

Bangor University

DOCTOR OF PHILOSOPHY

Advanced Optical Fibre Grating Sensors for Biochemical Applications

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Advanced Optical Fibre Grating Sensors for Biochemical Applications



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This thesis is submitted for the degree of Doctor of Philosophy

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Declaration

I hereby declare that this thesis is the results of my own investigations, except where otherwise stated. All other sources are acknowledged by bibliographic references. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree unless, as agreed by the University, for approved dual awards.

Yr wyf drwy hyn yn datgan mai canlyniad fy ymchwil fy hun yw'r thesis hwn, ac eithrio lle nodir yn wahanol. Caiff ffynonellau eraill eu cydnabod gan droednodiadau yn rhoi cyfeiriadau eglur. Nid yw sylwedd y gwaith hwn wedi cael ei dderbyn o'r blaen ar gyfer unrhyw radd, ac nid yw'n cael ei gyflwyno ar yr un pryd mewn ymgeisiaeth am unrhyw radd oni bai ei fod, fel y cytunwyd gan y Brifysgol, am gymwysterau deuol cymeradwy.

Abstract

This thesis describes a detailed study of advanced fibre optic sensors and their applications for label-free biochemical detection. The major contributions presented in this thesis are summarised below.

A self-assembly based in-situ layer-by-layer (i-LbL) or multilayer deposition technique has been developed to deposit the 2D material nanosheets on cylindrical fibre devices. This deposition technique is based on the chemical bonding associated with the physical adsorption, securing high-quality 2D materials coating on specific fibre cylindrical surface with strong adhesion as well as a prospective thickness control. Then a " Photonic-nano-bio configuration", which is bioprobes immobilised 2D-(nano)material deposited fibre grating, was built. 2D material overlay provides a remarkable analytical platform for bio-affinity binding interface due to its exceptional optical and biochemical properties. EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) and NHS (NHydroxysuccinimide) were used to immobilise bioprobes. This kind of configuration is considered to have many advantages such as: enhanced RI sensitivity, enrich immobilisation sites, improved binding efficiency, selective detection. Followed by this configuration, several label-free biosensors were developed. For example, graphene oxide coated dual-peak long period grating (GO-dLPG) based immunosensor has been implemented for ultrasensitive detection of antibody/antigen interaction. The GO-LPG based biosensor has been developed for label-free haemoglobin detection. Apart from biosensors, the black phosphorus (BP) integrated tilted fibre grating (TFG) has been proposed, for the first time, as BP-fibre optic chemical sensor for heavy metal (Pb²⁺ ions) detection, demonstrating ultrahigh sensitivity, lower limit of detection and wider concentration range.

Ultrafast laser micromachining technology has been employed to fabricate long period grating (LPG) and microstructures on optical fibre. The ultrafast laser micromachined polymer optical fibre Bragg grating (POFBG) has been developed for humidity sensing, showing the significant improvement with the reduced response time.

Key words: Fibre grating, Optical fibre sensor, Label-free biosensor, 2D materials, Graphene, Black phosphorus, Laser micromachining

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Chapter 1 Introduction

1.1 Introduction

Since the first fibre grating was demonstrated by Hill et al. in 1978 [1], it took another decade to become a hot topic when the controllable and effective fabrication method were devised [2]. Fibre gratings were then been wildly developed for many applications such as telecommunications, optical sensing [3], fibre lasers [4], amplifier gain flattening filters [5], WDM systems [6], dispersion compensators [7] and so on. Particularly in the field of sensing, due to their various advantages such as immunity to electromagnetic interference (EMI), low weight, compact size, large bandwidth, and multiplexing capabilities, optical fibre gratings were recognised as excellent candidates for sensors and have been commercialised decades ago [8].

However, with the increasing demands in sensitivity and application range, serval challenges were posed. The earlier developed fibre grating sensors were mostly based on fibre Bragg gratings (FBGs) or long period gratings (LPGs). Among them, conventional FBGs confined the light strictly in fibre core and hence no direct interact with the environment. As a result, FBGs were used in limited applications, which were mostly physical detections such as strain, temperature, and pressure [9]. Based on the mode-coupling scheme, LPGs demonstrated additional applications such as refractive index (RI) sensing, chemical sensing [10–12], and liquid level sensing [13]. However, the maximum RI sensitivity of conventional LPGs only occurred at the surrounding refractive index near that of cladding. For low RI range (1.33-1.35 RIU, refractive index unit) where bioassays and biochemical events were usually carried out, the RI sensitivity of conventional LPGs was quite lower. In addition, due to their RI based sensing nature, conventional LPGs based biochemical sensing provided no selectivity to different biochemical species. All above-said challenges required new techniques and developments to meet the modern requirement, especially for biochemical sensing applications.

As response to these challenges, three strategies are wildly recognised and frequently used: novel grating structures, fibre cladding modification, and thin film deposition. To date, novel grating structures such as large tilted fibre gratings (TFGs) and dual-peak

long period gratings (dLPGs) have been reported with enhanced performance [14,15]. Then for another two strategies, both can be categorised as post-sensitisation approaches, are able to provide further enhancement in RI sensitivity and other sensing performance. To reduce the fibre cladding thickness, several approaches have been reported, such as cladding etching, side polishing and fibre tapering [16–18]. However, these approaches are not only complex in procedures but also hard to control. In addition, these approaches can only provide simple modifications to the fibre configuration. Fortunately, advanced laser micromachining technique has opened up a new avenue for microfabrication due to the ultrashort pulse width and extremely high laser pulse intensity, which enable spatially localised modification either on the surface or in the bulk of materials. By lasers micromachining, the machining depth can be precisely controlled and inducing minimised mechanical damage to fibre. Additionally, even complex 3D structures can be created if necessary, which could also help to improve the sensing performance. Lastly, instead of sacrificing the mechanical integrity, thin film deposition is an alternative elegant approach. It was proposed by depositing a high refractive index (HRI) layers onto LPGs [19]. Shortly after, this approach has been proved both theoretically and experimentally for the significant enhancement of RI sensitivity [20-22]. Numbers of materials including sol-gel, polymers, metal oxide, and nanomaterials have been employed to enhance the RI sensitivity of fibre sensors. With the successful isolation of graphene, a new family of 2D materials were emerged and unsurprisingly been involved in the integration with fibre gratings. Due to the excellent properties, 2D materials have been integrated with fibre gratings opening a new direction for fibre grating-based sensors.

1.2 Project objectives and achievements

Bio-nano-photonics is one of the fastest developing modern research subjects in the 21st century. It will lead to a new area which links the photonics technology, nanotechnology to the biochemical and biomedical sciences. The main objective of this PhD programme is to develop advanced opto- nano- mechanics based sensors and devices for label-free biosensing and biomedical applications. This programme focuses on the implementation of functionalised advanced 2D materials-based sensors and devices for novel biosensing and biomedical applications.

The main achievement of this PhD project is the development of a photonic-nano-bio configuration, in which a 2D (nano)material layer is placed between fibre grating transducer (photonic) and bioprobes (bio). In which, 2D material linking layer not only enhance the bulk refractive index sensitivity of fibre grating, but also provides a remarkable analytical platform for bioaffinity binding interface due to its favourable combination of exceptionally high surface-to-volume ratio and excellent optical and biochemical properties. To build this configuration, a study has been made on developing a reliable method to deposit 2D nanomaterials onto the cylindrical fibre surface. As a result, an in-situ self-assembly based multilayer deposition technique based on chemical-bonding associated with physical-adsorption has been developed to create a stable and uniform coating overlay on the surface of fibre. The coating thickness can be controlled by the concentration of 2D material and depositing cycles. Based on this configuration, a number of fibre grating based-sensors have been developed for biochemical applications. An ultrasensitive label-free biosensors was developed with GO coated dLPG. In addition, an integrated black phosphorus (BP)tilted fibre grating (TFG) configuration has been developed for heavy metal chemical sensing. This BP-TFG was exploited as the first BP-fibre optic chemical sensor for heavy metal detection, demonstrating high sensitivity, low limit of detection and large sensing range.

Apart from these main achievements, serval other excellent results were also reported. Label-free biosensors like dLPG based DNA sensor and GO-LPG based haemoglobin sensors were fabricated. The humidity sensors based on polymer optical fibre Bragg gratings (POFBG) which have improved response time were developed with the assistance of excimer laser micromachining.

1.3 Thesis structure

This thesis consists of seven chapters where the main contents can be grouped into three parts and displayed in Table 1.3.1.

Part	Chap	Title		
	1	Introduction		
Ι	2	Theory of fibre gratings		
П	3	Two-dimensional materials deposition on optical fibre devices		
	4	Label-free fibre optic biosensors		
Ш	5	Laser micromachining		
	6	Fibre grating-based humidity and chemical sensors		
	7	Conclusions and future work		

Table 1.3.1 Thesis structure	Table	1.3.1	Thesis	structure
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Chapter 1 provides a brief introduction to fibre grating based sensors, where both of their advantages and limitations discussed. In addition, serval wildly recognised methods to overcome the limitations of fibre grating sensors are also described. At last, the thesis structure is listed.

Part I (Chapter 2) starts from the fundamental Maxwell equation to the theory of fibre gratings, such as guided-wave (and mode) theory in optical fibres, coupled-mode theory of fibre gratings and sensitisation principle of fibre grating sensors. The coupled-mode theory analyses the power exchange between waveguides and different modes, which is the core theory of fibre gratings. By applying coupled-mode theory, the analytical solutions and the simulated spectra can be achieved for both short- and long- period gratings. Furthermore, the underlying mechanism of sensitisation of fibre grating sensors is discussed in the last section of this chapter.

Part II consists of Chapter 3 and Chapter 4, which describes the core technology of this thesis, the 2D material deposition and label-free biosensors based on it. Chapter 3 focus on the integration of 2D materials (GO, BP) on fibre optic platform. An in-situ layer-by-layer deposition technique based on chemical-bonding associated with physical-adsorption was developed to create a stable and uniform coating overlay on the surface of fibre. In addition, for both GO and BP, the characterisations including thickness, morphology and optical effect of deposited layers were examined by multiple methods.

In agreement with the theoretic prediction, it is proved that the presence of the 2D material coating will enhance the light-matter interaction. Chapter 4 demonstrates several biosensors include label-free DNA biosensor, GO-dLPG based immunosensor, and GO-LPG based haemoglobin sensor. These label-free biosensors are all having enhanced sensing performances like low limit of detection and excellent bio-affinity efficiency.

Part III consists of Chapter 5 and Chapter 6, which focus on other achievements other than label-free biosensors. Chapter 5 describes laser micromachining techniques, which is a very attractive and important field in optics. In this chapter, laser micromachining is introduced as an effective technique for the fibre gratings inscription and microstructure fabrication. A series of microstructures such as micro-slot, D-shaped structure, microfluidic channels, and structural long period grating are fabricated with the excimer laser or fs-laser. Chapter 6 focuses on other fibre grating-based sensors including humidity and chemical sensors. The first BP-fibre optic chemical sensor has been proposed for heavy metal detection. The laser-modified polymer FBG has been developed for humidity sensing.

Chapter 7 provides an overall conclusion and some proposed future works.

Chapter 2 Theory of fibre gratings

2.1 Guided-waves in optical fibres

Light, as a propagating electromagnetic wave, can be described by the well-known Maxwell's equations:

$$\begin{cases} \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \\ \nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J} \\ \nabla \cdot \vec{D} = \rho \\ \nabla \cdot \vec{B} = 0 \end{cases}$$
(2.1-1)

where \vec{J} and ρ represent current density and charge density, respectively. \vec{E} and \vec{H} are electric and magnetic fields, while \vec{D} and \vec{B} are electric flux density and magnetic flux density, respectively (although in many case \vec{B} is still named magnetic field for historical reasons). They satisfy the relations of:

$$\begin{cases} \vec{D} = \varepsilon \vec{E} \\ \vec{B} = \mu \vec{H} \end{cases}$$
(2.1-2)

where $\varepsilon = \varepsilon_r \varepsilon_0$ is permittivity and $\mu = \mu_r \mu_0$ is permeability of the medium in which light propagates. Herein, ε_0 and μ_0 are free space (or vacuum) permittivity and permeability, respectively, while ε_r and μ_r are relative permittivity and permeability base on the properties of medium.

An ideal optical fibre is a steady and homogeneous medium, with no current and charge density. Therefore, by substituting the first two equations in (2.1-1) to each other, the electric field and magnetic field can be separated [23,24]:

$$\nabla \times \left(\nabla \times \vec{E}\right) = -\nabla \times \frac{\partial \vec{B}}{\partial t} = -\mu \frac{\partial^2}{\partial t^2} \vec{D}$$
(2.1-3)

With the assistance of the identity $\nabla \times (\nabla \times \vec{E}) \equiv \nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E}$ and the condition of $\nabla \cdot \vec{E} = 0$, Eq. (2.1-3) can be further transformed to:

$$\nabla^2 \vec{E} - \frac{n_i^2}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = 0$$
(2.1-4)

where c is the vacuum velocity of light which equals to $1/\sqrt{\varepsilon_0\mu_0}$, and $n_i = \sqrt{\varepsilon_{r,i}\mu_{r,i}}$ is the refractive index (RI) of fibre, where i denotes core, cladding or other parts of fibre. Most fibre is made of non-magnetic materials, such as silica which has $\mu_r = 1$, so in many literatures the RI could be written directly as $n = \sqrt{\varepsilon_r}$.

Assuming the propagating light is in the form of simple harmonic wave:

$$\begin{cases} \vec{E}(t) = \vec{E}e^{-i\omega t} \\ \vec{H}(t) = \vec{H}e^{-i\omega t} \end{cases}$$
(2.1-5)

the equations of light wave in fibre can be reduced as the Helmholtz equations:

$$\begin{cases} \nabla^2 \vec{E} + k_0 n_i^2 \vec{E} = 0 \\ \nabla^2 \vec{H} + k_0 n_i^2 \vec{B} = 0 \end{cases}$$
(2.1-6)

where wave vector $k_0 = \sqrt{\omega^2/c^2} = 2\pi/\lambda_0$ corresponds to the wavelength λ_0 .

In the particular case of optical fibre, the guided rays are considered as parallel to the fibre axis as most conventional fibres are weakly guiding. The longitudinal components of both electric and magnetic fields can be ignored as they are far weaker than that of their transvers counterparts. Hereby, the guided waves in a conventional optical fibre are considered as transverse electromagnetic (TEM) wave in nature. Hence, considering no azimuthal index variation in fibre, the guided waves are traveling along the z direction with propagation constant of β , and the variables of the fields can be further separated in the cylindrical coordinate as [25]:

$$U(r,\phi,z) = U^{+}(r)e^{il\phi}e^{i\beta z} + U^{-}(r)e^{il\phi}e^{-i\beta z}, \qquad l = 0, \pm 1, \pm 2 \quad (2.1-7)$$

where U represents either electric field \vec{E} or magnetic field \vec{B} , and the notes + and - represent forward and backward propagating direction, respectively. By applying this assumption, Eq. (2.1-6) can be converted as [25]:

$$\frac{d^2 U}{dr^2} + \frac{1}{r}\frac{dU}{dr} + \left((n_0^2 k_0^2 - \beta^2) - \frac{l^2}{r^2} \right) U = 0$$
(2.1-8)

which is the Helmholtz equation in cylindrical coordinate. Herein, $\beta = k_0 n_{eff}$ where n_{eff} is effective refractive index. Eq. (2.1-8) is one of the typical differential equations whose solutions are among the family of Bessel functions. Defining parameters of:

$$u_{i} = \sqrt{k_{0}^{2} n_{i}^{2} - \beta^{2}}, \quad when \, n_{eff} < n_{i}$$

$$w = \sqrt{\beta^{2} - k_{0}^{2} n_{i}^{2}}, \quad when \, n_{eff} > n_{i}$$
(2.1-9)

where *i* still denotes the core, cladding or other parts of the fibre. For the case of forward propagating, the solutions of (2.1-8) can be displayed as:

$$U(r) = \begin{cases} A_1 J_l(u_i r) + A_2 Y_l(u_i r), & \text{when } n_{eff} < n_i \\ A_3 I_l(wr) + A_4 K_l(wr) & \text{when } n_{eff} > n_l \end{cases}$$
(2.1-10)

where $J_l(u_ir)$ and $Y_l(u_ir)$ are the Bessel function of the first and second kind of *l*th order while $I_l(wr)$ and $K_l(wr)$ are the modified Bessel functions of *l*th order and A_{1-4} represent the amplitude of fields. As shown in (2.1-10), for each *l* which represents azimuthal order, there are a series solutions of propagation constants $\beta_{l,m}$, and for each of these $\beta_{l,m}$ there is a mode (an eigenfunction, in mathematics) of the wave. Herein, light wave is in the form of propagation wave when $n_{eff} < n_i$ and becomes evanescent wave while $n_{eff} > n_i$. In addition, u_i and w satisfy the relationship of $u_i^2 + w^2 = V$, where this V parameter $V = 2\pi \frac{r_i}{\lambda_0} NA$ is an important parameter that governs the mode numbers of the fibre.

In the case of a bare fibre, the light is well confined by the fibre core as propagating wave and becomes evanescent wave in cladding region. To satisfy the convergence condition, which prevents field intensity approach ∞ at r = 0 and $r \rightarrow \infty$, the solution for a particular bare fibre can be achieved by reducing (2.1-10) to:

$$U(r) = \begin{cases} A_1 J_l(u_i r), & r < r_{co} \\ A_4 K_l(wr) & r > r_{co} \end{cases}$$
(2.1-11)

To investigate the propagating mode in fibre core, it is necessary to solve the equation (2.1-11). By applying the boundary condition that all the fields and their derivatives must be continuous at the interface of the boundary, the characteristic equation (or dispersion relation) of propagation modes in fibre can be derived by eliminating the amplitude factors as:

$$\frac{u_{co}J_l'(u_{co}r_{co})}{J_l(u_{co}r_{co})} = \frac{w_{cl}K_l'(w_{cl}r_{co})}{K_l(w_{cl}r_{co})}$$
(2.1-12)

Herein, this equation can be solved by graphical method. For visible convenience, both left- and right-hand side (LHS and RHS) curves are plotted in Fig. 2.1-1. As u_{co} is the function of the effective refractive index of fibre core, it can be seen in Fig. 2.1-1 that each intersection point is a solution for one mode in fibre core. As the RHS curve decreases to 0 at when $u_{co} = V$, multiple modes can propagate in fibre core if the V parameter is large enough. However, as the first branch of LHS is starting from 0, there will be at least one mode allowed to propagate in fibre core, which is usually called fundamental core mode. In the case of V = 12.732 (Fig. 2.1-1), there are four modes allowed to propagate in fibre core.



Figure 2.1-1 The graphical construction of Eq. (2.1-12). The LHS and RHS are plotted separately as the functions of u_{co} . The V parameter in this case is 12.732. Figure adapted from Ref [25].

When V < 2.405 (for l = 1), there is only one intersection of the characteristic equation. Such a fibre is defined as single-mode fibre (SMF). For example, the most common commercial SMF, e.g. Corning SMF-28 with numerical aperture (NA) of 0.14 and core diameter of 8.2 µm, it can be calculated that the V parameter of SMF-28 at 1550nm is 2.327.

2.2 Coupled-mode theory

An ideal fibre is considered as an "unperturbed" and linear system, energy in one mode would not influence any other modes as they are orthogonal to each other in such a system. However, if there is any perturbation in fibre, it would cause energy transfer between different modes. As it was discussed in last section, there can be multiple modes propagating in the fibre, these modes can exchange power with each other if they are coupled. Optical fibre grating is one of the most typical structures to cause these "perturbation" in the fibre.

The presence of a fibre grating induces a dielectric perturbation which will violet the orthogonality of modes, and hence the energy in different modes can transfer between modes. The coupled-mode theory is a tool to analysis these energy transfers. Hereby, the coupled-mode theory caused by fibre gratings will be discussed based on the model provided by Erdogan [26–28].

Mathematically, if a fibre grating is inscribed by UV laser, the dielectric perturbation induced by it can be described as:

$$\Delta \varepsilon(r,\phi,z) = 2\varepsilon_0 n_{eff} \overline{\delta n_{eff}}(z) \left[1 + \nu \cos\left(\frac{2\pi}{\Lambda}z + \phi(z)\right)\right] \quad (2.2-1)$$

where ν is the fringe visibility of the index change, Λ is the grating period, $\phi(z)$ describes grating chirp, and $\overline{\delta n_{eff}}$ is the spatially averaged index change over a grating period. This results in a coupling between modes, in general, the transverse coupling coefficient between *j*th and *k*th modes, can be given by:

$$K_{kj}^{t}(z) = \frac{\omega}{4} \int_{0}^{2\pi} \int_{0}^{\infty} \left[\Delta \varepsilon(r, \phi, z) U_{k}(r) U_{j}(r) \right] r dr d\phi \qquad (2.2-2)$$

where $\omega = \frac{2\pi}{\lambda}$. This integral form indicates the strength of mode coupling is defined by two factors, the permittivity perturbation and the mode overlap. Meanwhile, the longitudinal coupling coefficients $K_{kj}^{z}(z)$ is an analogue to the transverse one. However, it is much smaller than that of transverse coupling and usually ignored.

In a grating contained fibre, the z direction component in transverse amplitude of field in Eq. (2.1-7) is no longer being oscillation only, instead, a pair of slowly varying amplitudes with mode coupling described is shown as:

$$U(r,\phi,z,t) = \sum_{j} \left[A_{j}^{+}(z)e^{i\beta z} + A_{j}^{-}(z)e^{-i\beta z} \right] U(r)e^{il\phi}e^{-i\omega t}$$
(2.2-3)

where the transverse mode field $U(r)e^{il\phi}$ describes either core, cladding, or radiation mode. $A_j^+(z)$ and $A_j^-(z)$ are those slowly varying amplitudes where of the *j*th mode and the superscript "+" and "-" denotes the travelling directions along z axis. Due to mode coupling, both amplitudes will vary during travelling. The evolution of these amplitudes can be described generally as:

$$\frac{dA_j^+}{dz} = i \sum_k A_k^+ \left(K_{kj}^t + K_{kj}^z \right) \exp\left[i \left(\beta_k - \beta_j \right) z \right] + i \sum_k A_k^- \left(K_{kj}^t - K_{kj}^z \right) \exp\left[-i \left(\beta_k + \beta_j \right) z \right]$$

$$\frac{dA_j^-}{dz} = -i \sum_k A_k^+ \left(K_{kj}^t - K_{kj}^z \right) \exp\left[i \left(\beta_k + \beta_j \right) z \right] - i \sum_k A_k^- \left(K_{kj}^t + K_{kj}^z \right) \exp\left[-i \left(\beta_k - \beta_j \right) z \right]$$

$$(2.2-4)$$

Above all, as the grating induced perturbation is approximately uniform across the core and not exists outside of the core, so $\overline{\delta n_{eff}}$ can be replaced by $\overline{\delta n_{co}}$. The general coupling can be further transformed to:

$$K_{kj}^{t}(z) = \sigma_{kj}(z) + 2\kappa_{kj}(z)\cos\left[\frac{2\pi}{\Lambda}z + \phi(z)\right]$$
(2.2-5)

where $\sigma_{kj}(z)$ is defined as "dc" coupling coefficient (period-averaged strength) while $\kappa_{kj}(z)$ is "ac" coupling coefficient (individual fringe strength) given by:

$$\sigma_{kj}(z) = \frac{\omega\varepsilon_0 n_{co}}{2} \overline{n_{co}}(z) \int_0^{2\pi} \int_0^{r_{co}} U_k(r) U_j(r) r dr d\phi \qquad (2.2-6)$$

$$\kappa_{kj}(z) = \frac{\nu}{2} \sigma_{kj}(z) \tag{2.2-7}$$

It is clear from the coupling coefficients that the strength of coupling depends on both refractive index perturbation and the mode overlap.

2.2.1 Fibre Bragg gratings

A fibre Bragg grating (FBG) is a type of Bragg reflector constructed in fibre, which can be considered as a segment of reflection filters. Therefore, the dominant interaction of FBG is the wavelength near an identical counter-propagating (backward) mode. By the synchronous approximation [5], Eq. (2.2-4) can be simplified to:

$$\frac{dR}{dz} = i\hat{\sigma}R(z) + i\kappa S(z)$$

$$\frac{dS}{dz} = -i\hat{\sigma}S(z) - i\kappa^* R(z)$$
(2.2-8)

where the amplitudes *R* and *S* are

$$R(z) \equiv A^{+}(z) \exp(i\delta z - \phi/2)$$

$$S(z) \equiv A^{-}(z) \exp(-i\delta z + \phi/2)$$
(2.2-9)

In (2.2-8) the coefficient κ is the cross-coupling factor, while $\hat{\sigma}$ denotes the general self-coupling factor defined as:

$$\hat{\sigma} \equiv \delta + \sigma - \frac{1}{2} \frac{d\phi}{dz} \tag{2.2-10}$$

where δ is the detuning factor, which is spatially independent along z axis for all type of gratings, is defined as:

$$\delta \equiv \beta - \frac{\pi}{\Lambda} = \beta - \beta_D = 2\pi n_{eff} \left(\frac{1}{\lambda} - \frac{1}{\lambda_D}\right)$$
(2.2-11)

where $\lambda_D \equiv 2n_{eff}\Lambda$ is the "design wavelength" for Bragg scattering by an extremely weak grating $(\delta n_{eff} \rightarrow 0)$ with a grating period of Λ .

For a single-mode Bragg grating, the coupling coefficients [26]:

$$\sigma = \frac{2\pi}{\lambda} \overline{\delta n_{eff}}$$

$$\kappa = \kappa^* = \frac{\pi}{\lambda} v \overline{\delta n_{eff}}$$
(2.2-12)

In this thesis, the chirped gratings would not be discussed, hence the factor ϕ and its derivative $\frac{d\phi}{dz}$ are always kept as 0. To solve Eq. (2.2-8), the boundary conditions should be applied, for example, the grating length is L. At the start point of Bragg grating, the forward coupling is in its full strength, [R(0) = 1], and the backward coupling does not exist at the end of Bragg grating [S(L) = 0]. Consequently, the reflectivity can be obtained as:

$$r = \frac{\sinh^2(\sqrt{\kappa^2 - \hat{\sigma}^2}L)}{\cosh^2(\sqrt{\kappa^2 - \hat{\sigma}^2}L) - \frac{\hat{\sigma}^2}{\kappa^2}}$$
(2.2-13)

It is depicted in Eq. (2.2-13) there are 3 controllable factors could influence the intensity of reflection power, the grating length *L*, the *v* which is implied in both coupling coefficients and the operation wavelength λ . The expression of the maximum reflectivity r_{max} can be derived from the Eq. (2.2-13) as [26]:

$$\mathbf{r}_{max} = \tanh^2(\kappa L) \tag{2.2-14}$$

and it occurs when $\hat{\sigma} = 0$, or at wavelength:

$$\lambda_{\max} \cong \left(1 + \frac{\overline{\delta n_{co}}}{n_{eff}^{co}}\right) \lambda_{\mathrm{D}}$$
(2.2-15)

As $\overline{\delta n_{co}}$ (~10⁻⁴ RIU) is usually several orders smaller than that of n_{eff}^{co} (~1.45 RIU), the actual resonance wavelength is very close to the designed wavelength. Based on this relation, the upper bound of FBG reflectivity would be 1 at $\kappa L \rightarrow \infty$, but usually 99% at $\kappa L \sim 3$ will be good enough for applications as Eq. 2.2-15 rapidly converges (for example, when $\kappa L \sim 8$ the reflectivity is 99.99995%). This relation is significantly nonlinear, to achieve 50% reflectivity, the value of κL only need to be 0.88. There are two different ways to achieve the same κL value during FBG fabrication, by the increase of the modulation depth or the grating length. However, these two ways yield different shape of Bragg peaks. Fig. 2.2-1 is plotted to illustrate this difference, with the designed wavelength at 1550 nm and grating fringe visibility $\nu = 1$.



Figure 2.2-1 FBG reflection spectra versus different κL values ($\kappa L = 0.88$, $\kappa L = 3$, and $\kappa L = 8$). (a) with a fixed grating length of 4 mm but different modulation depths. (b) with a fixed modulation depth of $\overline{\delta n_{co}} = 2 \times 10^{-4}$ but different grating length.

Fig. 2.2-1 (a) depicts the FBG spectra with the same grating length but different modulation depths. It can be regarded as the fabrication of FBG via the phase mask assisted UV exposure method. During the fabrication, the resonance peak would not only grow stronger, but also shift to longer wavelength [30,31]. In Fig. 2.2-1 (a), the resonance peak shows 0.116 nm ($\kappa L \sim 0.88$), 0.395 nm ($\kappa L \sim 3$) and 1.055 nm ($\kappa L \sim 8$) offset from the designed wavelength 1550nm. However, if the fabrication method is switched to "point-by-point" (for example, femtosecond laser inscription), the resonance wavelength is expected to have no shift during fabrication as the modulation strength doesn't change according to Eq. (2.2-15). This is in a similar situation as

shown in Fig. 2.2-1 (b), the modulation depth is kept as a constant of 2×10^{-4} , while the grating length is different. In such a case, the resonance peaks keep the same offset of 0.214 nm from the designed wavelength.

It is also noticeable that the bandwidth of the grating peak significantly increases against the exposure strength. Herein, the equation of bandwidth of FBG resonance peak can be indicated [26]:

$$\lambda_{bandwidth} \cong \frac{v \overline{\delta n_{co}}}{n_{eff}^{co}} \lambda_{\rm D}$$
(2.2-16)

Subsequently, for an existing FBG where κ and *L* are already fixed, the maximum reflectivity would occur at the minimum $\hat{\sigma}$. As the σ is now a constant, it requires the detuning factor at Eq. (2.2-10) $\delta = 0$, which yields:

$$\lambda_B = 2n_{co}^{eff}\Lambda \tag{2.2-17}$$

This condition is well known as the phase matching condition of fibre Bragg condition, where λ_B is called Bragg resonance wavelength.

2.2.2 Long period gratings

Long period grating (LPG) is another important type among the fibre grating family. A long period grating is typically a photoinduced periodic refractive index modulation in the order of hundreds of micrometres in fibre core. The perturbation of refractive index in fibre core results in cross coupling between the fundamental core mode and a series of forward-propagating cladding modes.

To investigate LPG's cladding modes, the first task is to calculate effective refractive indices of different cladding modes. There are two models for the calculations. The first one is called two-layer (geometry) model [32], which is an analogue to that of the calculation of the core mode. This is reasonable because the refractive index difference between core and cladding is very small and the diameter of core is very small compared to cladding. Therefore, by changing the core-related parameters to cladding-related, the same Eq. (2.1-12) can be also applied to calculate the effective indices of cladding modes. The second one is called three-layer (geometry) model, which is developed by Turan Erdogan to correct the inaccuracy of the two-layer model [27]. In addition, there are few research groups investigate the difference between these two

models, such as Felipe S. Delgado et al. [33]. Hereby, a more complicated form of the characteristic (or dispersion) equation of cladding is given by [27]:

$$\zeta_0 = \zeta'_0 \tag{2.2-18}$$

where:

$$\zeta_{0} = \frac{1}{\sigma_{2}} \frac{u_{2} \left(JK + \frac{\sigma_{1}\sigma_{2}u_{21}u_{32}}{n_{cl}^{2}r_{co}r_{cl}} \right) p_{l}(r_{cl}) - Kq_{l}(r_{cl}) + Jr_{l}(r_{cl}) - \frac{1}{u_{2}} s_{l}(r_{cl})}{-u_{2} \left(\frac{u_{32}}{n_{cl}^{2}r_{cl}} J - \frac{u_{21}}{n_{co}^{2}r_{co}} K \right) p_{l}(r_{cl}) + \frac{u_{32}}{n_{co}^{2}r_{cl}} q_{l}(r_{cl}) + \frac{u_{21}}{n_{co}^{2}r_{co}} q_{l}(r_{cl})}{\left(\frac{u_{32}}{n_{co}^{2}r_{co}} K \right) p_{l}(r_{cl}) + \frac{u_{32}}{n_{co}^{2}r_{cl}} q_{l}(r_{cl}) + \frac{u_{21}}{n_{co}^{2}r_{co}} q_{l}(r_{cl})}$$
(2.2-19)

$$\zeta_{0}' = \sigma_{1} \frac{u_{2} \left(\frac{u_{32}}{r_{cl}} J - \frac{n_{sur} u_{21}}{n_{cl}^{2} r_{co}} K\right) p_{l}(r_{cl}) - \frac{u_{32}}{n_{co}^{2} r_{cl}} q_{l}(r_{cl}) - \frac{u_{21}}{n_{1}^{2} r_{co}} q_{l}(r_{cl})}{u_{2} \left(\frac{n_{sur}^{2}}{n_{cl}^{2}} J K + \frac{\sigma_{1} \sigma_{2} u_{21} u_{32}}{n_{co}^{2} r_{co} r_{cl}}\right) p_{l}(r_{cl}) - \frac{n_{sur}^{2}}{n_{co}^{2}} K q_{l}(r_{cl}) + J r_{l}(r_{cl}) - \frac{n_{cl}^{2}}{n_{co}^{2} u_{2}} s_{l}(r_{cl})}$$
(2.2-20)

where the symbol definitions in Eq. (2.2-20)-(2.2-21):

$$\sigma_1 \equiv i ln_{eff} / Z_0$$

$$\sigma_2 \equiv i ln_{eff} Z_0$$
(2.2-21)

$$u_{21} \equiv \frac{1}{u_{cl}^2} - \frac{1}{u_{co}^2}$$

$$u_{32} \equiv \frac{1}{w_{ex}^2} - \frac{1}{u_{cl}^2}$$
(2.2-22)

where

$$u_j^2 \equiv (2\pi/\lambda)^2 \left(n_j^2 - n_{eff}^2 \right) \qquad [j = co, cl] \qquad (2.2-23)$$

$$w_3^2 \equiv (2\pi/\lambda)^2 \left(n_{eff}^2 - n_{sur}^2 \right)$$
 (2.2-24)

$$J \equiv \frac{J_l'(u_{co}r_{co})}{u_{co}J_l(u_{co}r_{co})}$$
(2.2-25)

$$K \equiv \frac{K_{l}'(w_{sur}a_{cl})}{u_{cl}K_{l}(w_{3}a_{cl})}$$
(2.2-26)

$$p_l(r) \equiv J_l(u_{cl}r)N_l(u_{cl}r_{co}) - J_l(u_{cl}r_{co})N_l(u_{cl}r)$$
(2.2-27)

$$q_l(r) \equiv J_l(u_{cl}r)N_l'(u_{cl}r_{co}) - J_l'(u_{cl}r_{co})N_l(u_{cl}r)$$
(2.2-28)

$$r_l(r) \equiv J'_l(u_{cl}r)N_l(u_{cl}r_{co}) - J_l(u_{cl}r_{co})N'_l(u_{cl}r)$$
(2.2-29)

$$s_l(r) \equiv J'_l(u_{cl}r)N'_l(u_{cl}r_{co}) - J'_l(u_{cl}r_{co})N'_l(u_{cl}r)$$
(2.2-30)

In all above equations, $Z_0 = \sqrt{\mu_0/\varepsilon_0} = 377\Omega$ is the free space electromagnetic impedance. For a given azimuthal number *l*, there are typically more than a hundred cladding modes in a conventional fibre with cladding diameter of 125 µm. There are two prerequisites of Eq. (2.2-18), the surrounding refractive index (SRI) must be smaller than that of cladding, $(n_{SRI} < n_{eff} < n_{cl})$, and the azimuthal index must be l = 1. Noting that in Erdogan's paper, the continuity condition is based on longitudinal field instead of transverse field [34]. Hence, the meaning of the longitudinal index is different from that of Eq. (2.1-12). Consequently, the solutions generated from Eq. (2.2-18) are mixed up with both LP_{0x} and LP_{1y} modes, for which Erdogan has not stated clearly in his papers [27].

To solve Eq. (2.2-18)- (2.2-20), the technique is very similar to that of Eq. (2.1-12). By identifying the intersections of LHS and RHS of the characteristic equation on a plotted graph, the effective refractive indices of cladding can be thus obtained.

Parameter term	Parameter value
Core radius (r_{co})	4.1 μm
Cladding radius (r_{cl})	62.5 μm
Core refractive index (n_{co})	1.465
Cladding refractive index (n_{cl})	1.460
Operation wavelength (λ)	1550 nm

Table 2.2.1 Parameters applied in the simulation.



Figure 2.2-2 Graphical construction of three-layer model for cladding effective indices calculation, each intersection represents a mode.

Here, an example is displayed in Fig. 2.2-2 with parameters given by table 2.2.1. There are 10 cross sections in n_{cl}^{eff} ranging from 1.458 to 1.460, which correspond to the effective refractive indices of 1st to 10th order cladding modes.

Based on this method, the effective refractive indices of various cladding modes can be obtained by applying the Eq. (2.2-18)- (2.2-20). For better illustration, the lowest 20 order cladding modes at wavelength from 1000 to 2000 nm together with that of core mode are plotted in Fig. 2.2-3. It is clear that the refractive indices of both core and cladding modes are wavelength-dependent. The effective refractive indices in shorter wavelength is smaller than that of longer wavelength. However, not all of these cladding modes belong to the same azimuthal order, to clarify this, the radial field distribution for serval lowest-order of cladding modes are displayed in Fig. 2.2-4 via the field distribution equation [27].



Figure 2.2-3 Effective refractive indices of fundamental core mode and first 30-order of cladding modes as a function of wavelength. The solid lines represent fundamental core mode and odd-order cladding modes, while the dashed lines represent even-order cladding modes.



Figure 2.2-4 Local intensity distribution profile of the four lowest-order cladding modes at l = 1 by Eq. (2.2-19). (a) The radial distribution profile (b) The field distribution profile at cross-section (c) The relation between even-order cladding modes (m=2) and LP₁₁ modes. All modes are normalised with the total transferring power of 1W. Figure adapted from Ref [27].

One may realize in Fig. 2.2-4 (a) and (b), the field distributions of low even-order modes are very close to 0 in the core region, whereas the odd modes have much larger portion.

This indicates that the even-order cladding modes are not a subset of LP_{0x} modes, but of LP_{1y} modes. This is because in Erdogan's model the field was no longer regarded as TEM mode, which considered the longitudinal continuity [34] instead of transverse continuity. As results, HE, TM and TE modes will also be considered. It is also worth to mention in Fig. 2.2-4(b) that the first order mode (m=1) in cladding starts from LP_{02} whereas the LP_{01} represents the fundamental core mode. Fig. 2.2-4(c) demonstrates the second-order cladding mode (m=2) is the superposition of sub-profiles of LP_{11} mode, which consists of TE_{01} , TM_{01} , and HE_{21} modes. This demonstration is also valid for higher even-order cladding modes.

As it was discussed in the beginning of this section, the dominant interaction of a LPG is forward coupling, which occurs between two strongly coupled modes 1 and 2. The coupling equation (2.2-4) for LPG can be rewritten as:

$$\frac{dR}{dz} = i\hat{\sigma}R(z) + i\kappa S(z)$$

$$\frac{dS}{dz} = -i\hat{\sigma}S(z) + i\kappa^*R(z)$$
(2.2-31)

where the amplitudes *R* and *S* are $R(z) \equiv A_1^+(z) \exp[-i(\sigma_{11} + \sigma_{22})z/2] \exp(i\delta z - \phi/2)$ and $S(z) \equiv A_2^+(z) \exp[-i(\sigma_{11} + \sigma_{22})z/2] \exp(-i\delta z + \phi/2)$, and the coefficient σ_{11} and σ_{22} are the self-coupling coefficients and $\kappa = \kappa_{12} = \kappa_{21}^*$ are the cross-coupling coefficients, respectively. Similar as FBG's case, $\hat{\sigma}$ is a general self-coupling coefficient defined as:

$$\hat{\sigma} \equiv \delta + \frac{\sigma_{11} - \sigma_{22}}{2} - \frac{1}{2} \frac{d\phi}{dz}$$
(2.2-32)

where

$$\delta \equiv \frac{1}{2}(\beta_1 - \beta_2) - \frac{\pi}{\Lambda} = \pi (n_{eff}^{co} - n_{eff}^{cl})(\frac{1}{\lambda} - \frac{1}{\lambda_D})$$
(2.2-33)

with $\lambda_D \equiv (n_{eff}^{co} - n_{eff}^{cl}) \Lambda$ is the design wavelength.

Assuming the refractive index distribution in grating region is:

$$n(r,z) = n_{co} + \overline{\delta n_{co}} [1 + \nu \cos\left(\frac{2\pi}{\Lambda}z\right)]$$
(2.2-34)

the coupling coefficient can be expressed as:

$$K_{kj}^{t}(z) = \kappa_{kj}(z) \left[1 + \cos\left(\frac{2\pi}{\Lambda}z\right) \right]$$
(2.2-35)
considering no azimuthal index variation in fibre, where:

$$\kappa_{01-01}^{co-co}(z) = \frac{\omega\varepsilon_0 n_{co}}{2} \overline{n_{co}}(z) \int_0^{2\pi} \int_0^{r_{co}} U_{co}(r) U_{co}(r) r dr d\phi \qquad (2.2-36)$$

$$\kappa_{01-m}^{co-cl}(z) = \frac{\omega \varepsilon_0 n_{co}}{2} \overline{n_{co}}(z) \int_0^{2\pi} \int_0^{r_{co}} U_{co}(r) U_{cl,m}(r) r dr d\phi \qquad (2.2-37)$$

To obtain a sense of the coupling strength between the LP_{01} core mode and the *m*th cladding modes, the coupling strength (for all l = 1, $\overline{n_{co}} = 2 \times 10^{-4}$) of cladding modes at 1550nm wavelength is plotted in Fig. 2.2-7 (a). Whilst the coupling strength of the 1st to 7th odd-mode at wavelength ranging from 1200nm to 1700nm is plotted in Fig. 2.2-5 (b) revealing the wavelength dependent characteristics.



Figure 2.2-5 Coupling strength κ_{01-m}^{co-cl} between core mode LP_{01} and *m*th cladding modes. In (a) the solid circle represents the odd cladding modes, and the hallow circle represents the even cladding modes. (b) The coupling strength as a function of wavelength. Figure adapted from Ref [25].

Fig. 2.2-5 (a) shows the coupling between core mode and low-order even cladding modes is very small, as they only have small portion inside fibre core. Therefore, the coupling strength of these modes are really weak compared to that of low-order odd modes. However, for higher-order even cladding modes, the oscillation inside fibre core region could arise because the energy distribution changes, where the coupling strengths of odd and even modes become comparable. In addition, for both odd and even cladding modes, as long as the energy distribution inside fibre core decreases, their coupling strength would drop as well. In some special case, they can drop back to a value near 0 if the cladding mode fields begin to exhibit "null" in the fibre core. In Fig. 2.2-5 (a), there are 5 complete cycles of the coupling strength with period about 32, the larger the fibre core diameter is, the smaller that period is.

Like an analogue of Bragg grating, the solution of Eq. (2.2-31) can be obtained by assuming [R(0) = 1, S(0) = 1]:

$$T_{=} = \cos^{2}\left(\sqrt{\kappa^{2} + \hat{\sigma}^{2}}z\right) + \frac{\hat{\sigma}^{2}}{\kappa^{2} + \hat{\sigma}^{2}}\sin^{2}\left(\sqrt{\kappa^{2} + \hat{\sigma}^{2}}z\right)$$
(2.2-38)

$$T_{\times} = \frac{\hat{\sigma}^2}{\kappa^2 + \hat{\sigma}^2} \sin^2 \left(\sqrt{\kappa^2 + \hat{\sigma}^2} z \right)$$
(2.2-39)

where $T_{=} = |R(z)|^2/|R(0)|^2$ denotes the transmission of mode "1" (core mode), while $T_{\times} = |S(z)|^2/|R(0)|^2$ denotes the transmission of mode "2" (cladding modes) at the end of the LPG. Subsequently, the maximum transmission power of cladding modes for a LPG with grating length of *L* is given by:

$$T_{x,\max} = \sin^2(\kappa L) \tag{2.2-40}$$

and it occurs at the wavelength:

$$\lambda_{\max} = \frac{1}{1 - (\sigma_{11} - \sigma_{22})\frac{\Lambda}{2\pi}} \lambda_{\rm D}$$
(2.2-41)

For the coupling between core and cladding, the σ_{11} equals to $\sigma = \frac{2\pi}{\lambda} \overline{n_{co}}$, and the selfcoupling of cladding modes are much smaller than that of core, e.g. $\sigma_{22} \ll \sigma_{11}$. There for, we can approximate as:

$$\lambda_{\max} \cong \left(1 + \frac{\overline{\delta n_{co}}}{n_{eff}^{co} - n_{eff}^{cl}}\right) \lambda_{\mathrm{D}}$$
(2.2-42)

Moreover, for a typical LPG, $\overline{\delta n_{co}}$ is about 2 orders smaller than the $(n_{eff}^{co} - n_{eff}^{cl})$, hence λ_{max} occurs almost at λ_D , where the phase matching condition (or resonance) yields:

$$\lambda_{R,m} \equiv (n_{eff}^{co} - n_{eff,m}^{cl}) \Lambda \qquad (2.2-43)$$

where m denotes the mth cladding mode.



Figure 2.2-6 Transmission spectra of different LPGs at wavelength ranging from 1200-1700 nm. (a) LPG spectra at different modulation depth (b) LPG spectra at different grating length (c) LPG spectra at different grating period.

Based on these, the simulated spectra of LPGs with different grating parameters are plotted in Fig. 2.2-6. In Fig. 2.2-6 (a), all LPGs have the same grating period (450μ m) and length (20mm), but different modulation depths. When the modulation depth increases, the resonance peaks grow stronger and reveal red-shift simultaneously, which matches to the description of Eq. (2.2-42). This series of spectra can be considered as an analogue of the spectral evolution during LPG fabrication with multiple UV exposure or the amplitude mask assisted UV exposure [35,36].

Apart from this, to increase grating length is the alternative way to achieve strong resonance, but the resonance wavelength tends to be no change theatrically. For a long period grating fabricated by a "point-by-point" method, the simulated spectral evolution during fabrication has been plotted in Fig. 2.2-6 (b). Fig. 2.2-6 (c) illustrates the influence of grating period to the grating spectra [37,38]. As the phase matching condition described, the resonance wavelength of mth cladding mode depends on the grating period.

The phase matching curves between resonance wavelength and grating period are plotted in Fig. 2.2-7. It can be seen that the phenomenon of "dual peak" occurs when the grating period is below 200 μ m. By recalling Fig. 2.2-3, the effective RI curvatures of cladding modes and fundamental core mode are different. For example, there are two points on the same phase matching curve of 21st cladding mode in the wavelength range of 1000 to 1700nm. The "dual peak" phenomenon demonstrates an interesting feature that two peaks from the same mode order will shift towards different direction in response of the external perturbation.



Figure 2.2-7 Resonance wavelength of 1-29th odd-order cladding modes versus the grating period. The open circles denote the simulated central wavelength of the dual-peaks corresponding to 19-21th cladding mode. Figure adapted from Ref [15].

2.2.3 Tilted fibre gratings

Another type of fibre grating is called tilted fibre grating (TFG). This type of grating is defined with a tilted angle of grating fringe against the fibre core axis. For a tilted grating, the expression of the induced index change in the fibre core needs a revision by considering the tilted angle [26]:

$$\delta n_{co}(x,z) = \overline{\delta n_{co}}(z') [1 + \nu \cos\left(\frac{2\pi}{\Lambda}z' + \phi(z')\right)] \qquad (2.2-44)$$

As shown in Fig. 2.2-8, the grating axis z' is no longer coincide with the fibre axis z, which is defined as $z' = z \cos \theta - x \sin \theta$ (for x-tilted grating) or $z' = z \cos \theta - y \sin \theta$ (for y-tilted grating).



Figure 2.2-8 Configuration of a grating with single-side tilt angle (a) x-tilted grating (b) y-tilted grating.

The effective grating period, i.g. the axial period $\Lambda = \Lambda_g/\cos\theta$ will determine the resonant wavelength instead of the inscribed period Λ_g . It is clear that the coupling direction of a TFG depends strongly on the tilted angle, which can be either backward, side, or forward coupling for different tilted angle. With wavevector-based ray optics [14], the strongest coupling occurs at the direction:

$$\vec{K}_R = \vec{K}_{core} + \vec{K}_G \tag{2.2-45}$$

where \vec{K}_R , \vec{K}_{core} and \vec{K}_G are wave vectors corresponding to the scattered light, core mode, and grating, respectively. As in general case, the refractive indices of fibre core and cladding are very close, the amplitude difference of \vec{K}_R , \vec{K}_{core} is neglected. Fig. 2.2-9 illustrates the phase matching condition for tilted fibre grating with different tilt angle $\theta <$, =, and > 45°.



Figure 2.2-9 (a) Phase matching condition defined by wavevectors. The parallel line on \vec{K}_G indicates the tilted condition of grating (b) Mode coupling regimes and β axis illustrate for TFG with different tilted angles.

As shown in Fig. 2.2-9, if the grating's tilted angle $\theta > 45^{\circ}$, the core mode will be coupled to the forward-propagating direction, and for grating angle $\theta < 45^{\circ}$ the coupling direction is reversed. However, there is a range of tilted angles where the total internal reflection is violated hence the light will be coupled to the radiation modes. This range can be defined by the critical angle:

$$\alpha_c = \arcsin \frac{n_{sur}}{n_{cl}} \tag{2.2-46}$$

where n_{sur} and n_{cl} are refractive indices of the surrounding-medium and cladding respectively., The critical angles are 43.8° and 67.0° when the fibre is surrounded by the air ($n_{sur} \sim 1.00$) and water ($n_{sur} \sim 1.33$), respectively.

By defining φ (shown in Fig. 2.2-9) as the incident angle, the ray optic relation can be given as $\varphi = |2\theta - \pi/2|$. When φ locates within the range of $\theta_{1c} < \theta < \theta_{2c}$, the core mode will be coupled to radiation modes.

$$\theta_{1c} = \frac{1}{2} \left(\frac{\pi}{2} - \alpha_c \right), \quad \theta_{2c} = \frac{1}{2} \left(\frac{\pi}{2} + \alpha_c \right)$$
(2.2-47)

. For the case of fibre surrounded by the air, the fundamental core mode will be coupled to the backward-propagating cladding modes when grating angle $\theta < 23.1^{\circ}$ or to the forward-propagating cladding modes when $\theta > 66.9^{\circ}$, respectively.

Consequently, the phase match condition of a tilted fibre grating is:

$$\lambda_{R,m} \equiv (n_{eff}^{co} \pm n_{eff,m}^{cl,i}) \Lambda \quad \text{i for TE and TM} \qquad (2.2-48)$$

where "+" denotes backward coupling and "-" indicates forward coupling.

For the fabrication of TFG, the UV side-exposure induces asymmetric RI change hence the strong birefringence in the fibre core, which is usually ignored in the non-tilted grating cases. For the effective refractive index of cladding modein Eq. (2.2-48), the polarisation effect should be taken into consideration. For a tilted grating, as the fibre cladding and surrounding-medium no longer satisfy the weekly guiding condition $(n_1/n_2 \approx 1)$, the TE_{0m} and TM_{0m} modes are no longer degenerate. The eigenvalue equations are given [39,40]:

$$\frac{J_1(u_{cl}r_{cl})}{u_{cl}J_0(u_{cl}r_{cl})} = \frac{K_1(w_{sur}r_{cl})}{w_{sur}K_0(w_{sur}r_{cl})} \quad \text{for TE}_{0m}$$
(2.2-49)

$$\frac{J_1(u_{cl}r_{cl})}{u_{cl}J_0(u_{cl}r_{cl})} = \frac{n_{sur}^2}{n_{cl}^2} \frac{K_1(w_{sur}r_{cl})}{w_{sur}K_0(w_{sur}r_{cl})} \quad \text{for TM}_{0m}$$
(2.2-50)

where $u_{cl} = \sqrt{k_0^2 n_{cl}^2 - k_0^2 n_{eff}^2}$ and $w_{sur} = \sqrt{k_0^2 n_{eff}^2 - k_0^2 n_{sur}^2}$. r_{cl}, n_{cl}, n_{sur} , and n_{eff} are cladding radius, cladding refractive index, surrounding-medium refractive index

and cladding effective refractive index, respectively.



Figure 2.2-10 (a) Effective refractive indices for both TE (solid curves) and TM (dash curves) cladding modes. (b) the refractive index difference between TE and TM modes as a function of wavelength. Figure adapted from Ref [39].

By solving Eq. (2.2-49) and (2.2-50), the effective refractive indices are calculated and plotted in Fig. 2.2-10 (a) with selected modes. It is clear that the effective refractive indices of TE and TM modes at *m*th order are slightly different in the value, where the

effective RI of TE modes show slightly high. The refractive index difference of the same order TE and TM modes can also display by Fig. 2.2-10 (b). It is clear that the RI differences relate to both operation wavelength and mode order. The RI differences increase when the mode order as well as the wavelength increase.

To investigate the polarisation effect of the largely tilted TFG, the resonance wavelength with selected TE and TM modes against the axial grating period is plotted in Fig. 2.2-11.



Figure 2.2-11 Resonance wavelength of both TE and TM modes as functions of axial grating period of a forward coupling grating. (a) m=1 to 10 (b) m=11 to 20 (c) m=21 to 30 (b) m=31 to 40 (e) m=41 to 50 (f) m=51 to 60. Figure adapted from Ref [39].

The wavelength difference is very tiny but still noticeable. For low-order cladding modes, TE modes are having slightly smaller resonant wavelength than its counterpart TM modes, while for high-order cladding modes, this wavelength sequence are reversed. This results in an interesting fact that TM modes will corresponding to larger wavelength than TE modes at lower order or lower wavelength, while this sequence will be reversed at higher order or higher wavelength with a turning point at around 11th mode with in the OSA detection range. For example, in the spectrum of large tilted fibre grating, TE modes will always on the right-hand side (higher wavelength) in a pair of peaks.

The tilted angle will also affect the coupling coefficient. The coupling coefficients in Eq. (2.2-12) shall be rewritten as [26,28,41]:

$$\sigma_{kj}(z) = \frac{\omega\varepsilon_0 n_{co}}{2} \overline{n_{co}}(z) \int_0^{2\pi} \int_0^{r_{co}} U_k(r) U_j(r) r dr d\phi \qquad (2.2-51)$$

$$\kappa_{kj}^{\pm}(z) = \frac{\nu}{2} \frac{\omega\varepsilon_0 n_{co}}{2} \overline{n_{co}}(z)$$

$$\int_0^{2\pi} \int_0^{r_{co}} \exp(\pm i \frac{2\pi}{\Lambda} r \cos \phi \tan \theta) U_k(r) U_j(r) r dr d\phi \qquad (2.2-52)$$

where the \pm notes on κ represent the propagation direction of the original modes. The fringe visibility is also had an effective value as [4]:

$$\nu_{kj}^{\pm}(\theta) = \frac{\int_{0}^{2\pi} \int_{0}^{r_{co}} \exp(\pm i\frac{2\pi}{\Lambda}r\cos\phi\tan\theta) U_{k}(r)U_{j}(r)rdrd\phi}{\int_{0}^{2\pi} \int_{0}^{r_{co}} U_{k}(r)U_{j}(r)rdrd\phi}$$
(2.2-53)

Based on all the information above, the spectrum of tilted fibre grating can be predicted by simulation. Fig. 2.2-12 plots the simulated spectra of TFGs with titled angle of (a) 8° and (b) 81° .

There is significant spectral difference between two types of tilted grating. In the case of small tilted gratings (e.g. 8°-TFG), the light will be coupled from fundamental core mode to the backward core mode as well as the cladding modes resulting Bragg peak at longer wavelength side (e.g. at 1550 nm) and a set of cladding mode resonances at shorter wavelength side (e.g. 1525-1547 nm). The polarisation effect for the backward coupling TFGs can be demonstrated by launching the polarised light [42]. In the case of largely tilted gratings (e.g. 81°-TFG), the separation between TE- and TM- polarised

modes is much larger. As shown in Fig. 2.2-12 (b), the separation between TE and TM is around 7 nm.



Figure 2.2-12 The simulated transmission spectra of TFGs with tilted angle of (a) 8° and (b) 81°. In particular, both small (backward-coupling) and large (forward-coupling) tilted fibre grating can be used in various sensing applications though based on different sensing mechanisms.

For small tilted fibre gratings (usually $2^{\circ}-10^{\circ}$), the cutoff wavelength and resonances point (based on surface plasmon resonance (SPR)) are two indicators which describe the environment change, where cutoff wavelength related to bulk refractive index and resonances point related to specific detection [42]. Based on this, many excellent sensing works are reported [42–44]. However, as small tilted fibre grating based sensors are heavily rely on SPR, it limits the sensor structure and also the coating material which has to be metal such as gold and silver. In addition, both the cutoff wavelength and resonance point based indicator can sometimes cause ambiguity as they are usually located in a range rather than a clear point.

For large tilted fibre gratings, the sensing performance is very close to the LPGs, whilst providing polarisation information in addition. The sensing work based on large tilted fibre gratings will provide more reliable results than the small one because it based on individual peak monitoring. Apart from this work, there are also many good publications based on large tilted fibre gratings [45,46]. However, they also having a drawback that having mixed sensitivity on the bulk refractive index and target detection.

2.3 The principle of fibre gratings sensitisation

Both LPG and TFG can couple the light from core to the cladding, leaving the evanescent field penetrating the cladding boundary into the surrounding-medium. Mathematically, the electromagnetic field at the interface of cladding and the surrounding-medium determines the boundary condition of characteristic equation. The variation of boundary condition (e.g. external perturbation) will change the value of effective refractive index of the cladding and/or coupling coefficient. Physically, this can be regarded as the light-matter interaction between the evanescent wave and the surrounding-medium. Although the property of LPG and TFG is different, the underlying mechanism of their refractive index sensitivity is similar. In this section, we will discuss the LPG as the example.

As indicated in Eq. (2.2-18) to (2.2-20), the SRI is an important factor for the calculation of cladding effective refractive indices. In Fig. 2.3-1, both the effective refractive index and wavelength shift as the function of SRI for the selected cladding modes are plotted. The response of grating spectrum to the SRI change is nonlinear. For low RI region, resonant peaks show small wavelength shift [47,48]. When the SRI is close to the refractive index of cladding, the response becomes dramatically larger. Due to both grating period and n_{co}^{eff} are constant, the wavelength shift matches the prediction of phase matching condition Eq. (2.2-43), showing negative sensitivities to the SRI change. However, when the SRI exceeds the refractive index of cladding, it will become radiation mode [49,50].



Figure 2.3-1 (a) Effective refractive index and (b) wavelength shift of cladding modes (LP_{02} , LP_{04} and LP_{06}) as the function of the surrounding-medium refractive index.

The RI sensitivity of a LPG relates to a number of factors which have been described in Shu et al. [15]:

$$\frac{d\lambda_{res}}{dn_{sur}} = -\lambda_{res} \gamma \frac{u_m^2 \lambda_{res}^3 n_{sur}}{8\pi r_{cl}^3 n_{cl} \left(n_{co}^{eff} - n_{cl,m}^{eff}\right) \left(n_{cl}^2 - n_{sur}^2\right)^{3/2}}$$
(2.3-1)

where γ is called waveguide dispersion and defined by:

$$\gamma = \frac{d\lambda_{res}/d\Lambda}{n_{co}^{eff} - n_{cl,m}^{eff}}$$
(2.3-2)

This dispersion coefficient is related to the curves' slope in Fig.2.2-9, which achieves the maximum at dispersion-turning-point (DTP). The DTP dominates the "dual peak" features, which usually provide the highest sensitivities among all types of LPGs.

Eq. (2.3-1) has indicated how to achieve high sensitivity for an LPG (i) to monitor the peak with larger wavelength. (ii) to reduce the cladding radius, or (iii) to increase the effective RI of cladding as the RI sensitivity is inversely proportional to r_{cl}^3 and $(n_{co}^{eff} - n_{cl,m}^{eff})$.

The first example is given by a LPG with the reduced cladding. For comparison, the RI responses of two LPGs with different radius are plotted in Fig. 2.3-2.



Figure 2.3-2 The evolution of transmission spectra (a) and the wavelength shift (b) against SRI for LPGs with different cladding radius ($r_{cl} = 62.5 \mu m$ and $r_{cl} = 40.0 \mu m$).

It is clear from Fig. 2.3-2 that the RI sensitivity of an LPG with reduced cladding is much larger than that of regular LPG. The regular LPG shows RI sensitivity of -9.1 nm/RIU (at RI region: 1.00-1.33), while that of cladding-reduced LPG gives - 23.2nm/RIU, which is significantly enhanced by more than 200%.

However, reducing radius of a fibre will sacrifice its mechanical strength and make it easy to be broken. During the last few years, extra layer deposition has been developed to sensitise the fibre gratings. To investigate the effect of overlay coating, a four-layer model has been proposed with the transverse field distribution given by [22,51]:

$$U_{m}(r) = A_{0}Z_{m,co}\left(u_{co}\frac{r}{r_{co}}\right) \qquad \text{for } r < r_{co}$$

$$A_{1}Z_{m,cl}\left(u_{cl}\frac{r}{r_{cl}}\right) + A_{2}T_{m,cl}\left(u_{cl}\frac{r}{r_{cl}}\right) \qquad \text{for } r_{co} < r < r_{cl}$$

$$A_{3}Z_{m,ly}\left(u_{ly}\frac{r}{r_{ly}}\right) + A_{4}T_{m,ly}\left(u_{ly}\frac{r}{r_{ly}}\right) \qquad \text{for } r_{cl} < r < r_{ly}$$

$$A_{5}K_{m,ly}\left(w_{sur}\frac{r}{r_{ly}}\right) \qquad \text{for } r > r_{ly} \qquad (2.3-3)$$

where

$$Z_{m,i}(x) = \begin{cases} J_m(x) & \mathbf{n}_{eff} < \mathbf{n}_i \\ I_m(x) & \mathbf{n}_{eff} > \mathbf{n}_i \end{cases}$$
(2.3-4)

$$T_{m,i}(x) = \begin{cases} Y_m(x) & \mathbf{n}_{eff} < \mathbf{n}_i \\ K_m(x) & \mathbf{n}_{eff} < \mathbf{n}_i \end{cases}$$
(2.3-5)

and *i* denotes the different layer region, such as core, cladding, overlay, and surrounding-medium. Similar to Eq. (2.1-11), J_m and I_m are the *m*th order ordinary Bessel functions of the first and second kind, while Y_m and K_m are the modified Bessel functions of the first and second kind. The overlay thickness is defined by $r_{ly} - r_{cl}$. Coefficients of A_0 to A_5 represent the amplitudes of the optical fields, which can be solved with the propagation constant β by the transfer matrix formulation [52].

Fig. 2.3-3 (a) displays the simulated effective RI corresponding to the cladding modes from LP_{0,2} to LP_{0,11} as a function of overlay thickness. The simulation conditions include the RI of the deposited material $n_{ly} = 1.7$, the operation wavelength at 1550nm, and external refractive index $n_{sur} = 1.33$.



Figure 2.3-3 (a) Effective refractive index of cladding modes as a function of the overlay thickness. Transverse field distribution of the LP_{04} cladding mode with overlay thickness of (b) 250 nm and (c) 500 nm.

The effective refractive indices of cladding modes shift to higher values when the material with higher RI than the cladding (HRI coating). More interestingly, when the out layer is thick enough, one of the cladding oscillations will be guided into the overlay. It results in an overall shift of the effective refractive indices of cladding modes. The effective RI of the *m*th mode will shift close to the RI region where the (m - 1)th mode used to be. This can be explained by Fig. 2.3-3 (b), the majority energy of transverse field is distributed in the core and cladding region, only a small portion of energy is in the overlay region. This kind of distribution is very close to the LP_{0,3} mode and so does the effective refractive index refer to the ray optics, but this mode still corresponds to the LP_{0,4} mode as there are 4 oscillations in total. This phenomenon will thus repeat when the overlay thickness further increases.

It is worth to note that there are some values of optimal overlay thickness according to the Fig. 2.3-3 (a), where the slope of each mode is maximum, where both the maximum evanescent field and penetration depth are achieved. Hereby, an example with the coating thickness of 170 nm has been simulated and shown in Fig. 2.3-3 (c), in which the evanescent field is examined. Consequently, a careful design of overlay thickness can help to get higher RI sensitivity.

As the grating resonance wavelength is directly related to the effective refractive index of cladding modes, the wavelength shift against the SRI change can be predicted. In Fig. 2.3-4, a simulation for the SRI response of two LPGs is shown in Fig. 2.3-4. These two gratings are assumed to have the same grating period $\Lambda = 400 \mu m$, but different coating thickness of 0 and 170 nm.



Figure 2.3-4 Resonance wavelength of the LP_{04} mode as a function of the SRI, the coating thickness of the second LPG is 170 nm with material refractive index of 1.7.

Based on the results of Fig. 2.3-4, the maximum sensitivity of the LPG with 170nm coating is shifted to the SRI region near 1.33, which agrees to the prediction discussed above. For that SRI region (~1.33), the sensitivity of the bare-LPG is less than -10.0 nm/RIU while that of the coated-LPG achieves -1700 nm/RIU, which is dramatically enhanced by more than 170 times. It is noticeable that the maximum sensitivity of coated-LPG at n=1.33 is lower than that of bare-LPG at 1.46, but the overlay deposition can move the most sensitive RI region from 1.46 to 1.33, which is the desired RI region for majority biochemical applications.

By now, the wavelength-based RI sensitivity has been discussed. However, the HRI coating would not only affect the wavelength but also the peak intensity. The peak intensity depends mainly on the coupling strength hence the variation of the field distribution will change the peak intensity. For a coated-LPG, if the coating material has complex refractive index, the coupling strength in Eq. (2.2-38) and Eq. (2.2-39)

will involve an extra factor related to the imaginary part of refractive index (the absorption coefficient) given by [53]:

$$\kappa_{j,j}' = \frac{1 - \exp[-\mathrm{imag}(2\beta_j)L]}{\mathrm{imag}(2\beta_j)L} \kappa_{j,j}$$
(2.3-6)

for self-coupling and,

$$\kappa_{k,j}' = \frac{1 - \exp[-\operatorname{imag}(\beta_j + \beta_k)L]}{\operatorname{imag}(\beta_j + \beta_k)L} \kappa_{k,j}$$
(2.3-7)

for cross-coupling.

For a bare-LPG, the resonant intensities barely change at low SRI region and show a significant change [47,48] for the region near the cladding RI. For a coated-LPG, the intensity response will be much stronger as the decaying factor leading to the reduction in peak intensity. Therefore, the HRI overlay deposition can enhance the intensity-based RI sensitivity.

2.4 Chapter summary

In this chapter, the underlying theory of three major types of fibre gratings was discussed. Starting from the fundamental Maxwell equations, the way that light propagates in fibre waveguide was derived as a series of propagating or radiation modes. These modes are orthogonal to each other in the ideal fibre waveguide and energy will not transfer between them. However, the grating-induced RI change in the fibre will violate this orthogonal condition resulting mode coupling.

Fibre grating is a structure with designed RI modulation in the fibre core. The different RI modulation will lead to different coupling between modes. For FBG, the coupling occurs between forward and backward propagating core modes, hence FBG is classified as reflection grating. For LPG, the light is coupled from core to the forward-propagating cladding modes. The LPG spectra, mode distribution, resonance wavelength and the sensitivity have been discussed. For TFG, the most unique type of fibre gratings, the detail mode coupling has been discussed and simulated. In the last section, the principle of fibre grating sensitisation has been discussed. The cladding-reduced method and the overlay deposition technique have been introduced.

Chapter 3 Two-dimensional materials deposition

3.1 Introduction of two-dimensional materials

Dimensionality is one of the most important parameters that defines material prosperities. As the name indicates, these two-dimensional (2D) nanomaterials (Fig. 3.1-1) are in layered form, with a typical thickness of a few nanometres or less. Hence, there can be dramatic differences between 2D-layered materials and its bulky counterpart, even the chemical compound of them are the same. Apart from those much-discussed advantages such as flexibility, robustness and high carrier mobilities, 2D materials are now considered to allow an exploration of the photonic applications due to their flexible bandgap. Encouraged by the successful study on graphene, innumerable researches have been carried out in the discovery and investigation of 2D materials.



Figure 3.1-1 Schematic illustration of different kinds of typical ultrathin 2D nanomaterials, such as graphene, h-BN, TMDs, MOFs, COFs, MXenes, LDHs, oxides, metals, and BP [54].

Till now, the family of 2D materials encompasses many other members such as transition metal dichalcogenides (TMDs), MXenes (where M represents Ti, Nb, V, Ta, etc and X represents C and N), hBNs (hexagonal boron nitride) and some monoelemental 2D semiconductors (phosphorene, silicene, germanene, borophene). Hereby, some popular 2D materials will be detailly discussed in the following sections.

Graphene

Graphene is the first-ever isolated 2D material (one atom thick) in nature. More than 50 years efforts have been placed on the obtaining a single-layer graphite (graphene), as the one-atom thick layer of sp² carbon are predicted to have tight bond nature. Eventually in 2004, Novoselov and Geim et al. have done this great job by a "scotch tape method" (mechanical exfoliation) [55]. Due to its excellent properties and early discovery, graphene is now the most investigated 2D materials. Experiments revealed astonishing properties of graphene in a wild range of electronic, optical, thermal, and mechanical fields.

First of all, graphene has a remarkable band structure (shown in Fig. 3.1-2) as its conduction and valence bands meet at the six locations in momentum space (on the edge of Brillouin zone), which are Dirac points. This makes graphene a zero-gap semiconductor, which behaviours as a semi-metallic material.



Figure 3.1-2 First Brillouin zone and band structure of graphene. The vertical axis is energy, while the horizontal axes are momentum space on the graphene lattice [56].

Therefore, graphene has excellent electronic properties, the electron mobility of graphene is reported to be $15,000 \text{ cm}^2/\text{V} \cdot \text{s}$ at room temperature, which is more than

10 times higher than that of silicon [57]. Moreover, this value can be achieved as high as 250,000 cm²/V · s in a cryogenic environment, exceeding the theoretical limit of 200,000 cm²/V · s [58]. Although this value will be limit to 40,000 cm²/V · s on glass substrate [59]. The corresponding resistivity of graphene is also significantly lower than that of regular materials as $\sim 10^{-6} \Omega \cdot$ cm. This value is less than the silver, which has the lowest resistivity among bulky materials, and 60 times less than that of SWCNTs (single wall carbon nanotubes) [60,61]. Apart from these, graphene is also considered to have high carrier density of $\sim 2 \times 10^{11}$ cm⁻² which is million times larger than that of copper.

The unique band structure of graphene also has great influences on its thermal properties. Graphene has an exceptionally thermal conductivity as high as 5300 $W \cdot m/K$ [62] at room temperature, more than 200% higher than the 2000 $W \cdot m/K$ of pyrolytic graphite. However, if the graphene is supported on an amorphous material, which causes the scattering of graphene lattice waves, the thermal conductivity will be reduced to about 500-600 $W \cdot m/K$ [63].

On the side of optical properties, the unique band structure of graphene results in an ultrabroadband (from FIR to UV) interaction with electromagnetic waves [64]. Even for terahertz wave, graphene can also have strong interaction with it, due to its intraband transition nature [65].



Figure 3.1-3 (a) Photograph of a 50-µm aperture partially covered by graphene and its bilayer [66].
(b) Optical image of graphene flakes with one, two, three, and four layers on a 285-nm thick SiO₂-on-Si substrate [67].

Remarkably, graphene shows an unexpectedly high opacity as each single layer graphene absorbs about 2.3% ($\pi \alpha \approx 2.3\%$, where α is a fine structure constant) of vertical incident light within the infrared to-visible spectral range (indicated in Fig. 3.1-3) [66], indicating a strong light-matter interaction. Despite that, as shown in Fig. 3.1-3, graphene is still considered to have good transparency as it is usually being few-layered [58]. In addition, it is reported that the refractive index of CVD-gowned graphene is n = 3.135 + 0.897i (where the imaginary part is also called extinction coefficient) at 670 nm [68].

Furthermore, graphene has also been reported to have strong nonlinear optic properties [69,70], based on its high third order susceptibility Among these properties, saturable absorption [71] and nonlinear refractive index change (basis of Kerr) [72] are vitally important for fibre laser technology. Consequently, a series work in fibre lasers based on graphene have been reported [73–75].

The mechanical properties of graphene are also remarkable, which is based on the strong bonding between carbon atoms and the mature fabrication technology. Graphene is considered to have the mechanical strength of 130 GPa which is highest ever tested among all of materials, 200 times higher than that of steel [76]. The young's modulus of graphene can be approximately 1 TPa (150000000 psi) as well [76]. Monolayer graphene can even be bent in a large angle without breaking if no strain applied, and more importantly carrier mobility in such extreme case can be reserved.

Graphene oxide

As an important precursor of graphene, graphene oxide (GO) is also a 2D material which contains various oxygen-containing groups. Researchers have identified that most of the oxygen function groups are hydroxyl and epoxy groups which located on the basal plane. There are also smaller amounts of carboxy, carbonyl, and sometimes phenol, lactone, and quinone at the edge of GO sheets [77–79]. The presence of the oxygenated functional groups induces structure defects to GO, leading to the reduction in electronic and mechanical properties compared with pristine graphene. However, these functional groups, on the other hand, provides significant advantages in chemistry. Firstly, thanks to the polar oxygen functional groups which are hydrophilic, GO is dispersible in many conventional solvents, particularly in water [80–82]. Consequently, many common methods including drop-casting, spraying, or spin-coating are enabled

for GO deposition via the stable GO dispersion. Moreover, these functional groups can serve as the chemical reaction or immobilisation sites for various biomolecules through either covalent or noncovalent bonds. Therefore, GO is a super flexible 2D material which can be engineered in either chemical, thermal, or electrochemical properties.

Due to the flexibility of GO in structure and chemical compounds, the electronic properties of GO can vary in different conditions. Generally, the as prepared GO films are reported to be insulating with the sheet resistance as low as $10^{12} \Omega/\text{sq}$ [83], depending on the amount of the sp³ C-O bonding in the GO sheet. This is because the presence of sp³ bonding will lead to a disruption to the sp² carbon clusters [84], which allows the carrier transporting [77]. However, by reducing the amount of oxygen in GO, the resistance of GO sheet can be decreased dramatically, turning GO into a semiconductor and ultimately into a graphene like material. The reported conductivity of a reduced GO can reach as high as 1000 S/m [85,86]. Above all, GO can be turned into insulating, semiconducting, or semi-metallic material, by controlling the oxidation parameters.

GO is also a photosensitive material as it shows remarkable absorptance in UV and visible spectral range. The refractive index (real part) of GO is reported to be around 2.0 [87,88], while the absorption plays remarkable role only around 230-300 nm due to $\pi \rightarrow \pi *$ and $n \rightarrow \pi *$ transition respectively [89,90]. Thereby, fluorescence labels [91] are become a common application based on this unique optical property of GO.

Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMDs or TMDCs) contains a group of 2D compound materials which are first isolated in 2010 (MoS₂) [92,93]. As the name indicated, these materials are in a MX₂ heterostructures structure, where M is a transition metal (Mo, W, Re, Nb, etc) and X is a chalcogen atom (S, Se, or Te), with one layer of M atoms sandwiched in the middle of two layers of X atoms (shown in Fig. 3.1-4). Properties of transition metal dichalcogenides can be very different due to the diversity of chemical compositions and structural phases. Depending on the combination of M and X elements, TMDs can manifest insulating to metallic or semimetallic properties. In addition, the bandgap of TMD materials is also variable in the range of 1.0 to 2.5 eV corresponding to mostly visible frequency and near inferred

(~400-1200 nm). Here for example, bandgaps of typical TMDs are shown in Table 3.1.1 [94].



Figure 3.1-4 Schematic of two and three-dimensional structure of a typical TMD material (MoS_2) where a single layers of 6.5Å can be achieved [95].

Material	Bandgap	Wavelength
WS ₂	1.95 eV	634 nm
MoS_2	1.90 eV	653 nm
WSe ₂	1.55 eV	800 nm
MoSe ₂	1.58 eV	785 nm
MoTe ₂	1.20 eV	1033 nm

Table 3.1.1 Bandgap of common TMDs and their corresponding emission wavelength

The band structure of bulk or multilayer TMDs is indirect, while by reducing the thickness of TMDs, the band structure will eventually turn into direct at monolayer condition. This phenomenon is due to the changed confinement effects and the interaction between the neighbouring layers [96]. According to the semiconductor photon absorption principle, the photoluminescence effect will be strongly enhanced for monolayer TMDs as they have a direct bandgap. For example, the emission efficiency of a monolayer MoS₂ can be 10^4 greater than its bulk form [97]. The direct band nature indicates promising optoelectronics application prospects of monolayer TMDs. For example, TMDs are reported as good photodetection materials, the photoresponsivity of a monolayer MoS₂ of 7.5 mA/W at its active region, which is

similar to that of graphene devices (6.1 mA/W), while for multilayer MoS₂ the photoresponsivity can be even higher, reaching 100 mA/W. This value is close to silicon devices and hence the ultrasensitive photodetector based on MoS₂ is reported [98]. With the assistance of a gold contact at the far edges.

Moreover, the mechanical properties of TMDs are also remarkable, particularly for MoS₂. It is reported the Young's modulus of a monolayer MoS₂ can reach 270 GPa, while that of bilayer MoS₂ is 200 GPa. The weakening in Young's modulus is believed due to the interlayer sliding and defects [99]. However, more interestingly, this value rises again if the flake thickness further increases, the measured Young's modulus is 330 GPa for 5-25 layers MoS₂ flakes [100]. For other TMD materials, it is also reported that the Young's modulus of 5-14 layers WSe₂ and monolayer WS₂ are 167 GPa [101] and 272 GPa [102], respectively.

Black phosphorene (phosphorus)

Phosphorene is a two-dimensional crystalline form of black phosphorus (BP), which is the most stable allotrope of phosphorus. Monolayer phosphorene was first isolated by mechanical exfoliation in 2014 [103–105] and was considered as a strong competitor to graphene. In Black phosphorus structure (shown in Fig. 3.1-5) the individual layers are stacked together by van der Waals force, where the thickness of each layer about 5.3 Å. As the phosphorus atoms have five electrons on their 3p orbitals, sp³ hybridisation is the majority structure within phosphorene, where the bond angle among atoms are 109°28'. However, in the hexagonal structure of phosphorene, the bond angle will slightly distorted, where the angle in the plane of the BP layer is about 96.3° while the angle between layers is 102.69°.

Despite the mono-atomic hexagonal structure and two-dimensional nature, phosphorene has substantially different properties to graphene. The most interested property is its band structure. BP has a thickness dependent bandgap of 0.3–2.0 eV, bridging the gap between graphene (zero bandgap) and large band TMDs. Detailly, the monolayer phosphorene shows a high bandgap of 2.0 eV and the bandgap decreases as the thickness increases and ended up in a 0.3 eV for bulk Black phosphorus [106]. It is believed that the absence of interlayer hybridisation near the top of the valence and bottom of the conduction band causes the rise in the bandgap [105]. It is also differ from that of TMDs, even the layer number changes, the bandgap of BP will always stay

direct [107]. Therefore, this property potentially makes BP a better semiconductor than graphene and many TMDs. In addition, for field-effect transistors (FETs) applications, BP are considered to be better than that of typical TMDs such as MoS_2 [95,108,109], as both mono- and few-layer BP show higher carrier mobility (1000 cm²/V · s). BP also reported to have larger current on/off ratio (1×10^3 to 1×10^5) than that of graphene transistors [104,110,111]. Unlike the in-plane centrosymmetric structure of graphene and TMDs, BP has a puckered lattice configuration along the armchair direction and a bilayer structure along the zigzag direction. Such unique structure of BP is considered to have anisotropic electrical and optical conductivity [105], which is experimentally proved in later works [112–114]. It is also noticeable that, many works have reported that the Raman spectrum of BP is polarise dependent as well. For example, as shown in Fig. 3.1-6 (c and d), the A_g^2 peak which corresponding to atom vibrate within the plane, shows significant difference for different scanning direction [115].



Figure 3.1-5 Structure information of (a) multi-layer and (b) monolayer black phosphorus (phosphorene) where a single layers of 5.3Å [116].

Furthermore, the optical properties of BP are highly tunable. Different thickness and doping will have different effect on the optical absorption of BP [117]. Due to its puckered structure, even local strain can have significant engineering effect on the optical properties of BP [118]. Generally, the optical absorption of monolayer is reported to be 2.8% [119], slightly higher than that of graphene.

BP is not only a promising 2D materials in electronic and optical applications, but also can be used as an excellent functional layer for (bio-)chemical applications. BP is

reported to have higher molecule absorption energy than graphene and TMDs [120]. All these properties make BP suitable material for biochemical sensing. In addition, despite BP is considered as air unstable [121], this defect is already minimised via advanced synthesis technique or extra protection [122–124].



Figure 3.1-6 Schematic of monolayer BP. (b) Optical micrograph of an exfoliated monolayer BP flake on 285 nm SiO₂/Si substrate. (c) Polarisation-resolved Raman spectra of monolayer BP with linearly polarised laser excitation. (d) Intensity of the A_g^2 mode as a function of the excitation laser polarisation angle in the x-y plane. [115]

Generally, for monolayer and multi-layer BP, they can sustain a tensile strain of up to 30% and 32%, respectively. The Poisson's ratio of BP is reported to be negative ($\nu = -0.027$) in the out-of-plane direction [125]. Moreover, due to its unique anisotropic structure, even the mechanical properties of BP are anisotropic as well, too. As it is predicted theoretically, BP has the in-plane Young's modulus and the ideal strain values of single-layer BP are 41.3 GPa and 0.48 in the direction perpendicular to the pucker, while these values become 106.4 GPa and 0.11 for the for the direction parallel to the pucker, respectively [126].

3.2 Two-dimensional materials deposition for photonic devices

As discussed in last section, the most 2D materials have unique optical properties such as strong light–material interaction, high nonlinearity, broadband optical response, fast relaxation, and controllable optoelectronics. Owing to these properties, 2D materials, in particular, graphene, TMDs and black phosphorous, have led to the explosive development for photonic devices. By engineering the physical properties, the optical response of 2D materials will also change as results. Hence, 2D materials are suitable for various photonic devices.

How to deposit 2D materials on conventional optical substrates is usually the major challenge in the fabrication of photonic devices. To date, there are many deposition methods have been reported, and all those methods play important role in the fabrication of photonic devices. In the following subsection, some conventional deposition methods will be briefly introduced.

3.2.1 Current 2D materials deposition methods

Mechanical exfoliation

Mechanical exfoliation is the most universal method for 2D materials deposition. The basic idea of mechanical exfoliation is to overcome the Van der Walls force between the layers of 2D material by a stronger force, which is the same method for the first isolation of graphene from graphite. Mechanical exfoliation contains many variations such as micromechanical cleavage, sonication, ball milling, fluid dynamics, which are all being wildly used to fabricate the devices.

Applications based on mechanical exfoliation are usually seen in all-fibre laser, where the 2D materials are used as a saturable absorber at the fibre end face. Mechanical exfoliation is chosen in these applications mainly due to its simplicity and reliability where all chemical procedures are absent. For example, the depositions of BP thin flakes on the fibre end are shown in Fig. 3.2-1a. By simply starching the prepared BP flake, the core area of FC/PC fibre end face is covered by BP flakes with different thickness. These BP flakes are moderately peeled from a big block of commercial BP via scotch tape. However, the defects of mechanical exfoliation method are also significantly exposed in Fig. 3.2-1b, where the material flakes are in limited size and the shape and thickness of them are hard to control. Hence, the deposited material is mostly applied on the fibre end facet (tip).



Figure 3.2-1 (a) SEM and AFM image of BP covered fibre connector end face [127] (b) Optical image of the fibre end face with thin (left) and thick (right) BP (fibre cladding diameter of 125 μ m, fibre core diameter of 9 μ m) [128].

Thermophoresis based optically driven

It is also worth to mention, for fibre laser applications, there are some works reported an unique method based on thermophoresis based optically driven [74,129]. For example, in graphene based fibre laser [74], a 25 mW laser diodes with operation wavelength at 974 nm were dipped into the graphene aqueous dispersion for serval minutes, and the graphene was deposited on the fibre ends after a 20 min evaporation process. As shown in Fig. 3.2-2, the end face of fibre core region is densely covered by graphene while the cladding region is covered by relative less graphene sheets. This is due to the laser intensity is mainly concentrated at fibre core region, where the optical absorption will achieve maximum.

However, despite the very different depositing mechanism, this optically driven deposition method shares similar limitations as the mechanical exfoliation technique. The thermophoresis affected area is limited at where the laser irradiation is relative strong, such as fibre core or cross section of waveguide, leading to relatively small depositing area. In addition, the shape and thickness of the deposited 2D materials are hard to control too. Therefore, this method is only seen in fibre laser applications [74,129].



Figure 3.2-2 (a) Schematic diagram for depositing graphene on the fibre end face by optical radiation. Images of the fibre end face (b) before and (c) after the graphene was deposited [74].

Wet transfer

Wet transfer is the most commonly used technique, for the fabrication of 2D materials based photonic devices, because it can deposit relatively large 2D material sheet with a well-controlled thickness. To apply wet transfer method, one will firstly need to grow target 2D material on an etchable base foil (mostly copper foil), and then cover the 2D material sheet by an extra layer of PMMA. As the schematic diagram in Fig. 3.2-3(a), the PMMA-graphene-copper foil sandwiched structure is floated on the etchant (mostly with trivalent ion such as Fe³⁺) with the copper side facing down. The copper will be turned into cupric ions in the presence of trivalent ion by oxidation reaction, as a result, the copper foil will totally "dissolved" in the etchant solution. Thereafter, the target substrate will be immersed into the liquid beneath the graphene/PMMA layer and lifted after the position be aligned (Fig. 3.2-3b). To achieve the robust deposition, the as combined material-substrate structure is usually rinsed and heated (Fig. 3.2-3c). Then, the PMMA protection layer will be eventually removed by acetone or other organic solvent. The wet transfer technique provides great advantages as the thickness of

deposited layer can be controlled at the grown procedure, whilst the size and shape of materials can be also controlled by a designed cutting pattern.



Figure 3.2-3 Schematic diagram of a typical graphene wet transfer method.



Figure 3.2-4 (a) In-fibre polariser based on graphene coated D-shape fibre [130] (b) Graphene-based mode-locked fibre laser [131] (c) Graphene coated D-shape MMF for gas sensing [132].

Owing to these advantages, there are plenty of photonic devices fabricated via wet transfer, such as fibre lasers [131,133], optical modulators [134–136], in-fibre polarisers [130,137] and photon detectors [138,139], and gas sensor [132].

Although all the photonic devices shown in Fig. 3.2-4 are deposited by a single 2D material, the wet transfer method can be applied for multiple times to obtain stacked layer even with different 2D materials (Fig. 3.2-5) [140]. The created multiple layer called heterostructures where are frequently used in semiconductor applications.



Figure 3.2-5 Schematic of the multi-layer wet transfer method [140].

Print transfer

There is another important variation branch of mechanical transfer, which has many different names such as print transfer, pick-and-lift, van der Waals technique or sheet stamping. Nevertheless, they are basically all describing a method to transfer the target 2D materials via a piece of "transfer stamp" material (usually PDMS) at dry condition. Typically, the "transfer stamp" will have stronger van der Waals than that of 2D materials, thus the 2D materials will be adhered on the "transfer stamp" and lifted. The adhered 2D material can subsequently be transferred by the stamp material to the target substrate and then remove the "transfer stamp". This print transfer method can be used in the cases where water is not allowed, for instance water-soluble substrate. In addition, the print transfer can also create heterostructures by repeating the procedure (Fig. 3.2-6). Many BP based photonic devices were fabricated via this print transfer method [141].



Figure 3.2-6 Schematic of the print transfer method. [142]

Drop casting

Apart from the materials prepared in dry condition, such as CVD grown graphene, many 2D materials are synthesised in liquid phase. The typical procedure of drop casting method consists of the mixing the material in a suitable solvent and then dip a small droplet of that solution/dispersion at the target substrate and then evaporate the solvent. This is a simple and efficient method when the precise control of thickness is not required. There are many photonic devices fabricated by the simple drop casting method, such as the GO waveguide polariser [143].



Figure 3.2-7 Schematic diagram of the proposed GO waveguide polariser structure and top view of drop-casted GO sheet for different number of solution drops [143].

The limitation of drop casting method is obvious. It is hard to control the thickness and shape of sheet because the material will random flow in the droplet during evaporation. The flatness of the drop casted sheet cannot be controlled as well.

Spin coating

Spin coating can be considered somehow as an upgraded drop casting. A spinner is introduced to obtain the relative controlled thickness and flat surface of deposition before the solvent evaporated. This is a mature method which evenly spreads the solution or dispersion of materials to the substrate by centrifugal force and then evaporate solvent. The advantage of this method is that the thickness of the deposited layer can be well controlled by carefully design the spin speed and the concentration of the material. However, this technique shares similar limitations of mechanical transfer, that it only works well for planar substrate and in addition demands high durability of substrate. Therefore, spin coating is relatively less used in fabrication of 2D material-based photonic devices.

3.2.2 In-situ self-assembly based multilayer deposition

For many applications, there are many advantages to deposit a thin layer of 2D materials on the surface of optical fibre devices. As previous discussed (Section 2.3), the high refractive index (HRI) coating will lead to a significant improvement of the performance of fibre sensors due to the enhanced sensitivity and light-matter interaction. Moreover, the 2D materials are usually more biocompatible than the silica surface of optical fibre. However, to deposit 2D nanosheets on cylindrical optical fibre surface remains big challenge if uniformity is required.

The above-discussed, deposition methods are usually transferring 2D layer on the flatten surface of the devices. However, the conventional deposition methods are not practicable for optical fibre-based devices with the cylindrical geometry. In addition, the cylindrical geometry of fibre makes it more challenging for achieving the uniformity coverage of 2D materials on entire fibre surface. Physical vapour deposition (PVD) is commonly used to deposit gold nanoparticles [42] or metal oxide materials [144,145] on the fibre surface. However, as most 2D materials can no longer keep their properties in a high temperature condition, PVD is not a good choice.

Hereby, in order to create robust coating layer of 2D materials on the surface of fibre grating, chemical assistance is added to establish covalent or electrostatic bonding between the 2D materials with the fibre surface.

In this work, an in-situ self-assembly based multilayer deposition technology based on chemical-bonding associated with physical-adsorption is developed [146]. The deposition will be carried out at a V-groove with the fibre horizontally placed (Fig. 3.2-8) and the reagents added. A silianisation process is started with APTES (3-aminopropyltriethoxysilane), across-linking agent, giving a chemical modification of the fused-silica fibre surface. Then the presence of the amino groups (NH₂-) on the fibre surface of enables the further chemical reaction of 2D nanosheets onto the fibre. 2D

nanosheets will be adsorbed on the fibre surface when the solvent of 2D material evaporates during the deposition process. In some case, the fibre will be rotated during the deposition. The detailed i-LbL deposition method will be described in following sections for different 2D materials (i.e. GO, BP).



Figure 3.2-8 Schematic the V-groove assisted deposition.

As for different materials coating the process is slightly different, the detail of the selfassembly based multilayer deposition method will be described in next two sections for GO and BP deposition respectively.

3.3 Graphene oxide deposition on fibre

3.3.1 Deposition of GO nanosheets

For GO deposited on fibre, the in-situ assembly based multilayer was applied. The schematic of this method is shown in Fig. 3.3-1. The fibre was initially cleaned with acetone to remove the residual contaminant on fibre surface. Subsequently, this fibre was alkaline treated by immersion in 1.0 M (1.0 mol/L) NaOH solution for 1 h at room temperature to enrich the number of hydroxyl group (-OH) on the surface, and then washed with deionised (DI) water thoroughly and dried (Fig. 3.3-1a). Then, a silanisation (Fig. 3.3-1b) process was implemented, the alkaline-treated fibre was firstly immersed in 5% APTES ((3-Aminopropyl)triethoxysilane) solution (v/v in ethanol) for 1 h at room temperature to form Si-O (siloxane linkage) bonding on the surface, followed by washing with ethanol to remove unbound monomers and baked in an oven

at 70°C for 30 min to improve the stability of APTES monolayer. After this silanised fibre was incubated in 1mL of 1.0 mg/mL GO aqueous solution contained in a custommade mini-bath, which was placed on a hot plate at 42 °C for 3 h. The carboxyl and epoxy group of GO reacted with amino group of APTES-silanised fibre surface, hence GO nanosheets were gradually deposited on the fibre surface (Fig. 3.3-1c) during this process, while the aqueous solution was slowly evaporated by heating. By repeating the GO deposition process, the multilayer will be formed. When the entire fibre was emerged out of the solution, a brownish coating was observed on the fibre surface (Fig. 3.3-1d). Thereby, the most efficient way to control the coating thickness is by control the concentration of the GO dispersion.



Figure 3.3-1 Schematic of GO deposition on cylindrical fibre surface. (a) alkaline treated fibre (b) APTES silanised fibre (c) Covalent bonding between amino group and carboxyl/epoxy group (d) GO coated fibre.

Followed with this technique, a group of fibre samples were deposited with GO nanosheets with different coating cycles. As demonstrated in Fig. 3.3-2, significant difference is shown between samples with different coating cycles, because this method induced ~150 nm thickness for per coating cycle. The optical microscope image in the right column show the clear boundaries between bare and GO-coated sections, demonstrating the successful deposition on fibre surface. It is also noticeable that the surface of thin GO overlay is much smooth than that of the thick coating, as the latter one shows a lot of wrinkles. In addition, to achieve thinner coating thickness lower than 150 nm, the concentration of GO would have to be reduced.

3.3.2 Surface morphology of GO-coated fibres



Figure 3.3-2 Optical microscope images of GO coated fibre, the left column is the central part of the coated fibre and the right column is the boundary between the coated and uncoated part, where the coating procedure is repeated for (A) 1 (B) 3 (C) 5 (D) 7 (E) 9 times, respectively.

Apart from the optical microscope image, the GO-deposited fibre surface was also examined by SEM, and AFM and Raman spectroscopy. Fig. 3.3-3 provides the SEM image of the thin (~50 nm, 1 deposition cycle with GO concentration 80 μ g/mL) and thick (~500 nm, 1 deposition cycle with with GO concentration 1.0 mg/mL) overlays, respectively, where both of the GO nanosheets have been deposited onto fibre to form a homogeneous layer over the entire cylindrical surface. It is clear that the thin overlay looks smooth while lots of wrinkles starts to show on the thick overlay which is in strong agreement with the microscope image. This may due to the defects on the basal plane would accumulate and enlarged.

Subsequently, the AFM images of coated and uncoated boundary are displayed to estimate the GO overlay thickness. As shown in AFM tapping mode topographic image (Fig. 3.3-4), the well-controlled GO-bare boundary can be used to estimate the thickness of the coating thickness. The thickness of GO overlay is identified as around 49.2 nm (with GO concentration 80 μ g/mL) for the thin coating and 501.8 nm (with GO concentration 1.0 mg/mL) for the thick layer, respectively.

In further, to examine the chemical composition of the deposited materials, Raman spectroscopy is one of the most powerful tools used to characterise the properties of carbon-based materials. Renishaw Raman Microscope 1000 (with 632.8 nm light) was used to characterise the coating. The Raman spectrum has been depicted in Fig. 3.3-5. In comparison with bare fibre, the Raman spectrum of GO coated fibre presented as red curve in Fig. 3.3-5 consists of three prominent peaks assigned to the first order D (1335 cm⁻¹) and G modes (1599 cm⁻¹) and the second order 2D mode (~2682 cm⁻¹) indicating the presence of GO. The D mode is assigned to local defect and disorder of GO caused by attachment of hydroxyl and epoxide groups on the carbon basal plane and edges. The G mode is due to the first order scattering of the E_{2g} plane of sp² carbon atoms. As other chemicals such as APTES and NaOH are not significant in the Raman results, this deposition technique is considered to have good performance.


Figure 3.3-3Scanning Electron Micrograph of GO-fibre surface with (a) thin overlay (b) thickoverlay, at 15 kV (Scale bar: $30 \ \mu m$).



Figure 3.3-4 Atomic Force Micrograph of step boundary with the measured GO overlay thickness of (a) 49.1 nm for thin overlay and (b) 501.8 nm for thick overlay.



Figure 3.3-5 Raman spectroscopy spectrum of the GO coated fibre surface.

3.3.3 Optical properties with GO deposition

The optical properties of the GO coated fibre gratings is also investigated as GO is predicted to have the potential to enhance the light-matter interaction. According to the analysis in Section 2.3, an overlay with well controlled thickness can enhance the sensitivity of the fibre grating to refractive index change, and the difference in coating thickness will also induce different optical effect to fibre grating. A long period grating (LPG) was used to characterise the optical evaluation. Multiple deposition cycles were implemented to deposit the GO nanosheets on the LPG. The SRI response was conducted with a set of aqueous sucrose solutions of that LPG was recorded. The solutions with concentrations of 0%, 10%, 20%, 30%, 35%, 40%, 45%, 50%, 55% and 60% were prepared with the measured refractive indices of 1.332, 1.347, 1.362, 1.378, 1.388, 1.400, 1.409, 1.419, 1.430, 1.441 and, 1.453 respectively. The bare or GO coated LPG was placed in a straight V-groove with two ends fixed and the solution was added into V-groove by careful pipetting to cover the entire grating region. After each measurement, both grating device and V-groove were rinsed with methanol and DI water thoroughly. The spectra evolution of transmission spectrum against different SRI for coating cycles at 0, 1, 4, 7 are plotted in Fig. 3.3-6.



Figure 3.3-6 The evolution of LPG transmission spectra against SRI of (a) bare LPG and GO coated LPGs at (b) one (c) four and (7) seven deposition cycle, respectively.

The spectrum behaviours of bare and GO-coated LPG show big difference against the surrounding RI change. For bare LPG (Fig. 3.3-6a). the grating resonance only shows the wavelength blue-shift and the peak intensity remains in similar level. For GO-coated LPGs (Fig. 3.3-6 b-d), the resonance shows dramatic shrink as well as the wavelength blue-shift whilst the surrounding RI increases. The wavelength shift against the SRI for bare LPG and one-cycle GO coated-LPG is plotted in Fig. 3.3-7(a), giving more than 50% enhancement at low RI region (1.33-1.36). For seven-cycle GO coated-LPG (thick coating layer), the spectral behaviour is significantly different with the bare LPG, where the spectral response to the SRI change starts to show irregular behaviour. The wavelength shift for a thick GO coating LPG is starkly reduced to near 0 in some RI region and even showing red-shift at very high RI region as the next order mode start to take place of the original cladding mode (Fig. 3.3-7b). This phenomenon was reported in some previous work with carbon nanotube coated LPG [147,148].

However, the intensity change of this case start to take place of the wavelength shift to be the key indicator of surrounding medium variation, as it becomes monotonic and significant as the SRI increasing. Additionally, form the spectrum of the C4 case, where the GO coating thickness is intermediate, the turning point of the wavelength domain towards intensity domain can be sensed.



Figure 3.3-7 LPG resonant wavelength shift against surrounding RI change. (a) 1-cycle GO deposition and (b) 7-cycle GO deposition.

3.4 Black Phosphorene deposition and its optical effect

3.4.1 Synthesis of BP nanosheets

The BP nanosheets were synthesised by using a liquid-phase exfoliation method [149], in this work the solvent was changed with absolute ethanol. As shown in Fig. 3.4-1, (i) 25 mg bulk BP was cut and grinded into small pieces then added to 25 mL absolute ethanol; (ii) The BP dispersion was sonicated by a cell crasher at 25 kHz and 1200 W for 3h to break the van-der Waals stack of BP, where the temperature of solution was kept below 277 K with an ice bath; (iii) The as-prepared dispersion was centrifuged at 5000 rpm for 15 min; (iv) the supernatant containing few-layered BP nanosheets was decanted gently for further usage.

The properties of the as-prepared BP nanosheets were consequently characterised by AFM and Raman spectroscopy. As shown in Fig. 3.4-2, the nanosheets size are ranging form 50-250 nm with the thickness from 7-24 nm. This indicates that the nanosheets are mostly having few layers structure. The Raman spectra of the BP nanosheets and bulk BP are also displayed in Fig. 3.4-2 (c), which present three characteristic peaks, including A_g^1 (at ~362 cm⁻¹), B_{2g} (at ~440 cm⁻¹) and A_g^2 (at ~466 cm⁻¹), where the A_g^1 corresponds to atoms oscillate out-of-plane while B_{2g} and A_g^2 correspond to atoms vibrate within the plane.



Figure 3.4-1 Schematic representation of synthesis of BP nanosheets (i-iv) and deposition process of BP nanosheets on fibre device surface (v-vii).



Figure 3.4-2 (a) Atomic Force Micrograph of the as-prepared BP nanosheets (b) The measured height profile of the typical nanosheets in the micrograph (c) The Raman spectrum of BP nanosheets compared with the bulk BP.

Moreover, it is also noticeable that the spectrum of BP nanosheets is slightly different from the bulk BP, an approximately 1 cm^{-1} shifts toward high wavenumber. This is due to the first-principles linear response method from Fei et al. [150], the effect of the zigzag and armchair strain on the puckered honeycomb structure of the black phosphorus [151].

3.4.2 BP deposition on optical fibre

For BP deposition procedure based on the in situ self-assembly based multilayer technique demonstrated in Fig. 3.4-1 (v-vii) The deposition process consists of: (v) The section of fibre over TFG region was rinsed with acetone to clean the surface from any contaminants. Thereafter, the alkaline treatment was carried out by immersing the fibre device in 1.0 M NaOH solution for 1 h to enrich the number of -OH groups on the fibre surface, then washed with DI water and ethanol thoroughly; (vi) A APTES-silanisation procedure was followed by incubating the fibre in freshly-prepared 5% APTES for 2 h to form Si-O-Si bonding; (vii) The fibre was fixed into a homemade microchannel container where 30 µL BP dispersion was carefully added. Due to positively charged amino groups on the APTES-silanised fibre surface, the negatively-charged BP nanosheets were adhered to fibre by electrostatic force. Upon solvent evaporation and drying, the physical adsorption effect played important role. After the solvent fully evaporated, the fibre surface was dried and coated with BP nanosheets. Subsequently, the second deposition cycle was conducted. In each cycle, BP dispersion (30 μ L) was added in microchannel container where ethanol solvent was evaporating gradually and totally, such drying process enhanced the physisorption of BP nanosheets on fibre surface. After multiple cycles (i.e. 8 cycles), the BP-coated TFG was rinsed by absolute ethanol to remove non-adhered BP nanosheets, dried and stored in a vacuum environment to enhance the self-assembly based multilayer adhesion before further uses. The transmission spectra of BP-TFG were monitored in real-time during the entire BP deposition process, which will be discussed later.



Figure 3.4-3 Microscope image of BP deposited fibre surface (a) without and (b) with APTES silanisation process.

It is worth mention that, for BP deposition, crosslink is even more important because BP doesn't have any functional groups. BP is not able to form covalent bond with the silica fibre directly, and the van der Waals force between fibre and BP nanosheets is usually too weak to form stable overlay on its own. Fortunately, the as-prepared BP is examined to have weak negative charge, hence the electrostatic force can be used to benefit the BP deposition. Here, APTES is used as the crosslink as the amino group can be electrolysed to be positive charged in liquid phase. However, the function of APTES here is differ from that of GO deposition, the positive charged amino group in this case is to enable electrostatic self-assembly (ESA) rather than form any covalent bounding in the case of GO deposition. To exam the effect of APTES-silianisation, two fibre samples were used for the test. The same deposition procedure was implemented, and only one of them was silanised by APTES-silianised fibre surface where only small amount BP nanosheets are adsorbed on the fibre surface without silanisation.

3.4.3 BP-fibre surface morphological characterisation

The surface morphological characterisation of BP on fibre was investigated detailly. In the microscope image of Fig. 3.4-4(a), it shows a successful overlay coated on fibre surface. Subsequently, Raman spectroscopy was used to characterise the coating material. The Raman spectrum in Fig. 3.4-4(b) presents three characteristic peaks as above, indicating the presence of black phosphorus [152] without significant property change. The surface coverage of BP was further examined by SEM with the magnification of $1000 \times$ (Fig. 3.4-4c) and $10000 \times$ (Fig. 3.4-4d). The BP nanosheets are densely covered on the fibre and BP overlay is quite homogeneous over the entire cylindrical surface demonstrating the high-quality BP deposition.



Figure 3.4-4Surface morphology of BP-coated fibre. (a) Microscope image (scale bar: $50 \ \mu m$), (b)Raman spectrum, SEM images with magnification of (c) $1000 \times$ (bar: $10 \ \mu m$) and (d) $10000 \times$ (bar: $1 \ \mu m$).



Figure 3.4-5 Atomic force micrograph topographic, profile of BP coating boundary (inset: height profile of BP overlay of (a) 3 cycles coating, (b) 5 cycles coating and (c) 8 cycles coating. (d) The 3D profile image at the boundary of 5 cycles coated fibre.

The thickness of BP overlay depends on the operation of deposition. With the flexibility of i-LbL deposition technique, the overlay thickness can be prospectively controlled by the number of coating cycles. As displayed in Fig. 3.4-5, the thickness of BP overlay with 3, 5 and 8 coating-cycles is 120.0 nm, 202.8 nm and 323.1 nm respectively. Moreover, the BP overlay thickness was kept in a good trend with about 40 nm per deposition cycle. Both 2D and 3D AFM images show the clear boundary between the uncoated and BP-coated fibre sections.

3.4.4 Optical effect of the BP coating

The RI sensitivity of the BP-coated TFG was also examined also by applying the aqueous sucrose solutions with RI ranging from 1.332 to 1.414 as surrounding media. The BP-TFG show the RI sensitivities of 189.6 nm/RIU (TM) and 172.1 nm/RIU (TE) for low RI region (1.333–1.347) refractive index, and 1563.3 nm/RIU (TM) and 1472.0 nm/RIU (TE) for high RI regions (1.430–1.441), revealing 10% to 15% SRI sensitivity enhancement overall.



Figure 3.4-6 Transmission spectra of (a) bare- and (b) BP-TFG with test solutions of different RIs. The wavelength shift comparison between bare- and BP-TFG for (c) TM and (d) TE modes.

Note that the SRI enactment seems less than that of GO coated LPG, but it does not mean the performance of BP is worse than GO, instead, it is due to various reasons. The most obvious one, there is only few information about the refractive index of BP, especially for its nanosheets form, the enhancement of BP-TFG thus may not be optimised. Even though, the existing enhancement still indicating that BP also have great potential to be a functional material in fibre optic investigations.

3.5 Chapter summary

In this chapter, the deposition techniques for GO and BP detailly investigated and discussed, in addition, the surface morphologies and optical properties were studied by employing optical microscope, AFM, SEM Raman spectroscopy and measurement of grating spectra. The AFM height profiles at the boundary of coated and uncoated section have been successfully referred to evaluate the 2D materials overlay. The results shown that this in-situ self-assembly based multilayer deposition technique can provide prospectively control to the overlay thickness as well as high quality of the overlay. The 2D materials-induced optical effect also have been investigated. The behaviour of the spectrum was also showing significant difference for different overlay thickness. The intensity change will become the key indicator if the coating layer is thick enough. Moreover, the optical modulation induced by coating shown obvious polarisation dependent, the TE mode will be more sensitive than TM mode in response of the increasing of coating thickness. The RI sensitivities of fibre grating devices have been enhanced by the nanomaterial coating.

Chapter 4 Label-free fibre optic biosensors

4.1 Introduction of optical label-free biosensors

The development of biosensor is extremely important for the healthcare, clinical analysis, drug discovery, and environmental and security sectors [153,154]. Biosensors are required to accurately quantify a single or a small group of specific disease marker molecules from a complex environment, which usually contains a large number of different molecules. Moreover, the analytes of small biomolecules, such as DNA, RNA, proteins, viral capsids, normally present an extremely low concentrations (i.e. smaller than the order of pg/mL). Hence, to meet all of these requirements, both sensitivity and selectivity are vitally important for biosensors.

Due to the small size, low weight and weak charge of typical biomolecules, it was challenging to detect biomolecules via physical properties. The traditional biosensors are usually based on label detection methods, where "label" is defined as any artificially induced foreign molecule attached to the target biochemical molecular. The labelled molecules are usually much easier to be measured and quantified. There are many labelling methods based on various techniques such as fluorescent labelling, isotopic labelling, chemiluminescent labelling, electrochemically active probe labelling, and nanoparticle labelling. Among them, the fluorescent-, chemiluminescent-, and nanoparticle- labelling are based on the covalent bonding while the electrochemically labelling only requires the temporary attachment. The isotopic labelling is the most unique one, where the "light" and "heavy" part of a biomolecule are separated to a detectable difference. However, these label-based detections are often suffering from the laborious labelling processes that may potentially change the intrinsic properties of the target molecule [155]. In addition, due to the number of labels on each target molecule is relatively flexible [156], quantitative analysis becomes challenging. Moreover, the labelling methods only provide endpoint results where continuous monitoring is not allowed and thus the information of binding kinetics would not be observed.

The traditional biosensor which is usually considered as time consuming, complicated, labelling required and hazardous, to overcome the defects, many of efforts have been placed to the development of label-free detection methods. For label-free biosensing, target molecules are detected in their nature forms without any label or modification, so that the in-situ detection is enabled. Furthermore, the label-free detection is not only easy and cheap to implement, but also allows for quantitative and kinetic measurement of molecular interactions. To date, many label-free detections are developed based on various techniques, including surface plasmon resonance, interferometers, slotwaveguides, ring resonators, photonic crystals and fibre gratings [157]. Despite all these techniques are fundamentally based on refractive index detection. For counterpart analytes, the biorecognition interaction will maximise the local RI change when probes and analytes are biorecognised, as the adsorbed analytes will form a "layer" on the surface of optical transducer [158]. However, for non-counterpart analytes, the adsorption effect would be low and so does the RI change. Then, selective biodetection is established based on this mechanism. It has been reported that the protein-protein interactions will lead to a RI increment at 0.18-0.19 ml/g [159,160].

In this chapter, label-free biosensors based on optic fibre gratings will be discussed. Fibre gratings can provide high sensitivity to the RI change, which is an ideal platform for label-free biosensing. Optic fibre has lots of advantages like low weight, small size, and immunity to electromagnetic interference. Moreover, Fibre gratings provide multiplexing, in-line, real-time and label-free detection. The first label-free biosensor based on fibre grating was presented in 2000 for anti-human IgG detection, with the limit of detection (LoD) of $2 \mu g/mL$ [161]. Followed by that, plenty of fibre gatingbased biochemical sensors were developed including long period gratings (LPGs) [162], tilted fibre gratings (TFGs) [43,46,163], microfibre Bragg gratings (mFBGs) [164], and LPGs in photonic crystal fibres [165] and surface plasmon resonance [44].

4.2 Principle of optical label-free biosensors

The mechanism of the fibre grating-based label-free biosensor is based on the local RI change against the biorecognition events. The probe biomolecules will be initially immobilised on the fibre device surface [161,162], the bio-recognition events between probe and target biomolecules will induce the change of local concentration of analyte hence the local RI surrounded fibre gratings [159,160], leading the optical signal change.

However, as discussed in Chap. 2, the fibre optic biosensor will not provide optimised RI sensitivity unless the surrounding RI approaches the value of fibre cladding RI. Normally the RI of the biomolecule analyte is close to buffer solution, far to the RI of fibre cladding [166,167], therefore, how to improve the sensitivity is a big challenge for the development of biosensors.

One of the early technologies is to reduce the cladding thickness by cladding etching, side polishing or fibre tapering [16–18,168], which can usually enhance the RI sensitivity by several times [19–22]. However, those approaches become more complex and increase cost in terms of requiring careful packaging to compensate for the inevitable reduction in the mechanical integrity of the fibre. Instead of sacrificing of mechanical integrity, more elegant approaches have been investigated either by novel design of grating structures and/or by the deposition of thin overlay of new materials.

Many novel grating structures were developed to enhance the sensitivity compared with regular LPGs. For example, large tilted gratings have been reported to provide a RI sensitivity of 340 nm/RIU at RI region near 1.33, which is six times higher than that of conventional LPGs [169] and becomes a good candidate for biosensing applications. In addition, TFGs can also provide higher Q-factor hence high accuracy in optical measurement [46]. Another type grating, dual-peak LPG (dLPG), has been reported to provide more than 20 times higher RI sensitivity than regular LPGs. There is a set of dispersion-turning-points exists in LPG phase-matching curves, where the extremely high RI sensitivity can be achieved [15]. These unique dLPGs have recently been developed as label-free biosensors [170,171].

An alternative strategy to enhance the RI sensitivity has also been proposed by depositing a thin film layer of a material with RI higher than that of cladding [22]. According to the simulation in Chapter 2 and previous papers [21,22], high RI layer

can enhance the RI sensitivity of fibre gratings. But, the bare silica surface of optical fibre is not ideal the immobilisation of biomolecules. A functional and biocompatible overlay is required.

To date, 2D nanomaterials are perfect candidates for the improvement of biosensing performance. Due to the unique properties of 2D materials, they are wildly involved in label-free biosensing applications. For example, graphene and graphene oxide show different affinities to ss- (single-stranded) and ds- (double-stranded) DNA. When a specific ss-DNA sequence adsorbed on the graphene basal plane, it would form a non-covalent π - π stacking binding between its rings and the hexagonal cells of graphene [172] then the graphene can be decorated. If the complementary sequence of such ss-DNA exists, the hybridisation effect between two ss-DNAs is much stronger than the former. These two ss-DNAs will form a ds-DNA and thus the π - π interaction between ss-DNA and graphene sheet is violated and so that the ds-DNA will leave the surface of graphene. Taking the advantages of 2D materials, many label-free DNA sensors have been developed [172–174].

Lack of functional groups on the surface of graphene, only a few graphene-based biosensors were reported. Alternatively, graphene oxide, an important precursor of graphene, has attracted great attentions. GO owns many properties of graphene such as large surface-to-volume ratio, high RI. It was reported the real part RI of GO is ranging from 1.7 to 2.0 [87,88], indicating it could be used to enhance the RI sensitivity. In addition, GO has excellent biocompatibility due to its rich oxygen-containing function groups. In recent years, the functionalised GO has been exploited to fabricate biosensors for drug delivery [175,176], bioimaging in living cells [175,177], the detection of cancer cell [178], glucose [179], DNA [180,181], enzyme [182], protein [183], peptides [184], and cellulose and lignin [185].



Figure 4.2-1 Schematic diagram of fibre optic biosensor comprising the dLPG coated with the graphene oxide linking layer, which provides a remarkable analytical platform for bioaffinity binding between pre-immobilised antigen and antibody (IgG and target anti-IgG).

In Fig. 4.2-1, the schematic of GO-fibre grating configuration-based biosensor is presented. A long period grating couples the light from fibre core to cladding serving as an optical transducer, the GO layer coated over the LPG surface is used to immobilise bioreceptor leaving the binding sites free for specific counterpart recognition. The kinetic binding between antibody and antigen altered the LPG transmission spectrum which can be monitored in real-time as a change of local RI, thereby eliminating the need of analyte labelling. This is able to enhance both optical sensitivity, stability and efficiency of fibre grating based biosensor. The optical signal will vary due to the effect of biochemical, bioaffinity, immunogenic interactions occurring within the evanescent field.

4.3 DNA biosensor based on dLPG

DNA biosensor technology becomes an important area of high throughput research in basic biological and disease pathways. Different immobilisation strategies have been proposed to bind oligonucleotides on the glass surface. Covalent linkage becomes the preferred approach as it allows a more stable attachment for hybridisation. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)-based conjugation is used routinely in protein immobilisation (via amino / carboxy-mediated coupling) and has also been applied to covalently attach DNA molecules to a diamond surface via the 5'-phosphate group [185].

4.3.1 Generation of the DNA biosensor

The materials used in this work include (3-Aminopropyl)triethoxysilane (APTES), 1ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 1-methylimidazole, phosphate buffered saline (PBS), and SSPE buffer Hydrochloric acid (HCl), deionised (DI) water, methanol and RI matching liquids (Range 1.300 to 1.458, Adjusted to \pm 0.0002).

The 5'-ends of oligonucleotides were modified during synthesis with the phosphate group. Oligonucleotides (Carl Roth, Karlsruhe) were designed as follows:

Probe: 5'- phosphate - GCA CAG TCA GTC GCC-3'

Complementary: 5'- GGC GAC TGA CTG TGC-3'

To obtain the dual-peak feature in the LPG, the periods ranging from 140µm to 160µm were selected and designed for the fabrication of dLPGs. 3cm-long dLPGs were UV inscribed in hydrogenated standard single-mode fibre (SMF28, Corning) by a CW frequency-doubled Ar laser (244nm) using the point-by-point fabrication method over multiple iterations. After UV inscription, the gratings were annealed at 80°C for 48 h to remove the residual hydrogen and to stabilise their optical properties.

To generate a dLPG-based biosensor, it is necessary to immobilise one of the two interacting biomolecules on the sensor surface. Fig. 4.3-1 depicts an overview of fibre optic biosensor including functionalisation steps from the bare glass fibre surface to immobilisation of bioprobes and the detection of the complementary DNA sequence. Individual steps are detailed below. The amino functionalisation has been well-documented for use in protein immobilisation [46,170,186] as determined by

fluorescent microscopy of the subsequently-immobilised protein [46,170]. Therefore, this with APTES-based silanisation was employed in this study. The glass fibre (in the region of the grating) was soaked in freshly-prepared 5 M HCl solution for 30 min, thoroughly rinsed with DI water then dried in the air (Fig. 4.3-1a). It was then immersed in a fresh, 10% solution of APTES for 50 min to generate surface primary amine groups (Fig. 4.3-1b), ready for EDC coupling. The fibre sensor was then rinsed with DI water and again air-dried.



Figure 4.3-1 Schematic diagram of biofunctionalisation of fibre optic biosensor: (a) Cleaned glass fibre surface. (b) Silanisation of glass fibre surface by APTES. (c) Covalent immobilisation of 5'-phosphorylated oligonucleotides via EDC-mediated reaction. (d) Hybridisation with the complementary oligonucleotides.

In this process, EDC and imidazole reagents led to the formation of a phosphoramidate linkage between the amino-silanised fibre glass surface and the 5'-phosphate group on the oligonucleotide, in a one-step reaction. An aqueous solution of 5'-phosphorylated oligonucleotide (5'- phosphate- GCA CAG TCA GTC GCC -3') was diluted with 30 mM 1-methylimidazole to a final concentration of 5 Mm, and 10 mg/ml EDC was added and mixed for 1 min. The amino-silanised glass fibre was immediately immersed into this oligonucleotide solution, which was placed in a closed container to avoid evaporation and incubated overnight at room temperature. After 16.5 h incubation, the glass fibre was thoroughly rinsed in DI water, dried in the air and stored in dry container at room temperature for further use (Fig. 4.3-1c). The oligonucleotide was now covalently linked to the biosensor and available for hybridisation to a complementary DNA strand (Fig. 4.3-1d).

4.3.2 Optical measurement system

All the biochemical experiments were performed in a fume cupboard (Labcaire Systems Ltd, UK). To minimise the bend cross-sensitivity, the fibre grating sensors were placed straight in a custom-made V-groove container on a Teflon plate and all the chemicals and solvents were added and withdrawn from the container by careful pipetting.

As shown in Fig. 4.3-2, in the interrogation system, broadband light sources (BBS: Agilent HP83437A, Agilent Technologies Inc.; LS-1 Tungsten Halogen Light Source, Ocean Optics Inc.) were used along with an optical spectrum analyser (OSA, Agilent HP86142A, Agilent Technologies Inc., range 600 nm to 1700 nm). The OSA was connected to a computer and the optical spectra were captured by a customised program. Data analysis was performed using that customised program which automatically defines resonance wavelengths, using the centroid calculation method.



Figure 4.3-2 Experiment setup for label-free DNA detection.

4.3.3 RI sensitivity characteristics of dLPG

An LPG in a single mode fibre couples the light from the core mode to co-propagating cladding modes resulting in the transmission spectrum containing a series of attenuation bands. Each attenuation band corresponds to the coupling to a cladding mode satisfying the phase-matching condition (Eq. 2.2-43). As discussed in Fig. 2.2-9, the "dual-peak" nature of the LPG has been reported that a set of dispersion-turning-points exists on the phase-matching curves due to the parabolic property of the group index of the higher cladding modes [24]. With a selected relatively short LPG period, the light coupling between the fundamental core mode and a higher order cladding mode leads to two attenuation peaks in the transmission spectrum with respect to the conjugate cladding mode. The graphic phase curves for a 157μ m-period dLPG are plotted in Fig. 4.3-3(a), where the dots marked on the top of the curves represent the dispersion-turning-points.

The intersection points of phase curves and the horizontal line are the wavelengths at which the phase-matching conditions are satisfied. For the 12th cladding mode, there are two resonances sitting on both sides of the turning point, and which are defined as 'blue-peak' (short wavelength) and 'red-peak' (long wavelength), respectively.



Figure 4.3-3 Dual-peak LPG fabrication process: (a) Phase-matching curves for analysis of movement of dual peaks. (b) Spectral evolution under UV exposure. Dual-peak LPG RI sensitivity experiment: (c) Wavelength shift of dLPG resonances. (d) Transmission spectrum change against SRI.

Point-by-point and multiple scanning methods were employed to inscribe the dLPG (3cm-long, 157 μ m-period). During the UV inscription process, the dLPG spectra were recorded. Development of the dual-peak characteristics can be clearly observed during the multiple scans (Fig. 4.3-3(b)). After the first cycle of UV exposure, there was no noticeable peak (Fig. 4.3-3(b), black). In the second cycle, two resonances initially appeared at 1180 nm (LP_{0,12}^{blue}) and 1630 nm (LP_{0,12}^{red}), (Fig. 4.3-3(b), green) which moved towards each other with subsequent inscriptions (Fig. 4.3-3(b), orange and purple). During the third cycle (Fig. 4.3-3(b), orange), dual peaks were moving closer and growing stronger while a new resonance corresponding to the LP_{0,11} cladding mode was generated at 1010 nm. With further UV exposure in fourth cycle (Fig. 4.3-3(b),

purple), the dual peaks moved more closer and became stronger, whereas the $LP_{0,11}$ peak showed only a small red-shift. The spectral evolution can be explained by Fig. 4.3-3(a). Success of UV exposure increased the core effective refractive index, causing the phase curve to move downwards (Fig. 4.3-3(a), green \rightarrow orange \rightarrow purple). Thus, the two intersection points ($LP_{0,12}^{blue}$ and ($LP_{0,12}^{red}$) corresponding to the same $LP_{0,12}$ cladding mode made a large movement wherein the separation between these intersections reduced from 450 nm to 150 nm (Fig. 4.3-3(a), red and blue dotted arrows). This movement, as dual peaks close towards the dispersion-turning- point, forms the basis for an extremely sensitive detector. Thus, as the UV inscription progressed, the blue-peak was red-shifted whereas the red-peak made the opposite blue-shift. In contrast, the movement of the phase curve with successive UV inscriptions has relatively little effect on the $LP_{0,11}$ peak, causing only a slight red-shift and a weak increase in intensity strength.

The RI sensitivity was investigated by immersing the dLPG in a set of index gels (Cargille Lab Inc. US). The spectrum was measured for each RI value, the wavelength shift of dLPG resonances are plotted in Fig. 4.3-3(c) and the spectral features are depicted in Fig. 4.3-3(d). Over the range of RIs from 1.30 to 1.44, the red-peak is further red-shifted with increasing RI, whereas the blue-peak is further blue-shifted. In contrast, the LP_{0.11} peak shows only a slight blue-shift with increasing RI. It can be seen from Fig. 4.3-3(c) that the resonances move nonlinearly with an increasing trend over the whole RI range. The total wavelength shifts of $LP_{0,11}$, $LP_{0,12}^{blue}$ and $(LP_{0,12}^{red})$ are -10.6 nm, -111.7 nm, and +225.0 nm respectively (with a calculated estimation for the final redpeak which had moved out of the detectable range). The detail of RI characteristics for different peaks are compared and listed in Table 4.3-1. It is particularly noteworthy that both the blue and red peaks show an ultrahigh RI sensitivity of -2914 nm/RIU and +7488 nm/RIU in the high RI range (1.432 to 1.44; Table 4.3-1), respectively, whereas the LP_{0,11} peak has a low sensitivity of -288 nm/RIU. The blue and red peaks also show high RI sensitivity of -564 nm/RIU and +794 nm/RIU, respectively, in low RI range (1.30 to 1.35; Table 1) - the range in which bioassays and biochemical events are usually carried out. The maximum RI sensitivity (794 nm/RIU) in low range RIs of 1.30-1.35 of this dLPG is more than 50 times higher than that of previously reported 370 µm-period LPG sensor, which only achieved an RI sensitivity of 15 nm/RIU around 1.33 RIU [187]. Hence, biosensors based on dLPGs should achieve comparable or

better performances with respect to the standard LPG or mFBG based biosensors [164,187].

Resonance	LP _{0,11}	LP ^{blue}	LP ^{red} _{0,12}
High RI (n: 1.432-1.44)	-288	-2914	+7488
Low RI (n: 1.30-1.35)	-26	-564	+794

Table 4.3.1 Parameters applied in simulation of this section.

4.3.4 Oligonucleotide immobilisation and evaluation

The bio-functionalisation of the dLPG sensor was determined by monitoring the spectral evolution of dLPG in situ throughout the cleaning, silanisation and immobilisation processes. A 3cm-long dLPG with a period of 158.5 μ m was used for this experiment. As shown in Fig. 4.3-4(a), there are three resonances within the observed wavelength range. Consistent with previous observations (Fig. 4.3-3(d)), when transmission spectra were measured in different RI media, separation between peaks in the 1300-1700 nm increases with increasing RI, which confirms that they are dual peaks corresponding to the same conjugate cladding mode. In this case, the blue-peak at 1422 nm (in water) was selected for the following experiments.

Fig. 4.3-4(b) shows the transmission spectra of this peak, captured in DI water, after HCl cleaning, APTES silanisation, and oligonucleotide immobilisation, respectively. A clear blue-shift has occurred in response to this biofunctionalisation procedure. Specifically, the silanisation has induced a relatively small blue-shift of -1024 pm whereas the immobilisation has moved the peak by a further -2320 pm. Clearly, the APTES- modification and the attachment of 5′-phosphorylated oligonucleotides on the fibre surface have changed the effective index of cladding, indicating the successful immobilisation.

The dLPG sensor with immobilised oligonucleotide was next hybridised with a complementary oligonucleotide (5'- phosphate- GCA CAG TCA GTC GCC -3'). Following DNA immobilisation (Fig. 4.3-1(c)), the dLPG sensor was washed in DI water and rinsed in 6×SSPE buffer (0.9M NaCl, 0.06M NaH₂PO₄, and 0.006M EDTA)

for 10 min, then immersed in fresh 2 μ M complementary oligonucleotide in 6×SSPE buffer and allowed to react at room temperature for 60 min.



Figure 4.3-4 Dual-peak (a) dLPG spectrum measured in different surrounding media. (b) Spectra captured in DI water after cleaning, silanisation and oligonucleotide immobilisation.

4.3.5 Label-free DNA detection

The blue-peak described above was monitored in situ throughout the whole hybridisation process. As can be seen from Fig. 4.3-5, the resonant peak shows a blue-shift of -1044 pm over the whole hybridisation process. There are three stages associated with the 60 min DNA hybridisation. A rapid reaction occurs in the first 3 min with the wavelength shift of -490 pm, which equates to a detection sensitivity of 245 pm blue-shift per μ M DNA (or 4 nM DNA per pm blue-shift). This initial reaction is followed by a steady process (3 to 20 min) with the wavelength shift of -216 pm, and finally a much slower reaction (20 to 60 min) with the shift of -338 pm. Thus, maximum sensitivity occurs in the first 3 mins.

The dLPG-based biosensor could be used to study binding kinetics. The sensor measurements were rapid (503 ms per full scan for the selected 'blue-peak') and in the current study the measurements were taken every 30s for the first 20 mins. However, the measurement time could easily be reduced to 1 scan/s and the resulting data used to give kinetic analyses of initial rates of binding. Finally, if the noise effect could be eliminated effectively by using an optical interrogation system with 1 pm resolution, this would theoretically lead to a detection sensitivity of 4 nM oligonucleotide concentration, which would be two orders of magnitude lower than the microfibre Bragg grating based DNA biosensor reported previously [164].



Figure 4.3-5 Wavelength shift against time during the DNA hybridisation (detection) process.

4.4 GO-dLPG based immunosensor

4.4.1 Fabrication of the fibre optic immunosensor

The following materials were used for generation of label-free immunosensor:

GO aqueous dispersion (2 mg/mL), Sodium hydroxide, APTES, EDC, NHydroxysuccinimide (NHS), Bovine serum albumin (BSA), Rabbit IgG, Goat Anti-Rabbit IgG, phosphate buffered saline (1×PBS, pH 7.4) HCl), methanol, ethanol, acetone, and DI water. All chemical and biochemical reagents were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with DI water. The silica single-mode fibre (SMF-28, cladding diameter of 125 μ m).

The dLPG with period of 162 μ m and length of 30 mm was inscribed in a hydrogenated single-mode fibre by a CW frequency doubled Ar laser at 244 nm wavelength. The point-by-point method over multiple iterations was employed to achieve the dual-peak

feature. After UV fabrication, the dLPG was annealed at 80 °C for 48 h to remove the residual hydrogen and to stabilise the optical properties 125 μ m) was purchased from Corning.

Fig. 4.4-1(a-c) demonstrates the GO deposition which is followed the procedures described in Section 3.3, here the GO concentration is 80 μ g/mL to make a relatively thin overlay. The surface morphology has been displayed Fig. 3.3-4(a).



Figure 4.4-1 Schematic illustration of fibre optic biosensor based on GO-coated dLPG: (a) dLPG silica fibre surface with alkaline treatment, (b) Silanisation by APTES, (c) GO deposition, (d) IgG immobilisation via EDC/NHS, (e) Passivation of unreacted sites by BSA blocking solution, (f) Binding interaction between probe bioreceptor (IgG) and target analyte (anti-IgG).

The biomolecules were immobilised to the surface of GO-dLPG. The covalent immobilisation of IgG on GO-dLPG surface might lead to improper orientation by masking antigen-binding sites. This shortcoming can be circumvented by using heterobifunctional cross-linkers of EDC/NHS combination [59]. The GO-coated dLPG was immersed into a mixture of 20 mM EDC and 40 mM NHS in 0.01 M PBS buffer for 1 h. Subsequently, the GO surface was immobilised by IgG through sinking the GOdLPG into a solution of rabbit IgG with a concentration of 1 mg/mL for 2 h. The large 2D aromatic surface of GO made it ideal for biomolecules binding. GO reacted with EDC to yield a stable active ester in the presence of NHS while the ester reacted with the amine group of IgG to form a covalent immobilisation leaving the binding sites free for angi-IgG recognition (Fig. 4.4-1(d)). The non-bound IgG was washed away by 1×PBS buffer solution which was adjusted to a pH of 7.4. The unreacted sites on GO surface were passivated by BSA, the IgG-immobilised GO-dLPG was immersed into 1% BSA solution for 30 min to block the remaining activated carboxylic group and to prevent non-specific adsorption onto GO surface (Fig. 4.4-1(e)). Here, the IgG-bound GO-dLPG was ready as a biosensor for the detection of target anti-IgG (Fig. 4.4-1(f)).

Then as discussed before, the RI sensitivity of the dLPG is doubled at the RI region where bioassays and biological events carried out.

4.4.2 Immuno-sensing set-up

In the interrogation system, broadband light source (BBS: Agilent HP83437A, Agilent Technologies Inc.) was used along with an optical spectrum analyser (OSA, Agilent HP86142A, Agilent Technologies Inc.). The OSA was connected to a computer and the optical spectra were captured by a customised program. Data analysis was performed using the customised program which automatically defined resonance wavelengths using the centroid calculation method. All biochemical experiments were performed in a fume cupboard. All procedures were conducted at a controlled room temperature of 22.0 ± 0.1 °C unless specified otherwise. The long period fibre grating was illuminated with the light from the broadband source and the transmission spectrum was monitored in real-time by using the OSA. To minimise the bend cross-sensitivity, the fibre grating region was placed straight in a custom-made V-groove container on a Teflon plate and all the chemicals and solvents were added and withdrawn by careful pipetting.

The schematic diagram of this set-up is basically a combination of Fig. 4.2-1 and Fig. 4.3-2 which contains similar structure with DNA detection but having a GO sensitising layer and BSA blocking layer at grating surface.

4.4.3 Refractive index sensitivity characteristics of GO-dLPG

The RI sensitivities of bare and GO-coated dLPGs were investigated and compared by immersing the devices in a set of aqueous sucrose solutions. The solutions with concentrations of 0%, 10%, 20%, 30%, 35%, 40%, 45%, 50%, 55% and 60% were prepared with measured RIs of 1.3326, 1.3471, 1.3625, 1.3820, 1.3917, 1.4004, 1.4101, 1.4218, 1.4300 and 1.4413, respectively. The fibre sensor was placed in a V groove while the sucrose solution samples were added by careful pipetting to cover the entire grating region. After each measurement, both fibre sensor and V groove were rinsed with methanol and DI water thoroughly.

Fig. 4.4-2 (a) and (b) plot the evolution of transmission spectrum against different sucrose concentrations for bare dLPG and GO-dLPG, respectively. Dual peaks move

to opposite directions when SRI increases, in which the red-peak $LP_{0,12}^{red}$ moves to the long wavelength while the blue-peak $LP_{0,12}^{blue}$ shows a blue shift. In contrast, the $LP_{0,11}$ peak only shows a slight blue shift. As it can be seen in Fig. 4.4-2 (b), the intensities of GO-dLPG dual-peaks are significantly reduced when the SRI increases, this is consistent with the previous results. For a long period grating coated with high RI and thin layer, the cladding guided modes are partially radiated to the overlay behaving as leaky modes. The coupling coefficient between optical modes is a function of the SRI. The increasing SRI reduces the overlap integral between core and cladding modes, hence the decreasing of resonant intensity. When the SRI approaches that of cladding, the core mode will be coupled to the broadband radiation mode with no distinct attenuation bands.



Figure 4.4-2 Transmission spectra of bare dLPG (a) and GO-dLPG (b) measured in different sucrose concentrations.

The SRI sensitivity of the dual peak case is not increased absolutely because the GO coating pushed the grating working point out of the turning point (described in Chapter 2, Fig. 2.2-8). However, if the key indicator is chosen as the separation of the dual peak, the sensitivity is still significant enhanced. In this case, the GO-dLPG show the RI sensitivities of 2538 nm/RIU and 8956 nm/RIU for low (1.333–1.347) and high (1.430–1.441) RI regions respectively, while the blue symbols of non-coated dLPG give sensitivities of 1255 nm/RIU and 5761 nm/ RIU for the corresponding RI regions. The RI sensing mechanism relies on the sensitivity of long period grating's attenuation bands to the properties of overlay material, such as refractive index and the thickness. With a proper GO thickness of 49.2 nm, the RI sensitivities of GO-dLPG have been improved 200% and 155% those of non-coated dLPG for low and high RI regions,

respectively. The GO deposition enhances the light-matter interaction between cladding and surrounding medium leading to the increase of RI sensitivity.

4.4.4 Optical response to the functionalisation

The optical responses of GO deposition and IgG immobilisation were determined by monitoring the transmission spectra. Fig. 4.4-3 depicts the transmission spectra captured in DI water for bare, GO-coated, , and IgG-immobilised dLPG. As shown in the figure, both the separation and the intensity of dual peaks have been increased with respect to the GO deposition and IgG immobilisation procedures. The GO deposition induces the wavelength separation from 120 nm to 155 nm while the IgG immobilisation expands it to 165 nm. It was reported that the rapid variation of the gradient of the phase matching curves near the dispersion turning points (DTP) caused the sensitivity of the particular resonant bands to environmental perturbation to be determined by its proximity to its DTP [15]. It should be noted that the GO deposition has tuned dual peaks away from its DTP (Fig. 4.4-3) which might sacrifice the bulk RI sensitivity of dLPG device.



Figure 4.4-3 Spectra evolution of bare, GO-coated, and IgG-immobilised dLPG.

4.4.5 Label-free anti-IgG immunosensing

The advantage of fibre grating based biosensor was that signal response was obtained continuously in the concentration- dependent manner in which signal was monitored in real-time. The feasibility of GO-dLPG immunosensor was performed by using rabbit IgG immobilised GO-dLPG to detect the kinetic binding with goat anti-rabbit IgG. Four consecutive processes for different goat anti-rabbit IgG concentrations of 1, 10, 50, and 100 μ g/mL were plotted in Fig. 4.4-4. For each process with the specific anti-IgG concentration, the LP^{red}_{0,12} peak of GO-dLPG was monitored in-situ throughout whole process.



Figure 4.4-4 (a) Wavelength shift against time during IgG and Anti-IgG binding interaction processes. Transmission spectra of GO-dLPG ($LP_{0,12}^{red}$ peak) (b) during PBS prewashing stage and (c) during kinetic binding in 1 µg/mL anti-IgG solution.

As shown in Fig. 4.4-4, each process was performed in three stages: i) Prewashing the rabbit IgG-immobilised GO-dLPG with PBS buffer (1×PBS, pH 7.4) for 5 min, providing a stable baseline over which the peak signal was monitored (Fig. 4.4-4(b)). ii) Kinetic binding stage when the IgG-immobilised sensor was immersed in goat anti-rabbit IgG solution. The first 3 min was a rapid reaction process during which the grating peak moved to the long wavelength dramatically (Fig. 4.4-4(c)), followed by a

27 min steady process when the signal was moving gradually and achieving the saturation finally. iii) A subsequent rinsing with PBS buffer thoroughly to remove unbound anti-IgG prior to the next measurement for another anti-IgG concentration. One may realise that for each binding stage, the wavelength response is a relative slow change process, and the resonance peak will not recover to the initial wavelength even after washing process.

This response behaviour can be explained by the dynamic interaction nature of the biomolecule. In this case, antibody and antigen will repeat binding and unbinding process even the analyte solution was kept static during detection. In first serval minutes, as most binding sites of bioprobes (IgG) were unoccupied, the reaction rate can be very fast. Then, when most binding sites were occupied in later minutes, the reaction reached equilibrium which means the binding rate is equal to the unbinding rate. In the washing stage, the remaining biomolecules on the bioprobes will be very hard to unbind due to the quickly rising binding energy. The PBS washing are thus not able to throughoutly remove the previous binding molecule, and hence the wavelength shift was accumulated.



Figure 4.4-5 Wavelength shift against time during IgG and Anti-IgG binding interaction processes. During four antibody-antigen binding processes, the grating peak wavelength shifts as absolute change in refractive index after deducting the baseline signal in PBS were 1470, 1730, 2415, and 1960 pm for anti-IgG concentrations of 1, 10, 50, and 100 μg/mL,

respectively. The slight decrease in the 4th binding process (e.g. 100 μ g/mL anti-IgG) indicated the gradual depletion of binding sites on sensor surface. The wavelength shift corresponding to the total amount of antibody-antigen binding was 4735 pm. The wavelength shift of LP_{0,12}^{red} peak as a function of the concentration of each anti-IgG solution has been plotted in Fig. 4.4-5. The red line provides the best logistic curve fitting of the experimental data, whereas the dashed line represents the wavelength change three times the standard deviation of the blank measurement in PBS buffer. For this GO-dLPG based biosensor, the limit of detection (LOD) of 7 ng/mL is achieved, which is defined as three times the standard deviation of the blank measurement (Fig. 4.4-5). This LOD is 10- fold better than non-coated dLPG based biosensor [162] and 100-fold lower than LPG-based immunosensor [161].

It is noticeable that the RI sensitivity enhancement is only about 200%, while the enhancement of biosensing performance is much larger than this value. It proves that the GO coating not only provides increasement in RI sensitivity at low RI region but also plays important role in the enhancement of binding efficiency. The mechanism of biosensing is that the bioaffinity binding changes local refractive index at the GO-analyte interface, where the evanescent light penetrates, and induces an optical signal change. The sensitivity of the GO-dLPG biosensor can be defined as the ratio of the change in optical signal to the changes in the measurement quantity. The biosensor sensitivity is given by:

$$s = \frac{\Delta\lambda}{\Delta C} = \frac{\Delta\lambda}{\Delta n} \frac{\Delta n}{\Delta C} = S_{RI}E$$
(5.4-1)

where $\Delta\lambda$ is the wavelength shift, ΔC is the change of the analyte concentration, and Δn is the corresponding refractive index change. The affinity binding between antibody and antigen alters the local analyte concentration (ΔC), increasing the local refractive index (Δn) at device and surrounding-media interface, hence induces the optical signal change with the corresponding wavelength shift ($\Delta\lambda$). Therefore, the biosensor sensitivity comprises of two parts: sensitivity to refractive index change S_{RI} and the binding efficiency E. The efficiency depends on the property of sensor surface, the number of binding sites, and the type of bio-analyte. Due to the inherently high surface-to-volume ratio, enriched functional groups and excellent optical and biochemical properties, the usage of GO as a bio-interface linking layer provides large number of binding sites, high immobilisation density, great biocompatibility and stability, and

strong interference of optical waves. The GO-dLPG exhibits not only the enhancement of RI sensitivity but also the extremely higher efficiency, ensuring remarkable performance for biosensing applications with the advantages of label-free, real-time, ultrahigh sensitivity and competitive limit of detection.





Figure 4.4-6 Reusability of the GO-dLPG based immunosensor.

For the practical applications, the reusability is an important and must-have function. To this end, the reusability has been demonstrated by regenerating the biosensor surface activity with HCl treatment. The above IgG/anti-IgG bound sensor was submerged into 0.01 M HCl solution for 10 min at room temperature, which formed a low pH environment (pH 2.0) and broke the bonds between IgG and anti-IgG, then rinsed with PBS buffer and dried. After stripping off the anti-IgG, its reusability was confirmed by detecting the binding interaction in 1 μ g/mL goat anti-rabbit IgG for multiple times. Fig. 4.4-6 presents the comparison results for three cycles with the percentages of peak signal and initial binding rate.

The maximum peak signal as the absolute change in RI after reducing the baseline signal in PBS prewashing stage retained 90% and 76% after 2nd and 3rd cycle, respectively. Likewise, the initial binding rate calculated with the data over the first 1

min of binding interaction kept greater than 89% and 94% after 2nd and 3rd cycle, respectively. These results confirmed that the GO-dLPG biosensor was possible to measure the antibody-antigen binding for multiple times. Herein, the detail of the kinetic binding interaction is shown in Fig. 4.4-7. It is clearly shown that despite the difference in the total wavelength change and binding rate, the majority trend of the interaction remains similar. This indicates reduction in response and binding rate are the results of bioactivity decreasing of the bioprobes.



Figure 4.4-7 Wavelength response corresponding to the kinetic binding interaction between antibody and antigen when IgG-immobilised GO-dLPG was incubated in 1 μ g/mL anti-IgG solution for (a) cycle 1, (b) cycle 2, and (c) cycle 3.

4.5 GO-LPG based biosensor for haemoglobin detection

Many diseases can be diagnosed by measuring the level of haemoglobin. For example, anaemia is a common concern in geriatric health with estimated prevalence increasing with advancing age [188,189]. Anaemia is typically defined using the World Health Organisation (WHO) criteria of haemoglobin levels lower than 130 mg/mL for men and 120 mg/mL for women [190]. Anaemia has serious consequences for some clinical and functional outcomes in the elder population. Abnormal blood haemoglobin concentrations always relate to other diseases, such as thalassemia, stroke and diabetes [191,192]. It has been reported that an almost 2-fold increase in the occurrence of Alzheimer disease among patients with anaemia [193]. The impact of anaemia on quality of life, functional abilities and recovery from illness must be received much clinical attention.

It was reported in previous work that hemin and graphene can also form a hybrid structure with the π - π stacking interaction [194]. With its high RI and biocompatibility, GO can be an ideal sensing layer for bio-detection. So far, the sensing performance for thin 2D material layer has been examined, while that of thick layer coated fibre grating (intensity-based sensing) is not demonstrated yet. On this side, there are some previous works have reported to achieve high intensity-based RI sensitivity by coating carbonnano-tube (CNT) and metal oxide layer on conventional LPGs [144,145,147]. To compare with their work and to demonstrate the intensity-based sensing, a relatively thick GO coated LPG were carried out as the sensing platform.

4.5.1 Materials and Device

In this subsection, the biosensor was functionalised with the assistance of following materials: GO aqueous dispersion, NaOH, APTES, human haemoglobin, methanol, ethanol, acetone, and DI water.

A 15 mm-long LPG with a period of 400 μ m was UV-inscribed in H₂-loaded single mode fibre with point-by-point fabrication technique. After the UV exposure, the grating was annealed at 85 °C for 24h to remove residual hydrogen and stabilize its optical properties.

Then the GO nanosheets were coated on LPG with the developed i-LbL deposition technique as described in Section 3.3.1. Here, the GO concentration was 1.0 mg/mL.

4.5.2 Interrogation system for bio-detection

The interrogation system was employed for the measurement of optical properties of GO-LPG and biochemical sensing. As shown in Fig. 4.5-1, a broadband light source (BBS) was used to launch the light into fibre device and the transmission spectra were captured by an optical spectrum analyser (OSA, Agilent HP86140, Agilent Technologies Inc.). The data was analysed using a customised program which automatically defined the resonant wavelength and intensity by the centroid calculation method. To avoid the thermal and bend cross-talk effects, the fibre device was mounted on a homemade straight V-groove container with two ends fixed and all chemical

experiments were performed in a fume cupboard at a controlled room temperature of 22.0 ± 0.1 °C.



Figure 4.5-1 Schematic illustration of measurement system.

4.5.3 Refractive index sensitivity characteristics of GO-LPG

The LPG transmission spectra of the 7th cladding mode [15] with the central wavelength at 1591.6nm (in the air) were monitored before and after the GO deposition. It can be seen from Fig. 4.5-2 that the GO coating induces a blue-shift of 3.8 nm in wavelength and an increase of 12 dB in intensity of LPG attenuation band.



Figure 4.5-2 LPG transmission spectra before and after GO deposition.

The change of LPG resonant wavelength as well as intensity induced by the thick GO overlay (thickness of 501.8 nm) is displayed in Fig 5.4-3. There are two different trends for the RI region below and above the CRI (1.445). For the RI lower than the CRI, the intensity of the attenuation band decreases as the RI increases. This is consistent with the theoretical analysis in Section 2.2. Once the RI equals to the CRI, the cladding

modes are no longer confined by the cladding layer, which is acting as an infinite medium and supports no discrete cladding modes, hence a broadband radiation mode coupling occurs with no distinct attenuation bands. When the RI is higher than the CRI, the fibre does not support any bound cladding mode and the re-appeared attenuation band corresponds to leaky mode coupling. By increasing the RI, the resonant intensity increases because the leaky mode is better confined by the Fresnel reflection while its wavelength is influenced with a blue-shift.

The intensity change of the attenuation band against the RI is plotted in Fig 5.4-3(b). For the RI region below the CRI, the intensity shows a nonlinear behaviour for a gradual decrease with RI which is consistent with those LPGs coated with CNT, ZnO, TiO2 [144,145,147]. The sensitivity achieves -76.5 dB/RIU and -234.2 dB/RIU for RI range of 1.33-1.38 and 1.40-1.44, respectively, exhibiting 2.5 times and 5 times higher than that of CNT-deposited LPG for the corresponding RI ranges [147]. For the RI higher than the CRI, the resonant intensity increases dramatically against RI. The sensitivity approaches +1580.5 dB/RIU which is 7.3 times higher than that of ZnO-coated LPG [145]. For the case of RI=1.4615, the resonant intensity reaches -28.35 dB, indicating that around 99.8 % of core mode has been coupled into leaky mode, which is extremely high than that of metal oxide-coated LPGs [144]. The enhanced RI sensitivity of GO-LPG may be caused by the unique features of GO material, such as extraordinary large surface-to-volume ratio, high carrier mobility, and excellent optical properties. GO provides strong light-matter interaction between evanescent field and external medium.



Figure 4.5-3 (a) Transmission spectra of GO-LPG with test solutions of different RIs. (b) The variation of attenuation band intensity against the RI.

4.5.4 Haemoglobin label-free detection

The GO-LPG was performed as a biosensor to detect human haemoglobin. A set of haemoglobin concentrations ranging from 0.0 mg/mL, 0.2 mg/mL, 0.4 mg/mL, 0.6 mg/mL, 0.8 mg/mL and 1.0 mg/mL were prepared with sucrose solution (RI=1.4610) acting as RI buffer. Fig. 4.5-4(a) shows the spectra of GO-LPG under different haemoglobin concentrations and Fig. 4.5-4(a) plots the evolution of resonant intensity. It can be seen that the resonant intensity increases by 1.91 dB when the haemoglobin concentration changes from 0.0 mg/mL to 1.0 mg/mL. Defining the concentration sensitivity as the change induced by 1 mg/mL haemoglobin, the device sensitivity is calculated to be 1.9 dB/(mg/mL). If use a low-noise interrogation system with a resolution of 0.1 dB, the GO-LPG could detect a haemoglobin concentration change as small as 0.05 mg/mL, which is far below the haemoglobin threshold value for anaemia. The increase of resonant intensity could attribute to the local refractive index change caused by the adsorption of haemoglobin molecules onto GO, where the measured pH values of haemoglobin concentrations are around 7.0, hence the strongest $\pi - \pi$ interactions lead to the most effective adsorption of proteins onto GO [195,196]. Taking into account the advantages of both enhanced RI sensitivity and favourable biocompatibility, GO provides a significant sensing linkage between evanescent field and target biomolecules with enhanced light-matter interaction, consequently exhibiting ultrahigh sensitivity for haemoglobin detection.



Figure 4.5-4 (a) Transmission spectra of GO-LPG resonance and (b) the intensity change of attenuation band against haemoglobin concentrations.
Based on the results above, and because the response is intensity based and the wavelength shifts are small, the BBS and OSA in the interrogation system can be replaced by a single or narrow wavelength laser and a power meter [197]. Which does not only lower the detection threshold and the cost, but also able to benefits the sensing performance. For example, if our experiment of haemoglobin detection was conducted with the same interrogation system reported in Ref [197], and assuming the tunable laser output is set to be 1609 nm, -15 dBm, one can convert our results from the logarithmic form to the linear form with maximum and minimum power to be 1.7 μ w and 1.1 μ w respectively. Based on this assumption, the corresponding sensitivity in linear form 0.06 μ W/(mg/mL) or 0.6 μ W/%. Moreover, because a standard detector with a minimum detection power of 1nW, this device can provide limit of detection as well as resolution of 16.7 dB/(μ g/mL) which is 0.00167 dB/% in percentage.

However, the response of the grating spectrum to different haemoglobin concentration was almost static where the binding kinetics still not investigated. This kind of detection can't provide binding kinetics information because the interaction between GO and haemoglobin was not dynamic and only limited species of biomolecules can be examined by a certain 2D nanomaterials. However, this probe-free detection also having many advantages. Apart from the low cost and simplicity reasons, the kinetic binding will usually take at least 10 mins to achieve the equilibrium, while the response of probe-free detection method is almost immediate. Hence, if conditions permitted this kind of biosensing based on the interaction between biomolecules and 2D nanomaterials are even more popular than the complementary based detection.

4.6 Chapter summary

In this chapter, three types of fibre grating-based label-free biosensors were demonstrated. Both novel design of grating structures and/or by the deposition of thin overlay have been used to improve the performance of the biosensors. In addition to simply enhance the refractive index sensitivity, this chapter also focusses on the of biofunctionalisation methodology such as immobilisation of bioprobes. Chemicals such as EDC and NHS can play important role in the biomolecules immobilisation. With the help of EDC, the unmodified oligonucleotides can be simply immobilised on the glass fibre surface in a one-step reaction. Furthermore, the GO linking layer provides a remarkable analytical platform for bioaffinity binding interface due to its favourable combination of exceptionally high surface-to-volume ratio and excellent optical and biochemical properties. A new GO deposition technique based on chemical-bonding in conjunction with physical-adsorption was proposed to offer the advantages of a strong bonding between GO and fibre device surface and a homogeneous GO overlay with desirable stability, repeatability and durability. The first label-free biosensor presented in this chapter is a label-free biosensor based on a dual-peak LPG to detect the hybridization of oligonucleotides in real-time. The dual-peak LPG with inherent ultrahigh / high RI sensitivity has been demonstrated to detect a quantifiable optical signal corresponding to the RI change of the bio-analytes in which the biological recognition events occurred. In addition, a one-step EDC-mediated procedure has been demonstrated to facilitate the covalent immobilization of 5'-phosphorylated oligonucleotide on an amino-modified glass fibre sensor surface. The dLPG biosensor was used to monitor the hybridization of complementary oligonucleotides showing a detectable oligonucleotide concentration of 4 nM.

The second biosensor is a label-free antibody-antigen immunosensor based on GO coated dLPG. The IgG was covalently immobilised on GO-dLPG via EDC/NHS heterobifunctional cross-linking chemistry leaving the binding sites free for target analyte recognition. The performance of immunosensing was evaluated by monitoring the kinetic bioaffinity binding between IgG and specific anti-IgG in real-time. The GO-dLPG based biosensor demonstrates an ultrahigh sensitivity with limit of detection of 7 ng/mL, which is 10-fold better than non-coated dLPG biosensor and 100-fold greater than LPG-based immunosensor. Moreover, the reusability of GO-dLPG biosensor has been facilitated by a simple regeneration procedure based on stripping off bound anti-

IgG treatment. The proposed ultrasensitive biosensor can be further adapted as biophotonic platform opening up the potential for food safety, environmental monitoring, clinical diagnostics and medical applications.

The third biosensor is GO-LPG based label-free haemoglobin sensor The GO-LPG device giving a sensitivity of 1.9 dB/(mg/mL) to haemoglobin and a detectable concentration of 0.05 mg/mL, which was far below the haemoglobin threshold value for anaemia defined by World Health Organisation. The proposed GO-LPG architecture can be further developed as an optical biosensing platform for anaemia diagnostics and biomedical applications.

Chapter 5 Laser micromachining and fabrication

5.1 Excimer laser and micromachining system

5.1.1 Fundamentals of excimer laser

The 'excimer' is a short term for 'excited dimer'. An excime laser is a form of ultraviolet laser. The most excimer lasers are working with the noble gas halide, where the rare gases are usually considered as "inert" because they cannot react with other atoms or molecules under normal circumstances.



Figure 5.1-1 Schematic diagram of the excimer laser system.

Fig. 5.1-1 shows the schematic of a typical excimer laser. In an excimer laser, the mixed gases including noble gas (argon, krypton, or xenon) and the reactive gas (fluorine or chlorine) will experience the electrical stimulation and high pressure in the excimer laser cavity to create the pseudo-molecules such as fluoride (ArF), krypton fluoride (KrF), xenon fluoride (XeF), krypton chloride (KrCl), or xenon chloride (XeCl). The pseudo-molecules have very short lifetime in the order of serval nanoseconds and the laser is then generated during this period through stimulated emission. The repetition rate of the excimer laser depends on the frequency of electrical discharge, which can be as high as serval kHz. The pulse duration of a typical excimer laser is in the range of a few nanoseconds to around 100 nanoseconds of full width half maximum (FWHM).

The wavelength of excimer laser is usually in the ultraviolet region and depends on the gain medium. The typical excimer lasers and their operation wavelengths are listed in the Table 5.1-1.

Laser gasArFKrFKrFKrClXeClWavelength193 nm248 nm351 nm222 nm308 nm

Table 5.1.1 Excimer lasers and working wavelengths

Since thirty years ago the first work using UV excimer lasers for polymers processing [198–200], investigation on excimer lasers is still an attractive field. Excimer laser is commonly used in the fabrication of microelectronic devices, miniaturised semiconductors, and micromachining. Excimer laser is now not only an excellent tool to complement photolithography techniques, but also provides a platform for the investigation of laser-matter interaction at UV region. Due to its high precision and structural flexibility, a number of prototyping of MEMS devices is produced by excimer laser processing. Excimer laser can directly produce a "complex" structure, which would need a multi-step lithographic process, such as a channel with different depth at different section.

When an electromagnetic wave enters opaque matter, the radiation will be absorbed. As a result, the energy will induce vibrational or electronic excitations inside the matter depending on the energy of photons. According to the photoelectric effect, if the energy carried by each photon is low, the laser exposure will only result in vibration or rotation inside the matter where thermal effects dominate. However, when the photon energy (usually by UV laser) is equal or exceeding the chemical bonding energy of the exposure matter, molecules in that matter will start to dissociation. Excimer laser can produce photons with sufficiently high energy, for example, 4.9 eV for the KrF laser and 6.4 eV for the ArF laser. The interaction between UV excimer laser and polymer materials is mainly an ablative photodecomposition effect [201], where the intra-chain covalent bonds of polymer materials are directly broken by UV absorption. In a decomposition reaction, small particles of matter are formed once the molecular bonds are broken, the exposed part of matter will be electronically excited, and then the polymer molecules dissociate into small particles. This process can be described as:

where A and B are the different atoms which are covalently bonded, hv is the photon energy which is assumed to exceed the bond energy of AB. The repulsive forces between species will lead to an explosive ejection of the dissociated species ("phase explosion") from the surface. The species will travel with a speed of 10^4 to 10^5 cm/s due to the explosion shockwave [202]. In addition, as the majority energy is absorbed by the bond-breaking process the temperature rises as well as the thermal damage to the substrate are restricted.

5.1.2 Excimer laser micromachining system

The Excitech Series 8000 is a commercial excimer laser micromachining system, which operates at wavelength of 248 nm (KrF) or 193 nm (ArF) with 20 ns pulse duration. This laser has repetition rate of up to100 Hz and maximum pulse energy of 225 mJ [203,204]. This micromachining system contains 400 mm × 400 mm (X&Y) airbearing translation stage and a 450 mm × 450 mm (X&Y) CNC (computer numerical control) controlled open-frame mask stages.



Figure 5.1-2 The typical beam path of the excimer laser with mask projection system and the schematic of projection optics. Figure adapted from Ref [205].

Fig. 5.1-2 shows the laser beam path working in the excimer laser micromachining system. As the raw beam of an excimer laser usually has rectangular shape, the components A and B are two orthogonal cylindrical lenses, which are used to shape the beam from rectangular to square shape. C-D is called fly's eye homogeniser [205,206], which consists of a 6x6 microlens array at each side. This structure can divide the incident beam into 36 beamlets and then redistribute the laser energy onto the condenser lens E, yielding a uniform flat-top beam profile at F.

After that a field lens F would image the reshaped and homogenised beam onto the mask G. The mask G is typically made from either chrome-on-quartz or a thin metal sheet. Finally, the laser beam will pass a projection lens H to demagnify the mask pattern onto the sample surface. For the beam size of $1 \text{ cm} \times 1 \text{ cm}$ square, the projection lens will project the beam to $1 \text{ mm} \times 1 \text{ mm}$ square with its 10x demagnification effect (NA=0.3). In the project process, the energy of laser will drop to 77.3% due to the exists of the aperture [207].

5.2 Femtosecond laser and microfabrication system

5.2.1 Introduction of femtosecond laser

Femtosecond (fs) is a time scale which represents 10^{-15} second, in such a short time, even light can only travel 0.3µm, some counterintuitive phenomenon can happen at femtosecond scale.

Ti:sapphire is a short term for the titanium ions (Ti³⁺) doped sapphire (Al₂O₃) crystal, which is widely used as the gain medium of femtosecond lasers. The Ti³⁺ ion has a large gain bandwidth ranging from 650 to 1100 nm allowing a wide wavelength tunability, while sapphire is providing excellent thermal stability. In addition, according to the time-bandwidth product ($\Delta v \Delta \tau = \text{const}$, by Heisenberg uncertainty), ultrashort pulses are also allowed to generate in the assistance of Ti:sapphire crystal. In 1982, the first Ti:sapphire laser was constructed by Peter Moulton at the MIT [208]. This kind of femtosecond laser based on Ti:sapphire is usually pumped by another laser at green

light region (514 to 532 nm), with the most efficient pumping occurring at wavelength near 800 nm. Herein, the typical structure of the fs-laser is shown in Fig. 5.2-1, which mainly consists of the laser cavity with Ti:sapphire crystal and a dispersion compensator [209].



Figure 5.2-1 Schematic diagram of a self-mode-locked Ti:sapphire laser.

5.2.2 Mode-locking and Kerr lensing effect

Mode-locking is a very important concept in ultrashort pulse laser. Usually, there are multiple longitudinal modes propagating in laser cavity and these modes are in random phase. The intensity of laser is thus randomly distributed against time (Fig. 5.2-2(a)). By the mode-locking technique, these modes can be modulated to have a highly coherent phase at a certain time point and hence the laser output intensity is "concentrated" at that point (Fig. 5.2-2(b)).

(a) Random phase



Figure 5.2-2 The intensity difference between random and locked phase.

Technically, mode-locking can be realised by either an active element (an optical modulator) or a nonlinear passive element (a saturable absorber). For a Ti:sappire fslaser, it is achieved through the action of the Kerr lensing effect induced by the laser crystal [210].

The optical Kerr effect is based on the nonlinear mechanism of medium refractive index. The medium RI is not a constant to the electromagnetic field, instead, it varies with the field strength [211]:

$$n(I) = n_0 + n_2 I \tag{3.2-2}$$

where n_0 and n_2 are the linear and nonlinear refractive indices of the medium, respectively [212]. The Ti:sappire crystal acts as an effective saturable absorber which provides self-phase modulation due to the temporal intensity variation. In addition, Kerr lensing effect can lead to a spatial self-focusing effect. For a Gaussian beam, the refractive index at the beam centre will be larger than that of the edge. As a result, the beam size of the laser is then reduced at the output side (shown in Fig. 5.2-3), hence the high spatial laser intensity is achieved.



Figure 5.2-3 The principle of Kerr lensing effect, where the laser is self-focused via the Kerr medium.

5.2.3 Multi-photon absorption

Based on its ultrashort pulse and super high intensity, the laser-matter interaction of a fs-laser is very different from that of the excimer laser. According to the photoelectric effect, such 800 nm laser pulses can lead to neither photodissociation nor photoexcitation to the exposure matter as the energy carried by each photon is lower than the band gap. The absorbed laser energy will lead to only temperature rise in the matter. However, this is only true for the weak field regime. Researchers discover that the multi-photon absorption is possible under intense field conditions [213–215], which opens new avenue for the investigation of laser-matter interaction.

In the quantum regime, whenever a system absorbs any photon, even if the photon energy is lower than the bandgap, the system will reach a virtual state and last for a very short lifetime, which is governed by the Heisenberg uncertainty principle:

$$\Delta E \cdot \Delta t = \hbar \tag{3.2-3}$$

where $\hbar = h/2\pi$ and *h* is the Planck constant $(6.6261 \times 10^{-34} \text{ J} \cdot \text{s})$, ΔE is the uncertainty in the energy, while Δt is the uncertainty in the lifetime which is considered equal to the lifetime itself. This relation indicates there exists the possibility for multiphoton absorption if the photon density per unit time on the atom or molecule is high enough. If a second photon arrives within the time Δt after the first one, the system will transit to the "two-photon" absorbed virtual state, and the lifetime becomes a smaller Δt as well. Then similarly, for n-photon absorption case, whenever a new photon arrives before the "de-excitation", the energy of that photon will be added up to the system, until there are no more photons can arrive in time or the system finally

reaches the excited state (in this case, ionisation condition). The probability of n-photon absorption is proportional to a nonlinear factor I^n , where I is the intensity of the incident laser [216].

In an intense field produced by fs-laser, transitions are no longer limited to single photon absorption case. Multiple photons can combine their energies for a transition which requires energy less than or equal to $n\hbar\omega$ in a relay, and thus multi-photon ionisation is energetically allowed (Fig. 5.2-4).



Figure 5.2-4 Schematic of the multi-photon ionisation.

Based on the multi-photon ionisation principle, although the operation wavelength of the laser is around 800 nm, a femtosecond laser is possible to process, cut or ablate almost any materials due to its extreme high energy density.

5.2.4 Femtosecond laser microfabrication system

The Excitech Series 2000 is a commercial femtosecond laser microfabrication system. The laser head (source) is "Hurricane i" system from Spectra-Physics, which amplifies the output of the mode-locked Ti:sapphire laser to produce high-power and ultrafast pulses. This fs-laser system consists of two main lasers, the Mai Tai seed laser and the Evolution-15 pump laser. The mode-locked Ti:sapphire Mai Tai seed laser contains its own pump laser, and the Evolution-15 is a diode-pumped, Q-switched, frequency-doubled Nd:YLF pump laser. This fs-laser has a pulse duration of 120 fs, a fixed repetition rate of 5 kHz, and the operation wavelength at range of 795~805 nm. The final projected beam spot size is about 20 μ m.



Figure 5.2-5 Schematic of the femtosecond laser direct 3D writing system.

Fig. 5.2-5 shows the setup of the femtosecond laser microfabrication system. Apart from the laser source, a laser shaping/control system is also included. The output laser beam is controlled by a tunable attenuator, an aperture, a mechanical shutter, mirrors and a galvanometer scanner. The galvanometer scanner together with a X-Y-Z translation stage with resolution of 1 μ m are working together to control the laser beam pointing and focusing. This computer-controlled galvanometer scanner provides more convenient and faster control to the laser beam. By these components, more complex pattern can be produced within shorter time. According to the multi-photon ionisation principle, femtosecond laser will only work around its focal point. If the energy density is not high enough, this femtosecond laser will have no effect to a transparent material. This tight focusing and the nonlinear absorption nature of the femtosecond laser make it possible to implement processing only inside the transparent matter without damaging the surface. Nowadays, the advantage of fs-laser system has been used to create structures like microfluidic inside a bulky glass [217,218].

5.3 Excimer laser-based micromachining

5.3.1 Ablation depth control on polycarbonate

Among all the polymer materials, polycarbonate (PC) has good ablation characteristics in the UV [219] and good optical transmission, thus it is widely used in many applications such as micro-lens fabrication.

The ablation effect of excimer laser on polycarbonate is investigated. As shown in Fig. 5.3-1(a), a 7x5 ablation matrix is shown with the laser passing rate ranging from 0.1 to 0.9 with the step of 0.2 (stands for different laser fluence), and the pulse shots from 20 to 140 with the step of 20. From the results, it is clear that the burning mark is more and more significant at the heavily ablated spots, which demonstrates the UV absorption of polycarbonate generates heat as a by-product. The best excimer laser machining quality was achieved by the low fluence just above the threshold. For better illustration, Fig. 5.3-1(b) and (c) show both of the top and bottom images of the spot at the deepest corner. Due to the beam shape, the laser ablated spots are in trapezium shapes with the bottom size smaller than that of the top. To examine the laser micromachining quality, the SEM image of the spot created by 200 shots has been shown in Fig. 5.3-1(d). Despite of some "debris" which may be adsorbed after machining, the bottom of the spot shows very flat and clean even 200 shots have been overlapped.



Figure 5.3-1 (a) Ablation matrix sample on polycarbonate by the use of excimer laser. The microscope image of (b) the top and (c) bottom view of the deepest spot, and (e) SEM image of the deepest spot.

Fig. 5.3-2 gives the measured ablation depth of the spots in the matrix (Fig. 5.3-1a) as a function of laser fluence and number of laser pulse. A series of non-linear curves in Fig. 5.3-2 (a) are in agreement with the Beer's law. By assuming the ablation threshold for a given polymer material is F_T [220] and the actual laser fluence is F, the etch rate d can be estimated by:

$$d = \frac{1}{\alpha} \ln \frac{F}{F_T} \tag{3.3-1}$$

where α is effective absorption coefficient of the given polymer. If the laser fluence is fixed, the ablation rate of a certain material will be fixed [221], which is demonstrated by a clear linear relation between ablation depth and the laser pulse number (Fig. 5.3-2b). The ablation rate is calculated as 0.028, 0.730, 0.106, 0.128, and 0.135 μ m/pluse corresponding to the laser fluence of 0.214, 0.508, 1.021, 1.356, and 1.476 *J/cm*², respectively. It is proved that the ablative threshold of polycarbonate is ~214 mJ/cm², which agrees with the previous work [219].



Figure 5.3-2 Measured ablation depth as a function of (a) laser fluence and (b) number of laser pulses.

5.3.2 Microstructure fabrication on polymer fibre

Polymer optical fibres (POFs) have similar merits with silica fibres, such as light weight, small size, immunity to electromagnetic interference and multiplexing capabilities. Furthermore, POFs can provide additional advantages of large strain limit, high fracture toughness, extensive flexibility in bending, large and negative thermo-optic coefficient, and excellent biocompatibility with potential for biomedical applications [222].

The advanced laser has opened up a new avenue for microfabrication due to the ultrashort pulse width and extremely high pulse intensity, which enable spatially localised modification either on the surface or in the bulk of materials. Excimer laser can provide UV light in deep region of the spectrum and the most polymer materials could absorb such UV radiation. Hence, the excimer laser is an excellent tool for micromachining on the polymer fibres, including grating inscription, microstructure fabrication, side ablation and polishing. The refractive index decrease in PMMA materials was photoinduced by deep UV irradiation at 248 nm whereas an incubation process was observed below the ablation threshold [223,224]. On the other hand, with the rise of laser parameters above the reported PMMA ablation threshold, the ablative process could occur [224]. The response of polymer materials to the laser pulse is complex because of optical absorption, photochemical reaction, thermal and mechanical effects, which are import but most of which are usually unknown completely [207,225].



Figure 5.3-3 Schematic diagram of (a) the excimer laser and mask projection scanning system, (b) slotted POF and (c) D-shaped POF.

In this section, the Excitech Series 8000 laser is used as a tool to micromachine the POF. With the laser setup shown in Fig. 5.3-4 several designed microstructures such as micro-slot or D-shape can be fabricated by moving the workpiece sample under the static aperture laser beam and triggering the laser output. The slotted structure was formed with the laser beam size (mask image) smaller than the fibre diameter while the D-shape was created with the beam size larger than fibre diameter. For example, using

a mask of 400 μ m × 400 μ m in size, a laser beam of 40 μ m × 40 μ m can be projected onto the POF sample surface and hence a slot with width of 40 μ m can be produced. Multiple scan with laser radiation fluences of 1.37 J/cm² and different masks have been used to generate the designed microstructures. Laser machined microstructures (Fig. 5.3-5) varying in width, ranging from a narrow slot, an open bay to a D-shape, can be achieved by the use of different masks with a size of 400 μ m, 800 μ m and 1.6 mm, respectively.



Figure 5.3-4 Microscope images of laser-micromachined microstructures on POF (a) slot, (b) open bay, (c) D-shape.

It is important to know the ablation rate of the excimer laser for the ablation of microstructures on the polymer fibres. Thereby, an ablation rate test was implemented with a series of slots with different stage moving speed were created on a group of polymer fibres from the same source. The depth of four ablated micro-slots were measured and shown in Table 5.3-1.

Pulse/area	10	20	30	40
Ablation depth (µm)	11.25	24.50	37.00	62.25

Table 5.3.1 Relation between ablation depth and number of laser pulse

With the data provided in Table 5.3-1, the ablation rate of the excimer laser to polymer fibre is estimated to be ~ 1.66 μ m/shot. The laser scanning speed was set as 555.6, 277.8, and 185.2 μ m/s in order to get 9, 18, and 27 pulse/area, hence the ablated depth of 15, 30 and 45 μ m, respectively. The images of those 6 fibres are displayed in Fig. 5.3-6, demonstrating both controllability and repeatability of the excimer laser. The target ablation depth is achieved within the range of reasonable error. However, the ablated surfaces of POFs become rough due to the presence of bubbles.



Figure 5.3-5 The images of ablated polymer fibre samples with the measured ablation depths where (a) the first sample (the top row) (b) the second row (the bottom row).

The cylindrical geometry of the fibre may be a challenge for high quality micromachining. By the top-side ablation, the cross-section of the POF is actually "gibbous moon" shape. Hence, the side ablation method has been employed. Fig. 5.3-7 demonstrates the images of side-ablated polymer fibre sample showing a clear ablated surface only with some small cracks. From the side view, it is remarkable that the ablated section is very flat, which is good than top-ablated method. However, there is also a significant drawback with the side ablation, to ablate a polymer fibre from side will waste a large portion of laser energy, leading to the method regards as low efficiency and time consuming. To remove 45 μ m-thickness cladding from the fibre, the top-ablated technique will finish in seconds time while hours may be required for the side-ablated method.



Figure 5.3-6 The images of side ablated polymer fibre with (a) left edge (b) the sideview.

5.3.3 Photodegradation effect of excimer laser on PPMA fibre

Due to its unique properties, PMMA has become one of the most common polymers used for the fabrication of gratings and waveguides. PMMA-based optical fibre Bragg gratings (POFBGs) were found to be sensitive to relative humidity, temperature, strain and pressure with high sensitivity [226–229]. The sensing performance of POFBGs can be significantly improved either by reducing the fibre diameter with chemical etching [227] or by spatial modification of fibre geometry using laser micromachining [230]. There has been a report recently that the sensitivity of chemically etched POFBG over strain, temperature, and pressure can be improved [231]. Since the first FBG was written in polymer fibre, the ultraviolet (UV) laser at 325 nm wavelength has become the preferred laser for grating fabrication in POFs [232]. The mechanism of photoinduced refractive index change of polymer is a key factor in the fabrication of fibre gratings. To date, the PMMA photosensitivity under UV radiation is still not completely understood. Early studies reported that the mechanism of photoinduced refractive index increase in PMMA at 325 nm UV radiation was a consequence of photopolymerisation of residual monomers [233,234] while other groups demonstrated that the PMMA photodegradation occurred at wavelengths below 320 nm [235,236]. The recent investigation reported that the main photosensitive mechanism of PMMA-based mPOF irradiated at 325 nm UV light is a competitive process between photodegradation and photopolymerisation [237]. Very recently, Oliveira et al. reported that FBGs can be inscribed in undoped PMMA-based mPOF using 248 nm UV laser within 30 seconds, in which the laser conditions of low fluences and low repetition rates were properly controlled to modify the refractive index of fibre core at the incubation regime hence avoiding polymer ablation [238].

To investigate the photodegradation effect, the top ablation method was applied to a polymer fibre with Bragg grating to replace the bare polymer fibre, by which one can analysis the refractive index changes by monitoring the spectrum evolution of the Bragg grating during ablation process. As the mechanical property of polymer fibre can be affected by the remaining stress in the fibre which may vary with environmental conditions generating variability in POFBG response, it is important to remove the majority of residual stress by pre-treated annealing process [239]. In this section, the PMMA-based step-index POF samples were annealed at 80°C over 7 hours prior to FBG inscription. After annealing, the polymer fibre length decreased to (93.7 ± 0.5) %

and the diameter increased to (104.2 ± 0.5) % of its original values, possibly leading the fibre to become few-moded.

The POFBG was inscribed by the scanning phase mask technique using a CW heliumcadmium laser (Kimmon model IK5652R-G) with an output wavelength of 325 nm, a beam diameter of 1.8 mm and a power of 30 mW. Due to the high transmission loss of POF in the 1550 nm wavelength region, a short POF with 7 cm length was used to construct a POFBG. The POF was mounted horizontally in a v-groove, the laser beam was focused vertically down on the fibre axis using a cylindrical lens of focal length 10 cm. A phase mask with period of 1.038 μ m (O/E Land Inc., Canada) was placed on top of the fibre to generate a periodic refractive index modulation in the core region. The laser beam was scanned 5 mm along the phase mask.

In this experiment the POFBG was moving along the fibre axial direction with fluence of 1.37 J/cm^2 , repetition rate of 20 Hz, and scan speed of 121 µm/s to achieve a designed depth of 45 µm. The PMMA-based POF (7 cm long) contained a 5 mm long FBG was connected to a single mode silica fibre down-lead using UV curable glue (Norland 76). The POFBG was launched via a 3-dB coupler with light from a broadband source (Thorlabs ASE730) and the spectrum was monitored by using an optical spectrum analyser (OSA, HP86142) during laser micromachining process.

When the laser was firing along the fibre axial direction, the spectra of POFBG were captured at start point of 0 (laser off), process points of 1, 2, 3, 4 (laser on), and final point of 5 mm (laser off) against grating region, which are plotted in Fig. 5.3-8 as curve (i), (ii-a, ii-b, ii-c, ii-d) and (iii), respectively (with offset). During laser micromachining, the grating spectra showed not only the wavelength shift but also the peak splitting and reunion characteristics. Curve i (before laser on) shows the multi-peaks at 1535.2 nm, 1534.3 nm and 1533.2 nm reflecting the few-moded POFBGs after pre-treated annealing process and FBG inscription. When the laser beam started to fire on the POFBG (curve ii-a), the grating resonances instantly shifted to the short wavelength side, whereas the peak splitting appeared simultaneously. During laser firing, all peaks were keeping blue shift (curve ii - a, b, c, d) until the laser was off (curve iii) at which the split-subpeaks merged again then moved back to long wavelength side when the POFBG was naturally cooling down.



Figure 5.3-7 POFBG spectral evolution during laser micromachining.

By zooming the Bragg peak at 1534.3 nm for detail analysis, the peak split into two subpeaks immediately when the laser beam was projected on the polymer grating. Two subpeaks were keeping blue shift with a nearly constant wavelength separation of 220pm during laser process (curve ii- a to d), finally merged into one peak then red shifted when the laser was off and fibre was cooling back to the room temperature. The total wavelength change caused by laser micromachining (curve i and curve iii, both measured at room temperature) is -180 pm. As it can be seen from the microscope image (Fig. 5.3-9), the PMMA fibre surface has been ablated in a " gibbous moon" D-shaped geometry over the POFBG region. The noticeable roughness on the ablated surface and edge was mainly due to the heating effect of high energy laser pulses.



Figure 5.3-8 Microscope image of laser micromachined PMMA-based fibre surface.

As it was discussed in Chapter 2, the Bragg wavelength depends on the effective refractive index of fibre core, n_{eff}^{co} , and the grating pitch Λ , both of which are a function of temperature T, and the water content ω . Hence Bragg wavelength of a POFBG can be expressed as [229]:

$$\lambda_B = 2n_{co}^{eff}(T,\omega)\Lambda(T,\omega) \tag{3.2-2}$$

For constant relative humidity, the Bragg wavelength change against temperature can be expressed as

$$\Delta \lambda_B = \lambda_B (\alpha + \xi) \Delta T \tag{3.2-3}$$

where α is the thermal expansion coefficient related to the volumetric change induced by thermal effect, ξ is the normalised thermo-optic coefficient which describes the refractive index as a function of temperature. It is well known that the thermo-optic coefficient of PMMA is negative [239,240] so the heat introduced negative refractive index change of fibre core is dominant the blue shift of Bragg resonance.

The mechanism behind the spectral characteristics during laser micromachining is more complex, which may be explained by the modulated refractive index profiles [241,242].

As depicted in Fig. 5.3-10, curve i is the core refractive index profile of initial POFBG before laser micromachining, curve ii is the profile during laser beam firing along the POFBG, and curve iii is the profile after laser off and the POFBG cooled down to room temperature. When the laser was projected onto the POFBG, the 200 µm width laser

beam acted as a heating source to spread the heat over the grating region where the negative thermo-optic factor yielded a decrease of mean refractive index of fibre core (see curve i and ii), leading to a blue shift of Bragg wavelength. During laser firing, all peaks were keeping blue shift due to further decrease of refractive index induced by the accumulated heat. The mean refractive index profile of POFBG was splitting into two parts (micromachined and un-micromachined) generating peak splitting feature. Compared to the un-micromachined part, the micromachined part of POFBG absorbed strong UV irradiation leading to a further photoinduced refractive index decrease. This is considered as the effect of photodegradation. As a consequence, a difference in RI of $\sim 2.1 \times 10^{-4}$ between two parts was observed, resulting in two sub-gratings with a peak separation of 220 pm. When the whole grating was micromachined, the split index profiles were reunited and reached to the same level. The index profile finally raised to curve iii after the fibre completely cooled down. The decrease of $\sim 1.7 \times 10^{-4}$ between mean refractive indices before (curve i) and after (curve iii) laser micromachining (both at room temperature) is the consequence of photodegradation, introducing a permanent blue shift of 180 pm in Bragg wavelength. The application of this laser ablated D-shape fibre will show in later chapters.



Figure 5.3-9 Schematic of core refractive index profile of POFBG.

5.4 Microfabrication with femtosecond laser

Femtosecond laser, due to its straightforward and highly accurate nature, is considered as promising technique in the microstructure fabrication [243–245]. Based on multiphoton absorption principle, femtosecond laser is able to ablate almost any materials, even to those which other lasers can't deal with. During the last decade, fs-laser has been extensively investigated and used for the fabrications of the microelectronic structures, miniaturised photonic components, and microfluidic devices.

5.4.1 Laser pulse on glass and ablation depth

Glass is an ideal material for the optofluidic device as it is both chemically steady and optical compatible. The light absorption of a transparent material has been proved to be nonlinear [246], hence the micromachining on the glass requires extremely high laser intensity [247]. Moreover, some glasses are even transparent to the UV light, and thus most of conventional lasers can have any effect. The recent development of femtosecond laser provides an excellent tool to process the glass.



Figure 5.4-1 Femtosecond laser micromachining on glass. The images of fs-laser ablated grooves on the glass (a) side view and (b) top view. (c) The relation between the measured ablation depth and number of fs-laser pulse.

The test of groove ablation on glass surface by the use of fs-laser was investigated (Fig. 5.4-1). The energy of fs-laser pulse was set as $20 \,\mu\text{J} \,(2.65 \times 10^{17} W/cm^2)$ whilst a 50-loop scanning associated with the scanning speed of 100, 50, 20, 10, 5, 2.5, and 1.25

mm/s was applied, the corresponding pulse/area was 50, 100, 250, 500, 1000, 2000, and 4000 respectively. Different groove depths were measured from the edge of the glass by the use of optical microscope (Fig. 5.4-1) whereas the grooves demonstrate the same width measured on the top, indicating the fs-laser (as an ultrashort pulse laser) is an excellent "cold" laser tool with no melting or micro-explosion to the exposure materials. The groove depth shows a non-linear effect of the laser pulses (Fig. 5.4-1c). The ablation depth grows fast for the pulse/area less than 200 and shows less change with the pulse/area of 400 and 800. This phenomenon is not caused by the saturation, actually it is in agreement with the multiphoton ionisation. At non-focal point, the laser energy density is not sufficient to ionise the glass, hence the depth of groove stops to grow.

As discussed in Section 4.2.6 that the fs-laser affect area will be strictly limited in the laser focal point where the multiphoton absorptions occur. Based on this concept, a micro-holder for fitting the optical fibre was designed and fabricated by fs-laser micromachining (Fig. 5.4-2a). The fat section is prepared for sitting the fibre with 250 μ m-diameter jackets whilst the slim slot is for fixing the bare fibre with standard 125 μ m-diameter (Fig. 5.4-2b).



Figure 5.4-2 The fs-laser fabricated miro-holder for fibre fitting. (a) Image of the micro-holder with the joint sections, (b) Image of the bare fibre fixing in the micro-holder.

5.4.2 Fabrication of microfluidic channel by fs-laser

"Microfluidics" is the science that investigates the behaviours, precise control and manipulation of fluids in sub-millimetre scale channel [248]. Many biomedical and biomedical applications can be actualised on the microfluidic platform. During the last

decade, the concepts of lab-on-a-chip (LOC) and micro total analysis systems (μ TAS) started to blossom, by integrating the multiple biochemical functions such as synthesis and analysis on a microchip [249].

Polytetrafluoroethylene (PTFE, or more commonly known as Teflon for its trademark) is a material owning unique physical and chemical properties such as thermal and chemical stability, low frictional resistance, and low dielectric constant. PTFE (Teflon) has been developed for numerous biochemical and biomedical applications. However, the PTFE shows almost no absorption to the light spectrum ranging from ultraviolet (UV) to infrared (IR) [250]. The femtosecond laser becomes the ideal tool to process the microscale structure on the PTFE.

In order to investigate the relationship between the fs-laser pulse and the ablation depth, a series of grooves on the PTFE were fs-laser ablated. The ablation depth shows a nonlinear effect to the fs-laser pulse numbers, the depth increases dramatically during the first 150 shots then grow gradually due to the beam divergence. These results are in good agreement with the previous reported work [251]. The ablation depth has also been plotted against pulse energy, demonstrating a linear response, which is shown in Fig. 5.4-3.



Figure 5.4-3 Measured ablation depth against (a) fs-laser pulse number per area and (b) pulse energy.



Figure 5.4-4 The results of (a) The image of the deepest ablated grooves at 203 μ m, and (b) image of the channel bottom.

The geometry and surface quality of the ablated slots were examined by the optical microscope. During the fabrication of microchannel, a multi-scan technique was applied where the fs-laser beam with 20 μ m in diameter was controlled to ablate the Teflon surface line by line with a separation gap of 4 μ m, the pulse numbers were multiplied by a factor 5. From Fig. 5.4-4(b), the vertical line mark at channel bottom is noticeable, which is corresponding to the laser beam scanning. For a smooth ablated surface, multi-scanning plus multi-direction may be applied.



Figure 5.4-5 (a) Schematic of opto-microfluidic chip. (b) Designed optofluidic chip from top view (c) The side view of microchannel with optical fibre-holder architecture.

The behaviour of fluids could be interesting and even counterintuitive in the device with several hundred micrometres scale. Down to microscale, the factors such as surface tension, energy dissipation and fluidic resistance become more significant, the behaviour of fluids in 'microfluidic' can be very different from that of 'macrofluidic'. For instance, the fluidic flow could become laminar instead of turbulent when the Reynolds number (which related to the inertial/viscous of a fluid) is less than 2500. Under such condition, two different fluids will not mix and show co-flowing phenomenon.

In our research, we intended to develop an opto-microfluidic biochip system where the fibre grating was embedded in the microchannel for bio- events detection in the realtime. As shown in Fig. 5.4-5, the microfluidic channel device is fabricated on a 12x5 cm PTFE. The multiple inlets and an incubation channel with both mixing and delaying function are designed for the microsystem. A twisting incubation microchannel with 10 corners is designed in front of the main straight channel [252]. With this microstructure, various functions such as mixing, diluting, multiple bio-liquid detection are enabled. Each period of this mcirochannel is set as 8 mm long, 600 μ m wide and 500 μ m high with round conjunction. A 10 cm long and straight microfluidic channel is designed for passing the bio-liquids as well as for embedding the fibre grating. The microchannel width and height are designed as 600 μ m and 500 μ m to form a 30 μ L volume microchannel for biomolecule liquid passing through. Considering optical fibre is in cylindrical geometry with 125 μ m diameter, which can leave enough space for bio-liquid to pass through.



Figure 5.4-6 The SEM image of (a) microfluidic channel junction in PTFE, (b) microchannel viewed from the top, and (c) a cross-section view.

The microchannel samples fabricated by fs-laser micromachining were examined by the SEM (Fig. 5.4-6), which demonstrate the good shape and smooth surface of the ablated microchannels. It is necessary to mention that the samples for SEM images are smaller than the designed microchannel chip, but with the same PTFE material. The channel depth on those SEM samples is only ~ 100 μ m. In general, a well-designed multiple scan can result in a very smooth surface of the micromachined area as well as the channel walls.

5.4.3 Long period grating inscription by femtosecond laser

The Long period gratings have been found to have widespread applications including optical communications and sensing [47,253–255]. In conventional single-mode fibres (SMFs), LPGs are usually inscribed through refractive index modulation of the fibre core by UV exposure [256]. However, as most conventional SMFs are photo-insensitive, a hydrogen load process is required for implement the UV exposure method. In addition, these UV inscribed gratings will degenerate at a high-temperature environment. Therefore, the femtosecond laser inscription is one of the most attractive alternative methods to fabricate LPGs due to its flexibility and direct writing.

Although it is near two decades passed since the first LPG fabricated by the infrared femtosecond laser [257], the evolving laser technique are constantly providing the possibility to improve the quality of the fabricated LPG. For examples, the efficiency of LPG fabrication can be enhanced by applying an axial tension to the SMF [258], and the background loss can be reduced with the help of highly precise controlled laser beam [259,260]. To date, LPGs fabricated by femtosecond laser in SMFs have been reported by many groups [37,257,261,262], however, these LPGs belong to "index-type" gratings as there is no significant modification on waveguide geometry. It has been reported that the structural LPGs have been successfully fabricated in photonic-crystal fibres (PCFs) [38,263] by making microstructures into the cladding of PCF. The structural LPG has significant advantages in its thermal stability, which can be used as devices and sensors in high-temperature environment. The grating is much easier to be fabricated in SMF than a PCF, also SMF is cheaper than PCF.

In this section, we discuss the fabrication of the structural LPGs in SMF by the use of femtosecond laser. The femtosecond laser has a pulse duration of 120 fs, repetition rate

of 5 kHz, 800 nm operation wavelength, and the laser energy set as 20 µJ. The Gaussian laser beam was focused onto the fibre by a microscope objective lens and the focal spot diameter is estimated to be 20 µm. During LPG fabrication, the SMF was mounted on a custom-designed glass slide with both ends fixed and ~0.05 N pre-strain applied. Then the glass slide holding the fibre was mounted on a computer-controlled three-axis translation stage with a tuning resolution of 1 µm. The laser beam scanning was controlled by the computer to enhance the accuracy. With the assistance of an optical microscope (Nikon 80i), the location of the focal point on the fibre can be accurately selected and controlled. The fs-laser was focused on fibre's upper cladding surface and aligned at the centre of the fibre. Then the laser beam was scanned perpendicular to the fibre axis with a constant speed of 10mm/s to inscribe a 'groove' structure on fibre surface. This fabrication of slots on fibre cladding was continued until the grating spectrum was successfully monitored. Throughout all fabrication process, the transmission spectra were real-time monitored via an optical system consists of broadband light source (BBS) and optical spectrum analyser (OSA). Fig. 5.4-7 shows the morphology of a single groove inscribed on the fibre surface.



Figure 5.4-7 The microscope images of the 'groove' inscribed on SMF, (a) the top view (b) the side view.

As shown in Fig. 5.4-7, the 'groove' has the width of 20 μ m and the depth of 16 μ m. One should be noticed that the area under the groove shows the burned mark across the fibre which may be caused by the fibre cylindrical geometry. A series of identical grooves were created one by one along the fibre and eventually formed the LPG. The separation between centre of the groove, e.g. the grating period was set as a fixed data (e.g. 500 μ m) during the laser fabrication process. The length of the LPG length can be

increased against the number of grooves. This kind LPG is considered as a "structural grating" because the fibre geometry is significantly modified by the laser.

LPG peak intensity against grating length

In order to investigate the effect of grating length to the grating resonant intensity, the laser power and scanning speed were maintained as the same, but the groove number (e.g. grating length) was different. As plotted in Fig. 5.4-8(a), 11 LPG spectra have been recorded where the resonant intensities increase when the inscribed groove number (LPG length) increases. The resonant strength increases nonlinearly with the number of grooves, the maximum intensity of -3.2 dB is achieved at grating length of 3.6-4.0 cm. It is wealth to note that the central wavelength of resonance does not change during the fabrication, which is in strongly agree to the theory discussed in Section 2.2.2, indicating the coupling strength is kept constant when grating length grows. In addition, the resonant intensity grows fast when grating length is from 1.5 cm to 3.5 cm while the increase is almost 0 for grating length short than 0.5 cm or longer than 3.6 cm. It may be explained by Eq. (2.2-40), the relation between peak intensity and grating length is determined by a squared sine function.

As the light coupling principle of fs-laser inscribed LPG is similar to that of corrugated LPG [264,265], the pre-strain applied on the fibre is necessary for the laser fabrication process, the tensile force can induce the refractive index perturbation in fibre core due to the differential strain distribution and the photoelastic effect.



Figure 5.4-8 LPG resonant intensity against the grating length. (a) The evolution of transmission spectra, (b) The peak intensity.

Fabrication repeatability

The repeatability of the LPG fabrication by fs-laser has been investigated as well. Five LPGs with the same parameters of grating period of 300 μ m and length of 1.8 cm (60 periods) were inscribed in SMFs. As shown in Fig. 5.4-9, the resonant central peak wavelengths at 1421 nm or 1488 nm are kept at the same locations for all of the 5 gratings, demonstrating excellent repeatability of the fs-laser fabrication technique. The slight difference in intensity and wavelength may be caused by the difference of initial fibre alignment as well as the pre-strain applied to the fibre samples.



Figure 5.4-9 Repeatability of fs-laser inscribed LPGs.

RI sensitivity of fs-laser fabricated LPG

The performance of the fs-laser fabricated LPG was finally examined by a series of index matching oil to investigate its RI response. To minimize the thermal and bend cross sensitivity, the LPG was fixed on the glass substrate and the experiments were conducted under constant room temperature environment. A careful clean-and-dry process after each measurement was applied to wash the LPG with methanol to remove the residual RI matching oil from both grating and glass substrate. It was ensured that the spectrum in air was recovered prior to each measurement. The evolution of the transmission spectra with different SRI is displayed in Fig. 5.4-10(a). The increase in

the SRI leads to the blue shift of all the grating peaks as expected. It is notable the peak 3 at around 1550 nm doesn't appear at the ambient air, while its intensity becomes stronger when the SRI increases. The wavelength movements of all three peaks of the LPG are plotted in Fig. 5.4-10(b). Where the peak with higher order shows lager RI sensitivity to the SRI which also agrees to the LPG theory. The SRI sensitivities are - 24.8, -52.1, and -68.5 nm/RIU in low RI region (1.00-1.33) and increase to -146.67, - 440.00, and -573.33 nm/RIU for high RI region (1.42-1.45), respectively.



Figure 5.4-10 (a) Transmission spectra and (b) resonant wavelength shifts RI change. (Note: the hollow square is the virtual point made by estimation.)

Comparing with a regular UV inscribed LPG with the same grating period (e.g. 300 μ m), which has resonant peak near 1550 nm with the RI sensitivity of ~ -15.8 nm/RIU [15], the fs-laser fabricated LPG shows 4 times higher RI sensitivity than that of the traditional UV-induced index LPG. The sensitivity enhancement can be explained by the reduction of the cladding, as it was discussed in Section 2.3. This enhancement is also examined experimentally in previous works [17,170]. Above all, the structural LPG shows good preforms than the index-modulated LPG in RI sensing application.

5.5 Chapter summary

In this chapter, two advanced ablation lasers: the excimer laser and femtosecond laser, were discussed including the working principle, the ablation effect and the applications, as they are now frequently used in various micromachining applications.

The ablation effect of excimer laser to different polymer materials were investigated. Particularly, the ablation rate of excimer laser to the PMMA based polymer fibre was estimated as 1.66 μ m/shot under the laser fluence of 1.49 mJ/m². Based on this, the designed microstructures can be precisely produced on the cladding of D-shape polymer fibre, which will be further used for humidity sensing in following chapters. Femtosecond laser, as a 'cold laser', has been employed to fabricate the microfluidic channels as well as the long period gratings. The systematic fabrication condition for fs-laser inscribed LPGs has been investigated. In addition, the structural LPGs shown better performance in RI sensitivity than that of convention index LPGs.

Chapter 6 Fibre grating-based humidity and chemical sensors

6.1 Polymer fibre Bragg grating for humidity sensing

6.1.1 Background of polymer optical fibre Bragg gratings

Apart from conventional silica material, polymers are also wildly used to fabricate optical fibre. Having the drawback of relatively high transmission loss, polymer optical fibres (POFs) are much less popular than the conventional silica fibres in communication applications. However, for sensing applications, the problem in transmission loss is minimalised as sensors are normally made in tiny scale, and polymer materials can provide unique advantages. The physical and chemical properties of polymeric materials are rather different to silica, potentially making them attractive for researchers to exploit in device and sensing applications. In particular, polymer optical fibre (POF) sensors can offer large strain limits, high fracture toughness, extensive flexibility in bending, large and negative thermo-optic coefficients and for some materials an affinity for water. In addition, polymers have excellent compatibility with organic materials, giving them great potential for biomedical application [222]. Over the last decade, fibre Bragg grating technology has been extensively developed to inscribe Bragg gratings in step-index [232] and microstructured optical polymer fibres (mPOFs) [239,266] made of poly(methyl methacrylate) (PMMA) materials [267], TOPAS [268], and polystyrene polymer [269]. PMMA based optical fibre Bragg gratings (POFBGs) were found to be sensitive to relative humidity, which is in contrast to FBGs in glass fibre which do not show any intrinsic humidity sensitivity [270]. The affinity for water of PMMA leads to a swelling of the POF and an increase of refractive index, both of which contribute to an increase in the Bragg wavelength of a POFBG written in the PMMA fibre [270]. The affinity for water of PMMA leads to a swelling of the POF and an increase of refractive index, both of which contribute to an increase in the Bragg wavelength of a POFBG written in the PMMA fibre [270]. This is a potentially very useful property, which has possible applications in chemical processing, agriculture, food storage, paper manufacturing, semiconductor and pharmaceutical industries, where humidity is monitored and controlled to ensure product quality.

POFBGs have recently been applied to quantify the small amount of water dissolved in aviation fuel [271].

A typical POFBG humidity sensor is made of PMMA based optical fibre. A change of environmental conditions could lead to a change in the water content of the PMMA, which is a function of time [226]. The process of water absorption or desorption in PMMA can be described by the diffusion theory of mass transfer. Although grating sensors made of different PMMA fibres may exhibit different response times and sensitivity, for the same type of PMMA fibre the humidity response time of POFBGs is determined by the fibre geometry [227]. In previous work [227], the response time of a POFBG was improved (lowered) by reducing the fibre diameter using chemical etching. Alternatively, a laterally accessible microstructured polymer fibre with a sideslotted cladding was suggested for further improvement in humidity time response [272,273]. However, such slotted specialty fibre is not commercially available and also has the drawbacks of high loss and butt-coupling difficulty [273]. Recently, the advanced ultrafast lasers have opened up a new avenue for microfabrication due to the ultrashort pulse width and extremely high peak intensity, which enable spatially localised modification either on the surface or in the bulk of materials [207,274]. In the last few years, different laser microfabrication methods have been explored, leading to microstructures with enhanced optical, chemical and biological properties [275,276].

6.1.2 Humidity sensing principle of POFBG

The Bragg wavelength of a PMMA-based POFBG depends on the core effective refractive index and the grating pitch, both of which are a function of temperature T and the water content w. For constant temperature, the Bragg wavelength change $\Delta\lambda_B$ of a POFBG against humidity can be expressed as [226]:

$$\Delta \lambda_B = \lambda_B (\eta + \beta) \Delta H \tag{6.1-1}$$

where λ_B is the initial Bragg wavelength, η is the normalised RI change with humidity, β is the swelling coefficient related to humidity induced volumetric change, and ΔH is the relative humidity change (%RH). The wavelength change in a POFBG sensor varies non-linearly with humidity, because both η and β can be temperature and humidity dependent. This process of water absorption or desorption in PMMA can be described by the diffusion theory of mass transfer. For a cylinder geometry, if the surface concentration, C_0 , is constant and the concentration, C_1 , is initially uniform throughout the cylinder, then the mass concentration due to diffusion can be expressed as [277]:

$$\frac{C-C_1}{C_0-C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0(r\alpha_n)}{\alpha_n J_1(n\alpha_n)}$$
(6.1-2)

where J_0 and J_1 are zero and first order Bessel functions of the first kind, D is diffusion coefficient, t is the time, r is the radial position, a is the cylinder radius, and α_n is the nth positive root of $J_0(a\alpha_n) = 0$. Eq. (6.1-2) can be used to define the water concentration in the polymer fibre for either water absorption (in-diffusion) or desorption (out-diffusion). In terms of normalised concentration, Eq. (6.1-2) can be rewritten for absorption:

$$C(t,r) = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0(r\alpha_n)}{\alpha_n J_1(n\alpha_n)}$$
(6.1-3)

From Eq. (6.1-1), one can see that there are two factors contributing to the wavelength change of a POFBG. One is the core effective RI change induced by the humidity change, i.e., the RI humidity dependence. The other is the volumetric change of the fibre induced by the moisture absorption. Since the fibre cladding, which is made of PMMA in this work, forms the largest portion of the fibre's volume or weight, the volumetric change of fibre can be dominated and approximated by that of PMMA cladding. If a POFBG is fabricated in a fibre with smaller diameter it will result in faster response time, as indicated in Eq. (6.1-3). In previous work different POFs were investigated by using chemical etching [227]. Some POF (e.g., POF1 in [227]) shows a slow response time. Significant reduction of fibre diameter therefore is required to improve response time, which usually leads to unstable POFBG performance by using laser micromachining.

6.1.3 POFBG fabrication and laser micromachining

Due to the high optical loss of POF in the 1550 nm wavelength region [266] a short length (7 cm) of POF is used to construct a POFBG sensor, which was connected to a standard single-mode silica fibre down-lead using UV curable glue. POF cannot be cleaved in the same fashion as silica fibre, neither can it be spliced using a fusion splicer. Hence, a UV gluing technique was developed [271] in which POF is cut by using hot
blade to get a clean end face, then butt-coupled with an angled single-mode silica fibre pigtail; the butt-coupling joint was glued with UV curable glue (Norland 76). The PMMA step-index POF contained a 5 mm long FBG, fabricated by illuminating the fibre with 325 nm ultraviolet (UV) light from a HeCd laser through a phase mask placed on top of the POF. It should be pointed out that before grating fabrication the POF was annealed at 80°C over 7 hours. Therefore, all the POFBGs were annealed. This is important because the mechanical property of polymer optical fibre is affected by the remaining stress in the fibre. This stress may vary with environmental conditions, generating variability in POFBG response. This effect exists in both step indexed and microstructured polymer fibres [239,278].

Excimer laser was applied to create post grating structures on a series of POFBG with the same diameter of 130 μ m, FBG length of 5 mm. The laser micromachining set-up is followed by Fig. 5.3-4, where multiple scan with laser radiation fluences of 1.37 J/cm² and different masks have been used to generate the designed microstructures. The mask size was chosen to be 400 μ m and 1.6 mm, for slot and D-shape fabrication respectively, while the length of each microstructure was fixed at 5 mm (the same as FBG length).

6.1.4 Enhanced performance for humidity snesing

The humidity sensing was carried out with four POFBG samples (listed in Table 6.1-1) where one of them was normal POFBG at 1536 nm without any modification, while the other three were having different microstructures; one was slotted POFBG at 1563 nm with slotted-depth of 33.1 μ m, and other two were D-shaped POFBGs at 1572 nm with depths of 44.5 μ m ('D-shaped 1') and 50.5 μ m ('D-shaped 2').



Figure 6.1-1 Experimental setup for humidity sensing.

As shown in Fig. 6.1-1, the POFBGs were placed inside an environmental chamber (Sanyo Gallenkamp) to allow operation in a controlled temperature and humidity environment. They were illuminated via a fibre circulator with light from a broadband source (Thorlabs ASE730) and the wavelengths of the POFBGs were monitored by using an IBSEN I-MON 400 wavelength interrogation system. The environmental chamber was set at constant temperature (24°C) and programmed to change the relative humidity (RH) varying from 40% to 90% with an increment of 10% RH.



Figure 6.1-2 Wavelength responses of four POFBGs step-changed from 40% RH to 90% RH at 24°C, the wavelength traces for four POFBGs were offset to give a better view. (b) Normalised wavelength changes of POFBG sensors against a 10% step relative humidity change.

The wavelength responses of the four POFBGs with humidity change were recorded and plotted in Fig. 6.1-2(a) where the wavelength traces for the four POFBGs were offset to give a better view. The step-changed RH in environmental chamber was measured by using a built-in RH sensor and is plotted in Fig. 6.1-2(a) as well. To fully observe the time response of POFBGs the dwelling time at each relative humidity level was set to 90 minutes. One can clearly see that it takes a very short time for the chamber to establish the relative humidity to the setting value; however, for a normal POFBG it takes a much longer time to reach a stable response. The micromachined POFBGs show different improvements in time responses.

To compare the performances of the different POFBG humidity sensors, the measured humidity responses for the humidity changed from 60% RH to 70% RH are shown in Fig. 6.1-2(b). To simplify the comparison of the sensors which have different Bragg wavelengths, we chose to plot the time response of the relative wavelength change, $\Delta\lambda/\Delta\lambda_{max}$, which is the ratio of the grating's Bragg wavelength deviation from its original value to the maximum wavelength deviation induced by the humidity change [226]. The response time was estimated as the time of relative wavelength change being increased to 90% for the humidity step rise. For the normal POFBG sample (without any laser micromachining), the response time was estimated as 54 min, which was in agreement with 53 min reported in previous work [227]. The measured result for the slotted POFBG with a depth of 33.1 µm did not show much improvement on response time. Its response almost overlapped with that of the normal POFBG. We then tried to remove more cladding of the fibre. Two D-shaped POFBGs were machined, which showed a much improved response time, estimated as 30 min and 24 min for 'Dshaped 1' and 'D-shaped 2', respectively. From the results it looks like the greater the volume of cladding removed, the faster the response of the POFBG. According to Eq. 6.1-1, the wavelength change of POFBG induced by environmental humidity consists of two parts: humidity dependent refractive index change and humidity induced volumetric change in the fibre core. Thus, there are two ways to improve the response time of a POFBG humidity sensor. Firstly, if the moisture can reach the fibre core in a short time it means a fast response time. Secondly, reducing fibre size would accelerate the moisture diffusion process, as suggested by Eq. 6.1-3. The slotted POFBG with a depth of 33.1 µm, which does not reach the fibre core but allows the moisture into the fibre core more quickly than a normal POFBG. Examining the wavelength response of the slotted POFBG in Fig. 6.1-2(b) reveals a quick change at the start, then it drops a little bit and eventually it rises and overlaps with that of the normal POFBG. This indicates that the moisture does reach the fibre core more quickly, producing a quick

change of Bragg wavelength in the initial stage as the core index changes. However, the volumetric change in the fibre core not only depends on the moisture reaching the core but also on the volumetric change in the fibre cladding. Since the volume of fibre cladding is much larger than that of fibre core, the humidity induced volumetric change is dominated by the fibre cladding response time. From the slotted POFBG response one can see that there is a kink after the quick start. This kink also exists in all the machined POFBG responses to different extents. We believe it arises from the time lag between the humidity induced refractive index change in the fibre core and the volumetric change contribution from the bulk of the fibre cladding.

This explains why the response of the slotted POFBG is almost overlapped with that of the normal POFBG after the kink. In the case of the D-shaped POFBGs, the laser micromachining takes off a significant part of the POFBG cladding and so the volumetric change of the cladding takes less time to complete. Consequently, the time lag is smaller than that of the slotted POFBG response, and overall response time is much improved, showing a smaller kink. The response time of the deeply machined POFBG ('D-shaped 2') exhibits the fastest response time of 24 min, showing great improvement over the normal POFBG.

The above analysis can be verified by further experiment. As aforementioned, both humidity dependent refractive index change and humidity induced volumetric change in the fibre core contribute to the POFBG wavelength change. If the quick wavelength change in the initial stage is induced by humidity dependent refractive index and overall response time is dominated by the volumetric change of fibre cladding, removing the volumetric change will accelerate the time response of the POFBG. We proposed a technique in [226] to remove the humidity induced volumetric change in a POFBG by pre-straining the POFBG. The POFBG was strained by 2000 µe using a translation stage and then glued to an INVAR bar. The length of the PMMA optical fibre between the two anchoring points did not vary with PMMA swelling (given that the applied strain was larger than any humidity induced fibre swelling). The device length change due to changing temperature in this case was not determined by the POF thermal expansion but by the INVAR (the influence of the glue was negligible as the glued points were very small). Due to the low linear thermal expansion of INVAR $(1.2 \times 10^{-6})^{\circ}$ C) the pre-strain applied may vary with a rate of only 1.2 $\mu\epsilon$ /°C. However, in any case during the experiment the thermal change was negligible as temperature was fixed in the environmental chamber. With this arrangement, the POFBG humidity responsivity only relies on the humidity induced refractive index change. The relative wavelength changes of the prestrained slotted POFBG over 10%RH step change (from 60% RH to 70% RH) is plotted in Fig. 6.1-3 together with that when it was unstrained.



Figure 6.1-3 Wavelength changes of pre-strained and unstrained slotted POFBGs to a 10% humidity step change.

It can be seen form 6.1-3 that in the response of the pre-strained slotted-POFBG there is no kink which exists in the responses of both the slotted and D-shaped POFBGs Fig. 6.1-2(b). Moreover, the response time of the pre-strained slotted-POFBG is around 20 min, which is reduced by a factor of 2.5 than that of the slotted POFBG with no strain applied. These two features clearly indicate that pre-straining can remove humidity induced volumetric change in the POFBG and the response time of a POFBG humidity sensor can be accelerated by this process. However, this acceleration is achieved at the cost of reduced POFBG humidity sensitivity as the contribution from humidity induced volumetric change is removed [226]. It can be seen from Fig. 6.1-3 that 0.2 nm and 0.6 nm of wavelength change in pre-strained and unstrained slotted POFBGs are induced by 10% humidity step change, respectively. The humidity sensitivity of the slotted POFBG was 60 pm/%RH with no strain applied and reduced to 20 pm/%RH when a pre-strain of 2000 µε applied. The reduction in sensitivity is not really problematic as current interrogation systems typically provide resolutions around 1 pm, readily enabling RH monitoring to better than 1%. The response time of the pre-strained slotted-POFBG is even shorter than that of D-shaped POFBGs. Therefore, we expect the response time of pre-strained D-shaped POFBGs can be further reduced. However,

the optical performance of a pre-strained D-shaped POFBG is not as stable as that of the pre-strained slotted-POFBG. When we applied strain to the D-shaped POFBG, the reflectivity dropped rapidly and then vanished, even though the fibre was not broken. Removing the strain did not recover the grating response. The response times of all the POFBGs used in this work are summarised in Table 6.1.1.

POFBG samples	Micromachined depth (µm)	Humidity response time (min)
Normal	0	54
Slotted	33.1	53
D-shaped 1	44.5	30
D-shaped 2	50.5	24
Pre-strained slotted	33.1	20

Table 6.1.1 Summary of humidity response times of POFBG sensors used in this work.

The response time of a POFBG to humidity changes is mainly influenced by the geometry and size of the fibre. Laser micromachining can provide a flexible method to modify POFBG sensor performance. In this section POFBGs with different microstructures (slot and D-shaped) are utilised in humidity sensing applications. The D-shaped structure provides an improved response time, similar to the existing technique of fibre etching. Unfortunately, fibres heavily machined in this way become difficult to handle and lack robustness, similar to very small diameter etched fibres. The slotted fibre provides a way of allowing water in the environment rapid access to the fibre core, whilst preserving the strength of the device. It has been discovered that this geometry does not of itself significantly improve response time due to the dominant contribution of the swelling of the fibre cladding material. By pre-straining the sensor, this contribution can be removed allowing a much faster response due to the core index variation (a factor of 2.5 in our experiment). The penalty for this approach is a reduction in sensitivity, but the magnitude of the wavelength shift observed is still large enough to allow sub-1% relative humidity resolution with typical interrogation systems.

6.2 BP-TFG based chemical sensor for heavy metal detection

6.2.1 Background of heavy metal

Heavy metals are metals with relatively high densities or atomic weights. However, there is no widely agreed criterion-based definition for heavy metal, different research will have different distinguishing criterion. Usually, atomic weights 63.5 and 200.6 g/mol and a specific gravity greater than 5 g/cm⁻³ are considered to be heavy metals [279,280]. Heavy metals are considered as "Low density chemical components those are highly toxic" [281], they are almost non-degradable and ubiquitously distributed, leading to a great risk to human health and environment [279,282–284]. The toxicity of heavy metal is because they can alter the biochemical lifecycle [279,284] by forming bond with thiol group of proteins [285]. Some heavy metals like cadmium (Cd), lead (Pb), chromium (Cr) and mercury (Hg) are considered as hazardous compounds even at low concentrations, causing most of the heavy metal-related disease [286–288]. It needs to be recognised that lead is exceptional compared with other chemical hazards. Exposure to lead is associated with a wide range of effects, including various neuro developmental effects, cardiovascular diseases, impaired renal function, hypertension, and impaired fertility. According to the guidelines for drinkingwater quality of World Health Organisation (WHO), the maximum permissible limit of lead in drinking water is 10 ppb [280], which represents the lead concentration does not exceed tolerable risk to the health. Therefore, the detection of heavy metal becomes a major public concern in modern days.

6.2.2 Fabrication of BP-TFG sensor

As it was discussed in Chapter 3, black phosphorus (BP) has a unique puckered orthorhombic structure and in-plane anisotropy, BP possesses much larger surface-to-volume ratio, extremely high hole mobility and superior molecular adsorption energy than those of other 2D materials [103,105,289]. The extraordinary properties of BP make it a very promising nanomaterial for widespread applications such as BP field-effect transistors (FETs), modulators, photodetectors, chemical sensors, bioimaging and biomedical therapy [103,113,122,149,152,289–291]. In addition, comparing with conventional LPG, tilted fibre grating (TFG) owns narrow band resonances demonstrating much higher Q-factor hence high accuracy in optical signal

detection [14,42,46,292]. In particular, the excessively tilted fibre grating shows much lower thermal and tension cross-talk effects and higher sensitivity in lower refractive index (RI) region [14]. Therefore, high sensitivity is expected to be obtained via the combination of these two techniques.

The 81°-TFG with length of 12 mm was UV-inscribed in hydrogen loaded Corning SMF-28 fibre by using a frequency-doubled Ar laser and mask scanning technique. A custom-designed mask with a pitch of 6.6 µm was purchased from Edmund Optics Ltd. The mask was rotated in the plane of incidence to realise grating fringes tilted by 81° with respect to the fibre axis. Multiple scans were applied to achieve a maximum forward cladding mode coupling at the wavelength determined by the following phase-matching condition described in Eq. 2.2-49. Then, the BP nanosheets were synthesised and deposited following the procedure presented in Section 3.4. The result of deposition was examined by a group of methods which shown in Figure 3.4-4.

6.2.3 **BP-induced** polarisation-selective coupling

The BP-induced optical properties were experimentally investigated by monitoring the spectra evolution of a tilted fibre grating over entire BP deposition process. For an 81°-TFG, the excessively tilted plane of index-modulated grating breaks the symmetry of mode coupling, inducing the significant polarisation dependent coupling characteristics. 81°-TFG exhibits two sets of comb-like split resonances in transmission spectra, which suggest that the light have been coupled into two sets of birefringence modes corresponding to two orthogonal polarisation modes, TM and TE modes [46]. The polarisation modes can be fully excited by launching the linearly polarised light. Spectra (i) in Fig. 6.2-1 (a) show a zoomed-pair of polarisation modes, in which TM and TE modes have been fully excited, respectively. The transmission spectra of BP-TFG were monitored during deposition process and recorded as (ii), (iii), (iv) and (v) in Fig. 6.2-1 (a) after 2nd, 4th, 6th and 8th coating cycle, respectively. It is apparent that the polarisation depends on BP overlay thickness. As can be seen from Fig. 6.2-1, optical signals (both TM- and TE-polarised resonances) show a significant red-shift in wavelength and a decrease in intensity against the increase of overlay thickness which was determined by number of coating cycles. The wavelength shift was attributed to the increase of cladding effective refractive index induced by high RI coating layer, and

consequently the phase-matching condition was tuned. The leaky radiation from cladding to coating layer could reduce the coupling coefficient between core and cladding modes hence decrease the resonant intensity.



Figure 6.2-1 (a) Spectral evolution during BP-deposition process revealing strong light-matter interface and optical tunable features, where (i-v) represent for 0,2, 4, 6, 8 cycles coating, respectively.(b) Wavelength shift and (c) intensity change of TM- and TE-polarised resonances against number of deposition cycles.

It should be emphasised that the extinction ratio has been extremely enhanced with the increase of BP overlay thickness, meanwhile a polarisation-selective coupling feature has been clearly observed. As shown in Fig. 6.2-1, the variation of TE mode is always larger than that of TM mode. After 8 cycles of BP deposition, TE mode has 16.9 nm in wavelength shift (Fig. 6.2-1b) and 4.35 dB in intensity decrease (Fig. 6.2-1c), which are 1.2 times and 2.1 times larger than those of TM mode, respectively. The separation between two polarised resonances of BP-TFG has been increased to 8.38 nm, giving an estimated birefringence of $\sim 3.0 \times 10^{-4}$ which is 150% enhancement that of bare 81°-TFG. In such BP-TFG architecture, TE-polarised radiative light can be strongly perturbed by BP overlay in terms of coupling and guiding, leaving the TM-polarised light passes through the fibre.

6.2.4 Stability performance of BP-TFG

Despite the great potential of BP on chemical sensing, black phosphorus is facing a great challenge on its poor air and water stability. BP degrades to oxygenated phosphorus (POX) quickly in ambient environment, and hence lead to the degradation of its electric properties and device performances. It is a severe problem for sensing applications. However, some works has reported that relative thick BP flakes can reduce the degradation effect [290]. Therefore, to minimise the degradation problem, the BP overlay coated on TFG for lead ion (Pb²⁺) sensing was designed to be ~300 nm and a relative fast operation could be applied.

Preliminary to the lead ion detection, a stability test was performed in DI water (without any Pb^{2+} ions). The BP-TFG was immersed into DI water for 120 s, and then dried in air for 180 s until the transmission spectrum become steady. This procedure was repeated for 3 times and the results are shown in Fig 6.2-2. The spectrum does not show significant difference where the standard deviation is calculated to be 0.003 dB.



Figure 6.2-2 Water stability of the BP-TFG.

6.2.5 Heavy metal chemical sensing

After the preliminary test, the BP-TFG was exploited for the implementation of heavy metal chemical sensing. The experiments were conducted with the setup illustrated in Fig. 6.2-3. The light from broadband source was launched into BPTFG and the output

was monitored by an optical spectrum analyser (OSA). By adjusting the polarisation controller, the TM polarised resonance was fully excited and selected for optical signal monitoring.



Figure 6.2-3 Experiment setup for lead ion sensing.

To avoid thermal and tension cross-talk effects, the BP-TFG was mounted on a homemade mini-bath with two ends fixed and all the experiments were implemented at room temperature. A series of aqueous solutions containing Pb²⁺ ions with concentrations of 0.1, 1.0, 10, 100, 1000, 1×10^4 , 1×10^5 , 1×10^6 and 1.5×10^7 ppb was prepared for the detection. The BP-TFG was firstly immersed into Pb^{2+} solution (0.1) ppb concentration) for 120 s, the solution was subsequently withdrawn by careful pipetting to expose the BP-TFG in the air for 180 s when the transmission spectrum achieved steady and was captured by OSA. Afterwards, the BP-TFG was washed with ethanol thoroughly to remove the adsorbed lead ions prior to next concentration measurement. The detection procedure was performed serval times with the same device and one of the typical transmission spectra at different Pb²⁺ concentrations are plotted in Fig. 6.2-4(a). By increasing Pb^{2+} concentration, the peak shows apparent intensity decrease indicating the strong optical absorption occurred between BP and lead ions. The slight wavelength red-shift could be caused by the increase of effective refractive index of cladding. This type of response is in strong agreement with the thick deposition case (7 cycles) discussed in Section 3.3.3, where the intensity change becomes the main indicator of the spectrum.

The intensity change as a function of Pb^{2+} ion concentrations of was extracted and plotted in Fig. 6.2-4(b), revealing a non-linear relationship with piecewise sensitivities of 0.5×10^{-3} dB/ppb, 7.7×10^{-7} dB/ppb and 2.3×10^{-8} dB/ppb for Pb²⁺ concentration ranges of $0 \sim 100$ ppb, $10^3 \sim 10^5$ ppb, and $10^6 \sim 10^7$ ppb, respectively. The proposed BP-TFG can effectively detect Pb²⁺ ions concentration over a wide range from 0.1 ppb to 1.5×10^7 ppb with no saturation effect, which is four orders of magnitude larger than that of BP-

FET based lead sensor [122]. The reported BP-FET sensor limited its detection for Pb^{2+} concentrations lower than 10 ppb and faced the saturation problem for concentrations higher than 1×10^5 ppb.



Figure 6.2-4 a) Transmission spectra of TM-resonance showing a clear up-shift as Pb^{2+} concentration increases. (b) Resonant intensity change against Pb^{2+} concentrations. The blue line is the best logistic fitting curve and the dashed horizontal red line represents three times the standard deviation of the blank measurement.

The limit of detection (LoD) is generally defined as three times the standard deviation of its blank measurement. To calculate the LoD, the logistic fitting of the experimental data is plotted in Fig. 6.2-4(b) with error bar displayed. The dashed red line represents intensity change three times the standard deviation (0.003 dB in last section). Therefore, the LoD of BP-TFG is 0.25 ppb for Pb²⁺ ions, which is 4-fold better than CNTs-based heavy metal sensor [293]. Meanwhile, this LoD of 0.25 ppb is only one fortieth of WHO's permissible limit of 10 ppb for lead in drinking-water [280]. In addition, the sensing range of the BP-TFG based sensor is also much larger than that of FET-based Pb²⁺ sensor [122].

For comparison, the similar detection was also conducted for light metal Na^+ ions (spectrum shown in Fig. 6.2-5(a)) with the results plotted as green symbols in Fig. 6.2-5(b), showing a very limited sensitivity. It reveals that BP exhibits strong adsorption of heavy metal ions hence the ultrahigh sensitivity for lead detection.



Figure 6.2-5 (a) Transmission spectra of TM-resonance showing a clear up-shift as Na^{2+} concentration increases. (b) Resonant intensity change against ion concentrations of Pb^{2+} (blue symbols) and Na^+ (green symbols). The blue line is the best logistic fitting curve and the dashed horizontal red line represents three times the standard deviation of the blank measurement.

In addition, the reusability of the BP-TFG was examined by repeating the detection procedure with highest concentration Pb^{2+} solution (1.5×10^7 ppb). With the results shown in Fig. 6.2-6, it is clear that only very slight difference is shown in the peak intensity, showing excellent reusability for lead ions detection, and potential to develop a more cost-effective and reusable chemical sensor.



Figure 6.2-6 Reusability of BP-TFG for heavy metal sensing. For all detection cycles, resonant intensities were monitored in the air under following conditions: i) (black symbol) the initial device; ii) (blue symbols) after detection of Pb^{2+} ions ($1.5x10^7$ ppb); iii) (red symbols) after Pb^{2+} ions were washed away by ethanol, demonstrating the recovered intensities.

It is believing that the basic mechanism underpinning the unique optical properties of BP-TFG is the adsorption of BP to heavy metal ions. It has been reported that BP band gap can be widely tunable by thickness, strain, electric field and dopant [150,294,295]. As the pristine BP behaves as a p-type semiconducting characteristic, its majority charge carriers are holes. The adsorption of heavy metal ions denoted charges and enhanced hole carrier concentration in BP. With increasing ion density, the electric field from the ionised donors gradually reduced band gap owing to the giant Stark effect and tuned the electronic state of BP from a semiconductor to a Dirac semimetal [294]. Due to its ultrahigh carrier mobility and superior molecular adsorption energy, BP has strong capability to attract heavy metal ions. When the carrier concentration was large enough, correlation effects became significant and resulted in an increase of carrier-induced refractive index change. Consequently, the fibre guided optical wave was modulated by perturbing phase condition and absorption coefficient.

6.3 Chapter summary

In this chapter, laser micromachined POFBG based humidity sensors and BP coated TFG based heavy metal chemical sensor have been demonstrated.

The humidity sensors based on POFBG respond to the water content change in the fibre induced by varying environmental condition. The water content change is a diffusion process. Therefore, the response time of the POFBG sensor strongly depends on the geometry and size of the fibre. By laser micromachining, microstructures such as Dshaped and slot can be created on the POFBG which can significantly improve the response time of the POFBG to humidity change. For slotted POFBG, due to the slow expansion of the bulk of the cladding, a pre-strain will be necessary to remove the humidity induced volumetric change, and the response time improvement would be revealed as a result. The BP-TFG was exploited as the first BP-fibre optic chemical sensor for heavy metal detection with significant performance. The BP-TFG sensor is benefited from the BP overlay where BP overlay has not only enlarged the light-matter interaction but also provides a sensing layer for heavy metal. By taking advantage of the in-situ self-assembly based multilayer deposition method discussed in chapter 3, the unique optical tunable features including coating thickness-dependent polarisation and polarisation-selective coupling have been experimentally observed. Furthermore, the BP-TFG was exploited for heavy metal Pb²⁺ ions detection, demonstrating ultrahigh sensitivity up to 0.5×10^{-3} dB/ppb, much lower limit of detection down to 0.25 ppb, and extremely wide concentration range from 0.1 ppb to 1.5×10^7 ppb. The BP-fibre optic architecture will open the path as an optical platform for superior chemical sensing and biomedical applications.

Chapter 7 Conclusions and future work

7.1 Conclusion

This thesis has detailed the study on advanced fibre grating technology and its applications for chemical and bio- sensing. Three strategies aiming at improving the sensing performance including novel grating structures, 2D material deposition and fibre cladding laser modification were proposed and investigated both theoretically and experimentally. Several biochemical sensors, such as dLPG-based DNA sensor, GO-LPG based haemoglobin sensor, GO-dLPG based immunosensor, BP-TFG based heavy metal chemical sensor and laser-modified POFBG humidity sensor were presented.

Starting from fundamental Maxwell equations, the theory behind fibre gratings (FBGs, LPGs and TFGs) was thoroughly discussed. By solving the coupling between propagating modes, the behaviour of light in a grating contained fibre can be described in spite of the grating type. Therefore, all of the properties including propagating modes, grating spectra, and resonance wavelength were discussed. In addition, the underlying mechanism of fibre grating sensitisation strategies were also demonstrated.

In the second part, two advanced technologies, i.e. 2D materials deposition and laser micromachining, have been employed as promising approaches for device sensitisation.

For 2D materials deposition, an in-situ self-assembly based multilayer deposition technique has been developed. Graphene oxide (GO) and black phosphorene (BP) nanosheets were successfully deposited on cylindrical fibre devices. The surface morphological characteristics were investigated by the use of optical microscope, AFM, SEM, Raman spectrum. The optical effect of 2D materials deposition on fibre gratings was also observed resulting the enhancement of the RI sensitivity. In addition, the 2D material-induced polarisation effect has been revealed.

For laser micromachining, the working principle and structure of both excimer laser and femtosecond laser were discussed. The excimer laser was used to produce D-shape and side-slot structures on polymer fibre device, which has been further utilised for humidity sensing. In addition, a novel photodegradation effect on PMMA under excimer laser exposure was discovered and discussed. Femtosecond laser was used not only for the fabrication of microstructures but also for the inscription of LPGs. A systematic study was carried out for the fabrication of LPGs, including grating length, grating period, repeatability, and its RI sensitivity.

In the application part, serval advanced fibre optic biochemical sensors were proposed and developed, including EDC-mediated DNA sensor, GO-LPG based haemoglobin sensor, GO-dLPG based immunosensor, BP-TFG based heavy metal sensor, laser modified POFBG humidity sensor. All these biosensors were proved to have significant sensing performance with the assistance of both novel design of grating structures and/or by the 2D material coating. The dLPG-based DNA sensor achieved a detectable oligonucleotide concentration of 4 nM. A sensitivity of 1.9 dB/(mg/mL) to haemoglobin and a detectable concentration of 0.05 mg/mL were presented by the GO-LPG based biosensor. GO-dLPG based immunosensor demonstrated an ultrahigh sensitivity with limit of detection of 7 ng/mL for the detection of anti-IgG, which is 10fold better than non-coated dLPG biosensor and 100-fold greater than LPG-based immunosensor. The proposed BP-TFG sensor was the first BP-fibre optic chemical sensor for heavy metal detection. It revealed an ultrahigh sensitivity up to 0.5×10^{-3} dB/ppb, a lower limit of detection down to 0.25 ppb than BP-FET based sensor, and extremely wide concentration range from 0.1 ppb to 1.5×10^7 ppb.

In conclusion, despite the fibre grating was developed for decades, there are still many spaces to improve the performance of these fibre grating sensors, such as sensitivity, stability and application range. Therefore, plenty of efforts have been made on both grating fabrication phase and post-modification phase. Many special designs on grating were developed, including but not limited in lager tilted fibre gratings, dual-peak long period gratings, and cascade gratings. In addition, advanced technologies, like the aforementioned laser micromachining technique and nanotechnology can be involved, opening new research fields for the fibre optics.

7.2 Future work

Biofunctionalised black phosphorus based biosensing

Due to its excellent properties, black phosphorus has been utilised in plenty of applications, including humidity, gas and chemical sensing. However, due to its air instability, it was seldomly used in biosensing applications. Fortunately, with the development of BP preparation and other aspects, BP based biosensors were started to be reported [296–298]. Without considering its instability, black phosphorus is considered as non-toxic material which is ideal for biosensing [299].

One challenge is that it is hard to immobilise biomolecules on black phosphorus sheets because BP does not have any functional group. However, it is recently realised that poly-L-lysine (PLL) can be a good candidate for crosslinking agent between BP and biomolecules. The poly-L-lysine (PLL) can have π - π interaction with BP basal plane to form covalent bonding with biomolecules via its amino group.

Neuron-specific enolase (NSE) is a typical biomarker for small cell lung cancer (SCLC). The biorecognition reaction between anti-NSE and NSE are now enabled the clinical detection of endocrine tumours.

Optofluidic based sensing

As a fascinating technology, the advantages of microfluidic include but not limited to reduced sample and reagent volumes, improved portability, high sensitivity, enhanced processing rate, low cost, and the potential to minimalize artificial error. Benefiting from these, the microfluidics has drawn great research interest from both academic and industry institutes. To date, various microfluidic structures such as micromechanical valves microchannels, micropumps, microfluidics mixers and other components have been developed to realise functions like focusing, separation and fractionation of biomedical or chemical particles. The type of microfluidic can be categorised as active and passive types depending on their source of the manipulation forces. In particular, passive microfluidic technology is always being very simple but efficient and is able to handle relatively higher flow rate.

Within decades, photonic devices are evolving towards a similar direction with fluidics, which is miniaturisation. Hence the idea of fabricating a compact and versatile chip with integrated function of microfluidics and photonic analysis devices has come up as

"optofluidic", which basically aims to manipulate fluids and light at microscale and exploit their interaction. Many applications such as integrated biochemical sensing is made not only available, but also tunable, reconfigurable, and adaptive. Among them, the "label-free" sensing which based on refractive index variation is becoming more and more competitive, as its counterpart, fluorescence-based detection, suffers from disadvantages like complicated labelling process and biochemical properties distortion. The "label-free" sensing does almost no alternations to the analytes, making it particularly suitable for real-time monitoring without interfering the reactions. So far, the reported "label-free" optofluidic sensors are including Mach-Zehnder interferometers (MZIs) [300], Young interferometers [301], and also fibre gratings [302,303].

Particularly, the integration with microfluidic channel will lead to many benefits to the fibre grating based biosensors, producing excellent optofluidic system. Firstly, the closure of microfluidic channel can provide stable environment for the biorecognition reaction, increasing the accuracy and reliability of the detection results. Furthermore, relatively small size of the channel will limit the biomolecule in a small space, where the sensitivity of the biosensing can be enhanced. In addition, both of probe and target biomolecules are usually hard to synthesis and expensive, the microchannel can also help to save the cost of a biosensing protocol.

Hereby, the designed microfluidic channel in Fig. 5.4-5 was fabricated and shown in Fig 7.2-1, the channel was fabricated by femtosecond laser on a Teflon bar and then assembled with a hard PMMA bar by physical pressure to constitute the microfluidic channel part. In addition, a fibre grating can be embedded in the channel to form the signal transducing part. This structure is made dispatchable, and thus for different biosensing applications, one may only need to change the grating core in the optofluidic system.



Figure 7.2-1 The fabricated microchannel for fibre grating integration (a) the image of dye test (b) the image of optofluidic system during biosensing application.

Multiplex biosensing

Multiplexed biosensing is vitally important for the point-of-care (PoC) testing, because many diseases often involve a complex panel of biotargets. Therefore, the diagnostic can be improved both in accuracy and reliability by analysing multiple biomarkers simultaneously. Multiplexed point-of-care biosensing is thus become a hot research topic within decade. The PoC testing usually requires portable, inexpensive, and userfriendly sensor platforms which also have high sensitivity and stability. The advanced configuration of optic fibre grating based sensors discussed in this thesis are considered to be the excellent candidates for the multiplexed PoC testing. Based on the configuration of biorecognition detection, where kinetic bioaffinity binding dominated by the immobilised bioprobes, multiplexed biosensing is naturally allowed on the fibre grating platform. For instance, as shown in the schematic of Fig. 7.2-2, on an optic fibre with multiple gratings, multi-spot detection system can be established by immobilising different bioprobes at different grating region. Then such multiple gratings-contained device can be used to detect serval target biomarkers simultaneously on a single biochip. Additionally, the interrogation system can be further simplified, fully integrated devices will allow the detection results to be displayed without all the optical instruments and data processing.



Figure 7.2-2 Schematic of multiplex biosensing based on fibre grating platform.

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