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Sol-gel based fabrication methods for photonic crystals

Yin Huang
Iowa State University

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Sol-gel based fabrication methods for photonic crystals

by

Yin Huang

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Major: Electrical and Computer Engineering

Program of Study Committee:
Meng Lu, Major Professor
Long Que
Sumit Chaudhary

Iowa State University
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ABSTRACT

Photonic Crystals (PhCs) composed of periodic change of dielectric materials are capable of manipulating the interaction between photon and materials and thus controlling the flow of light. Undergone a rapid theoretical and technical exploration during the past three decades, PhC structures have been implemented in numerous photonic devices and have been found useful for widespread applications, such as communication, optical sensor, energy harvest, and display. As PhC-based devices operating in the visible or near Infrared (NIR) wavelength regimes, the period of the dielectric constant modulation is sub-wavelength and below one micrometer. At such a length scale, the fabrication of PhC structure with a sufficient precision and size is challenging.

In this thesis, sol-gel based fabrication methods are demonstrated to fabricate PhC slabs on a glass substrate and three dimensional (3D) PhC inside a capillary tube. The one-dimensional (1D) and two-dimensional (2D) PhC slabs, which are also known as guided mode resonant (GMR) filters, have dielectric thin film with a high refractive index ($n = 1.78$), functions as the light confinement layer. Meanwhile, the imprinted periodic structure on hybrid inorganic-organic sol-gel thin film couples the light excitation into PhC slab mode. It has been studied for their capabilities of generating narrowband reflections in visible and NIR portions of the spectrum. The sol-gel based imprint method uses titanium alkoxides sol-gel solution to transfer desired patterns from a master mold to the glass substrate within 5 minutes. This one-step fabrication process warrants a simple, rapid, and low-cost formation of PhC slab structures over a surface area as large as 1 cm$^2$, which is currently limited by size of available imprint mold. Also, our sol-gel imprint approach enabled the tuning of PhC slab modes by pre- and post-imprint processes. The fabricated PhC slabs were characterized and their applications in refractometry-based biosensing were explored. The 1D PhC slab filter exhibited a $Q$ factor of 70 at resonant
wavelength while 2D PhC slab filter had Q factor of 158 at resonant wavelength. As for refractometric biosensor, a bulk sensitivity of 50 nm per refractive index unit and the detection of monolayer of polyamino acid have been measured.

In addition, efforts have been devoted to investigate the fabrication of 3D PhC inside a capillary tube, where the self-assembly polystyrene (PS) sphere was exploited as the template. Within a few simple steps, inverse opal PhC structures were generated inside glass tubes and can perfectly work as nanoscale optofluidics. With volume ratios of polystyrene and sol-gel solution from 5:1 to 7:1, the fabricated inverse opal PhC structures were discovered to be more compact and ordered. By trying different PS sphere diameters of 185nm, 236 nm, 269nm, and 307nm, the resonant wavelengths of inverse opal PhCs have been found a linear redshift with an increase of PS sphere diameter.
CHAPTER 1: INTRODUCTION

Since the discovery of PhCs composed of periodic dielectric structures with a photonic band gap, it has opened a new method for controlling light. With this unique property, PhCs have been extensively developed and have been used in area of communication, biosensor, energy harvest, and display. The mostly used method to fabricate 1D and 2D PhCs would be electron beam lithography which has an advantage of flexibly and precisely writing any arbitrary pattern but it is a time-consuming and expensive process. When it comes to 3D PhC, fabrication situation becomes tough and challenging. A suitable method proposed is laser interference lithography which is based on interference of four lasers [1]. However, after the advent of self-assembly based technique [2, 3], laser interference lithography is not so useful anymore. In this study, it is aimed to find fabrication methods of PhCs with goals of simplicity, low cost, large-scale fabrication, and high throughput.

1.1 Motivation

Recent works have demonstrated successes of transferring nanopatterns to substrates by imprint lithography and directly fabricating nanostructures by self-assembly technique. Both the imprint lithography and self-assembly technique do not require strict fabrication environment, for example clean room, and complicate fabrication tools. But, good fabrication techniques are not enough to achieve goals mentioned above. Therefore, the sol-gel technology is proposed. It is temporarily regarded as a one of fast growth of technologies. So far, with outstanding thermal, chemical and mechanical stabilities, uses of sol-gel technology to make chemical sensors and biosensors are very popular. This is because of several advantages: 1. an economical, quick, and ease fabrication with mass production. 2. a flexibility to change design of sol-gel process, for example adding dopant. 3. a flexibility at the bulk level to make sol-gel solution comfortable to arbitrary
configurations with a good surface quality. According to former reporters, the fabricated sensor configurations usually includes monoliths [4, 5], and thin film [6, 7] with micro and nano scale but few reports for nano periodic structure. In most sol-gel derived devices, microporous structures were often found so that it can be served as a matrix for entrapment of other small molecules for example chemical reagents [8] and biological reagents [9]. In addition, due to optical perspective, the sol-gel derived metal oxide materials (such as TiO$_2$ and SiO$_2$) with high refractive index possess low optical loss. So far, the sol-gel derived photonic devices conclude anti-reflector[10], waveguides [11], cavities, Brag reflector [12], dye-sensitized solar cell [13, 14], and so on. Based on advantages of sol-gel technology, it is believed that with the combination of sol-gel technology, imprint lithography and self-assembly technique are promising to fabricate PhCs.

1.2 Outline

Due to engineered properties of sol-gel technology and convenient fabrication techniques, a fast and economical fabrication method is proposed by combining sol-gel technology and imprint lithography to fabricate 1D and 2D PhC slabs (GMR filters). In addition, for the 3D PhC fabrication, a sol-gel based self-assembly technique is used.

Chapter 2 describes a basic chemistry of sol-gel technology at first. Based on sol-gel technology, sol-gel imprint lithography is introduced to fabricate PhC slabs. The final subsection is relative to a development of sol-gel technology in photonic devices.

Chapter 3 focuses on the fabrication of PhC slabs. A basic description of how PhC slabs work is presented at start of this chapter. It also includes simulation results as a basis to design PhC slab structures by using rigorous coupled wave analysis (RCWA) and the subsequent fabrication process is presented. The details of corresponding experiments
for characterizing PhC slabs are introduced. After that, rest of chapter is aimed to application of PhC slabs.

Chapter 4 is mainly on purpose of introducing how sol-gel based self-assembly technique is used to make 3D PhC. Meanwhile, the fabrication process and characterization of fabricated 3D PhC are presented. In order to find potential applications, simulation works were finished to discover how 3D PhC affects near electrical field distribution of gold (Au) nanoparticles by using Finite-different time-domain (FDTD) solutions (Lumerical solution, Inc).

Chapter 5 is a conclusion of thesis. A summary of works in this thesis is presented. Meanwhile, regarding fabrication methods and fabricated devices, the future plans and improvements are discussed.
CHAPTER 2: SOL-GEL PHOTONIC WITH IMPRINT LITHOGRAPHY

The goal in this chapter is to introduce the fundamental principles of sol-gel imprint lithography and development of sol-gel photonics. The common use of sol-gel technology is to fabricate glass. In figure 2.1, an overview of sol-gel technology is presented.

2.1 Sol-Gel Chemistry

The sol-gel technology is composed of two physical states which are called sol and gel respectively. Sol is not same as a solution because in sol, there is a giant number of small particles suspending in another major phase system for example in a liquid phase while the solution is purely one single-phase system. On the other words, the system of sol solution works as a membrane which cannot distinguish between pure liquid molecules and small particles while for the large size of particles, it is separated from sol system. When a sol solution does not become a gel state, it usually is as stable as s solution. It is because that for very small sizes of dispersed particles, gravitational forces and Van Der Waals forces are negligible to affect sol system. Once particles in a sol solution aggregate together and become heavy, the aggregated particles will participate. However, there is a way that the sol system can form a continuous network of polymer in three dimensions and not participate. This states that the sol solution has started to become gel. Gel is solid and usually soft with low elastic modulus. The composition of gel might not be same as sol solution due to chemical reactions inside. At the following subsection, details of sol-gel technology are presented.
Figure 2.1 an overview showing how to synthesize so-gel based thin film and sol-gel based powder [6]

Here, a titanium-based precursor is set as an example for introducing this technology. The chemistry of sol–gel process is mostly dependent on hydrolysis (Eq. 1) and condensation (Eqs. 2, 3) of metal alkoxides [15]. These two kinds of reactions are the basis of leading to the formation of gel.

\[
Ti(CH_3O)_4 + H_2O \xrightarrow{\text{yields}} Ti(CH_3O)_3 - OH + CH_3 - OH
\]  

\[
Ti(CH_3O)_3 - OH + CH_3 - O - Ti(CH_3O)_3 \xrightarrow{\text{yields}} Ti(CH_3O)_3 - O - Ti(CH_3O)_3 + CH_3 - OH
\]  

\[
Ti(CH_3O)_3 - OH + HO - Ti(CH_3O)_3 \xrightarrow{\text{yields}} Ti(CH_3O)_3 - O - Ti(CH_3O)_3 + H_2O
\]

It is generally agreed that hydrolysis reaction is proceed with the displacement of alkoxide groups. This reaction can be performed both in acid condition and base condition. When pH value of sol solution is below 7, alkoxide groups are protonated by positive hydrogen ions. The resulting precursors have become more electrophilic and the
water is inclined to attack precursors. The specific reaction showed in equation (1) is that water molecule react with precursor at result of making one alkoxide group leave from precursor. On contrast, when pH value of sol solution is above 7, sol solution has a lot of hydroxyl anions which are nucleophilic. The hydroxyl anions then are more willing to bond with precursors and the precursors become unstable. By leaving one alkoxide group, the precursors return to be stable. No matter what value of pH in sol solution is, the function of hydrolysis is to displace alkoxide groups of precursors with hydrogens.

As for condensation reaction, it is aimed to form small size of cluster. The widely accepted mechanism is that after lefts of alkoxide groups, the resulted titanium intermediates become nucleophilic and are inclined to attract neutral titanium precursors. The other kind of condensation is that the two precursors which are nucleophilic and electrophilic respectively can react with each other. Both these two kinds of condensation reaction involve chain reaction to form clusters with very small size. At same time, these clusters are likely to aggregate together to form gel with high viscosity.

Reports [15, 16] show that hydrolysis rate, condensation rate, and formation of small cluster during sol-gel process are affected by the pH value of sol solution. Under the acid condition, hydrolysis reaction is accelerated due to a large amount of protonation of alkoxide groups. But, the hydroxyl groups on the titanium intermediates have also been protonated and the condensation reaction between titanium intermediates is prohibited. Also, repulsion due to the protonation of clusters will overcome Van Der Waals force and clusters cannot aggregate together. Therefore, if sol-gel solution is under low pH, it will keep at state of sol for a long time. In basic conditions, alkoxide groups are deprotonated to be nucleophilic. It leads to the acceleration of reaction while the
hydrolysis reaction is suppressed. Due to the increase of condensation rate, it results in quick precipitation of clusters which are observable by human eyes and participated particles are porous.

The mechanisms presented above are general descriptions of chemical reactions in sol-gel technology. By adding base as a catalyst, the whole process of sol-gel technology is accelerated while it could be slowed down by adding acid. For producing sol-gel based powders, it is recommended to add base into sol-gel solution. But, in consideration of fabrication, it is beneficial to have sol-gel solution to be maintained at sol state for a long time of use. Acid-based catalyst is an option but condensation reaction is slowed down resulting in a slow change of sol-gel solution’s viscosity which is crucial for spinning-coating. Furthermore, if the homogeneity of fabricated structure is taken into consideration, adding base is not a good option due to a fast of participation of clusters in sol-gel solution. Therefore, in my fabrication, only a small amount of water is added into sol without any acid and base. It is because that due to short of water, the hydrolysis reaction and condensation reaction are slow at same time and only when there is a condensation reaction that is complete to release a water molecule, a precursor then can react with a water molecule. With step by step, alkoxide groups are replaced and the final products will be more homogenous. Meanwhile, with a slow reaction speed, the sol can be kept for longer time when desirable viscosities are met.

In addition to influence of pH value, the temperature of baking gel is key to decide whether there is a crystal structure inside. After heating reaction products above 300 °C, titanium-based gel starts to form anatase structure. As temperature increases up to 600 °C, the TiO₂ with rutile structure is also observed [15].
2.2 Sol-gel Imprint Lithography

Since the breakthrough of fabricating nano pattern with 25 nm resolution by imprint lithography [17], it has been already regarded as a promising techniques after years of development. This technique is not necessary to have complicated fabrication tools and strict fabrication environments. Besides that, the advantages of low cost, fast time of fabrication, and high production throughput attract societies’ eyes. One of useful applications for this techniques is the fabrication of photonic devices. In order to fabricate photonic devices by using imprint lithography, materials used should have satisfied several requirements: 1. mechanical and chemical stabilities at different temperatures. 2. the chemical stability to other chemicals should be high. 3. sometimes, the material also should not be sensitive to visible and UV light. The metal alkoxides based sol-gel solutions are good candidates to satisfy requirements above. Therefore, the sol-gel imprint lithography is developed and is known as an economical and simple method in fabrication of photonic device.

The basic fabrication process of sol-gel imprint lithography is showed as following in step by step shown in figure 2.2. Firstly, a droplet of sol-gel solution is dropped on a substrate and spreads to form a sol-gel thin film when sol-gel solution’s viscosity is good to be used. The viscosity is influenced by the progress of condensation. Usually, it is better to wait for a few days after preparation of sol-gel solution in order to have a better viscosity. A patterned polymer stamp made by polydimethylsiloxane (PDMS) is put onto surface of sol-gel thin film. For a better uniform shape of pattern, applying a force on PDMS might be a good choice. With help of capillary force, surface pattern on PDMS is filled with sol-gel solution. The substrate is sintered at a temperature
above 100 °C for removing solvent such as water and alcohol. After that, sol-gel solution turns into solid. These solvents are evaporated and diffuse through PDMS into air. By using this techniques, the nano patterns can be produced quickly and simply by using polymer molds.

Figure 2.2 a review of sol-gel imprint lithography to fabricate nanopattern. (a) drops of sol-gel solution are dropped on substrate and PDMS mold is brought to contact with substrate. (b) due to capillary force, the PDMS pattern is filled with sol-gel solution. (c) PDMS/sol-gel solution/glass sandwich is then dried under room temperature. (d) after removing PDMS, a heat treatment is performed to solidify sol-gel solution.

However, attentions should be paid to several problems. Firstly, it is hard to control the layer thickness of device because a droplet of sol-gel solution might have different thin film thicknesses after spread of sol-gel solution on substrate due to the influences of humidity condition, surface morphology of substrate, hydrophilic ability of substrate, and so on. An improvement to this problem is to spin sol-gel solution directly to PDMS stamp so that the layer thickness is controllable by spinning speeds. Then, the choice of precursor is important. Different precursors results different reaction products which have different tolerances to high temperature [18]. Some of reaction products might have cracks during sintering process. For the fabrication of photonic devices, this is a very serious problem. Finally, the shrinkage of sol-gel during sintering process
should be taken into consideration in the fabrication of photonic devices. The shrinkage might result in size difference between fabricated devices and designed devices. Therefore, the choice of precursor and shrinkage are important in sol-gel imprint lithography. In this thesis, a titanium-based precursor that is used results in a minimal shrinkage and no crack in reaction product when fabricated devices were under inspection of scanning electron microscopy.

2.3 Sol-Gel Photonics

The common application of sol-gel technology is served as a coating material. Due to transparent characteristic, the sol-gel solution can be coated on glass and metal surface. It either works as an anti-reflection layer to reflect sun light or a protection layer to prevent from chemical corrosion. After years of development of sol-gel technology, it has widened its applications to photonic devices [19, 20], biosensor [21], chemical substance indicator [8, 22], and so on. One of interesting applications is relative to photonic devices:

1. Tailoring properties of glass fibers

The traditional methods of tailoring properties of glass fibers are either to grow a gas-sensitive thin film to detect CO₂ [22] and O₂ [7] at side of core of glass fiber or directly dope materials inside, for example rare earth elements [23, 24]. For gas sensing, by passing light which matches absorption wavelength of gas-sensitive material in sol-gel thin film through the glass fiber, changes of fluorescence effect in glass fiber due to reaction of gas with material in thin film can be observed in real time. However, the thin film on side of core has changed refractive index around the core and the light can be
leaky out from a fiber. Thus, the collected light signal is attenuated at end of fiber. One of proposed solution is directly doping the material into sol-gel solution and it is infiltrated into glass fiber. It solves problem of leaking light while the surface volume ratio is also increased, which help improve quality of signal.

2. Planar and channel waveguides

Both channel waveguide [24] and planar waveguide [25] can work in area of telecommunication. The light is free to propagate inside but prohibited to propagate outside. The basic requirement for these waveguides is to have a higher refractive index than surrounding layers of materials. It can be achieved by using metal-alkoxide based sol-gel solution especially titanium based sol-gel solution. Although the optical loss of sol-gel based thin film is around 1 dB per centimeter [19], it is negligible when size of waveguide goes to millimeter or micrometer in the field of integrated photonic. Another way to improving optical loss of waveguide is to decrease optical loss by removing C-H bonds and O-H bonds. Due to flexibility of sol gel technology, it is possible to replace alkoxide groups with other elements for example elements from halogen groups. In addition to fabricate waveguides on silicon substrate, due to stretchable strength of sol-gel material, a fabrication of waveguide on a flexible substrate has been reported [26].

3. Dye-sensitized solar cell

Due to low cost and ease of fabrication, high conversion efficiency of light to electricity, and environmentally friendly properties, dye-sensitized solar cells (DSSCs) have been well studied. The DSSCs system involves a photoelectrochemical conversion. A sol-gel based porous structure of oxide (TiO₂ and ZnO) thin film works an entrapment of dye molecules and a photosensitized anode at same time [27]. Due to porous structure,
large surface area is provided to absorption of dye molecules. The resulting conversion efficiency has achieved more than 10% so far [28, 29]. With help of dye molecules, the DSSCs has extended its absorption spectra to infrared region.

4. Micro-optic elements

Micro-optic elements are very important in optical connection between fibers and light detection device or light emission device. The famous optic elements are micro-lens array [30] and diffraction gratings [31]. Taking micro-lens array as an example, the sol-gel based fabrication starts as a coating process. A thick layer of thin film is formed on the substrate after the coating process. A stamp with concave structure on the surface is then pressed onto sol gel thin film. After removing the stamp, the transferred micro-lens array is under high temperature for heat treatment to fix the shape of micro-lens array. The final production has a good heat stability compared to plastic-based or glass-based micro-lens array.

Of course, there are many other sol-gel based photonic devices fabricated. But, sol-gel based PhC fabrication has not been developed well. The PhCs are known as perfect devices to modulate transmission of light. It is widely used in large number of applications. Many fabrication methods have been proposed. However, there is very few report that the PhCs can be fabricated by sol-gel technology. The following two chapters are going to introduce sol-gel based fabrication of PhCs
CHAPTER 3: SOL-GEL BASED GUIDED MODE RESONANT FILTER

3.1 Guided Mode Resonant Filter

Since the observation of narrowband reflectance using sub-wavelength periodic grating nanostructures [32, 33], guided-mode resonance (GMR) filters, which are also known as PhC slabs or high contrast gratings, have attracted much attention. The GMR filter, shown in Figure 3.1, consists of a uniformly corrugated surface made from a material (e.g. TiO$_2$ and Si$_3$N$_4$) with a higher refractive index than its surrounding medium. Magnusson’s group studied in great detail optical resonances in waveguide-based GMR filters and showed that structures with a sub-wavelength modulation in refractive index along one dimension can function as filters with smooth line shapes and adjustable linewidths when the grating structure on planar waveguide satisfies the resonant condition to couple light from surrounding environment to waveguide [34-40]. Under resonant condition, the GMR filter is designed to provide high efficiency of reflection at resonance wavelengths while transmit all other wavelengths incident on the structure surface at a given angle. The spectral response of the GMR filters such as the resonance wavelength, peak reflection efficiency, and resonant linewidth are strongly dependent upon the dimensional parameters and the selection of filter materials. With an electromagnetic simulation tools, rigorous coupled wave analysis (RCWA), it is possible to engineer the structure of a GMR filter to achieve a desired narrow band reflection within the entire optical region of the electromagnetic spectrum. GMR filters have been successfully demonstrated in ultraviolet, visible, near infrared (NIR), mid-wave infrared (mid-IR) regions [41-42]. What is more, GMR modes recently have found widespread applications in displays [36,38], LEDs [43], biosensors [40,44,45], and
telecommunications [46-47]. Considering the popularity of GMR filters, many fabrication methods has been proposed. So far, the methods of fabricating GMR filter involve E-beam lithography, soft lithography, and nano imprint lithography. By taking the cost and complicity of fabrication into accounts, soft lithography and nano imprint lithography are more preferred than other fabrication methods. Here, a proposal of fabricating GMR filter is provided by using sol-gel imprint lithography.

3.2 Numerical Design of GMR Structure

GMR structures with zero-contrast grating were firstly proposed by Magnusson [48]. It works as bandpass filter at micro wavelength region. In this work, it is aimed to construct GMR structures serving as a biosensor at region of visible spectrum. Rssoft was used to simulate this structure because of its fast time of simulating periodic structure. For the simplicity of simulation, all GMR structures are restricted to be one period. From figure 3.1, it schematically illustrates the structures. The values of $\Lambda$ are fixed as 400 nm in 1D GMR and 500 nm in 2D GMR both with 50% duty cycle (same as silicon molds purchased from LightSymth). The $n_w$ represents refractive index of sol-gel material while the $d_w$ stands for grating height. In order to obtain the value of $n_w$, an ellipsometry is used to measure the refractive index of sol-gel thin film on silicon wafer. The $h_w$ is denoted thickness of waveguide layer. The other parameters such as $n_{sup}$ and $n_{glass}$ are based on refractive index of surrounding environment and glass. Here, the TE mode is defined as incident electrical field parallel to surface of gratings for the 1D GMR structure simulation while the TM mode is defined as incident magnetic field parallel to surface of gratings. 2D GMR structure has no requirement of polarization. From figure 3.2 to figure
3.4, all simulation results have a nice match to experiment results. It is proved that sol-gel based GMR filter is successfully fabricated.

Figure 3.1 schematic diagrams of the 1D and 2D sol-gel GMR filters. (a) 1D GMR structure, showing the patterned gratings on the glass substrate. The gratings period and grating depth were kept constant at $A_{1D} = 400$ nm and $d_w = 80$ nm. (b) 2D GMR structure with the period of $A_{2D} = 500$ nm at both in-plane directions and $d_w = 150$ nm. In the schematics, $h_w$ represents thickness of waveguide layer; $n_w$, $n_{sup}$, and $n_{glass}$ represent index of sol-gel material, superstrate, and substrate, respectively.

Figure 3.2 the simulated and experimental reflection spectra of sol-gel 1D GMR device with $h_w \sim 100$ nm. The light illumination was TE-polarized.
Figure 3.3 the simulated and experimental reflection spectra of sol-gel 1D GMR device with $h_w \sim 100$ nm. The light illumination was TM-polarized.

Figure 3.4 the simulated and experimental reflection spectra of sol-gel 2D GMR device with $h_w \sim 100$ nm.
3.2 Fabrication

3.2.1 Preparation of Sol-gel Solution

According to report [49], the precursor of titanium-based sol-gel solution is tetrabutylorthotitanate (Sigma-Aldrich) and ethanolamine (Sigma-Aldrich) is served as stabilizer. 4.2 mL of tetrabutylorthotitanate and 1.2 mL of ethanolamine were mixed together. The previous solution then was mixed with 16 mL of ethanol. The solution was stirred with magnetic bar inside for 2 hours. After that, 2.5 mL of ethanol and 0.25 mL of water (H₂O) were mixed together and added into the solution above. Finally, the solution was stirred overnight. Usually, after 4 to 5 day’s waiting, the viscosity of sol-gel solution is good enough to be used for spin-coating.

3.2.1 Sol-gel Imprint Process

Compared with listed fabrication methods in introduction, our fabrication method demonstrates advantages of low cost, simplicity, and fast time of fabrication. The figure 3.5 shows the process of fabricating 1D GMR structure. Hard polydimethylsiloxane (hPDMS) was used to replicate mold from silicon master mold while a layer of PDMS worked as a supporting layer. Basically, the hPDMS was spinning-coated on silicon mold at 1000 rpm and PDMS was poured onto hPDMS. After a few hours’ bake, the polymer mold was peeled off from silicon mold. Then, the sol-gel solution was spinning-coated on polymer mold under different spinning speed. The spinning speeds started from 2000 rpm to 4000 rpm with a step of 1000 rpm. The PDMS mold with sol-gel solution was transferred from spinner to a cover glass and the second cover glass was placed on the polymer mold as a sandwich structure. The whole structure was put on a hotplate with 200 °C with a controlled force on the surface of top cover glass for 5 minutes. After that,
the whole structure was removed from hotplate. By removing top cover glass and PDMS mold, the pattern was clearly observed at bottom cover glass. In figure 3.5 (g), it is a demo of fabricated 1D GMR device. For the optical experiments, the GMR devices were required continuously to be baked on hotplate around 40 minutes in order to remove all solvents inside. The 2D GMR devices have same fabrication process but do not show in figure 3.5.

Figure 3.5 Schematic of the fabrication process of sol-gel GMR devices. (a) the PDMS mold was replicated from the silicon master mold carrying the same periodic structure as the stamp template of sol-gel GMR devices. (b) After curing, the PDMS mold is separated from the mold and sol-gel solution was spinning-coated onto the PDMS mold as shown in (c) and (d). The sol-gel coated PDMS was brought into contact with the glass substrate. (e) The PDMS/sol-gel/glass sandwich was baked on a hotplate under a controlled pressure. (f) After the sol-gel layer was solidified, the PDMS mold was removed and the GMR structure was baked on the hotplate to improve the sol-gel film quality. The photograph of a 1D GMR device is shown in (f).
3.4 Characterization

3.4.1 Spectral measurement

The setup of measuring reflection is more complicated than measuring transmission. Thus, we built a setup to measure transmission and normalized the transmittance. By subtracting normalized transmittance with a unit of incident power, a normalized reflectance is acquired. The setup started with a tungsten halogen lamp as light source and the light then was perpendicularly incident onto cover glass with GMR pattern. The Ocean Optics USB2000 served as a detector to collect the transmitted light after light passed through cover glass. Since 1D GMR filter is sensitive to polarization of excited light, by adding a polarizer between light source and GMR structures, two different polarization modes (TE and TM) were obtained.

3.4.2 Nanostructure inspection and energy dispersive X-ray analysis

The GMR devices on cover glass have shown strong light diffractions at a certain angle, which are observed easily by eyes. However, this cannot suggest that the grating pattern was transferred well to cover glass because the sol-gel solution might not fully fill gaps between gratings on polymer mold during fabrication process and the light diffraction still could be observable. Also, there might be some cracks on GMR patterns during baking step. In order to find out how well patterns were transferred from the polymer mold, GMR patterns on cover glasses were inspected under scanning electron microscopy (SEM). From figure 3.6 (a)-(b), the top view and cross section view of 1D GMR pattern were observed. Based on scale bar, it is indicated that the transferred pattern has same period and height of depth as 1D silicon mold. Also, in figure 3.6(c), the
top view of 2D GMR pattern is periodically matched with 2D silicon mold. Besides to
inspection of nanostructure, an analysis of element in a GMR pattern is performed based
on energy dispersive x-ray spectroscopy (EDS). On the GMR pattern, two labeled
rectangular areas, in figure 3.6(d), with grating and without grating are selected to be
analyzed. Base on result in figure 3.7, it shows that main elements include Ti, O, C in
GMR pattern. Other elements are believed coming from either glass or Ir coating process
for obtaining a conducting surface on GMR device. The reason why there is carbon in
GMR pattern might be that there are still some alkoxide groups on precursor which are
not reacted completely with water and it is regarded as an impurity. Due to the existence
of carbon, our prepared sol-gel material is called as hybrid organic-inorganic material.

Figure 3.6 SEM images of the sol-gel GMR structures. (a) SEM image of top view of an 1D
grating; (b) Cross sectional SEM of an 1D GMR structure with $h_w = \sim 130$ nm and $d_w = \sim 80$
nm; and (c) top view of 2D GMR structure. (d) top view of an 1D grating: two rectangular
areas were selected for EDS analysis. (Scale bar: 1 μm)
3.4.3 Tuning of GMR resonant wavelength by thickness of sol-gel film

As figure 3.8 shows, as an increase of spinning speed, the locations of resonance wavelengths (reflection peak) linearly have a blueshift in TE mode. Same observation happens to TM mode. It is caused by thickness of waveguide layer. The waveguide layer works as a waveguide for the coupled light. The thickness and index of waveguide layer result in what wavelengths should propagate inside. Here, all devices have same fabrication process and baking time. The only difference between fabricated devices is spinning speed. At different spinning speeds, the waveguide layers below grating structures are different. An increase of spinning speed has a decrease of waveguide layer thickness since higher spinning speed causes thinner layer of coated material. The resulting waveguide layer thicknesses are different from spinning speeds. Therefore, the waveguide layer thickness is a key factor affecting optical properties of GMR device. By controlling spinning speed, the resonant modes of GRM device can be adjusted.

Figure 3.7 an EDS analysis result shows an increase of elements (Ti, O, and C) and a decrease of other elements such as Si, C, Na, and Zn.
Table 3.1 Different refractive index of sol-gel film at different baking times

<table>
<thead>
<tr>
<th>Baking time (mins) at 200 °C</th>
<th>Refractive index (600 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.616</td>
</tr>
<tr>
<td>5</td>
<td>1.726</td>
</tr>
<tr>
<td>20</td>
<td>1.762</td>
</tr>
<tr>
<td>60</td>
<td>1.787</td>
</tr>
<tr>
<td>180</td>
<td>1.875</td>
</tr>
<tr>
<td>300</td>
<td>1.912</td>
</tr>
</tbody>
</table>

Figure 3.8 Spectral characterizations of the sol-gel GMR devices with different waveguide layer thickness. Normalized reflection spectra were measured for the GMR devices with $h_w = 130$, 170, and 200 nm, respectively.
3.4.4 Tuning of GMR resonant wavelengths by refractive index of sol-gel film

During the characterization of GMR devices, one interesting phenomenon is found that as the baking time is extended to be longer, the locations of resonance wavelengths (reflection peak) have a redshift for all GMR structures. The figure 3.9 presents an example of GMR filter’s reflection spectra in TE mode at spinning speed 3000 rpm. One of reason causing this shift is that the higher refractive index of device duo to longer time of baking leads to redshift of resonant wavelength. In order to verify this conclusion, the refractive index of sol-gel thin film on silicon wafer was measured by ellipsometry (VASE, J.A. Woollam) during 5 hours of baking time at 200 °C as table 3.1 shows. However, under TM mode, GMR structure’s resonant wavelength is not so sensitive to baking time. Based on the control of baking time, the refractive index of GMR structure is adjustable so that resonant modes of GMR structure are controllable.

![Figure 3.9 Spectral characterizations of sol-gel GMR devices with different refractive indexes. Experimental results of GMR reflection spectra with $n_w = 1.726, 1.762, 1.787, 1.875$, and $1.912$, respectively. The refractive indexes were measured by ellipsometry.](image-url)
3.5 Application

3.5.1 Reflection measurements of solutions with different indexes

Sensitivity to changes in the refractive index of media exposed to the sensor surface was measured by placing a droplet of methanol ($n = 1.327$), water ($n = 1.333$), acetone ($n = 1.359$), and dimethyl sulfoxide (DMSO) ($n = 1.479$) upon a single GMR sensor with spinning speed of 3000 rpm in sequence. Single TE mode laser emission was measured for each solution shown in Figure 3.10, and a bulk refractive index sensitivity of $S_b = \Delta \lambda / \Delta n \approx 50 \text{ nm / RIU}$ was measured, with linear behavior over the $\sim 15 \text{ nm}$ tuning range in table 3.2.

Figure 3.10 Refractometric sensing using the sol-gel GMR sensor. Normalized reflection of the sol-gel GMR sensor in the response to changes in refractive index of the superstrate medium. Five different superstrate materials: air ($n_{\text{sup}} = 1.0$), methanol ($n_{\text{sup}} = 1.327$), water ($n_{\text{sup}} = 1.33$), acetone ($n_{\text{sup}} = 1.359$), and DMSO ($n_{\text{sup}} = 1.479$), were measured.
Table 3.2 GMR sensor’s resonant wavelengths at different solutions

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Refractive index</th>
<th>Resonant Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1</td>
<td>645.55</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.327</td>
<td>659.97</td>
</tr>
<tr>
<td>Water</td>
<td>1.33</td>
<td>662.14</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.359</td>
<td>663.71</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.479</td>
<td>670.78</td>
</tr>
</tbody>
</table>

3.5.2 Detection of Polymer Thin Film Deposition

Sensitivity to surface mass adsorption was characterized by introducing a solution of the protein polymer poly(Lys, Phe) (denoted PPL, Sigma-Aldrich) which has been shown to deposit a self-limited, single monolayer having a refractive index, thickness, and mass density of 1.45, ~15 nm, and ~2.5 ng/mm², respectively. By monitoring the spectral output of the sensor over time, the kinetic characteristics of mass adsorption can be recorded. Figure 3.11 illustrates the dynamic detection of the growth of a single PPL layer. These data were obtained by initially establishing a baseline depending on GMR sensor’s resonant wavelength when the sensor surface was soaked in a phosphate-buffered saline (PBS) solution with pH = 7.4. After 5 minutes, the PBS solution was replaced by PBS solution with PPL and GMR sensor’s resonant wavelength kept stable for 30 minutes. Then, the sensor surface was rinsed with PBS solution to remove any PPL that was not firmly attached to the sensor. In this manner, the sensor was observed to exhibit a resonant wavelength shift of ~0.25 nm shown in figure 3.11 for PPL monolayer adsorption and no shift after rinse. All measurements were performed with the sensor at ambient temperature.
Figure 3.11 Refractometric sensing of protein polymer poly using the sol-gel GMR sensor. The temporal shift of the GMR resonant wavelength was recorded when a self-limiting PPL monolayer was deposited onto the GMR sensor surface.
CHAPTER 4: SOL-GEL BASED 3D PHOTONIC CRYSTAL

4.1 3D Photonic Crystal

3D PhCs are highly ordered materials with periodic modulation of refractive index in three dimensions. This leads to a photonic band gap in which light propagation is prohibited. Photons can be confined, modulated, and guided in this structure. Most 3D PhCs fabrications are dependent on sol-gel-based inverse opal fabrication method because it is considered as a relatively simple and easy method. According to Ho’s group report [3], the titania based inverse opal PhC has been made. The fabrication process is briefly described as using colloidal polystyrene (PS) spheres as template to build 3D structure and TiO₂ nanoparticles as backbone of inverse opal 3D structure. The titanium sol-gel solution containing polystyrene spheres was spread on a substrate resulting in a self-assembly ordered 3D structure with PS spheres. Meanwhile, the titanium sol-gel solution was infiltrated into gaps between PS spheres. After a slow dry process, the PS sphere was burned out at high temperature while the titanium sol-gel solution turned into solid and formed a nanocrystal structure and the inverse opal PhC was obtained. It showed a face-centered-cubic structure under inspection of SEM. The fabricated devices demonstrate good resonant reflections at visible frequencies. By adjusting the size of polystyrene spheres during fabrication process, the optical properties of inverse opal PhC can be controlled. In this studies, a similar method is used except that the fabrication is relying on capillary tube as a substrate to make SiO₂ inverse opal PhC. The sol gel solution is infiltrated into capillary tube automatically due to capillary force. It can be used as optofludic application by incorporating gold (Au) nanoparticles into the system.
4.2 Fabrication

In this subsection, details of fabricating inverse opal PhC are presented as Figure 4.1 shows. 5 cm quartz capillaries with inner diameter of 180 μm were first calcinated at 500 °C to remove the polyimide coating and washed with acetone and ethanol respectively. Then they were treated with piranha solution (a 3:1 mixture of concentrated sulfuric acid with hydrogen peroxide) and dried with nitrogen after washing. Inverse opal PhCs were prepared by co-assembly of monodispersed polystyrene (PS) and silica (SiO2) nanoparticles in the capillaries. In our experiment, four sizes of 5 % PS spheres(185 nm, 236 nm, 269 nm and 307 nm) in aqueous suspension and 7 nm SiO2 nanoparticles (LUDOX SM, Sigma Aldrich) whose concentration was adjusted to 5 % were used. After the monodispersed PS and SiO2 nanoparticles were mixed thoroughly, they were infiltrated into the capillaries by capillary force and dried at room temperature. The mixing ratio of PS and silica nanoparticles was optimized between 2:1 and 7:1 so that ordered self-assembled structures were obtained in capillaries. Then the capillaries were sintered at 550 °C for 3 hours with a heating/cooling ramp of 1 °C/min to remove the PS spheres and inverse opal PhCs was generated.
4.2 Simulation

Due to property of modulating light in 3D PhC, an investigation of how gold (Au) nanoparticle can interact with light inside was performed to develop a potential application in surface enhanced Raman spectroscopy (SERS). In order to illustrate advantages of Au nanoparticles incorporated IO PhC capillaries, we simulated the near field distribution of the gold nanoparticles in water with silica PhC structure and in water without PhC structure. A commercial software package (FDTD Solutions, Lumerical Solutions Inc.) was used to simulate the optical responses of the IO PhC structures with gold nanoparticle. The optical properties of Au and SiO2 were taken from Palik’s handbook [50]. The simulated structure consisted of a face center cubic IO PhC with the lattice constant of 280 nm. Two Au nanoparticles with diameter of 80 nm were placed inside each opal. In the x-y plane, periodic boundary conditions were imposed to truncate the periodic structure at x and y boundaries. Perfectly matched layers are imposed at
boundaries of the propagation direction (z direction) to properly absorb outgoing radiation. The simulation included 15 layers of voids along the z direction. The structure was excited by a normally incident, a unit magnitude plane wave propagating in the z direction. The corresponding reflection spectrum (Figure 4.2) was obtained in the simulation and the near field distributions (Figure 4.3-4.4) at given wavelengths (488 nm, 532 nm, 633 nm, 785 nm) were plotted along the center cross-sectional plane of the IO PhC structure. In the reflection spectrum (Figure 4.2), wavelengths around 600 nm are highly reflected and the strength of electrical field between Au nanoparticles is obviously higher than other range of wavelengths. Also, a near filed distribution (Figure 4.5) at 785 nm was selected to see advantages of inverse opal PhC. It can be seen that the intensity of electric field around gold nanoparticles in PhC structure are higher than that in homogeneous water. The reason may be that the PhC can modulate the electric field distribution by interference of the periodic structure and hence the interaction of light and gold nanoparticles is thus enhanced. Since the strength of surface enhanced Raman signal is proportional to strength of electric field near Au nanoparticles, the inverse opal PhC definitely improves SERS signal based on simulation results above.
Figure 4.2 stimulated reflection spectrum of IO PhC with nano-void diameter of 236 nm

Figure 4.3 $|E/E_{inc}|$ profile of Au NPs incorporated IO PhC capillary at 488 nm (a) and at 532 nm (b) respectively. The white dashed circle outlines the voids of IO PhC. The diameter of the nano-voids of IO PhC is 236 nm.
Figure 4.4 $|E/E_{inc}|$ profile of Au NPs incorporated IO PhC capillary at 633 nm (a) and at 785 nm (b) respectively. The white dashed circle outlines the voids of IO PhC. The diameter of the nano-voids of IO PhC is 236 nm.

Figure 4.5 $|E/E_{inc}|$ profile of Au NPs in water (a) and Au NPs in IO PhC capillary (b) at 785 nm respectively. The white dashed circle outlines the voids of IO PhC;
4.4 Characterization

During the co-assembly of binary particle of PS and silica, the small silica colloids filled the interstices of the large PS nanoparticles as template. Therefore, in order to obtain ordered PhC structure, the volume ratio of the PS and silica should be optimized. In our experiment, six volume ratios were tried from 2:1 to 7:1 to form columns of co-assembly in capillaries. Figure 4.6 (a) - (d) are the end face structures of the co-assembly of 269 nm nanoparticles and 7 nm silica colloids at four different volume ratios after remove of the PS nanoparticles by calcination at 550 ºC. It can be seen that between 5:1 and 7:1, the co-assemblies are more ordered and the voids derived from the PS nanoparticles are arranged in hexagonal packing. And in Fig 4.6(c), when the ratio is 6:1, a typical IO PhC of FCC (face centered cubic) lattice is formed with a reflection peak at 568 nm. However, at the other end of the IO PhC column, the measured reflection peak is 556 nm which means that the ratio is not the best. Hence, by further fine tune of the volume ratio at 5.5:1, uniform IO PhC columns are obtained in capillaries with reflection peaks of both ends at 559 nm. And Fig 4.6(e) is one cross section of the IO PhC in the capillary which confirms the FCC structure. In Fig 19(f) are four IO PhC capillaries with inner diameter of 180 μm made from 185 nm, 236 nm, 269 nm and 307 nm PS templates. For visualization, capillaries were infiltrated with water to display the reflection color of the IO PhC except for the IO PhC from 185 nm PS template whose reflection peak is not in the range of visible. It can also be judged that by the as proposed binary particle co-assembly method, uniform IO PhC structure can be obtained reliably. From SEM images Fig 4.6(c) and (e), the size of interconnecting pores is about 1/3 of
that of the voids and both of them form zigzag nanofluidic channels in the capillary, which provides high surface to volume ratio.

Figure 4.6 (a)-(d), SEM images of the end face structure of co-assembly of 269 nm nanoparticles and 7 nm silica colloids mixed at volume ratio of 4:1, 5:1, 6:1 and 7:1 in capillaries, inset of (c) is cross-section view of the capillary tube; (e), the cross section of the structure inside the capillary of (c); (f), picture of four IO PhC capillaries; Scale bar in (a)-(e) is 1 micron, the scale bar in inset of (c) and (f) is 200 micron
CHAPTER 5: CONCLUSION

In this study, after series of characterization experiments and optical experiments, sol-gel based methods of fabricating sub-wavelength PhC structures are proved to be successful methods. These two fabrication methods have demonstrated advantages of simplicity, low cost, quick production time and high throughput. All PhC devices have exhibited strong resonant reflections at visible and NIR regimes of spectra. In fabrication of 1D and 2D GMR structures, with assistance of imprint lithography, GMR resonant modes are able to be engineered by changing process parameters in fabrication. Spinning speed and baking time have been found two important factors to affect GMR resonant modes. The evaluation of 1D GMR structure’s sensitivity as refractometric sensors is not so promising, which is considered as a shortcoming. The proposed solution to problem of sensitivity is to make GMR structure porous to increase surface to volume ratio. From SEM images, fabricated GMR structures are nonporous structures so far. According to former report of fabricating TiO$_2$ sol-gel powders [15], it can be porous by adding base solution into sol-gel solution. Therefore, adding a base solution during the preparation of sol-gel solution might make our GMR structures porous to enhance sensitivity.

As for fabrication of 3D inverse opal PhC in capillary tube, with the help of self-assembly technology, devices have also demonstrated a tuning of inverse opal PhC’s resonant reflection by adjusting diameter of PS sphere. Simulation results show an enhancement of near electrical field distribution between Au nanoparticles when inverse opal PhC is present. By incorporating Au nanoparticles into inverse opal PhC which is a 3D porous structure, a potential application of the surface enhanced Raman spectroscopy
(SERS) might be developed. Based on SERS analysis, the capillary tube with 3D inverse opal PhC could be implemented to detect analytes.

5.1 Future Work

In this study, GMR structures working as optical sensors have been explored. Instead of optical sensors, the GMR structure might also play a role of cavity. The GMR structures rely on waveguide layers with high refractive index as light confinement layers. By adding gain medium into sol-gel solution, for example erbium and neodymium, and with a laser pump, the GMR structures can work as amplified spontaneous emission devices. Furthermore, since the present GMR structures are composed of hybrid inorganic-organic materials, the optical losses might affect quality of confining light. Based on former report [15], a heat treatment above 400 °C can turn titanium alkoxide sol-gel solution to TiO$_2$ with crystal structure which has low optical loss. From these two suggestions, it is optimistic to predict that GMR structures might be suitable devices for amplified spontaneous emission.


