Liquid-filled hollow core microstructured polymer optical fiber

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Abstract: Guidance in a liquid core is possible with microstructured optical fibers, opening up many possibilities for chemical and biochemical fiber-optic sensing. In this work we demonstrate how the bandgaps of a hollow core microstructured polymer optical fiber scale with the refractive index of liquid introduced into the holes of the microstructure. Such a fiber is then filled with an aqueous solution of (-)-fructose, and the resulting optical rotation measured. Hence, we show that hollow core microstructured polymer optical fibers can be used for sensing, whilst also fabricating a chiral optical fiber based on material chirality, which has many applications in its own right.

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OCIS codes: (060.2370) Fiber optics sensors; (230.3990) Microstructure devices; (160.4760) Optical properties; (999.9999) Chirality

References and links

1. Introduction

Microstructured optical fiber (MOF), or photonic crystal fiber [1], offers huge potential to the field of fiber-optic chemical and biochemical sensing. The characteristic micron-sized holes that run along the length of MOF can be filled with a fluid, thereby bringing the species to be quantified in contact with the mode field propagating through the fiber over long lengths. Of particular importance is the ability of MOF to guide whilst being filled with low index materials such as aqueous solutions, which are important for biosensing, and gases. Sensing mechanisms can be based on the modulation of characteristics such as polarization, wavelength, intensity and phase.

Light may be guided in MOF by two distinctly different guidance mechanisms: in a solid core surrounded by a microstructured cladding providing index guidance [1], or, alternatively, in a hollow core surrounded by a necessarily regular microstructured region designed such that certain wavelengths cannot propagate through this region and are hence confined to the hollow core [2]. Correspondingly, there are several sensing regimes possible using MOFs. An advantageous feature common to all three cases of MOF chemical sensors described below is that sample sizes required are minute, since the volume of the holes of, say, a 50 cm length of MOF is typically of the order of microlitres.

Proposed by Monro et al. [3], the cladding holes of an index guiding MOF can be filled with a liquid or gas and the species sensed by the evanescent field that propagates in these holes. Careful design of the MOF incorporating features such as small core size and large air-fill fraction in the microstructured cladding allow a useable overlap of the mode field and sample material, whilst circumventing the problems of short length and fragility associated with traditional stripped cladding [4], and D-shaped [5], evanescent field fiber-optic sensors. Evanescent field gas sensing in the holes of a MOF [6], and in a random hole MOF [7], has been demonstrated. Fluorophore-labelled biomolecules in aqueous solution have been detected in the holes of a MOF by guiding in the silica segments between the holes of the microstructured cladding region [8].

Another sensing possibility made available by MOF is that within a liquid-core index guiding fiber [9], where the microstructured cladding is designed such that the air-filling fraction of the cladding is high and therefore the average index of the cladding is lower than that of the liquid core. A highly attractive aspect of this configuration is that the mode field is almost completely confined to the liquid sample. In this way the overlap of field and sample is increased and hence shorter fiber samples can be used, requiring a smaller volume of...
sample solution. Vienne et al. have demonstrated guidance in a water-core MOF [10], although the selective filling of only the central hole has proven somewhat problematic.

A third sensing configuration that avoids the problem of selective filling, whilst achieving almost total confinement of light to the sample fluid, is by use of a hollow core MOF (HC-MOF), in which both core and microstructured cladding holes are filled with the sample fluid. Widely referred to as photonic bandgap fibers, such waveguides exhibit a periodic spectral response. An example of a HC-MOF is shown in Fig. 1 [11]. Guidance in such a structure may be described by the antiresonant reflecting optical waveguide (ARROW) model [12, 13], by which light is confined to the hollow core of the waveguide unless it can couple to one of the high-index rods of the microstructured cladding (the high-index sites between adjacent holes). Only those frequencies that can be supported by the cladding rods will be lost, giving rise to guided frequency “bands” in the HC-MOF. The use of HC-MOF has been demonstrated for gas sensing [14].

![HC-MOF](image)

**Fig. 1.** The HC-mPOF used in this work.

Filling the holes of such a fiber changes both the refractive index of the core and the cut-off frequency of the cladding rods, and therefore changes the position and width of the frequency bands that are able to propagate in the core. However, the guidance mechanism itself remains the same. Such scaling of the bandgaps can be calculated by the following scaling law [15], which is based on the scalar waveguide approximation. When the holes of a HC-MOF are filled with a material other than air, the initial index ratio of the solid material and air $n_0$, is shifted to some smaller value $n$.

The corresponding shift in wavelength is then:

$$\lambda = \lambda_0 \left[ \frac{1 - \left(1/n^2\right)}{1 - \left(1/n_0^2\right)} \right]^{1/2}$$

(1)

where $\lambda_0$ is the wavelength at which the bandgap originally occurs, and $\lambda$ is the wavelength of the shifted bandgap. Wavelength shifting in silica MOF filled with D$_2$O has been demonstrated [16], and Eq. (1) agrees well with the experimental results obtained, although no further work in the field of sensing or otherwise with these liquid filled fibers has been reported to date.

Microstructured polymer optical fiber (mPOF) [17], offers some unique prospects to fiber-optic sensing. It is fabricated from polymethylmethacrylate (PMMA), which can be readily chemically modified on its surface to yield a variety of moieties, including those to which biomolecules can be easily attached [18]. Although not strictly necessary, biorecognition elements such as enzymes and proteins are often immobilized in a sensor so that their

#68268 - $15.00 USD

Received 21 February 2006; revised 12 April 2006; accepted 13 April 2006

(C) 2006 OSA 1 May 2006 / Vol. 14, No. 9 / OPTICS EXPRESS 4137
orientation is favourable for reaction and so that the device can be used for continuous monitoring. Jensen et al. have reported the physical binding of antibodies and antigens to the surface of the holes of a solid core mPOF, and fluorescence of the tagged matching molecules has been excited via side illumination of the fiber, which is then coupled to the core [19]. Since surface modification of PMMA does not require high temperatures or pressures, such reactions are possible at the fiber stage without damaging either the fiber structure or attached groups. Additionally mPOF is more flexible and biocompatible than its silica counterpart, making it well suited to \textit{in vivo} use.

In this paper we present the first demonstration of bandgap shifting in a hollow core mPOF (HC-mPOF), and also demonstrate how such a fiber can be used for chemical sensing. As an initial demonstration of the use of HC-mPOF for chemical sensing applications, we have chosen to measure the concentration of a chiral material in aqueous solution. Chiral molecules exhibit a ‘handedness’ where a mirror image of the molecule is not superimposable on the original. These two isomers are known as enantiomers, and a solution of each exhibits optical rotation. Optical rotation is commonly used to measure concentration in the sugar industry and enantiomeric purity in applications such as drug synthesis. It is hoped that a sensor such as the liquid filled HC-mPOF could measure such reactions \textit{in situ}, and would be especially useful in situations where only small sample volumes are available. Furthermore, a chiral optical fiber has applications in its own right, particularly in in-fiber technology such as polarization-mode converters [20], dispersion modification [21], and optical switching [22].

2. Bandgap shifting

The fiber used in this experiment was the proof-of-concept HC-mPOF described in detail in reference [11], and shown in Fig 1. The fiber consists of a hollow core of 68μm diameter, surrounded by three rings of air holes and has a length of 49.5 cm. Light from a supercontinuum source [23] was launched into the core of the HC-mPOF, and the output coupled to a spectrum analyzer. Judging from the output image, the fiber was clearly multi-moded. Care was taken that only light from the core of the fiber was launched into the analyzer, and the spectrum is shown in Fig. 2 below.

![Fig. 2. Transmission through an air filled (black curve) and water filled (gray curve) HC-mPOF.](image)

The fiber was then filled with Millipore water by attaching a 5mL syringe to one end of the fiber and placing the other in a beaker of the water. The syringe was held open and all holes of the fiber were filled in approximately 10 minutes. The volume of the fluid held by filled fiber is of order 1μL. The fiber was examined under a microscope, and no air-bubbles, which could cause loss or completely suppress guidance, could be seen in the core or cladding holes of the fiber. To ensure that no air entered the holes after filling, the fiber was mounted “under-water” in modified v-groove mounts that effectively kept the fiber submerged during
all measurements. The measurement described for the unfilled fiber was then repeated for the water-filled fiber. The spectrum of the water-filled fiber is also shown in Fig 2.

For both the unfilled and water-filled fiber spectra, there are two distinct transmission peaks observable. It is not clear whether these peaks are from two different transmission bands of the fiber or, alternatively, that it is one band fragmented due to defects in the structure. The size and shape of the air holes and PMMA rods in the fiber used are certainly not uniform, and variation in rod diameter can lead to resonances occurring in what would otherwise be a singular band. Broader bands more suitable for many sensing applications are certainly possible with improvement in the design and fabrication of the fibers, as has been demonstrated for silica MOF.

The unambiguous scaling of spectral features with refractive index of the holes support the proposition that the guidance mechanism is bandgap guidance. The phenomenon of bandgap guidance in a liquid core is of great importance for sensing applications, since the mode field is almost completely confined to the liquid core of the waveguide, and thus the interaction of the sample and field is maximised. As expected, the transmission peaks in the water-filled fiber have shifted to shorter wavelengths and are narrower. The shifts of these peaks agree to approximately 1% with the values predicted by the scalar frequency scaling law Eq. (1), as seen in Table 1.

<table>
<thead>
<tr>
<th>Air-filled fiber measured wavelength (nm)</th>
<th>Water-filled Fiber measured wavelength (nm)</th>
<th>Predicted wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1 1430</td>
<td>875</td>
<td>868</td>
</tr>
<tr>
<td>Peak 2 1140</td>
<td>700</td>
<td>692</td>
</tr>
</tbody>
</table>

It should be noted that only very poor transmission was observed for wavelengths longer than about 900 nm due to the high absorption of water in the infrared region of the spectrum. Hence, it may well be that with a wide band gap, the frequency limits of the fiber do not limit the sensing system overall, since it is the aqueous medium of the core itself that limits the spectral range of the waveguide. This is especially true for the sensing of biochemicals, which generally require strictly aqueous solutions. Furthermore, a fiber with only discrete transmission bands may prove advantageous in some schemes whereby unwanted ‘noise’ is effectively filtered out.

### 3. Chiral fiber

A fiber similar to that in section 2, although of slightly different cross-sectional dimensions, was used in this section. The fiber length was 3.5 cm. A solution of (-)-fructose (Sigma, 99%) was made up to a concentration of 0.7 g/mL. (-)-fructose has a specific rotation, \( \alpha \), of \(-92.7^\circ\) [24], where \( \alpha \) is the normalised rotation of the optically active species given by:

\[
\alpha = \frac{\alpha}{l_c}
\]

where \( \alpha \) is the measured optical rotation in degrees at 589 nm, \( l \) the sample path length in decimetres (dm) and \( c \) is the concentration of the optically active species in g/mL [25].

The fiber was placed in the same set-up as described in section 2, however the set-up was modified to include 2 polarizers at either end of the filled fiber. The source light is unpolarized, and the first polarizer linearly polarizes the light entering the sample. The second polarizer (or analyzer) was rotated such that maximum attenuation was obtained, for the case where the fiber is in place in the set-up and also without the fiber. The difference in the angle of the analyzer between the two cases indicates the degree to which the chiral
solution-filled fiber rotates the polarization of plane polarized light. All measurements were made at 589nm, which fell in one of the bandgaps of this particular fiber. A measurement was also made of the (-)-fructose solution in a 5cm reference cell.

The measurement of optical rotation through the sample cell was in good agreement by that predicted by Eq (2). Optical rotation through the fiber was measured to be \(-26.5 \pm 3^\circ\), whereas a value of \(-23^\circ\) is predicted by Eq. (2). It is possible that the fiber is birefringent and if the light is launched along one of the polarization axes and the fiber happens to be twisted, then optical rotation additional to that from the chiral solution could be measured. Thus the birefringence of the fiber was tested, and no measureable birefringence was observed. Speculations about the small discrepancy between expected and observed values include an increased path length traversed by higher-order modes resulting in a longer interaction length. More detailed work, possibly using a single-mode HC-mPOF is [16], will be undertaken to resolve this issue.

This is the first demonstration of liquid sensing with a HC-mPOF, or more generally a HC-MOF, by band-gap guidance. Furthermore, we believe this is the first report of the fabrication of a chiral fiber, certainly one that operates by bandgap guidance, to the best of our knowledge.

4. Conclusions

Initial exploration in the field of HC-MOF sensing has brought forth promising results. In this work we have established that chemical sensing in the liquid-filled hollow core of a HC-mPOF, or more generally in any HC-MOF, is indeed possible. The spectral shift upon filling the mPOF with liquid shows that in the fiber operates by bandgap guidance. This is of great importance since it implicates that almost the entire mode field propagating through the fiber exists in the liquid core. The large overlap of mode-field and sensing species has been an elusive goal for fiber-optic chemical sensing research, and the increased sensitivity of such a design opens up many new sensing possibilities. The myriad of surface chemistry reactions available for PMMA makes it an ideal material with which to fabricate biosensors, and the characteristics of flexibility and biocompatibility increase the potential of HC-mPOF for in vivo sensing use.

As an initial demonstration of how HC-mPOF may be used as a sensor, we have shown that optical rotation can be measured in a HC-mPOF that is filled with a chiral solution. Many biological species, sugars and useful drugs are chiral molecules and the measurement of optical rotation is an accurate way to determine the concentration of the enantiomers. However, the aim of this work was merely to demonstrate the use of HC-mPOF for sensing applications, and the modulation of other properties such as wavelength, intensity and phase are further exciting possibilities for sensing schemes that will be studied in future work.

The final conclusion that can be drawn from this work is that it is possible to fabricate a chiral optical fiber that is based on molecular chirality through use of a HC-mPOF. The applications of chiral optical fiber include polarization-mode conversion, dispersion modification, and optical switching.

Acknowledgments

The authors would like to acknowledge Ian Bassett and Yucheng Zhao for useful discussions about chirality and hollow core fibers, and Barry Reed and Martijn van Eijkelenborg for fabrication of the fibers.