



Optical fibre long period grating with a nanoporous coating formed from silica nanoparticles for ammonia sensing in water

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ABSTRACT

A fibre optic long period grating (LPG) with a nano-assembled mesoporous coating of alternate layers of poly(diallyldimethylammonium chloride) (PDDA) and SiO₂ nanospheres was used for the development of a highly sensitive fibre-optic chemical sensor. Sensor fabrication involves a 2-stage process: firstly, the deposition of the base mesoporous thin film (PDDA/SiO₂) over an LPG written in the optical fibre using a layer-by-layer technique, followed by the infusion of a functional material into the porous film. The refractive index of the base mesoporous coating, determined at a wavelength of 633 nm using ellipsometry, was found to be 1.2. The infusion of the functional material into the coating resulted in a significant change in the RI of the coating, producing a dramatic change in the transmission spectrum of the LPG. The sensing mechanism exploited is based upon chemically induced desorption of the functional material from the mesoporous coating. The sensing of ammonia in aqueous solution was chosen as an example to demonstrate the sensing principle of the LPG sensor. The operation of the sensor was characterized using two functional materials, tetrakis-(4-sulfophenyl)porphine (TSPP) and polyacrylic acid (PAA). The device showed high sensitivity to ammonia with a response time less than 100 s and a limit of detection of 140 ppb when the TSPP infused (PDDA/SiO₂) film was employed as a sensitive element.

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1. Introduction

Optical fibre long period gratings (LPGs) coated with chemically sensitive materials have emerged as a promising platform for fibre optic sensors [1,2]. Studies of the response of the transmission spectrum of an LPG to the layer-by-layer deposition of thin film coatings via processes such as the Langmuir–Blodgett [3] (LB) and electrostatic self-assembly [4] (ESA) techniques, and also by dip-coating [5,6] have shown that, for thicknesses of order 100 nm and refractive index (RI) higher than that of the silica cladding, the transmission spectrum of the LPG shows a high sensitivity to changes in the thickness and RI of the coating. The phenomenon has been studied extensively both theoretically [7,8] and experimentally [9,10]. Appropriate choice of coating properties such as thickness and RI [6], and of LPG parameters, such as the length and period [10], allows the optimization of the sensitivity of the device to changes in the optical properties of the coating. Based on this principle, sensors for organic vapours [11], metal ions [12],

humidity [13], organic solvents [14] and biological materials [15] have been reported. Similarly to surface plasmon resonance (SPR) devices, LPG sensors can provide highly precise analytical information about adsorption and desorption processes associated with the RI and thickness of the sensing layer. For instance, the sensitivity of LPG sensors is in the same order of magnitude as SPR sensors, showing a sensitivity of ca. 1 nM for antigen–antibody reactions [16,17]. An advantage of the LPG over SPR lies in the ability to fabricate a cheap and portable device that can be applied in various analytical situations.

Recently, LPG fibre sensors deposited with porous coatings have attracted a lot of interests. For instance, a sol–gel film of SnO₂ of thickness of order 200 nm was deposited onto to an LPG, facilitating the demonstration of an ethanol gas sensor [6]. The porosity and high RI of the coating material resulted in the LPG spectrum exhibiting a response due to diffusion of ethanol gas into the coating and the authors predicted that an optimized sensor would exhibit a detection limit of 100 ppb. We recently demonstrated a new approach to LPG based chemical sensing: the chemical infusion of analytes into a mesoporous coating that consisted of a multilayer film of SiO₂ nanoparticles (SiO₂ NPs) deposited using the ESA technique [18]. The initially low RI of the mesoporous coating, 1.2@633 nm, was increased significantly by the chemical infusion, resulting in a large change in the LPG's transmission spectrum. A

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similar approach was used in the development of a humidity sensor where condensation of the water vapour into the porous film changed the index of the coating [19]. SiO₂ NPs are commercially available with a range of diameters from 10 nm to 100 nm and their surface charge is selectable [20]. Their use to form the base coating allows the rapid deposition of a coating of the physical thickness required to optimize the sensitivity of the device.

In this study, the concept explored in our previous work [18] is developed further to demonstrate a species specific chemical sensor. A novel 2 stage approach to the development of the sensor is explored. The first stage involves the deposition of the mesoporous coating onto the LPG. In the second stage a functional material, chosen to be sensitive to the analyte of interest, is infused into the base mesoporous coating. The sensing of ammonia in aqueous solution was chosen to demonstrate the sensing principle. The operation of the sensor was characterized using two functional materials, tetrakis-(4-sulfophenyl)porphine (TSPP) and polyacrylic acid (PAA). TSPP is a porphine compound that changes its optical properties (absorbance and RI) in response to exposure to ammonia [18], while PAA has been employed previously as a functional compound that can strongly bind ammonia to the carboxylic (COOH) functional groups [21,22]. In the case of the PAA it is assumed that direct binding of ammonia to the COOH moiety will change RI of the mesoporous coating, while in the case of TSPP its desorption will result on RI change.

2. Experimental methods

2.1. Materials

Tetrakis-(4-sulfophenyl)porphine (TSPP, $M_w = 934.99$) was purchased from Tokyo Kasei, Japan. Poly(diallyldimethylammonium chloride) (PDDA, $M_r = 200,000\text{--}350,000$, 20% (w/w) in H₂O; monomer $M_w = 161.5\text{ g mol}^{-1}$), PAA₂₅ ($M_w = 250,000$, 35 wt% in H₂O) and ammonia 30 wt% aqueous solution were purchased from Aldrich. A colloidal solution of silica nanoparticles (SiO₂ NPs), SNOWTEX 20L (40–50 nm), was purchased from Nissan Chemical. All chemicals were reagents of analytical grade, and used without further purification. Deionized pure water (18.3 M Ω cm) was obtained by reverse osmosis followed by ion exchange and filtration in a Millipore-Q (Millipore, Direct-QTM).

2.2. Deposition of SiO₂ NPs on the LPG fibre

SiO₂ NPs were deposited onto the surface of the fibre using the ESA process, as illustrated in Fig. 1a. As the LPG transmission spectrum is known to be sensitive to bending, for the film deposition process and ammonia detection experiments the optical fibre containing LPG was fixed within a special holder, as shown in Fig. 1b, such that the section of the fibre containing the LPG was taut and straight throughout the experiments [23]. The detailed procedure of the deposition of the SiO₂ NPs onto the LPG and infusion of the TSPP compound has been previously reported [18]. Briefly, the section of the optical fibre containing LPG, with its surface treated such that it was terminated with OH groups, was alternately immersed into a 0.5 wt% solution containing a positively charged polymer, PDDA, and, after washing, into a 1 wt% solution containing the negatively charged SiO₂ NPs solution, each for 20 min. This process was repeated until the required coating thickness was achieved.

When the required film thickness had been achieved (i.e. when the development of the second resonance band was observed with the fibre immersed into water), after 10 deposition cycles, the coated fibre was immersed in a solution of TSPP or PAA as functional compound for 2 h, which was infused into the porous coating and provided the sensor with its specificity. Due to the

electronegative sulfonic groups present in the TSPP compound, an electrostatic interaction occurs between TSPP and positively charged PDDA in the PDDA/SiO₂ film. On the other hand, PAA is usually considered as a promising sensor element for ammonia sensing, owing to the presence of free carboxylic function groups that lead to high affinity towards amine compounds [10,21].

After immersion into the TSPP and PAA solutions, the fibre was rinsed in distilled water, in order to remove physically adsorbed compounds, and dried by flushing with N₂ gas. The compounds remaining in the porous silica structure was bound to the surface of the polymer layer that coated each nanosphere. This effectively increased the available surface area for the compounds to bond to. The presence of functional chemical compounds increased the RI of the porous coating and resulted in a significant change in the LPG's transmission spectrum, consistent with previous observations for increasing the coating thickness [23]. All experiments have been conducted at 25 °C and 50% of rH.

2.3. Characterizations of film structures

The morphology and porosity of the PDDA/SiO₂ films were studied using an Hitachi S-5200 field emission scanning electron microscope (FE-SEM). The film was deposited onto a silicon wafer and the substrate was cut into a number of samples, each of dimensions 2 mm × 2 mm, compatible with the sample holder of the FE-SEM. The films were vacuum-dried for more than 6 h and then coated with a thin (5 nm) platinum film using a Hitachi E-1030 ion sputter (15 mA, 10 Pa) to allow electrical discharge of the sample surface during the interaction with the electron beam.

2.4. Ellipsometry measurements

The thickness and RI of the (PDDA/SiO₂) films were measured using a SopraGES5 ellipsometer (Tarn Electronics SARL, France). Data were collected at a spectral resolution of 1 nm and measured in the wavelength range 400–800 nm; for simplicity the RI value of the mesoporous film was determined at one wavelength (633 nm). Measurements were also conducted on the films before and after infusion of TSPP.

2.5. UV–vis measurements

The UV–vis spectrum of the PDDA/SiO₂ film assembled on the quartz substrate and infused with the TSPP compound was measured with the aid of a fibre optic spectrophotometer, Ocean Optics S1024DW, and deuterium-halogen light source (DH-2000-Ball, Mikropack). In order to monitor the influence of ammonia on the absorbance spectra, the UV–vis measurements were conducted before and after exposure of the TSPP infused PDDA/SiO₂ film to ammonia.

2.6. Quartz crystal microbalance (QCM) measurements

A 9 MHz quartz crystal microbalance (QCM) electrode, manufactured by USI System, Fukuoka, Japan, was used to monitor the assembly of the PDDA/SiO₂ film and to determine the amount of the functional compound, TSPP, infused into the mesoporous film [24]. The deposition procedure used for QCM electrode surface modification was identical to that described in Section 2.2. The following relationship is obtained between adsorbed mass, M (g), and frequency shift, ΔF (Hz), using the Sauerbrey's equation [25,26] and by taking into account the characteristics of the quartz resonators used:

$$\Delta F(\text{Hz}) = -1.832 \times 10^{-8} \frac{M}{A} \quad (1)$$

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