A reflection-mode fibre-optic sensor for breath carbon dioxide measurement in healthcare

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A B S T R A C T

A reflection-mode carbon dioxide (CO_2) fibre optic sensor (FOS) is developed based on the colorimetric change of pH indicator dye thymol blue. The CO_2 sensing film comprises thymol blue and tetramethylammonium hydroxide in the form of an ion pair doped in an organically modified silica film. A dip coating process was conducted to coat the sensing film on the tip of optical fibre with a film thickness approximately $2.7 \pm 0.1 \mu m$. The observed reflection signal at a wavelength of 608 nm exhibits a reversible change for the concentration of CO_2 range from 0 to 6% with a response time of 19 s and recovery time of 170 s for 6% of CO_2. An optimal concentration of thymol blue in the preparation of coating solution that provides a highest sensitivity was found to be 2.9 mg/ml. Storing the FOS in a pure nitrogen atmosphere provided a stable film with a shelf-life of over 15 days as compared to a gradual degradation in film performance and complete loss of sensitivity after 10 days with storage in ambient air. The FOS response is affected by relative humidity (RH) and a humidity filter was demonstrated to reduce humidity levels in breath from 90% to 40–50% to reduce this effect. The developed FOS was used to measure the end-tidal breath CO_2 for testing its applicability in healthcare. The CO_2 measurement from breath sample using our FOS shows a good agreement (percentage error~3%) with a commercial CO_2 datalogger (K-33 BLG, CO_2 Meter, USA). Due to the limitation of response time, at present the FOS is limited to measuring variation of the CO_2 from slow breath to breath.

1. Introduction

In the human body, carbon dioxide (CO_2) is exhaled from the lungs where the exchange of inhaled O_2 and CO_2 in blood takes place. Insufficient exhaled CO_2 can lead to respiratory acidosis that can become life-threatening if left untreated [1]. End-tidal CO_2 ($ETCO_2$) can be used to evaluate the status of pulmonary diseases such as chronic obstructive pulmonary disease (COPD) and asthma [2], a series of diseases affecting the functionality of lungs. Moreover, $ETCO_2$ has been commonly used to verify the placement of breathing tubes in patients' lungs during endotracheal intubation and to detect inadvertent oesophageal intubation [3]. CO_2 moves from the lungs and out through the tube if it is properly placed and so an absence of CO_2 can be used to indicate incorrect intubation. CO_2 is generated by tissues as an end-product of cellular metabolism and transported in blood in a dissolved format (H_2CO_3). Reduced $ETCO_2$ may indicate reduced CO_2 transport secondary to low cardiac output. The reduced circulation in ischaemic tissue can lead to local elevation of tissue CO_2, and transcutaneous CO_2 of local tissue has been proposed as a reliable marker for early detection of pressure ulcers [4].

Commercial CO_2 sensors such as non-dispersive infrared (NDIR) have been widely used at the point of care to monitor patients' breath CO_2 level. NDIR relies on the strong absorption of CO_2 at specific wavelengths (2600 and 4300 nm) [5] and measures the gas density inside a sample chamber. Capnography is a type of NDIR sensor for the measurement of CO_2 commonly applied for breath analysis as its fast response time enables the capture of CO_2 levels from breath-to-breath [6]. The commonest type of capnography device in clinical use is the "sidestream" design, in which expired gas is withdrawn from the breathing circuit and analysed in a distant chamber. This process has a number of limitations due to sampling rates, transfer times and different conditions in the chamber compared to the breathing circuit, which can lead to inaccuracies. "Mainstream" analysis is also available, but requires relatively complex devices in the patient circuit. Both

mainstream and sidestream types can only measure CO_2 in expired gas outside the patient when the true measure of interest is the concentration of CO_2 in alveolar gas. As such measurement should ideally take place as close to the alveolus as possible, i.e. within the airways themselves. This is particularly true for neonates and infants. Current capnography devices generally are bulky and relatively expensive, which limits their use outside the operating room or intensive care environment. Many critically ill patients require CO_2 measurement either before arrival in hospital or during transfers and therefore a low cost portable device would be beneficial.

An optical fibre sensor employs an optical waveguide for detecting the change of absorption [7], fluorescence [8] or refractive index [9] for measuring CO_2. Such sensors are usually small (~few hundreds microns diameter); require cheap components for signal reading and interpretation (e.g. LED, photodetector) and have the potential to make cheap and portable quantitative devices. Moreover, the optical fibre based sensor is immune to electromagnetic interference making it attractive during magnetic resonance imaging [10] which is a problem for many electrochemical sensors. The lack of electrical activity is also attractive for an in vivo device in close proximity to the heart. Optical fibre sensors can transfer signals from the tip many hundreds of metres so these can be used at a remote location, for example away from the MRI scanner.

A colorimetric optical fibre sensor comprises (i) a sensitive film containing an indicator that changes its colour when exposed to an analyte and (ii) an optical fibre as a waveguide for collecting the change from the sensing film in either reflection or transmission mode. pH sensitive dyes such as thymol blue, phenol red and methyl red have been used in the construction of optical fibre sensors for measurement of CO_2 [11]. The pH dyes change their colour as a result of changing the protonation status. Thus, such substances require the quaternary ammonium hydroxide as a phase transfer agent to convert gas phase CO_2 into liquid phase (carbonic acid) in order to provide the proton needed. The sensitivity of such sensors are governed by the pK_a value of the indicator, the ionic strength and the buffer concentration in the sensing film. The response of such sensors that contain pH indicators changes rapidly at the pK_a value of dye [12], thus the pH value of the solid sensing layer determines the response to CO_2. The indicator substances work only when they are dissolved in a matrix material such as silica gel. The matrix materials provide a scaffold for supporting the substances coated on the optical fibre and their porosity allows gas exchange between the environment of interest and the sensing film.

This paper investigates key steps required to turn these sensors into useful measurement tools in end tidal CO_2 monitoring and other healthcare applications, specifically in terms of sensor longevity, dye concentration, response time and cross sensitivity to humidity and temperature. A reflection mode optical fibre CO_2 sensor is reported by dip coating the fibre tip with CO_2 sensitive film which comprises thymol blue and phase transfer doped inside of Ormosil. The tip-based CO_2 sensor significantly reduces the size of the sensing area (125 μm diameter) and has more flexibility in real world application compared with evanescent field sensors previously proposed [7] (10 cm length of sensitive region). It has been reported that sensors based on pH sensitive dyes completely lose sensing capability after ~1 week which may be attributed to the thermal degradation of the quaternary ammonium hydroxide catalyst or photo bleaching of the dye compound [8,11]. It is demonstrated that appropriate storage methods can be used to significantly extend longevity. Cross-sensitivity to humidity was studied and an in house-made humidity filter was demonstrated to reduce humidity levels in breath from 90% to 40–50% enabling End-tidal CO_2 from the breath to be measured. Although the FOS is imperfect for measuring the End-tidal CO_2 from breath-to-breath, the technique world have in principle a number of advantages which we have referred to above (close to lung, non-electrical, not bulky, inexpensive) and future improvements are discussed.
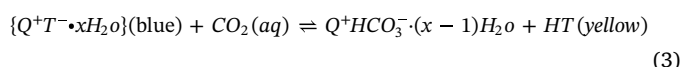
2. Materials and method

2.1. Materials

Tetraethyl orthosilicate (TEOS), triethoxymethylsilane (MTEOS), thymol blue, ethanol and tetramethylammonium hydroxide (TMAH) solution (10 wt%), calcium chloride anhydrous ($CaCl_2$) were purchased from Sigma-Aldrich, UK. Carbon dioxide (5% in argon mixture) was purchased from Ryvalgas, UK. Nitrogen (oxygen free) was purchased from BOC, UK.

2.2. Sensing mechanism for CO_2

Thymol blue, as a pH indicator, has two detectable ranges [13]. Its colour transitions from red to yellow when the pH rises from 1.2 to 2.8 and from yellow to blue at pH 8.0–9.2. The prepared porous silica sol-gel film doped with thymol blue and TMAH allows gas exchange between the film and atmosphere. The transition of colour during reaction of CO_2 can be explained by:

$$QOH + HT\ (red) \rightleftharpoons Q^+T^- \cdot xH_2o\ (\text{blue}) \tag{1}$$

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{2}$$

$$\{Q^+T^- \cdot xH_2o\}(\text{blue}) + CO_2(aq) \rightleftharpoons Q^+HCO_3^- \cdot (x-1)H_2o + HT\ (yellow) \tag{3}$$

where HT is the acidic form of thymol blue, QOH is TMAH, Q^+ is a tetramethylammonium ion and T^- is the deprotonated thymol blue molecule. $Q^+T^- \cdot xH_2o$ is the ion pair formed between acidic thymol blue and TMAH in the sol-gel film that causes the colour change from red to blue due to change of protonation status of thymol blue (Eq. (1)). Gas phase CO_2 (g) transitions into aqueous CO_2 (aq) when it permeates from outside into the matrix film. CO_2 (aq) reacts with the hydrated water molecule to produce a hydrogen ion that converts the T^- into protonated status HT as illustrated in Eq.(3) and the colour turns from blue to yellow correspondingly.

3. Method

3.1. Sensing film preparation

Ormosil was produced by mixing 200 μl of TEOS with 1.8 ml of MTEOS in a 20 ml volume of vial under stirring for 10 mins, subsequently adding 5 ml of ethanol and stirring for another 10mins. Six concentrations of solution mixture were made by adding 12/17/22/27/32 mg thymol blue into prepared Ormosil solutions for stirring of 15 mins. 500 μl of TMAH solution was dropwise added to each solution mixture, the vials are capped and stirred for 1.5 h prior to dip-coating. The final coating solutions that are prepared have dye (thymol blue) concentrations of 1.6/2.3/2.9/3.6/4.2 mg/ml.

The tip of an optical fibre with a diameter of 62.5/125 μm (F-CPL-M12855, Newport, UK) cleaved at 90° was dip coated using a home-made dip coater with withdrawal speed of 6 mm/s four times. A drying period of 2 mins between each coating was allowed. The coated fibres were left in ambient air for drying for 24 h before use.

3.2. Sensor characterization

The geometry of the coated film on the fibre tip was imaged and measured using scanning electron microscopy (SEM) (JEOL 7100F, UK). The fibre with the coated film was cut into a 4 cm length from the tip and mounted horizontally in SEM stubs. The sample was then coated with an 8 nm thick layer of Iridium using a sputter coater (Quorum and Polaron, UK) to increase the conductivity for electrostatic discharge.

For calibration of the FOS, the measurement chamber was initially filled with 100% dry N_2. The concentration of CO_2 in the chamber was

then built up step by step by regulating the CO_2 flow through the gas channel and allowing each step to stabilize for at least 5 mins. The reflection spectrum of the FOS and the CO_2 datalogger readings are recorded simultaneously with a frequency of 0.5 Hz and 0.05 Hz, respectively. The reflection value is defined as:

$$R = \frac{I_0}{I_1} \times 100\%$$ (4)

where I_1 is the intensity of light that is reflected from the tip when there is no film present and I_0 is the intensity of the light after interaction with the coated film. The absorbance is calculated from R using:

$$\text{Absorbance} = 2 - \log_{10} R$$ (5)

The reflection value at wavelength of 608 nm (highest absorption peak that has biggest amplitude change for sensing of CO_2) of the reflection spectrum was used as the optical signal. For the humidity cross-sensitivity test, the CO_2 and relative humidity level was initially brought down close to zero by filling up the chamber with dry N_2, and then flowing distilled water bubbled N_2 into the chamber to gradual increase the RH level step by step and maintain the CO_2 at an undetectable level (< 100 ppm). The sensitivity of the FOS is defined as the magnitude of the reflection change per unit of a given target analyte.

3.3. Experiment set up

The reflection absorption spectrum of the FOS was measured using the set-up illustrated in Fig.1a utilizing a multimode 1×2 optical fibre coupler (F-CPL-M12855, Newport, UK). A halogen light source (HL-2000, Ocean optics, UK) illuminates the tip and the reflected light is detected using a CCD spectrometer (USB 2000, Ocean optics, UK) which is connected to a computer for post processing.

The FOS is placed inside a gas chamber (15 cm (L) $\times$ 13 cm (W) $\times$ 8 cm (H)) which has an input channel and output channel for gas infusion and expulsion respectively. A commercial CO_2 data logger integrated with a humidity and temperature sensor (K-33 BLG, CO_2 Meter, USA) was positioned inside the chamber for calibration purposes. The concentration of CO_2 inside the chamber is regulated by mixing N_2 and CO_2 gas. For the humidity cross-sensitivity test, humidity is regulated by flowing humidified N_2/CO_2 created by bubbling the gas in distilled water into the chamber (Fig.1a). Very high humidity is created by adding 30 ml of distilled water to the bottom of the chamber for approximately 3 h, and then inserting the FOS into the chamber. An alternative set up used to measure response time replaces the gas chamber with a Tedlar bag (2 l, Sigma-Aldrich, UK) which was filled with CO_2 gas with concentration ~6% into which the FOS was inserted and removed.

For evaluating temperature effect on the FOS in response to CO_2, the FOS and the CO_2 data logger are placed inside a chamber that is initially filled with~6% CO_2. The chamber is then put into an oven with temperature programmed to increase from 25 to 40 °C (this range of temperature covers both ambient and physiological temperature of the human body).

Fig.1b illustrates the set-up for detecting CO_2 from human breath. The high level of humidity from breath sample needs to be reduced as it influences optical reflection spectrum and makes it difficult to interpret the measurements. More importantly, the humidity competitively reduces the permeability of CO_2 inside of film that reduces the intensity response of FOS. A heat and moisture exchanger (HME) (Clear-Therm™ 3, Intersurgical Ltd., UK) is connected to a mouthpiece used by a human volunteer to remove the condensation of moisture caused by the temperature change of breath gas from human body (37 °C) to ambient, a humidity filter is made by encapsulating 1.5 g of anhydrous $CaCl_2$ into a plastic venturi connector and connected to the HME. A Tedlar bag was used to collect the breath sample for sample analysis as illustrated in Fig.1b. The CO_2 data logger was sealed inside the bag as a reference

sensor. The evaluation of the home-made humidity filter was conducted by collecting the breath sample using the Tedlar bag through the HME without and with addition of anhydrous $CaCl_2$ for each three times. For quantitatively measuring the CO_2 from breath sample, the FOS was placed inside the Tedlar bag and the optical and reference CO_2 datalogger signals were recorded simultaneously during human volunteer breathing into the bag through the humidity filter.

Breath-to-breath measurement was conducted with a relatively slow breathing rate about 4 to 5 breaths per minute (BPM). The distal end of humidity filter is connected to a fitted Y-shape tube connector with the FOS mounted in the pathway of air flow (illustrated in Fig.1c).

4. Results and discussion

4.1. Characterization of FOS

Fig.2a shows an SEM image of the optical fibre tip with 4 layers of dip-coated film. It confirms that the film is successfully deposited on the tip of optical fibre with a film thickness of approximately 2.7 ± 0.1 μm. The reflected intensity at 608 nm decreases as each layer is deposited (Fig.2b) due to the higher absorption value caused by the thick film based on Lambert's law. A single dip coating is observed to have lower absorption value due to the thinner film. This is not suitable for the application as insufficient colour change is produced after interacting with CO_2. The absorption spectra of the FOS under CO_2 free (100% N_2) and 5% CO_2 are illustrated in Fig.2c. Two absorption peaks appear at wavelengths of 450 nm and 608 nm and the two peaks respond oppositely to the change of CO_2 concentration; the peak at 608 nm undergoes a decrease in the absorbance value at 5% CO_2 and the peak at 450 nm increases its absorbance value at 5% CO_2 atmosphere. Because the change of absorbance at wavelength of 608 nm is bigger than the wavelength of 450 nm, the wavelength of 608 nm is therefore used for the measurement of CO_2. As the reflection is correlated to the absorbance in Eq.(5), the reflection value of 608 nm is then used as the optical signal for the CO_2 measurement.

4.2. CO_2 measurement

4.2.1. CO_2 sensor response and repeatability

Fig.3a show a typical step response of the FOS (prepared using a thymol blue concentration of 4.2 mg/ml) to the concentration of CO_2 that was measured using the set-up shown in Fig.1a. The reflection intensity (at 608 nm) changes in accordance with the change of CO_2 concentration from the commercial CO_2 datalogger. The reflection of the FOS increases (absorbance decrease) with increasing CO_2 concentration from 0 to 60,000 ppm (6%). RH in the measurement chamber remains stable at a level of $13 \pm 1\%$ during the measurement of CO_2. The reflection intensity decreases as the CO_2 concentration decreases and the FOS exhibits a repeatable and reversible response as illustrated in Fig.3b. The reflection intensity is related to the CO_2 concentration via a polynomial as shown in Fig.3c. The FOS has a response time of 19 s when the FOS was exposed to a 6% of CO_2 atmosphere from ambient air (~400 ppm) and a recovery time of 170 s when the sensor is exposed to ambient air (Fig.3d). This indicates that the affinity for backward reaction of the equilibrium in Eq. (3) is lower than it is for the forward reaction.

4.2.2. Sensitivity with the concentration of dyes

Different concentrations of deprotonated dyes that are present in the Ormosil film provide different absorption values of the FOS. Fig.4 shows the response of FOS prepared from 5 different concentrations of thymol blue coating solution in response to different concentrations of CO_2. The result demonstrates that different concentrations of dye in the film will render different sensitivity that correlates well with the previously published reports on a different dye compound [20]. The sensitivity initially undergoes an increase and then a decrease with
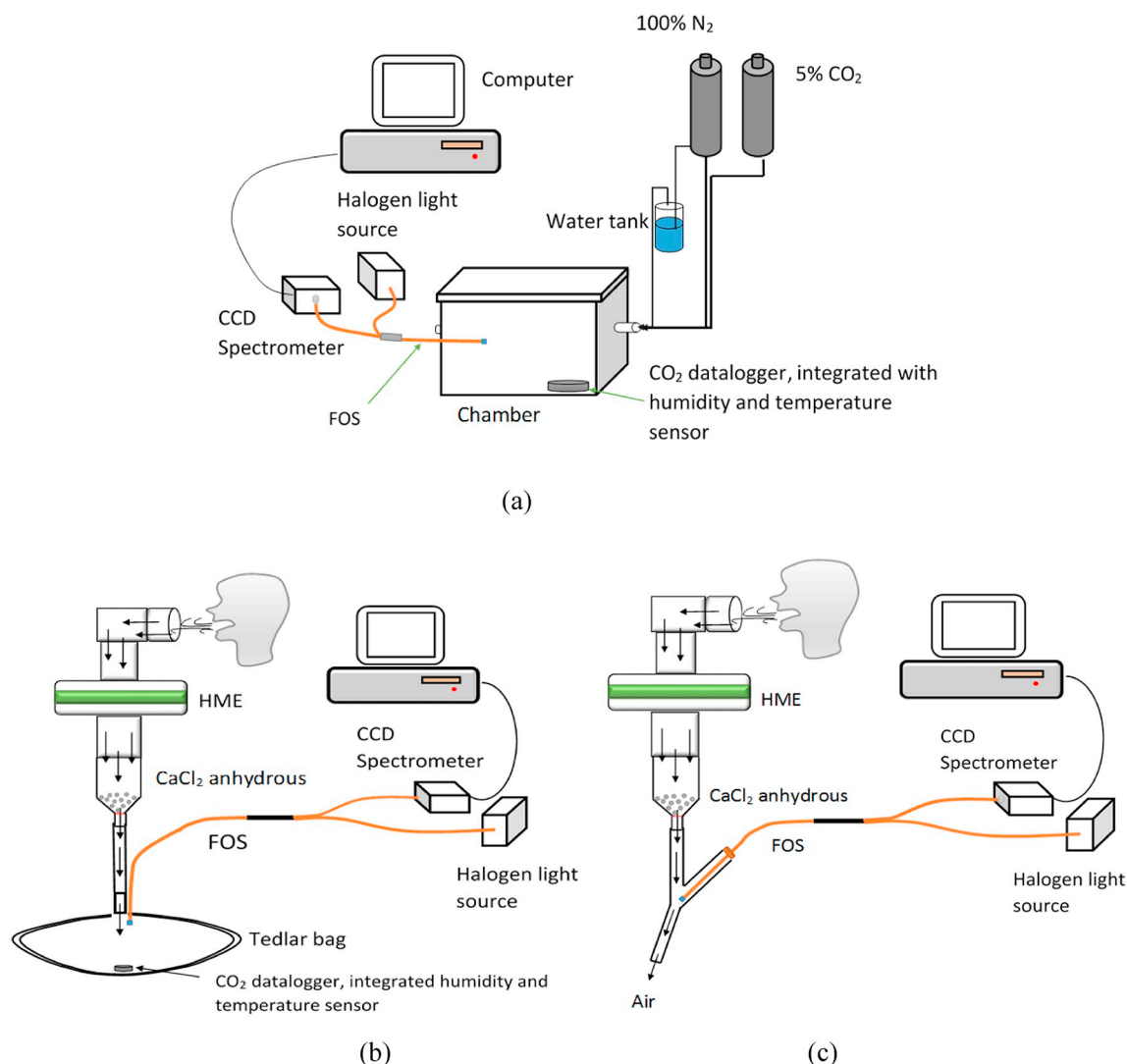
Fig.1. (a) Schematic of the experimental setup for FOS CO_2 calibration. Orange line - optical fibre. A commercial CO_2 datalogger was placed inside the chamber for recording the CO_2 and humidity inside of chamber. (b) Experiment set-up for breath CO_2 measurement using the developed FOS. The breath gas was filtered by the home-made humidity filter and collected by a Tedlar bag with commercial CO_2 datalogger and FOS sealed inside. Optical and datalogger signals were recorded simultaneously during breathing. (c) Experiment set up for breath-to-breath measurement using the FOS.

increasing the thymol blue concentration. The highest sensitivity is achieved with the concentration of 2.9 mg/ml. It reduces almost half after the concentration further increases. The concentration-dependent sensitivity may be explained by the limited solubility of the CO_2 in the silica film. When the concentration of the thymol blue above the optimal point, the excess of dye forms more hydrate molecule that reduces the permeability of CO_2 inside of the film. In this case, the CO_2 likely reacts only to out-layer of the film and reduces the sensitivity. The sensitivity in 4.2 mg/ml exhibits a slightly higher than that of 3.6 mg/ml, the reason of that remains unclear and one of the hypothesis is that the higher concentration of the thymol blue causes cracking in the silica film due to the limited dye solubility leading to higher gas permeability.

The selected dye, thymol blue has a $pK_a = 8.9$ which changes its colour for sensing of CO_2 as a result of pH change. The previous study has demonstrated that pH dyes whose pK_a is 7–9 are suitable for the CO_2 fibre-optic sensor [7]. It also demonstrated that the sensitivity of the dyes does not depend on the type of the dye if their pK_a value is within 7–9 [7].

4.2.3. Effect of humidity on sensor response

The reflected intensity increases as a result of protonation of thymol

blue during the measurement of CO_2. Humidity or water molecules containing protons may have the same protonation effect on the sensor. Moreover, the humidity existing in the CO_2 atmosphere may have either positive or adverse effect during the sensing of CO_2 depending on the pore size of the matrix film; the external water molecules existing in the pores of the Ormosil film may help to dissolve more CO_2 (promoting the reaction in Eq.(3)) due to the interaction of CO_2 with water molecules if the pore sizes are large enough to allow both humidity and CO_2 to freely travel without constraint. On the other hand, the water molecules could adsorb on the silica layer and block the transition of gas phase CO_2 (aq) from outside of film into CO_2 (aq) inside of the film (Eq. (2)). The effect of RH on the sensor response was therefore investigated. Fig.5 illustrates the reflection signal change with increasing the RH level in the chamber (set-up in Fig.1a) without and with CO_2 present. It shows that the reflection increases while increasing the RH level from 0 to 30% as the water molecule protonates the thymol blue. The reflection value remains stable while the RH concentration rises up to 62%. This is probably due to the saturation of humidity inside of the pore of the film above 30% RH. A drop of reflection at RH level above 70% is observed in the experiment which is caused by a reduced light reflectivity from the film that is due to the condensation of humidity on

(a)

(b)

(c)
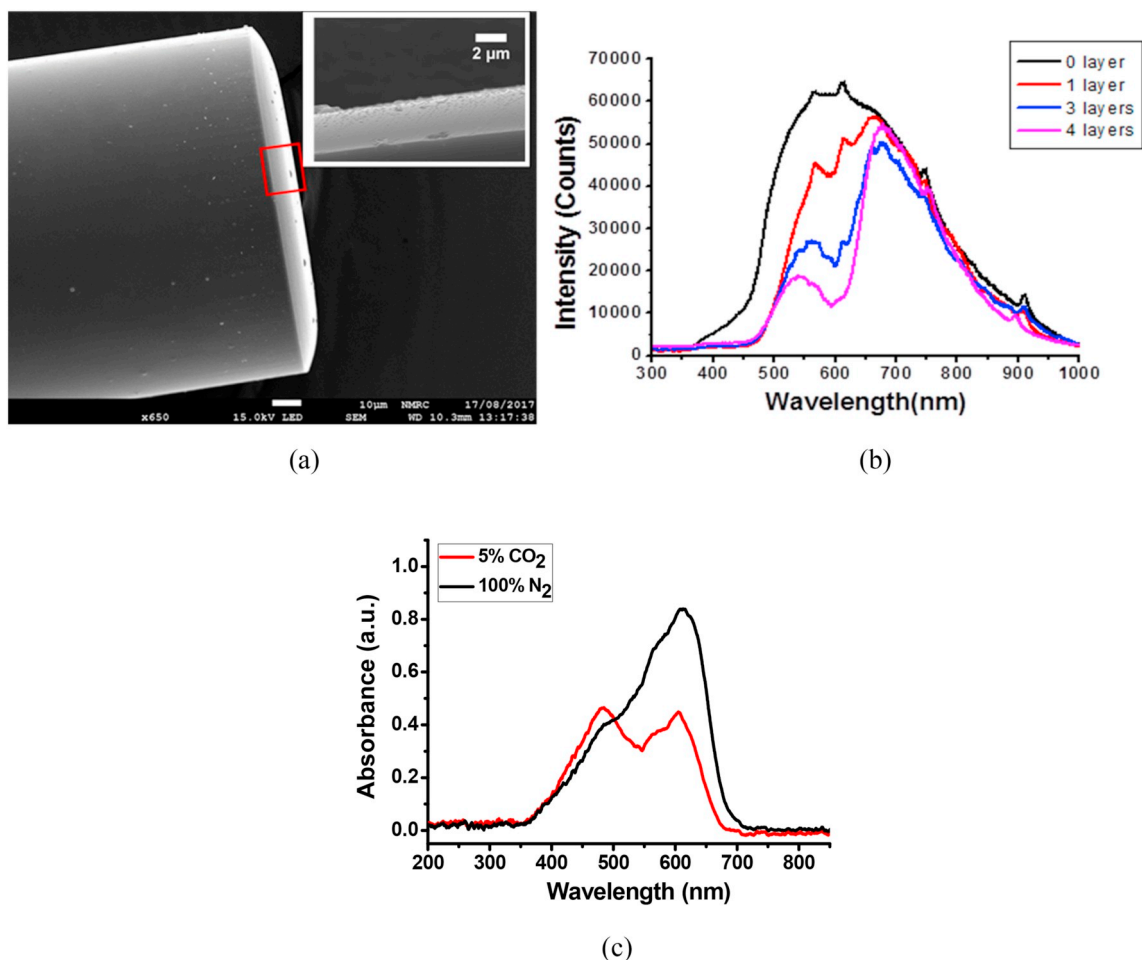
Fig.2. (a) SEM of the 4 layer dried film on the tip of optical fibre; the average film thickness measured at 10 different positions on the film in the inset is 2.78 ± 0.1 μm. (b) Reflection spectrum of FOS for 0 layer, 1 layer, 3 layers and 4 layers coating after drying. (c) Absorption spectra of FOS under N_2 and CO_2 atmosphere; FOS was coated with 4 layers and dried in air for 24 h. The absorbance value is calculated as Eq.(5).

the sensor surface or the accumulation of humidity inside the pores of the film. This effect limits the application of such sensor in very high humidity levels.

The CO_2 permeates into the Ormosil film and make interaction with the dye-ion pair producing reflection signal change. The sensitivity of such sensor depends on the permeability of CO_2 to the Ormosil film. Water molecules have higher permeability in the Ormosil film [14] that may reduce the permeability of CO_2 due to selective absorption by the silanol group (Si-OH) of the Ormosil film and a blocking effect to the pore gas channel. This effect highly depends on the pore size of film, drying condition of the film and gas pressure [15]. A high temperature (200 °C) annealing process can significantly reduce the number of silanol groups, but such high temperature will degrade the base catalyst (TMAH) resulting in insensitivity to CO_2 [7]. A decrease of reflection value at 6% of CO_2 while increasing the RH concentration (up to 50%) is observed confirming the blocking of humidity to the permeability of CO_2 (Fig.5). The magnitude of the signal change would be (incorrectly) interpreted as a CO_2 change of 2700 ppm (calculated from the yellow trace in Fig.4a).

4.2.4. Effect of temperature on sensor response

The dissolution of CO_2 in the coated film (Eq.(2)) obeys Henry's gas law, which defines the solubility of CO_2 in water according to the partial pressure of gaseous CO_2. As Henry's law constant is a temperature and pressure dependent parameter, it renders different CO_2 solubility at different temperature [16]. Besides, the dissociation constant of carbonic acid in Eq.(3) is also temperature dependent [17], it

increases as increasing of temperature at a temperature below 100 °C [18]. Consequently, it may also affect the pH value (high temperature, low pH) and the measurement of CO_2. The temperature effect of FOS to the measurement of CO_2 is, therefore, investigated. Fig.6 illustrates the reflection intensity of FOS at ~6% of CO_2 with increase of temperature from 25 °C up to 40 °C. During the measurement, the temperature that is read out from the data logger linearly increases and the reflection value exhibits a gradual decrease. The small reduction in the reflection attributes to the decline of the concentration of CO_2 that is caused by the imperfect sealing of the chamber. This change in CO_2 is also seen in the data logger. Therefore, the CO_2 measurement of FOS can be considered immune from temperature effect at 25–40 °C.

4.2.5. FOS stability

The sensing film will gradually become less sensitive due to degradation of base catalyst (TMAH) due to thermal degradation or the toxicity of air to the film. Previous research has demonstrated that this occurs after approximately 1 week [8,11]. It is therefore important to investigate methods of extending the lifetime of such films so that they can find practical application. Fig.7 shows the reflection value of two FOS during after storage in N_2 (CO_2 and humidity free) and ambient air atmosphere, respectively. It can be seen that the reflection of the sensor stored in ambient air gradually increases and most absorption is lost after 10 days after which sensitivity to CO_2 is lost. The FOS stored in N_2 exhibits a relatively stable reflection value compared to air storage and provides an extended lifetime. The storage method in N_2 creates isolation from the factors that could potentially degrade the pH of the film,
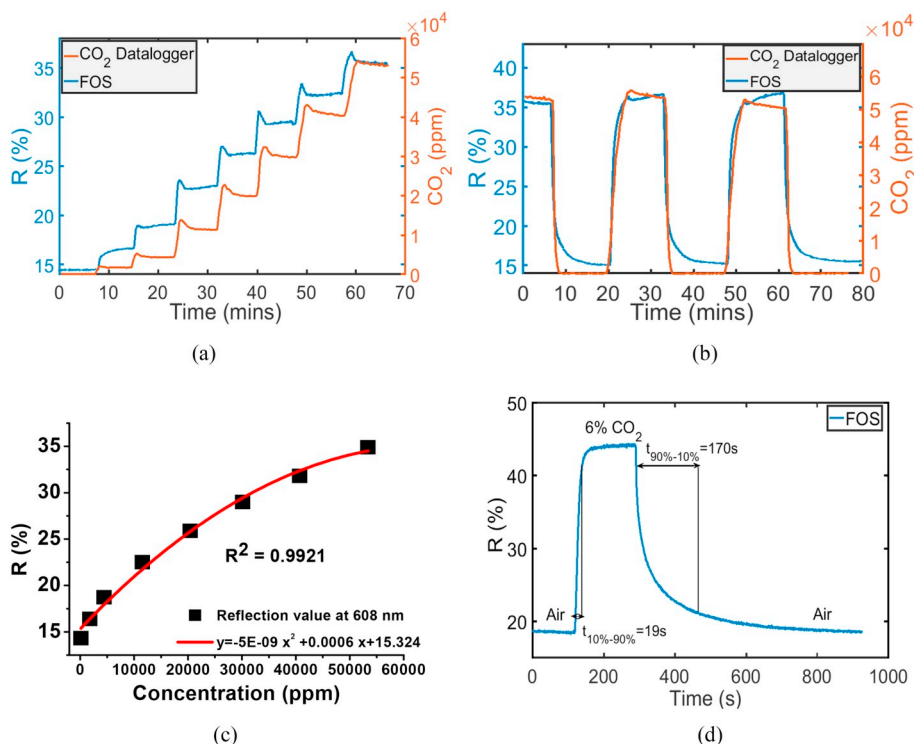
Fig.3. (a) Response of FOS to different concentrations of CO_2. CO_2 reading was achieved from a commercial CO_2 datalogger. (b) Reversibility of FOS to the concentration of CO_2. (c) Polynomial fitting of reflection value of FOS to the concentration of CO_2. Each point represents the average value of each stabilized step in (a), the error bar is smaller than the marker size. (d) The response time measurement of FOS for 6% CO_2. The response time and recovery time are calculated as the time between the signal change between 10% and 90%.
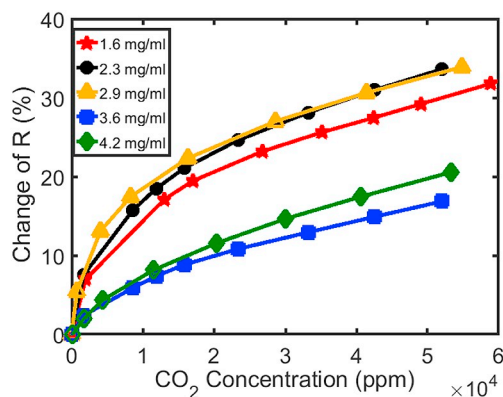
Fig. 4. Reflection change at wavelength of 608 nm against the concentration of CO_2 for different concentrations of thymol blue. Error bars are smaller than the marker size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
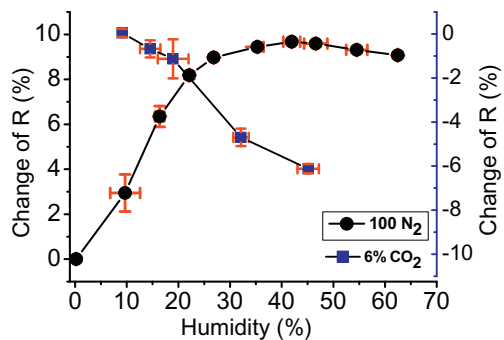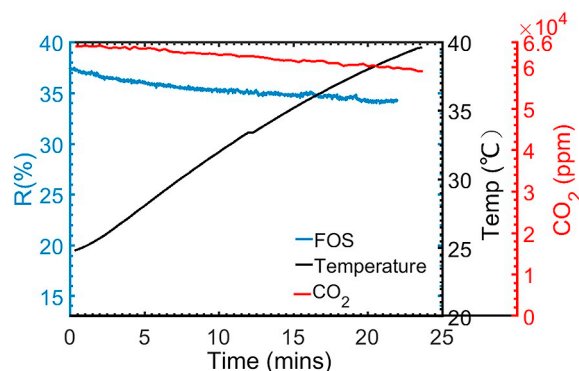

Fig. 6. FOS at CO_2 atmosphere in response to temperature variation.
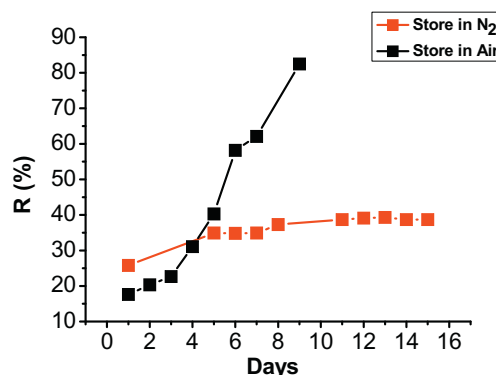
Fig. 7. Reflection value of FOS for consecutive days under N_2 and air storage condition.

Fig. 5. Change of reflection signal at wavelength of 608 nm against the relative humidity at low atmosphere CO_2 level (< 100 ppm) and 6% CO_2 level.

i.e. CO_2 and humidity. The sensor repeatedly exhibits a response to CO_2 after storage in N_2. For the sensor that loses its sensitivity in air, the sensitivity can be retrieved by immersing the sensor into a TMAH solution that changes the pH of the film. However, this process does not
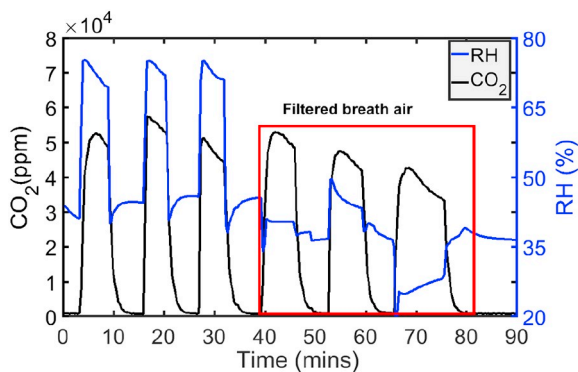
Fig. 8. The performance of the humidity filter; The first three spikes represent the three times breath sample collection without addition of the humidity filter, the last three spikes are the three times collection of the filtered breath sample. Both RH and CO_2 readings are achieved from the commercial CO_2 data-logger.

return the sensor to its baseline, and it is very unstable and sensitivity is lost very quickly (~1 h). This is because the base catalyst from the immersion process only interacts with part of the dye in the film which also decomposes after drying. In order to retain the base catalyst for CO_2 sensing, it has to be doped inside of the silica film before the film is formed.

4.3. Breath CO_2 measurement using FOS

The air exhaled from breath contains CO_2 and high humidity, which will condense as the air cools from body temperature to ambient. A filter containing calcium chloride anhydrous was used to reduce water molecules from the breath (illustrated in Fig.1b). The breath samples are collected from a healthy human using the set-up shown in Fig.1b and characterized using the commercial CO_2 data-logger. They contain 5% CO_2 and 70% RH (illustrated in Fig.8) when no $CaCl_2$ anhydrous was added in the plastic connector. Such high RH levels of the breath will make the measurement of CO_2 inaccurate. The RH level is reduced to an ambient level (ca.40%) after the $CaCl_2$ anhydrous powder was added. Meanwhile, the CO_2 level is maintained at the same level before filtering. The use of a humidity filter ($CaCl_2$ anhydrous) reduces the humidity level from breath and allows the FOS operate. Fig.9a illustrates the reading from the CO_2 data-logger during the breath sample collection with the application of $CaCl_2$ anhydrous and the FOS inside the Tedlar bag. The CO_2 concentration goes up gradually to about 5%, the time it takes to reach the stabilized value (5%) includes the process
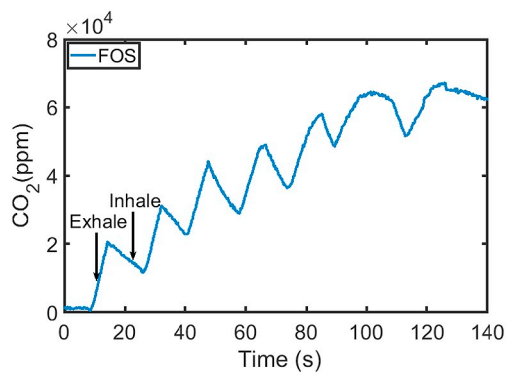
Fig. 10. FOS response of the measurement for breath-to-breath; the breathing rate was about 4 BPM.

of breath and gas sample diffusion. The average RH level remains almost unchanged before and after the breath. The CO_2 reading that is interpreted from the response of FOS as compared to the reading from the CO_2 data-logger is illustrated in Fig.9b. It is shown that the FOS takes less time to stabilize than the CO_2 data-logger, and the CO_2 reading from FOS shows a comparable result of 4.9% compared with the 5.0% from datalogger (percentage error of 3%). Fig. 10 illustrates the FOS response to the breath-to-breath measurement by using the set-up in Fig.1c. The FOS responds to each breath trace, the reflection value at 608 nm increases during exhalation and decreases during inhalation. However, the reflection value does not return to baseline after each breath and gradually increases with each breath which indicates an accumulation of CO_2 inside the sensor film.

The FOS exhibits a good agreement in terms of CO_2 measurement from one time breath sample and with a faster response time compared with the commercial CO_2 datalogger. However, due to the limitation of response time (19 s) and longer recovery time (170 s), the sensor did not show the capnography CO_2 pattern from breath-to-breath due to the insufficient interaction time of CO_2 with the film for each breath. This is the intrinsic limitation of the sensor. Therefore, the sensor is ideally applied to measure the CO_2 when the response time is not critical such as the measurement of CO_2 from a breath sample or to measure the CO_2 released from skin. In emergency medicine outside of hospital, some procedures are required to be done rapidly without the support of clinical devices in hospital due to their bulky size. The developed FOS has the potential to be integrated into a cheap, compact device for emergency medical support by simply replacing light source and spectrometer with a LED and photodetector. It can be used for
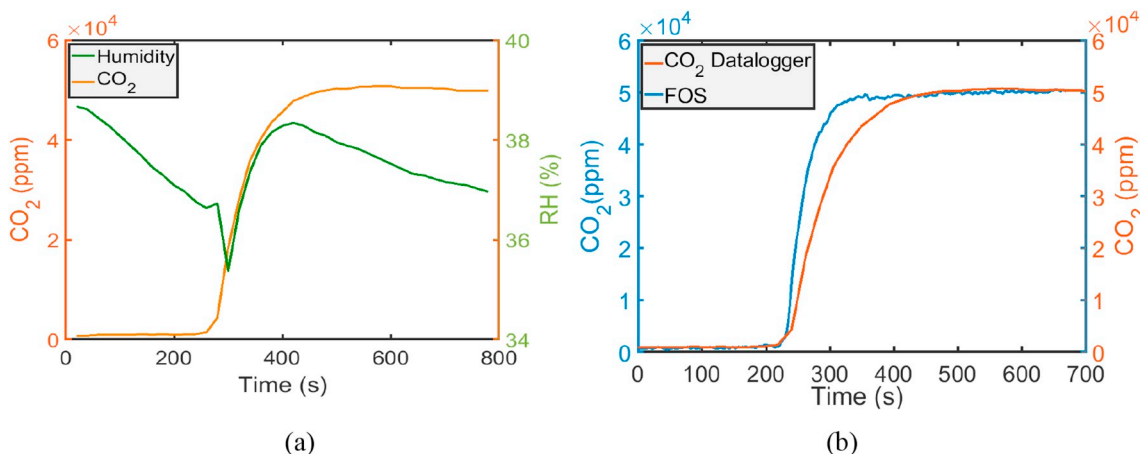
Fig.9. (a) Breath sample measured using CO_2 and humidity data-logger; (b) FOS and datalogger comparison. The CO_2 concentration of the FOS was obtained from the calibration curve illustrate in Fig.3c.

supporting the diagnosis of endotracheal intubation during emergency procedures and providing quantitative readings to facilitate control of CO_2 over time. Further work can be carried out by reducing the volume of the film which may reduce the time of CO_2 diffusing into film, but a higher dye concentration is likely to be used for producing sufficient colour change for compensating the reduced film thickness. Drying the film at supercritical condition will leads to a highly porous silica aerogel film which may also help to improve the sensor response time [19].

5. Conclusion

A reflection mode optical fibre CO_2 sensor is fabricated by dip coating a film that contains Ormosil doped with thymol blue and tetramethylammonia hydroxide. The colorimetric sensor showed a decrease of absorption value at wavelength of 608 nm when CO_2 concentration increases. The sensitivity of the FOS depends on the concentration of deprotonated dye inside the film. The optimal concentration of dye in coating solution was found to be 2.9 mg/ml. The sensor shows a gradual reduction in reflection value with each day after it was fabricated with a complete loss after 10 days when storing in ambient air. This can be significantly improved by storing the sensor in pure nitrogen in which the sensor showed a relative stable reflectivity and an extended shelf life ($>$ 15 days).

The sensor shows no interference with temperature for the tested range (25 to 40 °C), but is sensitive to humidity. A home-made humidity filter was made from anhydrous $CaCl_2$ for filtering breath samples and reducing the humidity levels to ambient. The FOS exhibited measurement of CO_2 from breath sample that was comparable to a commercial datalogger, but failed to achieve capnography during the breath-to-breath measurement due to the long response time (19 s) and recovery time (170 s). The FOS is therefore not yet able to replace IR methods for routine breath to breath monitoring in the operating theatre or intensive care settings. However, the reported FOS is suitable for measuring the CO_2 in the application where the response time is less important and the principle exhibits potential of making a low-cost, portable and quantitative CO_2 sensor for the supporting endotracheal intubation in the emergency medicine.

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