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An ammonia sensor based on Lossy Mode Resonances on a tapered optical fibre coated with porphyrin-incorporated titanium dioxide

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ABSTRACT

The development of a highly sensitive ammonia sensor is described. The sensor is formed by deposition of a nanoscale coating of titanium dioxide, containing a porphyrin as a functional material, onto a tapered optical fibre. The titanium dioxide coating allows coupling of light from the fundamental core mode to a lossy mode supported by the coating, thus creating a Lossy Mode Resonance (LMR) in the transmission spectrum. A change in the refractive index of the coating caused by the interaction of the porphyrin with ammonia causes a change in the centre wavelength of the LMR, allowing concentrations of ammonia in water as low as 0.1 ppm to be detected, with a response time of less than 30 s.

1. Introduction

Ammonia is regarded as a highly hazardous chemical requiring proper monitoring procedures [1]. Environmental studies have shown that ammonia presents a significant environmental hazard and contributes to acidification and eutrophication and impacts detrimentally on human health [2]. Devices based on optical techniques, particularly those that combine optical fibres and nanomaterials, provide a platform for the development of chemical sensors that offer high sensitivity and specific responses to targeted chemical species by undergoing changes in their physico-chemical properties (optical, electrical, and mass changes) [3,4]. These sensors offer several advantages over other sensing technologies, e.g. small size, biocompatibility, multiplexing, immunity to electromagnetic interference and remote sensing capability [5]. Chemical sensors based on long-period gratings [3,6], tapered fibres [7] and surface plasmon resonances [8] have been reported in the literature.

Tapered optical fibres have been used for the development of wide range of biomedical and chemical sensors [9]. A tapered fibre is fabricated by simultaneously heating and stretching a short section of optical fibre, resulting in a length of fibre that has a narrowed waist. The tapered waist region allows the evanescent field of the propagating mode to spread and thus interact with the surrounding medium. With the deposition of a sensitive layer onto the tapered region, any change in the optical characteristics of the sensitive layer will lead to changes in the optical spectrum obtained from the fibre, facilitating the use of tapered fibres for a variety of sensing applications [7].

LMRs are generated in the transmission spectrum of thin film-coated tapered or cladding-removed optical fibres, where the real part of the permittivity of the coating is positive and larger in magnitude than its imaginary part and is larger than that of the surrounding material [10]. Light, propagating through the coated optical fibre, experiences attenuation maxima at wavelengths that depend on the thickness and refractive index of the coating [11]. This effect is attributed to the coupling between the core mode and a particular lossy mode of the deposited thin film coating [12]. In recent years, LMRs have been studied in detail [13,14] and have been utilised as refractometers [13], demonstrating sensitivity higher than long period grating based sensors [3] and SPR [8].

The key element of the optical fibre chemical sensor is the sensitive layer that changes its optical properties in response to the presence of the particular analyte. The characteristics of fibre optic chemical sensors, such as sensitivity, response/recovery times and especially selectivity, depend strongly upon the performance capabilities and the properties of the sensitive layer. Research in the field of fibre optic chemical sensors has focused on the develop-

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ment of new materials that can be used as sensitive elements [15]. Generally, there are some requirements of the sensitive layer, such as: transparency in the appropriate spectral range, sensitivity (i.e. changes of their optical properties under the influence of the specific chemical species), fast response with a wide dynamic range, reversibility, selectivity, and low cost manufacturing.

Among the different deposition methods that can be applied for sensor development, inorganic and inorganic-organic hybrid materials have obvious advantages over those prepared from organic materials. Various deposition techniques, such as dip and spin-coatings, layer-by-layer deposition (LbL) electrostatic self-assembly, Langmuir-Blodgett deposition, and chemical and physical vapour deposition have been employed for the functional coating of optical fibres [16].

In the past decade a new approach for the fabrication of titanium dioxide (titania or TiO_2) thin films based on the liquid phase deposition (LPD) technique has attracted a lot of interest due to it being a cost-effective and simple fabrication process [17]. The deposition of TiO_2 thin films with desired physicochemical properties onto large and complex surfaces at relatively low temperatures and without the requirement for post fabrication thermal treatment can be achieved readily using this approach. In addition, it is relatively straight forward to functionalise the TiO_2 thin film by the addition of a functional compound into the film forming solution. Dye sensitised transparent thin TiO_2 films have potential in a wide range of applications. For example, tetracationic porphyrin was infused into a TiO_2 matrix, prepared by glancing angle physical vapour deposition, to fabricate an optically active and transparent composite film [18] which was used successfully for the detection of gaseous hydrochloric acid [19].

While there has been extensive characterisation of the evolution of the LMR spectrum during the deposition of coatings onto a range of optical fibre refractometers [13], this paper extends the previous research in LMR (discussed above) by utilising LMR for the development of an optical fibre based sensor for the detection of ammonia in water. LMR is achieved in a tapered optical fibre by depositing a nano-thickness coating composed of TiO_2 incorporating a porphyrin as a template and as the functional material. The coupling of light from the fundamental core mode to a lossy mode supported by the coating creates an LMR in the transmission spectrum of the fibre, which is shown to be sensitive to the changes in the optical characteristics of the coating. This work investigates the use of adiabatic and non-adiabatic tapered optical fibres to develop a lossy mode resonance (LMR) based ammonia sensor.

2. Experimental

2.1. Materials

Boric acid (BA, Mw: 61.83 g/mol), ammonium hexafluorotitanate (AMPF, Mw: 197.93 g/mol), 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate)(TMPyP), potassium hydroxide and ammonia 30 wt% aqueous solution were purchased from Sigma-Aldrich.

2.2. Tapered optical fibre fabrication

Adiabatic and non-adiabatic [24] tapers, of 17 μm and 40 μm waist diameters, were fabricated in a boron-germanium co-doped optical fibre (SM750) with cut-off wavelength 620 nm. The output from a Synrad 48-2 CO_2 laser, with a maximum output power of 25 W, was used to heat the fibre. A ZnSe plano-convex cylindrical lens in conjunction with progressively increasing laser power (2.6–11 kW/cm^2), was used to achieve the required energy flux at the fibre, so allowing the softening temperature to be maintained

as the fibre diameter decreased. The system used to fabricate the tapered optical fibres is described in detail elsewhere [20].

An adiabatic taper can be made by ensuring that the taper angle is sufficiently shallow (≤5.5 mRad) [20]. This was achieved practically by using the requisite laser scan length along the fibre. Adiabatic tapers with waist diameters of 17 μm and 40 μm were made with a laser scan length of 12.5 mm (ensuring an appropriate taper angle), while non-adiabatic tapers, also with waist diameters of 17 μm and 40 μm, were made using a scan length of 4.5 mm.

2.3. Preparation of sensing layers and ammonia sensing

Firstly, the section of optical fibre containing the tapered region was fixed in a holder that ensured that the taper was taut throughout the experiments. Next, the tapered region was immersed into a solution of potassium hydroxide (KOH) for 20 min to treat the surface so that it was terminated with OH groups. After that, the following solutions were prepared separately in water: 500 mM of BA, 100 mM of AMPF and 500 μM of TMPyP. The TMPyP was added to a 1:1 ratio (v/v) of BA and AMPF, and the tapered section of the fibre was immersed into the solution. The ammonia sensitivities of the TMPyP-TiO_2 coated tapered optical fibres were assessed subsequently by immersing the optical fibres into solutions of differing concentrations of ammonia in water; the solutions were prepared by appropriate dilution of the stock solution of 30 wt% ammonia.

2.4. Experimental setup

The experimental setup is shown in Fig. 1. The tapered section of the optical fibre was fixed in a holder with one end connected to a light source and other end connected to a spectrometer. A tungsten halogen lamp was used as the light source and a CCD spectrometer (Ocean Optics HR4000, resolution 0.02 nm) was used to monitor the transmission spectrum of the device.

3. Results and discussion

3.1. TMPyP/TiO_2 composite nanoscale film

The nanoscale TiO_2 coating was formed using the LPD method by the chemical reaction between BA and AMPF via the following mechanism [21]:

$$[NH_4]_2TiF_6 + 2H_2O \rightarrow TiO_2 + 2NH_4F + 4HF \tag{1}$$

$$H_3BO_3 + 4HF \rightarrow BF_4 + H_3O^+ + 2H_2O \tag{2}$$
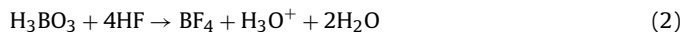
According to Eqs. (1) and (2), when fluorinated titanium ions ($TiF_6{}^{2-}$) are placed in an aqueous solution, firstly titanium hydroxide ions ($Ti(OH)_6{}^{2-}$) are formed, and gradually, the OH$^-$ ions are replaced by F$^-$ ions in titanium hydroxide leading to the formation of TiO_2 [22]. In order to characterise the surface morphology and thickness of the prepared films, films were deposited onto quartz microscope slides and studied using an SEM. The quartz slides were kept in the film-forming solution for five hours and then coated with a 5 nm layer of platinum particles using a Hitachi E-1030 ion sputter, to charge the surface. The deposited films were then analysed under an SEM. A comparison between the structures of the TiO_2 and TMPyP/TiO_2 films is presented in Fig. 2.

The deposited unmodified TiO_2 nanocoating was non-uniform (Fig. 2a) and did not generate LMR in the transmission spectrum of a coated tapered optical fibre. The quality of the film was found to improve significantly when the functional material was included in the solution (Fig. 2b). In this case, the electrostatic attraction between the TMPyP$^+$ cation and the $TiF_6{}^{2-}$ anion facilitated the binding between the template and the matrix [23]. In addition, it enabled the production of a highly uniform film owing to the
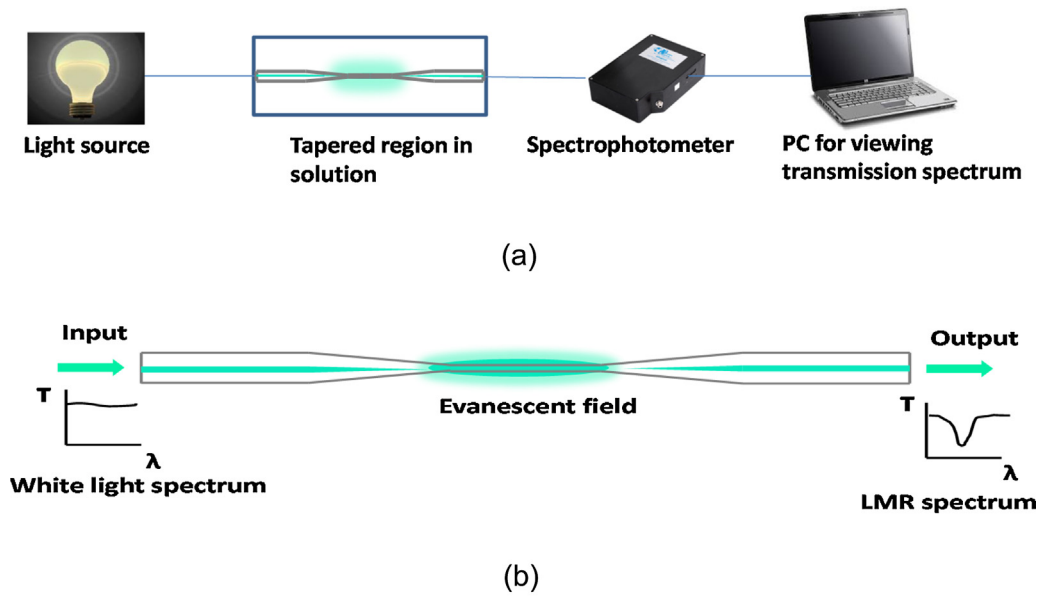
(a)

(b)

Fig. 1. (a) The experimental set-up and (b) the tapered region of optical fibre, illustrating the evanescent field and the LMR.

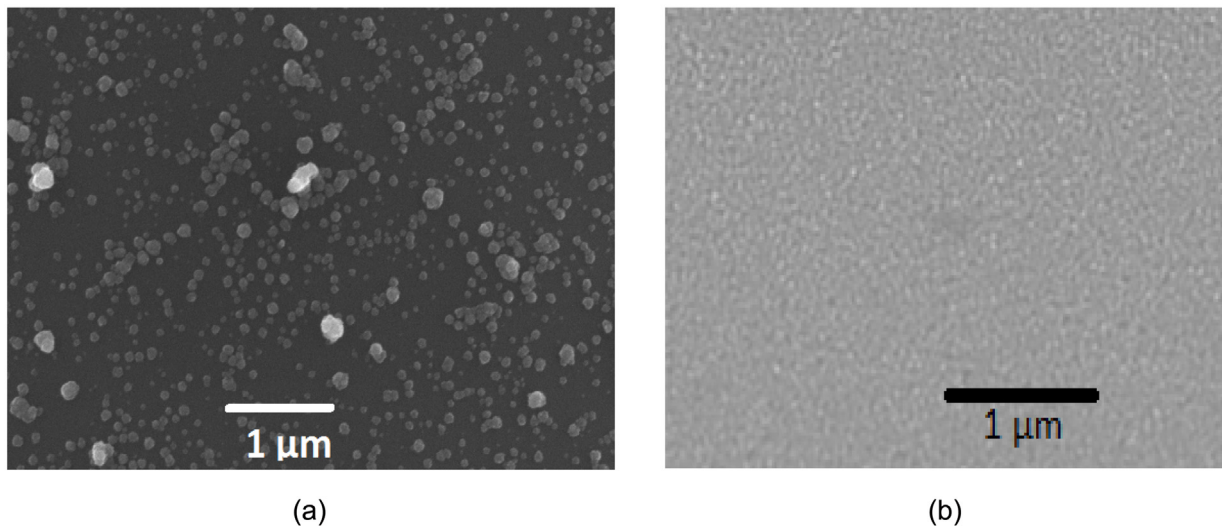(a)   (b)

Fig. 2. SEM images of coatings of (a) TiO_2 and (b) TMPyP-TiO_2 deposited onto glass microscope slides with the liquid phase deposition approach outlined in Section 3.1. In both cases, the glass slide had been kept in the film-forming solution for five hours.

slow hydrolysis of TiF_6^{2-}, resulting in a denser film with increased optical thickness.

3.2. Assessment of suitability of adiabatic and non-adiabatic tapers for LMR generation

The optical fibre tapers were fixed in a holder for the analysis of their transmission spectra in air and water. A taper can be classified as adiabatic or non-adiabatic taper based on its geometry [24]. Fig. 3(a) and (b) compare the transmission spectra of non-adiabatic tapered fibres with waist diameters 40 μm and 17 μm, obtained in air and water. The transmission spectrum was found to be dependent on the taper angle and on the diameter of the taper waist. A taper transition region with a non-adiabatic profile allows coupling of energy from the fundamental core mode to the higher order modes of the tapered section. Interference between the modes on recombination at the 2nd taper transition produces oscillatory features within the transmission spectrum [20]. In a non-adiabatic

taper of 40 μm waist diameter, a smaller proportion of light is coupled into the higher order modes; hence the transmission spectrum has fewer oscillations and is less sensitive to the surrounding RI. As the taper waist diameter is reduced to 17 μm, a higher proportion of light is coupled to higher order modes resulting in oscillations with increased visibility in the generated transmission spectrum. When immersed in water, the features in the transmission spectrum of the 17 μm taper showed a red shift of 19.4 nm, whereas the 40 μm taper showed a red shift of 8.9 nm.

The transmission spectra obtained from adiabatic tapers of waist diameters 40 μm and 17 μm are presented in Fig. 3(c) and (d). When immersed in water, the transmission spectrum does not show any significant change with respect to the surrounding RI. This is due to energy being confined to the fundamental mode and therefore less interaction between the evanescent field and the surrounding medium.

Following the experiments, the 17 μm diameter adiabatic taper was found to be the most suitable for LMR generation and devel-
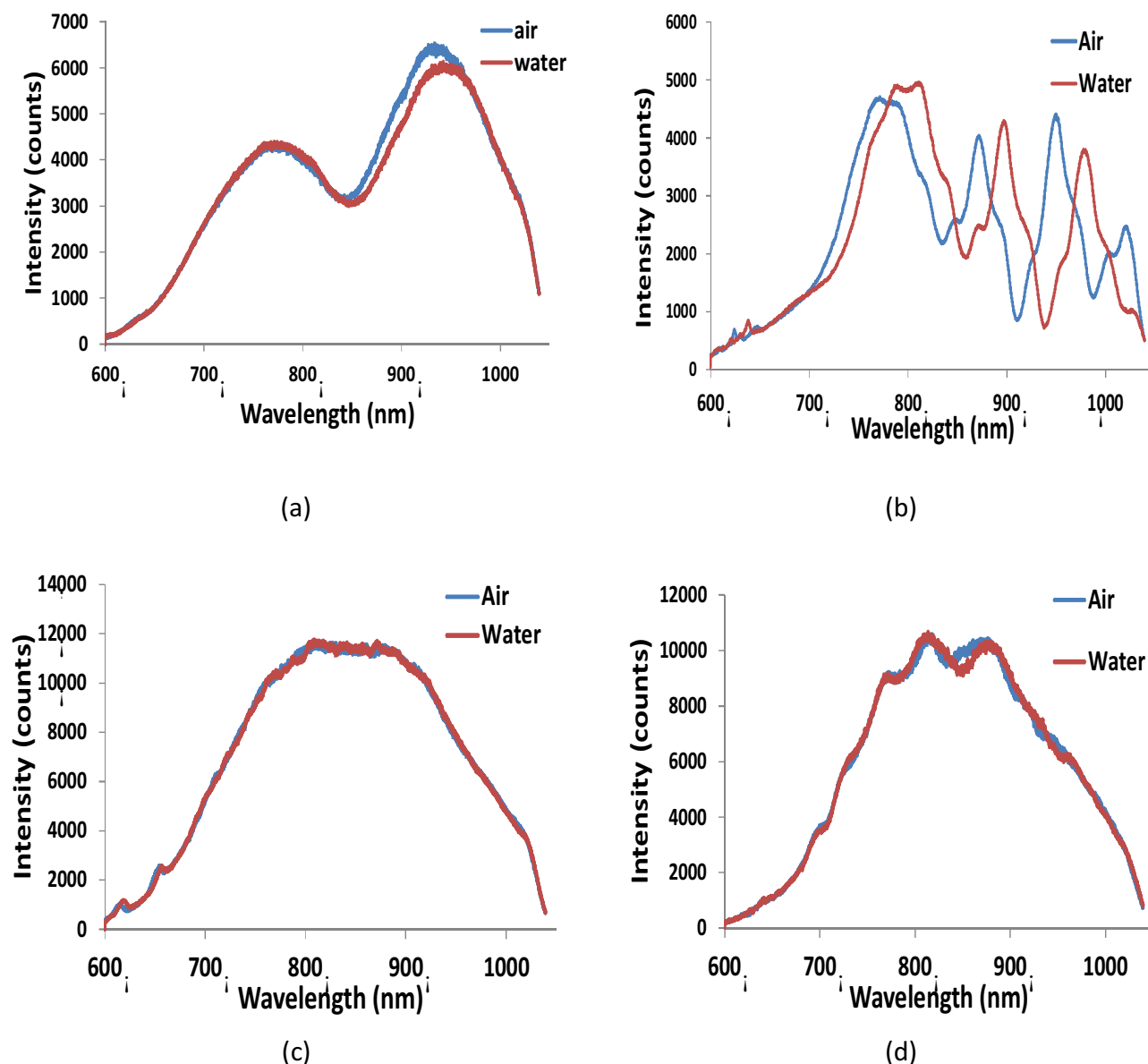
Fig. 3. The transmission spectrum obtained in air and water from optical fibre tapers: (a) 40 μm diameter non-adiabatic taper, (b) 17 μm diameter non-adiabatic taper, (c) 40 μm diameter adiabatic taper and (d) 17 μm diameter adiabatic taper.

opment of an ammonia sensor. LMR could not be generated on non-adiabatic and adiabatic tapers of 40 μm diameter owing to the low interaction between the guided modes and the surrounding medium. While previous work reports the generation of LMR on a 40 μm diameter adiabatic taper [25], we were unable to observe an interaction for taper of this diameter. This could be attributed to the differences in the cut off wavelengths of the fibres used. The evolution of the transmission spectrum of the 17 μm diameter non-adiabatic taper during film deposition is shown in Fig. 4. The formation of the LMR can be seen, which is accompanied by a change in phase of the oscillations in the spectrum. The presence of the oscillations could compromise the analysis of the spectrum when the device is used as a sensor, and thus attention was focussed on the use of adiabatic tapers.

3.3. LMR generation

The initial experiments explored the evolution of the spectrum with increasing coating thickness. The transmission spectrum of

the 17 μm waist diameter adiabatic tapered fibre was recorded whilst depositing the TMPyP-TiO$_2$ coating. Fig. 5 shows the evolution of the transmission spectrum, showing the development of the LMRs in response to the increasing optical thickness of the coating. As shown in Fig. 5(a), the first attenuation band appeared in the transmission spectrum after approximately 5.5 h in solution, when the thickness of coating was approximately 58 nm [26]. The second attenuation band appeared in the TS after 6.5 h in solution, when the coating thickness was approximately 70 nm (Fig. 5(b)). As discussed in Section 3.1, the coating thickness was measured using an SEM.

A grey scale plot showing the generation of LMRs and the evolution of the transmission spectrum is shown in Fig. 6, where the transmission value is represented by white and black, corresponding to 100% and 0%, respectively. The dark lines appearing at around 5.5 and 6.5 h at around 635 nm represent the first and the second LMRs. The generation of LMRs is attributed to the coupling between the core mode and the lossy modes supported by the TMPyP-TiO$_2$ coating. In accordance with previously reported work on LMRs
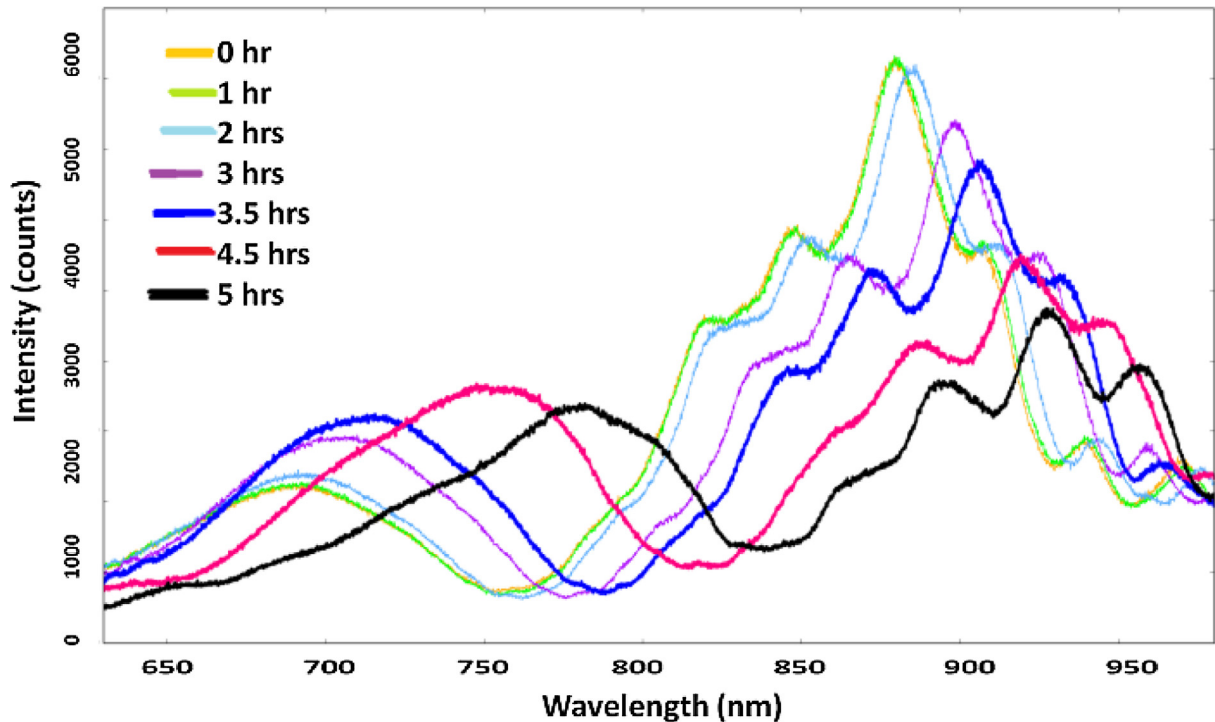
Fig. 4. Evolution of the transmission spectrum of the 17 μm diameter non-adiabatic tapered optical fibre with time and thus increasing thickness of the TMPyP-TiO$_2$ coating.
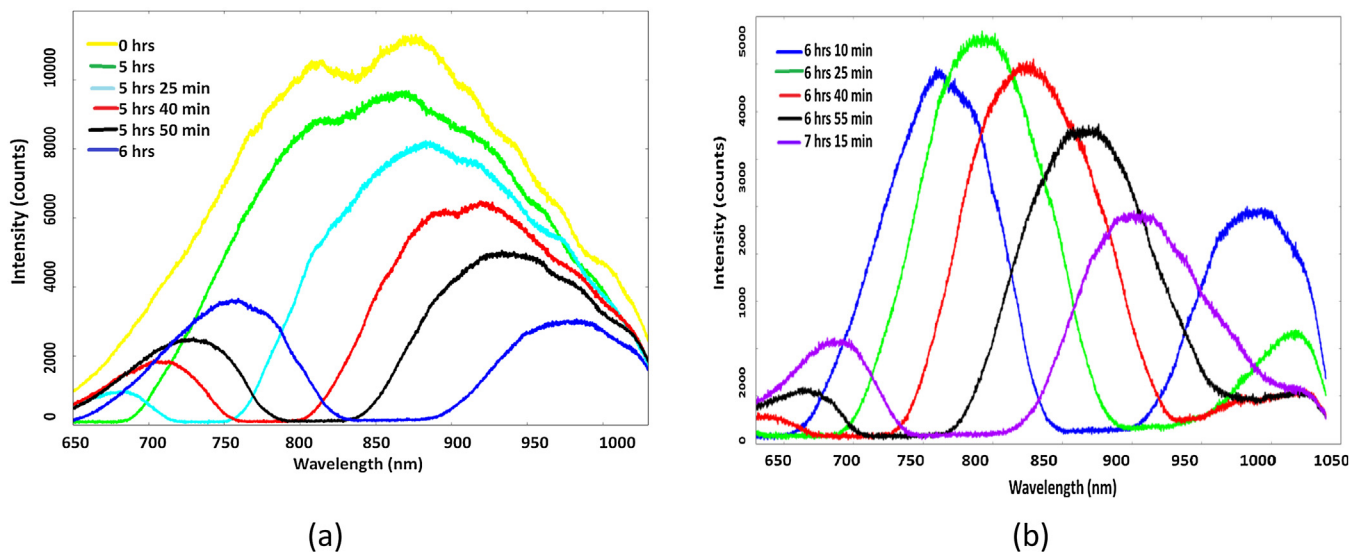

(a)

(b)

Fig. 5. Evolution of the transmission spectrum of an adiabatic taper of waist diameter 17 μm with time, and thus increasing thickness of the TMPyP-TiO$_2$ coating. The formation of the attenuation band generated by the first LMR is shown to occur after approximately five hrs in solution (a). The attenuation band generated by the second LMR is shown to occur after six hrs in solution (b).

[15], the attenuation band was found to be sensitive to the thickness of the coating. As the coating thickness increased, the central wavelength of the attenuation bands generated by the 1st and 2nd LMRs shifted to longer wavelengths, as shown in Fig. 7(a). Fig. 7(b) compares the transmission spectrum recorded with the taper surrounded by air and water and shows that LMR is generated only when the taper is immersed in water.

To form the device to be characterised as an ammonium sensor, a 17 μm diameter adiabatic taper was coated with aTMPyP-TiO$_2$ film. Whilst depositing the coating, the transmission spectrum was monitored and the coated-tapered region was removed from the solution when the central wavelength of the 1st LMR was approxi-

mately 850 nm. The taper was then rinsed with distilled water and dried with compressed air. The first LMR, which is known to be the most sensitive [14], was utilised in this work.

3.4. Ammonia sensing

The tapered section of optical fibre coated with the sensitive TMPyP-TiO$_2$ layer was exposed to varying concentrations of ammonia in water. All of the ammonia solutions, distilled water and coated tapered optical fibre were kept at room temperature (22 °C) for several hours before the experiments in order to eliminate effects arising due to temperature sensitivity of the LMR. The trans-
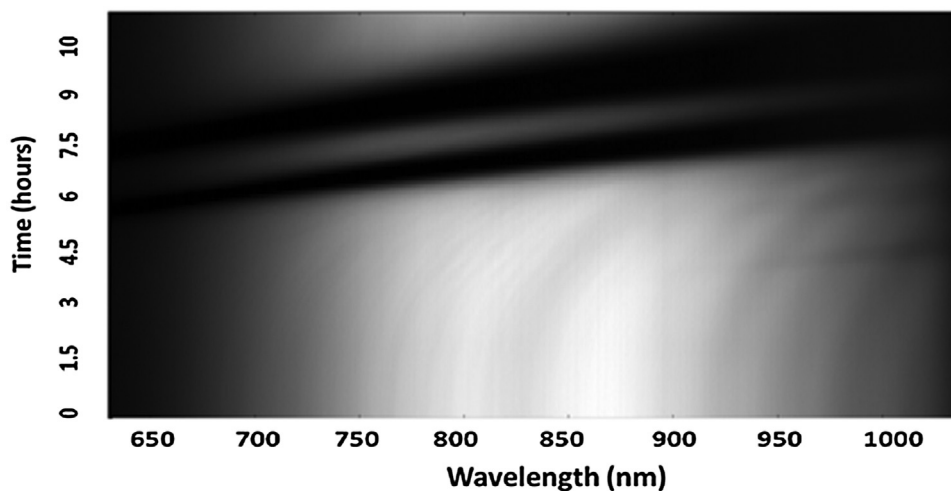
Fig. 6. The evolution of the transmission spectrum of the 17 μm diameter adiabatic tapered optical fibre when immersed in the TMPyP-TiO$_2$ film-forming solution. The grey scale represents the measured transmission, with white corresponding to 100%, and black to 0%.
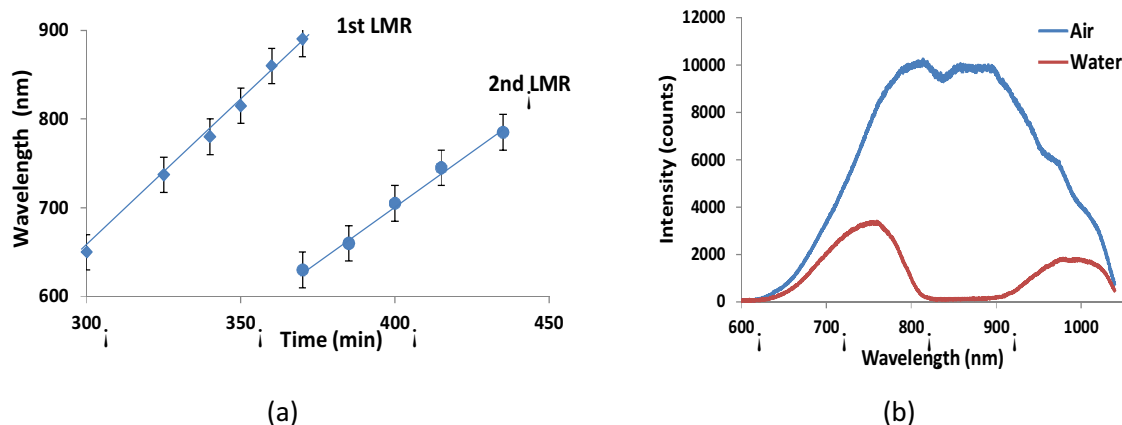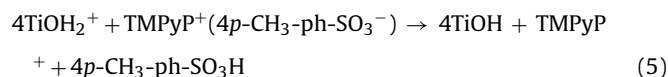

(a)

(b)

Fig. 7. (a) The shift in the central wavelengths of the attenuation bands of the first and second LMRs with respect to time, (b) the transmission spectrum recorded with TMPyP-TiO$_2$ coated tapered optical fibre of 17 μm waist diameter surrounded by air and water.

mission spectrum was observed in water and was monitored while exposing to 0.1, 0.3, 0.5, 1, 5, 10, 50 and 100 and 10,000 ppm concentrations of ammonia in water. Upon immersing the coating in the solution of 0.05 ppm ammonia concentration, no noticeable change in spectrum was observed. When the concentration was increased to 0.1 ppm, after 30 s in solution the attenuation band showed a red-shift of 3.25 ± 0.4 nm. After 2 min the bands stabilised showing a red wavelength shift of 4.1 nm. As the ammonia concentration was further increased to 0.3 ppm, the bands showed a red wavelength shift of 5.78 nm after 2 min. Fig. 8(a) and (b) depict the shifts in attenuation band in response to ammonia concentrations ranging from 0.1 to 1 ppm and 5 to 100 ppm, respectively. The results suggest that the observed red shifts of the LMR bands are due to an increase in refractive index of the coating upon exposure to ammonia in the solution.

Usually, the surface of TiO$_2$ is readily hydroxylated in aqueous solution to form two distinctive hydroxyl groups (Eq. (3)) and is subsequently protonated by the protons generated during the LPD process (Eq. (4)). As a result, during the preparation of TMPyP-TiO$_2$ film, TMPyP is bonded to the TiO$_2$ matrix via an ion-exchange reaction (substitution) of four counter anions (*p*-toluenesulfonate, *p*-CH3-ph-SO$_3$⁻) of the TMPyP with four protons bound to the TiO$_2$ matrix (Eq. (5)). When the TMPyP-TiO$_2$ composite is exposed to ammonia solution, the attraction between both components can

be much improved because the TiO$_2$ surface is negatively charged by hydroxide ion (Eq. (6)).

$$Ti–O–Ti + H_2O \rightarrow 2TiOH \tag{3}$$

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{4}$$

$$4TiOH_2^+ + TMPyP^+(4p\text{-}CH_3\text{-}ph\text{-}SO_3{}^-) \rightarrow 4TiOH + TMPyP$$
$$^+ + 4p\text{-}CH_3\text{-}ph\text{-}SO_3H \tag{5}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{6}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{7}$$

On the basis of the above equilibrium reactions, the electrostatic interaction between the TMPyP and the TiO$_2$ matrix becomes stronger in the composite film and the formation of TiO⁻TMPyP⁺ ion-complexes leads to modification of the refractive index, causing a modification in the transmission spectrum of the device. Porphyrins have high selectivity towards target compounds and typically have low cross sensitivity to non-amine compounds [6]. Therefore, similar phenomenon can be expected when the device is exposed with other amine compounds and the cross-sensitivity of the current system will be dependent on their pK$_a$ values or
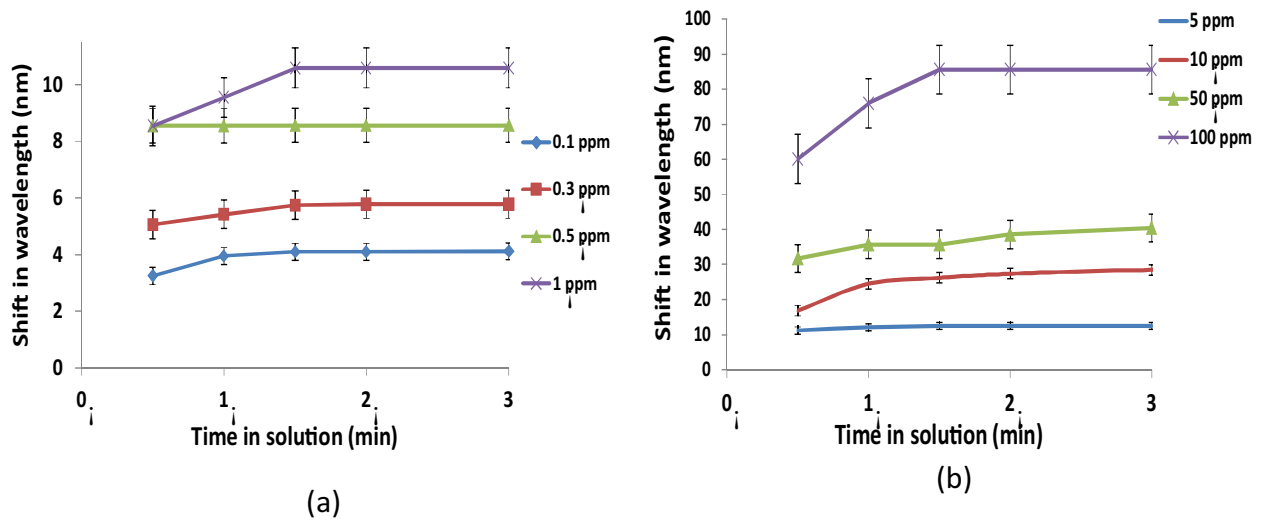
Fig. 8. The shift in wavelength of the attenuation band as a function of time for ammonia concentrations from: (a) 0.1 to 1 ppm and (b) from 5 to 100 ppm. The lines are guides to the eye.
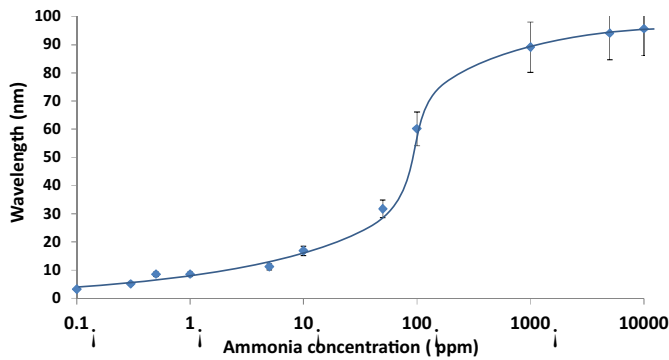

Fig. 9. The shift in wavelength of the attenuation band with respect to ammonia concentration from 0.1 to 10,000 ppm. The line is a guide to the eye.

molecular structures. However, the sensor will not be sensitive to non-amine compounds like alcohols and carboxylic acids. This issue will be examined in more detail in a future publication.

Fig. 9 shows the sensitivity to ammonia at various concentrations and saturation point of the sensor at 10,000 ppm. The current sensor system has a LOD of 0.16 ppm in the concentration range of 0.1–5 ppm. The LOD was defined according to LoD = $3\sigma/m$, where $\sigma = 0.32$ is the standard deviation and m is the slope ($\Delta I/\Delta c$) of the calibration curve, where c is the ammonia concentration and I is the measured intensity [27]. The sensor might be reversible when the amphoteric surface of TiO_2 is balanced with the acid-base equilibria in Eqs. (4) and (7). Furthermore, the sensor can be reactivated by removing all of the TMPyP from TiO_2 matrix and infusing it back in [26]. Previous work demonstrated the complete removal of TMPyP from a similar TiO_2 matrix deposited on optical fibre long period grating by using 0.1 M hydrochloric acid (HCl) and then infusing the TMPyP back in the TiO_2 matrix by immersing the fibre in TMPyP solution [26].

4. Conclusions

This work presents an LMR based optical fibre sensor for the detection of ammonia in water. The LMR was generated by depositing functionalised titania coatings incorporating porphyrin onto the 17 μm diameter adiabatic tapered optical fibre. The first order LMR which is the most sensitive LMR [14] was utilised for sensing of ammonia in water. The sensor allowed concentrations of ammo-

nia in water as low as 0.1 ppm to be detected, with a response time of less than 30 s.

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Biographies

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Dr. Sergiy Korposh received both his bachelor and master degrees in 2001 and 2002, respectively, in physics from Uzhgorod National University, Transcarpathia (Ukraine) and Ph.D. degree from Cranfield University in 2007. He worked as a postdoctoral researcher on development of the novel materials for chemical sensors in the Graduate School of Environmental Engineering of the University of Kitakyushu from 2008 to 2012. He joined Cranfield University as a research fellow in the Department of Engineering Photonics, with a focus on optical fibre-based chemical sensing. He is currently a Lecturer in the Department of Electrical and Electronic Engineering at University of Nottingham. His research interest lies in the field of application and development of fibre-optic chemical sensors modified with sensitive materials.

Professor Stephen W. James gained an MSc. in 1988 in Applied Optics from Imperial College, London, and a Ph.D. from the University of Southampton in 1992. He joined Cranfield University as a research fellow in 1993, where he developed his interest in the development and application of optical instrumentation and sensors. As a reader, he leads the optical fibre sensing activity in the Department of Engineering Photonics, with a focus on sensing chemical and physical parameters, and on deploying instrumentation in real world environments, ranging from foundation piles, railways, and aerospace structures to superconducting magnets. He is currently a Professor in the Department of Engineering Photonics at Cranfield University.

Professor Seung-Woo Lee obtained his Ph.D. degree in chemistry and biochemistry from Kyushu University, Japan in 1999. After postdoctoral work at Kyushu University, he worked for Frontier Research System, RIKEN, on projects based at Spatio-Temporal Function Materials group. He is a Professor at the Faculty of Environmental Engineering of the University of Kitakyushu, Japan. His current research interests include self-assembly and functionalization of organic/inorganic nanohybrids and nanoparticles, molecular imprinting using metal oxide or hybrid thin films, and chemical sensors for biomedical applications. He is a co-editor of the recently published MIP book entitled Handbook of Molecular Imprinting: Advanced Sensor Applications.

Professor Ralph P. Tatam, BSc (Hons), Ph.D., 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 Ph.D. in Physics in 1986. 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. 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.