

Fiber optic long period grating sensors with a nanoassembled mesoporous film of SiO₂ nanoparticles

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Abstract: A novel approach to chemical application of long period grating (LPG) optical fibers was demonstrated, which were modified by a film nanoassembled by the alternate deposition of SiO₂ nanoparticles (SiO₂ NPs) and poly(diallyldimethyl ammonium chloride) (PDDA). Nanopores of the sensor film could be used for sensitive adsorption of chemical species in water, which induced the changes in the refractive index (RI) of the light propagating in the cladding mode of the optical fiber, with a concomitant effect on the transmission spectrum in the LPG region. The prepared fiber sensor was highly sensitive to the change in the RI of the surrounding medium and the response time was very fast within 10 s. In addition, chemical infusion into the film was tested using a porphyrin compound, tetrakis-(4-sulfophenyl)porphine (TSPP), which could be saturated within a few min. The lowest detectable concentration of the TSPP analyte was 10 μM. The TSPP infusion led to the development of well-pronounced dual resonance bands, indicating a large increase in the optical thickness of the film. The RI of the film was dramatically increased from 1.200 to ca. 1.540.

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OCIS codes: (060.2370) Fiber optics sensors; (050.2770) Gratings; (310.1860) Deposition and fabrication.

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1. Introduction

Optical techniques have been considered as powerful tools for the development of chemical and biological sensors [1–3]. In particular, the combination of optical fibers and nanomaterials provides a prospect for the fabrication of sensors with high sensitivity and that offer specific response to targeted chemical species [4–6]. A long period grating (LPG) is a periodic modulation of the refractive index (RI) of the core of the fiber, with a period that typically lies within the range of 10 μm –1 mm [4]. The LPG couples the light from the forward propagating mode of the core to a discrete set of co-propagating cladding modes at wavelengths governed by the phase matching condition [7]:

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

where $\lambda_{(x)}$ represents the wavelength at which the coupling occurs to the linear polarized ($\text{LP}_{0,x}$) mode, n_{core} is the effective RI of the mode propagating in the core, $n_{\text{clad}(x)}$ is the effective RI of the $\text{LP}_{0,x}$ cladding mode, and Λ is the period of the grating.

The attenuation of the cladding modes results in the presence of a series of resonance bands in the transmission spectrum of the fiber [7], as shown in Fig. 1(b), centered at wavelengths that satisfy Eq. (1). A portion of the electric field of the cladding mode penetrates into the surrounding medium in the form of an evanescent wave and thus the effective RI of the cladding mode and the $\lambda_{(x)}$ of the resonance band within the optical transmission spectrum of the fiber will depend on physico-chemical parameters of the surrounding medium, such as RI, and concentration. Therefore, the central wavelength and extinction of the resonance bands are dependent on the period of the LPG and the thickness and refractive index of coatings deposited on the surface of the cladding.

Several approaches for depositing coatings of sub- μm thickness onto the surface of LPGs have been examined, such as Langmuir-Blodgett (LB) [4], electrostatic self-assembly (ESA) [5], layer-by-layer (LbL) and dip-coating [2,3] techniques. Such surface modification has enabled sensitive and selective measurements, with reports of demonstrations of specific optical sensors for pH, humidity, and chemical and biological components [8–14]. The sensitivity of the LPG's resonance bands to changes in the optical properties of the deposited

film is largest when the optical thickness of the coating (product of the physical thickness and refractive index) is of the order 300 nm [8]. The thickness of individual layers deposited by the LB and LbL techniques is in order of few nanometers and thus the deposition of at least 100 layers are required, which is a time consuming process.

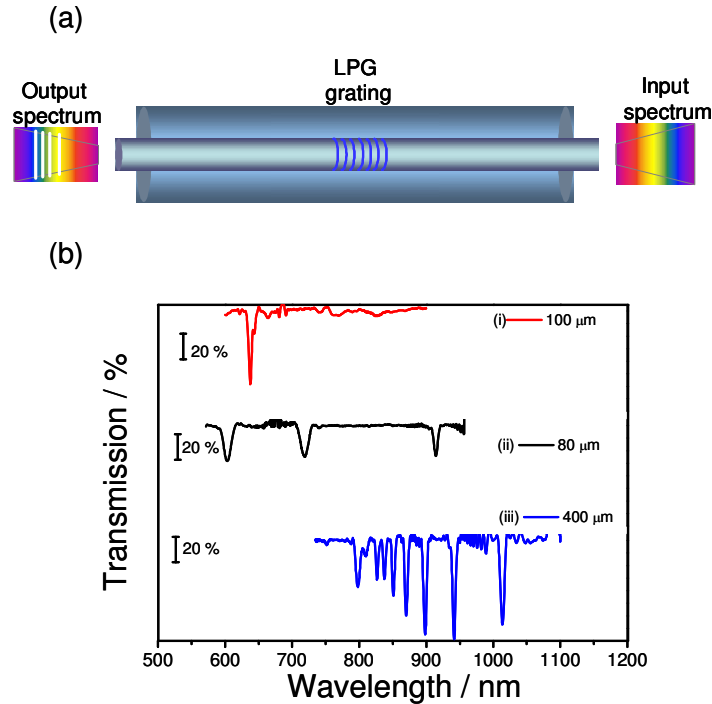


Fig. 1. (a) Schematic illustration of the LPG structure and (b) transmission spectra of uncoated LPG fibers with different grating periods: (i) 80 μm , (ii) 100 μm , and (iii) 400 μm .

In this work, we propose a novel approach for the efficient deposition of a functional coating with an optimized thickness on the surface of LPGs. The approach is based on the alternate deposition of silica nanoparticles (SiO_2 NPs) with a diameter in the range of 40–50 nm, using an LbL method. This allows the rapid film deposition for the required physical thickness [13]. The porous nature of the SiO_2 NPs coating results in a low refractive index. Increases in the refractive index of the coating, for example in response to the condensation of water vapor within the coating, will result in a change in the resonance wavelengths. This has been exploited to demonstrate a humidity sensor [14]. An additional advantage of the use of the LbL deposition technique to form the mesoporous coating, in comparison with the conventional sol-gel technique, lies in the ability to easily control the thickness of the coating layer by employing different diameters of SiO_2 NPs. In this paper we consider the mesoporous SiO_2 NPs coating as a base film that may then be modified to provide the coated LPG with species specific responsivity. Infusion of a functional material into the mesoporous film will have two effects; the first is to induce an increase of the RI and hence the optical thickness of the deposited layer, allowing the sensing of the infused material, the second is the provision of a species specific sensing capability and optimization of the characteristics of the sensor by control of the amount of material infused. This technique also means that the choice of functional material is not limited to those that may be deposited by the LB, LbL or dip coating techniques, broadening the potential of coated LPG sensors.

2. LPG Characteristics

LPGs of length 30 mm and with a period of 80, 100 and 400 μm were fabricated in a single mode optical fiber (Fibercore SM750) with a cut-off wavelength of 670 nm. The photosensitivity of the fiber was enhanced by pressurizing it in hydrogen for a period of 2 weeks at 150 bar at room temperature. The LPGs were fabricated in a point-by-point fashion, illuminating the fiber by the output from a frequency-quadrupled Nd:YAG laser, operating at 266nm. The transmission spectrum of the optical fiber was recorded by coupling the output from a tungsten-halogen lamp into the fiber, and by analyzing the transmitted light using a fiber coupled CCD spectrometer.

The response of the resonance bands of an LPG to the deposition of a coating is characterized by a coating thickness at which a cladding mode becomes phase-matched to a mode of the waveguide formed by the coating [8]. Under these conditions, a mode transition occurs whereby the remaining cladding modes are reorganized to fill the gap left by the loss of the cladding mode. The mode transition is accompanied by a rapid change in the effective index of the modes. This manifests itself as a regime in which the resonance bands show a high sensitivity to changes in the optical properties of the deposited film [8], and clearly for optimum sensor performance the coating thickness should lie within this regime.

A recent study showed that, in addition to optimizing the coating thickness, it is possible to enhance the sensitivity by appropriate choice of grating period [8]. This is achieved by selection of the grating period such that the sensor will operate at the *phase matching turning point* [15], which is observed when coupling to higher order cladding modes. This can be understood with reference to Fig. 2, where the phase matching curves for a number of higher order cladding modes are plotted. The data plotted in Fig. 2 were obtained using the LP approximation to calculate the dispersion of the core and cladding modes [16]. These values were used in Eq. (1) to calculate the resonant coupling wavelengths for each cladding mode. The curves here are provided to aid the explanation of the phenomenon, rather than to predict the actual resonant wavelengths, which is compromised by as a lack of knowledge of the exact fiber parameters. As indicated by the dotted line in Fig. 2, the phase matching curves exhibit a turning point at a given period where the coupling to a single cladding mode occurs at two wavelengths. As the grating period changes, the dual resonance bands move in opposite directions on wavelength. Similar effects can be observed from the difference ($n_{\text{core}} - n_{\text{clad}}$) of the RI of the core and cladding modes, for example, due to changes in temperature or in the RI of films deposited onto the cladding. It has been demonstrated theoretically and experimentally that the central wavelength of the LPG resonance bands exhibits the highest sensitivity to external perturbations near their phase matching turning points [15].

By selecting a combination of LPG period and optical thickness such that the LPG is operating at the phase matching turning point within the mode transition region, mode transition region, it is possible to ensure optimal sensitivity [8,17], the sensitivity of the central wavelength of the dual resonance bands could be maximized by optimal choice of LPG properties (grating period and optical thickness of the deposited film). Initially, a single broad resonance band appears in the spectrum, when the LPG couples light to the cladding mode at the phase matching turning point (indicated by the dashed line in Fig. 2). Subsequently, the amplitude of the resonance band is enhanced by the changes in n_{clad} ; however, the central wavelength is fixed and this band is split into dual resonance bands with further changes in n_{clad} [8,16,17].

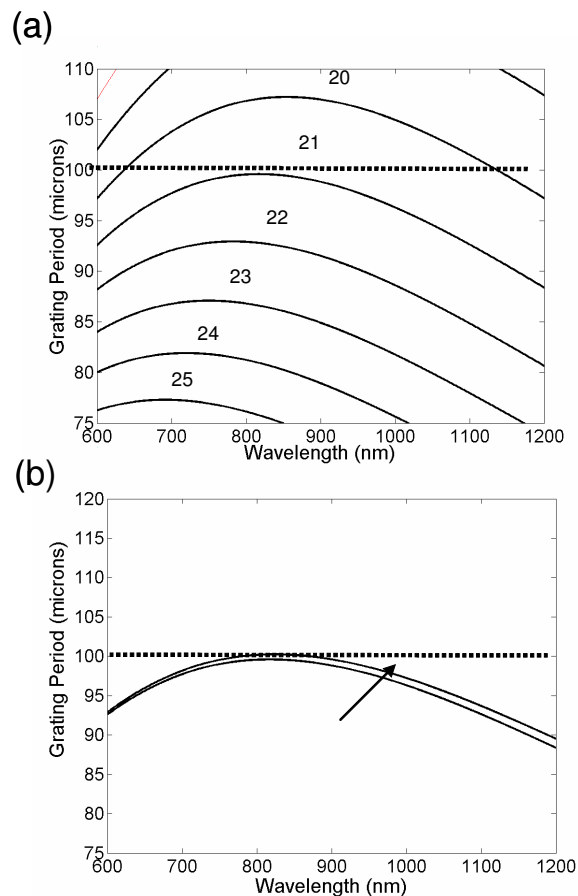


Fig. 2. (a) The relationship between the grating period and the wavelength at which coupling occurs to a set of symmetric cladding modes ($LP_{0,20}$ – $LP_{0,25}$), where numbers refer to the order of the cladding mode, $LP_{0,k}$, assuming that the LPG was fabricated in an optical fiber of a cut off wavelength of 670 nm. (b) The influence of an increase in the surrounding refractive index, analogous to the deposition of a coating onto the cladding, on the phase matching curve for $LP_{0,21}$. The surrounding refractive index is assumed to change from 1 to 1.4. The arrow indicates the direction of increasing refractive index. The dashed line is a guide to the eye to enable the reader to see the influence of different grating periods on the LPG transmission spectrum.

3. Sensor fabrication

Figure 3 shows a schematic illustration of the LbL deposition of SiO_2 NPs. Firstly, the region of the optical fiber containing the LPG is rinsed with deionized water and immersed into 1 wt% ethanolic KOH (ethanol/water = 3:2, v/v) for 20 min, leading to a negatively charged surface. The optical fiber is then sequentially immersed into an aqueous solution of positively charged polymer, poly(diallyldimethylammonium chloride) (PDDA, Mw: 200000–350000, 20% w/w in H_2O) and into an aqueous solution containing negatively charged SiO_2 NPs (SNOWTEX 20L, Nissan chemical industries) for 20 min, so that an alternate layer of PDDA and SiO_2 was deposited onto the fiber surface. The fiber is rinsed with distilled water, and dried by flushing with nitrogen gas after each deposition step. In the following text, films are expressed as $(PDDA/SiO_2)_x$, where x is the number of PDDA/ SiO_2 deposition cycles.

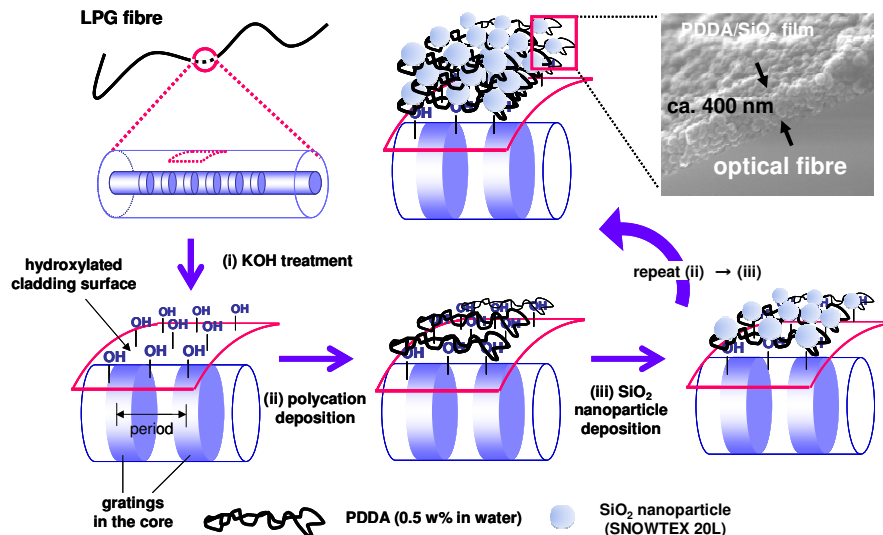


Fig. 3. Schematic illustration of the alternate deposition of SiO₂ NPs and PDDA onto the surface of an LPG. The inset shows an SEM image of the cross-section of a 10-cycle PDDA/SiO₂ film.

4. Results and discussion

4.1 Deposition of SiO₂ NPs

The inset in Fig. 3 shows the cross-section of a 10-cycle PDDA/SiO₂ ((PDDA/SiO₂)₁₀) film deposited onto an optical fiber and demonstrates that a uniform and highly porous film with a well-controlled thickness was deposited on the LPG. The porosity of the deposited film was measured using a Sorptomatic 1990 (Thermo Scientific) instrument operating on the static volumetric principle, due to porosity characterization via gas adsorption. The pore size distribution of the PDDA/SiO₂ film indicates a well developed mesoporous structure with a mean pore radius of 12.5 nm and specific surface area of 50 m² g⁻¹ [Figs. 4(a) and 4(b)]. In order to determine the thickness and RI of the PDDA/SiO₂ layer, a 1-cycle film was also assembled, using the same process as described for the LPG, on an activated quartz substrate and characterized using a SopraGES5 ellipsometer (Tarn Electronics SARL, France). The thickness and RI of the 1 layer-thick film were estimated to be 46 ± 3 nm and 1.2000 (at a wavelength of 633 nm), respectively. The measured RI is in good agreement with a previously reported result [18]. When the coating deposited onto the quartz substrate was viewed under the SEM and compared with the coating deposited on the LPG, there were no apparent differences in the morphology.

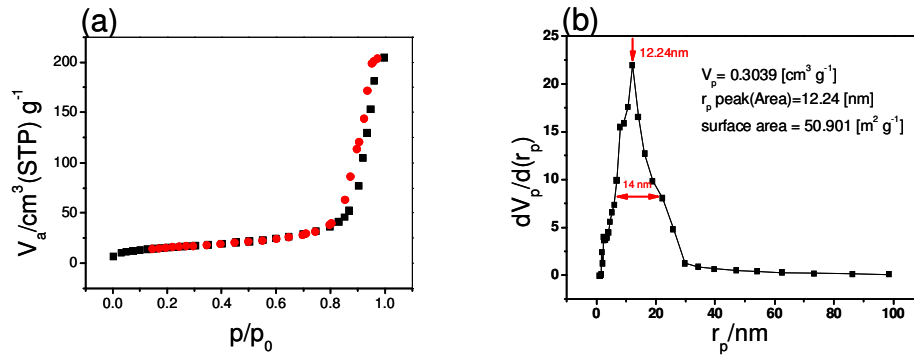


Fig. 4. (a) Adsorption isotherm of the PDDA/SiO₂ film: squares, adsorption part of the adsorption isotherm; circles, desorption part of the adsorption isotherm. (b) Pore size distribution in the PDDA/SiO₂ film.

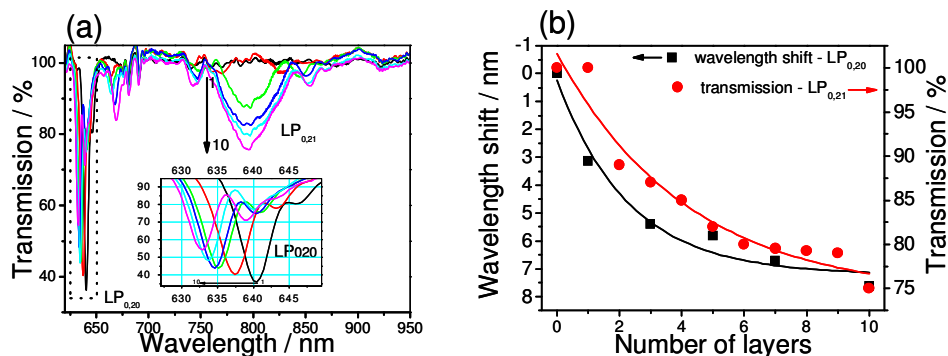


Fig. 5. (a) Changes in the transmission spectrum of the 100 μm period LPG of SiO₂ NPs and PDDA (each spectrum was recorded in the colloidal SiO₂ solution in water) and (b) wavelength shifts and changes in transmission as a function of the number of deposition cycles for the LP_{0,20} and LP_{0,21} resonance bands, respectively; the curve is a guide to the eye only.

Figure 5(a) shows the changes in the transmission spectrum of the 100 μm period LPG due to the alternate deposition of SiO₂ NPs and PDDA. The spectra were recorded with the LPG immersed in the silica colloidal solution. The resonance feature at 640 nm (corresponding to the coupling from the core mode to the LP_{0,20} cladding mode) exhibited a small blue wavelength shift of ca. 8 nm with increasing the film thickness [see the inset in Fig. 5(a)]. The same deposition of the (PDDA/SiO₂)₁₀ film was conducted on LPGs with 80 and 400 μm periods and similar effects, the shifts of the resonance features, in each case was observed (Fig. 6 and 7, respectively). The wavelength shifts of the resonance band for LPGs with 80 and 400 μm periods induced by the film deposition were 12 nm and 5.5 nm, respectively [Fig. 6(b) and 7(b)].

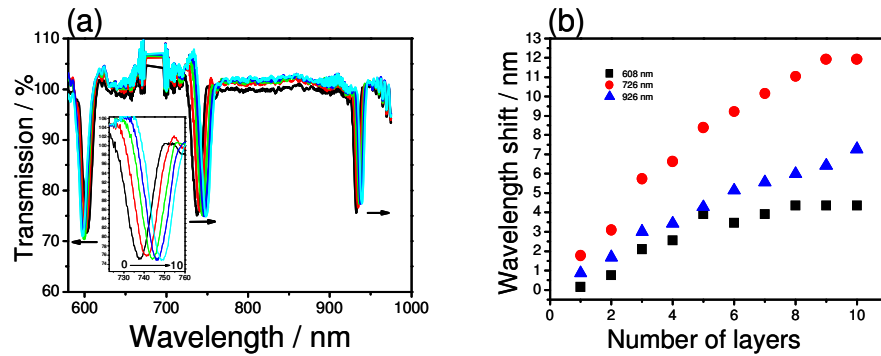


Fig. 6. (a) Changes in the transmission spectrum due to the alternate deposition of PDDA and SiO₂ NPs on the 80 μ m period LPG recorded in the colloidal SiO₂ solution; the inset shows enlarged view of the resonance band at 626 nm. (b) Wavelength shifts of the three resonance bands at 608, 726, and 926 nm.

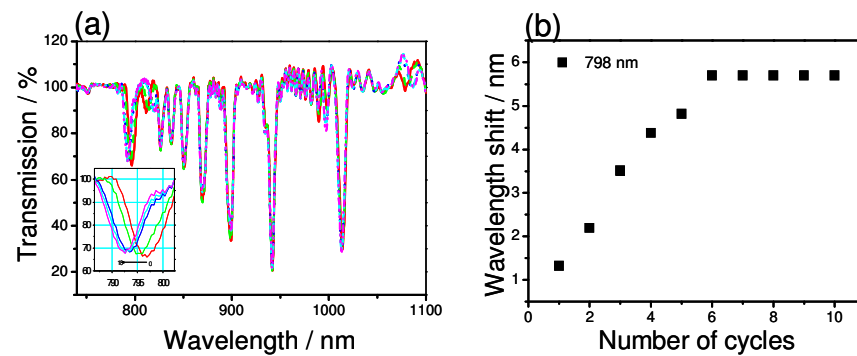


Fig. 7. (a) Changes in the transmission spectrum due to the alternate deposition of PDDA and SiO₂ NPs on the 400 μ m period LPG, recorded in the colloidal SiO₂ solution; the inset shows an enlarged view of the resonance band at 798 nm. (b) Wavelength shifts at 798 nm.

On the other hand, the 100 μ m period LPG has an additional resonance band centered at 800 nm. The development of the resonance band at around 800 nm, corresponding to the coupling to the LP_{0,21} mode, is a result of the change in the n_{clad} induced by the presence of the deposited layer, which makes coupling to this cladding mode at the phase matching turning point possible. Before film deposition, there is no band in the wavelength range at around 800 nm. As the number of the deposition cycles increases, the resonance band becomes more pronounced. However, because of the low RI (ca. 1.200) of the deposited SiO₂ NP layer, this resonance feature is not well developed for this film thickness. As previous studies have indicated the benefits of operating at the phase matching turning point [8,17], the demonstration of the sensing principles of the LPGs coated with mesoporous films infused with functional materials were carried out using the 100 μ m period LPG.

4.2 Effect of the coating on the LPG transmission spectrum

When the uncoated 100 μ m period LPG was immersed into water (RI = 1.323), a blue shift of the LP_{0,20} resonance band of 3 nm is observed. However, the sensitivity of the LP_{0,20} resonance band was much improved by the coating with a (PDDA/SiO₂)₁₀ film, showing a blue shift of 7 nm when the LPG was immersed in water, along with the appearance of the resonance band corresponding to coupling to the LP_{0,21} cladding mode at the phase matching turning point [Fig. 8(a)]. This indicates an increase in sensitivity of the LPG to the surrounding RI, being of interest when measuring the RI of low concentration aqueous

solutions, and has been observed previously for LPGs coated using the LB technique [19]. The response to the RI changes is fast (< 2 s, measurement limited by the integration time for the CCD spectrometer) and stable, as indicated by the response of the transmitted power at the centre of the $LP_{0,21}$ resonance band to repeated immersions in water [Fig. 8(b)].

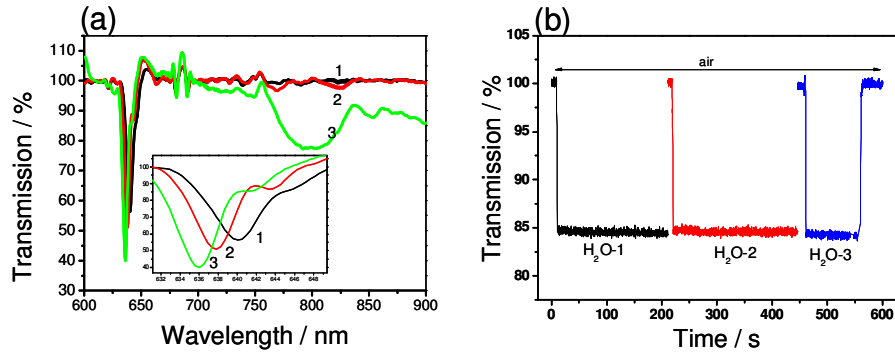


Fig. 8. (Media 1) (a) Transmission spectra of the 100 μm LPG fiber under different conditions: black line, in air without coating; red line, in water without coating; green line, in water after deposition of the $(\text{PDDA}/\text{SiO}_2)_{10}$ film. (b) Kinetic changes of the transmission spectrum of the SiO_2 NP coated LPG fiber measured at 800 nm in different phases from air to water.

4.3 Chemical infusion into the mesoporous SiO_2 NP film

The resonance bands ($LP_{0,20}$ and $LP_{0,21}$) could be used for the detection of chemical components that can be bound through an electrostatic interaction with the cationic groups of PDDA in the mesopores of the film. Figure 9(a) shows the transmission spectra recorded when the $(\text{PDDA}/\text{SiO}_2)_{10}$ film coated LPG was immersed in a solution of tetrakis-(4-sulfophenyl)porphine (TSPP, 1 mM in water). As the TSPP is infused into the film, the RI of the film increases (from 1.200 to ca. 1.540, measured using ellipsometry) and the phase matching condition for coupling to $LP_{0,21}$ is satisfied. A broad single attenuation band develops rapidly (within 60 s from the start of the infusion process) and then splits in two bands. This is consistent with previous observations of the response of the LPG resonance bands to increases in coating *thickness* at constant RI, but here is seen for changes in refractive index at constant thickness. The time required to complete the binding between the TSPP and PDDA moieties is less than 600 s [Fig. 9(b)]. It should be noted that transmission spectra in Fig. 9(a) corresponds to the time elapsed from the start of the TSPP infusion process rather than from the time at which the monitoring of the spectrum commenced. The observed response indicates a large increase in the optical thickness of the film, which is a result of the increase in the RI of the film that occurs, as the TSPP infuses into the mesoporous structure and is adsorbed to the PDDA moiety between the SiO_2 NPs.

The evolution of the transmission spectrum of the SiO_2 NPs coated LPG when immersed in the TSPP solution is shown in the grey scale plot shown in Fig. 10, where the transmission is represented by white and black, corresponding to 100% and 0%, respectively. The dark line at around 635 nm, which originates at a wavelength of 640 nm in the uncoated LPG, represents the resonance band that corresponds to the first order coupling to the $LP_{0,20}$ cladding mode.

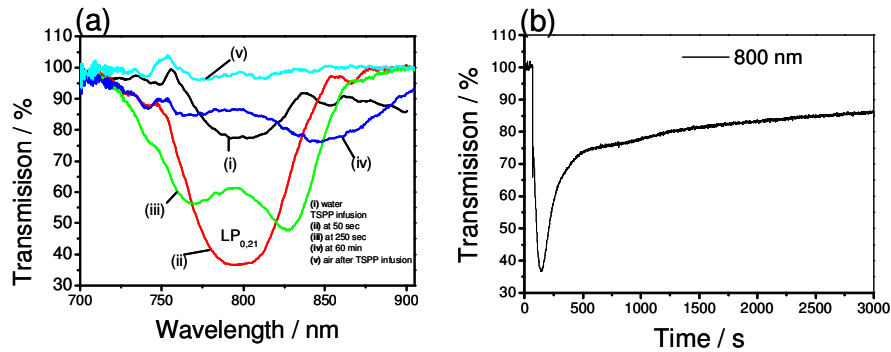


Fig. 9. (a) Transmission spectra of the SiO₂ NP coated LPG and (b) the dynamic transmission change recorded at 800 nm when the SiO₂ NP coated LPG was immersed in a TSPP solution (1 mM in water).

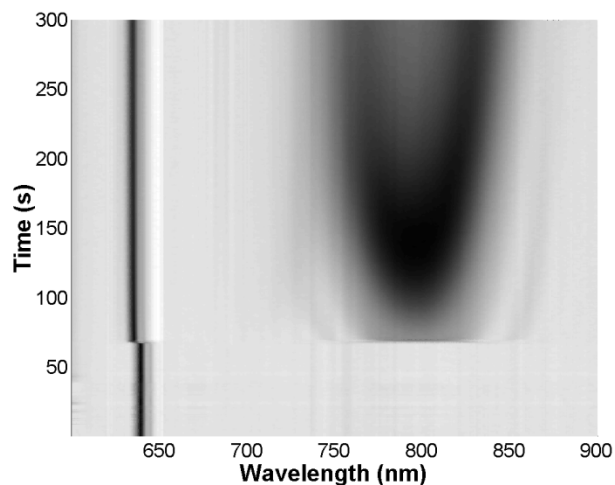


Fig. 10. The evolution of the transmission spectrum of the SiO₂ NP coated LPG (period 100 μ m), when immersed in an aqueous solution of TSPP (1 mM). The grey scale represents the measured transmission, with white corresponding to 100%, and black to 0%.

In order to assess the sensitivity of the optical device, the (PDDA/SiO₂)₁₀ coated LPG was exposed to different concentrations of TSPP, and the results are shown in Figs. 11(a) and 11(b). The increase of the TSPP concentration from 10 to 1000 μ M results in a decrease of the transmission measured at 800 nm, corresponding to the development of the LP_{0,21} cladding mode resonance. This is also accompanied by a blue shift of the LP_{0,20} resonance band, indicating the increase of the RI of the film. The response time of the sensor is observed to be slower at lower TSPP concentrations. For 1 mM TSPP, the increase in transmission at 800 nm shown in Fig. 11(b) is attributed to the splitting of the fully developed LP_{0,21} cladding mode resonance into dual resonance bands. Additionally, the infusion process can be observed in the multimedia file ([Media 1](#)).

The ability to reuse the device was tested by removing the infused TSPP molecules from the film using an ammonia solution (ca. 1000 ppm). The spectrum reverted to that observed for the (PDDA/SiO₂)₁₀ coated LPG before TSPP infusion. Subsequent immersion of the (PDDA/SiO₂)₁₀ LPG into the TSPP solutions showed that the performance was repeatable, as shown in Fig. 11(c). Note that this could also be used as a means for detecting ammonia, with the TSPP acting as the functional material.

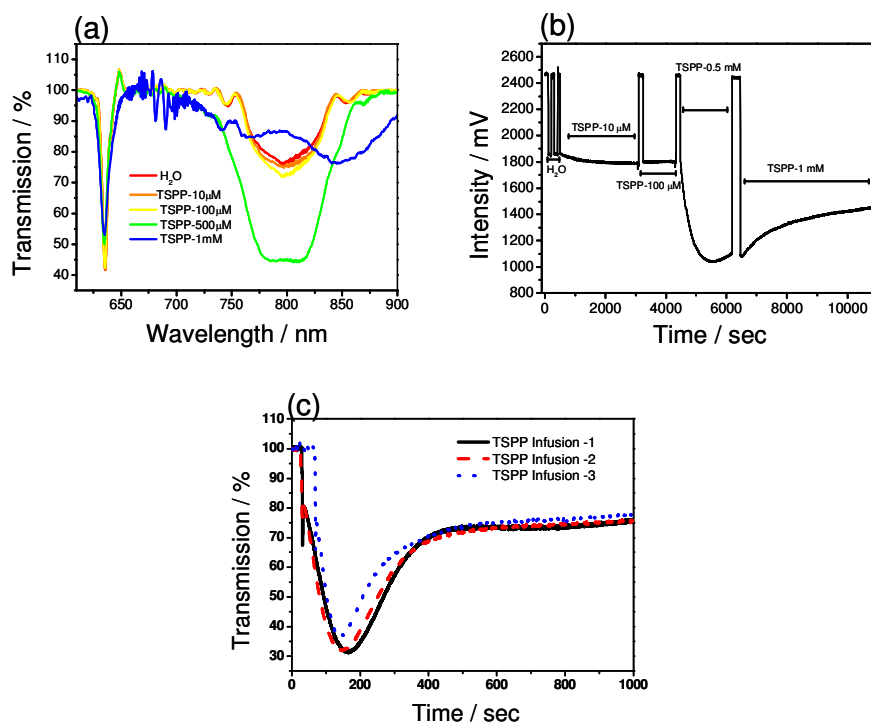


Fig. 11. (a) Transmission spectra of the (PDDA/SiO₂)₁₀ coated LPG; (b) transmission change recorded at 800 nm in response to different concentrations of TSPP (from 10 μM to 1 mM in water) and (c) dynamic response to the three infusions of TSPP into the PDDA/SiO₂ porous film recorded at 800 nm; the infusion was conducted after complete removal of TSPP from the PDDA/SiO₂ using NH₃ of 1000 ppm.

5. Conclusions

To date there have been a number of reports of chemical sensing based upon thin film coatings deposited onto LPGs. The approach adopted here, where mesoporous films were built from SiO₂ NPs, allows more rapid deposition of a base coating of required physical thickness. The mesoporous films were subsequently used for chemical adsorption, either of materials to be sensed, or of functional materials to facilitate sensing, potentially extending the functionality of this class of sensor. The results demonstrate the ability to use this approach to obtain quantitative measurements for the detection of organic compounds that can be infused into the porous film and that change the RI of the film. There is the potential for highly selective measurements by choosing the appropriate functional compound for infusion into the porous film preparation to interact specifically with the chemical analyte. The porous nature of the film may also allow the development of sensors with more rapid response time, and the analyte may penetrate deeper into the coating, even for small concentrations. The approach also offers different approach to providing optimal sensitivity, whereby to ensure that the LPG sensor operates with optimal sensitivity, i.e. at the phase matching turning point, the LPG period and the infusion time and concentration of the functional material may be controlled. This effect will be further explored for optical sensing of a variety of important chemical and biological compounds.

The TSPP compound used in this work is able to function as a sensitive element because of its extraordinary optical properties. In general, optical properties of porphyrins can be varied by metallation of the pyrrole ring, which in turn will lead to a higher sensitivity and selectivity to a wider class of chemical compounds [20]. Recently, we have used TSPP with a

cationic polymer for ammonia sensing [21,22] and the operation of the proposed device was based on the optical change due to the deprotonation from the *J*-aggregated TSPP to ammonia.

Acknowledgements

This work was supported by the MEXT via the 2nd Kitakyushu Knowledge-based Cluster Project and by the Ministry of Knowledge Economy (MKE, Republic of Korea) via the Fundamental R&D Program for Core Technology of Materials. The authors from Cranfield are grateful to the Engineering and Physical Sciences Research Council, EPSRC, UK for funding under grants EP/D506654/1 and GR/T09149/01.



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Fiber optic long period grating sensors with a nanoassembled mesoporous film of SiO₂ nanoparticles

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2010-06-07

Optical Society of America (OSA)

<https://doi.org/10.1364/OE.18.013227>

Korposh S, James SW, Lee S-W, et al., (2010) Fiber optic long period grating sensors with a nanoassembled mesoporous film of SiO₂ nanoparticles. Optics Express, Volume 18, Issue 12, June 2010, pp. 13227-13228