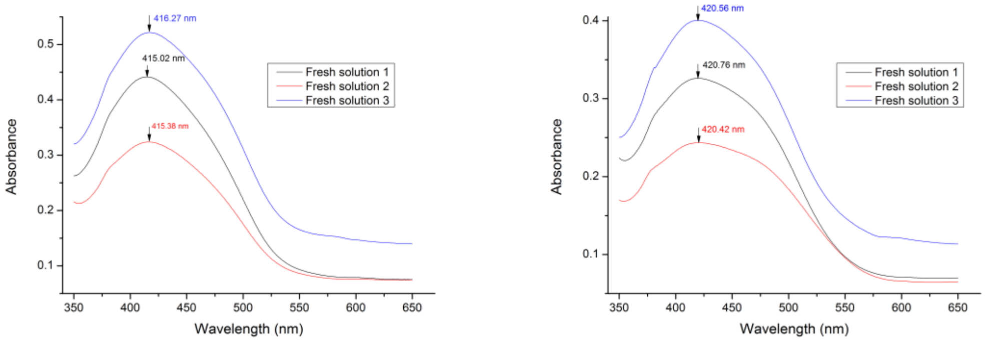

Figure 15 The spectra for the coated glass slides with $(PAH/BY)_6(APTMS/SiO_2)_2$ dipped into the fresh buffer solution for three times and each time for 60 minutes. Left: pH 6 (The sample is designated GS13), Right: pH 8 (The sample is designated GS14). The samples were cured at 120°C for 4 hours.

3. Results and discussion

In the layer-by-layer coating technique, the stability of the layers is seen to depend on type and concentration of the salt, the strength of ions and polyelectrolytes, the polymer molecular weight, the pH of the solutions and the thermal energy.

In order to form a stable multilayer thin film, a minimum charge density in each layer is needed. This minimum charge density depends on the salt concentration and the salt type; this was investigated [39] by the authors previously and also it was shown that to rely very strongly on the chemical identity of the charged units involved in forming the thin film [40]. Stronger ion pairing will also yield more stable multilayers [2] and moreover, high molecular weight polymers promote the stability of the layers [41-43]. High and low pH solutions can potentially discharge the ions and destroy the layers, while heat treatment causes a chemical reaction between the molecules of two adjacent layers and makes the bonds stronger and creates a more stable multilayer film, as can be seen in the first three experiments discussed (shown in Figure 2, Figure 3 and Figure 4). As the figures show, in this series of experiments there is a continuous decrease in the maximum absorbance for each pH buffer solution for two successive measurements while the values of the peak wavelength show a significant change from the first to the second measurement for the sample without heat treatment, and this represents an increase in stability of the thin film because of the thermal effect on the sample.

In the sample designated GS03 and examined in solutions ranging from pH 6 to pH 9, a dramatic decline in the maximum absorbance was seen, compared to other samples examined over the range from pH 6 to pH 8. The reduction in absorbance is a clear proof that leaching of the indicator is occurring and the decrease of the thickness of the thin film. In particular, in the case where a pH 9 solution is used, which causes greater destruction of the layers, a noticeable decrease takes place in the absorbance from the first to the second measurement. In addition to the absorbance, in all the samples studied the wavelength has not stayed stable during consecutive measurements and a small change of around 0 to 2 nm in the peak wavelength was observed; although with increasing the number of bilayers the amount of this change becomes reduced.

Covering the sensitive thin film with a couple of layers of silica nanoparticles leads to a coating which creates such a stable film that the wavelength continues to remain constant for a certain known pH, while the absorbance decreases irregularly during the two cycles of measurement, as shown in Figure 5. Referring to Figure 6, the duration and the temperature of thermal treatment used did not have any significant effect on the stability of the film as the values of the peak wavelengths for the first and the second measurements for both samples used, designated GS04 and GS05, were roughly the same. However, exposing the samples to UV light did not modify the molecular bonds. As Figure 7 shows there is not a regular change in the peak wavelength but a drastic decline is seen in both the absorbance and the peak wavelength values compared to previous experiments and also a dramatic absorbance reduction was observed in the first measurement. This means that by applying UV irritation, an increase in the strength of the inter-molecular bonds occurs temporarily. However, these inter-molecular forces are loss after a few times of dipping the sensor slide into the buffer solutions. As a result, the molecules of BY start to leach out from the sensitive thin film and this causes a steep decrease in absorbance and a very undesirable situation for a sensor system.

Adding silica nanoparticles to BY solutions shifts the absorbance spectra to the lower peak wavelength values, as shown in Figure 8. It can be seen in this figure that the absorbance has increased significantly compared to that of the other samples; however, the values of both the absorbance and the peak wavelength in the second measurement become close to the values seen from the previous tests. Looking more closely, it can be said that the higher values of maximum absorbance in the first measurement imply a larger number of molecules of brilliant yellow in the deposited layers. In other words, the SiO_2-PAH bilayers can protect the BY from significant damage, but not for a long time.

When the PAH was replaced by APTMS in the capping layers, the results showed that the peak wavelength for each pH solution used demonstrated almost same values as shown in Figure 12. Table 1 compares the peak wavelengths of three slides (designated GS04, GS08 and GS09) for two successive measurements over the range from pH 6 to pH 9 and then from 9 to 6. It is noticeable that the APTMS does not cause any significant changes to the peak wavelengths, compared to the use of PAH and the three tests carried out exhibited the same peak wavelengths, in spite of the difference in the peak intensity. The most striking result of this series of experiments is the remarkable reduction of the degradation of the probes and thus the improvement that would be seen to their shelf-life, as well as their re-usability, which are key considerations for the use of this type of coating in an industrial sensor system. Figure 13 shows that when the sensitive film is coated with a layer of APTMS, the peak wavelength for each pH value changes during successive measurements and also there is not a regular shift with different times of measurements. This therefore implies that the stability of the measured wavelength cannot be maintained because of the polycation properties. Moreover, the influence of SiO_2 is more effective in creating a stable sensor than does the polycation. However, the cross-comparison of the two sensor samples (designated as GS03 (without APTMS) and GS10 (with a layer of APTMS)) and shown in Figure 4 and Figure 13 confirms that the effect of APTMS on stability cannot be ignored. Indeed, as Table 1 shows, there is no significant difference in the stability observed between the situations where two capping layers of (PAH/SiO_2) and (APTMS/SiO_2) are applied. This may arise because of the similarity between the functional groups (amine groups) in both the PAH and the APTMS and thus the same interaction occurring between the polyanion and the polycation species.

In addition, a comparison of the last two columns of Table 1 shows that storing the samples for a week has had a negligible effect on the peak wavelength values. Applying these capping layers not only improved the sensor shelf-life but also enhances the re-usability of the sensor, as can be seen when sensors designated GS11 and GS12 are compared to GS13 and GS14, as illustrated in Figure 14 and Figure 15, respectively. Figure 14 shows a result which implies that destroying the deposited layers after 60 minutes exposure to the buffer solution results in the peak wavelength staying constant for those samples covered with two layers of APTMS/SiO_2, even after immersion on two separate occasions in the buffer solutions, for periods of 60 minutes in each case.

Table 1 The peak wavelength for two times consecutive measurements for the glass slides, designated GS04, GS08 and GS09 in pH solutions from 6 to 9 and then from 9 to 6.

pH	**Measurement**	**Peak wavelength (nm)**					
		GS04		**GS08**		**GS09**	
		$(PAH/BY)_6(PAH/SiO_2)_2$		**$(PAH/BY)_6(APTMS/SiO_2)_2$**		**$(PAH/BY)_6(APTMS/SiO_2)_2$**	
			error		error		error
6	First	415.26	-	415.10	-	415.18	-
7	First	417.24	-	417.26	-	417.36	-
8	First	423.19	-	423.4	-	421.92	-
9	First	468.25	-	461.5	-	463.12	-
8	Second	423.09	-0.02%	422.9	-0.1%	421.17	-0.2
7	Second	417.45	0.05%	417.06	-0.08%	417.06	-0.07%
6	Second	415.75	0.1%	415.75	0.1%	415.18	0%

4. Conclusion

In this study, the stability and the deterioration of wavelength-dependent optical sensor devices to pH changes using techniques to build up a series of nanolayer coatings was investigated and the results reported.

The stability of the pH sensors thus fabricated was studied using different pH buffer solutions. A variety of techniques was proposed and investigated to improve the stability of the film and to avoid progressive destruction of the indicator layer. One technique explored extensively was to build up capping bilayers using different materials i.e. silica nanoparticles as the polyanion and PAH or APTMS as the polycation. Another approach investigated was to apply thermal treatment after the layer building process and an alternative method considered was applying UV light irradiation.

The results of the experiments carried out, including covering the sensitive thin film with two layers of (APTMS/silica) nanoparticles was shown to improve the stability of the sensor (indicated by the stability of the peak wavelength) and also to enhances the stability and potential shelf life of the sample, when the nanolayers are deposited on the glass slide substrates. The most striking result is that the peak wavelength continues to remain constant for a particular pH while the layers were affected during repeated measurements over three cycles.

The durability of the sensors thus created makes the probe a suitable wavelength-dependent measurement device which is well suited to use as a high resolution pH sensor. To do so, the layers described can be coated directly on optical fibres of various diameters or coated glass substrates can be attached to the distal end of the fibre probes created. In that way compact optical fibre sensors can be created for a range of applications and as the work has shown, stored for some time before use.

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