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# A SUITE OF OPTICAL FIBRE-BASED CHEMICAL SENSORS FOR ENVIRONMENTAL MONITORING

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## ABSTRACT

This paper is to review the research activities at City University London in the development of a suite of optical fibre-based chemical sensors, including pH, humidity and heavy metal sensors, for environmental monitoring.

**Keywords:** *optical fibre sensors, chemical sensors*

## 1. INTRODUCTION

Optical fibres have demonstrated a strong resistance to chemical attacks. This feature has triggered extensive research at City University London into the development of optical fibre-based chemical sensors, which includes humidity, pH and heavy metal sensors, designed specifically for environmental monitoring.

The influence of humidity on a polymer-coated FBG was first reported by Giaccarri et al [1] and the technique described for humidity detection has been further explored by several research groups [2][3] including those at City University London.

Most of the fibre optic pH sensors can be fabricated by attaching a pH-sensitive element such as a membrane to the end face of a light-guiding optical fibre or fibre bundle [4]. pH sensitive membranes are usually made of a pH indicator immobilized on to or in a solid substrate (polymer, copolymer or glass) and the indicators applied are typically characterized by an absorption [5] or fluorescence [6] difference associated with the pH change.

Several fluorescent sensors that are selective for the mercury ion have been reported for aqueous systems or imaging in cells [7]. Liu et al developed a DNA-based sensor [8] for the detection of lead (II) ions in soil samples and spiked $Hg^{2+}$ in pond samples, that works by changes in fluorescence intensity but overall reports of chemosensors for measuring mercury as an environmental contaminant appear very scarce.

## HUMIIDTY SENSOR

A fibre Bragg grating (FBG) is made to act as the basis of the Relative Humidity (RH) sensor principle and the humidity sensing concept used in this sensor exploits the strain effect induced in a FBG through the swelling of a thin layer of applied polymer coating. The swelling of the polymer coating, arising from the absorption of moisture, changes the Bragg wavelength of the FBG, where this can be calibrated to give a direct indication of the humidity level. Thus the shift in the Bragg wavelength for a polymer-coated FBG can be given as follows.

$$\frac{\Delta\lambda_B}{\lambda_B} = (1-P_e)\alpha_{RH} \cdot \Delta RH + [(1-P_e)\alpha_T + \xi]\Delta T \quad (1)$$

where $\alpha_{RH}$ and $\alpha_T$ are the moisture expansion coefficient and the thermal expansion coefficient of the coated FBG.

Achieving temperature compensation is important as such grating-based devices are temperature sensitive and thus a second 'temperature-only' grating element is used to create the complete sensor system. To do so, a bare FBG is also included in the sensor design. Figure 1 shows the schematic diagram of the humidity sensor probe design, in which both grating elements can be seen – a bare FBG without coating is used for temperature measurement and for temperature compensation of the coated humidity sensor.

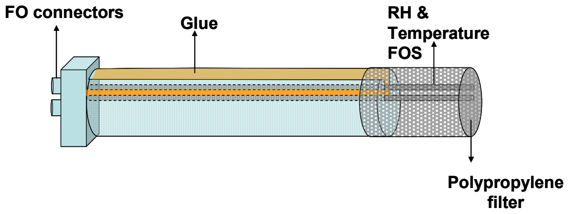


Figure 1 Schematic diagram of a RH sensor design, showing a coated grating as a RH sensor and a bare grating as a temperature sensor

## pH SENSOR

The development of an optical fibre pH sensor is basically based on the fluorometric determination of pH. In this work, a fluorescent indicator, HA, is used to induce pH sensitive changes in the measured fluorescence intensity. In aqueous solution, the following equilibrium can be reached:

$$HA \leftrightarrow H^{+} + A^{-} \tag{2}$$

The relationship between the protonation state of the indicator and the pH is governed by the Henderson-Hasselbalch equation below:

$$pH = pK_a + \log\frac{[A^{-}]}{[HA]} \tag{3}$$

where $[A^{-}]$ and [HA] are the concentrations of the dissociated and undissociated forms of the indicator and $pK_a$ is the acid-base constant. $[A^{-}]$ and [HA] are related to fluorescence intensities by $[A^{-}] = F - F_{\max}$ and $[HA] = F_{\min} - F$ where $F$ is a measured fluorescence intensity of the system, $F_{\max}$ is the fluorescence intensity of the fully protonated system and $F_{\min}$ is the fluorescence intensity of the deprotonated system. The expressions are then substituted into Equation (3) to provide Equation (4).

$$pH = pK_a + \log\frac{F - F_{\max}}{F_{\min} - F} \tag{4}$$

The above can be rewritten in terms of $F$ to give

$$F = \frac{F_{\max} + F_{\min} \times 10^{(pH - pK_a)}}{10^{(pH - pK_a)} + 1} \tag{5}$$

To meet the desired requirements discussed above, an appropriate fluorescent dye has been synthesized and coated onto the surface of the fibre to create a sensing probe as shown in Figure 2.

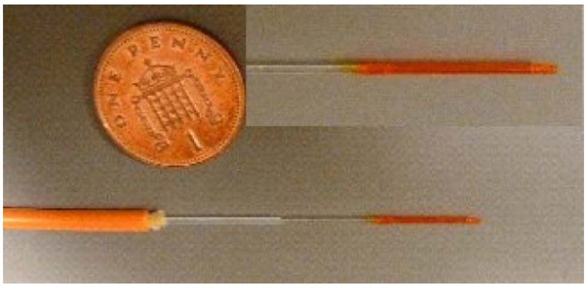


Figure 2 Optical fibre pH probe

Subsequently a sensor system has been set up in order to evaluate and calibrate the performance of the sensor. The sensing probe is illuminated by light from a 3mW LED emitting at a central wavelength of 375 nm via a 1x2 fibre coupler. When the probe is subjected to solutions with different pH values, the fluorescence signal generated is captured by an Ocean Optics mini-spectrometer and the spectra recorded as a function of pH are shown in Figure 3. It is noticeable that the fluorescence signal obtained increases with the increase of pH.

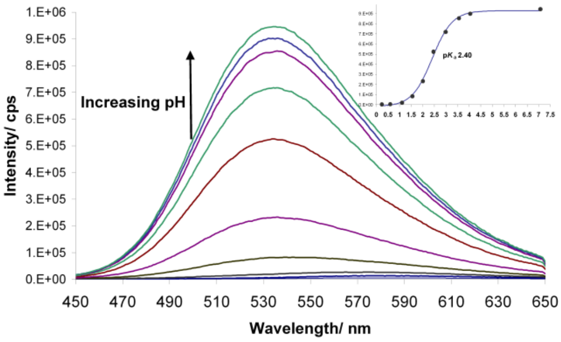
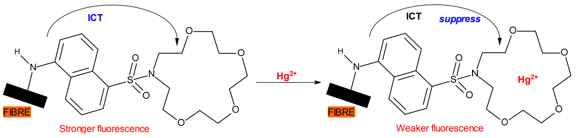


Figure 3 The fluorescence signal from the pH sensor increases with the increase of pH of the solution

## MERCURY SENSOR

The underpinning sensing principle for the mercury sensor design is highlighted in Figure 4 (a) where an intramolecular Charge Transfer (ICT) process was envisaged. Excitation by light leads to an ICT from the relatively electron rich fluorophore to the relatively electron-withdrawing crown ether, resulting in fluorescence. Mercury ion binding suppresses this ICT and consequently induces the spectral change (fluorescence quench). A picture of the mercury sensing probe created using the approach is shown in Figure 4 (b).



(a)

(b)

Figure 4 (a) Illustration of the sensing mechanism; (b) a mercury sensor probe developed

A similar set-up discussed in the above section has been used to evaluate the mercury sensor performance by replacing the pH probe with a mercury probe. The probe was immersed in different concentration of mercury (II) chloride in deionised water and Figure 5 summarises the spectral variation as a function of mercury concentration (at 500.15nm). It is noticeable that with the increase of the mercury concentration, from 247 ppb, through 2.47 ppm to 24.7ppm, the fluorescence signal is decreasing and this further confirms the 'fluorescence quenching' effect as illustrated in Figure 4 (a). The response time was ≤5mins in each case. Research is on-going with an aim to significantly improve the sensor sensitivity.

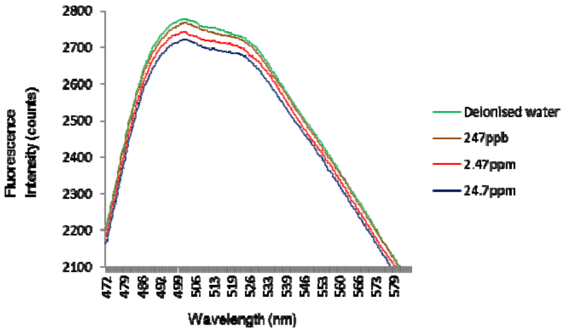


Figure 5 Fluorescence signal of the mercury sensor as a function of the mercury concentration

## SUMMARY

A suite of optical fibre-based chemical sensor systems has been specifically designed, fabricated and implemented, showing promise for environmental monitoring. Research is still 'on-going' both to expand the portfolio of novel sensors and instrumentation incorporating optical fibres and to widen the functionalities and scope of optical fibres to facilitate real-time and multi-parameter measurement.

## ACKNOWLEDGEMENTS

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