



## Strategies for fabrication of hydrogen peroxide sensors based on electrostatic self-assembly (ESA) method

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### Abstract

An optical fiber sensor has been fabricated for detection of 5  $\mu\text{M}$ –0.1 mM concentrations of hydrogen peroxide with a linear response. The deposition method used is electrostatic self-assembly (ESA) of polymer cationic and anionic layers. Prussian Blue (PB) has been included in the polycation layers. The optical fiber sensor is included in a reflection setup, where the measuring technique is based on the slope of the optical reflected power change caused by oxidation of Prussian White (PW) to Prussian Blue. The sensor recovers after immersion in a reductive agent and is immune against a variety of components. Measurement of hydrogen peroxide has been proved successfully in a wide range pHs between 3 and 9. Some techniques have been applied in order to avoid the lost of indicator.

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**Keywords:** Electrostatic self-assembly; Hydrogen peroxide; Optical fiber sensor; Prussian Blue

### 1. Introduction

Accurate estimation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is important in many fields. It is used in many industrial processes as an oxidizing, bleaching and sterilizing agent. It is also the waste product in industries such as atomic power stations. In these cases, concentration of  $\text{H}_2\text{O}_2$  is higher than in pharmaceutical, clinical and environmental analysis, where it is the product of reactions catalyzed by a large number of oxidase enzymes. These last fields require accurate sensors that can detect low concentrations. Consequently, in this work we fabricate a sensor adequate for detecting micromolar concentrations of  $\text{H}_2\text{O}_2$ .

To this purpose, three important characteristics must be taken into account. The first one is the detection technique. Since the determination of  $\text{H}_2\text{O}_2$  concentration has been a matter of research during the last years, and it still continues today, there are a wide variety of techniques. Apart from titration [1], there are two main groups: electrochemical detection [2–10] and spectroscopy [11–21]. Both of them are adequate for detection of micromolar range concentrations. The latter avoids the application of a voltage and the necessity of smart membranes to protect the electrodes. But, the main reason for the selection of spectroscopy is the idea of depositing the sensitive structure in an optical system where the substrate is optical fiber. The advantages of optical fiber are well known: immunity against electromagnetic interferences, capability of multiplexing several sensors, low losses and so forth. Among the variants of spectroscopy: chemiluminescence [11,12], spectrofluorometry [13–16] and spectrophotometry [10,17–21]; the last one has been chosen. The substance to detect oxidizes a chromogenic hydrogen donor.

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Its refractive index changes in the transition from the reduced to the oxidized state, which leads to an absorbance change that can be detected with a simple optical system. This phenomenon has been studied in the oxidation of Prussian White (PW) to Prussian Blue (PB) [10,20,21]. An important advantage of the PW/PB system compared with other sensors [2,4–7,11,14,15,18], is that no enzyme is needed in the sensitive structure. This permits to save costs. Enzymes such as horseradish peroxidase (HRP) are still expensive nowadays. Anyway, there are some less expensive mimics that avoid the usage of HRP [11,15]. However, most of them are organic, which reduces the lifetime of the sensor in an important way, in comparison with the sensor developed in this work, as it will be proved. Furthermore, the changes in the absorbance of PW/PB system are present in a wide range of wavelengths between 600 and 1000 nm. This permits the usage of the first optical telecommunications window, where LED sources and photodetectors are cost effective.

The second characteristic is the deposition technique. Electrostatic self-assembly (ESA) method has been selected. It is based on the construction of molecular multilayers by the electrostatic attraction between oppositely charged polyelectrolytes in each monolayer deposited, and involves several steps [22]. It is used to build up coatings on a wide variety of substrates such as ceramics, metals, and polymers of different shapes and forms, including planar substrates, prisms, and convex and concave lenses. Fiber optic is also included as a possible substrate [13,17,23], which is the one selected in this work. One advantage of this technique compared with others is the stable electrostatic attraction of the nanostructure deposited at the end of the fiber pigtail. Secondly, there is wide variety of different polymer structures where Prussian Blue can be deposited. This should permit to avoid the interference of some molecular species if an adequate structure is chosen. In addition to this, the thickness of the cavity created at the end of fiber is lower than the coherence wavelength of a LED source. This permits to avoid the necessity of an expensive laser device to monitor interferometric phenomenon caused by changes in the refractive index of the material deposited. Since the range of absorbance change of Prussian Blue is located in the first optical communications window, a simple LED source and a photodetector are adequate for the optical detection scheme.

The last characteristic is the measuring technique. This is one of the major novelties of this sensor. The detection is based on a reflection scheme where the slope of the change of absorbance of PW/PB system indicates the concentration of  $\text{H}_2\text{O}_2$ . This phenomenon is due to the diffusion time of  $\text{H}_2\text{O}_2$  inside the polymer structure, where Prussian Blue is included. The diffusion time is dependent on the concentration of  $\text{H}_2\text{O}_2$ .

The concentrations that can be monitored with a linear response range from 5  $\mu\text{M}$  to 0.1 mM. The pHs analyzed range from 3 to 9, which includes the physiological pH. This wide pH range is possible due to the lack of an enzyme in the structure deposited at the end of fiber.

## 2. Experimental

### 2.1. Reagents

The polycation poly(allylamine hydrochloride, PAH),  $M_w$  70000, and the polyanion poly(acrylic acid, PAA),  $M_w$  30000, were obtained from Aldrich. Prussian Blue soluble ( $\text{C}_6\text{Fe}_2\text{KN}_6 \cdot x\text{H}_2\text{O}$ ) was obtained from Riedel-de Haën AG. Ascorbic acid was obtained from Panreac. Acetic and phosphate buffer solutions of 25 mM ionic strength were fabricated in our laboratory. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of the polymers and Prussian Blue solutions. All water was filtered through a Milipore Q plus 185 purification system.

### 2.2. Instrumentation

Power measurements were obtained using a reflection scheme where the light source is a Hewlett-Packard 9537 HFBR 1424 LED at 810 nm and an Ophir LaserStar photodetector detects the reflected power measurements at the first optical communications window. The pH of the different solutions was adjusted with a Crison GLP22 pH meter. In order to obtain the spectrum of Prussian Blue deposited in the polymer structure, a halogen white source and an Avantes AVS S2000 spectrometer replace the LED source and the photodetector, respectively in the reflection scheme.

### 2.3. Assembly of multilayer films

The materials used for deposition of cationic and anionic layers are PAH and PAA, respectively. The concentration of PAH is 2 g/l and PAA 5 ml/100 ml. The method used for including Prussian Blue into the polymeric structure is premixing with the polycation [13]. In this method, the dye is mixed with a polyion with the opposite charge. Both of them will associate with the other oppositely charged polyion, leading to the construction of the structure. Some experiments were performed with conjugation technique. Prussian Blue was mixed with PAA, but changes in the signal were not as clear as with premixing. Annealing after concluding the construction of the LBL structure at the end of the fiber pigtail is another important parameter with consequences in the performance of the sensor. It has been proved that sensors must stay at 100 °C during at least 2 h for a good performance. On the other hand, the addition of capping bilayers at a different pH at the end of the structure causes an improvement in the sensitivity of the sensor.

### 2.4. Measuring technique

To perform each measure the same procedure is repeated: the sensor is immersed in a reductive agent, such as ascorbic acid solution, to reduce PB to PW. After this, the sensor is immersed in a buffer solution. When the signal is stabilized,  $\text{H}_2\text{O}_2$  is injected in the buffer, which oxidizes PW to PB. A

change in the reflected optical power is then produced. This process will be repeated for other measures, which indicates that it is a multiple use sensor. The response time of the sensor as a function of hydrogen peroxide concentration is exponential. To avoid this problem, another measuring technique is proposed: the quotient between two values: the difference of power between 90% and 10% of the complete signal level change, and the time elapsed between these two values. This slope leads to good linearity as a function of the concentration. That is the reason for selecting it. In Section 3 it will be referenced, for the sake of simplicity, as the slope of the reflected optical power detected by the reflection scheme.

### 3. Results and discussion

#### 3.1. Sensing mechanism

A reflection scheme for the sensor is represented in Fig. 1. The light launched by a LED source is reflected by the sensing arm of a coupler and detected at the photodetector. This system is used for the purpose of controlling the growth of the structure. Bilayers of  $[(\text{PAH} + \text{PB}^+ / \text{PAA}^-)]_n$  are deposited at the end of fiber. This creates a nano Fabry-Perot cavity between the fiber and the external medium. As more bilayers are deposited, the reflected power describes a sinus plot explained in terms of interferometry [24]. Once the structure has been deposited, the same setup is used for detecting variations in the reflected optical power if the absorbance of the PW/PB system is changed by the presence of  $\text{H}_2\text{O}_2$ .

#### 3.2. Choice of materials

Prussian Blue has been selected based on its applicability to the detection of  $\text{H}_2\text{O}_2$  in both electrochemical sensors [8,9] and spectroscopy [10,20,21]. The absorbance plot for the structure deposited at the end of fiber is strongly influenced by the presence of Prussian Blue. In [20,21], it is asserted that the maximum is located at a wavelength of 720 nm. This is actually the maximum for this pigment in bare solution. Nonethe-

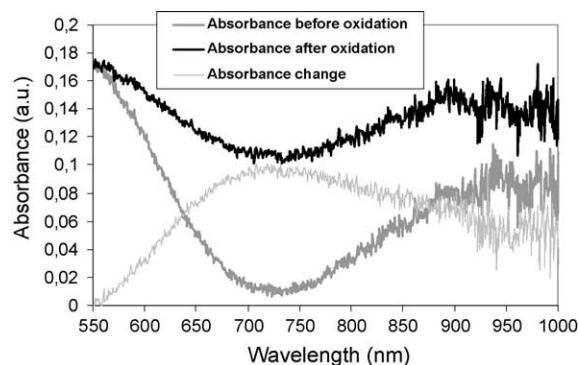


Fig. 2. Absorbance before and after oxidation, and absorbance change of PAH + PB/PAA structure with  $\text{H}_2\text{O}_2$  at pH 7.

less, there are some cases where this assumption is not valid. In [19], Meldola's Blue is immersed in a matrix. This causes a shift in the absorbance maximum that is characteristic of this colorant from 570 to 720 nm. As a result, we have obtained in Fig. 2 the spectrum absorbances of both Prussian White (the reduced form of Prussian Blue) and Prussian Blue. It is also included the difference between both absorbance plots. The reflection scheme of Fig. 1 has been modified by replacing the LED source with a white light source, and the photodetector with a spectrometer. Around 720 nm, it is located the maximum of absorbance change. Indeed, there is a wide range between 600 and 1000 nm, where measures can be taken. Consequently, it has been demonstrated that the polymer structure where Prussian Blue is immersed causes no appreciable shift in the absorbance spectrum of the colorant in bare solution. Any LED source, in the first optical communications window or even beyond, can be applied in the reflection scheme for detection of different concentrations of  $\text{H}_2\text{O}_2$ .

#### 3.3. Sensors without capping bilayers

In this section, homogeneous polymeric structures deposited at the end of fiber are analyzed. As an example, a sensor composed of 17 bilayers has been cured during 2 h at  $100^\circ$ . The thermal treatment avoids progressive desorption of the bilayers. However, sensitivity is an important parameter that is reduced if higher thermal treatment is performed. Consequently, a trade off must be maintained between sensitivity and robustness. Both factors cannot be improved at the same time. There is an additional trade off that optimizes the sensors response when 17 bilayers deposited. It was shown that the sensitivity of the sensors increased as the amount of Prussian Blue deposited augmented, i.e. as the number of bilayers increased. However, the stability of the structure decreased if too many bilayers were deposited. Seventeen bilayers were considered an optimum value in our experiments.

In Fig. 3, the response of the sensor against different concentrations of  $\text{H}_2\text{O}_2$  is analyzed. Measures have been taken 1 week later than its construction, once the sensor has stabilized its sensitivity. This phenomenon is explained in terms

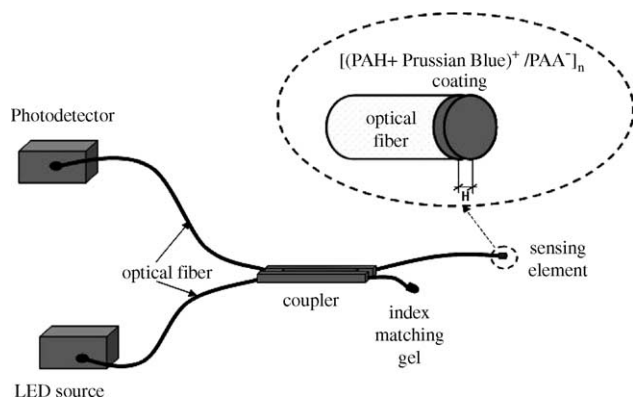


Fig. 1. Experimental setup to detect the reflected optical power by the nano Fabry-Perot cavity.

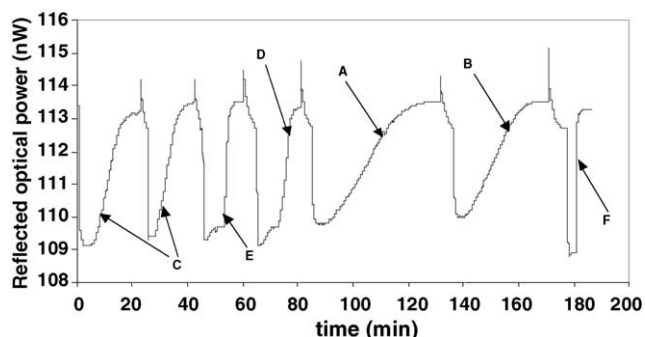


Fig. 3. Reflected optical power for different concentrations of H<sub>2</sub>O<sub>2</sub> at pH 4. A = 5 μM, B = 10 μM, C = 20 μM, D = 50 μM, E = 100 μM and F = 500 μM.

of lost of the pigment. During the first measures, Prussian Blue leached from the structure until the amount of Prussian Blue inside the polymer structure was stabilized. At this point, the response of the sensor is stable and results can be reproducible. The pH of the solutions is 4 and the concentrations analyzed range between 5 μM and 0.1 mM. It can be appreciated that the slope of the change in the reflected optical power increases, as the concentration of H<sub>2</sub>O<sub>2</sub> is higher. This effect is caused by the diffusion of H<sub>2</sub>O<sub>2</sub> in the polymer structure. As the concentration is higher the diffusion is faster, and the slope increases. The slope of the change of signal (see Fig. 4a) presents a linear dependence on the concentration of H<sub>2</sub>O<sub>2</sub>. The multiple-correlation coefficient  $R^2$  is indicated and is very close to one. Even a wider range of H<sub>2</sub>O<sub>2</sub> could be detected but the response was not linear. On the other hand, in Fig. 4b the response time of the sensor for different concentrations of H<sub>2</sub>O<sub>2</sub> presents an exponential shape.

To prove the durability of the sensor, in Fig. 5 the response of the same sensor 3 months after its construction and after many measures at different pHs is analyzed. In this case, the response of the sensor for the same concentration of 10 μM at pHs 3, 5, 7 and 9 is analyzed. It was checked that the structure desorbs for a pH 11. The conclusion is that there is a dependence of the response on the pH (see upper right corner of Fig. 5), but not as high as for other sensors where

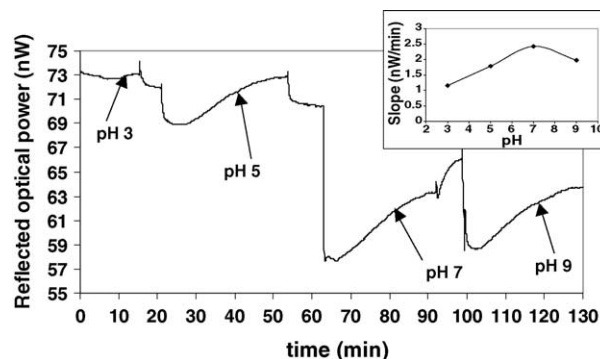


Fig. 5. Reflected optical power for 10 μM concentration of H<sub>2</sub>O<sub>2</sub> at pH 3, 5, 7 and 9. Upper right corner: slope of the change of signal for the four pHs analyzed.

the response is based on the change of signal level. In fact, in the range between pHs 6.5 and 7.5 the dependence is very low, which includes the physiological region.

### 3.4. Sensors with capping bilayers

It has been checked that for sensors of the type of previous section, there is a lost of Prussian Blue during the first measures due to the presence of a buffer solution. This effect has been demonstrated in [25] for Methylene Blue. If the sensor is introduced in a solution at a pH where binds between polymers and the pigment are broken, Prussian Blue leaves the structure. This leads to a lost of sensitivity.

Two strategies against this phenomenon are suggested in [25,26]. In both of them, some capping bilayers are added at the end of the structure. Following the strategy of [25], [PAH<sup>+</sup>/PAA<sup>-</sup>] bilayers at a pHs between 6 and 6.5 are added because they present a high ionic cross-link in comparison with lower pHs. In this way, they act as a barrier to avoid the leakage of pigment. The first design consists of 17 bilayers of [PAH + PB<sup>+</sup>/PAA<sup>-</sup>] at pH 5 and capping bilayers of [PAH<sup>+</sup>/PAA<sup>-</sup>] at pH 6. Three sensors have been analyzed in Fig. 6: one of them without capping bilayers, and the other two with two and six bilayers, respectively. If a

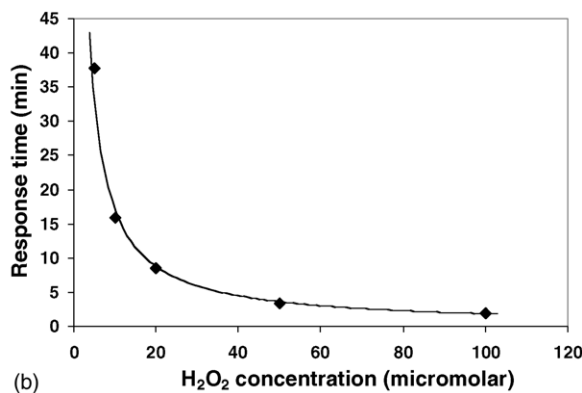
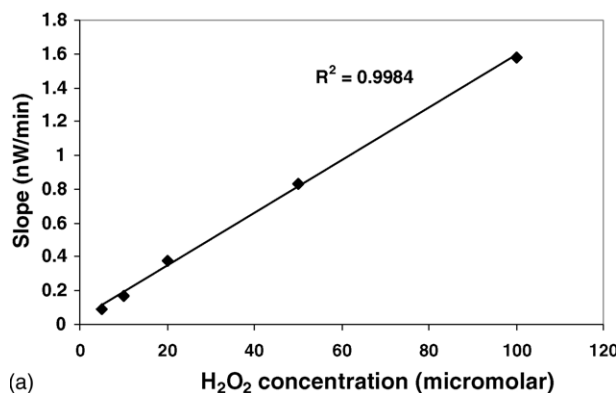


Fig. 4. (a) (Left) slope of the change in the reflected optical power for different concentrations of H<sub>2</sub>O<sub>2</sub> at pH 4. Linear tendency line. (b) (Right) response time of the change in the reflected optical power for different concentrations of H<sub>2</sub>O<sub>2</sub> at pH 4. Exponential tendency line.

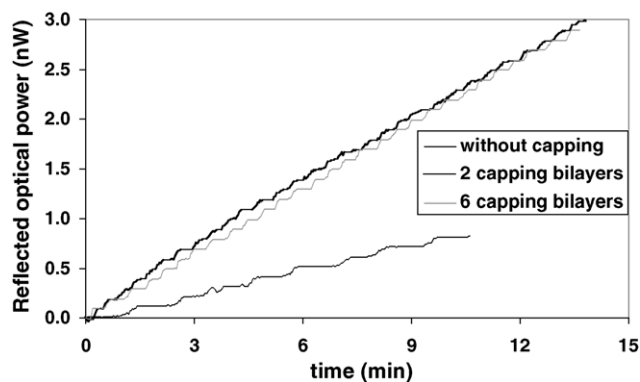


Fig. 6. Comparison of the change in the reflected optical power for three sensors with  $[PAH + PB^+ / PAA^-]_{17}$  at pH 5. One of them has no capping bilayers and the rest two and six of  $[PAH^+ / PAA^-]$  at pH 6, respectively. Measures have been taken at pH 7 and the concentration of  $H_2O_2$  is  $10 \mu M$ .

$10 \mu M$  concentration is analyzed at pH 7, both sensors with capping bilayers present a better response. The capping bilayers present no Prussian Blue, so the response should be equal. But, the barrier of  $[PAH^+ / PAA^-]$  bilayers at pH 6 provokes that Prussian Blue cannot leave the structure as easily. A second experiment (see Fig. 7) where the pH analyzed is again 7 and the concentration of  $H_2O_2$   $20 \mu M$ , consists of the same structure with the exception that in the first zone a pH 4.5 has been applied instead of a pH 5, and in the capping bilayers the pH was 6.5 instead of 6. The aim was to obtain a higher contrast of ionic strength between the two groups of bilayers, and in this way a better sensitivity. But, results obtained are very similar to those of Fig. 6. A small change in pH is sufficient to guarantee that the capping bilayers act as a barrier to avoid the leakage of Prussian Blue. This is corroborated in [27], where a fast variation of the ionic strength at pH 6 is detected for the combination of PAH and PAA. The other conclusion in this first design is that the number of capping bilayers plays no important role in the improvement of the sensitivity of the sensor. This is confirmed in the next strategy analyzed.

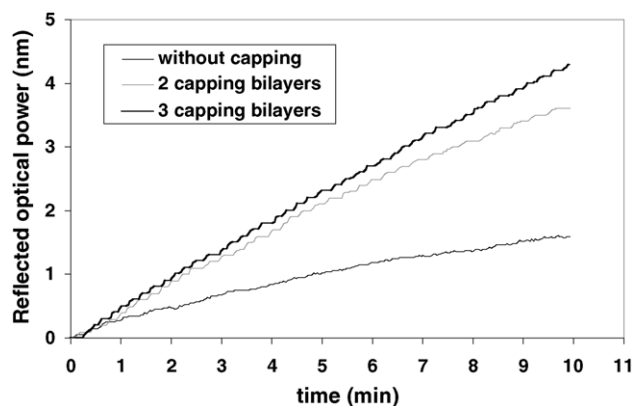


Fig. 7. Comparison of the change in the reflected optical power for three sensors with  $[PAH + PB^+ / PAA^-]_{17}$  at pH 4.5. One of them has no capping bilayers and the rest two and three of  $[PAH^+ / PAA^-]$  at pH 6.5, respectively. Measures have been taken at pH 7 and the concentration of  $H_2O_2$  is  $20 \mu M$ .

A second design consists of including a low pH zone between two high pH zones. In this way, two barriers avoid the loss of pigment. In the first zone 10 bilayers of the type  $[PAH + PB^+ / PAA^-]$  are deposited at a pH 6.5, in the second zone the same type of bilayers is deposited at a pH 4.5, and finally some capping bilayers are deposited with the same structure as the first zone and pH 4.5. There is a better response for the sensors where capping bilayers have been added at the end. This effect can be appreciated in Fig. 8a–c,

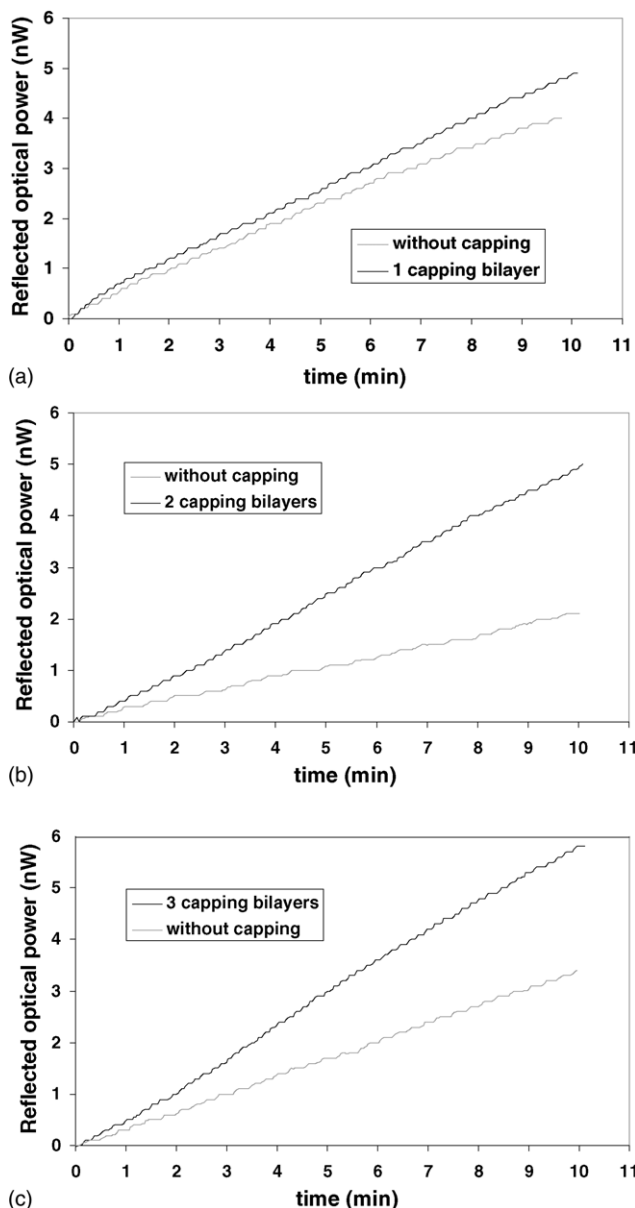


Fig. 8. Comparison of the change in the reflected optical power for six sensors with  $[PAH + PB^+ / PAA^-]_{10}$  at pH 6.5 and  $[PAH + PB^+ / PAA^-]_7$  at pH 4.5. (a) One of them has no capping bilayers and the other one has one capping bilayers of  $[PAH + PB^+ / PAA^-]$  at pH 6.5. (b) One of them has no capping bilayers and the other one has two capping bilayers of  $[PAH + PB^+ / PAA^-]$  at pH 6.5. (c) One of them has no capping bilayers and the other one has three capping bilayers of  $[PAH + PB^+ / PAA^-]$  at pH 6.5.

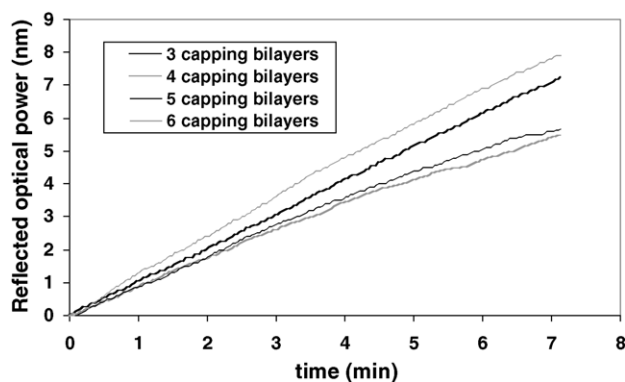


Fig. 9. Comparison of the change in the reflected optical power for four sensors with  $[\text{PAH}+\text{PB}^+/\text{PAA}^-]_{10}$  at pH 6.5 and  $[\text{PAH}+\text{PB}^+/\text{PAA}^-]_7$  at pH 4.5. They have respectively 3, 4, 5 and 6 capping bilayers of  $[\text{PAH}+\text{PB}^+/\text{PAA}^-]$  at pH 6.5.

where sensors with one, two and three capping bilayers are compared with sensors without capping bilayers that have been immersed the same time in buffer solutions. The pH analyzed is 7, and the concentration of  $\text{H}_2\text{O}_2$  is  $10 \mu\text{M}$ . If only one bilayer is deposited, the improvement of the response is not so important, whereas for both two and three capping bilayers there is an appreciable better response. This effect is logical because with one bilayer Prussian Blue can easily escape due to the spread of each individual layer [22]. Regarding the improvement in the overall response of this group of sensors compared with previous ones, this is obvious because more bilayers with colorant have been included. It is remarkable that the i.e. slope of the change of reflected optical power is different between Fig. 8a–c. The reason is that each pair of sensors was immersed a different time in buffer solution. As a result, the response of each pair is degraded in a different manner.

Finally, the same strategy as that of Fig. 8 has been used in Fig. 9. In this case, sensors with 3, 4, 5 and 6 capping bilayers have been constructed in order to analyze the influence of the number of capping bilayers in the improvement of the response of the sensor. The previous assumption that for more than one bilayer there is not a clear influence of the number of stacked bilayers is reaffirmed by the results. Differences between these sensors analyzed are caused by other factors.

### 3.5. Interferences

A wide group of interference compounds have been analyzed. Chloride, bromide, iodide, oxalate, thiocyanate, tartrate, urea, sulfate, phosphate and glucose produce no changes if 2.5 mM concentrations of them are injected in the solutions. Only arsenite (2.5 mM) produced a slight change of the signal but not in the state of Prussian Blue. This is true because the sensor recovered its signal after immersion in another solution without the need of an oxidizing or reducing agent.

## 4. Conclusions

An optical fiber sensor for detection of hydrogen peroxide  $\text{H}_2\text{O}_2$  based on electrostatic self-assembly (ESA) method has been fabricated. The polycation is composed of PAH and Prussian Blue, whereas PAA is used for the polyanion. A simple reflection scheme with a LED source and a photodetector in the first optical communications window serves for detecting changes caused by the presence of  $\text{H}_2\text{O}_2$ . The measuring technique is based on the slope of the change of signal produced by a specific concentration of  $\text{H}_2\text{O}_2$ . The dependence of the slope of the reflected optical power change as a function of the concentration of  $\text{H}_2\text{O}_2$  is linear in the zone analyzed, whereas the response time as a function of the concentration shows an exponential tendency. The concentrations with a linear response range between  $5 \mu\text{M}$  and 0.1 mM. A wide range of pHs is covered: from 3 to 9, with a low pH dependent zone located between pHs 6.5 and 7.5.

Some designs have been proposed to avoid the lost of indicator by adding some capping bilayers. Results show an improvement in the response of the sensors if more than one capping bilayer is added to the main structure of the sensor. Adding more bilayers does not lead to an appreciable improvement of the response.

Finally, the sensor has been tested against many interferants showing no cross sensitivity except for ascorbic acid, which is actually the reductive agent.

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