



Optical fibre long period grating gas sensor modified with metal organic framework thin films

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ABSTRACT

An optical fibre long period grating (LPG) modified with a thin film of ZIF-8, a zeolitic imidazol framework material and a subgroup of metal organic framework family, was employed for the detection of organic vapours. ZIF-8 films were deposited onto the surface of the LPG using an in-situ crystallization technique by mixing freshly prepared 12.5 mM zinc nitrate hexahydrate and 25 mM 2-methyl-imidazole solutions in methanol. The ZIF-8 film was characterized by scanning electron microscopy. The thickness and refractive index (RI) of films deposited after 1,2,3,5 and 10 growth cycles were determined by using an ellipsometer. The crystallinity of the films was confirmed by X-ray diffraction pattern. The LPG was designed to operate at the phase matching turning point to provide the highest sensitivity. The sensing mechanism is based on the measurement of the change in the RI of the film induced by the penetration of the chemical molecules into the ZIF-8 pores. The responses of LPGs modified with 2 and 5 growth cycles of ZIF-8 to exposure to methanol, ethanol, 2-propanol and acetone were characterised. The sensitivity of the measurements to humidity as an interfering parameter was also investigated.

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1. Introduction

Although numerous portable chemical sensors already exist, there is still a place and need for new technologies. New sensors could target the demand in areas of medical diagnostics, food quality control, in the monitoring of air quality (occupational exposure) and in various fields of environmental monitoring [1]. The fabrication of low-cost, portable, precise and real-time sensors for volatile organic compounds (VOCs) is of considerable interest as the gas chromatography – mass spectroscopy (GC-MS) approach used commonly for total VOCs detection is expensive and needs experienced personnel [2]. The key element of any portable chemical sensor is the sensitive layer that captures the analyte.

In this respect, metal organic frameworks (MOFs), because of their unique properties, offer an ideal platform for the development

of the sensitive layer. They can be considered as crystalline materials with tuneable porosity, large internal surface area and organic functionality. The strong metal–oxygen–carbon bonds imbue the materials with high chemical and thermal stabilities [3].

The applications of MOFs have been reviewed elsewhere [4–6], where main focus of their use is given to be selective hydrogen gas storage [7], selective gas adsorption [8], and separation [9] or catalysis [10].

The ability to adjust the pore size and to perform post-synthesis functionalization enables the development of MOFs that offer specific reactions with an analyte of interest, where only certain molecules (treated by size or functional group) are allowed to enter into the MOF's cavities. The initial research was based on the fabrication of a number of materials from the MOF family. Fabrication of these materials in the form of thin films is considered to be crucial for many applications, especially for sensors and membranes [1,11]. The fabrication of the films is challenging, particularly in ensuring uniform cover over the substrate and in providing control over the thickness and growth direction of the crystals [11].

There have been limited reports of MOF based sensors, but they indicate their potential to become powerful analytical devices [1].

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The main advantage is the high chemical selectivity possible by the selection of the MOF with appropriate properties [5]. However, there is a need to establish a suitable means of signal transduction to enable the use of MOFs for chemical sensing [12]. The pores for all MOF structures are scaled in Angstroms, which makes it difficult to measure the individual response from each pore and crystal. The most promising approach appears to be the adoption of a macroscopic perspective and to analyse changes in the properties of the whole film. This can be achieved by the use of optical transduction techniques, which requires the fabrication of a film, ideally with controllable thickness, on an optical sensing platform such as optical fibre sensors.

Among the variety of MOFs, zeolitic imidazole framework (ZIF)—ZIF-8 possesses properties that show promise for sensor development, such as its chemical robustness and thermal stability due to the sodalite (SOD) type of structure. The structure of ZIF-8 comprises zinc ions coordinated by four imidazolate rings with large cavities (11.6 Å) and small pore apertures (3.4 Å) [13], Fig. 1. ZIFs have been considered to behave as adsorbents with molecular sieving properties. An investigation of a ZIF-8 film demonstrated the adsorption of isopropanol in a selective manner versus water [14]. A ZIF-8 based Fabry–Pérot interferometer exhibited a concentration-specific reaction to a mixture of propane and nitrogen [12]. ZIF-8 film fabrication involves no substrate modification. The procedure works at room temperature and facilitates control over the thickness with one growth cycle that takes less than an hour [12,15].

Fibre-optic sensing platforms are small, lightweight, immune to electromagnetic interference and as such can be used in extreme conditions, enabling remote real time monitoring with no electrical power needed at the sensing point [17]. Fibre-optic sensing platforms based on long period gratings (LPGs) modified with appropriate functional coatings have been used to measure various measurands including relative humidity [18], ammonia [19] and volatile organic compounds (VOCs) [20]. In addition, when the proteins, enzymes and antibodies are incorporated, then optical fibres can be used for biological response measurement [21]. Among the various techniques used for the deposition of the sensitive element, layer-by-layer assembly is considered to be highly versatile, enabling control over the structure of the deposited material. This technique can be used to deposited a wide range of materials onto a range of substrates and represents a cheap, simple and rapid approach for the thin film deposition [22].

An LPG consists of a periodic perturbation of the refractive index of the core of an optical fibre, which couples the core mode to a set of co-propagating modes of the cladding of the fibre. This coupling is manifested in the transmission spectrum of the optical fibre as a series of loss, or resonance bands. Each resonance band corresponds to coupling to a different cladding mode and each shows different sensitivity to environmental changes [23].

The coupling wavelength can be obtained from the following phase matching equation

$$\lambda_x = [n_{\text{core}} - n_{\text{clad}(x)}] \Lambda \quad (1)$$

where λ_x represents the wavelength at which light is coupled to the LP_{0x} cladding mode, n_{core} is the effective refractive index of the mode propagating in the core of the fibre, $n_{\text{clad}(x)}$ is the effective index of the LP_{0x} cladding mode and Λ is the period of the LPG [23]. The central wavelength of the resonance band is sensitive to changes in environmental conditions such as strain, temperature, bending radius and refractive index of the surrounding conditions [19,23].

It has been shown that the phase matching condition for each cladding mode contains a turning point and that the LPG exhibits the highest sensitivity when phase matching turning point (PMTP)

is reached, which can be achieved by choosing the appropriate grating period and coating thickness [20,24].

In this work, an LPG based chemical vapour sensor was fabricated, using ZIF-8 as the functional coating. The ZIF-8 films were characterized by scanning electron microscopy (SEM). The thickness and refractive index (RI) of films containing of 1, 2, 3, 5 and 10 growth cycles were determined using an ellipsometer. The crystallinity of the films was confirmed by X-ray diffraction pattern (XRD). An LPG coated with a ZIF-8 thin film was exposed to methanol, ethanol, 2-propanol and acetone vapours, revealing a specific response to methanol. The response to water, a potential interfering measurand, was also investigated.

2. Experiment

2.1. Materials

Zinc nitrate hexahydrate, 2-methyl-imidazole, methanol, ethanol, 2-propanol and acetone were purchased from Sigma-Aldrich. All of the chemicals were analytical grade reagents and used without further purification.

2.2. Characterization of ZIF-8 film

2.2.1. SEM characterizations of film morphology

SEM was used to evaluate the structure and the thickness of the films deposited on glass substrates. Measurements were undertaken by Philips XL30 FEG ESEM electron microscope with 10 kV beam voltage. Glass slides of dimensions $1 \times 1 \text{ cm}^2$ and $2 \times 2 \text{ cm}^2$ were cut from standard microscope glass slides and then coated with ZIF-8 thin films, following the procedure described in Section 2.2. Samples coated with films consisting of 1, 2, 3, 5 and 10 growth cycles of ZIF-8 were characterized by SEM.

Thin Pt layers were sputtered on all samples before the SEM analysis. The sputter was set to 0.8 kV voltage and 0.7 mA current. The glass slides were sputtered by two layers of the Pt coating, with a deposition interval of 90 s.

2.2.2. Ellipsometry measurements

The thicknesses of the films on the glass substrates were further evaluated using an ellipsometer. The measurements were undertaken using an Alpha-SE Ellipsometer (JA Woolan) and the data processed using a model assuming a transparent film on a glass substrate. Data were collected at a spectral resolution of 1 nm and measured in the wavelength range of 380–900 nm; for simplicity the RI value of the mesoporous film was determined at one wavelength (632.8 nm).

2.2.3. Crystallographic analysis

X-ray diffraction patterns were collected using a Bruker-AXS D8 Advance diffractometer, using θ/θ goniometer geometry, a Cu-anode line-focus X-ray tube (powered at 40 kV & 35 mA), a Göbel mirror (producing a parallel Cu $K\alpha$ beam) with a 0.6 mm exit slit, a diffracted beam 0.12° Soller-slit collimator and a scintillation counter X-ray detector. The samples were scanned with a fixed glancing incident angle of 2.140 and 1.140°, over a 2θ range of 5° to 40°, with a 2θ step size of 0.02° and a step time of 32 s.

2.3. Sensor fabrication

LPG with grating period of 110.7 μm and of length 40 mm, was fabricated in a point-by-point fashion in boron–germanium co-doped optical fibre (Fibercore PS750) with cut-off wavelength 670 nm, side-illuminating the optical fibre by the output from a frequency-quadrupled Nd:YAG laser, operating at 266 nm [25].

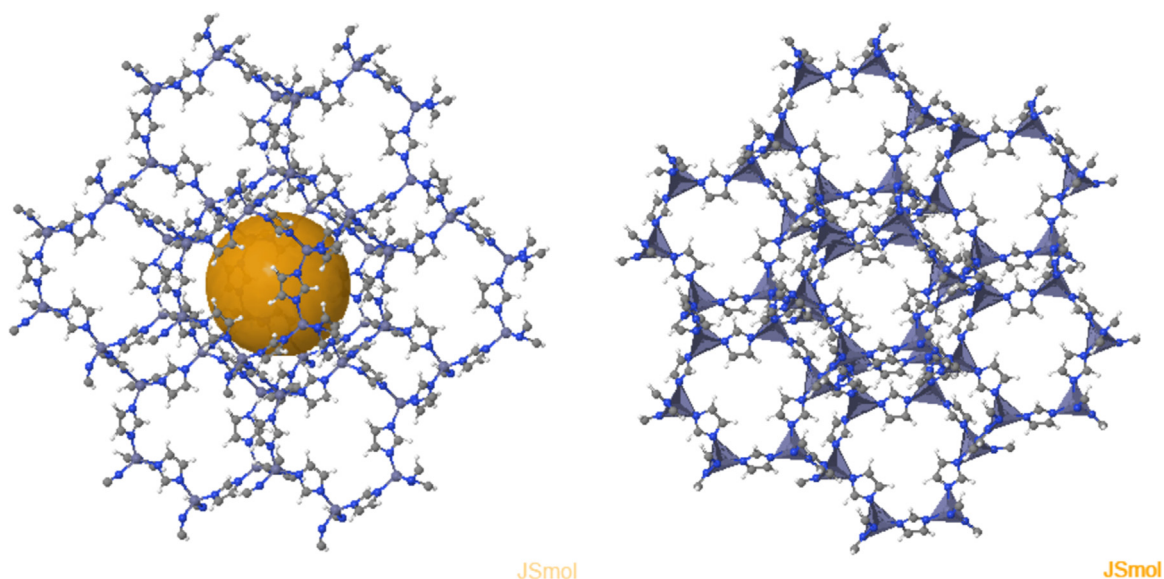


Fig. 1. ZIF-8 3D structure (the tetrahedra show the zinc–nitrogen bonds)/(the sphere represents the pore size within the framework which can be used for gas storage) [16].

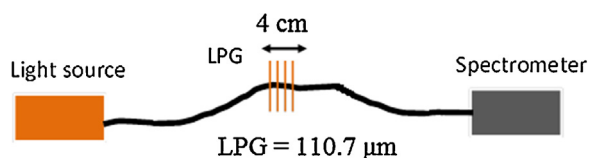


Fig. 2. Schematic illustration of the LPG sensor.

The transmission spectrum of the optical fibre was recorded by coupling the output from a tungsten-halogen lamp (Ocean Optics HL-2000) into the fibre, analysing the transmitted light using a fibre coupled CCD spectrometer (Ocean Optics HR4000), Fig. 2. The resolution of the spectrometer was 0.13 nm. The grating period was selected such that the LPG operated at or near the phase matching turning point [20,24], which, for coupling to a particular cladding mode (in this case LP_{019}), ensured optimized sensitivity.

2.4. Sensor modification

LPG was coated with ZIF-8 by an in-situ crystallization technique, Fig. 3 [12,15].

Briefly, solutions of 15 ml of 12.5 mM zinc nitrate hexahydrate and 15 ml of 25 mM 2-methyl-imidazole in methanol were mixed in a Petri dish. The LPG was fixed in a specially designed holder to keep the LPG taut and straight. The LPG was placed inside the Petri dish and immersed into the film forming solution for a period of 30 min. Then the LPG was washed by methanol and dried under nitrogen flow. The process was repeated to obtain thicker films consisting of 2 and 5 growth cycles. The transmission spectrum of the LPG was monitored during each deposition step.

2.5. Sensor performance

The performance of the coated LPG as a chemical sensor was investigated by monitoring the central wavelengths of the resonance bands while exposing the sensor to methanol, ethanol, 2-propanol and acetone vapours. VOCs samples of volume of 200 μ l were injected by pipette into a container containing the LPG (Fig. 4). The transmission spectra were monitored with acquisition interval of 10 s. A water droplet was also injected for comparison, with the aim of investigating the response to relative humidity, a potential interfering factor.

The response of the LPG to methanol was investigated with the fibre positioned in an environmental chamber composed of closed polytetrafluoroethylene (PTFE) box ($15 \times 15 \times 15$ cm). The LPG was fixed 5 cm above the base. Methanol (of volume 10 or 50 μ l) was injected from the top of the box by pipette and the transmission spectrum was monitored and recorded. The concentration was calculated according to the amount of methanol injected and the volume of the box.

Temperature and relative humidity (RH) were also recorded during all experiments with logging interval of 10 s by data logger (iButton® Hygrochron Temperature/Humidity Logger, part number DS1923, from Maxim Integrated™ with precision of $\pm 0.5^\circ\text{C}$ and ± 0.6 RH%) and a temperature resolution of 0.5°C .

3. Results and discussion

3.1. Film morphology

The SEM images allow an assessment of the coverage of the glass-slide substrate and of the uniformity of the thickness of the deposited ZIF-8 film, Fig. 5a. The density of the crystals over the substrates is affected by the concentration of the film forming solution, while the selected one (12.5 mM for Zn source and 25 mM methyl-imidazole) has been considered to be optimal [15].

The horizontal size of the crystals in the ZIF-8 film was observed to increase as a function of growth cycle, starting at approximately 100 nm and ending at 400 nm, in films of 1 and 10 growth cycles, respectively. This effect was observed through substrates coated with 1, 3, 5 and 10 growth cycles (Fig. S1) and it could be denoted by the agglomeration of the freshly crystallized ZIF-8 units onto the surface of the existing ones, in a similar way to that described for the seeded growth fabrication technique [11]. The increase of the crystal sizes with increasing number of growth cycles has been observed previously for substrates comprised of 1, 10 and 40 growth cycles [12].

Lu and Hupp characterized the surface area by applying the Brunauer–Emmett–Teller equation and obtained surface value $S_{\text{BET}} = 1530 \text{ m}^2/\text{g}$ and the micropore volume $V_{\text{micro}} = 0.59 \text{ cm}^3/\text{g}$ (estimated by SF method) [12]. As the same fabrication procedure has been followed here similar characteristics were expected.

The film thickness was evaluated with use of cross-sectional SEM imaging. A film consisting of 10 growth cycles has a thickness

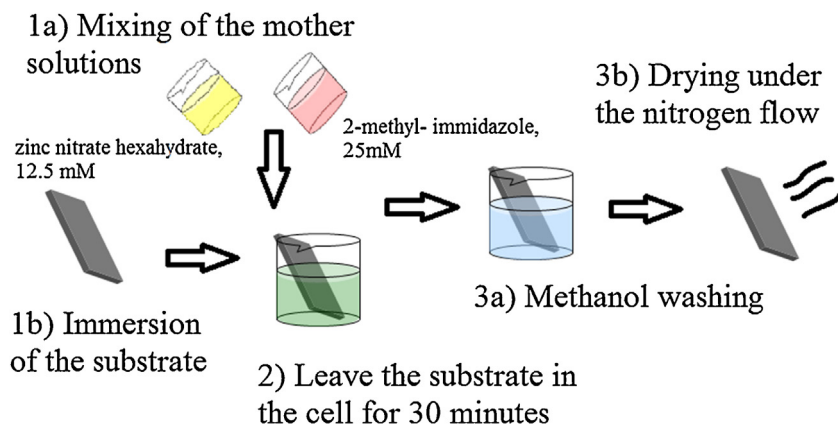


Fig. 3. ZIF-8 fabrication methodology [12].

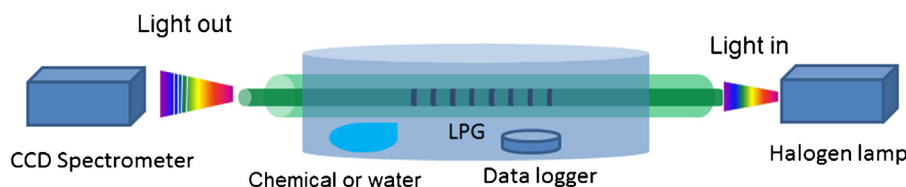


Fig. 4. Experimental set-up for chemical sensitivity experiments.

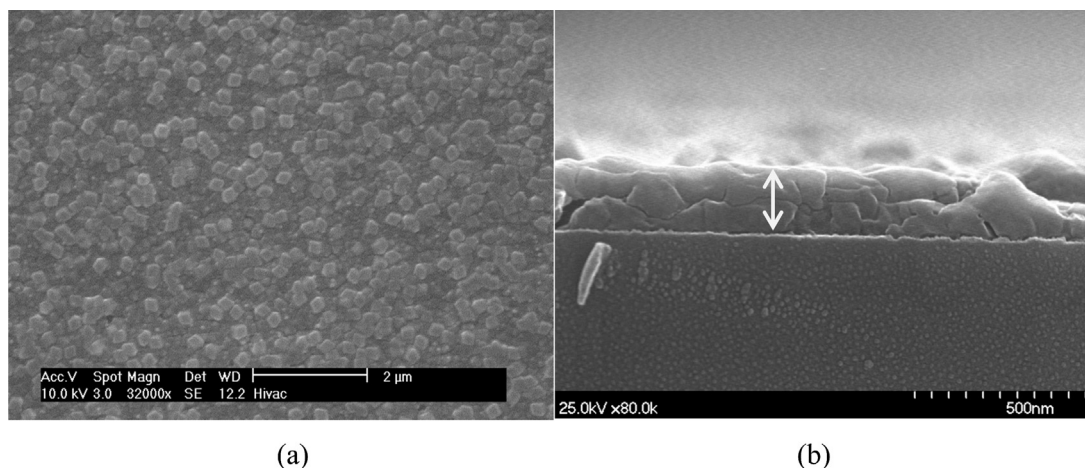


Fig. 5. (a) Top view and (b) cross sectional SEM images of ZIF-8 films grown on glass substrates with 5 and 10 growth cycles, respectively.

of about 400 nm, Fig. 5b, which is approximately about half of the level presented earlier with the use of the same deposition method [12]. This could well be due to the differences in the nitrogen flow rate or the exact vertical position of substrates in the Petri dish during the crystallization process in the film forming solution.

Ellipsometry measurements were conducted to investigate further the thickness of the substrates coated with 1, 2, 3, 5 and 10 growth cycles. A linear dependence of the MOFs film thickness on number of the deposited cycles was obtained with the slope of approximately 50 nm per growth cycle, Fig. 6. These results correspond well with the data obtained using SEM images (in Fig. 5b).

The RI of the coating was measured by ellipsometry and a non-linear relation between growth cycle and RI was observed. RI values varied from 1.48 to 1.40 for a film composed of 1 and 10 growth cycles, respectively (Fig. 6b). Interestingly, this change corresponds to the size of the crystals (Fig. S1). Larger crystals were observed on the substrates at the higher number of growth cycles which could denote presence of larger mesopores in the film structure [26]. Refractive index of ZIF-8 films depends strongly on the selected

crystallization method and conditions during fabrication. Large variations in RI values have been reported previously. Demessence et al. reported ZIF-8 films with RI ranging from 1.18 and 1.23 [14]. On the other hand, Cookney et al. obtained ZIF-8 films with much higher RI ranging from 1.54 to 1.58, which was related to the low porosity of these films [26].

3.2. Film structure

X-ray diffraction patterns establish that the films comprised ZIF-8 crystals, Fig. 7. The positions of the peaks (1 1 0), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (3 2 2) indicate a crystalline ZIF-8 structure. The highest intensity, at the (1 1 0) reflection peak, suggests that the orientation of the crystals is perpendicular to the substrate. The elevated plateau from 15 to 40 $^{\circ}$ relates to the amorphous structure of the glass substrate. The position and the intensity of the peaks in Fig. 7 are in a good agreement with the X-ray diffraction patterns presented in the literature and as well with the modelled diffraction pattern for ZIF-8 [12,27].

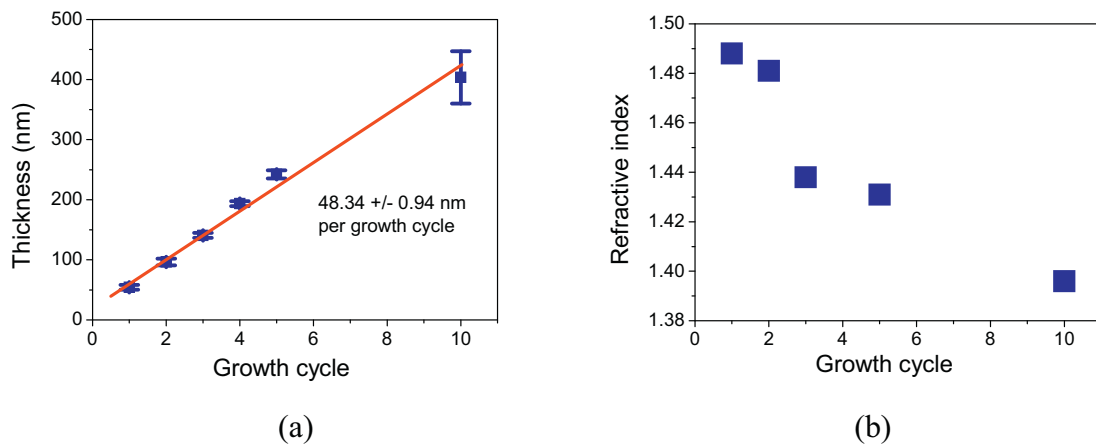


Fig. 6. Ellipsometry measurement: thickness of ZIF-8 film as a function of growth cycle (average value is shown and error bars were calculated as the standard deviation from the measurement over the three samples).

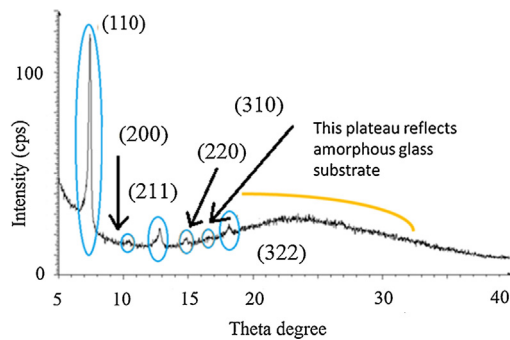


Fig. 7. In-plane X-Ray diffraction patterns of 20 growth cycles of ZIF-8 film on glass substrate, recorded at room temperature.

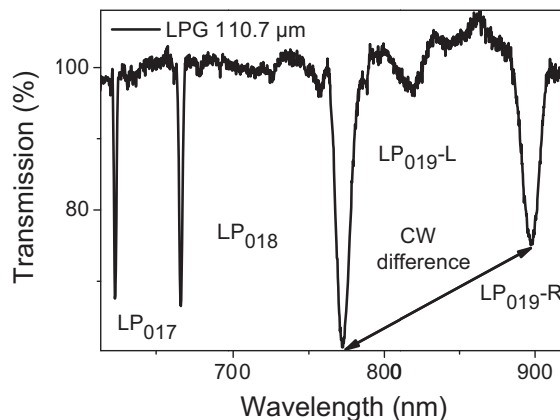


Fig. 8. Transmission spectrum of an uncoated LPG with period of $110.7 \mu\text{m}$ measured in air, with attenuation bands at 670 nm and 775 and 900 nm corresponding to the LP_{018} and LP_{019} cladding modes (the dual resonance was observed for the LP_{019} cladding mode denoted as LP_{019-L} (775 nm) and LP_{019-R} (900 nm)); CW, central wavelength.

3.3. LPG modification

The transmission spectrum of an unmodified LPG with period of $110.7 \mu\text{m}$ is shown in Fig. 8. Attenuation bands in the region of 775 and 900 nm correspond to the LP_{019} cladding mode and operate near the PMTP, while the other bands (region of 625 and 670 nm) correspond to lower order cladding modes and are less sensitive for this LPG period.

The cladding modes associated with the attenuation bands have been calculated based on the phase matching equation (Eq. (1)) and the known values of the central wavelengths and the grating period [28].

The cladding modes associated with the attenuation bands have been calculated through numerical modelling using the phase matching equation (Eq. (1)) and weakly guided approximation to determine the effective refractive indices of the core and cladding modes and the known values of the central wavelengths and the grating period [28].

Changes in the transmission spectra of the LPG when immersed into the film forming solution were monitored. The transmission spectra recorded 30 min after immersion are compared in Fig. S2a. The shifts of the central wavelengths of the LP_{019-L} , LP_{019-R} and LP_{018} resonance bands recorded in the film forming solution over the 1st to 5th growth cycles was observed to be of order nanometres, with the highest value for LP_{019-R} . Larger shifts of the central wavelengths of the attenuation bands were observed when the LPG was immersed in the solution than when the LPG was in air. This was expected, since the attenuation bands are known to show a dependence on the refractive index of the medium surrounding the fibre, with the response being larger for higher surrounding refractive indices [28] and previous work has also shown that the presence of a thin coating on the fibre can influence the sensitivity to surrounding refractive index [29,30].

Changes in the central wavelengths of all of the attenuation bands were observed in air after the deposition of each of 1st to 5th growth cycle of ZIF-8, Fig. 9a. The largest shift of the central wavelength during the deposition was observed for LP_{019-R} . The difference in the sensitivities of LP_{019-R} and LP_{019-L} to the film thickness can be explained by asymmetry in the phase matching curve around the PMTP [24,20]. The increasing separation of the attenuation bands corresponding to LP_{019-L} and LP_{019-R} can be expressed as the change of the difference between the central wavelengths and this change ranged from 150.61 to 174.19 nm for five growth cycles. The enhanced sensitivity that is achieved by operating at the PMTP is highlighted by the comparison of the response of the resonance band corresponding to coupling to LP_{018} with those of LP_{019-L} and LP_{019-R} in Fig. 9b. A linear dependence of the change in the separation of the central wavelengths of LP_{019-L} and LP_{019-R} on the number of growth cycles is shown in Fig. S3 indicating the uniform growth of the ZIF-8 film.

The smaller response of the central wavelengths of the attenuation bands for the first growth cycle agrees with the observations of Lu and Hupp when depositing ZIF-8 on silica substrates [12], where they reported that the thickness of the coating deposited on the first

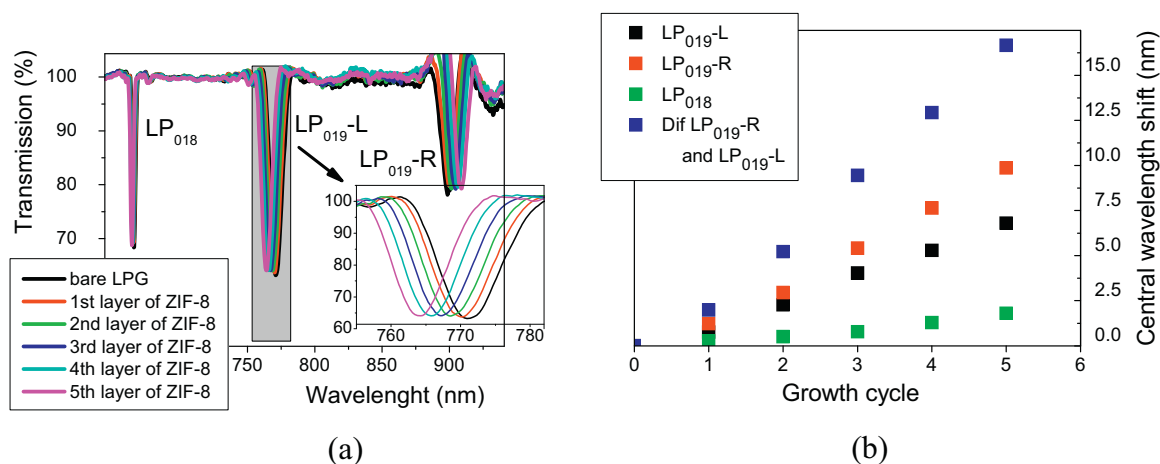


Fig. 9. (a) Transmission spectra of the LPG measured in air; black line, bare LPG and red, green, blue, cyan and magenta lines after the deposition of 1st to 5th growth cycle of ZIF-8; (b) change in the position of the central wavelength corresponding to LP₀₁₈, LP₀₁₉-L, LP₀₁₉-R cladding modes and the change in the difference between the central wavelengths corresponding to LP₀₁₉ cladding mode (blue) during the deposition of 1st to 5th growth cycle of ZIF-8. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

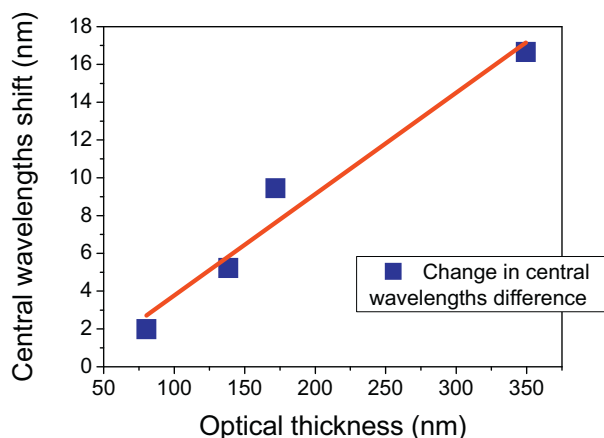


Fig. 10. The change in the separation of central wavelengths (LP₀₁₉-R minus LP₀₁₉-L) corresponding to LP₀₁₉ cladding mode induced by the deposition of ZIF-8 as a function of optical thickness.

growth cycle was less than the thicknesses of the layers deposited after subsequent growth cycles.

The linear relationship between the change of the separation between the central wavelengths and the number of growth cycles correlates well with the thickness measurements taken by the ellipsometer. The change in the central wavelength difference are plotted as a function of the optical thickness, i.e. the product of RI and thickness of the ZIF-8 film determined from the ellipsometer in Fig. 10, showing a linear relationship with a gradient of 4.7 nm wavelength shift/100 nm film thickness.

The transmission spectrum was monitored and recorded throughout the deposition process, and the separation between the LP₀₁₉-L and LP₀₁₉-R bands are plotted as a function of time in Fig. 11a. The plots show a number of interesting features. First, as indicated by the black lines, which are a guide to the eye, the central wavelengths of the resonance bands show a higher sensitivity to coating thickness when the LPGs are immersed in the growth solution than they do when the LPG is in air. Second, when the LPG is immersed in the growth solution, following the initial large step change in the central wavelengths in response to the increased surrounding refractive index, there is a continuous change as the ZIF-8 crystallises onto the optical fibre.

The oscillation of the central wavelength that occurred after the immersion process is likely due to the nitrogen flow that affects the spectra in two ways. First, the central wavelength change is caused only by the mechanical response of the LPG to the flow, which causes slight movement and bending. Second, the chemical process is taking place in the freshly crystallized ZIF-8 film, where methanol is being replaced by nitrogen and then subsequently replaced by air in the ZIF-8 pores until the final crystalline ZIF-8 structure is reached on the surface of LPG.

The rapid decrease of the central wavelength that can be seen to occur immediately after the immersion in the film forming solution indicates that the crystallization process starts rapidly and a high efficiency was observed within the first 10 min. The evolution of the transmission spectrum while the LPG was in the film forming solution (for the 1st growth cycle, labelled with the grey box in Fig. 11a), which is shown in Fig. S2b at selected time intervals for LP₀₁₉-L attenuation band, was used for the evaluation of the film fabrication process, Fig. 11b.

The measurement of the change in the difference between central wavelengths in real time provides an opportunity to observe the efficiency of the crystallization during the deposition in real time. It is possible to identify that the crystallization process starts rapidly, with a 50% and 90% of the central wavelength change reached within ~5 and ~20 min, respectively. The central wavelengths of the attenuation bands were determined in real time using the peak detection routine in LabVIEW to process the spectra recorded by the Ocean Optics spectrometer.

This finding is in a good agreement with real time measurements during the film deposition reported with use of Quartz Crystal Microbalance (QCM) measurement of ZIF-8 film growth where changes in frequency and mass were measured for 2 h and the 90% mass change taken a place within 30 min [12]. For this reason authors decided to set the growth cycle immersion for 30 min. Both the QCM and LPG data indicate that 50% crystallization is achieved within ~5 min following immersion in the solution.

3.4. VOCs sensing

The LPG transmission spectrum responded within 30 s to the injection of each of the tested VOCs to the chamber. The shift of the central wavelengths of the bands reached the saturation in less than 60 s for methanol and acetone and about 180 s for ethanol and 2-propanol. The response time correlates with differences in volatility of the solvents, where the highest value is expected for

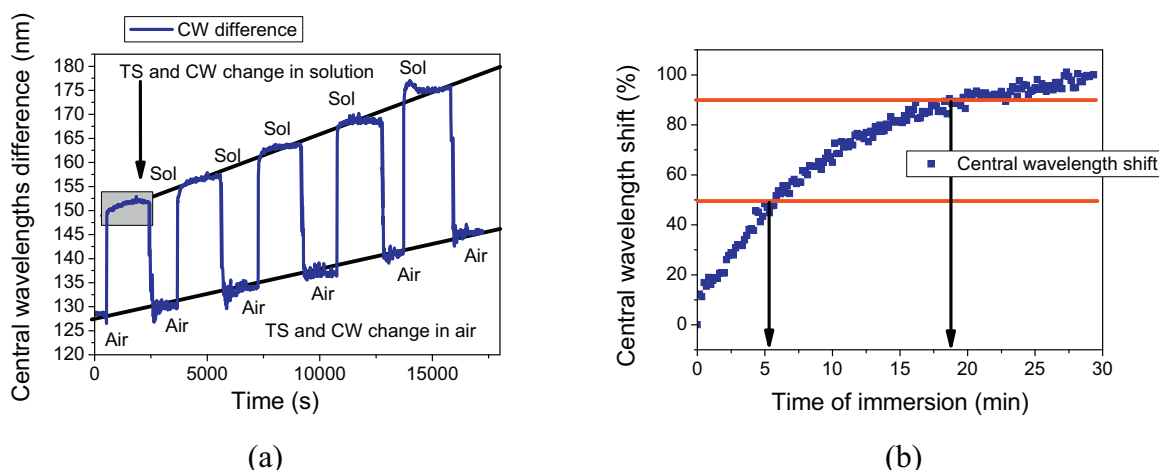


Fig. 11. (a) The dynamic shift of the central wavelength during the deposition of 1st to 5th growth cycle onto a surface of LPG and (b) relative shift of the central wavelength during the immersion in the film forming solution over the deposition of 1st growth cycle.

acetone, then methanol, ethanol and 2-propanol, respectively [31]. The evaporation rate is affected by the functional group, partial pressure of the saturated vapour, molecular weight, surface of the spill and air flow over the spill.

The highest response was observed for methanol, where the change in the bands' separation due to the concentrated vapours of 4.23 nm was obtained in comparison to 2.4 nm change induced by exposure to ethanol, for the sensor coated by 5 growth cycles, Fig. 12a. The inset shows the LP₀₁₉-L attenuation band in detail, where central wavelength shifts of 2.7 and 1 nm were observed for methanol and ethanol, respectively. Similarly, the transmission spectra are shown for acetone and 2-propanol, where the maximal change in the band separation reached 3.64 and 2.65 nm, respectively Fig. S4.

A decrease of the transmission due to exposure to the chemical vapours of the LP₀₁₉-L band was observed caused by the RI change. Similar to the central wavelength, the highest intensity change was observed for methanol.

Similarly, for the sensor coated with 2 growth cycles of ZIF-8 the highest response was to methanol, followed by acetone and with significantly smaller values for ethanol and 2-propanol, Fig. 12b. Similarly to the changes in transmission spectra during the deposition, the bigger shift of the central wavelengths was observed

for LP₀₁₉ in comparison to LP₀₁₈. The minimal response was observed for water corresponding to relative humidity increase from ≈ 40 to $\approx 70\%$ revealing high selectivity of the sensor towards VOCs over humidity.

The sensor response was reversible, as the transmission spectra returned to their initial positions within 10 min after the maximum shift of the central wavelength was observed and complete evaporation of the chemicals. The differences between the recovery times corresponded to the differences in volatility of the VOC, in the same way as for the response time (the recovery time was observed to be less than 3 min for acetone, about 5 min for methanol and about 10 min for 2-propanol and ethanol). It should be noted that the temperature difference was less than 1 °C from the average during the all experiments, Fig. 12b.

The monitoring of changes in the central wavelengths of the resonances bands takes advantage of the wavelength encoded nature LPG-based sensors. While it would be possible to monitor changes in intensity at the mid-point of the resonance band edge as the central wavelength changes, this would introduce the need for intensity reference correct for fluctuations in source intensity, in down lead losses, etc. While, using the current interrogation system, a wavelength lying outside the resonance bands could be used as a reference, care would need to be taken as the reference

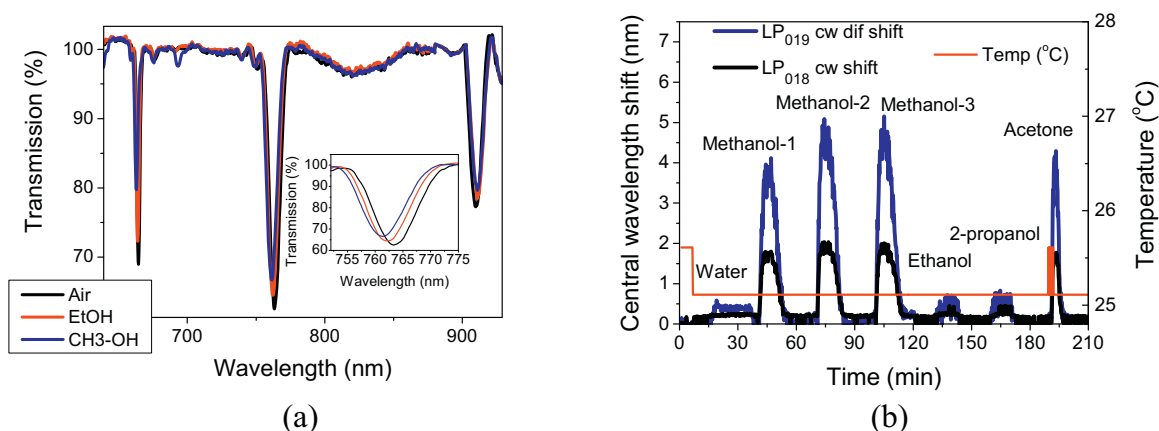


Fig. 12. (a) Transmission spectra of the LPG sensor with 5 growth cycles of ZIF-8 film measured in: black line, air and after exposure to: blue line, methanol and red line, ethanol; and (b) dynamic shift of the central wavelength of the LPG sensor coated with 2 growth cycles of ZIF-8 at the exposure to different organic vapours and water (for comparison); black line, LP₀₁₈ cladding mode and blue line, LP₀₁₉ cladding mode; red line, temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

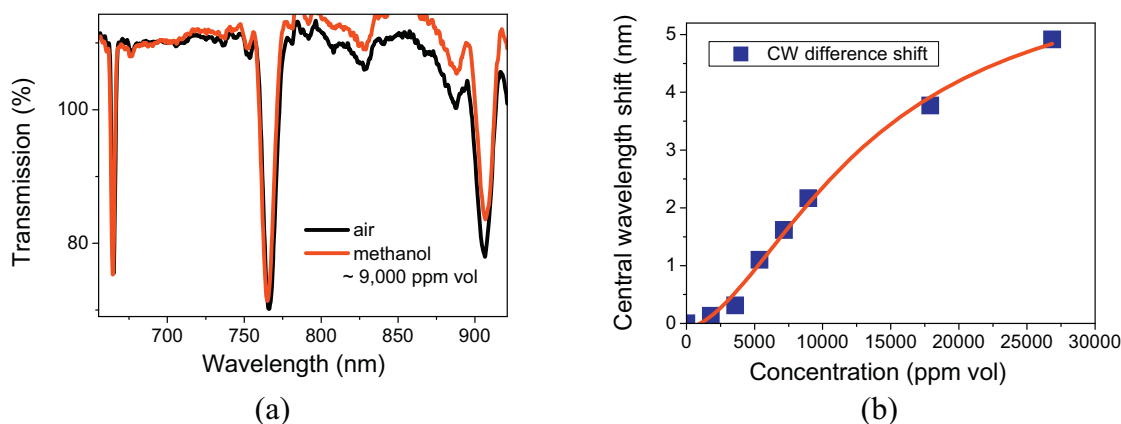


Fig. 13. LPG sensor with five growth cycles of ZIF-8: (a) shift in transmission spectrum corresponding to approximately 9000 ppm of methanol and (b) methanol calibration curve.

wavelength might be separated from the centre of the band by 10 s of nm, making the measurement susceptible to changes in the spectrum of the broadband light source.

While the experiments in the Petri dish showed the response of the LPG to different organic vapours, they don't allow proper comparison the effect of the number of growth cycles (thickness) on the sensitivity and don't enable to show concentration specific response and calibration. Methanol, for its highest response in these experiments, was chosen to examine the response of the sensor over the range of concentrations investigated. The experiments conducted in the environmental chamber showed the effect of the thickness of the film on the sensitivity and higher sensitivity was observed for the sensor coated with five growth cycles. Small changes in the intensity at the central wavelength were also observed. The transmission spectra of the LPG modified with the five growth cycles of ZIF-8 film measured in air and methanol is shown in Fig. 13a.

The sensor coated with five growth cycles was exposed to methanol concentrations ranging from 1790 to 27,900 ppm, the central wavelength shift was measured and the calibration curve plotted, Fig. 13b. Similar experiment had been conducted for the sensor coated with two growth cycles however the wavelength shift for the concentrations up 9000 ppm are shown, Fig. S5.

The limit of detection (LOD) of 1454 ppm was calculated using concentration from the calibration curve in Fig. 13b for the sensor coated with five growth cycles and this value corresponds to 0.065 nm shift of central wavelength. This LOD is 1.5 times lower as compared with two growth cycles film.

The binding constant of 14.70 μM has been calculated for ZIF-8–methanol interaction (data were taken from Fig. 13b) with use of the Langmuir isotherm (The Double Reciprocal–Lineweaver–Burk method was used for the linear transformation).

Although the obtained limit of detection demonstrated is currently too high for the direct real-world application, the results confirm the feasibility of sensors based upon LPGs coated with MOF thin films. In order to increase sensitivity and bring sensor closer to the potential real-world application, a number of optimization procedures are planned, including optimisation of the thickness of the ZIF-8 film and of the grating period, along with enhanced approaches to analysis of the spectrum.

4. Conclusions

ZIF-8 films with controllable thickness have been deposited successfully onto the surface of an optical fibre LPG and the response of the transmission spectra has been characterized. X-ray diffraction patterns allowed the crystal structure of the film to be assessed

and ellipsometry measurements revealed the direct relationship between the crystallization growth cycle and the film thickness, corresponding to a slope of approximately 50 nm per growth cycle. The change of the central wavelengths of the LPG resonance bands have been shown to be dependent upon the optical thickness of ZIF-8 film deposited onto the surface of LPG.

LPGs coated with two and five growth cycles of ZIF-8 exhibited sensitivity to methanol, ethanol, 2-propanol and acetone vapours. The highest sensitivity was to methanol. This can be explained by the use of methanol in the film forming solution and by the fact that the size of the pores matched well the size of the methanol molecule [13].

The measurement of the response times of the sensor was limited by the time taken for the solvents to evaporate (with an upper limit of 3 min).

A higher sensitivity was observed for the sensor coated with five growth cycles, which suggests that the sensitivity will increase with further increases in coating thickness. Issues associated with the decrease of attenuation of the resonance bands of the LPG at the deposition of the thicker films can be resolved by optimisation of the grating period. The lowest limit of detection for the given LPG sensor configuration was found to be 1454 ppm. This value can be decreased by optimising sensor parameters such as grating period, length of the grating and film thickness.

The concept of the LPG based sensor coated with a MOF material has been proved and represents the new strategy in the field of chemical sensing. The cross-sensitivity and the response of the sensor to the mixtures of gases is planned to be examined in our further work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2015.07.027>

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Professor Ralph P. Tatam BSc (Hons), PhD, DSc, CSci, CEng, CPhys, FInstP, FSPiE was appointed to a personal Chair in *Engineering Photonics* at Cranfield University in 1998. He graduated from Exeter University in 1981 (BSc Physics and Chemistry) and was awarded a PhD in Physics (1986) for work on dynamic Rayleigh–Brillouin laser light scattering studies of liquids. He worked as a Research Fellow and Lecturer in the Physics Laboratory at the University of Kent developing optical fibre sensors from 1985 to 1989. In 1989 he took up an appointment at Cranfield where he has established a research team investigating optical instrumentation and sensors applied to challenging measurement problems in engineering and more recently biomedical. He served as Dean of the Faculty of Engineering and Aerospace for 3.5 years from 2008. He is the European Editor for the journal *Measurement Science and Technology* and served as the Associate Editor for the SPIE journal *Optical Engineering* for 5 years and is on the editorial board of several other international journals. Ralph has been on the Technical Programme committee for numerous international conferences, including Symposium Chair for the SPIE *Optical Metrology* symposium, Munich in 2005 and 2007. He has published over 400 papers in the field of optical instrumentation and sensors, and won the UK National Measurement Awards *Frontier Science and Measurement* category in 2001 and 2004 for his work on *planar Doppler velocimetry* and *nanostructured films on optical fibres*, respectively. In 2005 he was awarded a DSc by Exeter University and elected as a *Fellow* of the SPIE.

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