U-bend fibre optic pH sensors using layer-by-layer electrostatic self-assembly technique

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Abstract. A layer-by-layer assembly technique is used to coat layers of nano-thin-films of pH indicator on a U-bend optical fibre to create an effective sensor, using neutral red as the active element. The experimental results characterizing such a pH sensor shows a wide pH sensing range (from pH5 to pH10) fast response.

1. Introduction

The layer-by-layer (LbL) nano-assembly technique [1] is a simple and robust technique to fabricate nano-films on a substrate. This technique has been used to create evanescent wave-based fibre optic sensors, where the original coating of the fibre had been removed prior to addition of the LbL coating. Therefore, the light propagating in the core of the fibre excites evanescent waves in the immediate environment of the core. When a pH indicator is coated around the core, the evanescent waves interact with the pH sensitive coating causing the optical characteristic to change, the effect of which can be captured by a photodetector or a spectrometer. As a result, the variation of the evanescent wave characteristics is dependent on the pH of the solution surrounding the fibre core.

As reported by Goicoecha et al [2], a pH sensor has been designed by coating nano-films of Neutral Red (NR)on an optical fibre. In so doing, a length of fibre, with its original coating removed and then recoated with the indicator, neutral red, is used as a sensing element, configured with a silver mirror deposited at the end surface of the fibre to make a reflective sensor probe. The sensor presented in this paper is based on the same coating technique as that described. However, in order to enhance the evanescent waves and their subsequent interactions with the pH-sensitive coatings, the fibre core can be bent into a U-shape and then coated with the indicator using the LbL technique. The details of the sensor fabrication, which includes the bending of the fibre and the use of the LbL coating technique, are described below.
2. Fabrication of the U-bend sensor

The optical fibre used in this work is a silica core fibre with polymer cladding. Its core diameter is 1mm and the cladding thickness is 10µm. To create the U-bend, both the buffer and the cladding are required to be removed, exposing the silica core. A flame is then applied to soften the glass so that the fibre can be slowly bent to create a U-shape, following which the fibre is ready to be coated by using the LbL technique [1]. This technique alternates the coating of layers of positively charged and negatively charged compounds. The layers are linked together by electrostatic attraction. The fibre surface is treated first in order to be charged to allow the interleaving layers to be deposited. In this work, the cationic polymers employed are poly(allylamine hydrochloride) (PAH) and 3-amino-7-dimethylamino-2-methylphenazine hydrochloride, known as Neutral Red (NR), which will act as a colorimetric indicator. The anionic polyelectrolyte was poly(acrylic acid) (PAA). Water based solutions of all chemicals were prepared with a concentration of 10−2 M. The pH of the solutions was adjusted to pH 6.0. This was made by adding a few drops of NaOH or HCl when necessary. A total of 25 bilayers were deposited along the fibre using this method.

The U-bend sensor thus created is shown in Figure 1, where the red thin film coating of the neutral red (NR) indicator can be seen clearly around the U-bend of the fibre.

![Figure 1: Fabricated U-bend pH probe. The red part of the fiber is the Neutral Red nano-film coating.](image)

3. Experimental set-up

In order to evaluate the sensor characteristics, a series of tests has been carried out using a simple experimental set-up, in which a broadband white light source is connected to one end of the U-bend fibre and a mini-spectrometer is connected to the other to capture the spectral content of the signal generated. The pH-sensitive neutral red indicator has a strong absorption peak in the visible spectral region; therefore through the comparison between the transmission spectrum and that of the white light source, the absorption characteristics of the sensor as a function of the pH can be obtained.

4. Experimental results and discussions

The colour of neutral red indicator dispersed in solution is known to change from red to yellow when the pH varies from 6.8 to 8, but its absorption peak is sensitive to a wider range of pH. To verify that this effect, which forms the basis of the sensor, is seen in the configuration in Figure 1, seven different pH buffer solutions with pH ranging from 4 to 11 are used for a series of calibration tests.

The probe is inserted into each of the buffer solutions for a few minutes and the absorption spectrum of the probe at each specific pH is recorded every 15s. When the probe is dipped into a new solution, the absorption characteristics of the probe are seen to change accordingly. The main reason behind this fast change is twofold. On one hand, the enhanced evanescent waves show a changing signals when the refractive index of the buffer solution varies, due to the U-bend shape. On the other hand, the nano-layer of NR indicator reacts to the new pH and this in turn changes the refractive index.
in the vicinity of the U-bend fibre. No change has been shown between the recorded first and second spectra, indicating the response time is shorter than measurement interval used there i.e. 15s.

The absorption spectra recorded at different pH buffer solutions are shown in Figure 2. Three absorption peaks can be seen clearly at around 500nm, 730nm and 890nm respectively. For the same buffer pH solutions, the absorption spectra of an uncoated U-bend probe have also been recorded, exhibiting two main absorption peaks at 730nm and 890nm respectively. In light of this, the conclusion can be drawn that the last two peaks present in the absorption spectra of the U-bend pH probe originate from the interaction between the U-bend evanescent wave and the refractive index change of the solution rather than from the NR coating with the solution.

![Absorption Spectra of U-bend pH Probe](image)

Figure 2: Absorption spectra of the U-bend pH probe for pH between 4 and 11.

The absorption peak around 500nm, however, arises from the absorption characteristics of the NR coating on the fibre as a function of pH. This peak wavelength is in good agreement with the absorption peak of NR reported in the literature, which is between 500nm and 550nm depending on the specifics of the molecule and thus the material supplied from a particular manufacturing company. When the pH is increased, the absorption peak wavelength decreases and this result agrees well with the results published [3].

As can be seen in Figure 2, the absorption signal observed is noisy. In order to estimate the wavelength of the absorption peak, a curve smoothing technique (termed ‘moving average’) is applied. This method makes the curve smoother by reducing the noise, but it cannot entirely suppress the noise. Figure 3(a) plots the variation of the absorption peak wavelength as a function of the pH. For pH less than 5, no significant variation of the wavelength is detected. Similarly, when the pH is greater than 9, no variation of the peak wavelength is detected. When the pH varies from 5 to 9, the total variation of the absorption peak wavelength is around 40nm and under this circumstance monitoring the absorption peak wavelength can be a method to estimate the pH. The advantage of this approach is that it is insensitive to any intensity variation, arising from, for example, the variation of the light source or the aging effect of the coating but this is at the cost of a narrowed sensing range of pH that can be measured.
Figure 3: (a) Variation of the peak wavelength as a function of the pH and (b) Absorption at 600nm as a function of pH.

Another approach is to look at the absorption intensity of the spectra at one specific wavelength. A close look at Figure 2 shows that when the absorption peak shift is not sufficiently large to allow unambiguous estimation of the pH, the absorption intensity change can be considered for sensing as this, by contrast, is more significant especially for the wavelengths longer than the absorption peak wavelengths. Figure 3(b) presents the absorption intensity as a function of pH at a wavelength of 600nm. In the range of pH tested, the intensity varies by 25%. More importantly, the sensing range has been widened from pH 4 to 10. Monitoring the intensity of absorption at one fixed wavelength, for example at 600nm in this work, can be an alternative method for the measurement of pH although it has the same disadvantages of any intensity-based technique has. To reduce the influence of light source variation, an intensity-ratio based technique can be investigated to minimize this effect.

5. Conclusion

A U-bend optical fibre coated with nanoscale layers of pH indicator, Neutral Red, by using the Layer-by-Layer technique has been investigated, specifically to create a sensor for a wide range of pH measurement. A preliminary characterisation has been undertaken, showing a blue-shift of the absorption peak when the pH is increased from 5 to 9 and the data agree well with the reported results. A wider range of pH detection can be realized, as shown, by using the intensity-based technique. In addition to this, the new probe has shown a fast response. Research is still on-going in refining the sensor design and fabrication, as well as optimizing the signal processing of the sensor system.

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