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Opening up optical fibres

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Abstract: A unique optical fibre design is presented in this work: a laterally accessible microstructured optical fibre, in which one of the cladding holes is open to the surrounding environment and the waveguide core exposed over long lengths of fibre. Such a fibre offers the opportunity of real-time chemical sensing and biosensing not previously possible with conventional microstructured optical fibres, as well as the ability to functionalize the core of the fibre without interference from the cladding. The fabrication of such a fibre using PMMA is presented, as well as experimental results demonstrating the use of the fibre as a evanescent wave absorption spectroscopy pH sensor using the indicator Bromothymol Blue.

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1. Introduction

The core of microstructured optical fibre (MOF) is generally a pure material whilst the cladding is composed of a two-dimensional microstructure consisting of two or more substances [1]. For the most common case of a solid core MOF, the cladding consists of an array of air holes in a solid material that run longitudinally along the length of the fiber. The cladding is thus characterized by an average refractive index value [2] less than that of the solid material, allowing the fibre to guide by total internal reflection. The solid material is usually silica although other materials may be used [3, 4]. Similarly, the holes of the cladding are not restricted to being air filled, and can be filled with any material that preserves the lower index condition of the cladding. The optical properties of the microstructured cladding, and thus those of the entire waveguide, depend on the optical properties of these constituent materials as well as the relative amount and arrangement of each. The corollary of this is that the constituent materials have a direct effect on the guidance properties of the fibre and it is this intrinsic link between materials and optical properties, coupled with the ability to freely exchange at least one of these materials via the microstructure, which make MOFs such interesting vessels for chemical sensing.

The evanescent field of a guided mode in an optical fibre travels in the cladding, and typically carries only very low power. Conventional fibre optic chemical sensors based on the use of the evanescent wave absorption spectroscopy involve removal of the cladding [5, 6] or tapering [7] of the fibre to achieve overlap of mode field and sample. These structures are fragile and therefore typically short in length. By filling the holes of an index guiding MOF with the analyte, overlap can be achieved without compromising the strength of the device [8-11]. Furthermore, the geometry of microstructured optical fibre can be designed to yield extremely large evanescent fields [12]. The detection of gases incorporated into the holes of MOF has been experimentally demonstrated [8], as has detection of analytes in the aqueous phase [9, 10].

Evanescent wave sensing schemes naturally lend themselves to the detection of surface-bound analytes due to the rapid exponential decay of the field away from the core surface. Such a technique is particularly important for biochemical sensing, where bio-recognition elements are often immobilized on a substrate. Jensen, *et al.* [11] have demonstrated the detection of fluorophore labeled antibodies through the immobilization of a complimentary antigen layer on the inside of the holes of a microstructured polymer optical fibre (mPOF). In this case, however, the fluorescence was excited by side illumination rather than the evanescent field of a propagating core mode.

An advantage of conventional fibre evanescent wave sensors such as the stripped cladding or tapered devices is that they can operate immediately when placed directly in the analyte solution. On the other hand, their microstructured counterparts require filling of the cladding holes with the analyte before any interrogation can occur. Capillary action may be the sole

driving factor for liquid filling of the microstructure holes, although pressure applied to one end of the fibre is often used to quicken the process. Diffusion of analytes in solution through pre-filled fibre capillaries is, however, an extremely slow process, making online sensing difficult. This is also true for the natural diffusion of gaseous analytes through a MOF [13]. The simultaneous coupling of both light and sample fluid into the fibre poses an additional problem.

We report on the fabrication of a laterally accessible mPOF device whereby fluid from the bulk can access the holes of the microstructured cladding along the length of the fibre. This is facilitated by a slot that is oriented laterally with respect to the fibre axis. Entry and exit of fluid through the endfaces of the fibre is avoided. Two examples of mPOFs with lateral slots are shown in Fig. 1. The diameter of the fibres in Fig. 1 is approximately 140 μm .

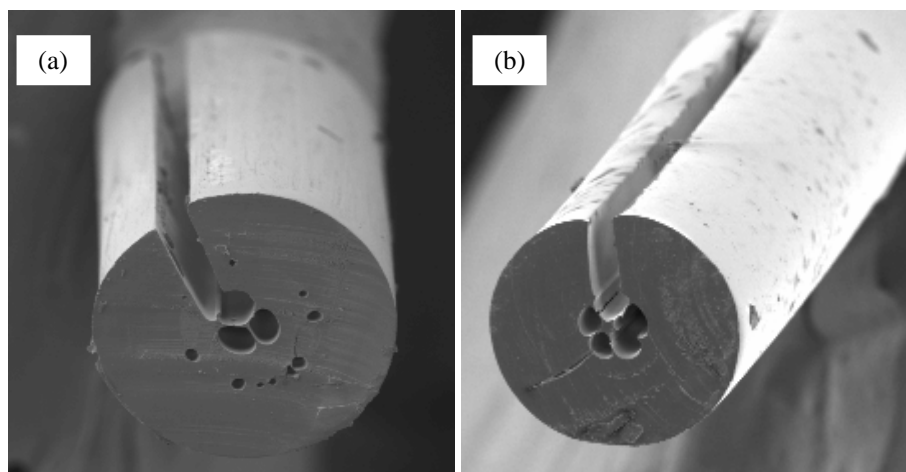


Fig. 1. Slotted microstructured polymer optical fibres (mPOF); a) 3-hole design and b) 5-hole design. In each case the fibre diameter is approximately 140 μm .

In this open sensing scheme, although the core is directly exposed to the analyte via the slot, the protective fibre jacket remains functional. If the midsection of such an exposed core fibre was placed in a reaction vessel, the reaction may be monitored optically in real time via absorption, fluorescence etc. The response time of the device would be limited by the time taken for the analyte to reach the vicinity of the core from the bulk. Since the slot is only $\sim 75\mu\text{m}$ deep and exists along the length of the fibre, the analyte is able to move into and out of the vicinity of the core unhindered, unlike the case of a regular MOF in which the cladding and fibre jacket remain intact.

Although it is possible to create lateral access to the microstructure of a fibre through laser drilling [14] or by bursting through the fibre wall through the simultaneous application of heat and pressure [15], such techniques produce a hole rather than a continuous slot and so the long diffusion times associated with analytes moving through the cladding capillaries remains. Furthermore, the incorporation of lateral holes at the fibre rather than an earlier stage can lead to significant losses, e.g. by disturbance of the core in the drilling process or deformation of structure due to the application of heat and pressure. An advantageous feature of both slotted fibres and those with holes into the microstructure is that since the analyte accesses the fibre laterally, such devices can be potentially spliced to conventional fibres without loss of access to the microstructure.

2. Fabrication of the fibre

Fabrication of the slotted devices requires only minimal deviation from standard drawing procedures as the only additional step was drilling lateral holes into the preform before being drawn to fibre. For the fabrication of mPOF [16], the process begins with an 8 cm preform

that is drawn down to an intermediate cane of ~ 0.6 cm diameter and then sleeved. Holes are then drilled into the sleeved cane, perpendicular to the cane axis. These holes intersect with a single air hole and do not impact the core. Cooling fluid is used when drilling the lateral holes and this is cleaned by rinsing both the lateral and microstructured holes with water and then blasting with compressed air. This cane is then drawn to fibre, with diameter ~ 150 μm , and each drilled lateral hole of the cane is stretched to form a slot in the fibre.

Shown in Fig. 1. are two examples of the exposed core mPOF. In Fig. 1(a), the lateral hole has been drilled into one of the holes of a 3-hole suspended core design, and in Fig. 1(b), it has been drilled into one of the holes of a 5-hole design. It is also possible to drill through more than one ring of holes to reach the innermost ring, although disruption of the cladding in such a way may change the guidance properties of the fibre.

In the case of a 1mm diameter hole drilled into the 0.8 cm cane, 5-6 m of 150 μm slotted mPOF with an approximately uniform diameter was produced. This length is increased by increasing the diameter of the drilled hole in the cane. Some fluctuation in fibre diameter was observed during the draw process, related to heat transport with and without an open slot. The result was that the slotted regions of fibre have a diameter about 70 μm smaller than the regions without a slot. However, the diameter within a single region i.e. with or without a slot, remains constant.

Significantly longer lengths of the slotted fibre were also produced by drilling ~ 15 overlapping holes in the cane. This formed a slot in the cane itself, and hence an extended slot in the fibre. Minimal fluctuations in fibre diameter were observed when drawing the cane with a slot rather than holes, and steady-state draw conditions were achieved. Other possible methods of forming a slot in the cane are through laser or hot-wire cutting.

The size of the hole drilled in the cane corresponds well to the slot width in the fibre. Shown below, in Fig. 2, are fibres in which holes of 1.0 mm, 1.6 mm, and 2.5 mm diameter were drilled. The diameter of the three fibres shown is approximately 150 μm , and all fibres were drawn under the same conditions. Ranging from a narrow channel to an open bay, varying the width of the slot can change the rate that new chemical species diffuse into the sensing region.

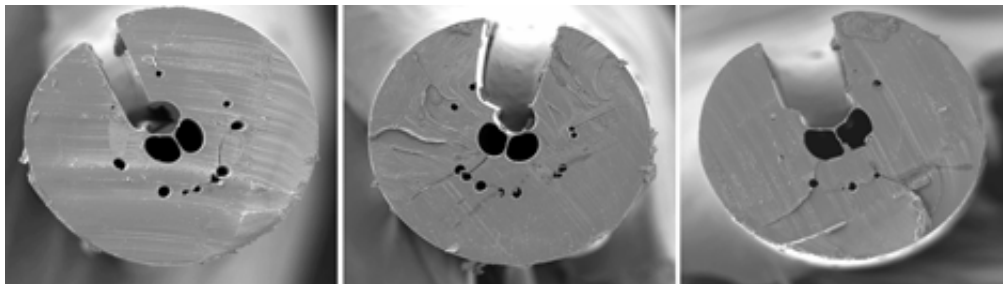


Fig. 2. Slotted mPOF with varying slot sizes. The slots were formed by drilling 1.0 mm, 1.6 mm and 2.5 mm holes into the intermediate preform or cane.

It can be seen from Figs. 1. and 2. that the microstructure experienced minimal, if any, distortion due to the presence of the lateral slot. The microstructure hole that connects to the slot is approximately the same size and shape as the other microstructure holes despite being open on one side. The slot remains open along its length, and the sides of the slot sustain an approximately parallel orientation. It appears that the existence of the slot induces no additional losses to the fibre.

3. Optical detection of chemical species

A simple test was conducted using the indicator bromothymol blue (BTB) (Sigma Aldrich) to test the sensing characteristics of the slotted mPOF. The colour change of BTB was used to show a change in the pH of a solution inside the fibre and demonstrate that the device is able

to function over a range of wavelengths. The set-up consisted of beaker filled with MilliQ filtered water, into which the mid-section of a slotted fibre was dipped. The ends of the fibre were secured on v-groove mounts on micropositioners. Since these mounted ends of the fibre were placed at a greater height than the submerged section, the height of solution in the slotted hole reached some maximum value rather than traveling the length of the fibre by capillary action. The fibre used was a slotted version of a 3-hole design with an outer diameter of $\sim 140\ \mu\text{m}$ with a slot width of $\sim 40\ \mu\text{m}$.

The transmission spectrum of a supercontinuum source [17] of a fibre immersed in water was taken using an Ocean Optics USB 2000 spectrophotometer. BTB is yellow in acidic solution and blue in basic solution. To make the solution basic, 0.1M NaOH was dropped in to the vessel bringing the solution pH to ~ 11.3 . The solution was stirred with a glass stirrer until it visually looked homogenous (approx 10s) and then a spectrum was recorded. 0.1 M HCl was then added (pH of solution ≈ 2.9) and the process repeated. In each case, the measurement was repeated 1 minute and 5 minutes after the initial measurement. No changes with time in the spectra were observed. The spectra recorded with acidic and basic BTB solutions were subtracted directly from the reference spectrum taken through a water filled fibre to yield the absorption spectra shown in Fig. 3.

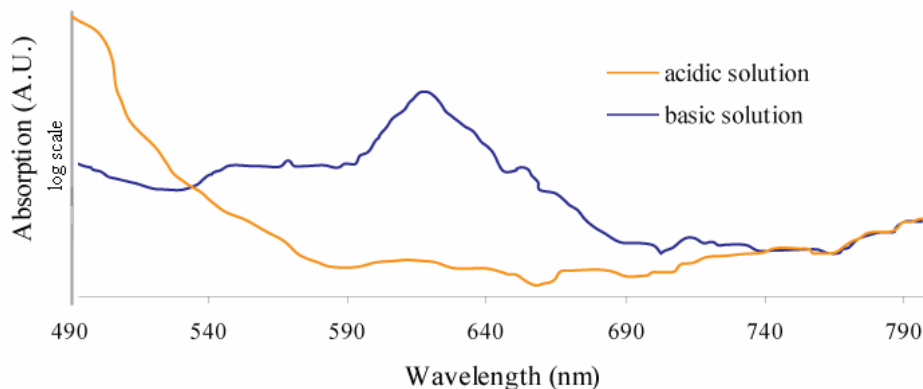


Fig. 3. Normalized absorption spectra through a slotted fibre in acidic and basic solution of BTB.

Figure 3 reveals two spectrally distinct forms of BTB, making evident the ability of laterally accessible mPOF to detect changes in absorption wavelength. The spectra were recorded immediately after addition and brief stirring of the acid or base, indicating that if any dead-time before the solution enters the fibres is experienced, it is shorter than the measurement time in this experiment,

An absorption peak centered at around 620 nm is evident in the spectrum of the basic (blue) form of the indicator, whilst an increasing absorption at shorter wavelengths down to 490 nm (approximately the lower limit of the supercontinuum source) appears in the presence of the acidic (yellow) form of BTB. BTB spectra for different pH values generally reveal much smaller absorption in the acidic form when compared to the basic form in aqueous solution. However, spectra obtained through the slotted fibre reveal a larger than expected absorption value for the acidic BTB form. This is because the acidic form of BTB is the protonated form which interacts strongly with the surface of the PMMA fibre, which has a slight negative charge. This leads to higher absorption on the surface than in the bulk of this neutral molecule. On the other hand, the basic form of BTB is the BTB^- anion. Anions of BTB have been recognized as surface inactive chromophores for surfaces that exhibit a slight negative charge, in this case the PMMA. This result agrees well with previous studies of BTB/BTB⁻ absorption based on planar waveguide geometries [18]. Despite the presence of surface interactions common to all evanescent wave sensors, mPOF filled with BTB solution is a feasible pH sensor, since the system at each pH would exhibit a distinct spectrum regardless of the relative amounts of the chromophore aggregating on the waveguide surface.

Indeed, surface interactions may be helpful in some systems to enhance the signal obtained via an evanescent field.

4. Conclusions

A MOF with a laterally exposed core along the length of the fibre has been fabricated for the first time without compromising the strength of the waveguide. The slot was simple to fabricate and the slotted mPOF was drawn under relatively standard draw conditions. Both 3- and 5-hole versions of the slotted mPOF were fabricated. Control over the width of the access slot was demonstrated through the choice of hole diameter drilled in the mPOF cane. Control of the length of the slot was also achieved by the choice of hole size in the cane and more significantly by fabricating an extended slot in the cane, which was drawn to long lengths of the laterally accessible fibre. It is possible to achieve steady state drawing if the holes in the cane are replaced by a slot that runs along the entire length of the cane, whilst maintaining the integrity of the microstructure.

Exciting variations on the current slot-access design will be explored in further work, including fabrication of a hollow core microstructured fibre [19, 20] with lateral access to the core. This would be a major development in the field of remote gas sensing, since large overlap of the field and sample can be achieved [21], in an online sensing scheme. A possibility to achieve extremely high overlap of sample and mode field for liquid phase analytes in a 'hollow' core also exists, however in this case the guidance mechanism would be index guidance [22].

We have demonstrated the laterally accessible mPOF can be used to sense the presence of chemical species. The slotted fibre is truly a sensor, rather than a probe, since it can deliver real-time and online information. Furthermore, this open fibre has the potential to be a quasi-distributed sensor, e.g. in combination with optical time domain reflectometry, because the analyte can enter the fibre anywhere along its length.

The colour change of Bromothymol Blue in solutions of different pH was used to test the basic lateral access mPOF sensor characteristics using evanescent wave absorption spectroscopy. The experimental results obtained here reinforce an important concept: that evanescent wave devices, especially those fabricated from polymers, are extremely surface sensitive and hence represent an ideal sensing scheme for substrate bound sensing. As this is the case for most biosensing, further research using solid-core mPOF opened by a lateral slot will focus on this area.

Apart from a new approach to chemical sensing with MOF, this laterally accessible mPOF opens up other possibilities for MOF devices, since the core of the fibre is now directly exposed. For example, deposition of thin films on the core of the fibre by metal evaporation for plasmonic fibre devices can be realized, as well as nanoparticle implantation and ion bombardment treatments of the surface and complex grating writing procedures that are hindered by interference from the microstructure.

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