All-in-fiber sensing and light generation based on specialty fibers

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**NANYANG
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UNIVERSITY**

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**ALL-IN-FIBER SENSING AND LIGHT GENERATION
BASED ON SPECIALTY FIBERS**

ZHANG NAN

**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

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Abstract

All-in-fiber sensing and light generation devices are facing increasing demand due to their distinct features of being free-standing and robust, great compactness, easy handling, low waveguide losses and low cost for mass production. Compared with conventional fibers, specialty fibers are able to provide better sensing and light generation performance since they offer great flexibility in manipulating light guidance property through simply tuning fiber cladding structure, and enhanced light-matter interaction by hosting aqueous matter in the air channels running along the entire fiber length. Currently, the development and applications of high-performance all-in-fiber sensing and light generation devices are still hindered by low sensing sensitivity, difficulties in the replacement or manipulation of liquids in the fiber cladding channels, and the small surface area of light emission from the fiber cross-section.

To address the challenges and limitations mentioned above, some all-in-fiber solutions for sensing and light generation are systematically investigated in this thesis. First, a side-channel photonic crystal fiber (SC-PCF) is designed, fabricated and manipulated for developing highly sensitive aqueous sensing platforms with in-line liquid circulation capabilities. The SC-PCF has a solid core and a triangular lattice cladding structure, while partial lattice cladding is intentionally removed to enable efficient liquid flow in the fiber channels and strong light-matter interaction. By precisely splicing this SC-PCF to side-polished single mode fibers (SMFs), a fiber long period grating (LPG) and a Sagnac interferometer are experimentally demonstrated to enable all-in-fiber optofluidic refractive index (RI) sensing and biological sensing, respectively. A high RI sensitivity of 1145 nm/RIU is achieved with the SC-PCF LPG, and a low limit of detection (LOD) of 1 ng/mL cardiac troponin T (CTT) protein is obtained with the highly sensitive Sagnac interferometer. To further improve the LOD, an ultrasensitive surface enhanced Raman sensing (SERS) platform is proposed and demonstrated with an optimized geometry of the SC-PCF, and an ultra-low LOD of 50 fM Rhodamine 6G (R6G) solution is achieved. Last, an all-in-fiber light generation is demonstrated based on a multilayer photonic bandgap (PBG) fiber laser with quantum dots (QDs) solution as the gain medium infiltrated in the hollow core. The PBG fiber laser platform has unique characteristics of large emission surface perpendicular to the fiber axis and remote pumping configuration, which provides a substantial impact on both studies of

lasing mechanism and future developments of a variety of applications ranging from omnidirectional displays to light sources for biomedical analysis and phototherapy with minimal invasion.

This thesis presents the design, fabrication, and application of specialty fibers for all-in-fiber sensing and light generation with high performance. Further investigations on the integration of all-in-fiber light generation with chemical or biological analysis will be carried out in the near future.

List of Abbreviations

4-ATP	4-Aminothiophenol
AR	Auger Recombination
AuNP	Gold Nanoparticle
BSA	Bovine Serum Albumin
CTT	Cardiac Troponin T
DI	Deionized
DL	Detection Limit
ERI	Effective Refractive Index
FEM	Finite Element Method
FP	Fabry-Pérot
FSR	Free Spectral Range
FWHM	Full Width at Half Maximum
LOD	Limit of Detection
LPG	Long Period Grating
MFD	Mode Field Diameter
MI	Michelson interferometer
MMF	Multimode Fiber
MZI	Mach-Zehnder interferometer
OSA	Optical Spectrum Analyzer
PAA	Poly (allylamine)
PBG	Photonic Bandgap Fiber
PBS	Phosphate Buffered Saline

PC	Polycarbonate
PCF	Photonic Crystal Fiber
PDMS	Polydimethylsiloxane
PL	Photoluminescence
PTFE	Polytetrafluoroethylene
QD	Quantum Dot
QY	Quantum Yield
R6G	Rhodamine 6G
RI	Refractive Index
RS	Raman Scattering
SC-PCF	Side-channel Photonic Crystal Fiber
SEM	Scanning Electron Microscopy
SERS	Surface Enhanced Raman Scattering
SMF	Single Mode Fiber
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
TIR	Total Internal Reflection
WGM	Whispering Gallery Mode

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Chapter 1 Introduction

1.1 Background and motivation

All-in-fiber schemes are attracting more interests in developing robust and versatile sensing networks owing to their distinct features of being free-standing and robust, immunity to electromagnetic interference, long lasting, low attenuation loss over long length, small size, low cost, good repeatability and enabling remote sensing configurations [1–3]. In particular, most of the optical fibers are made of silica which is a dielectric material, making them immune to the ambient electromagnetic signals. A single mode fiber (SMF) can technically achieve a transmission loss of 0.2 dB/km at the wavelength of 1550 nm, which is ultra-low compared with the value of 1.2 dB/m for chip-based optical waveguides [4–6]. The diameter of optical fibers is in the scale of hundred micrometers, making them very flexible and easy to be integrated into complex sensing networks. Optical fibers are generally fabricated using a fiber drawing tower. Due to the advanced fabrication technique, several hundred meters of fiber can be fabricated from a 1 meter-long preform with good consistency in the fiber geometry. By possessing these preferable features, all-in-fiber platforms can be easily adapted to wide applications from environment monitoring to biological detections.

As the main components in constructing all-in-fiber networks, fiber-based sensing elements and light sources have been intensively investigated. The early investigations on fiber-based sensing elements and light generation schemes are mainly done with conventional SMFs and multimode fibers (MMFs). Conventional SMFs and MMFs are composed of a germanium-doped-silica fiber core surrounded by a pure-silica cladding. The guided light is strictly confined in the fiber core through total internal reflection (TIR). By being integrated into interferometric sensors, SMFs and MMFs have been successfully applied to temperature [7], strain [8], curvature [9] and refractive index (RI) [10] analysis. However, they have some limits in realizing high-performance sensing and light generation schemes due to the fiber geometry and material. The geometry and optical properties of SMFs and MMFs result in extremely weak interaction between light and the ambient medium. This weak light-matter interaction limits the spectral response's sensitivity to ambient variations, as well as the efficiency in light

generation, resulting in either low sensing sensitivity or redundant and large setups requiring a long fiber.

To address the challenges and enhance light-matter interaction in conventional fibers, several advanced fabrication techniques have been proposed to create functional fiber structures based on SMFs and MMFs, such as fiber gratings [6], microbubbles [7], microfibers [11,12] and side-polished fibers [13]. In particular, fiber gratings are able to transfer modal energy between the core mode and high order cladding modes which have more interaction with the ambient analyte. Microbubbles are able to support Fabry-Pérot (FP) resonances and whispering gallery modes (WGMs), in which light keeps resonating in the structure to enable ultra-long effective interaction length with the analyte. In microfibers and side-polished fibers, a large portion of the core mode energy is exposed to the environment to significantly enhance the light-matter interaction efficiency. These fiber structures are small and can provide sufficient light-matter interaction with a very short fiber length, thus dramatically improving the sensitivity and usability of the all-in-fiber sensing network. However, these microstructures have low fabrication reproducibility and are fragile, causing difficulties in the integration and stability of sensing networks. Besides, the all-solid geometry of the conventional fibers makes it necessary to have external liquid/gas flow channels for light-matter interaction, which compromises the compactness of the system.

Therefore, to comply with the increasing demand of practical, compact, high performance and easy handling analytical all-in-fiber sensing networks, some specialty fibers, mainly photonic crystal fibers (PCFs), have been investigated to construct all-in-fiber platforms in the past two decades. A PCF consists of a periodic holey structure in the fiber cross-section. Owing to the fiber geometry, PCFs are able to provide unique capabilities of lightwave guidance in the fiber core and simultaneous liquid/gas transmission in some of the air channels running along the entire fiber length. Depending on the light guidance mechanism, PCFs can be divided into two categories: 1. Index-guiding PCFs; and 2. Bandgap PCFs. Index-guiding PCFs consist of a solid fiber core surrounded by a latticed cladding that has an averaged RI lower than that of the fiber core. Light is confined in the solid core by a modified total internal reflection (TIR) guiding regime. The first solid core index-guiding PCF was successfully fabricated in 1996, as shown in Fig. 1-1(a) [14]. For bandgap PCFs, the RI of the fiber core (or hollow core) is lower than that of the cladding, and light is confined in the fiber core by the bandgap of the periodic structure surrounding the fiber core. Normally, bandgap PCFs have relatively narrow spectral transmission windows. The first bandgap PCF was

Fig. 1-1 SEM photo of: (a) The first solid-core index-guiding PCF [14], (b) The first fabricated bandgap PCF [15].

fabricated in 1998 [15], and its structure is shown in Fig. 1-1(b). PCFs can provide much flexibility in the design of fiber geometry, thus enabling more design freedom in manipulating the wave guidance properties. Together with the capability of unprecedented long interaction paths between light and matter, PCFs offer a promising platform for plenty of applications.

Due to the advanced PCF fabrication techniques, several novel PCF structures have been fabricated and successfully applied for versatile applications, including in flow cytometers [16], lasers [17], label-free biosensors [18,19], and environmental monitoring systems [20–22]. For example, H. W. Lee *et al.* present a step-index PCF having a parallel hollow micro-channel, and use it to monitor the RI variations of the liquids flow in this parallel channel by tracing the shift of the resonant wavelength [23]. T. Monro *et al.* propose a suspended-core fiber with a jacketed-air suspended rod structure featuring an extremely high air-filling ratio, and they demonstrate to use this fiber for gas and liquid sensing applications [24–26]. A simplified hollow-core microstructured fiber with a large hollow core surrounded by one layer of air channels is investigated for fluorescence detection [27] and generating a radial laser emission by introducing a gain medium into its hollow core [28], *etc.*

Although PCFs have proved their capabilities in versatile all-in-fiber systems, existing PCF-based all-in-fiber platforms still have some limitations in meeting the increasing demand of ultra-sensitive molecular detection in aqueous environments, as well as laser light generation with a large surface emission area for massive sensing/detection in the environmental monitoring and clinical diagnosis fields. The challenges are listed as follows:

- 1) Low sensitivity due to insufficient light-matter interaction

The efficiency of light-matter interaction in the fiber systems can be affected by two factors: a). Mode coupling efficiency between the sensing fibers and in- (out-) coupled fibers, and b) The portion of modal energy that interacts with the surrounding media. Hollow core PCFs can provide maximum geometric overlap between the core modes and liquid/gas media, since light and the medium are both guided in the large fiber core. However, light that propagates in the liquid core suffers from strong attenuation due to absorption and scattering, and the modal mismatch between the large hollow core fiber and SMFs will result in low mode coupling efficiency. For solid-core PCFs, light transmitted in the fiber core interacts with the medium in the channels via evanescent fields. Low-loss light coupling to SMFs can be easily realized through splicing, whereas the evanescent field that interacts with the medium is usually small.

2) Inconvenient liquid/medium manipulation in the air channels

Currently, most of the PCF-based all-in-fiber platforms are built by direct splicing the PCFs with SMFs. In this way, the liquid/gas medium is sealed in the air channels, but the inconvenient insertion and extraction of the medium in the air channels

Fig. 1-2 All-in-fiber sensing schemes constructed with the assistance of: (a) CO₂ laser-based micromachining [31], and (b) Splicing with C-shaped fiber [32].

of PCFs lead to inconvenience to its practical applications. To have an in-line access to the air holes, several methods are proposed, such as drilling holes with a femtosecond laser or CO₂ laser micromachining [29–31], or inserting a 20- μ m-wide C-shaped fiber between the PCF and SMFs [32], as shown in Fig. 1-2. However, the micromachining technique requires expensive laser equipment and high-accuracy positioning stages. For the latter method, the tiny C-shaped fiber is very difficult to manipulate, and, more importantly, mode mismatch is inevitable because the C-shaped fiber has weak light guidance capability.

3) Relatively small mode area

In PCFs, light is generally confined in the fiber along the central symmetry axis, resulting in a relatively small light emission area from the fiber end. For an in-fiber laser source that is used for massive sensing/detection in the environmental monitoring and clinical diagnosis fields, small laser illumination area will increase the efforts for scanning the detecting area.

Consequently, in order to address all these issues/drawbacks, it is necessary to explore new PCF structures and configurations for fiber-based sensing platforms with strong light-matter interaction and convenient liquid manipulation in the channels, as well as for light generation platforms with large emission areas, both of which extending significantly the range of applications of all-in-fiber schemes.

1.2 Objectives

In this study, new fibers and setup configurations are investigated for constructing high-performance all-in-fiber sensing systems and light generation systems with preferable features for potential sensing applications. The objectives of this thesis are:

- 1) To demonstrate the design, fabrication, and characterizations of new PCF fiber structures that enable extensive light-matter interaction and low insertion loss when splicing with SMFs;
- 2) To apply these PCFs in all-in-fiber sensing schemes with in-line liquid insertion and extraction capability and explore their sensing capability as RI sensors and biological sensors. For the biological sensing, we use human cardiac troponin T (CTT) for demonstration;
- 3) To explore new sensing applications of the newly developed PCFs by adjusting the fiber geometry, investigating its adaptability for various sensing

applications;

4) To build a light source with a large surface emission area for the most important targeted application of *in situ* biological sensing.

1.3 Major contributions

The major contributions of this thesis are:

1) *Demonstrate a new PCF structure for all-in-fiber in-line sensing platforms.* The design, fabrication, and characterizations of a solid core side-channel photonic crystal fiber (SC-PCF), especially for all-in-fiber liquid sensing applications, are presented. The structure of the fiber enables efficient liquid circulation in the channel and convenient lateral access of the liquid, even when the PCF is spliced with SMFs. To maximize the power of the evanescent power in the fiber channel, a theoretical investigation on the dependence of the fraction of evanescent power in the channel on the structure parameters, including the pitch of the holey cladding and the ratio of the hole diameter to the cladding pitch, is carried out. Additionally, a novel way to integrate the SC-PCF into all-in-fiber sensing schemes is proposed. The SC-PCF consists of a large side-channel in the fiber cladding which hosts the liquid circulation. By splicing the SC-PCF with a side-polished SMF, the side-channel of the fiber can be exposed while the rest of the small holes are sealed. The side-polished SMFs are fabricated using a polishing machine and are polished to a desired depth.

2) *Present the fabrication of a long period grating (LPG) on the asymmetric all-silica SC-PCF.* An LPG is successfully fabricated on the asymmetric all-silica SC-PCF using a CO₂ laser, which is seldom reported. The grating consists of periodic structural deformations on the fiber surface. The LPG realizes mode coupling between LP₀₁ mode and LP₁₁ mode in the core of the SC-PCF. It can be used to sense the RI variations in the fiber side-channel with high sensitivity, and at the same time, reduce the fluctuations caused by the environment. Moreover, the fabrication method using a CO₂ laser offers much flexibility in tuning the grating pitch.

3) *Explore the sensing performance of the SC-PCF as an RI and biological sensor.* An SC-PCF LPG is used to construct an all-in-fiber sensitive liquid RI sensor with in-line liquid inlet and outlet, and its sensing performance is demonstrated with solutions with different RIs circulated in the fiber side-channel.

The sensing platform shows a sensitive spectral response to the liquid RI variations in the side-channel. Moreover, by introducing an intermodal interference, the detection limit (DL) of this RI sensor is significantly enhanced. The same SC-PCF can also be used for specific biosensing. An SC-PCF-based Sagnac interferometer was successfully employed to detect CTT protein via binding on it biological multilayers, which is enabled by the convenient liquid circulation of our sensing scheme. Moreover, this sensing platform can offer convenient spectral monitoring during the biological binding event.

4) *Extend the application of the SC-PCF to surface enhanced Raman scattering (SERS).* The geometric parameters of the SC-PCF are adjusted and optimized for the SERS excitation wavelength of 632.8 nm to achieve ultra-sensitive SERS measurements. As SERS gives fingerprint information of molecules, it is very promising in realizing specific molecular detection. With the optimized SC-PCF, a limit of detection (LOD) of 50 fM Rhodamine 6G (R6G) solution is achieved, which is a 4-order of magnitude improvement compared with the state-of-art value achieved by other fiber-based SERS platforms.

5) *Explore a fiber laser with large surface emission area.* A fiber laser source with large surface emission area is attracting great interest in applications such as omnidirectional imaging, biomedical detection and photodynamic therapy in large volume. A quantum dots (QDs) fiber laser with cylindrically symmetric radial emission from a photonic bandgap (PBG) fiber is demonstrated in this study. The resulting laser platform integrates the advantages of QDs (large wavelength tunability, broad absorption band, *etc*) and the unique characteristics of large emission surface and remote pumping, providing a substantial impact on both studies of lasing mechanism and future developments of a variety of applications, for example, detection or diagnosis of diseases in vessel structures.

1.4 Organization

The thesis is organized as follows:

Chapter 2 introduces the basic aspects and theories that are relevant to my work, including photonic crystal fibers, fiber gratings, fiber interferometers, Raman scattering, SERS, Mie scattering, lasing mechanism and laser characteristics.

Chapter 3 presents the literature review on optical fibers (including specialty fibers) integrated sensing platforms for refractive index sensing, and lasers that can

exhibit large surface emission area. In particular, for the fiber-based sensing platforms, we review the work on fiber RI sensors based on fiber gratings, fiber interferometers, microfibers, and photonic crystal fibers, and fiber-based SERS sensing. For the lasers, we review the work on sphere/micro-droplet lasers and fiber lasers that can emit with a large surface area.

Chapter 4 introduces the geometry of our SC-PCF, simulations on its geometric parameters, fabrication process, and basic characterizations, including mode profiles, transmission loss, and insertion loss.

Chapter 5 introduces a few SC-PCF-based all-in-fiber sensing schemes and their applications. Section 5.1 presents an all-in-fiber RI sensor constructed with an SC-PCF LPG. In this section, we introduce the method to fabricate an LPG on our SC-PCF, the sensing scheme, and the characterizations of its sensing performance, Section 5.2 presents an SC-PCF Sagnac interferometer applied for the specific detection of human CTT protein. In this section, we present the sensing scheme of this Sagnac interferometer, its RI sensing performance, the steps of multilayer binding events on the inner surface of the fiber side-channel, and the *DL* of CTT protein. In section 3.3, the geometry of the SC-PCF is optimized especially for SERS applications, and its sensing performance is demonstrated with 4-Aminothiophenol and R6G.

Chapter 6 introduces a QD fiber laser that has a large surface emission area. In this chapter, we present the structure of the PBG fiber, its optical waveguide properties, and the characterizations of this laser, including the laser threshold, Q-factor, and polarizations.

Chapter 7 summarizes the projects in this thesis and discusses the challenges we go through to fulfill these projects, the current limitations and practical applications of these built devices. Moreover, we also suggest possible future work including enhancing the sensing sensitivity of the SC-PCF based SERS platform with magnetic-core-gold-shell nanoparticles and applying the proposed PBG QD lasers for omnidirectional fluorescence sensing/imaging in vessel structures.

Chapter 2 Basic aspects and theory

In this chapter, basic conceptions and principles that are relevant to my work in this thesis are presented. Section 2.1 introduces the basics of PCFs, including the characteristics of fiber structures, wave-guiding mechanisms, fabrication techniques and splicing technique. Section 2.2 introduces several common techniques/configurations of fiber-based sensors, including fiber gratings, Fabry-Pérot interferometers, Mach-Zehnder interferometers, Michelson interferometers, and Sagnac interferometers. Section 2.3 introduces the conceptions and mechanisms of Raman scattering, surface plasmon resonance, SERS and Mie scattering. Section 2.4 introduces the working principles, the characteristics, and categories of lasers.

2.1 Photonic crystal fibers

2.1.1 Introduction to photonic crystal fibers

PCFs which have a periodic microstructure in the fiber cladding are extended from photonic crystal structures. They are proposed to overcome the limitations of conventional fibers and to prompt new applications of optical fibers [33]. Conventional SMFs and MMFs have an all-solid core-cladding structure and light guidance relies on TIR, limiting enhancement of laser or sensing interaction with liquid or gas media. Photonic crystal structures in the cross-section of PCFs enable light trapping capability in either a hollow core or a solid core while providing air channels for aqueous or gaseous media. The resulted enhanced light-matter interaction and possibility in choosing from diverse media dramatically extend new applications in fiber-based sensors and lasers.

The idea of extending the “stopbands” of periodic structures to create a new dielectric waveguide (PCFs) was first proposed by Prof. P. St. J. Russell and his colleagues in the University of Southampton in 1991. Light guidance in the axial direction of PCFs is realized through a 2-dimensional PBG structure, preventing light propagation in all directions in the cross-section (periodic plane). The initial design of a PCF is to introduce a defect (a large hollow core) in the center of a periodic PBG structure

to serve as the fiber core, and light is confined in the core defect. Air-core fibers have some inherent advantages over silica material based solid core fibers in some aspects. For examples, air-core fibers can help to dramatically diminish transmission loss caused by scatterings and material absorption and have higher damage threshold for high-power laser beam transmission. Therefore, PCFs have attracted intensive attempts to fabricate worldwide since it was first proposed. However, the fabrication of PCFs is not that straightforward. It is a long journey of exploration. The first successful fabrication of a silica-air PCF fiber was reported by Prof. J. C. Knight etc. in the University of Southampton in 1996 [14] by means of capillaries stacking. This PCF has a periodic air array in the cladding surrounding a solid silica core. Although the fabricated fiber structure did not present photonic bandgap, and it confined light through TIR (categorized as index-guiding fiber), it led to the invention of endlessly single mode fiber. After the successful trials of fabricating index-guiding PCFs, the first PBG PCF was fabricated in 1998 [15], as shown in Fig. 1-1.

Depending on the light guidance mechanisms, PCFs are mainly divided into index-guiding PCFs and PBG PCFs.

2.1.1.1 Index-guiding PCFs

In index-guiding PCFs, light is confined in the core area through TIR which requires a higher RI value in the core area compared with that of the cladding area. A typical structure of an index-guiding PCF, as illustrated in Fig. 2-1, consists of a solid core and a triangular air-lattice cladding. The period of the air holes (pitch) is indicated

Fig. 2-1 A schematic illustration of a typical index-guiding PCF.

by Λ and the air hole diameter is indicated by d . Normally, index-guiding PCFs are made of a single material – pure silica. Therefore, the presence of air holes results in an overall lower RI value in the cladding region since the RI of air (1.0) is smaller than that of silica (e.g., 1.444 at the wavelength of 1550 nm).

In a conventional step-index fiber, the number of transverse modes (M) guided in the fiber core can be theoretically calculated by the following equations:

$$V = \frac{2\pi}{\lambda} a \sqrt{n_{core}^2 - n_{cladding}^2} \quad (2-1)$$

$$M = \frac{V^2}{4} \quad (2-2)$$

where a is the radius of the fiber core, λ is the wavelength, and n_{core} and $n_{cladding}$ are the RIs of the fiber core and cladding, respectively. Step-index fibers support single mode propagation if $V < 2.405$. As for the conventional regular PCFs which have periodic air holes in the cladding, the definition of the RI of the cladding is not that straightforward. To quantify the requirements for the fundamental mode guidance in the fiber core, an effective index model is proposed. In terms of the effective index model, they define the RI of the cladding according to the propagation constant of the fundamental space-filling mode (β_{FSM}) of the infinite cladding, and reveal the importance of d/Λ in determining the number of modes [34].

According to the effective index model, an effective V value (V_{eff}) for a PCF can be defined as [35]:

$$V_{eff} = \frac{2\pi}{\lambda} \Lambda \sqrt{n_{core}^2 - n_{eff}^2} \quad (2-3)$$

$$n_{eff} = \frac{\beta_{FSM}}{k} \quad (2-4)$$

where $k = 2\pi/\lambda$. Taking into consideration the air filling ratio ($F = d/\Lambda$) in the conventional PCF structure. The expression of effective V value (V_{eff}) can be further simplified to [36]:

$$V_{eff} = \frac{2\pi}{\lambda} \Lambda \sqrt{(n_{core}^2 - n_a^2)F} \quad (2-5)$$

where, n_a is the RI of air ($n_a = 1$).

The geometry of index-guiding PCFs can be adjusted to support endlessly single mode propagation. Endlessly single mode propagation is the condition that the fiber only supports a single fundamental mode in the fiber core no matter what the wavelength is. For a typical index-guiding PCF structure, the fiber becomes an endlessly single mode fiber when the ratio of d/Λ is less than 0.43 [33].

However, our desired side-channel photonic crystal fiber (SC-PCF) presented in Chapter 4 of this thesis has an asymmetric and irregular geometry, so the effective index model cannot be used in this case. Therefore, for our SC-PCF, simulations based on finite element method (FEM) software COMSOL 3.5 were carried out to analyze the number of fiber core modes directly. The condition $d/\Lambda < 0.43$ for single mode propagation in the fiber core of a conventional regular solid-core PCFs is a good reference for any fiber design [37].

2.1.1.2 Photonic bandgap fibers

PBG fibers consist of a low index fiber core surrounded by a higher index periodic structure cladding. As the RI of the fiber core is lower than that of the cladding area, light cannot be confined through TIR. In PBG fibers, the light of certain well-defined bands of wavelength is guided in the low index air core by the bandgap of the photonic crystal structure cladding. Numerical computations suggest that a large air-filling ratio and a small pitch (distance between the center of two adjacent air holes) in the photonic crystal cladding are needed to obtain a photonic bandgap for light incident from vacuum [38]. The first PBG fiber was fabricated in 1998 with a honeycomb structure of air holes, as shown in Fig. 1-1(b). However, the guided mode of the fiber was observed to be evanescent in the central air hole but concentrated in the surrounding silica area due to the small air filling ratio in the cladding. Later, in 1999, the first fiber that supported single-mode PBG guidance in the air core was successfully demonstrated by R. F. Cregan in the University of Bath owing to the development in fabrication technologies [38]. This fiber has a triangular air-lattice cladding, and the large hollow core was created by removing 7 capillaries, as shown by the SEM picture in Fig. 2-2 (a). The air filling ratio and pitch in the cladding are ~39% and 4.9 μm , respectively. The optical micrograph of the transmitted modal intensity of a white light, shown in Fig. 2-2(b), indicates its characteristics of having discrete and restrict guidance bands decided by the photonic crystal bandgap. However, the loss study revealed that only 35% of an input laser was transmitted over a 40-mm long fiber sample due to low input coupling efficiency. Besides, the minimum transmission loss of a PBG is mainly limited by the scatterings caused by surface roughness. In 2005, the achievement of ultimate low-loss PBG fiber (1.2 dB/km) by reducing surface roughness promoted its practical applications [39].

Fig. 2-2 (a) SEM picture and (b) Optical micrograph of the transmitted mode intensity collected at the exit end of a single-mode PBG guidance fiber [38].

In addition, along with the developments of large hollow core PBG fibers, all-solid PBG fibers and Bragg fibers which also apply PBG guidance mechanism are investigated both theoretically and experimentally. The invention of all-solid PBG fiber is inspired by the experimental phenomenon of guidance mechanism transfer from index-guiding to PBG by infiltrating the air holes of index-guiding PCFs with high index liquid (larger than core) [40,41]. Compared with hollow core PBG fiber, all-solid PBG fibers have the advantage of easy fabrication. Moreover, all-solid PBG fibers show better coupling performance in the occasions where splicing with standard SMFs or MMFs are needed.

Different from the most PCFs which are made from silica material, Bragg fibers are usually made of polymer and soft glasses. Generally, Bragg fibers comprise a large hollow core surrounded by multilayers of thin films with alternating high index (soft glasses) and low index (polymers). The multilayers Bragg reflectors are used to confine light in the hollow core. The thickness of each layer (d) can be determined by:

$$d = \frac{\lambda}{4\sqrt{n_{layer}^2 - 1}} \quad (2-6)$$

where n_{layer} is the RI of the layer, and λ is the wavelength that be transmitted in the fiber core.

Bragg fibers have been used for delivery of mid-infrared radiation [42] and laser generation in visible wavelength range [43]. The SEM photos of an all-solid PBG fiber

Fig. 2-3 SEM photo of (a) An all-solid PBG fiber [44] and (b) A Bragg fiber [42].

that exhibit a low transmission loss of 2 dB/km [44] and a Bragg fiber that is used for CO₂ laser beam delivery [42] are shown in Fig. 2-3.

2.1.2 Fiber fabrication technology

Generally, there are two main steps involved in fabricating PCFs: preform preparation and drawing process using a furnace. Depending on different fiber structures and materials, a few techniques have been explored to prepare the large fiber preform, such as stacking [37], extrusion [45] and rolling [42].

The most widely used method for fabricating the preform of silica PCFs is stacking silica capillaries and rods. Generally, the capillaries are fabricated by drawing large silica tubes that have the same air filling ratio with that of the PCF, and have a length of 1 m and an outer diameter of a few millimeters. First, silica capillaries and rods are stacked carefully to form the designed photonic crystal pattern. Then the stack is inserted into a silica tube to provide an outer protecting silica layer surrounding the photonic crystal structure. The diameter of the cross-section of the fiber preform is around a few centimeters. Then, after mounting the preform in the preform holder on the top of a fiber drawing tower, the drawing process using high-temperature furnace (operating at above 1700 °C for silica fiber) can be carried out. The drawing process of silica-air PCFs is very challenging. There are a few parameters of the fiber drawing tower need to be adjusted during the drawing process to keep a fine fiber structure, including the furnace temperature, the pressure applied to the air channel, feeding speed and

drawing speed. Very often, vacuum environment may need to apply to suppress the small space between capillaries. More details will be discussed in Section 4.2 when describing the fabrication process of our SC-PCF. Due to its complex structure, special efforts are made to keep the structure of the SC-PCF preform and low furnace temperature are applied during the fiber drawing process because the size of the side-channel is quite large compared with that of other small air holes. Last, the polymer coating is applied to the drawn fiber immediately to protect the brittle silica fiber from damage during packaging.

Extrusion is an alternative method for fabricating complex patterns in fiber preform made of low melting temperature materials, for example, chalcogenide glass and polymers, when stacking is not readily applicable.

Rolling is applicable to fabricating structures like Bragg fibers which have periodic annular layers of thin films or polymer.

2.1.3 Splicing technique

Fusion splicing is the most common way to splice two fibers firmly and with low loss. Fusion splicing uses an electric arc to generate localized heats to melt the well-cleaved ends of two optical fiber and weld them. The generated heat can be controlled by changing electric arc power and duration. Throughout this thesis, we use a splicer (Sumitomo electric, TYPE-36) in all of the splicing procedure.

2.2 Conventional fiber sensors

2.2.1 Fiber gratings

2.2.1.1 Theories on fiber Bragg gratings and long period gratings

A fiber grating contains a periodic RI variation structure fabricated on the fiber. A typical illustration of a core index modulated fiber grating is shown in Fig. 2-4. Fabricating a grating on optical fibers is an effective method to manipulate mode energy transition and it can provide high precision and accuracy, and good repeatability in controlling mode coupling in optical fibers. There are two main parameters to describe the characteristics of the 1-dimensional grating: index difference and pitch period (δ).

According to mode coupling principles, fiber gratings can be divided into fiber Bragg gratings and long period gratings (LPGs). The period of a Bragg grating is equal

Fig. 2-4 Schematic diagram of a core index modulated fiber grating with a period of δ .

to or less than half of the working wavelength, and it is able to couple the forward-propagating fundamental mode to backward-propagating fundamental mode. With a fiber Bragg grating, a narrow selective wavelength (Bragg wavelength, λ_B) can be observed in the reflection spectrum when injecting a broadband light source into the fiber core. Accordingly, the selective spectral band is missing in the transmitted spectrum due to energy coupling to the backward-propagating fundamental mode. The Bragg wavelength can be determined by the following equation [46]:

$$\lambda_B = 2n_{co}\delta \quad (2-7)$$

where n_{co} represents the RI of the fiber core, and δ is the period of the grating.

The period of an LPG is in the range of sub-millimeter, larger than that of a Bragg grating. Fiber LPGs have previously been intensively investigated to manipulate the transmission modes in optical fibers. Fiber LPGs couple modal energy from the fundamental mode to a co-propagating high order core mode or cladding mode. As high-order core modes or cladding modes experience higher transmission loss compared with that of the fundamental core mode, there will be a series of low power bands in the transmission spectrum at the resonant wavelengths which satisfy the phase matching condition [47]:

$$\beta_{01} - \beta_{high\ order}^n = \frac{2\pi}{\delta} \quad (2-8)$$

where β_{01} and $\beta_{high\ order}^n$ are the propagation constants of the fundamental mode and high-order modes, respectively, and δ is the period of the grating structure. Since the propagation constant can be expressed as $\beta = 2\pi n_{eff}/\lambda$, the phase matching condition can also be expressed as follows:

$$n_{eff}^{01} - n_{eff}^n = \frac{\lambda_{res}}{\delta} \quad (2-9)$$

where n_{eff}^{01} and n_{eff}^n are the ERIs of the fundamental mode and high-order modes of the fiber, respectively, λ_{res} is the resonant wavelength at which the energy of the fundamental core mode is coupled to that of the co-propagating high-order core/cladding modes. Eq. (2-9) reveals that, with a certain grating pitch, the variations in the ERI

difference between two coupling modes result in a shift in the resonant wavelength. Therefore, any factors that induce the change of the ERI difference between two coupling modes can be detected by an LPG. Since LPGs have larger grating periods, its fabrication is much easier than that of fiber Bragg grating.

According to the mode coupling theory [48], In LPG, the normalized power (T) transferred from the fundamental mode to a cladding mode at the resonant wavelength λ_{res} is given by [49]:

$$T = \sin^2(\eta L) \quad (2 - 10)$$

where L is the total length of the grating, η is the coupling coefficient between the coupling modes, defined by [49]:

$$\eta = \frac{C\pi\Delta n_{mod}I}{\lambda_{res}} \quad (2 - 11)$$

where Δn_{mod} is the index modulation amplitude, I is the overlap integral between the coupling modes. C is a constant determined by the Fourier transform of the grating pitch shape. The total spectra width of an LPG that follows the first zero coupling efficiency of the grating is given by [49]:

$$\Delta\lambda_0 = \frac{2\lambda_{res}\delta}{L} \sqrt{1 - \left(\frac{\eta L}{\pi}\right)^2} \quad (2 - 12)$$

Moreover, from the Eq. (2-10) we can see that modal energy of the fundamental mode is transferred completely when $\eta L = \pi/2$. For a SMF LPG, the full width at half maximum ($FWHM$) of a resonance with complete modal power transferred can be estimated by [36]:

$$FWHM = \frac{0.8\lambda_{res}^2}{L(n_{eff} - n_{cladding})} \quad (2 - 13)$$

where n_{eff} is the effective refractive index (ERI) of the fundamental mode, and $n_{cladding}$ is the RI of the fiber cladding.

The sensitivity (S) of an LPG to the variation of the external RI (n) is defined as:

$$S = \frac{\partial\lambda_{res}}{\partial n} \quad (2 - 14)$$

2.2.1.2 Grating fabrication techniques

Several methods can be used to fabricate fiber LPGs, for example, point-by-point laser writing method [50], using phase masks [51], and electric arc technique [52]. Among these, CO₂ laser point-by-point imprinting method is an efficient way for LPG fabrication on silica PCFs. Together with its software and computer-controlled precise

moving stages, it can provide great flexibility in changing grating period, laser power, grating number and writing positions. Moreover, the gratings fabricated with a CO₂ laser are essentially permanent and are suitable for stable and long-lifetime applications.

In this method, a CO₂ laser beam with the wavelength of 10.6 μm is focused on the surface/core of the fiber to inscribe the grating on the fiber [50,53,54]. The illumination of the CO₂ laser beam imposes a thermal effect on the fiber. The periodic RI variations may come from three mechanisms [55]:

- 1) The thermal effect of CO₂ laser helps to release the stress introduced during the fiber fabrication process;
- 2) The thermal effect may result in a slight deformation on the fiber surface;
- 3) The RI perturbation induced by stretch force.

2.2.2 In-line fiber interferometers

In addition to fiber gratings, fiber interferometers also have been investigated for sensing applications due to the characteristics of easy fabrication, simple structures, high integration level and high sensitivity. The working principle of fiber interferometers is based on the interference effect between two optical beams traveling through different optical paths. In optical fibers, the interference can be realized with two different propagation modes in a single fiber or in two different fibers, as long as they travel through different optical paths when recombines. Normally, there are beam splitting components and beam recombination components in this kind of sensing scheme. In fiber interferometers, when the two optical beams recombine, the output intensity I can be expressed as

$$I = I_{1-out} + I_{2-out} + 2\sqrt{I_{1-out}I_{2-out}}\cos(\Delta\psi) \quad (2-15)$$

where I_{1-out} and I_{2-out} are the output intensities of the two interference beams, respectively, and $\Delta\psi$ represents the optical phase difference (OPD) of these two beams. When the OPD satisfies $\Delta\psi = (2m + 1)\pi$, where $m = 0,1,2,3 \dots$, the resonant dips appear.

Currently, there are four types of fiber interferometers, namely Fabry-Pérot interferometers, Mach-Zehnder interferometers, Michelson interferometers and Sagnac interferometers.

Fabry-Pérot interferometers (FPI) require two parallel mirrors to reflect the incident light signals. Depending on the formation of the cavity, FPIs can be divided into two categories: extrinsic FPIs and intrinsic FPIs. For extrinsic FPIs, the FP cavity is

located external to the fiber and generally filled by air or polymers [56]. For intrinsic FPIs, the FP cavity is embedded within the fiber [57]. Although extrinsic FPIs are easy to fabricate, they have the limits of difficult packaging and precise alignment, as well as low coupling efficiency since the cavity filled with air or polymer is not an effective waveguide. Several techniques have been used to fabricate intrinsic fiber FPIs, including micromachining with a laser beam [58,59], creating a microbubble within the fiber [60] and splicing PCFs [61]. When the partially reflective mirrors are parallel to each other, the optical phase difference between the two reflective beams can be expressed as:

$$\Delta\psi = \frac{4\pi nL}{\lambda} \quad (2 - 16)$$

where n and L represent the RI and length of the FP cavity, respectively, and λ is the working wavelength. Since the destructive interference ($\Delta\psi = (2k + 1)\pi, k = 0, 1, 2, 3 \dots$) results in a resonant dip. The dependence of the spacing between two adjacent resonant dips ($\Delta\lambda$) can be deduced as:

$$\Delta\lambda = \frac{\lambda_{res}^2}{2nL} \quad (2 - 17)$$

where λ_{res} represents the central wavelength between two adjacent resonant wavelength. As the interference pattern shifts when OPD changes, according to Eq. (2-16), FPI can be applied to temperature [62], RI [63], pressure [64], and acoustic sensing [65], *etc.*

Different from FPIs which utilize reflected beams to generate the interference pattern, in Mach-Zehnder interferometers (MZIs), Michelson interferometers (MIs) and Sagnac interferometers, incident light is split into two beams with different propagation paths, and then recombine and coupled into a single fiber to generate the interference pattern.

For early MZIs and MIs, the incident beam is split into two fiber arms through a coupler, one arm serving as the sensing arm and the other arm serving as the reference arm [8]. The difference between MZIs and MIs is that MZIs consists of two couplers (one is for beam splitting and another one is for beam combining), while MIs requires one coupler only and mirrors are placed at the other end of the fiber arms to reflect the beams. However, this kind of configurations have the drawbacks of being sensitive to the environmental perturbations since two beams propagate in two different fiber arms. To overcome this limitation, in-line fiber MZIs and MIs which utilize modal interference have been proposed and investigated [66,67]. In these sensors, partial energy of the fundamental mode is coupled to a high order mode by a coupling component. After propagating through the same fiber length, the two co-propagating modes are then re-

coupled back to the fiber core at the combining component to interfere with each other. For in-line fiber MZIs and MIs, the sensing arm and the reference arm are in the same fiber, and the accumulated optical phase difference comes from the modal dispersion. In such devices, mode coupling can be realized through several techniques, such as LPG [68], collapsing the air holes of PCFs [69], misalignment fusion splicing [70], tapering [66,71], *etc.* Although in-line fiber MZIs and MIs can provide ultra-high sensitivity in temperature and RI sensing and great compactness for real applications, they exhibit some limits when cooperating with PCFs. The mode coupling method of splicing with PCFs often excite numbers of high order cladding modes, thus, putting some limits on the repeatability of the interference patterns. The use of other mode coupling techniques, for example, tapering and LPG, increase the fabrication difficulty.

A Sagnac interferometer, also called fiber loop mirror [72], generally is constructed with a 3 dB coupler and a segment of fiber that possess a large birefringence, as illustrated in Fig. 2-5. It has a very simple configuration. The 3 dB coupler splits the light into two counter-propagating optical paths (indicated by P1 and P2 in Fig. 2-5) on a 50:50 basis. After propagating through the fiber loop, the two counter-propagating optical paths recombine at the 3 dB coupler, resulting in an interference pattern in the output spectrum. The interference pattern arises from the different modal ERIs.

For most of the PCFs, the energy is mainly coupled to the LP_{01} mode when applying a core-to-core splicing method. The interference pattern introduced by the birefringence (B) of the guided modes in the PCF/PM fiber is discussed in this section. To simplify the model and the calculation, the insertion loss of the fiber loop and the birefringence of the SMF are not considered. The transmittance (T) of the input optical

Fig. 2-5 Illustration of a Sagnac interferometer.

wave can be calculated according to the relative phase difference (ψ) by [20]:

$$T = \frac{1 - \cos(\psi)}{2} \quad (2 - 18)$$

$$\psi = \frac{2\pi BL}{\lambda} \quad (2 - 19)$$

where, λ is wavelength, and L is the fiber length as shown in Fig. 2-5, and $B = n_x - n_y$ is the birefringence coefficient of the specialty fiber spliced in the fiber loop. n_x and n_y are the ERIs of two orthogonally polarized modes, respectively. The resonance dips can be observed when its wavelength (λ) satisfies [73]:

$$\frac{2\pi BL}{\lambda} = 2m\pi \quad (2 - 20)$$

where m is an integer.

As T can be approximated as a periodic function of wavelength, the relationship of the spacing between two adjacent resonant dips ($\Delta\lambda$) and the birefringence (B) can be deduced as:

$$\Delta\lambda = \frac{\lambda_{res}^2}{BL} \quad (2 - 21)$$

where λ_{res} represents the central wavelength between two adjacent resonant wavelengths.

The spectral response sensitivity (S) to the RI variation can be obtained by taking derivative with respect to RI (n) on the both sides of Eq. (2-20) [74]:

$$S = \frac{d\lambda}{dn} = \frac{\lambda \cdot \partial B / \partial n}{B - \lambda \cdot \partial B / \partial \lambda} \quad (2 - 22)$$

The detection limit (DL) of an RI sensor is an essential factor that characterizes smallest RI variation of the samples that the sensor can accurately measure. It is determined by its RI sensitivity (S) and sensor resolution (R) by the relationship of [75]:

$$DL = \frac{R}{S} \quad (2 - 23)$$

where R is the smallest possible spectral shift that the resonant RI sensor is able to accurately measure, and its value is affected by the amplitude noise of the resonance peak ($\sigma_{ampl-noise}$), the thermal noise ($\sigma_{temp-noise}$), and the spectral limitations of the system setup ($\sigma_{spect-res}$) by the equation:

$$R = 3 \sqrt{\sigma_{ampl-noise}^2 + \sigma_{temp-noise}^2 + \sigma_{spect-res}^2} \quad (2 - 24)$$

Amplitude noise $\sigma_{ampl-noise}$ is the standard deviation of the spectral variance, and it can be approximately calculated via its dependencies on the $FWHM$ value of the resonance ($\Delta\lambda_{FWHM}$) and the signal to noise ratio (SNR) of the spectrum by the equation:

$$\sigma_{\text{ampl-noise}} = \frac{\Delta\lambda_{FWHM}}{4.5SNR^{0.25}} \quad (2 - 25)$$

Thermal noise $\sigma_{\text{temp-noise}}$ is introduced by the environmental temperature fluctuations. For many resonant RI sensors, a change in temperature (ΔT) induces a change in the RI of the liquid sample (Δn_s), thus, resulting in a spectra shift ($\Delta\lambda$):

$$\Delta\lambda = \eta \Delta n_s \frac{\lambda}{n_{eff}} \quad (2 - 26)$$

where η is the fraction of evanescent intensity that interact with the liquid sample, n_{eff} is the ERI of the resonant mode, and $\Delta n_s = \gamma \Delta T$, where γ is the thermal-optic coefficient of the liquid sample.

For large resonant mode linewidth RI sensors, in which a broadband light source and an optical spectrum analyzer (OSA) are used to measure the resonance, spectral limitations of the setup ($\sigma_{\text{spect-res}}$) is determined by the spectra resolution of the detector [75]. ”

2.3 Surface enhanced Raman scattering

2.3.1 Raman scattering

Raman scattering (RS) is an inelastic scattering process of light in which the energy of the incident photon is not conserved. The illustration of an RS process in a molecular energy level diagram and its corresponding Raman spectrum is shown in Fig. 2-6 (a) and (b) [76]. The incident photon has an energy of $h\nu_i$, and the emitted photon has an energy of $h\nu_e$, where h is the Planck constant, and ν_i and ν_e are the frequency of the photon. Depending on whether the excitation photon is in resonance with any real electronic transitions in a molecule, the RS process is divided into two categories: resonant and nonresonant. In nonresonant RS, the interaction between the incident photon and a molecule is due to scattering. As to resonant RS, the excitation photons are in resonance with electronic transitions, so the photon will be absorbed and a scattered photon will be emitted with another frequency, depending on the energy of transition.

To illustrate the RS process simply and clearly, the situation with only one molecule and one photon involved in the process is considered, as shown in Fig. 2-7 (a) [76]. The interaction of the incident photon with the molecule results in a change in the energy of the incident photon ($h\nu_L$) because of the inelastic scattering process, where ν_L represents the frequency of the incident light. The energy differences between characteristic vibrational modes ($h\nu_M$) in the molecule determine the difference in the

Fig. 2-6 (a)Schematic of Raman scattering in the diagram of energy levels, and (b) An example of a Raman spectrum [76].

energy of the incident photon and scattered photon [77–80], where ν_M is the frequency of the Raman scattered photon. The scattered photon can have either a lower or a higher frequency compared to that of the original incident photon, depending on whether the molecule involved in the interaction was in the a ground state or an excited vibrational state, as depicted in Fig. 2-7 (b). The so-called Stokes scattering process generates a scattered photon with a lower frequency when the incident photon interacts with a molecule in the ground state. By exciting a vibration, the incident photon will lose energy, and the scattered light will have a lower frequency ν_s . On the contrary, the photon gains energy when interacting with a molecule in an excited vibrational state, and the scattered light will have a higher frequency ν_{as} , called anti-Stokes scattering [79,81,82]. In general, Stokes scattering is much more likely to occur than anti-Stokes scattering, because the majority of the molecules are in the ground state, according to Boltzmann statistics for the molecule's energy distribution [81].

RS can give information of a molecule's vibrational levels, which in turn depends on the molecule's constituent atoms, their structural arrangements, and chemical bond strengths. Since each kind of molecule has its own specific set of vibrational modes, Raman spectroscopy has an inherent merit of label-free molecular fingerprint over other kinds of spectroscopy, for example, fluorescence spectroscopy which can only show broad band spectra.

Fig. 2-7 Schematic diagram of Stokes and anti-Stokes RS with (a) depicts the interaction between an incident photon and a molecule during the RS process, and (b) illustrates the energy levels of the molecule that involved in the RS [76].

In principle, the total intensity of RS signal ($P^{RS}(\nu_s)$) can be calculated with the following formula [76]:

$$P^{RS}(\nu_s) = N\sigma^R I(\nu_L) \quad (2 - 27)$$

where N represents the total number of molecules in the volume that can interact with incident photons, σ^R is Raman scattering cross section, and $I(\nu_L)$ represents the intensity of the excitation laser of incident frequency (ν_L). The Raman scattering cross section which is an inherent property of a molecule, and it relates the scattered intensity to the incident irradiance in RS process [83].

The applications of RS for vibrational imaging of biological samples [84], discriminating cell types [85], and structural analysis of molecule [74] has been explored over the last few decades [79]. However, the effective cross-section of RS is extremely small, which is around 10^{-30} - 10^{-25} $\text{cm}^2/\text{molecule}$ [83,86], and only resonant RS can provide a larger value of the effective scattering cross-section. Compared to the effective cross section of fluorescence, which is around 10^{-16} $\text{cm}^2/\text{molecule}$, the small scattering cross section of RS results in very weak Raman signals, and thus, hindering its applications for detection of analytes with relatively low concentrations.

2.3.2 SERS

To improve the sensing sensitivity and LOD for the ultimate purpose of achieving single molecule detection, several techniques have been developed, including SERS. SERS is a technique in which weak RS is amplified through the adsorption of a molecule onto (or is very close to) a roughened noble metal surface or substrate [87]. The roughened surfaces or substrates absorb the incident laser light and create an intense electromagnetic field due to the excitation of certain special coupling of surface plasmon.

Surface plasmon. resonance (SPR) is an electron resonant oscillations in the interface between two materials with positive and negative permittivity respectively [88]. It occurs when the parallel optical wave vector of the incident light and the propagation constant of the surface plasmon wave match. SPR has the characteristic of large absorption at a specific wavelength followed by a significant electromagnetic field enhancement on the metallic surface (normally noble metals). SPR can be divided into propagating surface plasmon resonance (PSPR) which is generally supported by continuous metallic thin films or gratings, and localized surface plasmon resonance (LSPR) which is supported by isolated metallic nanoparticles [89]. Therefore, the features of the metallic structures are extremely important, because the SPR absorption spectrum is highly sensitive to the characteristics of the metal structure, such as its chemical nature, the metal surface roughness or feature size, and period of the metal features.

Historically, in 1974, Martin Fleischman and his colleagues first discovered that high-intensity Raman signals could be observed when pyridine was attached to electrochemically roughened surfaces of silver electrodes [90]. This enhanced phenomenon was initially attributed to the presence of a large number of molecules on the roughened silver surfaces. But, later in 1977, Albrecht [91] and Jeanmaire [92] revealed that it was an intrinsic surface enhancement effect that was much more essential for the ultra-high intensity.

There are two main mechanisms that contribute to the enhanced Raman signals:

- (1) Electromagnetic enhancement: Molecules being close to the surfaces of the metallic structures experience a significantly enhanced electromagnetic field of the incident light induced by SPR, as shown in Fig. 2-8. Moreover, when the frequency of the Raman scattered light is close to that of the excitation light, the scattered electrical field can be amplified as well to further enhance the intensities of Raman signals.

(2) Chemical enhancement: The adsorption of a molecule onto the metallic surface induces the formation of an adsorbed molecule complex and an electronic coupling between the metal and the molecule, resulting in a larger effective Raman cross-section at the adsorption layer at the interface than free molecules [93,94].

Therefore, the modified formula for estimation of SERS signal power ($P^{SERS}(\nu_S)$) is [62]:

$$P^{SERS}(\nu_S) = N' \cdot \sigma_{inc}^R \cdot |A(\nu_L)|^2 \cdot |A(\nu_S)|^2 \cdot I(\nu_L) \quad (2-28)$$

where $A(\nu_L)$ and $A(\nu_S)$ represent the electromagnetic enhancement factors for the excitation laser and the scattered Raman light, respectively, σ_{inc}^R describes an increased effective Raman cross section of the adsorbed molecules, and N' is the number of molecules that actually contribute to SERS signal instead of a total number of the molecules in the volume.

As the chemical mechanism contributes to the SERS enhancement in the order up to 10^2 , and it varies with different analytes, we will only focus on the electromagnetic mechanism which plays the dominant role in the enhancement.

In order to understand the mechanism of electromagnetic SERS enhancement easily, consider a small sphere with a diameter of $2r$ much smaller than the wavelength of incident light, as illustrated in Fig. 2-8 [76]. The complex dielectric constant of the sphere is represented by $\epsilon(\nu)$, and the dielectric constant of the surrounding medium is ϵ_0 . A molecule located at a distance d from the central core of a sphere will experience a superimposed (or local) electrical field (E_M) of the incident light electrical field E_0 and

Fig. 2-8 A simple schematic diagram of the electromagnetic SERS enhancement [76].

a dipole field E_{sp} inspired by SPR. The field enhancement factor $A(v)$ can be defined as the ratio of the total power of the electrical field to that of the incoming field [62].

$$A(v) = \frac{E_M(v)}{E_0(v)} \sim \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \left(\frac{r}{r+d} \right)^3 \quad (2-29)$$

According to Eq. (2-29), if the real part of the complex dielectric constant ε is equal to $-2\varepsilon_0$, the enhancement factor $A(v)$ can reach the maximum value. Besides, a small imaginary part of ε is necessary for a strong the electromagnetic enhancement, which indicates a relatively low loss [76,95].

Similarly, the scattered Stokes or anti-Stokes field is amplified if it can resonate with the surface plasmons of the metal sphere. Taking into consideration the enhancement effects for both the excitation laser and Raman scattered light, the electromagnetic enhancement factor for SERS can be expressed as [62]:

$$G_{SERS}(v_S) = |A(v_L)|^2 |A(v_S)|^2 = \left| \frac{E_M(v_L)}{E_0(v_L)} \right|^2 \left| \frac{E_M(v_S)}{E_0(v_S)} \right|^2 \quad (2-30)$$

This formula describes all the peculiarities and properties of SERS enhancement with a simple model. $E_M(v_L)$ and $E_0(v_L)$ refer to the local and incident electrical field intensities at the excitation wavelength. $E_M(v_S)$ and $E_0(v_S)$ refer to the local and Stokes electric field intensities at the Raman scattered frequency. Generally, because of the weak spectral dependence, as well as ease of calculation, this formula is simplified as:

$$G_{SERS}(v_S) = \left| \frac{E_M(v_L)}{E_0(v_L)} \right|^4 \sim \left| \frac{\varepsilon(v_L) - \varepsilon_0}{\varepsilon(v_L) + 2\varepsilon_0} \right|^2 \left| \frac{\varepsilon(v_S) - \varepsilon_0}{\varepsilon(v_S) + 2\varepsilon_0} \right|^2 \left(\frac{r}{r+d} \right)^{12} \quad (2-31)$$

which indicates that the electromagnetic enhancement factor is proportional to the fourth power of the local electric field of the metal structure relative to the incident photon when both of the excitation laser and Raman scattered field are in resonance with its surface plasmons [76,96–100]. Although direct contact of the molecule with the metal structure is not necessary for electromagnetic SERS enhancement, the gain factor actually decreases rapidly with distance, as the decay of the field over distance is $\left(\frac{1}{d}\right)^3$.

Considering both the electromagnetic enhancement and chemical enhancements, the overall SERS enhancement factor (EF) can be defined as the ratio of surface enhanced Raman signal per molecule to normal Raman signal per molecule generated without surface enhancement effect.

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{vol}} \quad (2-32)$$

where N_{SERS} is the average number of analyte molecules that contribute to the SERS signal (adsorbed molecules), and N_{vol} represents the average number of analyte

molecules that are involved in the scattering volume for non-SERS active Raman measurement [101,102].

In general, for SERS on a roughened noble metal layer or film, the electromagnetic enhancement factor is on the order of 10^3 - 10^5 [103–105]. For SERS using isolated metal nanoparticles, mainly silver and gold, the enhancement is on the order of 10^6 [82,98,106–114]. Moreover, when the nanoparticles cluster into aggregate, the electromagnetic enhancement factor can be increased up to 10^{11} . The reason for this significant increase in the enhancement is demonstrated to be the stronger electrical field at the sharper edges or junctions of nanostructures. It is theoretically proved that in the midpoint between two adjacent gold or silver spherical nanoparticles (NPs) separated by a gap of 1 nm, the electromagnetic enhancement factor can be as large as 10^{11} [115]. Taking advantage of the “hot spots” in the nanoparticle aggregates, even larger enhancement factors up to the order of 10^{14} have been reported involving the attribution of chemical absorption induced resonant RS [116–118].

2.3.3 Mie scattering

Mie scattering describes the scattering process of an electromagnetic wave when interacts with a homogeneous nanoparticle. When an electromagnetic plane wave is incident on a nanoparticle, partial of the wave power will be extinct due to the absorption and scattering of the nanoparticles.

Fig. 2-9 An illustration of the interaction between the fundamental core mode and the nanoparticle. The Green region depicts the evanescent wave of the fundamental core mode.

In solid-core fibers, the fundamental mode transmitted in the fiber core interacts with nanoparticles via evanescent wave. The power decay coefficient of a single nanoparticle α can be calculated through [119,120]:

$$\alpha = -\eta_{particle} Q_{ext}$$

where, Q_{ext} is the extinction coefficient of the nanoparticle, and $\eta_{particle}$ represents the fractional optical power casted on the geometric cross-section of a single nanoparticle that lies within the evanescent field of the guided fiber mode and can be calculated through [119,120]:

$$\eta_{particle} = \iint_{\Omega_s} \frac{P(r, \varphi) r dr d\varphi}{P} \quad (2-33)$$

where, $P(r, \varphi)$ is the modal power density in the cross section of the optical fiber, and P is the overall power of the fundamental mode. Ω_s denotes the geometric cross-section of the nanoparticle.

The extinction coefficient of a nanoparticle Q_{ext} is a sum-up of its scattering coefficient and the absorption coefficient, and can be calculated through the Mie Theory [119,120]:

$$Q_{ext} = \frac{2}{a^2 k^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (2-34)$$

where, a_n and b_n are the scattering coefficients. We assume that the sphere has a RI of $n_s = n + ik$, where n and k are the real part and imaginary part of its RI, respectively. The RI of the surrounding medium is defined as n_m . The relatively RI (m) and the size factor (x) of the sphere is defined as:

$$m = \frac{n_s}{n_m} \quad (2-35)$$

$$x = \frac{2\pi n_m a}{\lambda} \quad (2-36)$$

where, a and λ is the diameter of the sphere and incident wavelength, respectively. The scattering coefficients can be expressed by:

$$a_n = \frac{\mu m^2 j_n(mx) [x j_n(x)]' - \mu_1 j_n(x) [mx j_n(mx)]'}{\mu m^2 j_n(mx) [x h_n^{(1)}(x)]' - \mu_1 h_n^{(1)}(x) [mx j_n(mx)]'} \quad (2-37)$$

$$b_n = \frac{\mu_1 j_n(mx) [x j_n(x)]' - \mu j_n(x) [mx j_n(mx)]'}{\mu_1 j_n(mx) [x h_n^{(1)}(x)]' - \mu h_n^{(1)}(x) [mx j_n(mx)]'} \quad (2-38)$$

where μ , μ_1 , j_n and $h_n^{(1)}$ are the permeability of the surrounding medium, the permeability of nanoparticle, the spherical Bessel functions of the first kind, and the Hankel functions.

2.4 Lasers

2.4.1 Working principle

A laser oscillator is generally comprised of a resonator (cavity) to provide optical feedback, and a gain medium within the resonator to amplify the light signal circulating in it based on stimulated emission. Stimulated emission is a process that the atoms/molecules of a gain medium pumped to excited states with electrons occupying higher-energy state emit a photon in the same direction and same energy as the incident photon through energy relaxation. The energy of the emitted photon ($E_{emitted}$) is expressed by the following equation:

$$E_{emitted} = h\nu = E_2 - E_1 \quad (2 - 39)$$

Where, h and ν are the Planck constant ($6.62607004 \times 10^{-34} J \cdot s$) and the frequency of the incident photon, and E_2 and E_1 represent the energy of the upper energy level and ground energy level, respectively. The illustration of absorption and stimulated emission are illustrated in Fig. 2-10.

To amplify the light signals trapped within the optical resonator, the gain medium needs to be externally pumped into the condition of population inversion in which the number of atoms/molecules in excited states is larger than that in ground state. In this case, the gain of specific light photons in a single travel round exceeds the loss caused by medium absorption or the resonator, realizing the amplification of the light signal. The pumping can be either electrical currents or optical light. Apart from the gain medium which offers light amplification, laser resonators are used to provide necessary optical feedback for producing standing waves for certain wavelengths. When the

Fig. 2-10 An illustration of processes of absorption and stimulated emission.

pumping energy exceeds the lasing threshold, laser emission will be coupled out of the cavity.

Laser emission is different from the natural sunlight or light bulbs. It exhibits good coherence, spatially or temporally. Spatial coherence enables it to be focused to a tiny spot and to propagate over long distance without large divergence. Temporal coherence enables it a narrow optical spectrum, show good monochromaticity. The laser emission can be either continuous or pulsed.

A typical schematic diagram of a laser with two parallel mirrors is plotted in Fig. 2-11 (a), and a typical spectrum of the laser emission is plotted in Fig. 2-11 (b) for easy understanding. Only the laser modes that are covered by the bandwidth of the gain medium can be amplified. Two key parameters regarding the lasing spectrum are the free spectral range (FSR, $\Delta\lambda$), and full width at half maximum ($FWHM$) as indicated in Fig. 2-11 (b). FSR is determined by the optical cavity length of the laser, and $FWHM$ is determined by the quality of the laser cavity.

There are a few types of laser cavities. The most common one is made of two

Fig. 2-11 (a) A typical schematic diagram of a laser with an FP cavity. (b) Cavity resonance modes and the bandwidth of the gain medium.

reflective objects, either by plan or spherical mirrors [121], or realized through other techniques such as grating structures [122]. Normally, one of the two reflective objects needs to be partially transparent to allow laser output. The simplest configuration of this type of cavities is the FP cavity consisting of two parallel plane mirrors. However, for FP cavities, a slight misalignment will induce beam spilling from the side of the cavity. Compared with FP cavities, a confocal cavity with two equal-radii spherical is more commonly used. Besides, spherical cavities also have been intensively investigated due to its unique capability of generating ring lasers. A spherical cavity is usually a gain medium doped liquid droplet [123,124] or microspheres [125–127], and most of the laser emission is based on the excitation of whispering gallery mode (WGM). In addition to the conventional mirror constructed laser cavities and spherical laser cavities, there is another kind of laser cavity which does not have pre-defined cavity length, called random laser cavity [128–130]. The resonance of light in the random laser is supported by a large amount of scattering in the highly disordered gain medium, and this kind of laser cavity can be realized by introducing particles with larger scattering cross section into the gain medium.

2.4.2 Laser characteristics

2.4.2.1 Threshold

Laser threshold is defined as the minimum excitation power/energy above which the light output is dominated by stimulated emission. Below laser threshold, the light output has a broad spectral bandwidth due to the spontaneous emission, and the output power grows slowly with the increase of the excitation power. Above laser threshold, a narrow peak will occur above the broad spontaneous emission spectrum due to the stimulated emission. The wavelengths of the emission are determined by the energy bands of the gain medium.

Theoretically, the lasing threshold enables an optical gain that can balance the round-trip loss in the cavity. This can be expressed by the equation [131]:

$$R_1 R_2 \exp(2g_{threshold}l) \exp(-2\alpha l) = 1 \quad (2-40)$$

where R_1 and R_2 represent the reflectivity of the mirrors on each side, l is the cavity length, $g_{threshold}$ is the threshold parameter, $\exp(2g_{threshold}l)$ is the round-trip threshold gain and $\exp(-2\alpha l)$ represents the round-trip total cavity loss. Therefore, the threshold parameter can be deduced to [131]:

$$g_{threshold} = \alpha - \frac{1}{2l} \ln(R_1 R_2) \quad (2 - 41)$$

2.4.2.2 Laser spectrum

The key parameters regarding the lasing spectra are the free spectral range (FSR, $\Delta\lambda$), and full width at half maximum ($FWHM$). $\Delta\lambda$ reflects the laser cavity length by:

$$\Delta\lambda = \frac{\lambda_0^2}{n d_{round}} \quad (2 - 42)$$

where λ_0 , n and d_{round} are the lasing wavelength, the RI of the gain medium, and the distance of the one round trip of the cavity. $FWHM$ reflects the quality-factor (Q , describes the damping of an resonator) of the cavity by

$$FWHM = \frac{\lambda_0}{Q} \quad (2 - 43)$$

The Q-factor of a symmetric FP cavity can be determined by:

$$Q = \left(\frac{2\pi n L f \sqrt{R}}{c(1 - R)} \right) \quad (2 - 44)$$

where n , L , f , R , and c represents the RI of the medium in the cavity, the length of the cavity, the resonance frequency, the reflectivity of the mirror, and the light speed in vacuum, respectively. Particularly, low Q-factor results in a broadened resonant peak, and high Q-factor results in a fine resonant peak.

2.4.2.3 Polarization

The polarization state of a laser beam is normally characterized with an external polarizer and a spectrometer, as shown in Fig. 2-12. The red arrow is the laser beam, and the light blue arrows indicate the electrical field with an amplitude of E . The dashed line

Fig. 2-12 Schematic diagram for the characterization of the polarization state of a laser beam.

of the polarizer indicate its transmission axis direction. θ is the angle between the oscillation direction of the electrical field of the laser beam and the transmission axis of the polarizer. Therefore, we can see from the Fig. 2-12 that if the electric field oscillate only in one direction, the power transmitted through the polarizer (T) can be represented as:

$$T = (E \cos(\theta))^2 \quad (2 - 45)$$

2.4.3 Various types of lasers

The common types of lasers are:

(1). Solid state lasers.

Solid state lasers often use an ion-doped glass or crystalline to generate laser output with high power, good beam quality or ultrashort pulse duration (picosecond or femtosecond) [132]. The ion-doped glass or crystalline is optically pumped with a flashtube or a laser diode that emits a shorter wavelength than the desired lasing wavelength. The most common dopants include erbium, ytterbium, neodymium, titanium, and holmium, emitting in different wavelength ranges. The most common crystals include yttrium aluminum garnet and sapphire, *etc.*

(2). Semiconductor lasers.

Semiconductor lasers which use semiconductor materials to provide optical gain play an essential role in our daily use, owing to its advantages of cost-effective and compactness. For example, laser pointers. It is usually pumped electrically, and the recombination of electrons and holes across material bandgap supplies the required optical gain. Semiconductor lasers are often used to pump other types of lasers with high efficiency. Special types of Semiconductor lasers includes vertical cavity surface-emitting lasers [133] which emit laser in the perpendicular plane to the wafer surface and Quantum cascade lasers [134] which use intersubband transition.

(3). Gas lasers

Gas lasers use gas discharges to amplify light, and have the characteristics of the highly coherent laser output. The most commonly used gas lasers are helium-neon lasers, carbon dioxide lasers, and argon ion lasers. The gain medium of helium-neon lasers is a mixture of helium and neon gas (normally 85% helium and 15% neon), and it can operate at a few wavelengths with the most widely used one being at 632.8 nm [135]. A carbon dioxide laser operates at 10.6 μm and are often used for welding and cutting due to its thermal effect [136]. Argon ion lasers which operate in the blue and green wavelength

range with narrow bandwidth have been used in medical applications [137]. A special type of gas laser is excimer lasers which use excimers as the lasing medium and typically emit light at ultraviolet wavelength range [138].

(4). Fiber lasers

Fiber lasers are a kind of lasers that the gain medium is doped or infiltrated in an optical fiber. As an optical fiber is an effective optical waveguide, it enables ultra-long gain active region and a high ratio of surface area to volume, which is good for laser cooling.

2.4.4 Fiber lasers

Compared with other types of lasers, fiber lasers (especially those with all-in-fiber configurations) provide much convenience and flexibility in the configuration design, light generation, packaging and practical use owing to the wave guidance capability of optical fibers. Fiber laser cavity can be formed via various methods, such as utilizing cleaved or coated fiber end [139], fusion splicing [140], fiber Bragg gratings [141], fiber loop [142], and fiber cladding structure [28,143–145].

Along with the development of fiber fabrication technology, the integration of gain medium and optical fiber cavity are becoming more diverse. For example, rare earth ions like ytterbium and neodymium can be doped into the core area of fibers to generate high power lasers [146], a large variety of gases or aqueous gain media can be introduced into the holey structure of PCFs to generate lasers with various wavelengths and lasing pattern [43,147].

In particular, PCFs have the inherent advantages to generate laser emission at visible wavelength range by combining with liquid gain media such as laser dye solutions and QD solutions. Depending on the fiber structure, the direction of laser emission can be either along or perpendicular to the fiber axis. Organic dyes have the drawback of fast-bleaching which limits its lasing performance under long exposure time, and it further deteriorates in the laser cavity as both of the pumping energy and emission intensity are high in the cavity [148]. In addition, the inherent optical properties of broad emission spectrum, narrow excitation band and sensitivity to ambient solvent conditions make organic dyes less applicable in constructing bio-analytical systems. Semiconductor QDs have enabled intensive studies as alternatives to organic dyes in light emitting diodes (LEDs) [149], biosensing [150,151], imaging [152,153] and versatile lasers [154,155]. On the contrary to organic dyes, QDs have unique advantages: are less susceptible to photo-bleaching, exhibit great tunability over a wide spectral range, have

temperature-insensitive lasing threshold, broad excitation band, and narrow emission peaks [148,156,157]. In particular, their broad absorbance bands allow the capability of simultaneous excitation of multicolor emission by exciting different QDs with single pumping wavelength. The narrow emission peaks of QDs, which have a typical *FWHM* value of 20 to 30 nm, can be easily tuned from 400 nm to 2 μm by altering the size and material of QDs owing to the quantum confinement effect [156]. Furthermore, the high absorption cross-section, high quantum yields and enhanced photochemical stability achieved with core/shell structured QDs enable to construct robust and low threshold QDs lasers [157–159]. Therefore, combining the wave-guidance capability of optical fibers and the advantageous gain medium characteristics of QDs, QDs fiber laser are attracting more attention among researchers, and show great potential for the applications of bioimaging, phototherapy, *etc.*

Chapter 3 Literature review

In this chapter, we present the literature review on our related topics. For the sensing platforms, we focus on all-in-fiber optofluidic sensing, including RI sensing and SERS, as they both are highly related to the realization of ultra-sensitive molecular detection in aqueous environments. For the light generation systems, we focus on the fiber lasers with a large surface emission area for the potential applications of mass sensing/detection in the environmental monitoring and clinical diagnosis fields.

In section 3.1, we first introduce various types of all-in-fiber optofluidic sensing configurations and then focus on photonic crystal fiber based all-in-fiber optofluidic RI sensors. In section 3.2, we introduce the development of SERS and the works on fiber based SERS detection. In section 3.3, we introduce the works on lasers with a large surface emission area, including sphere or droplet-based ring lasers, microfiber-based ring lasers and PCF-based ring lasers.

3.1 All-in-fiber optofluidic RI sensing

Measuring RI of an aqueous solution is a very important method to analyze the presence of analytes in the aqueous solutions and its concentrations. It is a label-free detection method which does not require pre-labeling, and the detection is carried out through quantitatively distinguishing the RI variation induced by the presence of an analyte compared with the background solutions. Liquid RI detections have been intensively extended to the detection of chemical and biological samples, such as explosive trinitrotoluene [160], virus [161] and CO₂ dissolved in water [162], combined with the advanced technologies of surface plasmon resonance, gratings, and interferometric structures.

3.1.1 All-in-fiber optofluidic sensing configurations

Both conventional fiber and specialty fibers have been explored to construct all-in-fiber optofluidic sensing configurations.

Conventional optical fibers (standard SMFs and MMFs) have been used to sense liquid RI variations in a few all-in-fiber configurations, including fiber gratings [163,164], SMFs/MMFs based interferometers [8]. To improve RI sensing

sensitivity, splicing SMFs/MMFs with specialty fibers or applying misalignment splicing are adopted to excite high order cladding modes to enhance the interaction between light and the ambient medium. A few setups of this kind have been investigated, such as an SMF-MMF-thin core fiber-SMF MZI sensing structure [165], an MMF-coreless silica fiber-MMF structure [166], and a core-offset MZI combined with a fiber Bragg grating [167]. But, these devices show low RI sensitivities in the order of tens of nanometer per refractive index unit (RIU). For fiber LPGs, a research on the RI sensitivity of an SMF LPG [168] reveals that higher-order modes coupling can give higher ambient sensing sensitivity due to the fact that more evanescent wave extends to the ambient environment. But even with 10th order mode coupling, the resonant wavelength only shows a shift of 35 nm when the ambient refractive index change from 1.0 to 1.44 (which is very close to the RI of silica at around 1550 nm). An LPG fabricated on a Boron-Germanium co-doped fiber show an ambient RI sensitivity of ~ 30.5 nm over an RI range of 1.330 to 1.374 prepared with salt solutions [169]. A fiber MZI formed by a pair of LPGs with rotary RI modulation is reported to have a sensitivity of 58.8 nm/RIU in the RI range of 1.3344 to 1.3637 with an interaction length of 40 mm [170]. The RI sensitivity of these configurations is extremely low. The low spectral sensitivity to ambient RI variations is induced by the weak light-matter interaction resulted from the geometry of SMFs and MMFs.

To address these challenges and enhance light-matter interaction in conventional fibers, several advanced fabrication techniques have been proposed to create functional structures on SMFs and MMFs, such as tapering [8], exposing the fiber core (through side-polish [13] or micromachining [171]), fabricating microfibers/nanofibers [11,12] and, splicing with specialty fibers [165,172].

Tapering can help to release more modal energy to its evanescent wave, thus, to enhance the interaction between propagation modes in the fiber and the ambient medium surrounding the fiber. An in-fiber MZI formed by two LPGs and a tapered fiber section having a waist diameter of 38.75 μm placed between the gratings is reported to have a higher ambient RI sensitivity of ~173.8 nm/RIU with an interaction length of ~51 mm [173]. The sensitivity is enhanced by around 5 times compared with its counterpart—a normal pair of LPG on single mode fibers. Another inline MZI constructed with 3 cascaded SMF tapers with a 60 mm-long interaction length is reported to have an RI sensitivity of ~28.6 nm/RIU [174]. This kind of devices still exhibits low RI sensitivity.

Exposing the fiber core enables the direct interaction between the ambient medium and fundamental mode in the fiber core, dramatically enhance light-matter

Fig. 3-1 (a) Microscope images of the microchannel [171]. (b) Schematic diagram of the inline fiber FPI [175]. (c) Schematic diagram of the inline fiber MZI contains a micro-channel [67].

interaction. In 2006, Y. Lai and his colleagues fabricated a $4\ \mu\text{m}$ microchannel (penetrating the fiber in the plane perpendicular to the axial direction, as shown in Fig. 3-1 (a)) into a single mode fiber by femtosecond laser micromachining and hydrofluoric acid etching, and the sensing sensitivity to the RI of the liquid flows through the microchannel was measured to be $0.56\ \text{dB}/10^{-2}$ by analyzing the transmitted power [171]. In 2008, T. Wei, *et al.*, demonstrated an inline fiber FPI by fabricating a micro-notch cavity on an SMF (Fig. 3-1 (b), using femtosecond laser micromachining), and obtained a high RI sensitivity of $1163\ \text{nm}/\text{RIU}$ [175]. In 2010, with the same micromachining method, Y. Wang reported an inline MZI (Fig. 3-1 (c)) in which one arm consisted of a fluidic micro-channel fabricated by removing part of the core of an SMF, and the other arm remained in the fiber core. This device achieves an ultra-high RI sensing sensitivity of $-9370\ \text{nm}/\text{RIU}$ in the RI range of 1.31 to 1.335 [67].

Microfibers/nanofibers with a fiber diameter reduced to be several micrometers or even hundreds of nanometers have attracted large attention in sensing applications due to its large fraction of evanescent fields [176]. Several microfiber based all-in-fiber RI sensing configurations have been investigated, and indeed, they exhibit higher sensitivity compared with normal fibers. In particular, by inscribing a fiber Bragg grating on a silica microfiber using focused ion beam milling technique, a high RI sensitivity of $660\ \text{nm}/\text{RIU}$ is achieved at the RI value of 1.39 [177]. For this device, the waist diameter of the microfiber which is fabricated by tapering a standard SMF is $1.8\ \mu\text{m}$ and the grating pitch is $576\ \text{nm}$ with the resonance wavelength being at $\sim 1540\ \text{nm}$. Besides, theoretically, the RI sensitivity of a microfiber Bragg grating can be improved with a fiber with smaller diameter and higher order mode resonance [178]. Microfiber LPGs also have been demonstrated [179,180]. H. Xuan, *et al.*, fabricated a LPG with a period number of 20

Fig. 3-2 (a) Scheme of the MZI using a 2 μm as the sensing arm [181]. (b) Scheme of the polarimetric interferometer using a high-birefringence microfiber [182]. (c) Scheme of the polarimetric interferometer using the twist of a high-birefringence microfiber [183]. (d) Schematic diagram of the microfiber coupler [184].

and a pitch of 120 μm on a 7.4 μm -diameter microfiber, and obtained an estimated RI sensitivity of ~ 1900 nm/RIU [179]. Higher RI sensitivities can be achieved with microfiber-based interferometers. In 2012, J. Wo *et al.* reported a microfiber MZI using a microfiber with a diameter of 2 μm as the sensing arm (Fig. 3-2 (a)), and it exhibited a high RI sensitivity of 7159 nm/RIU over the RI range of 1.3322 to 1.3646 [181]. In 2017, S. Gao *et al.* reported a polarimetric interferometer (Fig. 3-2 (b)) constructed with a high-birefringence microfiber and obtained an ultra-high sensitivity of 13488 nm/RIU in the RI range of 1.333 to 1.3393 for the dip wavelength at 1500 nm [182]. The sensitivity can be further improved to 18987 nm/RIU by the use of a rectangular microfiber with similar configuration [74] or to 24373 nm/RIU by the use of a twisted highly-birefringent microfiber (Fig. 3-2 (c)) [183]. Another sensing configuration that using a microfiber coupler (with a diameter of 1.4 μm , scheme is shown in Fig. 3-2 (d)) working at near its turning point of the effective group index difference between even and odd supermodes were demonstrated to have an ultrahigh sensitivity of 39541.7 nm/RIU at a RI of 1.3334 [184].

The aforementioned fiber structures have their own advantages and disadvantages in constructing all-in-fiber optofluidic sensing schemes. The advantages are that all of them enhance the RI sensing sensitivity compared with SMFs and MMFs via enlarging light-matter interaction, and can provide sufficient light-matter interaction with very short fiber length, thus dramatically improve the sensitivity and practicability of the all-in-fiber sensing network. However, the disadvantages are also non-negligible. The RI sensitivity of using a slightly tapered fiber is still low. Exposing fiber core requires expensive femtosecond lasers and highly precise moving stages, and the fabricated samples are fragile. Microfibers have a low reproducibility in fabrication and are fragile, causing difficulties in the integration and stability of sensing network. Besides, the all-solid geometry of the conventional fibers makes it necessary to have external liquid/gas flow channels upon light-matter interaction, which compromises the compactness of the system.

A PCF consists of a periodic holey structure in the fiber cross-section. Owing to the fiber geometry, PCFs are able to provide unique capabilities of lightwave guidance in the fiber core and simultaneous liquid/gas transmission in the air channels that are adjacent to the fiber core as well as runs along the entire fiber length. In this way, it enables intact interactions between fiber core modes and aqueous analytes in the air channels to enhance sensing sensitivity. As aqueous solutions can be transmitted in the holey cladding, no external fluidic cavities are needed, improving the compactness of the sensing platform as well as protecting the samples from contamination. Therefore, PCFs are more comply with the increasing demand for practical, compact, high performance and easy handling analytical all-in-fiber optofluidic RI sensing networks.

3.1.2 Photonic crystal fiber based all-in-fiber optofluidic RI sensors

Several types of PCFs based all-in-fiber optofluidic RI sensing have been demonstrated, combined with SPR, directional couplers, fiber gratings and interferometric configurations. Generally, the PCF RI sensors with liquid samples in the voids are more sensitive than those with RI surrounding the outer cladding of PCFs due to the modal energy distributions. Therefore, we will focus on the work that enables liquid infiltration into the holey fiber cladding.

PCF SPR sensors are reported to show high RI sensitivities that can reach as high as 5500 nm/RIU [88]. However, the deposition of uniform gold or silver layer onto the

inner wall of the air channels of PCF is difficult. Therefore, most of the PCF SPR sensors are demonstrated with simulation results only. The first PCF SPR sensor that has a proper rough metal coating on the channel surface was realized with an exposed core PCF, and it shows an RI sensitivity of 1800 nm/RIU [185].

In 2009, D. Wu *et al.* in Prof. B. Eggleton's group demonstrated a directional coupler architecture with an index-guiding solid-core PCF and reported an ultra-high RI sensitivity of 30100 nm/RIU [186]. In this device, they selectively introduced the analyte (with a slightly higher RI than silica) into a single air channel in the fiber cladding, and the resonant dips in the transmission spectra induced by the mode coupling between the solid core and liquid core (analyte) can be monitored to trace RI variations of the liquid core. In 2011, H. W. Lee *et al.* in Prof. P. Russell's group constructed another similar directional coupler using a step-index fiber with a parallel hollow micro-channel, and experimentally demonstrated a high RI sensitivity of ~3000 nm/RIU [23]. The novel structure of this PCF enables convenient liquid insertion and avoid complex selective channel introduction process. However, this kind of directional couplers can only work with a liquid that has a higher RI value than silica, and not suitable for water-based molecular detection.

PCFs based fiber gratings are reported to be able to offer a high RI sensitivity of 1500 nm/RIU which is almost 2 orders of magnitude larger than that of a SMF LPG near a RI value close to water [187]. In this device, the authors inscribed a LPG with a resonance wavelength at 1050 nm on a large-mode-area PCF, and the RI sensitivity was experimentally measured by heating the methanol solution in the PCF. Although amounts of PCF gratings have been demonstrated [188–191], seldom has been reported for molecular detections due to the inconvenient liquid manipulation in most of the configurations. Because, the PCFs are often spliced with SMFs in these configurations. In 2006, L. Rindorf *et al.* demonstrated the potential of using a PCF LPG to detect the thickness of poly-L-lysine and double-stranded DNA immobilized on the inner wall of the air channels [192]. In 2011, Z. He first realized a PCF LPG biomolecule sensor by

Fig. 3-3 Schematic diagram of the PCF LPG [18].

carrying out multilayer biomolecular binding events in the air channel of PCF cladding [193]. The schematic diagram is shown in Fig. 3-3. This configuration he demonstrated not only allowed continuous liquid flow through the channels of PCF LPG, but also enabled the capability of monitoring each step of binding event on the wall of channels by monitoring the shift of LPG resonant wavelength.

Besides, PCFs has also been integrated into interferometric configurations for highly-sensitive sensing demonstration, including FPI [194,195], MZI [196] and Sagnac interferometers [197]. In particular, an FP cavity was formed by splicing a 50- μm -long simplified hollow-core PCF with SMFs at its both ends, and this sensor had an RI sensitivity of $\sim 851.3 \text{ nm/RIU}$ near the RI value of water measured by heating the water infiltrated into the hollow core of PCF (water is infiltrated into the hollow core through the micro-holes in the middle of the fiber drilled with a femtosecond laser) [194]. Another FPI based on a concave-core PCF exhibits an RI sensitivity of 1635.62 nm/RIU [198]. By combining with Vernier effect, the sensitivity of PCF based FP cavities can be enhanced [63]. In 2012, J. J. Hu *et al.* demonstrated a highly sensitive PCF based MZI by splicing a PCF with SMFs, and the channels of the PCF were completely collapsed in the splice region serving as mode splitting and combining

Fig. 3-4 Schematic diagram of the proposed selective-filling PCF (SF-PCF) based Sagnac interferometer. The two red dots on the fiber cross section are the 2 channels filled with high index liquids [197].

components [196]. The RI sensitivity was demonstrated to be 320 nm/RIU. In 2013, T. Han *et al.* reported a Sagnac interferometer using a PCF that had two channels selectively filled with high RI index liquids [197]. The scheme of this device is shown in Fig. 3-4. The two channels are in the innermost ring of the fiber cladding, and the RI of liquid is higher than that of silica. The selective-filling PCF exhibits both index-guiding and bandgap guiding, and its unique birefringence characteristics enable an RI sensitivity of 63882 nm/RIU estimated from its temperature sensitivity. Most of the PCF based interferometers for RI sensing still have limits for realizing biomolecule detection due to the inconvenient liquid manipulations. In 2013, C. Wu reported an in-line optofluidic PCF RI sensors by inserting C-shaped fibers between PCF and SMFs to create liquid inlet and outlet [199]. The schematic diagram is shown in Fig. 1-2 (b). This configuration enables simultaneous light injection into the fiber core and liquid flow in the two relatively large channels of PCF cladding adjacent to the fiber core. By changing the RI solutions (sodium chloride solutions) that flows through the fiber, its RI sensitivity is measured to be 8699 nm/RIU. This device shows great potentials in chemical and biological molecular detections.

In conclusion, though PCFs have inherent advantages in constructing highly-compact, highly-sensitive and easy handling analytical all-in-fiber optofluidic sensing networks, current PCF based RI sensors still have some limits in realizing ultra-sensitive molecular detections in aqueous media. The limits either come from the low RI sensitivity due to insufficient light-matter interaction or inconvenient liquid manipulation/replacement in the air channels. To get in-line access to the air holes, drilling holes with femtosecond laser micromachining technique, using extra components to do free space coupling and inserting a 20- μm -width C-shaped fiber between the PCF and SMF have been proposed. However, the micromachining technique requires expensive femtosecond laser and high-accuracy positioning stages. For the latter method, the tiny C-shaped fiber brings difficulty in manipulation, and, more importantly, mode mismatch is unavoidable because C-shaped fiber has weak light guidance capability. Therefore, to overcome these limitations, a new PCF structure that enables sufficient light-matter interaction and easy process to realize in-line access to the air holes is preferable.

3.2 Fiber-based surface enhanced Raman sensing

SERS has been a powerful tool for label-free molecular detection with high sensitivity, and it is even able to trace single molecules when using a surface with a thin but rough layer of noble metals that increase the effective Raman scattering cross-section. Since it has the combined capabilities of label-free molecular fingerprinting and single molecule detection, SERS has been intensively investigated for various chemical and biomedical sensing applications, such as 2,4-dinitrotoluene vapor detection [200], haemoglobin detection [201], virus signature [202], gene probe [203], and environmental analysis [204]. Therefore, developing sensitive, simple, flexible and inexpensive SERS platforms is highly desirable.

Optical fiber-based SERS sensing platforms have many advantages over SERS substrate platforms, such as compactness, flexibility, and capability of remote sensing [101,205–210]. Moreover, fiber-based SERS is able to achieve a more stable and repeatable result compared with substrates-based SERS platforms since the Raman signal collected from fiber platforms is actually an averaged value along the interaction length.

3.2.1 Multimode optical fiber SERS probes

The features of the large surface area, large mode area, and the ability to transmit large optical power made multimode optical fibers (MMFs) widely applied in the SERS applications in the past two decades. Generally, the surface of the fiber facet or tip is roughened with some techniques, such as polishing [206], chemical etching [211] and femtosecond laser micromachining [212], and Ag or Au nanoparticles (AgNPs or AuNPs) are coated to form an active SERS sensing region through electrostatic self-assembly technology [211], optical trapping [213], slow evaporation [214], *etc.*

In 1991, Mullen and Eeith integrated an extended SERS sensing region on to the surface of an optical fiber for the first time [206]. They directly deposited Ag onto the angled (20° to the fiber axis) cross-sectional surface of a multimode optical fiber probe which was made from roughening a 600-μm core silica fiber with polishing papers to obtain high-quality Raman spectra. In 1992, the same group reported using SERS for pH sensing [215]. A SERS-active tapered fiber-optic nanoprobe developed for intracellular pH sensing in living human cells has also been reported [216]. This nanofiber with coated Ag layer as the SERS-active substrate was fabricated by tapering an MMF down

Fig. 3-5 (a) SEM photograph of a tapered optical fiber core, (b) TEM photograph of gold nanoparticles prepared by Frens method and microwave heating method, (c) SEM photographs of nanoprobe modified with gold nanoparticles, (d) Distribution of gold nanoparticles on the nanoprobe surface [211].

to the scale of 100 nm in diameter, and its success of sensing pH in living cells proved the inherent merits of fiber probes for *in vivo* monitoring and analyses. The capability of remote sensing with a SERS fiber tip was also demonstrated by using a nanoscale tapered fiber with AgNPs deposited on its surface (illustrated in Fig. 3-5) which exhibited a LOD for an R6G solution of 10^{-8} mol/L [211]. Taking advantage of a combined tapered and cylindrical fiber probe, the detection sensitivity for R6G solutions could reach 10^{-13} M in remote sensing configuration [117].

Because of a great versatility for a large range of applications, various types and sizes of SERS fiber tips have been tested, such as tapered [211], flat [217], and angled [218], by dipping them into the sample solution. Tapered and angled fiber tips can increase the magnitude of the evanescent field and transmit it to the surroundings, according to the evanescent wave theory. Thus, it is obvious that tapered or angled fiber tips can increase the interaction between light and analyte samples and show a better collection of Raman signal to get stronger SERS signals [211]. Moreover, for tapered or angled fiber tips, the surface enhanced Raman signal from the tips can be enhanced significantly by optimizing the geometry of the tip. A previously reported geometry-optimized tapered fiber tip with immobilized silver aggregates was demonstrated to have a LOD of 10^{-8} mol/L R6G [219].

An investigation on the effect of the angle of polished fiber tips revealed that the

intensity of SERS signal is further enhanced with the increase in the angle [218]. Various novel structures with flat fiber tips exhibiting large SERS enhancement and good performance have been reported as well, for example, the “sandwich” structure [220]. In this structure, a segment of MMF with incorporated Ag nanoparticles is dipped into a mixed solution of analyte and AgNPs, and sample molecules can be sandwiched in between randomly formed structures of Ag nanoparticles or aggregates, resulting in a significant enhancement in Raman signal according to the theory shown in the reference [221].

Since AgNPs and AuNPs serve as the SERS active medium, to achieve stable and significant enhancement of RS, plenty of studies have been conducted to investigate the effects of the parameters of nanoparticles. When excited by the incident laser beam, isolated NPs support the generation of localized surface plasmons, and their resonant frequency is determined by the particle morphology, size, and the distance between particles [200,222]. It is proved that electrical field intensity “hot spots”, where the electrical field will be amplified tremendously, exists in the regions between closely-spaced nanoparticles in nanoaggregates or clusters [100,221,223,224]. Theoretically, the maximum enhancement factor of RS on the order of 10^{11} , due to electromagnetic enhancement alone, is achieved when the molecule is localized equidistantly between two separated nanoparticles with a gap of 1 nm. However, the formation of the aggregates is random, so, in colloidal SERS, experiment errors can be easily caused by the variability in the shapes and sizes of nanoparticles or aggregates. Hence, in most cases, this kind of structure is less reproducible and stable.

To overcome this drawback, several techniques have been explored or developed to fabricate well designed periodic nanostructures on the cross section of MMF, such as electron beam lithography [101], nanoskiving [99,225], shadow evaporation [226], nanoimprinting [227] and focused ion beam [228]. Periodic metallic patterns support propagating plasmons, and their resonant frequency will be controlled by the pattern periodicity. Ordered patterns have plenty of advantages: they are robust, stable and reproducible. Meanwhile, they can provide enough SERS enhancement that satisfies most practical applications. The periodic metal nanostructures fabricated on the fiber cross-section can form the shape of a star [229], crescent moon [118], nanoring (as shown in Fig. 3-6), *etc* [106,230]. Numerical calculations and analytical studies suggest that the average electromagnetic enhancement factor of RS can reach up to 10^{11} for Ag nanodisks and 10^9 for nanospheres [82]. Moreover, the advanced sub-micron scale

Fig. 3-6 SEM images of Cr nanorings (top) and Au nanowells (bottom) on Si substrate [230].

manufacturing techniques are able to precisely fabricate nanostructures with dimensions of tens of nanometers or even a few nanometers. Prof. Capasso and co-workers successfully fabricated nanorods on the cross-section of an MMF through electron beam lithography and transfer method with an electromagnetic enhancement factor on the order of 10^5 [101] and the capability of detecting several kinds of analyte simultaneously is tested as well. All these techniques and findings hold a significant promise for the fabrication of highly sensitive fiber SERS sensors.

However, the performance of MMF SERS sensing platforms is limited so far either by the small amount of SERS active particles in active regions or by the low electrical field power in sensing areas. In order to overcome these problems, PCFs are investigated for SERS applications.

3.2.2 Photonics crystal fiber SERS sensors

By synergistically enabling flexible design of optical waveguide properties and liquid transmission cell in a single fiber, PCFs show great potentials in constructing high-performance SERS sensing system. Both bandgap PCFs and index guiding PCFs have been investigated for SERS analyses and measurements [231–233].

The performance of PCF SERS sensors is mainly affected by the structure of the PCF and substrates used for SERS. Generally, there are two methods to integrate PCF with SERS measurements. One is to infiltrate the air channels with a mixture of AgNPs/AuNPs and analyte solution [234], and the nanoparticle aggregates and clusters serve as SERS substrates. The other method is to immobilize AgNPs/AuNPs inside the

Fig. 3-7 SEM images of silver deposition profiles obtained under deposition experimental parameters: (A) Deposition time= 0.5 h with a 5 mg/mL precursor. (B) Deposition time= 0.5 h with a 10 mg/mL precursor. (C) Deposition time= 2 h with a 10 mg/mL precursor. (D) Deposition time =3 h with a 15 mg/mL precursor [95].

air channels or on the surface of the fiber by specific techniques, for example, high-pressure chemical deposition, as illustrated in Fig. 3-7 [95]. The bandgap-guiding hollow core PCFs enable direct interaction between analyte and excitation light, while the solid core PCFs generate SERS signal through the evanescent field in the cladding channels. Compared to solid core index-guiding PCFs, hollow core PCFs have the advantages of obtaining Raman spectra of samples with low silica background, but the feature of a narrow transmission window coming along with the bandgap confinement impedes their use for obtaining broad RS spectra. A combination of hollow PCF platform and an index-guiding light transmission mechanism, called liquid core PCF, has been investigated [234]. M. K. Khaing Oo et. al. compared a few PCF structures for SERS applications, and summarized that the PCF microstructure has a significant effect on the evanescent wave-based sensing and detection [231]. They have also reported a LOD of 10^{-10} M R6G in aqueous solution achieved with a suspended core PCF without any post-processing, which is reported to be state-of-the-art. Moreover, an accumulative Raman effect along the fiber length has been observed in the SERS experiment [235] and theoretically analyzed [236].

Therefore, for the fiber-based SERS technique, the effect of both the “hot spots” effect and the fiber length are worthy of exploration for sensitivity enhancement. However, the performance of PCF SERS sensors is limited either by the large attenuation caused by strong absorption and scattering in solution or by the weak Raman signal due to the low evanescent field power in the liquid filled channels.

3.3 Fiber lasers with a large surface emission area

3.3.1 Conventional implementations of lasers with a large surface emission area

Fig. 3-8 Schematic diagram of the quantum dots microdrop laser [154].

Fig. 3-9 (a) A sphere is suspended in ethanol in the large channel of a PCF. (b) SEM of the cross section of the sphere inserted PCF. (c) The launch and collection schemes. Green path indicate core input/scattering output scheme and light pink path indicate sphere input and core output scheme [240].

Lasers with a large surface emission area have great potential in the fields of mass sensing/detection in environmental monitoring and clinical diagnosis. Typical lasers emissions with a large surface emission area are realized by exciting whispering gallery mode (WGM) in the ring cavity [237]. WGM lasers emit along the circumference of a ring cavity and it has been widely used as a laser source with large surface emission area due to the easy fabrication of ring cavity. The ring cavity can be made of several materials, such as water [154], silica [238] and polymers [126]. However, generally, the excitation and collection of WGM lasers often involve bulk optical components, and the fixation of the ring cavity needs external supports, which compromise its compactness. For example, in 2008, J. Schafer *et al.* demonstrated a QD microdrop laser. The microdrop is levitated using electrodynamic endcap trap, and the excitation and collection of WGM are realized through free space coupling with an optical lens. The schematic diagram is shown in Fig. 3-8. Although in some setups, tapered fiber with a waist diameter of a few micrometers is used to couple WGMs [239], the requirements of precise alignment of tapered fibers and the bulky configurations still make it less compactness and limit its practical applications. Placing a microsphere resonator in the channel of a PCF to excite WGM resonance has been demonstrated, which simplifies the excitation of WGM [240]. The scheme is shown in Fig. 3-9. This configuration supports two launch and collection schemes. One is core input, and scattering output. The other one is sphere input and fiber core couple the output. But, no active laser output has been reported with this kind of simplified configuration.

3.3.2 Fiber lasers with a large surface emission area

Optical fiber-based lasers usually have compact configurations and can provide much flexibility in handling. Therefore, they can be applied to complex application scenarios.

Microfibers which have the characteristics of low transmission loss and large evanescent field have been investigated to generate ring lasers combined with gain medium owing to the high quality factor of the microfiber loop resonators [241–245]. In particular, In 2006, X. Jiang *et al.* demonstrated a microfiber knot laser in air using a microfiber that drawn from a erbium:ytterbium-doped phosphate glass [243]. The drawn microfiber has a diameter of 3.8 μm , and the fabricated knot has a diameter of 2 mm. The microfiber knot has dual functions of serving as gain medium and resonance cavity. Another method to combine a microfiber knot resonator is to immerse the knot resonator into gain solutions [244] or attach the gain medium onto the smooth surface of the

Fig. 3-10 (a) The scheme of the microfiber knot laser immersed in an R6G gain solution [244]. (b) The scheme of the double-knot microfiber laser [241].

microfiber knot [242]. The interaction between the light guided in microfiber and the gain medium is realized through the evanescent wave that penetrates into the gain region. In 2007, a microfiber knot laser was demonstrated by immersing a silica microfiber knot with an R6G solution, as shown in Fig. 3-10 (a). The knot has a diameter of $350\ \mu\text{m}$, and the laser peaks were observed when the pump energy of a $532\ \text{nm}$ nanosecond laser exceeds $9.2\ \mu\text{J}/\text{pulse}$. Later in 2012, a single wavelength microfiber knot laser is reported using a double-knot structure [241]. The scheme is shown in Fig. 3-10 (b). The microfiber that has a diameter of $1.88\ \mu\text{m}$ is drawn from an erbium³/ytterbium³ co-doped phosphate glass fiber. Though microfiber knot lasers show preferable characteristics of small size, low threshold, and stable laser output, they are fragile and have difficulties in handling.

A simplified hollow-core PCF has been investigated for generating ring lasers by pumping a $3\ \text{mM}$ R6G ethanol solution plug in the large hollow core of the PCF using a $532\ \text{nm}$ nanosecond pulsed laser [28]. The simplified hollow-core PCF is made of silica and consists of a large hollow core and a ring of 6 large channels surrounding the fiber core. The optical micrograph of the PCF is shown in Fig. 3-11 (a). The thin silica microring surrounding the hollow core supports resonance along its circumference. When the pump energy exceeds $185\ \text{nJ}/\text{pulse}$, a stable ring pattern radiation appears in the azimuthal direction of the fiber. Moreover, the authors demonstrated that the wavelength could be tuned through changing the circumstance of the hollow core. Later, in 2015, the same group demonstrated a tunable optofluidic microring laser by tapering the simplified hollow-core PCF [144]. The pumping configuration is changed from side-pumping to axial-pumping, as shown in Fig. 3-11 (b). As the laser is generated at the interface of the gain plug and air, the output wavelength of the ring laser is tuned through moving the position of the gain plug. This laser show an ultra-low threshold of 16

Fig. 3-11 (a) Optical micrograph of the PCF and a brief illustration of the side-pumping configuration [28]. (b) The schematic diagram of the tapered PCF based microring laser. Insets show the laser emission pattern with different gain media [144].

nJ/pulse. However, with this fiber structure, power fluctuations (nonuniformity in the density) exists in the ring pattern laser emission which probably comes from the interferences between the radiations or diffraction from the crown-like cladding.

A polymer PBG fiber consists of a cylindrical Bragg cavity are proposed and investigated for laser generation in its circumferential surface [43,246]. The fiber consists of a large hollow core surrounded by a bandgap structure formed by alternative high-index and low-index multilayers, and an outer thick polymer layer. The multilayer bandgap structure supports an axial transmission band for the optical pump (wave vector

is in the axial direction) and impose a normal-incidence (axial wave vector equals to 0) bandgap covering a broad wavelength band to provide necessary optical feedback for laser emission in the radial direction. Within this fiber cavity, the photons resonance along the diameter of the hollow cavity. Azimuthally polarized radial emissions have been demonstrated with an R6G water plug [43] and gain medium doped copolymers [246], by axially pumping the gain medium in the hollow core. The lasers exhibit low threshold (165 nJ/pulse for R6G) and perfect ring-shaped pattern.

Therefore, compared with microfiber knot lasers and the simplified hollow-core PCF, the polymer PBG fiber with a cylindrical Bragg cavity is preferable for generating lasers with large surface emission area owing to its easy coupling configuration, easy handling, and perfect ring-shaped laser emission pattern.

Chapter 4 Side-channel photonic crystal fiber

A new fiber structure is proposed here to address the challenges of weak light-matter interaction and inconvenient liquid manipulation in the fiber channels that limit the applications of all-in-fiber sensing platforms [247,248].

Hollow core PCFs can provide extremely large geometrical overlap between the transmitted light and the aqueous medium in the fiber core. However, the transmission band is affected by the RI of the aqueous medium filling the fiber core, and the attenuation loss is also large due to the strong absorption and scattering by the analytes (especially those have large molecules) present in the liquid-core. At the same time, the difficulties in creating lateral liquid access to the central fiber core limit its integration into compact all-in-fiber sensing system. In contrast, in solid-core PCFs, light interacts with the analyte via an evanescent field, thus can providing a more stable sensing performance. Therefore, the newly proposed fiber, side-channel PCF (SC-PCF), has a solid core and latticed cladding structure.

This chapter presents the design, fabrication and basic characterizations of the SC-PCF. Section 2.1 introduces the theoretical investigations on the fiber geometry. Section 2.2 describes the fiber fabrication process. Section 2.3 presents the basic optical properties of the fabricated fiber samples.

4.1 Geometry of SC-PCF

The SC-PCF, which contains a solid core and a large side-channel at the holey cladding region, is specially designed for all-in-fiber liquid sensing applications. Fig. 4-1 depicts the fiber geometry. The fiber is made of pure silica without any dopant material. One sixth of the cladding is intentionally removed to form a large side-channel that enables efficient liquid circulation, enough space for carrying cells for the potential application of detecting molecules on cells, and easy lateral access via splicing with SMFs. In SC-PCF, light is guided in the solid core by the well-known index-guiding mechanism and the information regarding the liquid analytes is obtained via the

Fig. 4-1 Geometry of the SC-PCF. Blue solid color indicates silica, and white indicates the air channels. Λ and d represent the pitch and the inner diameter of the small air holes, respectively.

interaction with the evanescent field in the side-channel adjacent to the fiber core.

The most important factors that affect the waveguiding properties of the SC-PCF are the pitch (Λ , the distance between two adjacent air holes) and the inner diameter (d) of the periodic air channels. The values of these two parameters should be chosen so that they would reduce the number of core-guided modes and mode coupling loss (butt coupling) to SMFs, but enlarge the fraction of evanescent power in the fiber side-channel.

As for the fraction of evanescent power in the fiber side-channel (FP_{ch}), theoretical investigations on its dependence on the Λ and d/Λ are done with FEM as well. The fraction of evanescent power in the fiber side-channel (FP_{ch}) is calculated by the equation:

$$FP_{ch} = \frac{P_{ch}}{P_{all}} \quad (4 - 1)$$

where P_{ch} and P_{all} represent the evanescent power in the fiber side-channel and the total power of the mode, respectively.

In the simulations, to mimic the experimental scenario, the side-channel is filled with water with an RI of 1.333, and the rest of the air channels are empty, with an RI value of 1.0. The wavelength used in the simulation is 1200 nm. The RI of silica material is extracted from its Sellmeier equation [249]. The simulation results show that smaller pitch (Λ) and larger air hole diameter ratio (d/Λ) values give a higher fraction of evanescent power in the side-channel, as shown in Fig. 4-2. This is not difficult to understand, because smaller pitch and larger air hole diameter ratio result in a smaller.

Fig. 4-2 Dependence of the fraction of evanescent power in the side-channel on the Λ and the ratio of d to Λ [248].

fiber core diameter.

Though, for the SC-PCF, a smaller fiber core diameter results in a larger fraction of evanescent power in the fiber side-channel, but its mode coupling loss to SMFs may be very large due to the mismatch between their mode field diameters (MFDs). The mode coupling loss can be estimated using the equation [250]:

$$\alpha = -20 \log \frac{2d_{SMF}d_{SC-PCF}}{d_{SMF}^2 + d_{SC-PCF}^2} \quad (4-2)$$

where d_{SMF} is the MFD of the SMF, and d_{SC-PCF} is the MFD of the SC-PCF [250]. For a Gaussian-shaped modal power distribution profile, the MFD can be estimated to be from the position where the power drops to $1/e^2$ of the maximum value. With this fiber geometry, we find that the minimum coupling loss can be achieved with a pitch of $\sim 6 \mu\text{m}$.

By running simulations, we find that the SC-PCF supported single mode propagation in the fiber core when the value of d/Λ is equal to or less than 0.45. To achieve single mode propagation in the core of the SC-PCF, the value of d/Λ is determined to be 0.45. Although a pitch value of $5 \mu\text{m}$ can give a slight higher evanescent power in the fiber side-channel than with a pitch value of $6 \mu\text{m}$, we determine the pitch value of the SC-PCF to be $6 \mu\text{m}$, considering that its mode coupling loss to SMFs is

Fig. 4-3 The modal intensity distribution of the fundamental mode in SC-PCF depicted by (a) an intensity profile and (b) a contour plot.

minimized at $6\ \mu\text{m}$. With these parameters, the fraction of evanescent power in the fiber side-channel is $\sim 0.145\%$, the mode coupling loss to SMFs is minimized, and only the fundamental mode is guided in the fiber core of the SC-PCF. The number of air hole rings is set to be 6 to ensure enough space for a cell (the diameter is $\sim 25\ \mu\text{m}$), and avoid the redundant use of capillaries. The simulated fundamental mode profile obtained with COMSOL for the above geometric parameters is shown in Fig. 4-3. The modal intensity distribution is Gaussian-shaped. The intensity is normalized to its maximum value.

4.2 Fiber fabrication

For pure silica PCFs, the most commonly used fabrication technique is the stack-and-draw technique [37].

The proposed SC-PCF was fabricated in Xlim Research Institute, France. First of all, small capillaries are fabricated from drawing large tubes, and the length of each capillary is around 1 m. The ratio of inner diameter to outer diameter of the tube is supposed to be the same as the d/Λ value of the fiber.

Second, all the capillaries and the fiber core rod are stacked together to form the preform of SC-PCF. Special efforts are made to keep the SC-PCF structure in the preform because the size of the side-channel is quite large compared to other small air holes. To maintain the preform structure during the drawing process, a short segment at each end of the preform is fully stacked with capillaries, and thus, only a 40 cm-long segment in the middle part of the preform would constitute the desired structure of the SC-PCF, as shown in Fig. 4-4.

Fig. 4-4 Illustration of the preform of the SC-PCF [248].

Third, the preform is drawn through a high-temperature furnace in a fiber drawing tower. The complete drawing process consists of two steps:

- (1) The large preform is drawn into canes, with the outer diameter reduced to a few millimeters.
- (2) After adding an extra silica jacket tube, the canes are drawn into fibers.

For the fabrication of our SC-PCF, the 2-step stack-and-draw works better than the 1-step stack-and-draw, because the ratio of preform diameter to fiber diameter is too large, and there is a big difference between the thermal expansion coefficients of silica and air.

The second step of drawing canes to SC-PCF is the most challenging part, and it is a process of trial and error. When the cane is heated up at the high temperature of $\sim 1700^\circ\text{C}$ (close to the melting temperature of silica), the large side-channel is prone to expand significantly, and hence squeeze and destroy the fiber structure. To obtain a fine fiber structure, there are a few parameters that can be adjusted during the drawing process, including the furnace temperature, the pressure applied to the air channel, preform feeding speed and drawing speed. For air cladding PCFs, the temperature applied to the preform/cane is an essential factor for maintaining the cane/fiber structure. If the temperature is too high, the air in the holey channels can expand and destroy the fiber structure (silica web). If the temperature is too low, the fiber is easily broken during the drawing process. We can control the temperature applied to preform/cane through changing the furnace temperature, as well as the feeding speed of the preform/cane since fast feeding speed can help reduce the thermal expansion effect.

At the same time, during the drawing process, the feeding speed (speed of the preform/cane, V_{seed}) and drawing speed (speed of the cane/fiber, V_{fiber}) need to be precisely controlled to obtain the accurate size of cane/fiber and good structure. The corresponding speeds can be calculated through the following relationship:

$$V_{seed}R_{seed}^2 = V_{fiber}R_{fiber}^2 \quad (4-3)$$

where R_{seed} and R_{fiber} are the radii of the seed preform/cane and the corresponding

cane/fiber, respectively.

In general, when drawing a fully stacked PCF preform to cane, a vacuum is applied to suppress the interstitial holes. However, in our case, applying vacuum will cause the collapse of the side-channel, therefore, is infeasible. As a result, there are some small interstitial holes in the fabricated fiber which actually provide better confinement of light in the core region opposite the side-channel and therefore further enhances the evanescent power in the side-channel.

The scanning electron microscope (SEM) photo of the fabricated SC-PCF is shown in Fig. 4-5. The structure of the SC-PCF is in good agreement with our design, and the shape of the side-channel is maintained well. The outer diameter, the size of the side-channel, Λ , and d/Λ , are measured to be 118 μm , 30 μm , 6.08 μm and 0.6, respectively.

4.3 Basic characterizations

4.3.1 Analysis of modes in the fiber core

After fabrication, the d/Λ value of the fabricated fiber is a bit different from that of the initial design. COMSOL simulations here therefore run with the practical geometry of the fiber to investigate its mode properties. All of the small air holes and the side-channel are empty without any liquid presence. The simulation results reveal that

Fig. 4-5 Cross-sectional SEM photo of the fabricated SC-PCF.

Fig. 4-6 Simulated intensity distributions of (a) LP_{01} mode and (b) LP_{11} mode at the wavelength of 1550 nm and their contour plots zoomed into the core area. The intensities are normalized to its corresponding maximum values.

the SC-PCF can support the LP_{01} and LP_{11} mode in the fiber core over a wide wavelength range of 1200 – 1700 nm. The simulated mode profiles of both the LP_{01} and LP_{11} modes are shown in Fig. 4-6.

In addition, the fiber core mode profiles are experimentally characterized with a tunable laser source (ANDO, AQ4321D), objective lenses (20x), and a normal InGaAs camera (not cooled), as shown in Fig. 4-7 (a). The tunable laser source has a fiber output (SMF). In this experiment, the laser wavelength is tuned to 1550 nm (single wavelength output with a power of ~0.5 mW). The 1550 nm laser light was collimated and then focused into the core of the SC-PCF by 20x lenses. After propagating through a 20 cm long SC-PCF, the transmitted laser light was then captured by the InGaAs camera. By adjusting the coupling position on the fiber core at the input end of the SC-PCF, we are able to couple the laser light into LP_{01} and LP_{11} mode. In particular, for the LP_{11} mode excitation, we need to apply a slight core-offsetting light coupling at the fiber input. The characterized mode profiles of LP_{01} and LP_{11} modes at the fiber output end and their

Fig. 4-7 (a) Schematic diagram of the mode profile measurement. Measured modal intensity profiles of (a) LP_{01} and (b) LP_{11} modes. Contour plots of the modal intensity profiles of (d) LP_{01} and (e) LP_{11} modes.

contour plots are shown in Figs. 4-7 (b)-(e).

4.3.2 Characterizations of the optical properties of the fiber

First, the bending loss of SC-PCF was investigated since it was related to the flexibility and stability of the sensing system. In this investigation, a tunable laser source (ANDO, AQ4321D) at 1530 nm was launched into a 2-m-long SC-PCF through SMF splicing at one fiber end. After passing through the SC-PCF which was wrapped around a 0.5-inch-diameter rod, the near-field transmitted mode profile was captured at the output end of SC-PCF with a 20x objective lens and an InGaAs camera with a step of

Fig. 4-8 (a) Schematic drawing for the bending loss measurement. Transmitted mode profiles at the output end of SC-PCF (b) without wrapping, (c) with 5-coils wrapping, and (d) with 10-coils-wrapping around a 0.5-inch-diameter rod measured under exactly the same light coupling conditions [248].

one turn. The measurement setup is shown in Fig. 4-8 (a). We chose the bending diameter of 0.5-inch because the power attenuation with a larger bending diameter was too small to be detectable, and the fiber was easily broken with a smaller bending diameter. The transmitted mode profiles without wrapping, with 5-turns wrapping and 10-turns-wrapping around a 0.5-inch-diameter rod are shown in Figs. 4-8 (b)-(d). The transmitted laser powers were measured to be -4.11dBm, -4.27 dBm and -4.35 dBm accordingly. The very small drop of 0.24 dB after 10-coils-wrapping around a 0.5-inch-diameter rod indicates an ultra-low bending loss. Therefore, the fabricated SC-PCF can be flexibly applied in a compact sensing platform.

Second, the transmission loss of the SC-PCF at 1550 nm was measured to be 0.27 dB/m by a cut-back method with an initial fiber length of 5 m. The cut-back method is a common way of measuring fiber transmission loss. By comparing the transmitted light powers after propagating through different fiber lengths, fiber transmission loss can be calculated. In this measurement, we used a stabilized broadband source (Infinon Research, IRBL-11111-F) with an SMF output. It has a low degree of polarization and can cover a wide wavelength range of 1250-1650 nm. The power spectrum of this broadband light source is shown in Fig. 4-9 (a)). The light coupling between the SMF

Fig. 4-9 (a) The emission power spectrum of the broadband light source. (b) Scheme for measuring the transmission loss. (c) Scheme for measuring the insertion loss.

and SC-PCF was realized through butt-coupling using a precise 3-axis nanopositioning stage. The output end of the SC-PCF is directly connected to an OSA (Yokogawa, AQ6370C) using a fiber adapter for measuring transmission spectra, as shown by the schematic drawing in Fig. 4-9 (b). To avoid power variation at the input end of the SC-PCF and ensure accuracy for the measurements, the light launching end of the SC-PCF needed to be fixed for the spectrum measurements. After collecting the transmission spectra, the SC-PCF is then shortened from the fiber output end to a fiber length of 10 cm. The transmission loss of the SC-PCF was calculated to be ~ 0.27 dB/m by comparing the output power with these two fiber lengths at the wavelength of 1550 nm. The measured low transmission loss together with the ultra-low bending loss of the SC-PCF allows long length usage of the SC-PCF in sensing devices.

Third, the total insertion loss after splicing with an SMF was measured to be less than 1 dB. The measurement steps are shown in Fig. 4-9 (c). After inserting a section of SMF by butt-coupling, the transmission power dropped by about 0.22 dB at 1550 nm. After fusion arc splicing (Sumitomo electric, TYPE-36), the transmission power dropped another 0.54 dB. The splicing can be further improved by optimizing the splicing parameters or using assistant technics.

4.4 Summary

In this chapter, the design, fabrication, and characterizations of a new PCF structure, the SC-PCF, are demonstrated. Our proposed SC-PCF structure has a solid core and triangular lattice cladding. One sixth of the lattice cladding was removed intentionally to enable efficient liquid infiltration and convenient lateral liquid access to the fiber channel even when the SC-PCF is spliced with SMFs. In this SC-PCF, the light transmitted in the fiber core interacts with the liquid/gas medium in the fiber side-channel via the evanescent wave. The dependence of the evanescent power in the side-channel on the fiber geometry was theoretically investigated using FEM. The simulation results showed that smaller Λ and larger d/Λ values result in a higher fraction of evanescent power in the fiber side-channel. However, a too small core diameter causes low modal coupling efficiency when splicing with an SMF. To balance the mode coupling efficiency, the fraction of evanescent power in the side-channel, and the number of core modes, the value of Λ and d/Λ were determined to be 6 μm and 0.45, respectively. The SC-PCF was fabricated with a 2-step stack-and-draw method. After fabrication, the outer diameter, the size of the side-channel, Λ , and d/Λ , were measured to be 118 μm , 30 μm , 6.08 μm and 0.6, respectively. With the fabricated fiber samples, the optical properties of the SC-PCF were then characterized, including the core modes, bending loss, transmission loss and splicing loss with SMFs. The fabricated SC-PCF supports LP_{01} and LP_{11} core modes. Our SC-PCF exhibited ignorable bending loss measured by wrapping a few coils of fiber around a 0.5-inch-diameter rod. The transmission loss of our SC-PCF was calculated to be 0.27dB/m, and the insertion loss of splicing to SMFs was measured to be less than 1 dB. These very advantages of our SC-PCF pave new ways to the realization of all-in-fiber sensing schemes.

Chapter 5 SC-PCF based all-in-fiber sensing devices

Our proposed SC-PCF is specially designed to enable easy liquid lateral access for constructing all-in-fiber sensing applications. In this chapter, a few all-in-fiber sensing devices are investigated for high-sensitivity liquid sensing applications, taking advantages of the characteristics of our SC-PCF.

In this chapter, section 3.1 introduces the integration of an LPG with the SC-PCF for highly-sensitive in-line optofluidic RI sensing application. Section 3.2 introduces an SC-PCF based all-in-fiber Sagnac interferometer for human CTT protein detection through multilayer functionalization on the fiber core surface. Section 3.3 presents the optimization and fabrication of a new SC-PCF fiber geometry for ultra-sensitive SERS measurements and detection, and demonstrates its sensing performance with standard Raman tags.

5.1 An in-line optofluidic RI sensor based on an SC-PCF LPG

In this section, an in-line optofluidic RI sensor is realized by splicing an SC-PCF LPG directly to side-polished SMFs. In this experiment, an LPG combined with an intermodal interference between LP_{01} and LP_{11} core modes is used to achieve a high extinction ratio of the interference pattern for sensing the RI of the liquid in the side-channel with the targeted application of water solution-based chemical and biological sample detection. First, the mode properties of LP_{01} and LP_{11} modes in SC-PCF fiber core are investigated to see the responses of their modal ERIs to the RI variations of the liquid flows in the fiber side-channel. Second, the LPG design, the theory of the

intermodal interference, and the fabrication of LPG on SC-PCF using a CO₂ laser are introduced. The LPG is used to monitor the RI variation of the liquid in the side-channel with a high sensing sensitivity. Last, the sensing performance of this all-in-fiber SC-PCF LPG is analyzed with RI solutions.

5.1.1 Mode properties of SC-PCF

The fabricated SC-PCF can support both LP₀₁ and LP₁₁ modes in the fiber core over a broad wavelength range between 1200-1700 nm. FEM simulations with the geometry of the fabricated fiber structure were carried out to theoretically analyze the effective refractive indexes (ERIs) of the two modes. In the simulations, the geometry of the practical structure of our designed and fabricated SC-PCF was imported into COMSOL 5.0 software from its SEM image. To investigate the effect of liquid presence in the side-channel on the mode guiding properties of the SC-PCF, simulations were performed with two scenarios. One scenario was selective water presence in the side-channel only, and the other scenario considered that all of the channels (including side-channel) were filled with air. As the simulations were carried out over a broad wavelength range, the material dispersion of silica and water also need to be considered in the simulations to ensure the desired accuracy. Therefore, the RI values of the silica and air at different wavelengths were calculated according to their Sellmeier equations [199,249].

The simulated modal intensity distributions (normalized to its maximum intensity) of LP₀₁ and LP₁₁ at the wavelength of 1550 nm are shown in Fig. 5-1 for both scenarios. The SEM photo of the fabricated SC-PCF is shown in Fig. 5-1 (a) again to make an easy comparison. The simulated mode profiles for selective water presence in the side-channel scenario are shown in Figs. 5-1 (b) and (c). The mode profiles for the “all air” scenario are shown in Figs. 5-1 (d) and (e). By comparison with those in the “all air” scenario, more fraction of the evanescent power is located in the side-channel for both LP₀₁ mode

Fig. 5-1 (a) SEM image of the SC-PCF. The gray lines depict the fiber structure in simulations. Simulated intensity distributions at the wavelength of 1550 nm of; (b) and (c) LP_{01} and LP_{11} modes with water in the side-channel, respectively; (d) LP_{01} and (e) LP_{11} modes in “all air” scenario; Contour plots of intensity distributions of (f) LP_{01} and (g) LP_{11} modes of the “all air” scenario.

(increased from 0.06% to 0.34%) and LP_{11} modes (increased from 0.099% to 0.485%) in the selective water presence scenario. It indicates that when the side-channel is filled with liquid, light-matter interaction in the side-channel can be enhanced. Figs. 5-1(f) and (g) show the contour plots of the intensity distributions of LP_{01} and LP_{11} modes of the “all air” scenario, respectively.

Then, the ERIs of LP_{01} and LP_{11} modes in the wavelength range 1400-1700 nm were calculated and their plot can be seen in Fig. 5-2. As can be observed from the figure, the ERIs of the LP_{01} and LP_{11} modes decrease a bit along the increase of wavelength in both scenarios. At a certain wavelength, the ERIs of LP_{01} and LP_{11} modes in the selective water presence scenario are slightly larger than those obtained from the “all air” scenario, and the ERI difference between the LP_{01} and LP_{11} modes in the selective water presence scenario is slightly smaller than that in the “all air” scenario. It means that when the air in the side-channel is replaced with water, the ERIs of LP_{01} and LP_{11} core modes increase slightly and the ERI difference between LP_{01} and LP_{11} core modes decreases.

Fig. 5-2 Calculated modal dispersion curves for LP₀₁ and LP₁₁ modes when the side-channel is filled with water (black squares and red circles, respectively), and when the holey cladding is all filled with air (green and blue triangles, respectively).

5.1.2 LPG design and fabrication

5.1.2.1 Simulations

In order to choose the appropriate LPG parameters for liquid sensing, the relationship between the LPG pitch and the resonant wavelength under the selective water presence condition was calculated based on the ERIs shown in Fig. 5-2. The simulation results were plotted in Fig. 5-3 as the black curve. In the simulations, the material dispersion of silica and water were calculated according to their Sellmeier equations [199,249]. For comparison, the relationship between the LPG pitch and the resonant wavelength in the “all air” scenario was also plotted in Fig. 5-3 as the blue curve. The simulation results indicated that, for SC-PCF, the LPG resonance shifts to a longer wavelength for the same grating pitch under the selective water presence condition.

Fig. 5-3 Calculated dependencies of the LPG pitch (left Y-axis) on the resonant wavelength for selective water presence (black curve) and the “all air” (blue curve) conditions, respectively, and the plot of the group ERI difference (right Y-axis) between LP_{01} and LP_{11} mode for selective water presence in which only the side-channel is filled with water.

Depending on the pitch calculation for the selective water infiltration condition, an appropriate grating pitch for aqueous sensing is 157 μm at the wavelength of 1520, taking into consideration the wavelength range of the broadband light source (1250-1650 nm, its power spectrum is shown in Fig. 4-9 (a)), the predict that the resonant wavelength will shift to longer wavelength with the increase of the liquid RI (simulation results were plotted in Fig. 5-11), and the absorption band of the water. Water has a broad absorption band that is centered at 1440 nm, and with its specific absorption coefficient reduced to less than half of the maximum value at ~ 1520 nm [251].

For the intermodal interference between the LP_{01} and LP_{11} modes, It was assumed that both the LP_{01} and LP_{11} modes are excited when the light is coupled to the SC-PCF and the modes coupling occurs in the center of the LPG [252]. After propagating over a length of SC-PCF (L_1), the LP_{01} mode energy is transferred to the LP_{11} mode by the LPG and continues to travel through the rest of the fiber length (L_2) as LP_{11} mode. In a similar

way, the energy of the excited LP₁₁ mode is coupled to LP₀₁ at the center of LPG, and propagates as LP₀₁ mode along the rest of the SC-PCF. When converging at the other splicing point, the light traveling along the paths interfere to generate an interference pattern. The relative phase (Ψ) of the two light beams can be calculated as [253]:

$$\begin{aligned}\Psi &= |(\beta_{core}^{11} \cdot L_1 + \beta_{core}^{01} \cdot L_2) - (\beta_{core}^{01} \cdot L_1 + \beta_{core}^{11} \cdot L_2)| \\ &= |(\beta_{core}^{01} - \beta_{core}^{11}) \cdot (L_2 - L_1)|\end{aligned}\quad (5-1)$$

where β_{core}^{01} and β_{core}^{11} are the propagation constants of the LP₀₁ and LP₁₁ core modes. By taking into consideration the expression of the propagation constant $\beta = 2\pi n_{eff}/\lambda$, where n_{eff} is the ERIs difference between LP₀₁ and LP₁₁ modes, the wavelength spacing ($\Delta\lambda$) between two adjacent resonant peaks (λ_1 and λ_2) can be calculated by:

$$\Delta\lambda = \left| \frac{\lambda_1 \lambda_2}{\Delta n_g (L_2 - L_1)} \right| \quad (5-2)$$

where the group ERI difference Δn_g can be calculated by:

$$\Delta n_g = \Delta n_{eff} - \lambda \frac{d}{d\lambda} \Delta n_{eff} \quad (5-3)$$

where Δn_{eff} is the ERIs difference between LP₀₁ and LP₁₁ modes.

5.1.2.2 LPG fabrication

The LPG was fabricated through a CO₂ laser point-by-point inscription method which can offer much flexibility in the grating pitch [254,255]. The minimum period step of our CO₂ laser system is 10 μm . For this SC-PCF LPG, we desire a grating pitch of 157 μm , and a large extinction ratio (> 6dB, which correspond to a 75% power transfer from the fundamental mode).

As can be seen from Eqs. (2-10) and (2-11) that the normalized power transferred from fundamental mode is a periodic function of the coupling efficiency of the two modes and the total grating length. The coupling efficiency is affected by the irradiation of a CO₂ laser from three aspects [48]: the RI perturbation caused by the residual stress relaxation, RI perturbation due to the periodic deformation, and RI perturbation due to

the stretch force. Moreover, these RI perturbations rely on the practical fiber structure. Therefore, with our SC-PCF, to obtain a resonant dip with high coupling efficiency, it is more practical to try different fabrication parameters and get the desired resonance. In principle, we will try small laser power but a large number of period, because large laser power may cause huge insertion loss to this fiber due to the collapse of air channels.

In order to monitor the exact resonance wavelength in the liquid sensing scenario during the grating fabrication process, the side-channel of the SC-PCF was initially filled with water before the grating fabrication. To selectively introduce water into the side-channel only, we first used a fusion splicer to collapse all the small air holes at one end of the SC-PCF by applying electric-arc discharge [256]. In details, a well-cleaved end of the SC-PCF was mounted close to the electrodes of the splicer, and then melted by the electric-arc discharge activated at the electrodes. Moderate arc power collapsed all the small air holes only and left the side-channel open since the diameter (approximately estimated by the diameter of the inscribed circle) of the side-channel is almost 10 times larger than that of the small air holes. Then, water advanced into the side-channel through capillary force when this collapsed fiber end was dipped into a water container. After the selective water filling of the side-channel, both of the SC-PCF fiber ends were cleaved carefully and spliced to SMFs to avoid water evaporation/leakage during the fabrication process and to monitor the spectrum variation in real time with the broadband light source and an OSA. The spectrum of the broadband light source can cover a wavelength range 1250-1650 nm (the power spectrum is shown in Fig. 4-9 (a)). The number of the grating array that fabricated on the SC-PCF was 50. After fabrication, a distinct attenuation band with a central wavelength at ~ 1520 nm was obtained, as shown in Fig. 5-4. The transmission spectrum is normalized to the light source spectrum. The resonance band has an extinction ratio of ~ 7 dB. The *FWHM* value of the resonance band is measured to be ~ 23 nm, and this value is close to an approximately predicted value of ~ 21 nm according to Eq. (2-11). Moreover, this *FWHM* value is comparable

Fig. 5-4 Normalized transmission spectra, and (insets) measured intensity distribution at the resonant wavelength (1512 nm) and a non-resonant wavelength (1570 nm) under same excitation power.

Fig. 5-5 Microscope photo of the fabricated LPG with measurement of the pitch in 3 locations.

with that of other PCF LPGs which have typical values of tens of nanometers [257]. The fluctuations on the spectrum might come from the interferences among LP_{01} core mode, LP_{11} core mode, and high order cladding modes of the SC-PCF.

To verify the exact grating period, the surface of the fiber grating was observed under a microscope. The actual period of the fabricated LPG was measured as shown in Fig. 5-5 and found to have an average value of $\sim 153 \mu\text{m}$. The theoretical grating pitch for the resonant wavelength at 1520 nm is 157 μm , as indicated in Fig. 5-3. There is a slight deviation in the grating pitch. due to 3 probable causes:

- 1) The required period of the grating ($\sim 157 \mu\text{m}$) is very close to the diameter of the focused CO_2 beam diameter, which is in the range of 100 to 200 μm . Therefore, it is hard to precisely control the period and consistency of the grating fabricated on the fiber surface.
- 2) There exist unavoidable measurement errors when measuring the period of the grating under a microscope. The measurement error is approximately in the order of micrometers.
- 3) The irradiation with the CO_2 laser introduces a decreases the ERI difference between LP_{01} and LP_{11} modes [258], resulting in a blue shift of the resonant wavelength for the same grating pitch. In other words, although the theoretical grating period for a resonance wavelength of 1520 nm is 157 μm , the experimentally obtained resonance wavelength is probably smaller than 1520 nm with a grating period of 157 μm because of the effects of the CO_2 laser irradiation. Hence, in order to experimentally obtain a resonance wavelength of 1520 nm, the grating period should be smaller than its theoretical value of 157 μm according to the plot in Fig. 5-3 for the SC-PCF.

To confirm the mode coupling between LP_{01} and LP_{11} modes, the modal intensity distributions were measured at the fiber output for different wavelengths with a tunable laser source. The laser source is a tunable laser source (ANDO, AQ4321D) with a tunable wavelength range of 1480 nm to 1580 nm, and it has an SMF output. The output power we use in the experiments is $\sim 2 \text{ mW}$. The output mode profile was analyzed by a beam diagnostics system with a vidicon camera (Coherent, E-7290). This camera has a maximum active sensor area of 9.4 mm in the vertical direction and 12.5 mm in the horizontal direction, respectively. The pixel spacings is 19.5 μm for the vertical direction and 17.3 μm for the horizontal direction, respectively. The sensitivity is characterized as 10 $\mu\text{W}/\text{cm}^2$ at 632.8 nm. The measurement setup is the same as the one we used for characterizing the mode profiles in section 4.3.1, illustrated in Fig. 4-7 (a). The modal

distributions shown as the insets in Fig. 5-4 indicate that light is efficiently coupled to the LP_{11} mode near the resonant wavelength (e.g. 1512 nm) and propagates mainly in the LP_{01} mode at a non-resonant wavelength (e.g. 1570 nm).

5.1.3 All-in-fiber sensing scheme construction

After the characterization of the fiber grating, this SC-PCF LPG was employed in an in-line optofluidic sensing scheme by re-splicing it to side-polished SMFs.

In order to construct an all-in-fiber sensing scheme, our SC-PCF needs to be fusion spliced with standard SMFs which are commonly used in commercial fiber optical components or equipment. However, the diameter of a standard SMF is 125 μm and it is larger than that of our SC-PCF (118 μm). Therefore, the fusion splicing between SC-PCF and standard SMFs will definitely seal all of the air channels in the SC-PCF cladding. In order to expose the side-channel of the SC-PCF, we polish the SMFs from one side to an appropriate dimension that allows the exposure of side-channel to the environment after fusion splicing with the side-polished standard SMFs.

5.1.3.1 Preparation of side-polished SMFs

First, a striped standard SMF was buried in the groove of a glass substrate (cuboid) with wax. The glass cuboid was made of pure silica and its dimension was 40mm $\times$ 8mm $\times$ 8mm (length $\times$ width $\times$ height). A photo of the setup for grooving is shown in Fig. 5-6 (a). A segment of a steel wire with a diameter of 0.3 mm was fixed on a mounted aluminum frame, and the glass cuboid was mounted on an electrically driven swing arm. The steel wire was in tight contact with one surface of the glass cuboid. When the glass cuboid swings back and forth (shown as the gold arrow in Fig. 5-6 (a)), a groove in the longitudinal direction was fabricated on it because the glass that in contact with the steel wire was gradually grinded away. A schematic illustration of an SMF buried in the groove of a glass cuboid is shown in Fig. 5-6 (b).

Fig. 5-6 (a) A photo of the setup for grooving. (b) A schematic illustration of the way to bury an SMF into the groove of a glass cuboid (dimensions are not to scale). (c) Illustrations of the cross-sections of SMFs before and after polishing (dimensions are not to scale).

Second, the SMF and the glass cuboid are polished together using a polishing machine (Buehler, MetaServ 250). The use of the glass cuboid containing a groove is to reduce the polishing speed and protect the SMF during the polishing process.

Third, after having been polished to a position that is $\sim 36 \mu\text{m}$ from the center of the fiber core (check the dimension of the polished side of the SMF under a microscope), the side-polished SMF is released from the glass cuboid by heating the wax. The illustrations of the cross-sections of the SMFs before and after polishing (dimensions are not to scale) are shown in Fig. 5-6 (c). Last, the side-polished SMF was rinsed with dichloromethane to remove the residual wax on the fiber surface, and the side-polished SMF was cut at the position with maximum polishing depth for further use. The dimensions of the side-polished SMFs were specially designed to expose the side-channel and seal the rest of the small air channels when spliced with the SC-PCF to realize simultaneous efficient liquid circulation in the side-channel and light coupling to the fiber core.

5.1.3.2 Sensing scheme

Fig. 5-7(a) is the schematic diagram of our SC-PCF LPG sensing platform. A segment of the SC-PCF with an LPG inscribed on it was spliced to the side-polished SMFs at its both ends. While splicing, the polished side of the SMF was oriented to the direction of the side-channel of the SC-PCF. The connection of SC-PCF and side-polished SMFs is illustrated in the inset of Fig. 5-7(b).

As shown in Fig. 5-4, the initial *FWHM* value of the LPG resonance band is ~ 23 nm, and there also are some perturbations in the spectrum. The large *FWHM* of the resonance band and the perturbations on the spectrum unavoidably introduced measurement errors in the following sensing experiments. To address this problem, an intermodal interference between the LP_{01} and LP_{11} core modes was excited to achieve

Fig. 5-7 (a) Scheme of the in-line optofluidic sensing platform. (b) The details on the connection region between SC-PCF and side-polished SMFs.

high extinction ratio in the resonant band of the LPG, and thus, to minimize the effect of the disturbance [252].

We know from the Eq. (5-2) that the spectral spacing of the intermodal interference in this case depends on both the group ERI difference Δn_g of LP_{01} and LP_{11} modes and the fiber length difference $(L_2 - L_1)$ between the part before the LPG and that after the LPG on SC-PCF. L_1 and L_2 are indicated in Fig. 5-8. Δn_g at different wavelengths were calculated based on the Eq. (5-3) and the calculated ERIs of LP_{01} and LP_{11} modes shown in Fig. 5-2, and the results of Δn_g were plotted in Fig. 5-3 attached to the right Y-axis. Therefore, by adjusting the position of the LPG on the SC-PCF, we are able to tune the spectral spacing of the interference pattern. In particular, the larger the fiber length difference, the smaller the spectral spacing ($\Delta\lambda$) of the intermodal interference. As the *FWHM* of the LPG is ~ 23 nm, we expected the $\Delta\lambda$ value of the interference pattern to be in the range $11.5 \text{ nm} < \Delta\lambda < 23 \text{ nm}$ to ensure having strong intermodal resonance dips as well as a clean spectrum for easy tracing. Since the resonant wavelengths are simply assumed equal to the central wavelength of the LPG (1520 nm), and the simulation results of Δn_g show that $\Delta n_g = 0.0078$ at the wavelength of 1520 nm, the desired fiber length difference $(L_2 - L_1)$ is calculated to be in the range $13 \text{ mm} < |(L_2 - L_1)| < 25 \text{ mm}$. In our setup, $L_1 = 1.6 \text{ cm}$, and $L_2 = 3.6 \text{ cm}$ were measured.

A slight core-to-core offset was deliberately applied when splicing the SC-PCF to the side-polished SMFs to excite the intermodal interference. To balance the coupling

Fig. 5-8 Definitions of the length L_1 and L_2 in the SC-PCF.

efficiency of the injection light and the interference extinction ratio, the offset between the center positions of the two cores is around 2 μm .

Bending a fiber near the splicing region can easily damage its splicing point. To protect the splicing points and enable fast filling up with liquid, the fiber splicing regions were placed and sealed in the space between a glass plate (35 mm $\times$ 20 mm $\times$ 2 mm (length $\times$ width $\times$ height), indicated by yellow colored supports placed beneath the fiber in Fig. 5-7 (b)), and a square solidified polydimethylsiloxane (PDMS) chip (indicated by the blue colored fiber holders) with dimensions of 30 mm $\times$ 15 mm $\times$ 10 mm (length $\times$ width $\times$ height). The PDMS chip consists of a 30 mm $\times$ 200 μm $\times$ 200 μm (length $\times$ width $\times$ height) groove at the bottom and a 1.4-mm-diameter hole punched through the chip from top to the bottom. The center of the hole was located at the middle point of the groove. The fibers were placed in the groove of the PDMS chip, and the splicing points were adjusted to the hole region in the middle of the PDMS chip to ensure exposure to the environments for liquid insertion, as illustrated in Fig. 5-7(b). Extra PDMS is used to seal the space between the fiber, chip and glass plate to fix the fiber and avoid liquid leakage. A syringe pump and a reservoir were connected to the PDMS chips with polytetrafluoroethylene (PTFE) tubes with an inner diameter and an outer diameter of 1 and 1.4 mm, respectively.

5.1.3.3 Spectrum analysis

The measured transmission spectrum obtained using an intermodal interference is shown in Fig. 5-9. By introducing the interference, the *FWHM* of each single resonance dip is significantly decreased to 3 nm, the extinction ratio is increased by ~ 3 times, and the perturbations can be ignored in the resonance band.

The spectrum spacing between the central wavelengths of Dip 2 and Dip 3 (as indicated in Fig. 5-9) was theoretically calculated to be around 15 nm, given that $L_1 = 1.6$ cm, $L_2 = 3.6$ cm, and $\Delta n_g = 0.0078$ at 1520 nm.

Fig. 5-9 Normalized transmission spectra of the LPG.

However, the spectral spacing between the central wavelengths of Dip 2 and Dip 3 was experimentally measured to be ~ 11.3 nm. The deviation between the values of the calculated fringe spacing and the experimentally measured one may originate from of the calculation of Δn_g and the measurement error in the length difference ($L_2 - L_1$). Besides, it is possible that the simulated value of Δn_g is slight lower than the practical value of Δn_g in the experiment by 1.73×10^{-5} , which might arise from the slight non-uniformity of the fiber introduced in the process of fiber drawing, slight modifications of the fiber geometry induced by the LPG fabrication with a CO₂ laser, and the extraction of the fiber geometry from SEM picture to the simulation software. Moreover, the measurement error in the fiber length is unavoidable under a microscope. In the length measurement, it is hard to find the precise starting, middle and ending points of the LPG, and this also induces errors in the length measurements. Besides, in the theoretical model, the energy coupling between the LP₀₁ and LP₁₁ modes is assumed to finish in the middle point of the grating (which is about after 25 periods of the grating). However, in the real experiment, the energy coupling may end after passing through the first 15 periods of the grating referring to a fiber grating structure with a similar LP₀₁ and LP₁₁ mode coupling

efficiency [258]. This position mismatch of ~ 10 grating periods will result in an increase of ~ 3.2 mm in the length difference, and then result in a theoretical wavelength spacing of ~ 13 nm. Consequently, we believe that the error between the measured wavelength spacing (between Dip 2 and Dip 3) and the predicted value is mainly due to the discrepancies between the theoretical and practical values of the parameters used in the calculation of Δn_g , the length measurement error and the assumption that the energy transfer of LP_{01} and LP_{11} modes coupling finishes exactly in the middle point of the grating in the theoretical model.

5.1.4 RI sensing experiments

5.1.4.1 Method

RI solutions (sodium chloride solutions with different concentrations) were prepared to test the RI sensing performance of this SC-PCF LPG integrated optofluidic sensing platform. The RI values of the RI solutions were measured with a Reichert

Fig. 5-10 Normalized transmission spectra recorded when the side-channel is filled with liquids with different RIs.

refractometer which works in the visible wavelength range. The RI solutions covered an RI range over 1.3330 - 1.3961. During the measurements, the syringe pump worked in withdrawal mode. Liquid samples entered from the liquid inlet, flowed through the side-channel of SC-PCF, and liquid samples were pulled out of the fiber and flowed into the syringe via the liquid outlet tube. To avoid contamination, the RI liquid samples were injected in ascending sequence of RI value. The spectrum for each measurement was recorded after fully stabilized when the side-channel is fully filled with the measured sample (it took around ~6 s for a 52 mm-long SC-PCF). Selective spectra for our measured RI solutions were plotted in Fig. 5-10. The spectra show a distinct red shift with the increase of the liquid's RI value in the side-channel.

5.1.4.2 Sensitivity

To investigate the sensitivity of the platform, the dependence of the wavelength shift of Dip 2 on the RI value of the solutions present in the side-channel of the SC-PCF were measured and analyzed. Besides, for comparison, the theoretical RI sensitivity of the SC-PCF LPG was also calculated with COMSOL 5.0. The RI of deionized (DI) water was calculated according to its Sellmeier equation at the wavelength of ~1520 nm. The wavelength of resonance (Dip 2 and Dip 3) versus the RI of the liquid was plotted in Fig. 5-11. Both the wavelength shift of resonance Dip 2 and Dip 3 exhibit a nonlinear relationship with the increase of the liquid RI. This phenomenon matches well with the simulation results. This nonlinear response can be explained by the fact that both of the ERIs of LP_{01} and LP_{11} modes change nonlinearly against the liquid RI variation in the side-channel. Similar shifting trend has been observed before by V. Bhatia [259].

Moreover, within the RI range of 1.3330 to 1.3780 (which is compatible with the RIs of most chemical and biological aqueous solutions), the RI response is approximately linear. The sensing sensitivity of this RI band can be fitted to be around 1145 nm/RIU. Dip 3 has a slightly higher sensitivity of ~1150 nm/RIU. The RI sensitivity of the SC-

PCF LPG based optofluidic sensor is comparable with that of other highly sensitive specialty fiber-based optofluidic RI sensor and LPG based RI sensors. For example, an RI sensor constructed using a step-index fiber with a parallel hollow micro-channel are reported to have a high RI sensitivity of ~ 3000 nm/RIU [23]. But this RI sensor only works for detecting an RI value that is higher than silica (1.444 at 1550 nm). An LPG fabricated on a microfiber show an external RI sensitivity of ~ 1900 nm/RIU [179]. Though some other kinds of RI sensors [260–262] are reported with ultra-high sensitivities that can be one order of magnitude higher than this value, It is difficult to realize in-line replacement of the liquid sample in their setups. In this sensing scheme, the in-line liquid manipulation and replacement are much more convenient and compact for chemical and biological sensing in real applications.

Fig. 5-11 Measured (black squares and simulated (blue triangles) evolutions of the resonance wavelength of Dip 2, and measured evolution of the resonance wavelength of Dip 3 versus the RI of the liquid present in the large channel of the SC-PCF. The black line and the red line are the linear fits to the measured wavelength shift of Dip 2 and Dip 3, respectively, over the RI range of 1.3330-1.3780.

5.1.4.3 Detection limit

For this device, R is dominantly determined by the amplitude noise, considering that water has a very low thermal-optic coefficient of $8 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ [263], and the OSA we use has a very high resolution at ~ 1 pm. Therefore, according to Eqs. (2-23) to (2-25), the DL of this sensor can be calculated by following the equation:

$$DL = \frac{R}{S} \quad (5-4)$$

$$R = \frac{3\Delta\lambda_{FWHM}}{4.5SNR^{0.25}} \quad (5-5)$$

where $\Delta\lambda_{FWHM}$, SNR and S are the $FWHM$ value of the resonance, signal to noise ratio, and the sensitivity of this RI sensor. SNR is defined as the signal to noise ratio of the resonance, and can be calculated by the equation :

$$SNR = 10\log_{10}\left(\frac{P_{signal}}{P_{noise}}\right) \quad (5-6)$$

where P_{signal} and P_{noise} are the power of the signal and noise.

By introducing interference between LP_{01} mode and LP_{11} mode, $\Delta\lambda_{FWHM}$ is reduced from 23 nm to ~ 3 nm (Dip 2) at the RI of 1.3330. This results in an improvement of DL by approximately 8 times compared with that of the LPG without interferometer.

Referring similar sensing device, SNR can be assumed equals to 20 dB [75,260]. Therefore, with this device, R is calculated to be 64 pm, and DL of the resonance Dip 2 is calculated to be $\sim 5.6 \times 10^{-4}$ RIU. The $\Delta\lambda_{FWHM}$ of Dip 3 is smaller (~ 1.7 nm), giving more than one order of magnitude improvement on the DL value (3.2×10^{-4} RIU) compared with the LPG sensors without the interferometer. The parameters (assume that SNR is the same in the same spectrum) and the resulting DL s of all of the 4 dips (indicated in Fig. 5-10) are compared in Table 1. Although, the DL of this SC-PCF LPG is not very high compared with a ultralow value of 4.6×10^{-7} RIU achieved by a PCF-based directional coupler [260], the DL can be further improved via enlarging the extinction ratio of the interference pattern.

Table 1. Comparison of the detection limit of the 4 Dips

	Dip 1	Dip 2	Dip 3	Dip 4
<i>S</i>	1170 nm/RIU	1145 nm/RIU	1150 nm/RIU	1130 nm/RIU
<i>SNR</i>	20 dB	20 dB	20 dB	20 dB
<i>FWHM</i>	7.81 nm	3 nm	1.8 nm	3.255 nm
<i>R</i>	166.6 pm	64 pm	38.4 pm	69.45 pm
<i>DL</i>	1.5×10^{-4} RIU	5.6×10^{-4} RIU	3.2×10^{-4} RIU	5.94×10^{-4} RIU

5.1.5 Summary

In this section, an LPG interferometer-assisted SC-PCF all-in-fiber in-line optofluidic sensing platform was demonstrated for monitoring RI variations of liquid samples present in the large side-channel of the SC-PCF. The RI responses of resonant dips show a non-linear increase over the RI range of 1.3330-1.3961. Over the smaller RI range of 1.3330-1.3780 which is compatible with biological and chemical aqueous solutions [168,264,265], the resonance wavelengths respond linearly to the liquid RI variation in the side-channel, and exhibit a sensitivity of 1145 nm/RIU. Moreover, by introducing the interferometer, the *DL* of this sensing scheme is improved by around one order of magnitude. The great capabilities of in-line manipulation of liquid samples, working in a continuous-flow configuration and detecting RI in a range below that of silica with high sensitivity make this sensing platform very promising for biological and chemical sensing.

5.2 A Sagnac interferometer for liquid RI and specific biological sensing applications

This section details the design and testing of an SC-PCF based Sagnac interferometer for human cardiac troponin T (CTT) detection. The SC-PCF can be easily integrated into compact all-in-fiber sensing schemes with in-line inlet and outlet. By providing fast liquid introduction speed and sensitive modal ERI response to the RI variation in the side-channel, the SC-PCF based sensing platform is very suitable for biological sensing applications that require multilayer treatment on the fiber core. First, the design of this sensor is introduced. Second, the scheme construction is described. Last, the investigations on the spectrum response to RI variations in the fiber side-channel and its application for the specific biological detection of the Human CTT protein are carried out.

5.2.1 Design of the Sagnac interferometer

According to the Eqs. (2-18) to (2-21), the length of the SC-PCF has an effect on the spacing between two adjacent resonant dips ($\Delta\lambda$) and the *FWHM* of the resonance peak. Ideally, the longer the fiber length, the smaller the $\Delta\lambda$, the smaller *FWHM* of the resonance. Referring to other related work that the immobilizations of multilayer biological molecules can introduce a total wavelength shift of ~15 nm measured with a highly sensitive PCF LPG with liquid samples introduced in the fiber air channels [193], for easy tracing of the resonance peak, we would prefer to choose the value of $\Delta\lambda$ to be slightly larger than 15 nm. As SC-PCF has a birefringence of 2.77×10^{-4} when water present in the fiber side-channel, according to Eq. (2-21), a proper fiber length should be slightly shorter than 570 cm.

5.2.2 Measurement setup

In order to conveniently introduce the liquid into the SC-PCF and perform detection, a similar splicing method of the SC-PCF to the side-polished SMFs was applied to construct the Sagnac interferometer. The schematic diagram is shown in Fig. 5-12.

A 535 mm-long SC-PCF was spliced to the side-polished SMFs with the core-to-core positions adjusted to obtain maximum transmission power. In this way, the light power from SMF fiber is almost completely coupled to the LP_{01} modes of SC-PCF.

The splicing point was placed in-between a PDMS chip and a glass plate for protection and to enable fast liquid introduction speed. The details about sealing method were the same as described in the section 5.1.3.

Fig. 5-12 (a) Measurement setup for the liquid sensing using the Sagnac interferometer with the SC-PCF. (b) The details on the splicing point of the SC-PCF and the side-polished SMF.

In this experiment, just as in the previous realization, the syringe pump works in withdrawal mode, forcing the liquid sample to be pulled into the side-channel of the SC-PCF at the inlet from the liquid reservoir, and exit the fiber from the outlet after flowing through the entire fiber length of the SC-PCF's side-channel. In this manner, the achieved flow rate of the liquid's injection is calculated to be $\sim 0.4 \mu\text{L}/\text{min}$ by taking into consideration the total water volume ($40 \mu\text{L}$) and the total time needed for it to flow through the side-channel (100 mins). Actually, in the practical RI sensing experiments, the transmission spectrum gets stable as soon as the fiber side-channel is fully filled with the liquid sample. The volume of the liquid that can fully occupy the side-channel of a 535 mm-long SC-PCF fiber is $\sim 0.378 \mu\text{L}$. Therefore, taking into consideration the characterized flow rate of $0.4 \mu\text{L}/\text{min}$ in the fiber side-channel, the measurement time for a single RI sample test is possible to be reduced to less than 1 minute.

Fig. 5-13 Transmission spectra of the SC-PCF in the Sagnac interferometer biosensing setup for the “all air” scenario (air infiltration, black curve) and selective water presence in the side-channel only (red curve).

The transmission spectra for the “all air” infiltration condition and selective water presence scenarios are plotted in Fig. 5-13.

As it can be seen from the spectra of Fig. 5-13 that the period of the interference pattern increases when the medium in the side-channel is changed from air to water. This indicates that when the medium RI in the side-channel increases, the birefringence coefficient decreases slightly. The periods of the interference patterns in the “all air” scenario and the selective water presence scenario were measured to be 10.75 nm and 16.36 nm, respectively, near the wavelength of 1550 nm. According to Eq. (2-21), we can calculate the birefringence in “all air” scenario to be 4.17×10^{-4} , given that the fiber length is 535 mm.

5.2.3 RI sensing experiments

5.2.3.1 Method

To test the RI sensing performance of the SC-PCF-based Sagnac interferometer, solutions of different RI values were introduced continuously into the side-channel of the fiber and the corresponding transmission spectra were recorded for analysis. The prepared RI solutions cover the RI range of 1.3322-1.3371, which was measured with a Reichert refractometer.

The RI solutions were introduced into the side-channel for measurement in ascending order of the RI value to avoid contamination. Once one measurement was finished, a higher RI value solution was pumped into the side-channel of SC-PCF to replace the previous sample. The spectra were collected after a few minutes when the spectra get stable.

The transmission spectra for the RI range 1.3322-1.3371 were plotted in Fig. 5-14 (a). An obvious red shift of the resonance wavelength was observed when the liquid's RI in the side-channel increases.

Fig. 5-14 Measured results of the SC-PCF-based Sagnac interferometer when inserting solutions of different RI values: (a) Transmission spectra of the Sagnac interferometer corresponding to different RI in the fiber side-channel, (b) Dependence on the RI variation for the resonance wavelength of the peak at 1550 nm. The red straight line linearly fits the experimental data.

5.2.3.2 Sensitivity

To analyze its sensitivity for RI sensing, the shift of the resonant wavelength was monitored, starting from the default value of 1549.45 nm when the side-channel was filled with water (the RI value was experimentally characterized to be 1.3322). The resonance wavelength shift was plotted in Fig. 5-14(b) with error bars. In the detection RI range of 1.3322-1.3371, the resonance wavelength of the peak at ~1550 nm shows a linear response to the liquid RI variation in the side-channel. The sensitivity is linearly fitted to be ~2849 nm/RIU which matches well with the calculated value of ~2780 nm/RIU at 1550 nm according to Eq. (2-22). Each data plot in Fig. 5-14 (b) is the average of 5 independent measurements, and the corresponding standard deviations were also

Table 2. The values of the means and standard deviation values for each point in Fig. 5-14(b).

Refractive index of liquid	Mean value of the resonant wavelength (nm)	Standard deviation
1.3322	1549.45	0.12675
1.333	1551.95	0.03639
1.3337	1554.0993	0.08497
1.3343	1555.78115	0.05597
1.3356	1558.87788	0.1022
1.3365	1562.37381	0.08791
1.3371	1563.25596	0.10663

calculated for each peak and are shown as well. The small standard deviations indicate the excellent stability and reproducibility of this sensing platform. A summary of the values of the means and standard deviation values for each point in Fig. 5-14 (b) are shown in Table 2.

5.2.3.3 Detection limit

The *DL* of this sensing platform was also investigated using the same method as that previously described in section 5.1.4.3. Similarly, in this estimation, the thermal noise was not considered in the calculation of sensor resolution (*R*). Thus, the *DL* of this sensing platform is dominant by the *FWHM* value of the resonance peak ($\Delta\lambda_{FWHM}$) and the *SNR* value. In this experiment, *SNR*, as the ratio of the peak power of the signal to the variation of noise distribution, can be estimated to be ~20 dB. Given that the λ_{FWHM} is measured to be around ~1.08 nm, sensitivity $S=2849$ nm/RIU, we can obtain that $R = 23$ pm , and $DL = \sim 8 \times 10^{-5}$ RIU. This *DL* achieved with our SC-PCF Sagnac interferometer is comparable with those achieved with other evanescent filed refractometric sensors which have typical values in the order of 10^{-5} or 10^{-6} summarized in the reference [266].

5.2.4 Demonstration of biological sensing capability with human cardiac troponin T (CTT) protein

The convenient liquid introduction in the fiber side-channel and the ultra-sensitive spectrum response to the ambient RI surrounding the fiber core make this Sagnac interferometer promising for the biological sensings that require multilayer surface functionalization. Therefore, after the characterization of the RI sensing performance of the SC-PCF based Sagnac interferometer, its biological sensing capability was demonstrated with CTT protein detection. The CTT protein is a biomarker for the diagnosis of acute myocardial infarction (AMI) since it is found in heart muscle only. The high selectivity in biological sensing can be obtained using the biological binding of antibody and antigen, and this method can be easily adapted to the sensing of various kinds of biological samples. Normally, the detection of the antigen is realized via its binding to the pre-immobilized antibody on the sensing device.

5.2.4.1 Presentation of the biological sensing protocol

The binding of molecules on the surface of fiber core will correspondingly modify the ERI of the guided mode in the fiber core, and, therefore the presence and concentrations of desired molecules in the liquid samples, can be monitored using the shift of the resonance wavelength at ~ 1550 nm.

The immobilization of the CTT antibody on the fiber core surface was realized through a multilayer biological binding method that uses electrostatic interaction [18,267]. The binding method will be described in the following paragraphs. In the following experiments, liquid samples were introduced into the side-channel of the fiber continuously from the liquid reservoir to ensure a constant pressure in the fiber.

The entire biological binding events for the immobilization of CTT antibody consists of the deposition of layers of OH^- , poly (allylamine) (PAA), and CTT antibody

in sequence. The detailed methods are shown as follows:

First, a 5 mM sodium hydroxide (NaOH, Alfa Aesar) water solution was prepared and circulated into the side-channel of the fiber for 10 minutes. This step aimed to immobilize a layer of OH^- group onto the surface of the fiber core. As the NaOH may corrode the silica core, a longer exposure time was not recommended. After 10 minutes, the side-channel of the SC-PCF was rinsed with DI water for another 20 minutes to remove the molecules that were not adsorbed onto the fiber core surface.

Second, a single-layer of PAA (Sigma-Aldrich, Molecular weight: ~65000) was immobilized on the fiber core through electrostatic interaction with the OH^- group because PAA is positively charged. To immobilize PAA, a 0.5% (mass percent) PAA water solution was introduced in the side-channel for 30 minutes to allow sufficient interaction with OH^- group. The pH value of PAA solution is adjusted to 9. After a thorough adsorption of PAA, the side-channel of the SC-PCF was rinsed with DI water for 20 minutes to remove redundant PAA molecules. The side-channel of SC-PCF is then pumped with a pH 7.4 phosphate buffered saline (PBS, Vivantis) solution for 20 minutes to ensure a pure PBS infiltration environment for the sufficient adsorption of the active CTT antibody (Abcam), and to provide a reference spectrum for the following measurements since the CTT antibody and protein were dispersed in PBS solutions.

Third, a monolayer of CTT antibody was immobilized onto the fiber core via the binding event with PAA. The CTT antibody was dispersed in PBS solutions. In this step, different concentrations of CTT antibody solutions were introduced into the side-channel for the investigations on the binding capability of the molecules and sensing capability of the platform. The CTT antibody solutions were prepared with several concentrations ranging from 1 pg/mL to 10 ng/mL. The step for the concentration is one order of magnitude. The CTT antibody solutions were measured in ascending order of concentration. Each CTT antibody solution was introduced into the side-channel continuously for 20 minutes for sufficient binding, and then replaced by another CTT

antibody solution with a higher concentration. After the immobilization of the CTT antibody (10 ng/mL), the side-channel was rinsed with PBS solutions for 30 minutes.

Fourth, to bind with unoccupied PAA molecules and avoid unspecific binding to the core surface, bovine serum albumin (BSA, Aladdin) solutions were used to act as the block protein after finishing the binding of CTT antibody. In this step, a 1 mg/mL BSA solution was introduced into the SC-PCF for 30 minutes and followed by 30 minutes PBS rinsing.

Last, CTT protein (Abcam) solutions of different concentrations are infiltrated into the side-channel of the SC-PCF for detection. The concentration of CTT protein is prepared from 1 pg/mL with a step of one order of magnitude.

The resonance wavelength at each binding step and the depictions of the biological binding events were plotted in Fig. 5-15 for easy understanding and comparison. The large wavelength shift after the immobilization of PAA layer comes from the change of liquid media from water to PBS with a higher RI value.

The spectrum for each biological binding step was recorded and plotted in Fig. 5-16 for analysis. The resonance wavelength shift indicates the great capability of the sensing platform in characterizing the binding event for biological detection.

Fig. 5-15 The shift of the resonance wavelength of the peak at ~1550 nm at each binding step and (inset) the depictions of the binding events.

5.2.4.2 Results and discussion

Fig. 5-16 Measured spectra corresponding to each biological binding step.

As can be observed from the measured spectra in Fig. 5-16, and as expected from the behavior deduced from Fig. 5-14 (b), the resonance wavelength of the peak at ~1550 nm shifts to longer wavelengths with more layers deposited onto the fiber core surface. This phenomenon can be explained by the fact that the binding of additional layers of biomolecules increases the ambient RI surrounding the fiber core. There is a significant wavelength shift of ~1.0 nm after the binding event of a 10 ng/mL CTT antibody solution, compared with the resonant wavelength with PAA layer bound (the spectra collected after rinse plotted in Fig. 5-16). In addition to the 1.0 nm wavelength shift after the immobilization of CTT antibody, there is another shift of 0.5 nm after the BSA layer is introduced. For the last step, when the CTT protein solutions were introduced into the side-channel of the SC-PCF for detection, no distinct wavelength shift was observed until the concentration is increased to 1 ng/mL. Therefore, 1 ng/mL can be regarded as the

limit for the detection of CTT protein with this sensing platform. After the introduction of 1 ng/mL CTT protein, the spectra exhibit a wavelength shift of ~1.35 nm.

Additionally, the binding event of PAA and CTT antibody was investigated in detail to evaluate the sensing performance of the SC-PCF-based Sagnac interferometer. The spectra corresponding to the binding of the CTT antibody with different concentrations were plotted in Fig. 5-17 (a). To make the shift more distinct, the spectra were plotted over a narrower wavelength range. The resonance wavelengths were recorded in Fig. 5-17(b) respectively. The dark blue squares are the experimental data, and the purple curve is fitted with Langmuir isotherm. The parameter of the fitting function was listed in the inset of Fig. 5-17(b). The experimental result shows that the resonance wavelength first shifts rapidly to longer wavelength with increasing the CTT antibody concentration and then becomes saturated, indicating that the binding event

Fig. 5-17 (a) Transmission spectra corresponding to the binding event of CTT antibody solutions with different concentrations, (b) Shift of the resonance wavelength collected under different concentrations of CTT antibody solutions. The dark blue squares are the experimental data points which were fitted with a Langmuir isotherm curve. The equation and parameters are shown in the inset.

between the CTT antibodies and the PAA molecule on the fiber core surface was gradually completed. The binding of CTT antibody is almost entirely saturated for CTT concentrations above 1 ng/mL.

5.2.5 Summary

In this section, an SC-PCF based Sagnac interferometer was constructed and demonstrated to exhibit ultra-high RI sensing sensitivity and great capability for specific biological detection. For the liquid RI sensing capability, this Sagnac interferometer shows a high RI sensitivity of 2849 nm/RIU with great stability. Besides, it shows a good *DL* of $\sim 8 \times 10^{-5}$ due to the small *FWHM* value of the resonance dip. Owing to the great features of ultra-sensitive spectrum RI response, convenient liquid introduction in the side-channel of the SC-PCF, and sufficient light-matter interaction, this SC-PCF based Sagnac interferometer has great potential in realizing specific biological detection that requires multilayer treatment on the fiber core surface. By applying the multilayer binding method, a LOD of 1 ng/mL human CTT protein was achieved with this sensing platform. This sensing platform can be flexibly adapted to detect a wide range of analytes, with the applications ranging from environmental monitoring to biological diagnosis.

5.3 Optimized geometry of SC-PCF for ultra-sensitive SERS application

In this section, the application of the SC-PCF is extended to SERS measurements.

Since the performance of PCF SERS sensors is limited either by the large attenuation caused by the strong absorption and scattering in the liquid core or by the weak Raman signal due to the low evanescent field power in the liquid-filled channels, it is worth to explore the new parameters of the SC-PCF structure that can give high-sensitivity SERS sensing performance.

As the initial geometry of the SC-PCF was not designed for sensing application at the typical excitation wavelength (632.8 nm) for SERS measurements, the essential optical properties of our SC-PCF, such as evanescent power at 632.8 nm, are not optimized for SERS sensing. When optimizing the new geometry of the SC-PCF, we would like to achieve high evanescent power in the air channels at the wavelength of 632.8 nm, low transmission loss, high light coupling efficiency, and have large space in the fiber side-channel (the diameter of the side-channel should be above 25 μm) for fast liquid circulation as well as enough volume for the cells based sensing which is a promising application of SERS measurement.

In this section, first, the pitch, the ratio of air hole diameter to pitch, and angle of side-channel of SC-PCF are optimized to achieve a large evanescent field (above 0.5%) at a typical excitation wavelength of 632.8 nm for SERS measurements, as well as to ensure a large channel space for potential cell-based sensing applications. Then, the SERS sensing performance is demonstrated via the bio-sensing measurements of 4-Aminothiophenol (4-ATP) and Rhodamine 6G (R6G) molecules. Last, an investigation about the effect of SC-PCF fiber length on SERS intensity is carried out to give a guideline for achieving better LOD. The integration of the SC-PCF with SERS measurements may pave a new way to the development of all-in-fiber ultra-sensitive molecular detection for biosensing applications.

5.3.1 New geometry of SC-PCF

First, the theoretical investigation is made on the fiber geometry for the purpose of increasing the fraction of evanescent power in the fiber channels at 632.8 nm.

In principle, a smaller core size/pitch is able to provide higher evanescent power in the fiber side-channel. However, with the previous fiber structure shown in Fig. 4-1, a smaller pitch will result in a smaller fiber side-channel if we keep the structure of 6-rings air-hole cladding. To ensure large space in the fiber side-channel and avoid using

Fig. 5-18 3D model of our SC-PCF. The size of the side-channel is 25 μm .

too many layers of capillaries, the angle of the fiber side-channel is enlarged to $\sim 120^\circ$. The new geometry of the SC-PCF is shown in Fig. 5-18, in which one-third of the air-hole cladding is removed intentionally to create the large side-channel. The size of the side-channel is around 25 μm (indicated in Fig. 5-18) which is comparable to the size of a single cell.

5.3.1.1 Simulation

To construct a high-performance SERS sensor, the designed PCF should meet the requirements of enabling high light coupling efficiency, low transmission loss, and a large fraction of the evanescent power. To deduce the optimal SC-PCF parameters for SERS applications, the mode profile and evanescent field power in the fiber channel were simulated at the wavelength of 632.8 nm using COMSOL 5.0. All of the air channels were filled with water, the same as the practical experiment scenario. The simulation results show that only the innermost ring of channels and the analyte solution inside contribute to evanescent field-based sensing. The fiber shows good capability of confining light in the core when the number of rings of air channels exceeds 4. So, we consider the effects of the diameter of the air channels and pitch.

Fig. 5-19 (a) The dependence of the fraction of evanescent power in the side-channel and (b) The dependence of the ERI of LP_{01} mode on pitch Λ and d/Λ when all the air holes are filled with water.

First of all, the dependencies of the fraction of evanescent power in the side-channel (ratio of the power in the side-channel to the overall modal power) on Λ ranging from 2.0 μm to 5.0 μm in steps of 0.5 μm and d/Λ ranging from 0.4 to 0.8 in steps of 0.02 are investigated. The total fraction of the evanescent power that can interact with the analyte in the air channels is around 3 times of that in the fiber side-channel. These simulation parameters were selected because generally smaller Λ and larger d/Λ result in larger evanescent power. The simulation results shown in Fig. 5-19 (a) reveal that the fraction of the evanescent power in the side-channel increases if the pitch (Λ) gets smaller or the ratio of d/Λ decreases. The trends are similar when only the side-channel is filled with liquid and all other small air holes are empty. The focused spot size of the excitation laser in our Raman system is $\sim 1 \mu\text{m}$. Balancing the evanescent power in the side-channel, the coupling efficiency as well as the difficulty in preparing the fiber preform (more capillaries are required if the fiber has a smaller pitch for maintaining the large size of the fiber side-channel), the air hole diameter and pitch are chosen to be 2.1 μm and 3 μm , respectively. A 9-rings solid core lattice cladding structure with side-channel are applied for the following simulations to ensure low-loss light guidance in the fiber core, and a size of $\sim 25 \mu\text{m}$ for the fiber side-channel. The SC-PCF has a total fraction of the evanescent power of $\sim 0.6\%$ when all of the air channel are filled with water.

After optimizing the parameters of the SC-PCF structure, the fundamental mode profile and the evanescent power under different RI value of the filling liquid were simulated. Two experimental conditions were considered: filling all the small air holes and the side-channel with analyte liquid (full-filling configuration) and filling only the side-channel with the analyte liquid (selective-filling configuration). The simulated mode intensity profiles for full-filling configuration were shown in Fig. 5-20 (a) and (b), with the intensity normalized to the maximum value. Light is confined well in the fiber core with $d=2.1 \mu\text{m}$ and $\Lambda=3.0 \mu\text{m}$ for both of these two conditions, indicating that the SC-PCF has excellent capability of transmitting light via the index-guiding mechanism.

The dependency of the fraction of evanescent power in the side-channel on the RI of the filling liquid is plotted in Fig. 5-21 (a) and (b). It is clear that the fraction of evanescent power in the fiber side-channel is slightly higher when only the side-channel is filled with liquid. This information is useful for its potential application in cell-based SERS sensing as cells can be inserted into the fiber side-channel only.

Fig. 5-20 The modal intensity distribution of the fundamental mode in the fiber core (for full-filling configuration) depicted by (a) an intensity profile and (b) a contour plot.

Fig. 5-21 Plotted dependence of the fraction of evanescent power in the side-channel on the RI of the sample liquid for (a) the configuration when only the side-channel is filled with liquid (red circles and black squares represent two different polarizations of LP_{01} mode) (b) Comparison of the two configurations: filling only the side-channel, and filling all the air channels and the side-channel.

5.3.1.2 Fiber fabrication

The proposed SC-PCF was fabricated during my visit in Xlim Research Institute, France. The fiber was fabricated by a 2-steps stack-and-draw method and the design of the preform depends on glass tube stock. Similarly, all the capillaries were stacked together manually to form the preform of SC-PCF, as illustrated in Fig. 5-22. The stacking process of the preform was more challenging for this case compared with the previous geometry of SC-PCF since the capillary was smaller and the number of rings is larger. In this case, small capillaries with a length of 1 m were stacked carefully to maintain the stability of the SC-PCF structure in the preform. To further stabilize this structure during the consequent high-temperature drawing process, both ends of the preform need to be fully filled with the capillaries. A photo of the fully stacked preform was shown in Fig. 5-23 (a). The drawing process of this new SC-PCF was similar to that of the previous SC-PCF but was more difficult because the angle of the side-channel is almost 120° and its size was quite large compared to other small air holes. Thus, the fabrication parameters need to be adjusted carefully to get the most appropriate parameters. Fig. 5-23 (b) shows the photo of the fabricated cane. The SEM image of the fabricated fiber was illustrated in Figs. 5-24 (a) and (b). The fabricated SC-PCF has a pitch of $2.87\ \mu\text{m}$, an air filling fraction of 0.81, and a side-channel with a size of $28\ \mu\text{m}$.

Fig. 5-22 Illustration of the preform for the SERS SC-PCF. The preform has a total length of 1 m, and the outer diameter is ~6 cm.

Fig. 5-23 (a) A photo of the fully stacked preform of the SC-PCF for SERS, (b) Microscope image of the fabricated cane.

Fig. 5-24 (a) Cross-sectional SEM images of the SC-PCF. (b) Zoomed in image of the fiber's central lattice cladding and the fiber core.

5.3.1.3 Characterization

The practical mode property was investigated with a simple characterization system consisting of a supercontinuum light source (NKT, SUPERK COMPACT K90-130-00) that has a flattened emission power over a broad range of 0.6-1.3 μm , objective lenses (100x), a beam diagnostics system with a vidicon camera (Coherent, E-7290, described in section 5.1.2.2) and a segment of the fiber sample. The scheme was the same as shown in Fig. 4-7(a). Light emitted from the supercontinuum light source was coupled

into one end of the 5 m-long fiber sample through an objective lens. After propagating through the fiber sample, the light output from the other end of the fiber was collected onto the sensitive area of the camera. The measured fundamental mode profile and the simulated fundamental mode are both Gaussian-shaped, as shown in Fig. 5-25.

Next, the transmission loss of SC-PCF at the wavelength of 632.8 nm was investigated, which plays an important role in enhancing the intensity of the collected Raman signals. The transmission loss was measured through a cut-back process. The experiment was conducted with a free space coupling spectrum measurement system

Fig. 5-25 (a) Experimentally characterized and (b) Simulated modal intensity distributions of the fundamental core mode, side-channel (SC) is outlined in blue dashed lines. (c) A contour plot of the intensity distribution of the fundamental mode in the fiber core.

consisting of a supercontinuum light source (the same as the one for mode profile measurement), an objective lens, a 3-dimension translation stage, and an OSA (Yokogawa, AQ6370C). To begin with, the position of one end of the SC-PCF which had been mounted on a 3-axis translation stage was adjusted in all of the 3 directions to maximize the coupling efficiency from the supercontinuum light source, and the other end of the fiber was connected directly to the OSA for measurement. To achieve the maximal coupling efficiency, we minored the transmission power with OSA continuously while adjusting the position of the input end of the fiber to obtain the largest transmission power. After maximizing the light coupling, the input end of the SC-PCF was fixed and the fiber was cut off from the output end by 1 m each time. The corresponding spectra were recorded after each cutting. The transmission loss at the wavelength of 632.8 nm was calculated to be 0.26 dB/m by analyzing the spectra, and the results were shown in Fig. 5-26. Moreover, the SC-PCF did not exhibit a large transmission loss when it was bent with a radius down to 5 cm, which is highly advantageous in many practical applications. The transmission loss of the fiber can be further reduced by applying all cleaning steps and processes (such as, keeping the preform/cane away from dust, and wearing gloves when operating to avoid contamination) during the fiber fabrication. The insertion loss of this SC-PCF was characterized to be ~1.5 dB.

Fig. 5-26 Transmitted power at 632.8 nm as a function of fiber length.

5.3.2 SERS experiments

5.3.2.1 Raman sensing scheme

The performance of the SC-PCF SERS sensor was tested in a commercial Renishaw Raman system which has a backscattered SERS measurement geometry, as schematically illustrated in Fig. 5-27. The Raman system consists of a HeNe (633 nm) excitation laser, a microscope stages, a spectrometer and necessary objective lens for light coupling. All of these parts are enclosed in a chamber to avoid effects of the external light source (such as a lamp) during the SERS measurements. The HeNe laser beam at the wavelength of 632.8 nm was launched into the SC-PCF from one end of the fiber, after being focused onto the fiber core through a 50x objective lens. In the experiment, the excitation light was guided in the fiber core, and SERS was consequently excited by the evanescent field in the cladding air channels. The evanescent field interacts with the mixture of AuNPs and analyte solution within the air channels along the SERS active fiber length. The generated Raman signal was coupled back into the fiber core, and the backscattered component propagating along the fiber core towards the same launch end

Fig. 5-27 Schematic diagram of the Raman measurement setup in a backscattered geometry.

was collected and analyzed by the spectrometer in the Raman system. This backscattered setup was provided by the Singapore Bioimaging Consortium (SBIC), and all the experiments below were done at SBIC with the assistance from a researcher in the group led by Dr. Malini Olivo.

5.3.2.2 4-ATP as the analyte

A Raman active tag, 4-aminothiophenol (4-ATP), was used to test the performance of SERS sensors based on the fabricated SC-PCF. The dependence of the SERS intensity on the concentration of 4-ATP solutions was investigated. The 4-ATP solution was mixed with 60 nm gold nanoparticles (AuNP) at one to one volume ratio to achieve strong SERS enhancement. The 4-ATP concentration of the sample solutions used in experiments was prepared from 5 pM to 50 nM in steps of one order of magnitude.

To begin with, the SC-PCF was cut to a length of 20 cm and both ends were carefully cleaved. The excitation light at 632.8 nm was launched from one end of the fiber which was fixed on the microscope stage in the chamber to avoid the variation of any factors that may affect the Raman intensity, such as intensity of the focused beam and light incident position on the fiber core. In this experiment, we introduced liquid samples into all of the air channels of the SC-PCF. The measurements started with pumping the lowest concentration of 4-ATP sample solution from the other end of the fiber into all the air-holes as well as the side-channel along the SC-PCF. Once the measurements were finished for one concentration, a 4-ATP solution with another concentration was pumped into the same fiber in the increasing order of concentration to avoid contamination. As the RI of the mixed sample solutions is lower than that of silica, the light is still guided in the solid fiber core through index-guiding mechanism. Simulation results show that, when all of the air channels are filled with water, the fraction of evanescent power is still $\sim 0.6\%$. Therefore, it will not cause a large

attenuation to the light transmitted in the fiber core. The power of the Raman excitation light is about 1 mW. The measured Raman spectra were illustrated in Fig. 5-28(a), in which the Raman baselines have been removed for the convenience of tracing the changes in Raman intensities. Notable peaks at 1004 cm^{-1} , 1075 cm^{-1} , 1138 cm^{-1} , 1180 cm^{-1} , 1387 cm^{-1} , 1428 cm^{-1} , and 1579 cm^{-1} are associated with the vibration of 4-ATP molecules, which is consistent with what was measured in other literature [268]. Other peaks, which have been identified to be resulted from the SC-PCF or solvent by measuring the Raman spectrum collected from SC-PCF filled with AuNP solutions only, will be ignored.

The LOD of 4-ATP using an AuNP coated silicon substrate is around 100 nM [112]. However, the Raman intensity of the 4-ATP solution using our proposed SC-PCF at 1075 cm^{-1} is still around 14731 counts even at a concentration as low as 5 pM, as shown in the Fig. 5-28 (a). The overall Raman intensities become stronger at higher concentrations. By tracing the intensity at 1075 cm^{-1} , the variation of the Raman intensity against the 4-ATP concentration was deduced and plotted in Fig. 5-28 (b). The SERS signal intensity gradually gets saturated at high concentrations. This phenomenon can be

Fig. 5-28 (a) SERS spectra of various concentrations of 4-ATP solutions, (b) SERS intensity for 4-ATP and AuNP solutions measured using a 20 cm long SC-PCF as a function of the 4-ATP concentration of the peak around 1075 cm^{-1} . (Insets) The equation and parameters of the fitting function.

explained by the adsorption process of the molecules. The enhanced Raman signal is mainly generated by the analyte molecules that are adsorbed onto or being close to the AuNPs. The concentration of the AuNPs is constant for all different concentrations of analyte solutions. With low concentrations of the analyte, the number of the molecules that are close/adsorbed to AuNPs increase rapidly with the increase of the concentration of the molecules, resulting in a fast growth of the SERS signal. When the concentration of the Raman molecules keep increasing to high concentrations, the number of the Raman molecules that can interact with AuNPs (close to AuNPs) gradually get saturated, then, resulting in a relatively slow growth of the SERS intensity [269].

5.3.2.3 R6G as the analyte

In order to be able to do a direct comparison with other published results, a more commonly used Raman active tag of R6G was subsequently used to test the SERS sensing capability of our SC-PCF platform.

Generally, with the same fiber length, the SERS intensity is mainly affected by the fiber geometry, the excitation laser power, the morphology of AuNPs and their concentration. As the morphology and concentration of AuNPs used in the experiments have not been changed for all the measurements, the sensing calibrations among side-channel photonic crystal fibers (SC-PCFs) were discussed from the effect of the variations of fiber geometry and the coupling of laser light into the fiber core.

First, our SC-PCF was fabricated using a state-of-the-art fiber drawing tower which can provide great stability during the drawing process. Therefore, good consistency in the dimensions of fiber geometry was obtained, with the variation of the outer diameter less than 1 μm .

Second, as the spot size of the focused laser beam is around 1 μm , which is smaller than the diameter of the fiber core ($\sim 3 \mu\text{m}$), whether the incident position of the laser beam on the fiber core has an effect on the SERS signal intensity or not needs to be

verified. The circles in the center of the Fig.5-29 illustrate the light incident positions on the fiber core. Two different incident positions were selected to test. One was in the center of the fiber core (Fig. 5-29(a)) and the other position was close to the edge of the fiber core (Fig. 5-29(b)). The collected SERS spectra in both conditions showed that, with the same incident power and exposure time, the SERS peak intensities of a 5 mM R6G solutions mixed with 60-nm-diameter AuNPs solution show almost no differences. This probably because that in both of these two excitation conditions, only the fundamental mode was excited and involved in the SERS measurements. Therefore, a small variation of the incident position of the laser beam on the fiber core will not affect the accuracy of the measurements.

Third, the repeatability of the experimental results with this SC-PCF platform was investigated by collecting SERS spectra 8 times in succession at the same incident position (in the center of the fiber core). The collected SERS spectra showed a maximum variation of less than 10%, which indicated good repeatability of the proposed fiber platform for SERS sensing applications.

Since SC-PCFs possess good consistency in the dimensions of fiber geometry, high tolerance of incident light coupling, and good repeatability of the experimental results, they are highly suitable for biological/chemical sensing in general.

Fig. 5-29 Illustration of the light incident positions on the fiber core (a) in the center of the fiber core, (b) close to the edge of the fiber core.

The LOD of the SC-PCF based SERS sensing platform was tested with different R6G concentrations. 60-nm-diameter AuNP solutions (150 pM) were used to dilute the R6G solutions at a one-to-one volume ratio. The concentration of the R6G in the mixture solutions covered a range of 50 aM-5 nM in steps of one order of magnitude, while the concentration of AuNPs in the mixture was kept constant, at around 75 pM. To start with, the SC-PCF was initially cut to 17 cm in length, and both fiber ends were well cleaved. The backscattered Raman signal was collected and analyzed from the same end by using the Renishaw Raman system.

To minimize the fluctuations of the coupled laser power that may affect the SERS signal intensity, one end of the SC-PCF was fixed with the high-precision nano-positioning stages under the microscope lens. The incident laser power and the laser exposure time were 2.057 mW and 10 s, respectively, for the following SERS measurements. These setting parameters were chosen to achieve high SERS signal intensities and, at the same time, to avoid over-heating of liquid samples in the side-channel, and fast intensity decrease due to long excitation time.

The measurements started with pumping the lowest concentration of R6G solution mixed with AuNPs from one end of the fiber into all cladding air channels running along the entire fiber length. Once one measurement was done, the measured solution was pulled out of the fiber, and an R6G solution with higher concentration was introduced into the SC-PCF in the increasing order of the concentration to avoid contamination. The light was guided in the fiber core through index-guiding mechanism since the RI of the solution is around 1.33 which was much lower than that of the silica. The measured Raman spectra for different R6G concentrations were plotted in the inset of Fig 5-30, in which the baselines have been removed for the convenience of tracing the changes in the Raman intensities. The notable peaks at 1184cm^{-1} , 1310cm^{-1} , 1495cm^{-1} , 1567cm^{-1} are relevant to the vibration of R6G molecules [270]. R6G with a concentration below 50 fM was hard to detect, so the spectra were not shown here.

Therefore, the LOD is of 50 fM R6G solution for this SERS-active platform. The state-of-the-art LOD achieved by PCFs-based SERS sensors without post-processing is reported to be 10^{-10} M R6G [231] using a suspended core fiber, with the excitation light power of 5 mW. Compared with the sensitivity achieved by suspended core fibers, the ultra-high sensitivity achieved in our work is mainly contributed by several factors: 1) Improved light coupling efficiency compared with that of the suspended core fiber at the laser beam launching end enabled, as the core diameter of the suspended core fiber is $\sim 1.1 \mu\text{m}$ which imposes some difficulties in light coupling. 2) low transmission loss of the excitation light and scattered Raman signal, 3) strong evanescent field in active sensing areas, and 4) low absorption of AuNPs and liquid samples.

Fig. 5-30 SERS intensity as a function of the concentration of R6G solutions. The red line is fitted with the Langmuir isotherm. (Inset) SERS spectra of various concentrations of R6G solutions, and the equation and parameters of the fitting function.

As can be observed from Fig. 5-30, the Raman intensity at 1310 cm^{-1} increases distinctly with the increase of concentrations, as well as the overall Raman peak intensities. Also, we can observe similar saturation phenomenon at higher concentrations as the tests with 4-ATP. Moreover, the LOD of R6G in selective filling configuration (only the side-channel is filled with the mixture solution) is 1 pM , which still shows improved performance compared with previously reported results.

As the state of AuNP has a significant effect on the intensity of SERS signal, a new segment of the SC-PCF infiltrated with a 75 pM AuNPs solution was prepared to investigate whether the AuNPs were adsorbed on the channel surface or clustered. After one hour, the AuNPs solution was pushed out of the fiber by air pressure with the help of a syringe. After being rinsed by pumping DI water into the channels, the fiber was dried in an oven at $120\text{ }^{\circ}\text{C}$ for 4 hours. The dried fiber was cut into several pieces for examination under SEM. It can be clearly seen in Fig. 5-31 that there are very few AuNPs adsorbed on the silica channel (highlighted in light blue circles). Therefore, the strong SERS signals predominantly arise from discrete AuNPs in the solutions. Meanwhile, these isolated AuNPs adsorbed on the silica surface, to some extent, reflect that the AuNPs do not aggregate massively.

Fig. 5-31 SEM photos show that few AuNPs are adsorbed on the silica wall.

5.3.2.4 The accumulative effect of SERS signal

A cut-back experiment was conducted to explore the effect of the SC-PCF's fiber length of on the SERS signal intensities with a 50 nM R6G solution (mixed with the AuNPs). Similarly, one well-cleaved end of the 14 cm long SC-PCF was fixed on the microscope stage after aligning with the launched excitation light. The mixture of R6G and AuNPs was pumped into the air channels of fiber from the other end using a syringe. Later, the fiber was cut off by 1 cm each time from the pumping end after each measurement. During the cutting procedure, we tried to stabilize the cutting end and avoid bending the fiber too much in order to minimize the solution leakage, and thus to ensure measurements accuracy and the reliability of the following analysis. The inset of

Fig. 5-32 The measured SERS intensity (black squares) of a 50 nM R6G solution as a function of fiber length and SERS spectra of 50 nM R6G solution with different fiber lengths (inset). The red curve is fitted with a polynomial function ($y=3144.5+11352.32x-1380.6x^2+57.7x^3$).

Fig. 5-32 showed the Raman spectra measured with fiber length cut back from 14 cm to 7 cm, in which the baselines were removed as well. By tracing the changes of Raman intensities at 1310 cm^{-1} window, it can be seen clearly that the intensities increase rapidly with longer fiber length, as demonstrated in Fig. 5-32. This nonlinear accumulative phenomenon can be explained by the complicated interplay between the Raman gain and the attenuation of the light propagating in the fiber.

To explore the accumulative effect, a numerical-analytical model was applied to analyze the dependence of SERS intensity on fiber length for backward scattering scheme, referring to the models for forward scattering scheme [236,271]. In this model, AuNPs are assumed to distribute evenly in the colloidal solution, and there is no interaction between AuNPs. Since the concentration of R6G (50 nM) is much higher than that of AuNPs ($\sim 75\text{ pM}$), the adsorption of R6G onto AuNPs can be regarded as saturated. As AuNPs distribute sparsely and the SERS signal is generated by the molecule adsorbed onto the surface of AuNPs, the overall Raman intensity that can be collected from the fiber end can be regarded as a sum of the intensity of SERS signal that is generated by individual AuNP.

The analysis of the intensity of SERS signal takes into consideration the power decay of the excitation light (α_{in}) and scattered Raman light (α_{Raman}) due to the absorption and scattering caused by the AuNPs along the propagating path, the Raman signal enhancement factor (S) which is regarded as constant for a certain type of AuNPs, and the coupling efficiency of scattered Raman light into the fiber core (C) which is assumed to be constant for a certain concentration in our case. Fig. 5-33 illustrates schematically the Raman backscattered process. Theoretical intensity of SERS signal can be deduced as follows.

The SERS signal generated by the i^{th} AuNP ($P_{Raman,i}$) can be expressed by:

$$P_{Raman,i} = P_{in} e^{-(i-1)\alpha_{in}} \cdot S \cdot C_i \cdot e^{-(i-1)\alpha_{Raman}} \quad (5-7)$$

The total SERS signal $P_{SERS,backward}$ generated by the AuNPs is:

$$\begin{aligned}
P_{SERS,backward} &= P_{in} \times S \times C \times \sum_{i=1}^n \exp(-(i-1)(\alpha_{in} + \alpha_{Raman})), \\
&= P_{in} \times S \times C \times \frac{1 - \exp(-n\alpha_{in} - n\alpha_{Raman})}{1 - \exp(-\alpha_{in} - \alpha_{Raman})} \quad (5-8)
\end{aligned}$$

where P_{in} represents the intensity of excitation laser, i represents the sequence of individual AuNP along the fiber length counting from the excitation light launching end, and n is the amount of AuNPs in active region. The simulated dependence of Raman intensity on fiber length for the full-filling configuration is illustrated in Fig. 5-34. For this simulation, α_{in} and α_{Raman} were computed to be 0.2102 and 0.0828, respectively, by using Mie theory (section 2.3.3) and taking into consideration the energy distribution of the fundamental mode in SC-PCF obtained with COMSOL. It can be seen clearly from Fig. 5-34 that increasing fiber length can be an effective way to further enhance the SERS sensitivity and the saturation length is longer with lower AuNPs concentrations. Moreover, in this backscattered scheme, the value of Raman intensity will be constant after reaching saturation length, which gives much convenience in practical applications as it is exceedingly time and effort consuming to calculate the precise saturation length by taking into consideration the attenuation coefficients for both of the excitation and

Fig. 5-33 A Numerical-analytical model for backscattered SERS signal. The green arrow indicates the excitation laser, and the red arrow represents the Raman signal. The gold solid circle is AuNP. The number on top of the AuNP indicates its index number.

scattered Raman light determined by the feature of AuNPs (such as the diameters of the gold sphere or their clustering), fiber structure, concentration of AuNPs, and transmission loss.

According to the theoretical calculations, the saturation fiber length for the full-filling configuration with 75 pM AuNPs is around 70 cm. As the maximum fiber length used in our experiment is 14 cm, the Raman intensity keeps growing as the fiber length increases. In contrast with the simulated curve, the slow growth or disorder of the intensities measured with our shorter fiber length in Fig. 5-32 is likely caused by two factors:

- (1) Excitation of radiative modes in the coupling end. When the fiber is short, the collected Raman intensities are contributed by both the fundamental mode and the radiation modes, while in the simulation only the fundamental mode is considered.
- (2) Accumulation of AuNPs attached to the silica core. More AuNPs are depositing onto the silica during the experiments when the fiber length is shortened, resulting in larger Raman intensities.

Fig. 5-34 Dependence of backscattered Raman intensity on fiber length with different concentrations of AuNPs for backward scattering scheme.

5.3.3 Summary

In this section, the geometry of a solid-core SC-PCF with a large side-channel in its lattice cladding was optimized for SERS sensing applications. An ultra-low LOD of 50 fM R6G solution mixed with AuNPs has been achieved using this SC-PCF, revealing its high sensitivity. Compared with previous state-of-the-art LOD of 0.1 nM R6G solution obtained with a suspended core PCF-based SERS platform, this SC-PCF SERS platform achieved almost 4 order of magnitude improvement in LOD. An accumulative increase of the Raman signal collected along the increasing length of the SERS-active SC-PCF has also been demonstrated, which indicates that increasing fiber length can be an effective way for further enhancing the SERS sensitivity. Moreover, the deducing theoretical dependence of the SERS intensity on fiber length in this backward scattering scheme gives guidelines for constructing high sensitivity, easy handling, and versatile PCF-based SERS optofluidic sensor. In addition to its high sensitivity, the simple design of the SC-PCF together with the easy preparation of the SERS-active medium is expected to offer more opportunities for diverse and high-performance optofluidic sensing applications, including environmental analysis, single molecular detection on cells and clinical diagnosis in various kinds of liquid samples like urine and blood.

Chapter 6 Cylindrically symmetric laser emission from a photonic bandgap fiber

Cylindrically symmetric laser emission in the transverse plane of the fiber axis is of great interest for applications in omnidirectional imaging, biomedical detection and photodynamic therapy for a large volume, providing extended laser emission surface area compared with the common fiber laser emission/guidance from a relatively small area along the fiber axis [246,272]. As indicated in literature reviews on the fiber lasers that can exhibit large surface emission area, a polymer PBG fiber is suitable for realizing an omnidirectional emission with easy pumping configurations, great compactness and low lasing threshold [43]. However, the fast-bleaching of organic dyes limits the lasing performance under long exposure time, and it further deteriorates in the laser cavity as both of the pumping energy and emission intensity are high in the cavity [148]. In addition, the inherent optical properties of broad emission spectrum, narrow excitation band and sensitivity to ambient solvent conditions make organic dyes less applicable in constructing bio-analytical systems.

To overcome these drawbacks and expand the applications of omnidirectional lasers for biological detection in vessel structures, a microfluidic quantum dot (QD) fiber laser that shows cylindrically symmetric radial laser emission at ~640 nm is presented for the potential application of pumping Cyanine 5 fluorescence bio-marker.

In this chapter, section 6.1 introduces the optical properties of the QDs we use in the experiments. Section 6.2 gives the detailed information on the waveguide properties of the PBG. Section 6.3 describes the laser scheme, and finally, section 6.4 presents thorough characterizations of the laser output.

6.1 Quantum dots (QDs)

CdSe/CdZnS/ZnS QDs were selected for this experiments owing to its high quantum yields (QY). It was synthesized using the ‘one-pot’ method [273] with

modification. Both cadmium and zinc precursors ($\text{Cd}(\text{OA})_2$ and $\text{Zn}(\text{OA})_2$) were first made and heated to 300 °C, where OA was oleic acid. Selenium (Se) precursor was further injected with an optimized rate to form CdSe core. To cap the CdSe core, alkyl thiol was used as sulfur (S) precursor to form CdZnS shell, and then trioctylphosphine dissolving S (TOPS) was added to produce ZnS shell. The resulting CdSe/CdZnS/ZnS QD has an emission centered at 636 nm and an *FWHM* value of ~30 nm, as shown in Fig.6-1 with the red curve. The absorbance spectrum reveals that the resulting QDs had a continuous absorption band below 650 nm and a larger absorbance to the shorter wavelength pump photons, as shown by the black curve. The average size of the QD was estimated to be around 7 nm from the transmission electron microscopy (TEM) image shown in the inset of Fig. 6-1. A high QY of 65% was obtained by exciting the QDs in hexane solution with a 405 nm laser in an integrating sphere. Here, QY can be defined as the ratio of the number of the emitted photons to the number of absorbed photons. All the characterizations were carried out at room temperature under ambient conditions. The high QY is beneficial to reduce the lasing threshold which is essential in facilitating its practical applications. The CdSe/CdZnS/ZnS QDs were then dispersed in the hexane with a concentration of 100 mg/mL for subsequent use.

Fig. 6-1 Absorbance and photoluminescence (PL) spectra of CdSe/CdZnS/ZnS QDs, and (inset) the TEM image of CdSe/CdZnS/ZnS QDs.

6.2 Photonic bandgap fiber

The multilayer photonic bandgap (PBG) fiber used in this experiment consisted of a hollow air core surrounded by 25 annular alternating layers of high index chalcogenide glass ($\text{As}_{25}\text{S}_{75}$, with a refractive index of ~ 2.5 at 550 nm and a layer thickness of ~ 60 nm) and a relatively low index polycarbonate (PC, with a refractive index of 1.59 at 550 nm and a layer thickness of ~ 110 nm), and a pure PC cladding, as shown in scanning electron microscope (SEM) images in Fig. 6-2. The inner diameter and outer diameter of the PBG fiber are measured to be around $250\text{ }\mu\text{m}$ and $1060\text{ }\mu\text{m}$, respectively. To eliminate surface modes in the cavity, the multilayer geometry is ended with a layer of high index $\text{As}_{25}\text{S}_{75}$ as the innermost layer.

This kind of PBG fiber has the capability of generating low-threshold radial laser emission due to the coupling of isotropic spontaneous emission of the gain medium to high order TE_{0n} mode characterized by an azimuthal polarization state [43]. The energy density plot for a high-Q TE_{0n} fiber cavity laser mode is shown in Fig. 6-3.

Fig. 6-2 SEM images of the PBG fiber, and the schematic diagram of the fiber structure with layer thickness on it (Dimension not to scale, gold color indicate $\text{As}_{25}\text{S}_{75}$ layer and light blue color indicate PC layer).

Fig. 6-3 Schematic diagram of the radially emitting fiber laser structure with R6G introduced in the hollow core serving as the gain medium, and energy density plot for a high-Q TE_{0n} fiber cavity laser mode. The arrows indicate the polarization state of a TE_{0n} mode [43].

To characterize the light confinement capability of the multilayer bandgap structure of the fiber we used in the experiments, simulations were carried out with Lumerical FDTD solutions to obtain the normal-incidence (axial wave vector equals to 0) bandgap of the multilayer structure. The alternating high-index and low-index multilayers surrounding the hollow core impose a normal-incidence (axial wave vector equals to 0) bandgap covering a broad wavelength range from 520 nm to 660 nm. The normal-incidence bandgap provides necessary optical feedback for laser emission in the radial direction. The simulation result of bandgap calculation was plotted in Fig. 6-4 as the black curve. The photoluminescence (PL) spectrum of the QDs was plotted as the red curve in Fig. 6-4 as well. Since the normal-incidence bandgap of the multilayer structure covers the PL spectrum of the gain medium, this PBG fiber is able to provide necessary optical feedback for laser emission in the radial direction. Concurrently, the PBG structure of the hollow cavity is able to support an axial transmission band centered at 550 nm for the optical pump (the wavevector is in the axial direction). Without the multilayer, light cannot be confined in the hollow region because the RI of gain medium (hexane, 1.3749) is lower than that of the PC cladding (1.59).

Transmission spectral response of this PBG hollow cavity was theoretically investigated with FDTD solutions and a theoretical FSR of 0.59 nm (Fig. 6-5) was obtained.

Fig. 6-4 Simulated reflection band of the multilayer structure (black curve), and measured photoluminescence spectrum of the QDs used in the experiments.

Fig. 6-5 Simulated transmission spectral response of the PBG structure cavity.

6.3 Laser scheme

The scheme of pump arrangement and the laser emission are shown in Fig. 6-6. QD doped hexane solution (concentration: 100 mg/ml) was injected into the hollow core of a 5-cm-long PBG fiber by capillary forces to act as the gain medium. The cylindrically symmetric laser emission was obtained by axially pumping the liquid gain medium in the hollow cavity of a PBG fiber with an Nd:YAG laser with a pulse duration of 5 ns at 532 nm. The laser light was collected and analyzed by a spectrometer from a direction perpendicular to the fiber axis.

Fig. 6-6 Scheme of the laser emission with the red arrows indicating the radiation direction.

Fig. 6-7 The wavefront of the laser emission in the far field.

6.4 Laser characterizations

6.4.1 Wavefront

Experimental observations confirmed that light was emitted from the fiber cavity in the transverse plane to the fiber axis with cylindrical symmetry. The laser wavefront was registered as a perfect ring in the far field with the assistance of a paper funnel and a 550 nm long-pass filter, as shown in the Fig. 6-7.

The cylindrical geometry of the laser emission from is determined by the circular cross-section of the fiber core and the penetration depth of the optical pump in the gain medium instead of the actual length of the gain plug which is in the order of centimeters. In our experiment, the penetration depth along the fiber axial direction for the 100 mg/ml QD hexane plug is $\sim 500\ \mu\text{m}$. The cylindrically symmetric emission stems from the interplay between the isotropic fluorescence of QDs and the cylindrical fiber resonator.

6.4.2 Laser resonant cavity

A high-resolution laser spectrum was collected with a high-resolution spectrometer (Ocean Optics, HR 4000, resolution: 0.11 nm). The laser is excited by a 532 nm Nd:YAG laser with a pulse duration of 5 ns and a pulse energy of $\sim 290 \mu\text{J}$. The distinct laser peaks in the spectra (Fig. 6-8) further verify the lasing phenomenon.

The averaged spacing between adjacent lasing peaks was measured to be around 0.58 nm for the fiber core with a diameter of $\sim 250 \mu\text{m}$. Given that in a Fabry-Pérot (FP) cavity the free spectral range (FSR, $\Delta\lambda$) of longitudinal modes is calculated by the formula:

$$\Delta\lambda = \frac{\lambda_0^2}{2nd} \quad (6-1)$$

where λ_0 is the wavelength of central lasing peak ($\lambda_0 = 642 \text{ nm}$) and n represents the RI of the gain medium plug ($n = 1.3749$), using the measured value $\Delta\lambda = 0.58 \text{ nm}$, the size of the fiber cavity (d) results to be $\sim 258 \mu\text{m}$, which matches well with the diameter of the hollow core of our fiber. Therefore, the calculation result reveals that the lasing mode is occupied by the photons propagating along the radial direction.

Fig. 6-8 High-resolution spectrum of the radially emitted QD fiber laser collected at the pump energy above the lasing threshold.

6.4.3 Threshold

To characterize the laser threshold, the emission spectra under different pump pulse energies were collected using a low-resolution spectrometer (Ocean Optics, USB 2000, resolution: 4 nm), as shown in Fig. 6-9 (a). Each spectrum was collected at a single shot of a 532 Nd:YAG laser with a pulse duration of 5 ns, and using an absorptive neutral density filter with a power transmittance of 5% placed between the fiber and the spectrometer to avoid saturation. At low pump energy, the spectrum showed only broadband spontaneous emission of QDs. A narrow peak occurs at ~ 642 nm in the spontaneous emission band of the QDs when the pump pulse energy exceeded a specific value (~ 238 $\mu\text{J}/\text{pulse}$). The narrow emission peaks on the spectra confirm the lasing phenomenon and indicate that the isotropic spontaneous emission is coupled to specific low threshold laser modes supported by the cylindrical fiber resonator.

The lasing threshold was estimated to be ~ 238 $\mu\text{J}/\text{pulse}$ by comparing the relationship between the peak intensities and pump pulse energies, as plotted in Fig. 6-9 (b). Compared with dye molecule counterparts, this relatively larger laser threshold with QDs mainly results from their relatively low QY (the QY of R6G is normally above 90% [274]) and the competitive highly-efficient nonradiative Auger recombination (AR) [156] in QDs. The low QY of our QDs may be attributed to the unsaturated dangling bonds at the surface of QDs and defects at the core/shell interface. These defects

Fig. 6-9 (a) Spectra of radial emission from the laser cavity collected under different pump pulse energies. (b) The dependence of the peak intensity on the pulse energy. Black squares are the experimental data points. The red line linearly fit to the experimental data.

act as traps for electrons or holes, which increase the ratio of nonradiative decay. Besides, in strongly confined QDs, the highly-efficient AR dominates when the QDs are pumped under high-energy excited states, resulting in a limit on the gain lifetime and an increase of laser threshold. The threshold of our QDs laser emission can be reduced by increasing the QY of QDs and/or suppressing the AR process through engineering the structure of QD interface [275].

6.4.4 Laser emission characteristics

6.4.4.1 Q-factor

In the experiments, the averaged *FWHM* value ($\Delta\lambda$) of the lasing peak was approximately 0.18 nm, indicating a high quality factor (Q-factor) of ~3600 according to the definition of the Q-factor

$$Q = \frac{\lambda_0}{\Delta\lambda} \quad (6-2)$$

where λ_0 is the wavelength of laser peak. Based on Eq. (2-44), the theoretical Q-factor of the PBG structure was estimated to be ~15000 for a mirror reflectivity of ~0.8 at near 642 nm calculated with an ideal PBG structure (estimated from Fig. 6-4). The slight deviation in the Q-factor value is acceptable taking into consideration a few practical factors that may cause it; the fact that the PBG structure of the fabricated fiber is less ideal than that in the simulation due to the slight deformation in cavity length or layers during cutting, the loss induced by absorption and scattering of the gain medium and the limited resolution of the spectrometer. This Q-factor value is one order of magnitude higher than the dye doped counterpart [276], indicating a more promising lasing performance when using with QDs as the gain medium.

6.4.4.2 Polarization

To characterize the polarization state of the laser emission, the intensity variation of the output laser with different polarization angles under a fixed pump energy of ~245 $\mu\text{J/pulse}$ was analyzed. As the generated laser was emitted in the radial direction of the fiber cross-section, the spectrometer collected the spectra from the perpendicular direction of the fiber axis, and a linear polarizer placed in-between the fiber and the spectrometer to characterize its polarization state. The measurements were carried out by rotating the linear polarizer in the perpendicular plane of the laser output direction. By analyzing the intensity of the output intensity that passes through the polarizer, we

Fig. 6-10 Dependence of the output intensity on the polarization angle. The black squares are measured data, and the red curve fits the experimental data with a cosine-square function. Inset: the scheme of the polarization measurements. The blue arrows label the directions of transmission axis of the polarizer placed in-between the fiber and a spectrometer. The green arrow represents the excitation laser beam at the wavelength of 532 nm. The red segment is the gain medium.

are able to identify the polarization state of the laser emission. The scheme is illustrated in the inset of Fig. 6-10, where the blue arrows on the fiber indicate the direction of the transmission axis of the polarizer, the red segment is the QD hexane plug, and the green arrow indicates the excitation laser beam that has a wavelength of 532 nm. Assuming that the polarization angle equals to 0 when the transmission axis of the polarizer is perpendicular to the fiber axis, the measured laser intensities (normalized to the maximum intensity) against polarization angles are plotted in Fig. 6-10. The dependence of the laser intensity on the polarization angle fit well with a cosine-square function, demonstrating that the radial laser emission is dominantly azimuthally polarized.

6.4.4.3 Thermal stability

The thermal stability of the laser was analyzed from two aspects: the thermal stability of the QDs and the thermal stability of the hexane solvent.

In our experiments, we used CdSe/CdZnS/ZnS QDs. Their PL spectrum variations corresponding to a temperature change from 100k to 300k have already been analyzed experimentally and reported in the literature [277]. According to the published data, the PL spectrum of this kind of QDs exhibits relatively good stability against temperature variation either in terms of peak wavelength, *FWHM* or the integrated PL

intensity. For example, when increasing the temperature from 275 K to 300 K, the peak wavelength shows a red shift of less than 3 nm, and the *FWHM* and the integrated PL intensity are almost unchanged.

We then consider the thermal stability of the hexane solvent. Hexane is regarded as volatile. The stability of this fiber laser operating over a long time can be ensured either by sealing hexane in the fiber cavity with other immiscible liquids plugs to suppress its evaporation, or by replacing the hexane with another less volatile solvent. One possible factor that may cause the instability of this fiber laser is the optical heating effect imposed by the pump pulse. However, as long as the usage of an ultra-high energy pump pulse is avoided to prevent the overheating of the solvent (the boiling point for hexane is $\sim 342\text{K}$), the laser should be able to function with good thermal stability in room temperature without large external thermal perturbations.

In addition, our experimental results also confirm the good thermal stability of this QD fiber laser. By increasing the ambient temperature from 25°C (room temperature) to 45°C , we only observe a slight shift of the emission wavelength (less than 2 nm to the longer wavelength). Moreover, the intensity variation of the laser output is less than 15% after a 2 hours continuous pumping with a pulse energy of $245\text{ }\mu\text{J}$ and a repetition rate of 3 Hz at an ambient temperature of 45°C .

6.5 Summary

In conclusion, a QD fiber laser with azimuthally polarized radial emission has been demonstrated, and it can provide a large emission surface area. The laser was realized by axially pumping a CdSe/CdZnS/ZnS QDs-doped hexane plug in the hollow cavity of a PBG fiber using a nanosecond Nd:YAG laser at 532 nm. The cylindrically symmetric radial emission results from the isotropic fluorescence of QDs and its coupling to low-threshold TE_{0n} modes. The laser emission exhibits a threshold of $\sim 238\text{ }\mu\text{J/pulse}$ and a high Q-factor of ~ 3600 . As the PL spectrum of CdSe/CdZnS/ZnS QDs is relatively stable at room temperature, the fiber laser can work stably as long as avoiding using ultrahigh-energy pump pulse.

The resulting laser platform integrates the advantages of QDs as the gain medium and the unique characteristics of large emission surface and remote pumping, providing a substantial impact on both studies of the lasing mechanism and future developments of a variety of applications. The ability to provide a large area cylindrically symmetric laser emission, combined with ultrasonic circular-array detectors, can enable photoacoustic

computed tomography (PACT) systems to generate full-view and high-quality images in round objects with fast data acquisition speed [278]. Similarly, this fiber laser could be integrated into photoacoustic endoscopy (PAE) systems for easy and convenient circumferential cross-sectional scanning. Besides, taking into consideration the characteristics of large wavelength tunability and the broad absorption band of QDs, this fiber laser can serve as a flexible optical pump for activating various kinds of molecules for detection or diagnosis of diseases in vessel structures, or in conjunction with drugs for photodynamic therapy. Finally, the convenient pump arrangement and extended laser emission surface make this fiber laser suitable for constructing omnidirectional or textile fabric displays.

Chapter 7 Summary and future work

7.1 Summary and discussion

In this thesis, novel PCF structures and a few fiber integrated configurations for all-in-fiber sensing and light generation applications have been explored.

Optical fiber based sensing platforms have the advantages of being free-standing and robust, enabling easy light coupling, and exhibiting low guiding losses, low cost for mass production, and being highly suitable for remote sensing. In particular, PCFs have been regarded very promising in constructing compact all-in-fiber platforms that interact with liquid/gas media, due to their unique capability of enabling unprecedented long interaction lengths between analyte and light by transmitting liquid/gas samples in the micrometer-sized channels running along the entire fiber length. There is an increasing demand for in-line ultra-sensitive molecular detection and light generation with large surface emission area in environmental monitoring and biological diagnosis fields. However, the performance of current all-in-fiber sensing and light generation platforms is still hindered by low sensing sensitivity, inconvenient replacement or manipulation of liquids in the air channels and relatively small mode area in the fiber core. Therefore, it is essential to investigate new PCF structures and schematic structures that can fulfill these requirements.

First and foremost, an SC-PCF structure with a solid core and a cladding consisting of air holes arranged in a triangular lattice pattern was demonstrated. One sixth of the lattice cladding was removed intentionally to enable liquid circulation and convenient lateral liquid access to the fiber channel even when splicing with SMFs. The geometry of the fiber structure was then investigated and optimized using FEM method to achieve enhanced light-matter interaction in the fiber side-channel as well as low coupling loss to the SMFs. The fabricated fiber samples supported the LP_{01} and LP_{11} modes in the fiber core. More importantly, SC-PCF showed low transmission loss and splicing loss, while the bending loss was negligible, which are essential factors for easy integration into compact all-in-fiber sensing systems.

Second, this SC-PCF was successfully applied to construct a few all-in-fiber sensing platforms for RI and biological sensing. In this part, a novel method to splice the SC-PCF with side-polished SMFs was proposed to enable in-line liquid insertion and extraction. The direction of the fiber side-channel was oriented to the polished side of the SMFs during the splicing process, and the side-polished SMFs has a polishing depth that exposes the side-channel of the fiber only and covered the rest of small air channels. By applying this splicing method, several sensing schemes with fast liquid infiltration speed and ultra-high sensing sensitivity have been successfully constructed with the SC-PCF.

In particular, we demonstrated an all-in fiber optofluidic RI sensor by inscribing an LPG on the SC-PCF. In this experiment, the fabrication of an LPG on the SC-PCF was challenging because of the asymmetric fiber structure of the SC-PCF. This work is also the first demonstration of the LPG fabrication on an asymmetric PCF structure. When we fabricated the LPG, we need to precisely align the direction of the fiber channels, and ensure that the CO₂ laser beam was focused on the silica-air lattice cladding instead of the fiber side-channel. With a grating pitch of 153 μm , the mode coupling between the LP₀₁ and LP₁₁ core modes of SC-PCF was realized. The SC-PCF LPG exhibits spectral responses to the RI variation of the liquid flows in the fiber side-channel, and the sensitivity is characterized to be $\sim 1145 \text{ nm/RIU}$. Moreover, with the assistance of an intermodal interference introduced by slight core offsetting splicing, the *DL* of the resonance spectrum was significantly improved by almost 10 times. As the SC-PCF is made of pure silica which has a low thermal-optic coefficient to the environmental temperature, this SC-PCF can have broad applications in chemical and biological sample detection.

We also fabricated an all-in-fiber Sagnac interferometer using the SC-PCF, and demonstrated its specific biological sensing capability with human CTT protein. The SC-PCF based Sagnac interferometer has the advantages of easy fabrication. Owing to its convenient in-line liquid replacement in the side-channel, this SC-PCF based interferometer was eligible for multilayer surface functionalization on the fiber core for biological detection. Moreover, it had a highly sensitive spectrum response to the RI variation in the fiber side-channel with a sensitivity of $\sim 2849 \text{ nm/RIU}$. This sensing platform showed a LOD of 1 ng/mL CTT protein solution and the real-time spectra monitoring during the biological binding event was applicable as well. With the successful demonstration of CTT protein detection, it proved to have great potential for the applications of highly-sensitive and specific biomolecular detection, and

biomolecule-labeled cells detections. Currently, one limitation of this SC-PCF Sagnac interferometer is that the fiber length of SC-PCF is a bit long (535 mm) which compromises the compactness of the sensing configuration. This limitation can be overcome via proper optimization of the fiber geometry to achieve a higher modal birefringence.

Third, to extend the application of SC-PCF and achieve more sensitive and specific sensing performance, an optimized geometry of SC-PCF was presented and applied to SERS measurements. The geometry of the SC-PCF was optimized for the typical SERS excitation wavelength of 632.8 nm with a large side-channel angle of 120° . The fabrication of the new SC-PCF was challenging because of the large air filling ratio in the air cladding and the asymmetric fiber structure. Fabricating the new SC-PCF was a trial and error process, the parameters of the fiber drawing tower including furnace temperature, preform feeding speed and drawing speed, and air pressure, need to be controlled precisely. The fabricated SC-PCF consisted of a photonic crystal structure with a pitch of $2.87\ \mu\text{m}$ and an air filling fraction of 0.81, and the diameter of the side-channel was around $28\ \mu\text{m}$. With this new SC-PCF, an ultra-low LOD of 50 fM R6G solution mixed with AuNPs has been achieved, which is 4 order of magnitudes better than state of the art value reported with other PCF-based SERS platforms. Moreover, the dependence of SERS intensity on fiber length in backward scattering scheme was theoretically and experimentally explored to give guidelines in constructing high sensitivity, easy handling, and versatile PCF-based SERS optofluidic sensors. Our SC-PCF SERS platforms have the characteristics of high sensitivity and easy processing of SERS-active medium. Therefore, it is expected to offer more opportunities for diverse and high-performance optofluidic sensing applications, including environmental analysis, single molecular detection on cells and clinical diagnosis in various kinds of liquid samples like urine and blood.

Fourth, a PBG fiber-based light generation platform with large surface emission area for the potential applications of in-fiber *in situ* biological detections was demonstrated. QDs as the gain medium was integrated with a PBG fiber to generate a cylindrically symmetric radial laser light emission. Precise coupling of the pump laser beam to the guided mode in the hollow core of the PBG fiber is required in this experiment. As the PBG is made of polymer materials (PC), its bandgap structures can be damaged if large pump laser energy illuminates on the cladding structure. To ensure precise light coupling to the hollow core, we use a small home-made microscope to monitor the light input end of the fiber while adjusting the focus positions on the PBG

fiber. The laser emission exhibited a threshold of $\sim 238 \mu\text{J}/\text{pulse}$ and a high Q-factor of ~ 3600 . As the PL spectrum of CdSe/CdZnS/ZnS QDs is relatively stable at around room temperature, the fiber laser can work stably as long as the hexane solvent filled in the fiber core is not overheated. The resulting laser platform can be integrated into photoacoustic computed tomography (PACT) systems to generate full-view and high-quality images in round objects with fast data acquisition speed and photoacoustic endoscopy (PAE) systems to provide much convenience for the application of circumferential cross-sectional scanning. Besides, taking into consideration the characteristics of large wavelength tunability and the broad absorption band of QDs, this fiber laser can serve as a flexible optical pump for the detection of various molecules or for diagnosis of diseases in blood vessel structures or in conjunction with drugs to realize photodynamic therapy. Finally, the convenient pump arrangement and extended laser emission surface make this fiber laser suitable for constructing omnidirectional or textile fabric displays. The current limitation of the laser for practical use is that the laser threshold is still relatively high, and it can be reduced by increasing the QY of QDs and/or suppressing the AR process through engineering the structure of QD interface.

Our work paves the ways towards realizing all-in-fiber sensing with ultra-sensitive spectra response, and light generation systems with stable and large surface emission. Moreover, by providing unique features of great flexibility and easy integration, the fiber-based sensing and light generation systems proposed can be easily combined with other techniques to inspire new applications.

7.2 Future work

For the future work, a few interesting experiments are listed as follows.

1. *Enhanced sensing sensitivity with magnetic-core-gold-shell nanoparticles.* In this experiment, the sensing sensitivity and LOD of our SC-PCF based SERS sensors can be further improved. One efficient way to enhance the sensing capability is to involve more molecules in the light interaction region. Magnetic-core-gold-shell nanoparticles dispersed in water can be easily introduced by an external magnetic field. Besides, the gold surface of the nanoparticles can be functionalized with various molecules by chemical/biological binding. Therefore, in this experiment, taking advantage of the asymmetric structure of the SC-PCF, the molecular detection capability for the molecules immobilized on the magnetic-core nanoparticles in the fiber side-channel is expected to be improved by applying an external magnetic field. The use of the magnetic field gathers

the molecules in the region close to the fiber core to enhance the light-matter interaction efficiency, thus improving the sensing sensitivity and LOD.

2. *Omnidirectional fluorescence sensing/imaging in blood vessels structures.* In this experiment, a PBG QD laser could be built to perform molecular sensing in blood vessel structures. The QD laser realized with a PBG fiber has large surface emission area. The cylindrically symmetric laser light is emitted from the radial direction of the fiber, forming a perfect ring pattern. The resulting laser platform has the unique characteristics of large emission surface and convenient remote pumping configuration. When it is combined with large wavelength tunability and the broad absorption band of QDs. Therefore this fiber laser can serve as a flexible and compact optical pump for activating various kinds of molecules for detection or diagnosis in blood vessel structures. In the next step, we will try to prompt the practical application of this QD laser. First, we need to do thorough sensitivity characterizations on the laser to identify which environmental factors or structural parameters may have a significant effect on the laser output according to the practical scenario. Then, the QD fiber laser can serve as a pump source for specific molecular fluorescence sensing in blood vessels with the assistance of cyanine 5 labeling. Cyanine 5 is a popular dye for biological labeling and it has the large absorption cross section at ~640-650 nm and emission peak wavelength at ~670 nm. Moreover, the aqueous gain medium can be easily driven by pumping pressure. This makes it possible to contribute to high-resolution fluorescence sensing/imaging.

Publications

Journal

1. **N. Zhang**, K. Li, Y. Cui, Z. Wu, P. P. Shum, J.-L. Auguste, X. Q. Dinh, G. Humbert, and L. Wei, "Ultra-sensitive chemical and biological analysis via specialty fibers with built-in microstructured optofluidic channels," *Lab Chip* 18(4), 655-661(2018).
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Conference

1. **N. Zhang**, K. Li, G. Humbert, P. P. Shum, Z. Wu, T. Zhang, Y. Cui, X. Q. Dinh, J.-L. Auguste, L. Wei, "Optofluidic Sensing With a Side-channel Photonic Crystal Fiber based Sagnac Interferometer", *CLEO PR, OECC&PGC 2017*, (Accepted).
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