Femtosecond laser additive manufacturing of nonlinear and fluorescent optical structures

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**FEMTOSECOND LASER ADDITIVE
MANUFACTURING OF NONLINEAR AND
FLUORESCENT OPTICAL STRUCTURES**

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**SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2020

**FEMTOSECOND LASER ADDITIVE
MANUFACTURING OF NONLINEAR AND
FLUORESCENT OPTICAL STRUCTURES**

JIAO JIANNAN

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University

in partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

13 October 2020

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JIAO Jiannan

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

13 October 2020

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Prof. SU Pei-Chen

Authorship Attribution Statement

This thesis contains material from 7 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 3 (**Sec. 3.3**), Chapter 4 (**Sec. 4.3**) and Chapter 5 (**Sec. 5.2**) are published as **Jiao, Jiannan**, Yi Gao, Shufan Li, Nguyen Duy Anh, Pei-Chen Su, Seung-Woo Kim, CS Suchand Sandeep, and Young-Jin Kim. "Surface third-harmonic generation at a two-photon-polymerized micro-interferometer for real-time on-chip refractive index monitoring." *Optics express* 27, no. 20 (2019): 29196-29206.

The contributions of the co-authors are as follows:

- Young-Jin Kim suggested the ideas, provided the initial project direction and edited the manuscript drafts.
- I and Shufan Li set up the FsLDW system.
- I and Yi Gao set up the observation system.
- I fabricated the sample.
- I and CS Suchand Sandeep mainly prepared the manuscript drafts.
- I analyzed the experimental data with CS Suchand Sandeep.

- All authors reviewed the results and provided guidance on the manuscript drafts writing.

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- Young-Jin Kim suggested the ideas and provided the initial project direction.
- I and Shufan Li set up the experimental system and did the experiment. I also developed the control software.
- I and Shufan Li analyzed the data.
- Shufan Li and Young-Jin Kim prepared the manuscript.

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- I, CS Suchand Sandeep and Young-Jin Kim developed the methodology.
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- I, Donglei Zhou, Shufan Li, Yi Gao and CS Suchand Sandeep performed the experiments.
- I, Seungchul Kim, Kyujung Kim, CS Suchand Sandeep and Young-Jin Kim analyzed the data.
- I, Donglei Zhou and CS Suchand Sandeep prepared the original draft.
- Pei-Chen Su, Seung-Woo Kim and Young-Jin Kim supervised the project, provided resources and revised the manuscript.
- All authors reviewed the results and approved the final manuscript.

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Abstract

In the past few years, the state-of-the-art additive manufacturing (AM) via femtosecond laser direct writing (FsLDW) has become a powerful tool for flexible microfabrication of complex 3D structures and it is promising to utilize this technology to fabricate optical structures integrated into optofluidic chips, because of its unnecessary of pre-patterned masks and higher manufacturing throughput compared to traditional manufacturing methods such as mask-based photo-lithography and mask-less electron-beam lithography.

Varieties of micro-sized optical structures are successfully additively fabricated and applied to real on-chip applications, which are mainly based on the linear optical phenomenon and are passive optical structures. Micro-sized nonlinear-optics-based active structure additively fabricated via FsLDW is promising for generating new flexible light sources and has not been studied too much, which is the research gap to be fulfilled in this research. In the research, on-chip optofluidic sources of small volume are the targets to be realized and the objective of this research is three-fold: (1) establishment of 3D and 2D FsLDW systems to realize additive manufacturing of basic micro-sized optical structures for optofluidic applications, (2) characterization and utility of surface third harmonics (THs) from the flexible two-photon-polymerized structures to provide

coherent sources for metrology and sensing applications such as micro-interferometer for real-time monitoring of gas refractive index changes and diffractive lens for generation of Bessel-like THs with a large non-divergent range, and (3) demonstration of fabricated active optical structures that contain gain mediums (upconversion nano particles and fluorescent dye) for micro laser sources (high repetition-rate pulsed upconversion micro-laser) and waveguides to be integrated into micro-sized optofluidic chips.

Our demonstrated nonlinear-optics-based active optical structures over traditional ones have three main advantages: firstly, the active optical structures containing a gain medium works well for the external photon excitation and efficient collection of the emission signals; this lowers the system complexity, optical delivery loss, and integration cost. Secondly, highly tunable small volumetric light sources can be realized in terms of beam size, output intensity, polarization, spectral position and distribution. Flexible patterned and diffracted surface optical harmonics and upconversion lasing can work as coherent light sources for micro sensing and detection applications. Finally, the need for in-coupling and out-coupling of the lights from or to the integrated photonic devices and relevant alignment issues can be much relieved with additively manufactured waveguides. In the future, complex optofluidic systems will be fabricated based

on our nonlinear-optics-based active structures for applications such as sensing the micro/nano particles and chemical characterization of fluids.

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List of Abbreviations

2D: two-dimensional
3D: three-dimensional
AM: additive manufacturing
Ar: argon
ASE: amplified spontaneous emission
BS: beam splitter
BTF: buy-to-fly
CCD: charge-coupled device
CMOS: compact complementary metal oxide semiconductor camera
CR: cross-relaxation
CSU: cooperative sensitization upconversion
CW: continuous wave
DFT: discretized Fourier transform
DOE: diffractive optical element
EMCCD: electron multiplying charge-coupled device
ESA: excited-state absorption
ETU: energy transfer upconversion
FFT: fast Fourier transform
F-OBJ: focusing objective
FP: Fabry-Perot
Fs: femtosecond
FsLDW: femtosecond laser direct writing
FWHM: full width at half maximum
FZP: Fresnel zone plate
GBL: gamma-butyrolactone
GM: Galvano mirror
GO: graphene oxide
GT: gray-tone
GUI: graphical user interface
HAR: high-aspect-ratio

HG: harmonic generation
HWP: half-wave plate
IFTA: inverse Fourier transform algorithm
I-OBJ: imaging objective
L: lens
Laser: Light Amplification by Stimulated Emission of Radiation
LC: liquid crystals
Ln: lanthanide
LPF: long-pass filter
M: mirror
MP: moving pattern
NA: numerical aperture
ND: neural density
NIR: near-infrared
O: objective
PA: photon avalanche
PBS: polarizing beam splitter
PC: personal computer
PDMS: poly dimethylsiloxane
PR: photoresist reflow
PZT: piezo-electric transducer
QWP: quarter-wave plate
RF: radio-frequency
RI: refractive index
SEM: scanning electron microscope
SHG: second harmonic generation
SPF: short-pass filter
STPA: simultaneous two-photon absorption
TH: third harmonic
THG: third harmonic generation
TPA: two-photon-absorption
TPP: two-photon-polymerization

UC: upconversion

UCNP: upconversion nano particle

UCL: upconversion luminescence

UV: ultraviolet

VBA: variable beam splitter/attenuator

WGM: whispering-gallery-mode

ZnO: zinc oxide

Chapter 1 Introduction

1.1 Background and motivation

Additive Manufacturing (AM) based on layer-by-layer construction has been penetrating the world of manufacturing since the late 1980s, and with the development of the technology, 3D printers can be used to process various of engineering materials (plastics, ceramics, plastics, etc.) and even non-traditional materials (drugs, food, bones, human tissue, etc.)[1]. Among the many kinds of AM applications, interest in three-dimensional microfabrication is driven by applications in the fields of photonics greatly, with the advantages of easier integration of small volumetric light sources into the micro-scale devices for on-chip applications. Femtosecond laser based direct writing is able to fabricate micro and complex structures with minimal lead time and less material waste, lowering the barriers of academic and commercial utilities[2-5].

Optical micro- and nano- structures can be manufactured through mask-based photo-lithography, mask-less electron-beam lithography[6], and focused ion beam processes[7]. Since these are subtractive manufacturing processes, repetitive coating, patterning and etching processes are necessary. Photolithography supports mass production well, but as pre-patterned masks are required, it is not well-suited for producing anything more complicated than high-

aspect-ratio (HAR) two-dimensional structures. The electron- and ion-beam lithography provide higher patterning resolution without masks but with a lower manufacturing throughput. Classic UV laser stereolithography and 3D inkjet printing can be used for producing 3D structures, however, resolution is not very high in these techniques. Because there exists the nonlinear two-photon-absorption (TPA), strong absorption in even transparent materials can be induced via ultrafast pulsed lasers with strong peak intensities, arbitrarily shaped 3D micro-sized structures can be additively manufactured in reasonably short build time with high design flexibility[2, 5, 8-11]. Furthermore, the problem of traditional optical diffraction limit can be solved with TPA-based processing of materials, which motivates the research of using TPA-based processing of materials for additive manufacturing of various novel micro-sized optical structures. However, the inexpensive TPA-based additive manufacturing has drawbacks when simple and large scale 2D patterns are the targets to be fabricated, it is inefficient to apply this method.

For the properties of fluids, there are unique properties that cannot be found in solids, and important applications in areas such as chemical synthesis, biotechnology, and analytical chemistry can be realized through optofluidics. For on-chip applications, sensing performance can be enhanced and the design of

microsystems can be simplified by the synergistic integration of photonics and microfluidics[12, 13]. Generation of new wavelengths and delivering light of small volume to small targets for on-chip optofluidic applications are full of promise.

New wavelengths can be generated with photon conversion processes, and nonlinear optical responses from materials can be used for decreasing the wavelength of the incident light. Both optical harmonic generation (HG) and upconversion (UC) can be used to transform long wavelength (infrared) photons into shorter wavelength (visible) photons, suitable to develop optofluidic light sources such as lasers and other lighting devices[14, 15]. Optical harmonic generation originates from coherent electron motion induced by a tightly focused input laser beam[16], while UC luminescence occurs in lanthanide-doped materials, which arises from the sequential absorption, an emission of one higher energy photon upon the excitation of several lower energy photons[17, 18]. For the wide-spread application of delivering desired light sources, the optical systems should be miniaturized and easily integrated into the microsystems. Active optical components that contain a gain medium such as fluorescent dyes have the advantages of remote excitation and optical signal collection, which alleviates some of the practical limitations of passive optical components[19].

Since the femtosecond laser pulses have unique characteristics of extremely high peak intensities and ultrashort pulse widths, this can be used for both surface and internal three-dimensional modification and microfabrication of transparent materials, making it possible to fabricate three-dimensional micro-sized optofluidic structures via femtosecond laser direct writing (FsLDW)[11]. During the fabrication of micro-sized structures, the femtosecond laser pulses interact with the material by layer-by-layer scanning, thus the 3D structures are additively manufactured. Exploration of additive manufacturing of nonlinear-optics-based active functional structures with FsLDW may pave novel design flexibility to the optical light sources for microfluidic and microelectronic devices.

1.2 Objectives and scope

Based on the research background and motivation, the objectives of the research are defined as below.

1. Establishment of TPA and micro-sintering based femtosecond laser direct writing system to realize additive manufacturing of basic micro-sized optical structures for optofluidic applications. Mask-less FsLDW is well-suited for additive manufacturing of micro-sized passive and active optical components. Dependent on the dimensions and features of the target objects to be fabricated, both 3D and 2D FsLDW are necessary. 3D FsLDW is used for

manufacturing of 3D structures with smaller dimensions and precise features. On the other hand, 2D FsLDW can be used for fast two-photon-polymerization (TPP) of 2D structures with planar geometries and sintering of micro-sized optical resonators. Optical sources and waveguides are important parts in the optofluidic system, and the fabricated 2D and 3D structures integrated into the optofluidic chips can provide desired sources and deliver the wave efficiently. SU-8 has the characteristics of good mechanical properties, low polymer volume shrinkage, and high thermal stability[20, 21], both pristine and Rhodamine B doped SU-8 structures are fabricated for developing micro-sized optical structures of high quality. The organic film containing upconversion nano particles (UCNPs) is used for developing active micro-sized laser resonators via 2D FsLDW.

2. Characterization and utility of surface third harmonics (THs) from two-photon-polymerized SU-8 structures to provide coherent sources for metrology and sensing applications. The conversion efficiency of third harmonic generation (THG) from two-photon-polymerized structures is dependent on the input polarization states and excitation positions. In the research, surface THG from two two-photon-polymerized SU-8 cuboids employed for the development of a micro interferometer is demonstrated, which can be easily integrated to microfluidic devices for the real-time

refractive index (RI) monitoring. Non-divergent beam with a maintained small spot size during propagation is necessary for particle trapping and imaging in the fluidic chip system, and axicon can transform the TH with a Gaussian profile into a Bessel-like beam which can propagate a long distance without divergence [22-24]. In the research, the two-photon-polymerized diffractive axicon works as a focusing lens with a large non-divergent range is demonstrated and non-divergent Bessel-like TH pattern is achieved, this feasibility exploration can be used for long thin beam illumination integrated into optofluidic chips in future applications.

3. Demonstration of fabricated active optical structures that contain gain mediums for optical sources and waveguides to be integrated into micro-sized optofluidic chips. UC luminescence occurs in lanthanide-doped materials, and UCNPs can be used for increasing the optical harmonic generation of the materials. With the 2D FsLDW system, fabricated ellipsoids containing $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ particles can work as whispering-gallery-mode (WGM) resonators to generate upconversion lasing. Input parameters such as incident polarization, pumping position and incident energy are studied to characterize the UC laser. Two-photon-polymerized Rhodamine B doped SU-8 active waveguides, suited to remote excitation, are demonstrated to efficiently guide

the wave signals under a simple vertical pumping, which can be integrated with developed novel optical sources in the future lab-on-a-chip applications.

1.3 Organisation of thesis

The thesis consists of seven chapters and is organized as below.

Chapter 1 gives a brief introduction that covers the research background, motivation, objectives, and scope of this thesis.

Chapter 2 is a literature review of this thesis. State-of-the-art technologies and materials for manufacturing of the micro-sized functional optical structures, photonic theories applied to the applications and various on-chip optofluidic applications are reviewed and discussed.

Chapter 3 introduces the establishment of the 3D and 2D FsLDW systems used for additive manufacturing of optical structures with different dimensions and features. Specifications of the laser sources and scanning control system are discussed. Both basic passive and active structures are fabricated based on the parametric study.

Chapter 4 studies the characteristics of THG from the two-photon-polymerized SU-8 structures. The optical observation system is established to check the incident ellipticities, linear polarization direction, and excitation position

dependent THG. THG conversion efficiency is quantitatively studied for providing coherent sources for optofluidic microsystems.

Chapter 5 focuses on the utilities of surface TH for real-time metrology applications. A micro-interferometer based on surface THG at two-photon-polymerized SU-8 cuboids for real-time monitoring of the refractive index changes of target fluids is demonstrated. The refractive axicon is simulated using the Zemax program to characterize the non-divergent Bessel-like pattern and the scalar diffraction algorithm is used to explain the working principles of diffractive optical elements (DOEs). A micro-sized two-photon-polymerized diffractive axicon is demonstrated to shape the surface TH with a Gaussian profile into a Bessel-like beam, which can be used for miniaturized illumination system for detecting small particles and cells in optofluidic systems in future applications.

Chapter 6 introduces the active optical structures contain a gain medium such as UCNPs and Rhodamine B for the basic components of optofluidic chips. High repetition-rate UC pulsed laser from whispering-gallery-mode (WGM) resonators fabricated by fast sintering with 2D FsLDW is demonstrated for the novel optofluidic source, and the two-photon-polymerized Rhodamine B doped SU-8 active waveguides can be used for delivering the wave to target positions.

Chapter 7 draws conclusions from the projects and discusses future works.

The content of this thesis is summarized in the flowchart as shown in figure 1.1.

Figure 1. 1 Flowchart for the overall structure of this thesis.

Chapter 2 Literature review

2.1 Preamble

In this chapter, the state-of-the-art technologies of laser microfabrication and TPA-based FsLDW for additive manufacturing will be presented. SU-8 photoresist is introduced as a good candidate for fabrication of the precision 3D micro-sized optical structures. Optical harmonic generation and upconversion mechanisms are introduced for the application of active nonlinear optical structures to be studied in this thesis. Basic on-chip optical structures such as beam shaping structures, laser resonators, and waveguides are presented separately. After that, the promising applications of optofluidic microsystems are reviewed, which gives the potential research directions and applications in future based on the current research result of this thesis.

2.2 Laser microfabrication and TPA additive manufacturing

Laser, which has an acronym for Light Amplification by Stimulated Emission of Radiation, has been used for modifications and structuring of the materials ever since it was invented. Compared to ordinary light, laser light consists of coherent photons (same frequency and phase)[25]. Because of a highly directional light beam and focusing into close to the diffraction-limited spot size of the laser, and the arrival of pulsed lasers, laser-based material processing is developing fast in

both the fields of conventional subtractive machining processes and additive manufacturing. In the field of laser machining, the difficult-to-machine materials can be processed with laser-based micro-machining, and its major applications are in welding, cutting, marking, drilling, treating material surfaces[4, 12].

Compared to machining, which is a subtractive manufacturing processing and defined as removal of materials to realize the desired geometries, additive manufacturing (AM) creates the desired shape via adding the materials, which has much lower material consumption and the reduced buy-to-fly (BTF) ratio[1, 26, 27]. AM has great advantages that the design of novel geometries and complex internal structures used for enhancement of component properties can be flexibly and easily realized, as shown in figure 2.1, are the advantages of AM over conventional machining.

Figure 2. 1 Benefits of additive manufacturing[4, 26].

Laser has been playing a core role in the development of AM technology because of its following advantages[4]:

- (1) A wide range of wavelengths can be produced.

- (2) A wide range of incident energy levels at the surface of a workpiece to be processed can be produced. With a non-contact interaction, the physical state of the workpiece can be changed, from solid to melt.
- (3) Manipulating the beam easily, which can be realized through a computer-based numerical control program, for the unnecessary mechanical contact with the workpiece.
- (4) Shaping the laser beam to interact with the workpiece both temporally and spatially, thus processing of various materials with complex shapes can be realized.

The arrival of ultrashort lasers has made the laser microfabrication become a fast-growing technology in the fields of industry and academy for varieties of applications, such as microelectromechanical systems (MEMS), nanophotonics, microelectronics and microfluidics, among which the 3D microfabrication of photopolymers via femtosecond laser pulses has developed quite fast over the last decade[10, 28]. Many techniques have been used for the microfabrication of photopolymers, like photoresist reflow (PR) technique, gray-tone (GT) photolithography, moving pattern (MP) lithography, etc.[29]. Compared to such techniques, mask-less additive manufacturing via TPA-based FsLDW has great advantages that arbitrary designability and reasonably high spatial resolution can

be realized via a simple and high-speed writing approach[30, 31]. Figure 2.2 illustrates the basic theory of TPA for producing 3D microstructures[10] and figure 2.3 shows a typical layout of the TPA-based FsLDW for precise microfabrication.

Figure 2. 2 Fundamentals of TPA induced by a focused laser beam[10].

Figure 2. 3 Schematic illustration for an example of TPA-based FsLDW configuration[32].

In the process of TPA, two near-infrared photons are absorbed by the materials simultaneously in a single quantum event whose collective energy corresponds to the UV region of the spectrum. In general, the molecular TPA efficiency is quite small. To enhance the TPA, a large TPA cross section of novel compounds can be designed. Another useful method is to focus the ultrashort laser pulses with high peak intensity into the common photopolymers and the rate of TPA is proportional to the square of the laser beam intensity, so that the strong absorption of the near-infrared source only happens at the focal point within the photopolymer, which can be used for additive manufacturing. Because of the quadratic intensity dependence of TPA, the solidification to submicron

dimensions is allowed, which is beyond the diffraction limit of light. During the manufacturing, 3D structures with pinpoint accuracy can be realized by scanning the laser spot in pre-designed paths, as shown in figure 2.4[8, 10, 33, 34].

Improvement of resolution and fabrication efficiency of micro/nano structures is promising for various applications such as 3D scaffolds for tissue or organ regeneration[35, 36]. Many researchers have studied the strategies to improve the resolution and fabrication efficiency of 3D structures via TPA-based manufacturing, for example, 3D nanofabrication efficiency in TPP can be increased by a subregional slicing method[37]. Nano-sized structures can be successfully obtained when scanning algorithm is optimized[38] or TPP involving a long laser-exposure technique is applied[39].

Figure 2. 4 An example of TPP of various of micro-sized optical structures. All scale bars, 20 μm [8].

2.3 SU-8 photoresist

SU-8 is a favorite negative photoresist developed by IBM in the late 1980s and now marketed by MicroChem Corporation for three-dimensional and high-aspect-ratio (HAR) lithographic microfabrication. SU-8 is prepared by dissolving the resin SU-8 in gamma-butyrolactone (GBL), which has 8 epoxy groups per SU-8 molecule, as shown in figure 2.5[20, 21, 40, 41].

GBL

SU-8 contains acid-labile groups and a photoacid generator, which makes it have an absorption in the deep UV. SU-8 is virtually transparent at near-infrared wavelengths, so it will have negligible one-photon absorption at the near-infrared.

If it is tightly focused by a beam at infrared wavelength, it will simultaneously absorb two photons and the solidification happens in a small volumetric area near the focal region. For the process of cross-linking of the polymer, a low concentration of a strong acid which will act as a catalyst is generated by the irradiation. Cross-linking is activated and the acid catalyst is regenerated via subsequent heating of the polymer[21]. Because SU-8 has the advantages of good mechanical properties, low polymer volume shrinkage, and high thermal stability, it is widely used for producing high-quality micro-optical devices[20, 28, 30], as shown in figure 2.6.

Figure 2. 6 SEM images of 3D high-aspect-ratio SU-8 structures[20].

Figure. 2.7 illustrates the general process steps to fabricate micro-sized optical structures via mask-less laser direct writing (LDW) of SU-8 photoresist[45].

Figure 2. 7 Fabrication steps for the polymerization of the modified SU-8 via mask-less laser direct writing[45].

2.4 Nonlinear optical harmonic generation

Light is electromagnetic radiation, which has electric and magnetic field components and can propagate in the vacuum. Linear or conventional optics is widely used in all photonic applications[46-50]. Laser has four basic properties, they are amplitude (intensity), phase, frequency (wavelength), and state of

polarization. Wave-particle duality is an important characteristic of light, and particles are photons. Photon is an elementary particle, and it has zero rest mass and is always moving at the speed of light. Photons can carry energy and momentum, which may be imparted when they interact with matter[51]. As for the linear optics area, when light interacts with matter linearly, the relative change of intensity is independent of the used intensity. In general, dispersion, reflection, refraction, luminescence, absorption, birefringence, diffraction, and scattering can be observed in the linear range, however, when the input intensity is high enough, these linear interactions may become nonlinear. Nonlinear optics deals with phenomena where conventional linear optical properties change as a function of the intensity of the light propagating through the media. Thus, nonlinear optics deals with the propagation of electrical fields through different materials, i.e. interaction of light and matter[51-53].

To study optical phenomena of linear and nonlinear interactions with matter, it is important to describe how an electromagnetic field changes during its propagation through matter. When an electric field E is applied to a dielectric material, its molecules respond by forming microscopic electric dipoles. Their atomic nuclei move a tiny distance in the direction of the field, while their electrons move a tiny distance in the opposite direction. This produces a

macroscopic bound charge density in the material even though all of the charges involved are bound to individual molecules and the total charge remains zero. As shown in figure 2.8, two layers of different bound charges are produced via these tiny movements of charges: a layer of positive bound charge on one side of the material and a layer of negative charge on the other. The term polarization, $\mathbf{P}$, is used to describe the bound charge[54].

Figure 2. 8 Induced polarization in material[54].

From Maxwell's equations, the relationship between polarization $\mathbf{P}$ and the applied electric field $\mathbf{E}$ can be expressed as

$$\mathbf{P} = \chi \epsilon_0 \mathbf{E} \quad - (2.1)$$

Here the factor χ is suggested to be a useful parameter when considering the material response to the fields oscillating in the optical frequency range. However, if the electric field is increased significantly, the nonlinear interactions can be observed, thus the polarization can be split into linear and nonlinear parts:

$$\mathbf{P} = \mathbf{P}^L + \mathbf{P}^{NL} \quad - (2.2)$$

The nonlinear polarization results from a nonlinear material response to an incident electric field, and the relationship between polarization and the electric field is nonlinear, then polarization is expanded as:

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \dots \quad - (2.3)$$

The polarization makes a significant contribution to the nonlinear optical process, since it results from charges oscillating within the medium that is produced by the incident oscillating electric field and re-radiate, thereby adding to that field[55]. Based on the orders of the susceptibility, nonlinear effects can be classified as different orders of effects, for example, $\chi^{(2)}$ effects, which result from squaring the electric field.

Nonlinear optical responses of materials have been successfully used in varieties of applications, such as short-wavelength light generation, optical modulation, and non-destructive study of the sample characteristics[56-65]. As shown in figure 2.9, it is the summary of nonlinear optical applications in our daily life[56].

Figure 2. 9 Summary of nonlinear optical applications in life[56].

Among a range of nonlinear optical responses, optical harmonic generation is one of the most desirable nonlinear optical processes[16], widely used in the generation of new light sources and noninvasive metrology of objects for both academic and industrial applications as shown in figure 2.10[57, 64, 66].

Figure 2. 10 Applications of optical harmonic generation. (a) Apparatus for high-harmonic generation by electric field enhancement[66]. (b) Depth-resolved THG images of two-photon-polymerized SU-8 micro-sized structures. Scale bars: 5 μm [57]. (c) Metrology of cell structures with THG microscopy. Scale bars: 10 μm [64].

Second harmonic generation (SHG) is very sensitive to the characteristics of heterointerfaces, and many researchers have used SHG to study the sample's structure noninvasively. If the material has no center of inversion symmetry, there will be quite a strong SHG signal from the bulk, while the surface effect is weak and can be ignored. If the bulk has a structure with a center of inversion symmetry, there will not be a SHG signal from the bulk[67]. Compared with SHG, the third harmonic generation (THG) occurs in all materials, even though the crystal has a center of inversion symmetry[63]. As all materials exhibit a non-vanishing third-

order susceptibility, it is promising to study the third harmonic generation characteristics and mechanisms depending on different states of pumping laser beam. When a laser beam focuses onto a nonlinear crystal, the polarization state of the outcoming beam is dependent on the polarization state of the incident beam and the position of the focused spot inside the sample[59, 68, 69]. These phenomena give good prospective scientific and industrial applications. For example, when optical components or waveguides are manufactured in a crystal based on nonlinear optics, the polarization dependence will determine the quality and efficiency of microfabrication[25], and polarization dependence of harmonic generation can help distinguish the nonlinear phenomenon from other phenomena occurring inside the material and study the material characteristics like structural symmetry as well. By controlling the position of the focused spot inside the crystal and choosing a suitable orientation of the crystal with respect to the light beam, phase matching can be realized, which has effects on the laser microfabrication as well[12]. With the help of flexible micro optical structures fabricated by TPA additive manufacturing, nonlinear phenomena can be studied easily, and the structures can provide more nonlinear-optics-based applications such as enhancement of harmonic generation, nonlinear beam shaping, etc[24, 70, 71].

For the applications of enhancement of optical harmonic generation, there are many parameters affecting the efficiency of harmonic generation. The effective forward coherence length is dependent on the axial extension of the Gouy shift, so the relative THG signal from objects of different sizes depends on the excitation numerical aperture (NA). As shown in figure 2.11, THG signal is a function of the NA. Besides the effects of NA, the object's size is also a factor of THG signal. when several objects or objects of different sizes are present within the excitation volume, interference effects can result in increased or decreased THG intensity[72].

Figure 2. 11 NA dependent THG signals. (a) Centered sphere geometry. (b) Calculated THG from a centered sphere as a function of size, for three different excitation NAs. (c, d) THG images of cells in a zebrafish embryo at cleavage stage recorded using NA = 0.75 and NA = 1.2. Scale bars: 50 μm (c), 30 μm (d)[72, 73].

The optical harmonic generation response is dependent on the input ellipticities as well. Figure 2.12 shows an example of high harmonic spectrum for various input laser ellipticities. It shows different ellipticities of the incident laser beam can cause different intensities of the high harmonic signals[16, 70].

Figure 2. 12 Incident ellipticity dependent optical harmonic generation. (A) Simulation of incident ellipticity dependent intensity distribution in a single ZnO wedge structure. (B) Experimental check of incident ellipticity dependent fifth-harmonic signals[70].

When the incident beam has different polarization states, the generated harmonic signal can also have different polarization states (figure 2.13) and can be used to detect the characteristics of certain samples like cells[74-76].

Figure 2. 13 Schematic layout of the experimental setup of four-channel polarization resolved second harmonic generation and the measurements of collagen[75].

2.5 Optical beam shaping structures

Redistributing the irradiance and phase of a beam of optical radiation can be realized via the process of beam shaping, and the properties of the beam profile of shaped beam are mainly determined by the factor of phase. As designed beam shapes of the laser beam exist in various applications, it is useful and necessary to design and fabricate optical components to shape the laser beam efficiently[77].

In the fields of ultrashort optics, femtosecond laser provides advantages over conventional laser sources such as the necessary timescale for measuring fundamental molecular, it is critically promising and necessary to transform femtosecond laser source into designed shapes for better applications[78]. In general, beam shaping techniques are mainly used for shaping coherent light sources, and there are many shaped beam patterns attracting great interests in both academic and industrial applications. For example, a flat-top laser irradiance with steep sides is widely used in laser machining, because of the same interaction over the illuminated area[55, 77, 79]. Bessel beam has lots of applications in both linear and nonlinear optics fields. The fabricated micro axicons can transform the Gaussian beam into Bessel beam and one of the typical applications is to help trap the cells, because Bessel beam with a transverse ring-like shape intensity pattern exhibits little or no diffraction over a limited distance. Figure 2.14 shows the example of generated Bessel beam with the fabricated axicon for trapping applications[23].

Figure 2. 14 Generation of Bessel beam with fabricated axicon for trapping applications. (a) Fabricated axicons. (b) Bessel beam profile through the axicon. (c) Schematic illustration for trapping applications. (d) Real trapping experiment using Bessel beam[23].

Moreover, because much thinner light sheets can be obtained with scanned Bessel beams, some researchers used the Bessel beam-based structured plane illumination to rapidly image three-dimensional cells with very high resolution, as shown in figure 2.15[80].

Figure 2. 15 An example of structured plane illumination for 3D cell imaging using Bessel beam. Scale bars, 10 μm . Insets, 3 μm [80].

In the nonlinear optics field, the new wavelength can be generated with the optical harmonic generation, at the same time, the wavefront can be shaped via beam shaping structures, which opens exciting new possibilities such as self-shaping of beams and all-optical self-routing[71]. With the technology of laser direct writing, flexible micro-sized structures can be integrated at the crystal facets for the spatial-mode conversion of the generated beams with new wavelengths. Figure 2.16 illustrates the fabricated micro-sized spiral wave plate

and refractive axicon to transform the second harmonics into a vortex beam and Bessel beam[24].

Figure 2. 16 Shaping of second harmonics into vortex beams and Bessel beams by structures integrated directly at the crystal facet. (a) Optical layout. (b) SEM figure of fabricated spiral wave plate. (c) SEM figure of fabricated axicon. (d) Comparison of Bessel beam and Gaussian beam along with propagation[24].

Besides shaping the generated harmonics into Bessel beams, shaping the pumping beam into Bessel beam can affect spatial profile, generation efficiency, dispersion and quality of the harmonics as well. As shown in figure 2.17, it is an example of pumping beam profile dependent dispersion of THG[81-85]. As Bessel beam exhibits a phase and intensity distribution near focus different from the Gaussian beam, there will be distinct THG phase matching properties and

coherent scattering directions, which can be used for rapid probing of large volumes[84].

Figure 2.17 THG generated from a slab with pumping beams of different profiles. (A) Gaussian beam. (B) Bessel beam[84].

With the diffractive optical elements (DOEs), the harmonics can be shaped via diffraction rather than refraction, with the advantages that light can be manipulated in complicated ways and yet in compact systems simultaneously, which is usually necessary for imaging and sensing applications[86-88]. As shown in figure 2.18, a self-focusing harmonic generation source in silicon is achieved via diffracted beam shaping with a gallium-implanted Fresnel zone plate (FZP)[70]. Because of the advantages of DOEs to shape the wavefront, it is promising to design and simulate DOEs, which can be achieved with either self-developed scripts via general programming languages and algorithms or

commercial software, such as Comsol Multiphysics, RSoft, Lumerical FDTD, VirtualLab Fusion, and Zemax[86, 87, 89-93].

Figure 2. 18 Shaping of high-harmonic generation source with the FZP. (A) Third-harmonic pattern recorded at the sample plane. The inset is a SEM of the structure. (B) Focus scans of the third-harmonic patterns. (C) Focus scans of the fifth-harmonic patterns. (D) Focus intensity line[70].

2.6 Optical micro resonators and upconversion lasing

Compared to other conventional light sources, the laser source has characteristics of high temporal coherence, narrow frequency bandwidth, high intensity in focal spot and low beam divergence. However, without an optical resonator, the radiation emitted by the laser mediums such as gas, solid state material and liquid dye, cannot be utilized in any applications[55, 94, 95]. With the development of integrated optical techniques, micro/nanoscale lasers have been widely used in

the applications from on-chip information promising to high-throughput sensing, which has captured broad research interest[96-100]. Thanks to the development of micro/nano manufacturing technology, the micro lasers with reasonably designed resonators are further promoted[5, 8, 101, 102].

To stabilize the output of a laser system to the desired level, feedback is necessary, and this feedback is accomplished by an optical resonator in all laser systems[55, 103, 104]. In a laser system, as shown in figure 2.19, with the help of spontaneous emission, the light is generated then bounces back and forth in the active medium inside the resonator. When the light bounces off the partially transmitting mirror, its intensity will be decreased by a loss factor of mirror reflectivity, and a gain factor G can increase the intensity when it passes through the active medium. If the loss and gain per round trip are balanced, the laser can attain a steady state intensity inside the resonator. An external pumping process can be used to generate the gain factor G , that the energy is transferred into the active medium for generation of a population inversion between atomic or molecular energy levels[52, 94, 105].

Figure 2. 19 Schematic illustration for a laser resonator with an active medium[52].

Small or micro lasers are those have modes sizes or dimensions close to or smaller than the wavelength of emitted light, with the development of manufacturing technology and novel materials, significant progress about improving the characteristics and reducing the dimensions has been realized. Varieties of applications such as optical integration and high-resolution bioimaging are attracted considerable attentions[96, 97, 106-108]. Figure 2.20 illustrates the development timeline of small lasers.

Figure 2. 20 Development timeline of small lasers[96].

Varieties of materials, both organic and inorganic, can be used for fabrication of optical micro resonators for small or micro lasers[98, 102, 109-114]. Among the inorganic resonators, silicon is widely used in the integrated photonic circuits and micro lasers, and all of the core optical functions can be performed at a competitive level within the integrated silicon photonic platform[115-117]. Figure 2.21 shows a typical silicon-based ultrahigh-Q resonator[118].

Figure 2. 21 An example of a silicon wedge-resonator. (a) Optical top view of the wedge-resonator (1-mm-diameter). (b) SEM of the side view of a resonator. (c) Fundamental-mode intensity profiles in the resonators[118].

Despite there exists great progress in the development of inorganic micro resonators, these inorganic materials based resonators have drawbacks as well, it is necessary to concern mechanical rigidity, heat effect, limited tunability, processing speed, high-cost processing, etc. during fabrication of the inorganic resonators[100]. Because of broad emissive bands and weak intermolecular interactions, organic resonators have lots of advantages over inorganic materials such as broadband tunability, easy integration, flexibility, etc. and the

reproducible organic functional structures can be fabricated with laser microfabrication flexibly[96, 98, 100, 102, 114, 119-122]. As shown in figure 2.22, it illustrates varieties of optical micro resonators to generate lasers and an example of 3D printed WGM resonators for full-color laser displays[100, 101].

Figure 2. 22 Typical organic micro resonators for micro lasers. (a) Varieties of micro optical resonators[100]. (b) 3D Printed organic WGM resonators for full-color laser displays All scale bars are 200 μm [101].

Among the micro resonators used for lasing, Fabry-Perot (FP) Resonator and Whispering-Gallery-Mode (WGM) resonators have relatively simple geometries that can be fabricated easily via additive manufacturing, and they are widely used in the fields of micro lasers and sensors[5, 100-102, 114]. FP resonator is widely used for spectroscopy, interference filters, and stabilization of laser oscillation,

and it is based on selectively transmitting or reflecting a particular wavelength. As shown in figure 2.23, it is the schematic of an FP resonator. In the resonator, the left and right reflecting plates sandwiching a center medium constitute the basic structure. The reflecting plate has a refractive index n_1 that is larger than the refractive index n_2 , which is the refractive index of the center medium. Light with amplitude E_0 is normal to the reflecting plates and is incident from the left to the right and. The spacing between the reflecting plates should be adjusted because of the interference, to be an integral multiple of a half-wavelength of the light[123].

Figure 2. 23 Schematic illustration for the Fabry-Perot resonator. (a) Basic structure of FP resonator ($n_1 > n_2$). (b) Phasors at resonance. (c) Phasors off resonance[123].

For the Whispering-Gallery-Mode (WGM) resonator, the light in microscopically small volumes can be stored for long periods of time and the WGM waves are produced in the varieties of geometries including hemispheres, capillaries, bubbles, bottles, fiber, knots, ellipsoids, toroids, rings, and disks. As for the materials, they can be amorphous or crystalline, and organic or inorganic[19, 114, 124]. WGM is the optical resonance arising from light being trapped due to total internal reflection at the boundary of a dielectric structure, and the structure has at least one axis of symmetry. When the light is propagating

along the inner surface of the resonator, after each round trip, if the light returns in phase there will be constructive interference[19]. Figure 2.24 illustrates a WGM resonator with the shape of micro disk[120]. Thanks to the small size of the WGM resonator, densely packaged optical elements can be realized for on-chip applications. Because of the intrinsically high quality (Q) factors of WGM resonators[125, 126], they can reduce the attenuation in photonic circuits, with lots of applications in lasing, optomechanical cooling, frequency comb generation, and sensing.

Figure 2. 24 Schematic illustration for a WGM resonator. (a) Geometry of the WGM resonator. (b) Electric energy density distribution of the WGM[120].

The resonators can be either passive ones or active ones. In recent years, there have been many applications of passive resonators, for example, integrating resonators onto a sensing chip[19]. However, the passive resonators have drawbacks that an evanescent-wave coupler to integrate resonance signals is usually required. The prism and tapered optical fiber are the common couplers, with the taper waist diameter chosen to fulfill the required phase matching

conditions. If passive free space coupling strategies are used, it will be at the cost of reduced performance. Compared to passive resonators, the active resonators that contain some gain mediums are particularly suited to remote excitation and collection of the resonance signals, which alleviates some of practical limitations of general passive resonators[19, 127-130]. For the active resonators, the gain medium is important to generate the required emission. The gain media can be either organic or inorganic. Fluorescent dyes are widely used as organic mediums, with lots of applications used in active FP and WGM resonators[102, 119]. Organic fluorescent dyes can be mixed with a polymer, such as PMMA, SU-8, PDMS, Polystyrene, etc., then the mixed polymer can be subtractively or additively manufactured into waveguides, rings, and disks. Alternatively, the fabricated polymer resonators can be coated with the fluorescent dyes on their surface.

The inorganic material can also be used as gain media, which allows continuous wave laser excitation. The main advantages of the inorganic gain mediums are chemically robust, stable and several accessible excitation wavelength windows can be offered as well, depending on their energy level structures[19, 99, 114, 128, 131].

Upconverting nanomaterials are one of the inorganic gain mediums, can be used for upconversion laser[131, 132]. In nature, most emissions are down conversion (DC), which means the emission energy is lower than the excitation energy. In contrast, upconversion (UC) emission is the emission of one higher energy photon upon the excitation of several photons with lower energy. In lanthanide (Ln) doped materials, near-infrared (NIR) photons are converted to higher energy photons ranging from ultraviolet (UV) to NIR. Varieties of applications based on upconversion luminescence have been demonstrated, spanning from photovoltaics to lighting to volumetric 3D displays[15, 133].

The physics of the UC luminescence can be explained by several mechanisms, including excited-state absorption (ESA), energy transfer upconversion (ETU), cooperative sensitization upconversion (CSU), cross-relaxation (CR), and photon avalanche (PA), as illustrated in figure 2.25[17]. In the case of ESA, excitation takes the form of successive absorption of pump photons by a single ground-state ion. ETU is similar to ESA. Compared to ETU, ESA is operated within a single lanthanide ion, while ETU involves two neighboring ions, which is the essential difference between ETU and ESA. The CSU is a process where the interaction among three ion centers is involved, that ion1 and ion3 generally can be considered as sensitizers in ETU process.

Compared to the ESA and ETU process, the CSU generally has orders of magnitude lower efficiency. In the process of CR, one excited ion can transfer part of its energy to another neighboring ion and both end up with some intermediate levels. For the PA-induced upconversion, there exists an unusual pump mechanism that a pump intensity above a certain threshold value is required. With the help of resonant CR between the excited ion and another adjacent ground state ion, the PA-induced UC process can make a feedback loop, which induces a rapid accumulative effect of the intermediate-level population, and finally leading to strong UC emission as an avalanche process[15, 17, 18].

Figure 2. 25 Schematic illustration for principal upconversion. (a) ESA-based upconversion. (b) ETU-based upconversion. (c) CSU-base upconversion. (d) CR-based upconversion. (e) PA-based upconversion[17].

Compared to simultaneous two-photon absorption (STPA) and optical harmonic generation, which are anti-Stokes-shift emissions as well, upconversion is more efficient to emit a photon having higher energy than the absorbed one, with no requirement of coherent or high-intensity radiation[134]. By patterning the UCNPs doped materials, flexible novel light sources can be developed, as shown in figure 2.26, it is an example of micro upconverting QR codes that can be used as stickers to tag a variety of products. They can be decoded and authenticated by UC and a smartphone application, however, are invisible to the naked eye [18, 135].

Figure 2. 26 Upconverting QR codes (a) Optical image of fabricated upconverting QR. (b) Photoluminescence spectrum of the UC QR code[18].

Active resonators with UCNPs doped gain mediums can be used for upconversion lasers, and the laser emission has been demonstrated in both continuous and pulsed modes. Because of a large anti-Stokes-shift of UCNPs,

upconversion lasers are widely used as the coherent visible and near-ultraviolet radiation sources[131, 136-138]. As shown in figure 2.27, it is an example of using a microsphere-based WGM resonator to achieve upconverting lasing[132].

Figure 2. 27 Schematic of excitation and lasing in an active WGM resonator with the UCNPs gain medium[132].

2.7 On-chip optofluidic system

Optofluidics has been used to analyze biological and chemical samples for a long time, which is a class of optical systems that are synthesized with fluids[13, 139].

Compared to solid materials used in optical systems such as glasses, metals and semiconductors, fluids are widely used in optical applications of liquid mirrors[140], oil-immersion objectives[141], liquid-crystal (LC) displays[142], as shown in figure 2.28.

Figure 2.28 Fluids-based applications in optical systems. (a) Magnetically deformable liquid mirrors[140]. (b) A high-NA oil-immersion microscope objective lens[141]. (c) Displays with graphene oxide liquid-crystal displays[142].

Because of unique properties of fluids that cannot be found in solid equivalents, micro-sized on-chip fluidic devices have undergone rapid development, which enables on-chip small-volumetric sample handling and sensing for chemical and biological analysis to be miniaturized, such as particle sorting and separation, cell culturing and concentration gradient formation, monitoring the refractive index of fluids[11, 143-146]. As shown in figure 2.29, it is an example of an optofluidic sensing system[147].

Figure 2. 29 Illustration for an optofluidic sensing system. (a) Real image of the optofluidic sensing system. (b) to (e) Schematics for the design of the optofluidic sensing system[147].

There are three major groups for optofluidic devices based on the materials used for fabrication and sensing[13]:

- (1) Solid-liquid hybrids device, in which both the liquid and solid's optical properties are applied in the device.
- (2) Complete fluid-based device, in which the function is only based on the optical properties of the fluids.
- (3) Colloid-based device, in which the solid particles in liquid and unique optical properties of colloidal solution are used to realize the functions.

There are two major advantages associated with optofluidics: integration and reconfigurability. In terms of on-chip optofluidic integration, optics and micro fluids on the same chip are combined by building the optics out of the same fluidic toolkit. At the same time, manipulating fluids can reconfigure the optical properties of the devices to realize novel functions[13, 148]. An important aspect of the commercial development of optofluidics is the development of the technology for manufacturing optofluidic devices. Varieties of technologies are utilized in fabrication of optofluidic devices. Planar microfabrication techniques are based on the modification of the entire surface of the sample during each manufacturing step such as conventional semiconductor processing or soft lithography using poly (dimethylsiloxane) (PDMS) substrates, which is rapid and cost effective[139, 149]. However, optofluidic chip fabrication based on planar microfabrication techniques cannot be used to directly form 3D microfluidic structures such as buried microchannels and microchambers without stacking and bonding[11, 12, 25]. These drawbacks can be overcome via ultrafast laser additive manufacturing, and arbitrarily shaped 3D polymer structures can be fabricated with high design flexibility and easy on-chip integration in reasonably short build time[8, 150-153]. As shown in figure 2.30, it is a highly integrative optofluidic refractometer fabricated via two-photon-polymerization[154].

Figure 2. 30 An example of two-photon-polymerized optofluidic structures (a) Schematic of the optofluidic device. (b) Top-view optical microscopy image of the device. (c) Enlarged SEM image of the grating. (d) Enlarged side view image of the coupling region. (e) Transmission spectra[154].

2.8 Summary

In this chapter, a comprehensive literature review on ultrafast-laser-based microfabrication, nonlinear and fluorescent optical theories used for functional optical structures, micro-sized functional structures for beam shaping and wave resonance, and on-chip optofluidic applications is presented. The state-of-the-art femtosecond laser direct writing is widely used for additive manufacturing of on-chip optofluidic components such as waveguide and micro-sized optical

resonator for generating novel sources. For the generation of new light sources, optical harmonic generation, upconversion luminescence and fluorescence from dye are successfully used in both academic and industrial fields.

Compared to laser microfabricated linear and passive optical structures, additively manufactured micro-sized active optical structures based on nonlinear optical response of the two-photon-polymerized materials provide new coherent sources from flexible patterns, which is promising to be studied. On the other hand, optical harmonic generation coherently amplified by UCNPs in WGM resonators additively fabricated via FsLDW can work as seed pulses to generate upconversion lasing as optofluidic sources. All these are the research gaps to be fulfilled in this research, which will be presented in the following chapters. Table 2.1 summarizes the main contributions of this thesis and the related research areas with their characteristics based on the literature review.

Table 2. 1 Summary of the contributions of this thesis

Micro manufacturing methods			Research in this thesis
Literature review	Advantages	Drawbacks	Additive manufacturing of micro-sized optical structures via TPA and
Photolithography	Mass production	2D, simple shape, mask-based,	

electron- and ion-beam lithography	High resolution	low manufacturing throughput, expensive	micro-sintering based femtosecond laser direct writing
Additive manufacturing via femtosecond laser direct writing	High resolution, mask free, complex shapes	Inefficient for large scale simple structures	
Linear and nonlinear optical phenomena for light sources			Research in this thesis
Literature review	Advantages	Drawbacks	Characterization of surface THs from two-photon-polymerized SU-8 structures, refractive index monitoring with surface THs based interferometer
Linear optics	Easy to observe, common phenomenon in nature	Optical phenomena (dispersion, reflection, refraction, diffraction, etc.) in the linear range with limited ways to generate new light sources	
Nonlinear optics	Generation of new wavelengths, promising for super resolution in metrology and manufacturing	Weak signal, difficult to observe, requiring strong pumping intensity	
Refractive and diffractive optical elements			Research in this thesis
Literature review	Advantages	Drawbacks	

Refractive optical elements	Typical high efficiency and the wide useful wavelength range	Heavy, limited degree of freedom in optical design	Transforming the surface TH into a Bessel-like beam which can propagate a long distance without divergence with a two-photon-polymerized diffractive axicon
Diffractive optical elements	Additional degree of freedom in optical system design, light in weight and compact	Strong dispersive behavior	
Passive and active optical resonators			Research in this thesis
Literature review	Advantages	Drawbacks	Injection-seeded high-repetition-rate short-pulse upconversion laser based on UCNPs doped WGM resonator
Passive resonator	Tremendous performance, ultra-small mode volumes	Complex coupling configurations	
Active resonator	Remote excitation and collection of signals, simple configuration	Reduced Q-factors	

Chapter 3 Femotesecond laser additive manufacturing system establishment and fabrication of micro optical structures

3.1 Preamble

As discussed in Chapter 2, additive manufacturing via FsLDW has great advantages that can provide significant opportunities for the design of novel geometries and complex internal structures at a micro-sized scale. In this research project, we will fabricate basic structures for the applications of guiding wave, beam shaping, enhancement of nonlinear phenomena, micro resonators, etc. As shown in figure 3.1, it is the schematic of basic structures to be fabricated. To additively fabricate these structures, we designed two kinds of FsLDW systems (3D and 2D), dependent on the dimensions and features of the target structures to be fabricated.

Figure 3. 1 Schematic of basic micro-sized structures to be fabricated with FsLDW. (a) Waveguides. (b) Refractive axicon. (c) Ellipsoid. (d) Disk. (e) Ring.

One system is a TPA-based FsLDW system with a Multi-Axis Positioner to control the movement of the sample, realizing flexible TPP of precise 3D structures. The other one is a 2D FsLDW system used for TPP of 2D planar structures and micro-sintering, controlled by a Galvano scanner. This system is used for TPP of 2D patterns with a little larger size such as waveguides and disks at a very high speed or sintering micro resonators for the application of whispering-gallery-mode microlasers.

3.2 Optical system establishment for femtosecond laser additive manufacturing

3.2.1 3D TPA FsLDW system for TPP of 3D structures

The experimental setup for 3D TPA FsLDW system can be seen in figure 3.2. The femtosecond laser source has a center wavelength of 780 nm with a repetition rate of 80 MHz, the light pulses typically exhibit a duration of fewer than 100 fs with the average power of more than 140 mW. The femtosecond laser source is focused by a 60× objective lens with a numerical aperture (NA) of 0.7. Table 3.1 gives the detailed specifications of the laser source.

Figure 3. 2 Schematic illustration for 3D TPA-based FsLDW system setup. Abbreviations: HWP: half-wave plate, PBS: polarization beam splitter, BS: beam splitter, BD: beam dump, PM: power meter, LED: light-emitting diode, M: mirror, O: objective, L: lens, and CCD: charge-coupled device

Table 3. 1 Specifications of the laser source of FemtoFiber pro NIR.

Specifications	
Second-harmonic wavelength	780 nm
Laser output power	150 mW
Pulse width	100 fs
Repetition rate	83 MHz
Linear polarization	>75% (horizontal)

Beam shape	TEM00 $M^2 < 1.2$
Beam size	1.2 mm
Beam divergence	< 1 mrad (780 nm)

To realize the fabrication of 3D micro-sized structures with high accuracy and precision, a piezo-electric transducer (PZT) stage is a good choice to control the ultra-high precision movement of the sample, while the femtosecond laser is fixed. The movement of the sample to be fabricated is controlled by E-545 PI nano® piezo controller and Multi-Axis Positioner (figure 3.3).

Figure 3. 3 E-545 PI nano® Piezo Controller and Multi-Axis Positioner.

The system can control the sample to move along x, y, and z directions, and each axis has a closed-loop travel range of 200 μm with the resolution less than 1 nm. The system can be connected to personal computers (PCs) with the communication interfaces such as Ethernet, USB, RS-232, and serial SPI high-speed interface. In the experiment, we used the Labview drivers from PI nano®

to build our own program for the purpose of flexible integration of control functions, thus 3D micro optical structures can be fabricated flexibly.

As the line width and line depth of the TPA FsLDW system are determined by the dose of the laser illumination, which is the combination of laser power and writing speed[155], the average power of the incident laser and sample movement speed are controlled in our system.

Figures 3.4 and 3.5 are the figures of incident power control layout and movement speed control layout of the real 3D TPA FsLDW system, respectively. As shown in figure 3.4, the average power of incident laser beam is controlled by a variable beam splitter/attenuator (VBA), which is a combination of a half wave plate (HWP), a polarizing beam splitter (PBS), and a beam dump. The ratio of transmitted light and reflected light on PBS depends on the state of polarization of incident beam that can be adjusted by tuning the HWP. When the laser source is delivered to the sample, the sample attached to the Multi-Axis Positioner will move as pre-defined paths and speeds, thus the laser spot scans the designed 3D patterns (figure 3.5). Table 3.2 gives the detailed specifications of the PI Multi-Axis Positioner for high accuracy movement control.

Figure 3. 4 Real image for control of the incident power. Inset shows how VBA works to control the power. Abbreviations: HWP: half-wave plate, PBS: polarization beam splitter.

Figure 3. 5 Real image for the PI Multi-Axis positioner to control the sample movement.

Table 3. 2 Specifications of Multi-Axis positioner.

Active axes	X, Y, Z
Integrated sensor	Piezoresistive

Travel range, closed loop	$200 \times 200 \times 200 \text{ }\mu\text{m}$
Resolution, closed loop	1 nm
Push/pull force capacity	50/30 N
Recommended load	0.5 kg
Operating temperature range	15 to 40 °C
Mass	1.2 kg
Cable length	1.7 m
Material	Aluminum

3.2.2 2D high-speed FsLDW system for fast TPP and micro-sintering

For TPP of 2D planar structures with larger dimensions and micro-sintering optical resonators, a Galvano scanner based 2D FsLDW can be used to fabricate optical waveguides and micro resonators at a high speed, as shown in figure 3.6.

In the system, the lens used in combination with the scanner is an f-theta lens. Compared to standard lenses, f-theta lenses have lots of advantages and are widely used in various applications from laser machining, confocal microscopy, and biomedical research. In comparison, standard spherical lenses focus the laser beam on a spherical plane in contrast to an ideal flat or plane field, however, the use of f-theta lenses provides a plane focusing surface and almost constant spot

size over the entire XY image plane or scanning field. The position of the spot on the image is directly proportional to the scan angle[156-158].

Figure 3. 6 Schematic figure for the FsLDW system based on a Galvano scanner. Abbreviations: M: mirror, GM: Galvano mirror.

The Yb-doped fiber femtosecond laser is used as the laser source of the 2D FsLDW system. The Yb-doped fiber laser (Amplitude Systems, Satsuma HP) with a 220-fs pulse duration and a repetition rate of 500 kHz has three different central wavelengths: 1060 nm, 515 nm and 343 nm, respectively. Dependent on the wavelengths and materials, micro-sized structures can be fabricated via TPP or fast thermal quenching. The laser spot can be scanned along with the sample film with a scan speed from 0.1 to 100 mm/s. The average size of the polymerized

or sintered structures can be controlled by either the laser power or the scanning speed.

3.3 Parameter optimization to fabricate the pristine and doped optical structures

3.3.1 Parametric study for additive manufacturing of 3D pristine SU-8 structures via 3D TPA FsLDW system

Additive manufacturing of 3D structures using 3D TPA FsLDW system requires flexible control of scanning routines, and a scanning control program based on Labview drivers from PInano® was developed. The core part of Labview driver used for constructing the connection to the controller is “E517_Configuration_Setup.vi”, as shown in figure 3.7, it is the block diagram of the initialization part of the whole software and the instruction for “E517_Configuration_Setup.vi”.

Figure 3. 7 Block diagram of the initialization part of the driver for the connection to stage controller.

The Graphical User Interface (GUI) of the program can be seen in figure 3.8 and it mainly contains the sections: (a) connection and initialization, (b) z-direction (scanning layers) control and (c) lateral scanning patterns control.

Figure 3. 8 Graphical User Interface (GUI) of the scanning control program.

After the connection is built, from the monitoring section the current positions and velocities of the x, y and z axes can be checked. The initialization section is used to set the original coordinates and velocities of the axes. In the pattern selection tab, we can choose different lateral scanning patterns in x-y plane during the scanning. Arbitrary lateral scanning patterns can be selected flexibly by either clicking the points in the figure or inputting the position coordinates in the arbitrary tab. Section b is used for controlling the scanning layers in z direction to fabricate 3D structures. In this section, after setting the start point to move along the z axis in the edit box (start position), the sample will move several layers, which is controlled by the layer number input. The distance between the layers is controlled via step size. The velocity input is used to control the movement velocity of the z direction.

For the purpose of fabricating complex structures, reading the points cloud of the combined structures from a data file is helpful. As shown in figure 3.9 (a), it is the program interface of loading data from a file, and figure 3.9 (b) shows the points cloud patterns of the pre-designed rings and waveguides as an example.

Figure 3. 9 Example of inputting complex and combined patterns by loading data from a file. (a) Program interface of loading data. (b) Pre-designed patterns in the file.

To fabricate 3D pristine SU-8 structures, we first pre-bake the sample one minute at 65 °C and 25 minutes at 95 °C. After pre-baking, the SU-8 film is slowly cooled down to the ambient temperature (25 °C) over 10 minutes, then the focal spot of the near-infrared femtosecond laser is scanned laterally per layer in the SU-8 film by controlling the Multi-Axis Positioner. After laser scanning, the sample is post-baked at 65 °C for one minute and at 95 °C for 5 minutes. The sample is cooled down to the ambient temperature and then immersed into the developing solution (Microchem) for 10 minutes to remove the unreacted photoresist.

Because the quality of two-photon-polymerized structure is dependent on the dose of the laser illumination, it is necessary to check whether the dose threshold of damage exists for our FsLDW system. To check the illumination dose threshold, the scanning speed (20 $\mu\text{m/s}$) and scanning intervals (1 μm) are kept

constant, only the laser power is controlled. As shown in figure 3.10 (a) to (d), when the laser source has a low power, the spot can scan different patterns (line, square, and circle) without burning. When the laser power was above 60 mW, the SU-8 was burnt immediately (figure 3.10 (e)), thus the illumination dose threshold of damage really exists for TPP of SU-8 via our FsLDW system.

Figure 3. 10 Burnt threshold check for TPP of SU-8. (a) Optical image of the laser spot pattern at 20 mW. (b)-(d) Basic laser spot scanning patterns at 20 mW. (e) Burnt patterns during laser spot scanning at 60 mW. All the images have the same scale bar.

During the parametric study, the structure usually has a better lateral resolution than the vertical resolution. If we need to fabricate a structure with a slope or shorter thickness, we need to decrease the illumination dose to decrease the thickness of the single polymerized layer. However, if the illumination dose is too small, the structure will not be very stable and will be easily damaged during the procedure of development. After the parametric study for fabricating our functional optical structures, the desired incident power, scanning speed, scanning interval are 10 mW, 20 $\mu\text{m/s}$ and 1 μm , respectively. Other combinations of the parameters can fulfill the requirement as well. As shown in figure 3.11, a designed cylinder with a diameter of 60 μm and a height of 5 μm

(5 layers) were fabricated with our 3D TPA FsLDW system as an example. We can see the lateral resolution was much higher than the vertical resolution. The diameter was around 60 μm , however, the height was larger than the designed height, which was around 15 μm . For fabrication of on-chip functional optical structures without the slope, the quality and resolution of the structures can fulfill the requirement well.

Figure 3. 11 Quality check of fabricated cylinder. (a) Confocal microscopy check. (b) SEM check.

3.3.2 Parametric study for additive manufacturing of 3D fluorescent dye doped SU-8 structures via 3D TPA FsLDW system

Based on the parametric study of the fabrication of basic pristine SU-8 structures, fabrication of active structures with a gain medium such as Rhodamine B doped SU-8 waveguides and conical structures was studied. As shown in figure 3.12, the rectangle waveguide with optimized thickness and conical structure (the designed apex angle was 90 degree and diameter was 30 μm) were fabricated as

an example. From the SEM measurement result, it shows that the height of single layer can be optimized to be around 10 μm that single mode active waveguide can be fabricated. The cone with a sharp tip is able to be fabricated, however, the shape of the cone is not totally the same as the designed geometry because of a relatively low vertical resolution during the TPP of SU-8. Depending on the target applications, reasonable shapes can be achieved by optimizing the laser power and scanning speed. For our purpose of developing active functional optical structures, the fabricated active conical structures can be used for enhancement of the amplified light sources with the Rhodamine B gain medium.

Figure 3. 12 Optical image and SEM check of fabricated Rhodamine B doped basic structures. (a).and (b) Optical image and SEM check of the fabricated active waveguide with optimized thickness. (c) and (d) Optical image and SEM check of the fabricated active conical structure. View angle: 45 degree.

Active Rhodamine B doped 3D high-aspect-ratio (HAR) structures can be fabricated by increasing the writing power to increase the thickness of single

polymerized layer. As shown in figure 3.13, waveguides of different sizes were fabricated via single-layer scanning with a higher illumination dose. The lengths of the waveguides were 180 μm , 140 μm , 100 μm and 60 μm , respectively. All the waveguides had the same width of 8 μm and the thickness was ~ 50 μm . The laser power we used was 20 mW and the scanning speed was 20 $\mu\text{m/s}$. Dependent on the applications, 3D HAR active SU-8 structures can be realized by optimization of the parameters.

Figure 3. 13 Microscopic image and SEM check of the fabricated HAR Rhodamine B doped waveguides. (a). Microscopic image of the doped waveguides. (b) Confocal image to check the thickness of the waveguides. (c) and (d) SEM check of the doped waveguides viewed at 0 degree and 30 degree, respectively.

3.3.3 Parametric study for fast manufacturing of 2D planar structures and micro resonators via 2D FsLDW system

When we want to additively manufacture large scale 2D structures with large sizes at a high speed, the 2D FsLDW system with a Galvano scanner to control the laser spot scanning will be used. The control program named MarkingMate from Sino-Galvo is used for controlling the scanning routines. The basic structures for parametric study of TPP of SU-8 at 515 nm are a ring and a line, and both the ring diameter and line length are 50 μm , as shown in figure 3.14. The scanning speed and average power are the parameters to be studied, as shown in table 3.3.

Figure 3. 14 Basic structure and the structure arrays for parametric study of TPP.

Table 3. 3 Parameter list for optimization of 2D TPP.

Material:	Wavelength of the incident laser: 515 nm				
	1mm/s	2mm/s	3mm/s	4mm/s	5mm/s
SU-8					

5 mW					
6 mW					
7 mW					
8 mW					
9 mW					
10 mW					

Parameters of TPP of 2D structures with 2D FsLDW system were studied.

As shown in figure 3.15, it is the fabricated pattern we used for parameters study.

In the experiment, different writing powers and scanning speeds were tried to optimize the fabrication quality based on table 3.3. Lower power and faster scanning speed make the structure have smaller features; however, the structure may be deformed and unstable, easy to be damaged after development. If the power is too high or the scanning speed is too slow, the structure may be burnt. Before development, the reasonable parameters for generating precise patterns are marked with the red box (figure 3.15(a)). After development, the structures were washed when the power was below 9 mW. When the power was 10 mW, the residual SU-8 damaged the pattern and the structure was dirty. Based on the optimization of parameters, reasonable structures can be fabricated when the laser power was 9 mW and the scanning speed was 1 mm/s in the experiment with the 2D FsLDW system.

Figure 3. 15 Parametric study based on the parameter list for 2D FsLDW. (a) Before development. (b) After development (1mm/s, 9 mW).

Several micro-sized ring and line structures with the laser power of 9 mW and scanning speed of 1 mm/s were fabricated to check the quality using confocal microscopy. As shown in figure 3.16, the average height of the fabricated structure was 20 μm and the average width of the line was 10 μm . The ring pattern had a precise shape with the inner diameter of ~ 40 μm and the outer diameter of ~ 60 μm . The fast fabricated 2D structures can be used for waveguides and resonators in future research and applications.

Figure 3. 16 Confocal microscopic check of fabricated ring and line with 2D FsLDW system.

The 2D FsLDW system can be used for fast sintering of the micro-sized resonators for lasing as well. Micro ellipsoids can be fabricated by controlling the scanning speed and laser power at a certain wavelength. We did the parametric study for fabrication of UCNP's doped micro ellipsoids, and a thin film of $\text{NaYF}_4\text{:Yb,Er}$ dissolved in cyclohexane solution was sintered using the laser wavelength of 343 nm. The $\text{NaYF}_4\text{:Yb,Er}$ UCNP's were synthesized using a typical solvothermal method[159]. Figure 3.17 shows the schematic illustration for sintering of UCNP's doped micro-ellipsoid via 2D FsLDW system. The right inset shows the transmission electron microscope (TEM) and scanning electron microscope (SEM) images of the $\text{NaYF}_4\text{:Yb,Er}$ UCNP's. It can be seen that the $\text{NaYF}_4\text{:Yb,Er}$ UCNP's are well-crystallized and display uniform hexagonal shape

with an average particle size of 25 nm. The UCNP film was fabricated using an interfacial assembly method by placing the glass substrate vertically in the UCNP solution, which is dense and uniform as seen from SEM image.

Figure 3. 17 Schematic illustration for sintered upconversion micro-ellipsoid via 2D high-speed FsLDW system.

Different average incident powers at a fixed speed (1mm/s) were used to scan the film, as shown in figure 3.18, the sizes of the sintered ellipsoids were dependent on the power and the film was burnt if the power was too high (above 15 mW). The scanning speed dependence was checked by setting the laser power a constant, and figure 3.19 shows the sintered ellipsoids at different scanning speeds when the laser power was 11 mW. Both the laser power and scanning speed work together to control the dimensions of the UCNPs doped ellipsoids, and reasonable sizes can be obtained by controlling the laser power and scanning speed for the laser resonator applications.

Figure 3. 18 Power dependence check of the FsLDW system to fabricate the micro UCNPs doped ellipsoids. The scale bar is 50 μm .

Figure 3. 19 Laser spot scanning speed dependence check of the FsLDW system to fabricate the micro UCNPs doped ellipsoids. The scale bar is 20 μm .

3.4 Summary

To summarize, we set up the 3D TPA FsLDW system for flexible TPP of 3D micro-sized structures and develop its control program. A 2D FsLDW system is established as well for fast TPP of 2D planar structures and micro-sintering.

Based on the parametric study, both 3D pristine and Rhodamine B doped SU-8

structures are successfully fabricated with the optimized scanning speed and femtosecond laser power. 2D structures can be two-photon-polymerized or sintered by scanning the laser spot at a high speed via the 2D FsLDW system. The fabricated optical structures with both systems can be easily integrated into other optical components and used for on-chip applications for sensing, illumination and delivering small volumetric light sources.

Chapter 4 Characterization of surface third harmonic generation at two-photon-polymerized SU-8 structures

4.1 Preamble

As discussed in chapter 3, both 3D and 2D micro-sized optical structures can be fabricated via TPP or micro-sintering. Nonlinear optical responses of the transparent SU-8 structures can be used for generation and delivering coherent light sources for lab-on-a-chip applications. The THG occurs in all materials, even though the crystal has a center of inversion symmetry. In this research, we studied the THG conversion efficiency at two-photon-polymerized pristine SU-8 structures by controlling the ellipticities and polarization directions of the incident femtosecond laser, focusing positions in the structures. The characterization of surface THs at two-photon-polymerized pristine SU-8 structures can be used for optimization of the THG conversion efficiency and measurement of the transparent structure thickness in a noninvasive manner.

4.2 Optical observation system setup

In the optical observation system, the polarization states of the incident beam and the excitation position need to be controlled, and the output should contain both the image and spectrum information of the samples. Based on the necessary input

and output information, the optical observation layout is designed as shown in figure 4.1, the inset is the spectrum of incident laser source.

Figure 4. 1 Optical layout of the TH analysis system. Abbreviations: HWP: half-wave plate, QWP: quarter-wave plate, LPF: long-pass filter, SPF: short-pass filter, BS: beam splitter, M: mirror, F-OBJ: focusing objective, I-OBJ: imaging objective, L: lens, CMOS: compact complementary metal oxide semiconductor camera and EMCCD: electron multiplying charge-coupled device.

In the system, a wavelength-tunable supercontinuum fiber mode-locked femtosecond laser (Toptica FemtoFiber pro SCIR, 980-2200 nm, 80 MHz) is used as the incident laser source and the center wavelength is 1588 nm. The ellipticity of the incident Fs laser's polarization state is controlled by employing a half-wave plate (Thorlabs WPH10M-1550) and a quarter-wave plate (Thorlabs

WPQ10E-1550). To remove any residual short wavelength light present in the excitation beam, an 800 nm long-pass filter (Thorlabs FELH0800) is placed in front of the focusing objective lens. After passing through a 40 $\times$ objective lens (Newport LI-40X) with a numerical aperture (NA) of 0.65, the beam is focused to a small spot of 7.6 μm diameter (FWHM: full-width-half-maximum) on to the two-photon-polymerized SU-8 structures. The nonlinear optical harmonics generated from the SU-8 structures are collected using a 20 $\times$ objective lens (Olympus LUCPLFLN 20X) of 0.45 NA. Before the optical harmonics are delivered to the spectrometer and camera, a 750 nm short-pass filter (Thorlabs FES0750) is adapted to remove the excitation wavelength and the collected light is directed to a broadband spectrometer (Andor Shamrock 193i) connected to a highly-sensitive electron-multiplying charge coupled device (EMCCD, Andor IXon Ultra) for the spectral analysis. The real-time image is captured by a compact CMOS color camera (Thorlabs, DCC1645C) to analyze the optical harmonic patterns.

4.3 Experimental procedures for characterization of THG at two-photon-polymerized SU-8 structures

4.3.1 THG characterization with elliptical polarization states and different interfaces

The two-photon-polymerized SU-8 structures for characterization of the THG were cylinders with a diameter of 40 μm and a height of 50 μm (a base structure was included to keep stable), as shown in figure 4.2.

Figure 4. 2 Two-photon-polymerized cylinders for characterization of THG.

To control the ellipticities of the input femtosecond laser source, the quarter-wave plate was rotated while the half-wave plate was fixed, as shown in figure 4.3.

Figure 4. 3 Schematic illustration for measuring THG with different excitation ellipticities. Abbreviations: HWP: half-wave plate, QWP: quarter-wave plate, LPF: long-pass filter, OBJ: objective, M: mirror.

To check the THG intensity at surfaces, three different interfaces were selectively excited: air-glass, glass-SU-8, and SU-8-air interfaces. Figure 4.4 shows the TH spectrums at different interfaces. When the incident beam was focused on an interface, the quarter-wave plate (QWP) was rotated with a step size of 5 degrees from the initial position, which was set as 0 degree such that the fast axis of the QWP was parallel to the fast axis of the half-wave plate (HWP). The spectrometer recorded the TH spectrum generated at each QWP rotation step. It shows THG was very sensitive to the different ellipticities and there were periodical patterns. When the rotation angle was either 45 degree or 135 degree, the resulting TH intensity decreased to 0, where the incident laser beam was circularly polarized. The TH reached to its maximum when the incident laser was linearly polarized, where the rotation angle of QWP was 0, 90 or 180 degrees

(figure 4. 4(a) to (c)). Figure 4.4 (d) shows the THG dependence on the ellipticity of the excitation beam when the incident beam was focused at the three different interfaces. The highest conversion efficiency of THG (2.6×10^{-7}) was obtained when the linearly polarized incident beam focused on the SU-8-air interface, and the conversion efficiency was 4.93 times higher than that from SU-8-glass interface, and 12.17 times higher than that from glass-air interface.

Figure 4. 4 THG dependence on different input polarization ellipticities and focused target interfaces. (a) to (c) Normalized peak intensity spectra from air-glass, glass-SU-8, and SU-8-air interfaces with different polarization ellipticities of the incident beam. (d) Comparison of the TH intensities at different interfaces with different ellipticities of the incident beam.

It has been reported that THG vanishes when an isotropic media is excited with circularly polarized light, even at interfaces[160, 161]. The polarization components of the THG in the case of an isotropic medium can be written as[162],

$$P_x^{(THG)} = \varepsilon_0 \chi_{xxxx}^{(3)} E_x (E_x^2 + E_y^2) \quad - (4.1)$$

$$P_y^{(THG)} = \varepsilon_0 \chi_{yyyy}^{(3)} E_y (E_x^2 + E_y^2) \quad - (4.2)$$

where P_x and P_y are the nonlinear polarization components in x and y directions, ε_0 is the permittivity of free space, $\chi^{(3)}$ is the third order nonlinear susceptibility, and E_x and E_y are the x and y components of the incident electric field. For a circularly polarized incident beam, E_x and E_y are related to each other as $E_x = iE_y$. The equations show that the nonlinear polarization components for THG will vanish for a circularly polarized pumping, hence no THG can be observed if the excitation is circularly polarized. To measure the TH signal at an interface, the parameter governing the signal level is not the absolute value of $\chi^{(3)}$, but rather the spatial variations of $\chi^{(3)}$ at interfaces[72], thus the maximum intensity of TH can be detected when the incident beam is focused on the SU-8-air interface because of the largest spatial variations of $\chi^{(3)}$ among the interfaces.

Figure 4.5 shows the optical spectrum of the generated TH when the excitation was focused on the SU-8-air interface. During these measurements, to

check the second harmonic generation (SHG), the 750 nm short-pass filter was removed from the beam path so that all the wavelengths of the collected beam were allowed to fall on the spectrometer for the initial characterization. No SHG was detected at the half the excitation wavelength of 794 nm in the experiment, because all the materials in the sample are isotropic (namely air, glass, and SU-8) and SHG is forbidden in the materials with inversion symmetry. However, as an electric dipole allowed process, THG occurs in materials with inversion symmetry[63]. The central wavelength of the generated TH was 551.4 nm which was at the one-third of the pumping wavelength. The harmonic generation nature was double-confirmed from the emission spectral bandwidth (0.005 eV) normalized by the harmonic order[163]; the optical harmonic generation provided a similar spectral bandwidth compared to the original bandwidth of the fundamental laser, which was 0.008 eV in our case, as shown in figure 4.5 (b).

Figure 4. 5 TH spectrum with linearly polarized excitation at SU-8-air interface. (a) Optical spectrum of the generated TH. (b) Normalized TH bandwidth compared with that of the fundamental beam.

4.3.2 Linear polarization direction dependence check of THG

To check the linear polarization direction dependence of the THG at the interfaces, the QWP was removed and the HWP was rotated gradually with a step size of 5 degrees, as shown in figure 4.6 (a). Figure 4.6 (b) to 4.6 (d) show the THs generated from air-glass, glass-SU-8, and SU-8-air interfaces were independent of the polarization direction of the excitation laser source, because all the materials in the sample (namely SU-8, glass, air) is isotropic and there is no direction preference for THG. To use the interface THG as the coherent light source, the TH intensity is not dependent on the linear polarization directions.

Figure 4. 6 Linear polarization dependence of THG. (a) System schematic for measuring THG with different linear polarization states by rotating the half-wave plate. (b) to (d) Normalized peak intensity spectra from air-glass, glass-SU-8, and SU-8-air interfaces with different input linear polarization states. Abbreviations: HWP: half-wave plate, LPF: long-pass filter, OBJ: objective, M: mirror.

4.3.3 Excitation position dependence of THG and thickness measurement

To find the excitation position dependence of the THG, the focused laser beam having a fixed linear polarization state was scanned through the polymerized SU-8 structure along the z-axis with a 10 μm scanning step size. Figure 4.7 shows the TH intensity map in the sample at various excitation depths. The observed

TH intensity was stronger at the interfaces and decreased to 0 within the bulk volumetric part of SU-8 and the glass substrate. The TH intensity reached its maximum when the laser beam was focused on the SU-8-air interface.

Figure 4. 7 TH intensity distribution at different excitation depths along with the sample

The strong THs from interfaces can be explained by Gouy phase shift. For a tightly focused beam, the Gouy phase shift creates a phase difference of π between the THs generated before and after the focus and hence they destructively interfere, resulting in a low TH intensity in the bulk[72, 164, 165]. Since the symmetry along the optical axis is broken at the interface, and the Gouy

phase shift no longer results in total destructive interference at the interfaces. The TH intensity at the interface between two media 1 and 2 scales approximately as $(\alpha_1 - \alpha_2)^2$, where $\alpha = \chi^{(3)}/n\Delta n$, and $\chi^{(3)}$ is the third order susceptibility, n is the refractive index and Δn is the dispersion[160]. Since the third-order susceptibility difference at the SU-8-air interface is larger than that of air-glass and glass-SU-8 interfaces, the highest TH intensity is observed from the SU-8 air interface.

Based on the characterization of polarization and excitation position dependent THG from two-photon-polymerized structures, signal with peak intensity can be observed at interfaces with linearly polarized pumping, independent of the input polarization direction. The surface THs from two-photon-polymerized 3D structures offer novel interface-sensitive light sources for measurement applications and can be used for measuring the thickness of complex transparent micro structures.

The strong surface THs from the different interfaces among two-photon-polymerized structures, air, and glass substrate can be utilized as the signal to measure the thickness of the polymerized SU-8 structure. The distance of two TH peaks from air-SU-8 and SU-8-glass interfaces in figure 4.8 is 60 μm , thus the height of the two-photon-polymerized SU-8 cylinder is 60 μm based on the

interface THs peaks. To check the reasonability of the thickness measurement based on THG, a confocal microscopic image of the sample was supplemented. As shown in figure 4.8, the two-photon-polymerized SU-8 structure (cylinder and base) had a thickness of around $50\text{ }\mu\text{m}$, corroborating the reliability of our system. In real measurement, correction should be concerned such as medium refractive index mismatch and the linear mechanical stage errors. When the measurement is scanned along the whole structure with a scanner, the 3D profile of the two-photon-polymerized structure can be obtained, even though the structure is transparent and with a high slope.

Figure 4. 8 Confocal microscopic check of the two-photon-polymerized SU-8 structure thickness.

4.4 Summary

To conclude, we have thoroughly characterized THs excited at different interfaces of two-photon-polymerized SU-8 structures with different input polarization states, and excitation depths. The highest conversion efficiency was observed at the SU-8-air interface (2.6×10^{-7}) when excited with linearly polarized light, which was 4.93 times higher than that at SU-8-glass interface, and 12.17 times higher than that at glass-air interface. Due to the isotropic sample nature, the generated TH has no dependence on the linear polarization state of the pumping beam. In the area of microfabrication, it is necessary to measure the surface profile of the 3D transparent structures or layers in noninvasive manner, which remained, however, practically difficult to date if the transparent structure has high slopes. Strong surface THG provides a good way to measure the profile of 3D transparent structures. In our research, the strong THs from air-SU-8 and SU-8-glass interfaces were used to measure the thickness of the two-photon-polymerized micro cylinders, which was reasonable based on the confocal microscopy measurement. After correction to suppress the errors, THs-based noninvasive metrology can be used for real transparent structure profile measurement in the future.

Chapter 5 Generating and delivering light sources of small volume for high precision on-chip measurement via surface THG

5.1 Preamble

As discussed in chapters 2 and 4, the optical harmonic generation of transparent materials has been widely used in short-wavelength light generation, optical modulation, and non-destructive study of the sample characteristics. Though THG is usually a weak process, it becomes relatively stronger at the material interfaces. Therefore, the surface THG from micro-sized two-photon-polymerized structures can be used as novel micro-sized light sources, which can be easily integrated into other on-chip optical systems, removing both the need for insertion and alignment of the light sources. To use the surface THG, we demonstrated a micro interferometer and a diffractive axicon, respectively. The two-photon-polymerized micro-sized THG interferometer is used for the real-time on-chip monitoring of micro-fluidic refractive index changes. To get the optical harmonic generation, a tightly focused pumping beam must be used, and the TH will diverge greatly. It is necessary to shape the THG wavefront to have a longer propagation distance, the diffractive axicon can be used for transforming the Gaussian TH into a Bessel-like beam, which can propagate a longer distance.

5.2 Micro two-photon-polymerized interferometer for real-time on-chip monitoring gas index changes

5.2.1 Fabrication of the micro-sized TH interferometer using two-photon-polymerized cuboids

Figure 5.1 illustrates the fabricated THG-based interferometer for sensing micro-optofluidic refractive index (RI) changes. A simple vertical pumping of these two-photon-polymerized structures results in highly coherent compact TH light sources within a small volume near to target samples for real-time on-chip RI monitoring. The inset shows how the fabricated micro-sized TH optical interferometer can be easily integrated into an optofluidic device. The RI variations of target fluids can be analyzed via the related spatial frequency changes in the TH interferogram.

Figure 5. 1 Illustration for micro-optofluidic refractive index sensing with TH interferometry.

As strong TH comes from the surface of two-photon-polymerized SU-8 structures, when the cuboids are pumped with a defocused vertical incident femtosecond laser beam, generated TH sources at the edges of the cuboids can interfere when propagating a certain distance. Figure 5.2 shows the fabricated cuboids to be used for generating interferogram. Figure 5.2 (a) and (b) show the micro-sized two-photon-polymerized cuboids of different scales as an example, which can be flexibly integrated into the chip systems dependent on the applications. In our experiment, the cuboids used to generate the interferogram is shown in figure 5.2 (c). The SU-8 cuboids with identical dimensions were fabricated; the width was 10 μm , the length was 40 μm , and the spacing between these cuboids was 8 μm .

Figure 5. 2 Generation of interferogram with two-photon-polymerized SU-8 cuboids. (a) Optical and (b) SEM images of the two-photon-polymerized cuboids of different lengths as an example; the scale bars are 20 μm . (c) Schematic illustration of the Young's two slits interferometry created by the two coherent TH sources. The scale bar is 10 μm .

To excite both cuboids simultaneously, a slightly defocused incident pump beam was used with a beam waist of 28 μm . THs generated at the SU-8-air interface of the cuboids act as two coherent light sources and make the interference pattern during propagation. As shown in figure 5.3, for efficient THG, a stronger pumping beam was required which was realized with a high average power of 170 mW and sub-100-fs short pulse duration at 1545 nm center wavelength. The TH generated from the cuboids had the central wavelength of 533 nm and the spectral bandwidth of 21.85 nm. The spatial intensity profile of the THG emission from both cuboids had high quality Gaussian shape with an R^2 value of 0.991, as shown in figure 5.3 (c).

Figure 5. 3 Coherent TH sources at the edges of two-photon-polymerized cuboids. (c) Spectrum of the incident laser beam. (d) Spectrum of the TH generated at the SU-8-air interface of the cuboids. The inset shows the optical image of the TH sources. (e) Spatial intensity distribution of the TH sources along the width of the cuboids. The scale bar is 10 μm .

Figure 5.4 shows the TH patterns when the imaging objective was scanned along the propagation direction of TH sources. During the scanning, the start was the position the objective focused at the TH sources and two TH point sources

were observed. When the imaging objective moved far away from the TH sources, a distance of 50 μm , the TH interferogram pattern was generated.

Figure 5. 4 TH patterns along propagation direction of TH sources. (a) TH images at different imaging positions. (b) Normalized intensity map of the horizontal profile of the patterns along propagation of TH sources. The scale bar shown is 10 μm .

The TH interferogram imaged at 50 μm away from the TH sources was analyzed using the simple Young's double slits interference theory, whose interference equation is given by[166]:

$$\Delta x = \frac{\lambda D}{nd} \quad - (5.1)$$

where Δx is the period of the interference fringes, λ is the central wavelength, D is the distance between the source and the imaging plane, n is the refractive index of the medium and d is the separation between the two sources. Figure 5.5 shows the spatial domain and frequency domain features of the interferograms. In order

to determine the peak position of the spatial frequency, a second order polynomial fitting was applied to the first significant spatial frequency peak. The spatial frequency from the experimental data was $0.574 \mu\text{m}^{-1}$, and its reciprocal was the period of the interference fringes, namely $1.74 \mu\text{m}$. Theoretical calculation based on Young's double slit theory yields the period to be $1.72 \mu\text{m}$, corroborating the reliability of our system.

Figure 5.5 Spatial and frequency domains of TH interferogram imaged at $50 \mu\text{m}$ from the TH sources. (a) Interference pattern imaged at $50 \mu\text{m}$ from the TH sources. (b) Spatial frequency distribution of the imaged interference pattern. (c) Zoom-in view of the first spatial frequency peak. The inset shows a second order polynomial fitting of the peak.

5.2.2 Real-time on-chip monitoring of fluidic refractive index changes

The spatial frequency of the interferogram created by the coherent TH sources can be used for real-time monitoring of RI changes of fluids in micro-fluidic devices. A correction factor is required when applying the Young's double slit equation to account for the microfluidic system's characteristics to the interferogram periods; the spatial frequency remains linear to the RI of the fluids.

The SU-8 micro-interferometer in figure 5.2(c) was incorporated into a

microfluidic device to monitor the RI changes created by argon (Ar) gas flow through the device, and figure 5.6 shows the real image of the experiment.

Figure 5. 6 Real image of real-time on-chip gas refractive index monitoring using surface THG interferometer.

In the measurement, the Ar gas pressure was controlled by a precision flow controller (Alicat Scientific MC-200), from 14.5 to 15.0 psi with a 0.1 psi step while the temperature of Ar was maintained at 28.1 °C. Figure 5.7 shows the TH interferograms recorded under different Ar pressures. The imaging position was set to be at 50 μm distance from the TH sources. When Ar pressure was controlled from 14.5 to 15.0 psi, the spatial frequency of the interferogram was found to increase from 0.495 to 0.605 μm^{-1} , as shown in figure 5.7 (b) and (c). According

to Gladstone-Dale model, the refractive index change of a gas (Δn) is linear to the change of gas pressure (ΔP), given by[167]:

$$\Delta n = \frac{K_{GD}}{RT} \Delta P \quad - (5.2)$$

where KGD is the Gladstone-Dale constant, R is the ideal gas constant, and T is the temperature. The dependence of the TH interferogram's spatial frequency to Ar pressure is plotted in figure 5.7(d). The spatial frequency of interferogram indicated a linear relationship with the Ar pressure with R^2 value of 0.995, which matched well with the theoretical prediction. These results confirm that the RI change of Ar induced by its pressure change can be efficiently monitored in real-time using the TH interferograms generated from two-photon-polymerization micro-sized SU-8 cuboids with a high sensitivity of $0.22 (\mu\text{m})^{-1} (\text{psi})^{-1}$.

In this study, the demonstrated two-photon-polymerized micro-sized third-harmonic optical interferometer can realize real-time, on-chip monitoring of microfluidic refractive index, with the advantages of compact coherent light sources for high-precision refractive index measurements within a small volume near to target samples. A simple vertical pumping via optical microscope enabled us to detect the resulting third-harmonic optical interferogram without complex light in- and out-coupling or precision alignment. The fundamental pump beam

was filtered out, thus background-noise-free third-harmonic interferogram at the target volume was well extracted out.

Figure 5. 7 Real-time monitoring of the refractive index changes of Ar gas under different pressures. (a) Recorded interferograms under different Ar pressures imaged at a 50 μm distance from the TH sources. The scale bar is 10 μm . (b) Normalized FFT domain of the central horizontal profiles of interference patterns under different argon pressures (c) Polynomial fitting of the data points near peaks in (b). (d) Pressure dependence of the spatial frequency of interferogram.

5.3 Shaping surface TH using a two-photon-polymerized diffractive axicon

5.3.1 Introduction to methods of generating non-divergent Bessel-like beam

Surface TH is generated from a tightly focused incident beam, and it can diverge greatly during propagates. In the field of beam shaping, the axicon can be used for transforming the Gaussian beam into a Bessel-like beam. The Bessel beam is an excellent illumination source since it maintains the central spot size for a distance more than hundreds of times the spot size, as well as it is capable to maintain the Bessel profile along the propagation distance. Both the refractive and diffractive axicons can be used for transforming the incident Gaussian beam into Bessel-like beam. To characterize the propagation of Bessel beam, a refractive axicon is simulated with Zemax and compared with theoretical analysis[23]. Feasibility exploration of shaping divergent Gaussian THs was realized via the two-photon-polymerized diffractive axicon.

The refractive axicon for generation of the Bessel beam is based on the light refraction, which can be illustrated in figure 5.8. Because of refraction, the refracted light interferes with each other, and it will generate a diffractionless beam with a Bessel shape. The intensity distribution of the perfect Bessel beam in the transverse plane is independent of propagation distance z , so the beam does

not diverge and is narrower than the first dark ring of the Airy disk pattern. The lateral intensity distribution structure of the Bessel beam can be expressed by[23, 168, 169]:

$$I(r, z) = \frac{4\pi^2 E^2(R)}{\lambda} \frac{R \sin \beta}{\cos^2 \beta} J_0^2 \left(\frac{2\pi r \sin \beta}{\lambda} \right) \quad - (5.3)$$

$$n \sin \alpha = \sin(\alpha + \beta) \quad - (5.4)$$

$$z_D = R(\cot \beta - \tan \alpha) \quad - (5.5)$$

Figure 5. 8 Schematic illustration for Bessel beam generation through a refractive axicon[23].

To characterize the Bessel-like beam generated by the refractive axicon via simulation, an axicon with general parameters is randomly selected, the ray-tracing program Zemax is used to simulate the wave propagation and the wave profile is compared with the Bessel function based on the theoretical calculation.

An axicon with an apex angle of 150 degree, a base diameter of 20 mm, and a

refractive index of 1.51 was modeled. For the parameter setting of the source in the simulation, the source was a collimated Gaussian beam, the power was 0.1 mW, the wavelength was 800 nm, the number of layout rays was 100, the number of analysis rays was 10^7 and the beam size was 0.9 mm. As shown in figure 5.9, it is the layout of the simulation and the detected Bessel-like pattern when the distance between the detector and the axicon base was 4 mm.

Figure 5.9 Layout of the simulation and the detected Bessel pattern. (a) Layout of the settings. (b) Detected Bessel pattern when the distance between the detector and axicon base was 4 mm.

Based on the Bessel beam shaping theory, the intensity distribution of the ideal Bessel beam in the transverse plane should be independent of propagation distance z , thus the beam does not diverge and is narrower than the first dark ring of the Airy disk pattern. Figure 5.10 shows the overlay between the horizontal central profile of the simulated Bessel pattern (detector to the apex angle of

axicon: 3 mm) and the square of Bessel function (J_0^2), confirming the reasonability of simulation.

Figure 5. 10 Comparison between of Zemax simulation and Bessel function.

Figure 5.11 shows the propagation of the generated Bessel-like beam, and the non-divergent beam can maintain its peak intensity and narrow spot size for a certain distance.

Figure 5. 11 Simulated Bessel patterns along propagation. (a) Bessel pattern profiles along propagation. (b) Peak intensity along propagation.

Because diffractive optical elements (DOEs) are light in weight and compact compared to their refractive counterparts, and are capable of manipulating light in ways not possible by conventional refractive optical elements (ROEs)[87], it is advantageous to use the diffractive axicon to transform the TH into non-divergent Bessel-like beam. The Bessel-like pattern generated by the diffractive axicon can be explained using scalar diffraction formulation since the features of the diffractive axicon are larger than the wavelength of TH. The diffractive axicon can work as either an amplitude type or a phase type transmittance to modulate the input wavefront. As shown in figure 5.12, the concentric-rings-made structure can work as a diffractive axicon to transform the THs into a Bessel-like pattern with a large non-divergent range.

Figure 5. 12 Schematics for shaping the divergent THs into the Bessel-like pattern using a diffractive axicon.

In the numerical analysis, Fresnel or Fraunhofer approximation can be used depending on the distance between the diffraction plane and observation plane. To numerically solve the scalar diffraction integrals, fast Fourier transform (FFT) can be applied to realize the discretized Fourier transform (DFT) efficiently. Besides explain the diffractive patterns using the scalar diffraction formulation, complex diffractive elements can be initially designed via the scalar diffraction algorithm based method, for example, inverse Fourier transform algorithm (IFTA), and the general steps to design a phase type DOEs based on IFTA is shown in figure 5.13[86, 87]. For demonstration purposes, figure 5.14 shows an example to initially design a phase type DOE to transform a plane wavefront into the target pattern (NTU logo) at Fraunhofer range, and the algorithm can be used for the design of real DOEs after the binarization of generated phase profile in future applications.

Figure 5. 13 Flow chart of the IFTA[87].

Figure 5. 14 Design of a phase type DOE to transform a plane wave into a target pattern. (a) Target pattern. (b) Designed phase distributions of the transmittance via IFTA. (c) Generated far-field diffractive pattern.

5.3.2 Shaping surface TH using a micro-sized two-photon-polymerized diffractive axicon

Because of the non-divergent characteristics of the Bessel beam, a diffractive axicon was fabricated to shape the surface THs, working as a focusing lens with a large non-divergent range. The fabricated diffractive axicon is shown in figure

5. 15 for the feasibility check. The designed period of the axicon was $10\text{ }\mu\text{m}$ with a fill factor of 0.5. The phase of the DOE is controlled by the thickness of the structure, and the thickness was $\sim 50\text{ }\mu\text{m}$ in our case.

Figure 5. 15 Two-photon-polymerized micro-sized diffractive axicon for shaping the surface TH. (a) Optical image. (b) SEM check viewed at 30 degree.

When the incident femtosecond laser is focused on the glass-air interface, strong THG can be observed. Figure 5.16 shows the spectrum of the THG from the glass-air interface with a center wavelength of 520.6 nm .

Figure 5. 16 THG spectra from the glass-air interface. The inset is the incident wavelength.

During the propagation of the TH wave, it diverged greatly. Figure 5.17 shows the TH pattern when the imaging objective was focused at the other glass-air interface.

Figure 5. 17 Divergent surface TH during propagation. (a) Initial TH at glass-air interface. (b) Divergent TH when it propagates to the other glass surface. (c) Horizontal profile in (b). The scale bars are 10 μm .

The divergent TH can be transformed into a Bessel-like beam with the diffractive axicon integrated at the surface of the glass substrate. The axicon

works as a focusing lens with a large non-divergent range. During the z scan of the imaging objective, the focal point with the highest intensity was observed, with a FWHM of $\sim 2 \mu\text{m}$, as shown in figure 5.18. When the imaging objective was moved far away from the axicon, a ring-like pattern in its far field was observed, and it is in the Fraunhofer diffraction range[87].

Figure 5. 18 Shaping the divergent surface TH with a diffractive axicon. (a) Highest intensity focused by the axicon. (b) Central horizontal profile of (a). (c) Far field diffractive pattern. (d) Central horizontal profile of (c). The scale bar is $10 \mu\text{m}$.

The diffractive axicon can transform the Gaussian beam into the Bessel-like beam with a longer non-divergent range during beam propagation[170]. Figure

5.19 shows the central horizontal profiles imaged at different positions. In the experiment, we defined the depth of focus as the range in which the diffractive pattern can maintain its peak intensity at least half of the highest intensity in the focal point. Within the depth of the focus (115 μm), a narrow and stable FWHM can be maintained. Based on the feasibility check, with the theoretical design and precise fabrication, the diffractive axicon can be integrated into real optofluidic chips for generating non-divergent light sources. The Bessel-like surface THs can be applied in light-sheet fluorescence microscopy, providing new coherent wavelength and removing the bulky illumination objective.

Figure 5. 19 Horizontal profile intensity map of the diffractive patterns at different imaging positions. Positive direction is moving away from the axicon (a) Normalized intensity map along the propagation direction. (b) Peak intensity of the diffractive pattern along the propagation. (c) FWHM of the diffractive pattern along the propagation.

5.4 Summary

To summarize, strong surface THG can be used as a coherent source to be integrated into on-chip applications. Coherent THs from two two-photon-polymerized cuboids were employed for the development of a micro interferometer which can be easily integrated to microfluidic devices for the real-time RI monitoring. The real-time monitoring of Ar gas pressure was

demonstrated in a micro-fluidic chamber with a high sensitivity of $0.22 (\mu\text{m})^{-1}$ $(\text{psi})^{-1}$. Optical harmonic generation arises from a tight focusing pumping beam, which diverges greatly along propagation. An axicon can transform the TH into a Bessel-like beam which can propagate a long distance without divergence. Bessel beam propagation was characterized by simulation of a refractive axicon using Zemax. Based on the characterization of Bessel beam, diffractive axicon was fabricated to shape the surface TH, which can be explained by scalar diffraction formulation. The fabricated diffractive axicon worked as a focusing lens with a large non-divergent range and Bessel-like TH pattern was observed through the axicon, thus the feasibility for future on-chip applications was demonstrated. Furthermore, background-free TH sources can be easily realized by removing the incident laser wavelength with band-control filters, and pure new generated wavelength can be applied in the on-chip systems.

Chapter 6 Fabrication of active optical components for integrated photonic chips

6.1 Preamble

As discussed in chapter 3, both passive and active (containing gain mediums) optical structures can be fabricated. In this chapter, both UCNPs and Rhodamine B doped micro-sized optical structures are discussed. Compared to passive structures without gain mediums, active structures with a gain medium can amplify the optical signals and be suited to remote excitation and collection, alleviating some limitations of passive ones. Upconversion luminescence (UCL) occurs in lanthanide-doped materials, and UCNPs can be used for enhancement of the nonlinear optical phenomena such as THG. Micro-sized ellipsoids containing NaYF₄:Yb,Er particles were sintered via 2D FSLDW system, which worked as WGM resonators to produce a high repetition rate pulsed green laser from near infrared excitation. Besides the active resonators were fabricated for providing laser sources, two-photon-polymerized Rhodamine B doped SU-8 waveguides were fabricated to deliver the light sources with a simple vertical pumping, which can be integrated into photonic chips in the future applications.

6.2 Fabrication of a high-repetition-rate pulsed upconversion micro-laser via 2D FsLDW

6.2.1 Optical observation system layout and sample fabrication

The experimental setup used for the observation of upconversion lasing from sintered micro spherical caps is presented in figure 6.1. A wavelength-tunable supercontinuum fiber mode-locked femtosecond laser (Toptica FemtoFiber pro SCIR, 980-2200 nm, 83 MHz) with a high average power of 170 mW and 100-fs short pulse duration at 1545 nm center wavelength is pumped at the edge of the sintered micro UCNPs ellipsoids. A half-wave plate (Thorlabs WPH10M-1550) and a quarter-wave plate (Thorlabs WPQ10E-1550) are employed to control the ellipticity of the incident laser's polarization state. An 800 nm long-pass filter (Thorlabs FELH0800) is placed in front of the focusing objective lens to remove any residual short wavelength light present in the excitation beam. The beam is focused to a small spot of 7.6 μm diameter (FWHM: full-width-half-maximum) on to the sample using a 40 $\times$ objective lens (Newport LI-40X) with a numerical aperture (NA) of 0.65. A 20 $\times$ objective lens (Olympus LUCPLFLN 20X) of 0.45 NA is used to collect the lasing signal at the micro UCNPs ellipsoids. The excitation wavelength is removed with a 750 nm short-pass filter (Thorlabs FES0750). A polarizer (Thorlabs LPVISE100-A) works as an analyzer to analyze

the lasing polarization directions and the collected light is directed to a broadband spectrometer (Andor Shamrock 193i) connected to a highly-sensitive electron-multiplying charge coupled device (EMCCD, Andor IXon Ultra) for the spectral analysis. A compact CMOS color camera (Thorlabs, DCC1645C) is used for capturing sample images and WGM patterns. The radio-frequency (RF) domain analysis of the upconversion lasing is realized by a photomultiplier tube (PMT) (Thorlabs PMT1001M) connected to a spectrum analyzer.

Figure 6. 1 Optical layout of observation system. The inset shows the pumping laser with a center wavelength of 1545 nm. Abbreviations: HWP: half-wave plate, QWP: quarter-wave plate, LPF: long-pass filter, SPF: short-pass filter, BS: beam splitter, M: mirror, F-OBJ: focusing objective, I-OBJ: imaging objective, PMT: photomultiplier tube, L: lens, CMOS: compact complementary metal oxide semiconductor camera, EMCCD: electron multiplying charge-coupled device.

To fabricate the micro-sized UCNP ellipsoids for the WGM resonators, a thin film of NaYF₄:Yb,Er was sintered at a high speed using the 2D FsLDW introduced in chapter 3. The average size of the ellipsoids can be controlled by either the laser power or the scanning speed, and the sintered micro ellipsoids in figure 6.2 (a) were fabricated using the laser power of 11 mW. figure 6.2 (b) shows the energy diagram of NaYF₄:Yb,Er UCNP. Upon excitation, the electrons in the ground state $^4I_{15/2}$ are first excited to $^4I_{13/2}$ state through ground state absorption, and then further pumped to $^4I_{9/2}$ through excited state absorption. The electrons on $^4I_{9/2}$ can either nonradiatively relax to $^4I_{11/2}$ or be pumped onto $^2H_{11/2}/^4S_{3/2}$, generating green $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions. The electrons on $^4I_{11/2}$ can be pumped to $^4F_{9/2}$ generating the red emission of $^4F_{9/2} \rightarrow ^4I_{15/2}$, or be excited to $^2H_{11/2}/^4S_{3/2}$, generating green emissions of $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$. In addition, the excited state energy of $^4I_{11/2}$ can be transferred to Yb³⁺ through the nonradiative process of $^2F_{7/2} + ^4I_{11/2} \rightarrow ^2F_{5/2} + ^4I_{15/2}$. The Yb³⁺ ions on $^2F_{5/2}$ can help to pump Er³⁺ on $^4I_{11/2}$ to higher excited state $^4F_{7/2}$ through back energy transfer from Yb³⁺ to Er³⁺. The electrons on $^4F_{7/2}$ level can relax to the $^2H_{11/2}/^4S_{3/2}$ level, which further contributes to the green emissions of $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$. Therefore, the green emission constitutes the main part of the upconversion spectrum. It should also be noted that the one-third of the central wavelength (TH) of the pump laser used also falls in this green emission region. This enables the resonance of the incident

NIR femtosecond laser (working as the fundamental pump light), its third harmonic (working as the seed light), and UCL (working as the secondary pump light) to enable the upconversion lasing process. Because of the smooth surface, when the input femtosecond laser is pumped at the edge of the UCNPs ellipsoid, WGM waves will be generated. As shown in figure 6.2 (c) and (d), the bright ring-shaped pattern was observed at the outer boundary, indicating the formation of WGM resonances. As shown in inset figure, the UCNPs film has upconversion luminescence at peaks of 543 nm and 665 nm, respectively. The combination of WGM resonance and upconversion luminescence contributes to generating lasing at the peak wavelength of 526 nm, as shown in figure 6.2 (e).

Figure 6. 2 Fabricated UCNP ellipsoids and observed WGM lasing. (a) Sintered micro ellipsoids. The inset shows the SEM check. (b) UCNP energy transfer and emission mechanisms. (c) Schematic illustration for induced WGM. (d) Observed WGM pattern. (e) Lasing spectrum at the fabricated UCNPs doped micro ellipsoid. The inset shows the spectrum of upconversion luminescence of the UCNP film.

6.2.2 Observation of upconversion lasing spectra

Different observation areas of the sample can be realized by controlling the slit size of EMCCD and the slit with a narrow width is used to check the WGM lasing spectrum at the edge of the UCNP ellipsoid. As illustrated in figure 6.3, an ellipsoid with a diameter of 10 μm was observed at its edge. Figure 6.3 (b) shows the lasing spectra from different slit widths (from 100 μm to 300 μm). When the slit width was 100 μm, the actual imaging area was 5 μm because of the 20X

imaging objective. With the increasing of slit width, the whole area of the structure can be captured and UCL emission peaks can be observed. When the slit width was from 100 μm to 300 μm , the UCL emission peaks at 548 nm and 661 nm were detected. Figure 6.3 (c) shows the profile of the upconversion lasing spectrum (534 nm) pumped by 5 nJ, observed from a narrow slit width (100 μm). It had a Gaussian shape with $R^2=0.9996$. Figure 6.3 (d) shows the RF domain analysis of the upconversion lasing. The laser had a pulse repetition rate of 83.3 MHz, which corresponds to 12 ns in time domain. The laser has the same repetition rate to the input femtosecond pulses and it is a high repetition rate pulsed upconversion laser source with a pulse-to-pulse time spacing of 12 ns.

Figure 6. 3 Observation of upconversion lasing with different slit widths. (a) Schematic illustration for observation of the upconversion lasing using the slit. (b) Upconversion lasing spectra observed through different slit widths. (c) Upconversion lasing spectrum with a

narrow slit width located at the edge of the WGM pattern. The inset is the Gauss fitting of the peak part. (d). RF emission pattern of UCNP lasing.

The input pumping energy dependent characteristics are shown in figure 6.4.

There was a slope change of the peak intensity when the pumping pulse energy was 1.86 nJ, which corresponds to the lasing threshold. The FWHM of the lasing bandwidth decreased with the increasing of the pumping energy, and it reached to the minimum of ~ 3 nm.

Figure 6. 4 The input pumping energy dependent characteristics of upconversion lasing. (a) Input pulse energy dependent upconversion lasing intensity. (b) Input pulse energy dependent upconversion lasing spectrum width.

Figure 6.5 shows the pumping position and input pulse energy dependence of upconversion laser at a UCNP ellipsoid with a diameter of $15.6 \mu\text{m}$. A larger slit width of $1000 \mu\text{m}$ was used to capture both the UCNP lasing and UCL emission. To check the pumping position dependence, the input femtosecond laser was pumped from the center to the edge of the ellipsoid, and a case of pumping at the background (pure UCNP film) was used for reference. The lasing

peak position had a shift when the pumping laser focused close to the edge of the ellipsoid, because of the WGM resonance. There were similar spectrum distributions when the input focused at either the ellipsoid's center or the pure UCNP film outside the ellipsoids. When pumped at the center and outside of the ellipsoid, besides of UCL emission peaks, only the THG emission was observed, with an emission peak at 515 nm. In comparison, when the input laser was focused at the edge of the ellipsoid, lasing peaks at 521 nm and 514 nm were observed. The peak wavelengths of UCL emission were kept constant (535 nm and 651 nm) when the input focused at different positions. When the ellipsoid is small and can be covered totally with the input spot, a stable spectrum can be obtained, independent of slit widths. The inset shows the stable lasing spectrum from a small ellipsoid with a diameter width of 5 μm , having a peak spectrum of 535 nm.

Figure 6. 5 Lasing and UCL at different pumping positions. (a) Normalized spectrum distributions when the input pumped at different positions of spherical caps and background (pure UCNP film). (b) Spectrum differences when pumped at the edge of the sample and

background. The inset shows the slit width independent upconversion lasing spectrum at an ellipsoid of 5 μm diameter.

Different input pulse energies were used to check the pumping energy dependence of upconversion lasing and UCL emission. Figure 6.6 illustrates the input pulse energy dependent lasing peaks and UCL peaks. The dependence of light output on pumping energy reflected the occurrence of radiation processes in the UCNPs doped micro ellipsoid resonator. For the peak wavelength of 521 nm and 514 nm, the slope suddenly changed at a threshold of ~ 0.8 nJ/pulse because of the stimulated emission. In contrast, the intensity of UCL was linearly dependent on the input energies and no lasing process happened.

Figure 6. 6 Input pulse energy dependent upconversion lasing and UCL. (a) and (b). Slope change check of input pulse energy dependent upconversion lasing. (c) and (d) Slope change check of input pulse energy dependent UCL. (e) Input pulse energy dependent whole spectra distributions.

6.2.3 Polarization direction check of femtosecond laser induced upconversion laser

The direction of the upconversion laser can be checked using the analyzer. As shown in figure 6.7 (a), the quarter-wave plate was removed from the optical layout shown in figure 6.1 and the linear polarization of the incident femtosecond laser can be changed by rotating the half-wave plate. The half-wave plate was rotated with a step size of 5 degrees while the analyzer was kept fixed, thus the light of different polarization directions passes through the analyzer had different intensities. Figure 6.7 (b) shows the input linear polarization dependent periodical pattern of the laser wavelength. The laser wavelength (526 nm) had an input linear polarization dependent polarization direction, only the polarization direction parallel to the transmission direction of the analyzer had the strongest intensity. As the lasing arises from the THG amplified by the UCNPs, the laser has the same polarization direction as the input femtosecond beam.

Figure 6. 7 Polarization direction of upconversion lasing dependent on the pumping laser polarization directions. (a) System schematic for checking the upconversion laser polarization directions by rotating the half-wave plate. (b) Linear polarization dependence of lasing wavelength. Abbreviations: HWP: half-wave plate, LPF: long-pass filter, SPF: short-pass filter, M: mirror, F-OBJ: focusing objective, I-OBJ: imaging objective, L: lens and EMCCD: electron multiplying charge-coupled device.

In contrast, the polarization direction of UCL (545 nm and 658 nm) has no dependence on the polarization direction of the pumping femtosecond laser, as shown in figure 6.8.

Figure 6. 8 Polarization direction check of UCNP lasing and UCL. (a) Emission spectrum intensity distributions with different linear polarizations of pumping laser. (b) Polar plot of the lasing wavelength and UCL wavelength with different input linear polarization states. The intensity of UCL is magnified by a factor of 3.

6.2.4 Input polarization ellipticities dependent upconversion laser

To check the upconversion laser intensity under different polarization ellipticities of the pumping beam, the analyzer was removed from the optical layout shown in figure 6.1. The ellipticity of the input polarization state was controlled by rotating the quarter-wave plate while keeping the half-wave plate fixed, as shown in figure 6.9 (a). In the experiment, the quarter-wave plate was rotated with a step size of 5 degrees from the initial position, which was set as 0 degree such that the fast axis of the quarter-wave plate was parallel to the fast axis of the half-wave plate. Figure 6.9 (b) shows the laser wavelength (520 nm) distribution pattern. The laser intensity decreased to the minimum when the rotation angle was either 45 degree or 135 degree, where the incident laser beam was circularly polarized. The laser intensity was at the maximum when the incident laser was linearly polarized that the rotation angle of QWP was 0, 90 or 180 degrees.

Figure 6. 9 Upconversion laser intensity dependence on different input polarization ellipticities. (a) System schematics for measuring upconversion laser with different

excitation ellipticities. (b) Polarization ellipticities dependence of lasing wavelength. Abbreviations: HWP: half-wave plate, QWP: quarter-wave plate, LPF: long-pass filter, SPF: short-pass filter, M: mirror, F-OBJ: focusing objective, I-OBJ: imaging objective, L: lens and EMCCD: electron multiplying charge-coupled device.

Figure 6.10 (a) shows the spectrum distributions with different pumping polarization ellipticities. Compared to upconversion lasing, there was no periodical pattern for the UCL, as shown in figure 6.10 (b). Because of the isotropic characteristics of the UCNP ellipsoids, the nonlinear polarization components for THG vanishes for a circularly polarized light, hence no THG can be amplified by the UCNPs and no WGM laser can be observed.

Figure 6. 10 Ellipticity dependence check of UCNP lasing and UCL. (a) Emission spectrum intensity distributions with different polarization ellipticities of the incident beam. (b) Polar plot of the lasing wavelength and UCL wavelength with different input polarization ellipticities. The UCL intensity is magnified by a factor of 3.

Based on the characterization of upconversion lasing, the injection-seeded high-repetition-rate, ultrashort-pulse upconversion micro-laser created from a UCNP micro-ellipsoidal cavity fabricated using femtosecond direct laser writing was demonstrated. This study can make a significant contribution to microfluidic

and microelectronic devices, nanophotonics, and optical sciences because it provides a novel method for generating high-repetition-rate, upconversion micro-laser using a simple and fast fabrication method.

6.3 Amplification of guided wave via two-photon-polymerized Rhodamine B doped waveguide

The active waveguide contains a gain medium can be used for delivering the small volumetric light sources to small targets, suited to remote excitation and collection, and some limitations of the passive ones can be alleviated. For the materials used for TPP, the Rhodamine B was first dissolved in SU-8 developer (10 mM dye concentration) and subsequently mixed with SU-8 in the liquid form at a ratio of 10% (developer + Rhodamine B) to 90% (SU-8). Figure 6.11 shows the real image of Rhodamine B doped SU-8 for fabrication of waveguides and spectrum characteristics of Rhodamine B used for the experiment.

Figure 6. 11 Rhodamine B doped SU-8 for fabrication and its emission spectrum. (a) Real image of Rhodamine B doped SU-8. (b) Absorption and emission characteristics of Rhodamine B. (c). Normalized emission profiles with different excitation wavelengths.

With the 3D TPA FsLDW system shown in chapter 3, different dimensional Rhodamine B doped waveguides can be fabricated. As shown in figure 6.12, for demonstration purposes, splitter Rhodamine B doped waveguides (average width: 10 μm) were fabricated with a scanning speed of 20 $\mu\text{m/s}$ and the average power of 10 mW. The thickness can be controlled by the number of scanning layers and the layer interval and it was $\sim 45 \mu\text{m}$ in the fabricated structure.

Figure 6. 12 Fabricated Rhodamine B doped splitter waveguides. (a) Optical image of the waveguides (before development). (b) Optical image of the waveguides (after development). (c) SEM check of waveguides viewed at 0 degree. (d) SEM check of the waveguides viewed at 30 degree.

To check the function of amplifying the optical signals using the two-photon-polymerized Rhodamine B doped SU-8 waveguides, the waveguides with

different dimensions were fabricated and a defocused continuous wave (CW) laser (532 nm) was used to pump the structures. As shown in figure 6.13 (a), the width of the waveguides was 10 μm and the lengths were 40, 60 and 80 μm , respectively. The number of scanning layers was 5 thus the waveguides had a thickness of ~ 15 μm . A simple vertical pumping of the polymerized waveguides is shown in figure 6.13 (b) and the defocused beam (3.15 mW) was used to cover the whole waveguides simultaneously. A bandpass filter (600-40 nm) was used to remove the incident laser wavelength. As shown in figure 6.13 (c), the guided wave intensity was stronger at the end of the waveguide than the center area because of Fabry-Perot resonance. Guided wave spectrum at the end of each waveguide is shown in figure 6.13 (d). The 60 μm waveguide was at the center of the defocused beam, so it had strongest signal. Figure 6.13 (e) illustrates the optical observation system of the experiment.

Figure 6. 13 Checking of the optical signal amplification of the Rhodamine B doped waveguides. (a) Fabricated different dimensional waveguides. (b) Pumping the waveguides with defocused incident laser (without bandpass filter). (c) Patterns of removing the incident laser wavelength with a bandpass filter. (d) Spectrum of the guided wave. (e) Optical layout of the imaging system. Abbreviations: CW: continuous wave, ND: neural density, M: mirror, OBJ: objective, L: lens and EMCCD: electron multiplying charge-coupled device.

Figure 6.14 shows the dependence of the emission of the Rhodamine B doped structures on the pumping power. A square (side length: 10 μm , height: $\sim 15 \mu\text{m}$) instead of the waveguide was used for checking to remove the asymmetry geometry effects on the emission. The focused laser was pumped at the center of the Rhodamine B doped structure. When the pumping power reached the threshold, 3.5 mW, there was a slope change, where the amplified spontaneous emission (ASE) happened. When the pumping power is above the threshold of the ASE, the emission spectra will have a blueshift[171], as shown

in figure 6.14 (b). Compared to lasing, ASE has a lower temporal coherence and a reduced speckle noise. However, its higher spatial coherence can be used for tight focusing of the radiation.

Figure 6. 14 Power dependence check of the Rhodamine B doped structure emission. (a) Dependence of the peak intensity on the pumping power. (b) Emission spectra profile with different pumping powers.

As shown in figure 6. 15, the spatial patterns of the guided wave through the Rhodamine B doped waveguide was checked. The waveguide had a width of 10 μm and a length of 40 μm . Five layers were scanned during fabrication to make the waveguide have a thickness of $\sim 15 \mu\text{m}$. To check the wave propagation characteristics, one horizontal profile at the pumping point and the other horizontal profile at the end of guided wave were checked. The propagated wave maintained its mode at the end of the waveguide, as shown in figure 6.15 (c), and the profile of the propagated wave had a FWHM of 8.45 μm . Based on the feasibility exploration, the two-photon-polymerized Rhodamine B doped

waveguide can amplify and guide the optical signals for integrated photonic applications.

Figure 6. 15 Spatial patterns of guided wave with Rhodamine B doped waveguides. (a) Microscopic image of guided wave. (b) Profiles of the wave at the pumped position and the propagated wave at the end. (c) Shape check of the propagated wave.

6.4 Summary

To summarize, both UCNPs and Rhodamine B doped micro-sized optical structures were fabricated for the purpose of generating laser source and delivering waves. The active structures with a gain medium can amplify the optical signals and be suited to remote excitation and collection, alleviating some limitations of passive ones. We have realized the high repetition rate pulsed upconversion lasers from the micro-sized UCNPs doped ellipsoids. The smooth surface of the ellipsoids can work as WGM resonators and the amplified THG by UCNPs resonates inside them can generate laser, with a narrow bandwidth of ~ 3 nm and a pulse-to-pulse time spacing of 12 ns (83.3 MHz in RF domain). The upconversion laser was linearly polarized and its polarization direction was

parallel to the input polarization direction. Because of the isotropic characteristics of the UCNPs doped ellipsoids, its strongest THG induced upconversion lasing comes from linearly polarized pumping. To deliver and amplify optical signals for on-chip photonic applications, Rhodamine B doped waveguides were fabricated via TPP. Based on the feasibility exploration of the dye doped waveguide, which can be flexibly integrated into optofluidic systems with simple vertical remote excitation, the guided wave maintaining its mode can be observed. Our scheme for realizing high repetition rate pulsed upconversion laser sources and dye doped waveguide opens a new window for applications from on-chip information processing to high-throughput sensing, which can be integrated into optofluidic micro systems in the future applications.

Chapter 7 Conclusions and recommendations for future work

7.1 Discussion and conclusions

In the past few years, the state-of-the-art additive manufacturing via FsLDW has become a powerful tool for flexible microfabrication of 3D optical structures, which can be integrated into optofluidic chips easily. It is promising to generate new optical sources of small volume and deliver them to small targets. In this research, novel optical sources from nonlinear-optics-based active optical structures via additive manufacturing are demonstrated, which opens up a new avenue for on-chip optofluidic sources.

There are three representative advantages in our nonlinear-optics-based active optical structures over traditional ones. Firstly, the active optical structures containing a gain medium works well for the external photon excitation and efficient collection of the emission signals; this lowers the system complexity, optical delivery loss, and integration cost. Secondly, highly tunable small volumetric light sources can be realized in terms of beam size, output intensity, polarization, spectral position and distribution. Flexible patterned diffracted surface optical harmonics and upconversion lasing can work as coherent light sources for micro sensing and detection applications. Finally, the need for in-

coupling and out-coupling of the lights from or to the integrated photonic devices and relevant alignment issues can be alleviated with additively manufactured active fluorescent waveguides.

Three major contributions drawn from the thesis are highlighted as follows.

1. TPA and micro-sintering based FsLDW systems are set up for additive manufacturing of micro-sized optical structures. Dependent on the target structures to be fabricated, the 3D FsLDW system is used for precise fabrication of 3D complex structures while the 2D FsLDW system is for fast manufacturing of 2D planar structures and micro resonators with a high-speed laser spot scanning. Based on the parametric study, both 3D pristine and Rhodamine B doped SU-8 structures are successfully fabricated with the optimized scanning speed and femtosecond laser power. In terms of 2D FsLDW system, it is successfully used to realize TPP of SU-8 planar waveguides and micro-sintering of active WGM resonators with UCNPs as gain mediums at a high-speed.
2. Coherent nonlinear optical sources of small volume based on surface THG from two-photon-polymerized structures are realized for high precision on-chip measurement and sensing. We have thoroughly characterized THs from two-photon-polymerized SU-8 structures with different incident powers,

input polarization states, and excitation positions. The highest conversion efficiency comes from SU-8-air surface via linearly polarized pumping and the intensities of generated THs have no dependence on the linear polarization direction of the pumping beam. Coherent THG from two two-photon-polymerized cuboids is employed for the development of a micro interferometer, which is successfully used for real-time on-chip monitoring of Ar gas pressure. The two-photon-polymerized diffractive axicon can work as a focusing lens with a large non-divergent range to shape the divergent Gaussian TH into a Bessel-like beam. The small volumetric background-free TH sources from band-control filters can be easily integrated into microfluidic devices for on-chip photonic applications.

3. Active optical structures contain UCNPs and Rhodamine B gain mediums are successfully fabricated for optofluidic sources and waveguides, respectively. We have achieved upconversion lasing at a high repetition rate from micro-sized UCNP doped ellipsoids, which can be fabricated using the 2D FsLDW at a high speed. The smooth surface of the ellipsoids can work as WGM resonators and when intense, near-infrared femtosecond laser pulses are focused on to this WGM resonator, the input pulses generate optical TH which works as the seed light; at the same time, they also work as the pump light for the upconversion processes. As a result, the weak TH

seed pulses are coherently amplified in the WGM resonator. In our study, different input ellipticities are checked and the upconversion lasing has the maximum intensity with linearly polarized input pulses. When pumped with linearly polarized input, its polarization direction is parallel to the input polarization direction. The generated pulsed upconversion laser has a pulse-to-pulse spacing of 12 ns which provides potential new sources for optofluidic chips. Rhodamine B doped waveguides are fabricated through 3D FsLDW system, which can be used for coupling and delivering the light sources in the future applications.

7.2 Recommendations for future work

In current study, the FsLDW systems are developed and nonlinear-optics-based active optical functional structures are successfully fabricated to generate small volumetric coherent sources, which are suitable to be integrated into optofluidic chips. Herein, I would like to summarize some recommendations for future work to extend and supplement the current research.

1. Further increasing the THG efficiency from two-photon-polymerized structures fabricated via AM. Surface THs with flexible patterns can be realized by flexible patterned 3D polymer structures, which can be easily additively manufactured using the FsLDW system. However, strong

pumping intensity causes damage of the structure because of the damage threshold, which limits the intensity of the generated THs from polymer structures. Coating the polymerized structures with nano particles is possible to provide solutions for high THG signals from polymer structures. Thus, 3D two-photon-polymerized structures with complex shapes coated with nano particles can be used for providing strong THs for on-chip sources in future applications.

2. Coupling and delivering the coherent surface harmonics or upconversion laser source via waveguides fabricated by a combination of AM and traditional planar processing methods. On-chip light sources and two-photon-polymerized waveguides are successfully fabricated and demonstrated separately. However, for real complex optofluidic applications, the generated sources should be coupled and delivered into the target positions. Varieties of materials and manufacturing methods will be utilized together to realize the on-chip photonic circuits. With traditional planar processing methods, large-area waveguides can be fabricated efficiently, on which the micro-sized structures for light sources and guiding waves will be flexibly patterned with FsLDW. Thus, the combined manufacturing methods to realize coupling and delivering nonlinear-optics-based sources can be worked as novel sources for optofluidic applications.

3. Design and fabricating the diffractive optical element to be integrated onto nonlinear optical mediums such as sapphire for real applications. Two-photon-polymerized diffractive axicon has been demonstrated to work as a focusing lens with a large non-divergent range to transform the divergent TH with Gaussian profile into a Bessel-like pattern. In the future work, the relationship between the structure parameters (dimension and material) and the target diffractive pattern will be quantitatively analyzed. Dependent on the sizes of the structures, scale diffraction algorithm or vectorial algorithms (finite element method, finite difference time domain method, etc.) will be utilized to design diffractive optical elements. The purpose of our two-photon-polymerized DOE is for shaping optical harmonics, and in real applications, a nonlinear optical medium will be used for efficient harmonic generation. Thus, using the two-photo-polymerized DOEs integrated on the nonlinear optical medium such as sapphire, diffractive patterns with new wavelengths can be used for on-chip sensing and illumination.
4. Development of optofluidic chips using the fabricated integrated photonic circuit for analysis of biological and chemical samples. Optofluidics has long been used to analyze biological and chemical samples since they are invented. In our study, fabricated nonlinear-optics-based active optical structures are designed for future optofluidic applications. With our developed on-chip

micro interferometer, the application of monitoring the refractive index and pressure changes of Ar gas has already been realized. However, the analysis of biological and chemical characteristics of a certain sample is more promising and necessary. In the future, complex optofluidic systems will be fabricated for sensing the particles such as cells and chemical characterization of fluids.

List of Publications

Journal papers

1. **Jiao, Jiannan**, Yi Gao, Shufan Li, Nguyen Duy Anh, Pei-Chen Su, Seung-Woo Kim, CS Suchand Sandeep, and Young-Jin Kim. "Surface third-harmonic generation at a two-photon-polymerized micro-interferometer for real-time on-chip refractive index monitoring." *Optics express* 27, no. 20 (2019): 29196-29206.
2. **Jiao, Jiannan**, Donglei Zhou, Shufan Li, Mun Ji Low, Yi Gao, Jianing An, Pei-Chen Su, Seung-Woo Kim, Seungchul Kim, Kyujung Kim, CS Suchand Sandeep, and Young-Jin Kim. "Injection-seeded high-repetition-rate short-pulse micro-laser based on upconversion nanoparticles." (In peer review)
3. Gao, Yi, Hyub Lee, Wen Xu, **Jiannan Jiao**, Peng Chen, Dong-Hwan Kim, and Young-Jin Kim. "Coherent power amplification of third-order harmonic femtosecond pulses at thin-film up-conversion nanoparticles." *Scientific reports* 9, no. 1 (2019): 1-9.
4. Gao, Yi, Hyub Lee, **Jiannan Jiao**, Byung Jae Chun, Seungchul Kim, Dong-Hwan Kim, and Young-Jin Kim. "Surface third and fifth harmonic

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Conference papers

1. **Jiao, Jiannan**, Yi Gao, and Young-Jin Kim "Surface profile measurement of 3D-printed transparent objects using nonlinear optics." 3rd International Conference on Progress in Additive Manufacturing (Pro-AM), (2018).
2. **Jiao, Jiannan**, Byung Jae Chun, Yi Gao, and Young-Jin Kim. "Third harmonic generation at sapphire wafers with different cut axis." In 2017 Conference on Lasers and Electro-Optics Pacific Rim (CLEO-PR), pp. 1-3. IEEE, 2017.
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