Laser additive manufacturing using nanofabrication by integrated two-photon polymerization and multiphoton ablation

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9.1 Introduction

9.1.1 Brief review of laser direct writing for micro/nanofabrication

Methods of micro-/nanofabrication of three-dimensional (3D) structures are of increasing interest because of their importance for the creation of compact 3D devices and their assembly into functional 3D systems. Recent years have witnessed a phenomenal increase in 3D micro-/nanofabrication techniques from diversified fields, such as microelectromechanical systems (MEMS)/nanoelectromechanical systems (NEMS), nanoelectronics, micro-/nanophotonics, biomedical engineering, bio-inspired architectures, and micro-/nanofluidics, with the aim of developing neoconceptual and high-value-added products [1–8]. Most current 3D micro-/nanofabrication techniques are based on traditional two-dimensional (2D) fabrication techniques such as photolithography, using layer-by-layer strategies [1–8]. However, such 3D micro-/nanofabrication techniques provide only limited 3D micro-/nanofabrication capabilities [1–8]. Broad applications of such 3D micro-/nanofabrication are limited because of expensive facilities, a time-consuming layer-by-layer strategy, high cost, low throughput, and the inability to fabricate 3D micro-/nanostructures of arbitrary geometry and increased complexity [1–8]. Some applications would be extremely challenging using conventional micro-/nanofabrication techniques, such as the controlled introduction of defects into 3D photonic crystals to achieve required functionality, fabricating 3D movable components in MEMS/NEMS devices, and constructing micro-/nanofluidic devices [1–8]. Therefore, a 3D micro-/nanofabrication technique that is capable of fabricating 3D micro-/nanostructures of arbitrary geometry at a nanometric resolution using a cost-effective process is highly desirable.
Femtosecond laser direct writing (FsLDW) is a precise, laser-based 3D micro-/nanofabrication method and has been recently recognized as a promising candidate to address existing challenges [9–14]. In FsLDW, a tightly focused laser beam penetrates a bulky material without obvious loss of absorptive energy; it scans according to a designed pattern from the bottom slice to the upside slice or vice versa until the entire 3D structure is fabricated [14]. Because of the extremely high transient power density, photons are absorbed in a nonlinear manner at the focal point in a volume much smaller than the cubic wavelength, $\lambda^3$, achieving high spatial resolution beyond the optical diffraction limit [14]. Therefore, FsLDW can be simply understood as a laser direct writing technique that involves nothing more than converting a 3D digital design into a target material. FsLDW also distinguishes itself from other micro-/nanofabrication methods as a universal tool applicable to diversified materials, including organic materials, biomaterials, dielectrics, metals, and semiconductors, only if a proper photon-material strategy is determined [14]. Compared with conventional 3D nanofabrication techniques, FsLDW demonstrates several advantages, including (1) single-step, noncontact, and mask-free direct 3D fabrication; (2) capability to fabricate arbitrary geometries and irregular structures; (3) capability to fabricate movable components; (4) realization of real 3D nanofabrication; (5) capability to work on a broad range of materials such as polymers, ceramics, metals, and hybrid materials; and (6) easy fabrication of voids, channels, and holes inside a bulk material [14].

This chapter introduces our research efforts in 3D micro-/nanofabrication based on FsLDW. Two different 3D micro-/nanofabrication strategies are demonstrated, including the additive 3D micro-/nanofabrication by two-photon polymerization (TPP) and the subtractive 3D micro-/nanofabrication by multiphoton ablation (MPA). The advantages and disadvantages for both fabrication techniques are shown and analyzed. Finally, a comprehensive 3D micro-/nanofabrication method by seamless integration of the additive TPP and subtractive MPA is demonstrated. The established comprehensive 3D fabrication method not only inherits the merits of both TPP and MPA in achieving ultrahigh writing resolution beyond the diffraction limit and features of sharp and clean edges, but it also offers the possibility to produce novel device structures that are difficult to be fabricated by either TPP or MPA alone.

9.1.2 Linear and nonlinear optical absorption in laser direct writing

In TPP an intensity laser threshold exists below which no polymerization occurs. In the specific case of resins that polymerize through a radical mechanism, the presence of this threshold is a direct consequence of the chemical nature of the resins’ components. The growth of macromolecular chains within the resin depends greatly on the delicate ratios of the rate constants among several processes that occur at the same time: initiation, propagation, recombination, and termination. If radicals are not continuously
generated during the initial stages of the polymerization reaction, no chains will be formed. In polymerization induced by light absorption, this mechanism results in the presence of an intensity threshold.

In the first approximation, the accumulated exposure dose $D$ of a single voxel induced for an $N$-photon-absorption process can be described as:

$$D \propto (P - P_{\text{th}})^N t,$$

where $P$ is the laser average power, $P_{\text{th}}$ is the laser threshold power, and $t$ is the exposure time [15].

According to this model, in one-photon polymerization ($N = 1$) the exposure dose is linearly proportional to the laser average power. In TPP ($N = 2$) the exposure dose becomes proportional to the square of the average laser power. To take advantage of this model from an experimental point of view, a series of voxels are fabricated using different values of both laser average powers and exposure times. Among these voxels there will be some with identical widths that are created with different combinations of laser average powers and exposure times. Assuming that identical voxels are fabricated when the same exposure dose is used, a log–log plot of exposure times and laser average powers used to create identical feature sizes can reveal the value of $N$ in Eq. (9.1). Hence, careful dosimetry experiments such as the ones described in the previous section not only produce useful information regarding writing conditions to use when performing high resolution TPP; they can also offer insightful evidence on the nature of the light absorption process that starts polymerization.

### 9.1.3 Challenges and opportunities

All of the grand goals for nanoscience are dependent upon reliable ways to fabricate nanostructures. Methods that use a laser direct writing process to achieve these goals show promising results in the fabrication of various nanomaterials and micro-/nanostructures of various dimensions, which are challenging to fabricate via conventional fabrication methods. Although TPP is almost ready to be implemented in a complimentary fashion with other more conventional microfabrication methods for industrial production, there are still three challenges that need to be addressed. The first is scalability. Being a serial process, TPP can produce only one object at a time slowing manufacturing progress and increasing its cost. The second challenge is the limited range of nonlinear photosensitive resins available for TPP, which seriously limits the functionality of the as-fabricated 3D micro-/nanostructures. The third challenge is the lack of comprehensive femtosecond laser 3D micro-/nanofabrication techniques combining both subtractive and additive fabrication capabilities. It is then imperative to focus future research activities to solve these three challenges in order to fully unleash the potential of 3D laser micro-/nanofabrication for various industrial applications such as MEMS/NEMS, 3D electronics, integrated optics, lab-on-a-chip, biomimetics, and metamaterials.
9.2 Additive nanofabrication using two-photon polymerization

9.2.1 Characterization of two-photon polymerization

TPP is one of the additive FsLDW techniques making use of photosensitive resins in 3D micro-/nanofabrication. Compared with other micro-/nanofabrication approaches, additive TPP offers both high resolution and relatively high throughput. TPP lithography is a typical nonlinear optical effect that, in general, requires a femtosecond laser to provide short pulses with photon energy well below the one-photon absorption edge of a photoresist. The photoresist polymerizes if the light intensity is high enough for two-photon absorption inside the material, which is in the focal volume of a microscope objective. This process causes a chemical and/or physical change of the photoresist within a small-volume pixel ("voxel"). This voxel typically is of ellipsoidal shape and is the basic building block in the 3D fabrication process. By moving the sample relative to the fixed focal position, arbitrary paths can be written into the photoresist. It can be simply described as using a laser beam to inscribe 3D nanostructures. Because of the threshold behavior and nonlinear nature of the process, a resolution far beyond the diffraction limit can be realized by controlling the laser power and scanning speed. As a result, the technique provides much better structural resolution and quality than conventional stereolithography.

9.2.1.1 Characterization of voxel dimensions

The "voxel" of a polymer is the basic building block of TPP. To obtain the highest fidelity of fabrication when writing a complex 3D microstructure by TPP, it is of uttermost importance to characterize the voxel’s lateral and axial dimensions. One experimental technique used to retrieve this information is the so-called ascending method. Separate voxels are fabricated on the substrate’s surface, keeping all writing conditions the same but positioning the laser focal volume in reference to the substrate—resin interface. Because a polymerized voxel will have a defined length, some of the voxels will be fully anchored to the substrate, whereas others will lay sideways because of their weak adhesion to the substrate. By imaging these latter voxels using scanning emission microscopy (SEM), it is possible to measure both their length and diameter. Although this method has the advantage of reveling in one image both dimensions of a voxel, it has the drawback of not giving a direct measure of the voxel size when performing TPP. In almost all cases, TPP occurs by moving either the sample around a fixed laser beam or the laser beam within a fixed resin. In both cases the microstructure is fabricated with a continuous overlap of voxels. Hence a more direct way to get information on the feature size used in TPP is to fabricate lines suspended from the substrate by means of tall supports. These lines, generated by a single laser passes, can reveal both the width and length of the polymerized feature size when imaged by SEM at different angles. An example of such a study is shown in Fig. 9.1.
9.2.1.2 Raman spectroscopy of TPP

Although TPP has become an enabling technology for several applications, there are still some fundamental aspects that have not yet been fully characterized. One of these is the influence of the scanning pattern on the mechanical properties of the microstructures. Even if the same object can be realized using different writing strategies, some approaches are better than others in producing accurate and dimensionally robust microstructures. Another aspect of TPP that requires a better understanding is the influence of the developing process on polymer swelling and solvent inclusion, which might have a large impact on the structural integrity of the microstructures. To answer these and other questions, an analytical technique capable of investigating the materials used in TPP at the molecular level is required before and after laser processing. Raman spectroscopy is a formidable tool for the characterization of microstructures fabricated by TPP. It allows for in situ and nondestructive monitoring of specific molecular bond vibrations with high spectral resolution and minimal sample preparation [16].

Raman spectroscopy provides comprehensive information about the vibrational modes of molecules using light scattering. The Raman-scattered light from the molecules in the probed sample is shifted in the frequency domain relative to the excitation light center frequency, and it contains information about the vibrational frequencies and anisotropy of molecular vibrations. Vibrational modes are like fingerprints of molecules. Therefore, Raman scattering is endowed with the sensitivity to discern different molecular species. Raman spectroscopy has broad applications, ranging from fundamental physical chemistry, inorganic chemistry, biochemistry, art, and archaeology to highly practical forensic examinations.
Most TPP has been performed using acrylic-based resins that are composed mainly of two molecular components: a photoinitiator and a mixture of monomers/oligomers [17]. The first one is the molecule capable of undergoing excitation by two-photon absorption and of generating active species (radicals) that start the polymerization process. In the presence of excited photoinitiators, the monomer/oligomer mixture forms a complex linked network — a polymer. Monomers and oligomers are present in the resin in much larger numbers than photoinitiators. Radicals generated during laser irradiation react with the monomer/oligomer mixture to form high-molecular-weight materials through a chain growth mechanism. Several reactions with different rates for initiation, propagation, chain transfer, and termination occur at the same time. In chain polymerization monomers and oligomers react only with the propagating reactive center, not with other monomers and oligomers, and chain addition ceases when the active species are depleted by a number of termination reactions. The molecular weight of chain polymers increases rapidly during polymerization and monomer/oligomer-to-polymer conversion (degree of conversion) can widely range between 20% and 90%, depending on the chemical nature of the monomers and oligomers. In acrylic monomers and oligomers, chain addition takes place in the carbon–carbon double bonds (C==C) present in molecules’ ester moiety. Thus, during TPP, the number of C==C bonds diminishes in favor to the formation of new intermolecular carbon–carbon single bonds (C–C).

The Raman spectra of a typical resin used in TPP before and after polymerization are shown in Fig. 9.2. Two distinctive peaks are observed at 1635 and 1723 cm⁻¹, which

![Figure 9.2](image-url) Raman spectra of a typical acrylic-based resin used in two-photon polymerization (TPP) before and after polymerization. The inset shows a scanning electron micrograph of a solid cube created by TPP and used to perform Raman spectroscopy (scale bar: 5 mm) [16]. a.u., arbitrary units.
are ascribed to the vibrational modes of C–C and the carbonyl (C=O) groups of the monomer, respectively. As a consequence of the diminished concentration of the C–C bonds following polymerization, the intensity of the peak at 1635 cm\(^{-1}\) in the polymerized resin is smaller than in the unpolymerized resin. On the other hand, the intensity of peak at 1723 cm\(^{-1}\) remains the same before and after polymerization because the carbonyl group does not participate in the chain reaction. The area of a peak in a Raman spectrum is proportional to the concentration of the oscillators responsible for that particular Raman active mode. Thus, spectra such as the ones in Fig. 9.2 can be used to measure the degree of conversion (DC) in resins following TPP. DC represents the number of C–C bonds consumed during polymerization and is a major factor influencing the mechanical properties of the ultimate microstructure; the higher the DC, the stronger the polymer. Since the number of carbonyl groups in the resin remains the same before and after polymerization, the peak at 1723 cm\(^{-1}\) can be used as internal reference for DC estimation. The percentage of DC is obtained using Eq. (9.2):

\[
DC = \left[1 - \frac{A_{C=C}/A_{C=O}}{A'_{C=C}/A'_{C=O}}\right]
\]  

(9.2)

where \(A_{C=C}\) and \(A_{C=O}\) are the integrated intensities of the 1635 and 1720 cm\(^{-1}\) peaks in the polymerized resin, respectively, whereas \(A'_{C=C}\) and \(A'_{C=O}\) are the integrated intensities of the same peaks in the unpolymerized resin.

A series of microcubes were fabricated first and then characterized using a confocal Raman microspectrometer. An SEM image of a microstructure used in the study is shown in the inset of Fig. 9.2. The microcubes were fabricated using several laser average powers and writing speeds. For each microstructure, Raman spectra like the ones in Fig. 9.2 were recorded and then used to measure DCs with Eq. (9.2). The results are shown in Fig. 9.3. At constant writing speeds, DC values monotonically increase with increasing average laser power. The highest DC value is around 43%; larger DCs are not attainable because the resin starts to boil if higher average laser powers were used. During TPP, highly cross-linked macromolecules are formed that can severely limit molecular mobility. The probability that an unreacted C–C bond will encounter a radical is dramatically reduced with the evolving polymerization, and a complete conversion (DC = 100%) is not achieved.

### 9.2.2 Additive nanofabrication of 3D micro-/nanostructures

Fig. 9.4 shows a schematic and a photo of a typical 3D lithography system (Photonic Professional; Nanoscribe GmbH), which mainly consists of a femtosecond laser, a piezoelectric 3D scanning stage for fast writing of small-area structures, and a motor-driven linear positioning system. The laser is a compact femtosecond-fiber laser (T-Light II; Menlo Systems) with 65-mW average power, 780-nm center wavelength, a pulse duration <120 fs, and a repetition rate of 100 MHz. The piezo positioning system, with x-y-z axes, provides a maximum travel distance of 300 µm in each direction. The Zeiss optical microscope equipped with a charge-coupled device camera enables real-time process monitoring. The whole system is installed on a
vibrational isolation table from Thorlabs Inc. Table 9.1 summarizes the specifications of the 3D lithography system.

TPP micro-/nanofabrication generally requires three steps. First, a glass substrate is coated with a layer of photoresist and loaded into the lithography system. The second step is structure programming using a specialized GWL. Alternatively, the structure data can be also imported from a computer-assisted design or a stereolithography file. The 3D lithography system visualizes the loaded structure data and automatically approaches the designated samples and adjusts the focus to the interface. Third, the 3D lithography system conducts the TPP process by tightly focusing the laser beam inside the photoresist and making a 3D scan according to the geometry design. After the TPP lithography, the samples are developed and processed for further experiments.

In addition to the calibration of voxel dimensions with different laser powers and scanning speeds, laser scanning modes should be optimized. Practical applications of micro optical devices, such as microlenses, generally require high-quality surface profile and sufficient smoothness. Therefore it is important to optimize the TPP process for the fabrication of 3D micro-/nanostructures with sufficient surface smoothness. In the TPP process, we found that conventional parallel linear scanning mode hardly achieves a high-quality surface. In fact, during parallel linear scanning the width of the fabricated line not only deforms the circle dimension but also causes protrusions at the edges of the lens surface, as shown in Fig. 9.5(a)—(c). To obtain a smooth microlens with better optical performance by TPP lithography, an annular scanning mode coordinated with continuous variable scanning steps was adopted. Using this new scanning method, a spherical microlens with a high surface quality was readily produced in a shorter processing time (see Fig. 9.5(d)).

Figs. 9.6 and 9.7 show a variety of 3D photonic crystal structures fabricated using the additive TPP technique, including woodpile and spiral photonic crystal structures.

Figure 9.3 Polymeric degree of conversion of microstructures fabricated by two-photon polymerization using Raman spectroscopy [16].
Figure 9.4 (a) Schematic of the two-photon polymerization three-dimensional (3D) lithography system (Nanoscribe GmbH). (b) Photo of the Photonic Professional 3D lithography system installed in the Laser-Assisted Engineering Lab.

### Table 9.1 Specifications of the 3D lithography system

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
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<tbody>
<tr>
<td>Lateral feature size</td>
<td>150 nm</td>
</tr>
<tr>
<td>Maximum writing speed</td>
<td>2 mm/s</td>
</tr>
<tr>
<td>Positioning accuracy</td>
<td>&lt;5 nm</td>
</tr>
<tr>
<td>Positioning repeatability</td>
<td>2 nm</td>
</tr>
<tr>
<td>Piezo range</td>
<td>300 × 300 × 30 0 μm</td>
</tr>
<tr>
<td>Maximum laser power</td>
<td>100 mW</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>780 nm</td>
</tr>
<tr>
<td>Working distance</td>
<td>160 μm to 4 mm</td>
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</tbody>
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with a spatial resolution around 150 nm. Compared with 2D photonic crystals, 3D photonic crystals provide the ability to manipulate light regardless of the polarization direction because of their omnidirectional photonic band structures coming from corresponding solid network structures [18]. Therefore, 3D photonic crystals can avoid many disadvantages of 2D photonic crystals. However, such 3D photonic crystals are very challenging and costly to fabricate using conventional approaches. It was demonstrated that TPP provides a powerful tool in the convenient fabrication of functional 3D photonic crystals. Other than 3D photonic crystal structures and materials, many other 3D optical components and structures were successfully fabricated using the additive TPP fabrication process. Figs. 9.8 and 9.9 demonstrate scanning electron micrographs of microlens arrays, optical cavity structures, and various complex 3D micro-logos. The fabrication results demonstrate the capability of the TPP method in precisely fabricating 3D micro-/nanostructures of complicated geometries.

9.3 Subtractive micro-/nanofabrication using multiphoton ablation

MPA is another typical FsLDW technique that has been established as a useful subtractive manufacturing technology in 3D micro-/nanostructuring of solid materials.
by direct ablative writing \cite{19-21}. MPA requires the simultaneous absorption of multiple photons in a single quantum event to initiate the ablation \cite{22}. Multiphoton absorption produces initial free electrons that are further accelerated by the femtosecond laser electric field \cite{22}. These electrons induce avalanche ionization and optical breakdown and generate localized plasma \cite{22}. The subsequent expansion of the localized plasma results in the fabrication of a void structure at the focal point \cite{22}. Because of the nature of nonlinear interaction, a high resolution beyond the diffraction limit can be obtained \cite{22}. A variety of micro-/nanostructures have been fabricated by the MPA process. Chichkov et al. \cite{22} reported the fabrication of a photonic crystal structure with a defect cavity at the center by creating periodic nanostructures in sapphire using MPA. Sun et al. \cite{23} reported the fabrication of 3D photonic crystals within silica. Zhou and Gu \cite{24} fabricated the first void-dot face-centered

Figure 9.6 (a, b) Woodpile structures, (c, d) pyramid structures, and (e, f) slanted-pore structures.
cubic 3D photonic crystal in lithium niobate with a pronounced high-order stop gap at a 1.5—2-μm wavelength. It is noteworthy that, because of the femtosecond pulse duration, electron—photon interactions ranging in the picosecond regime are minimized, and thus thermal effects are almost negligible with minimal edge effects [20]. Therefore, MPA is especially capable in fabricating structures such as channels, holes, and voids in various materials [19—21, 25—27].

We used the same laser lithography system to carry out subtractive MPA fabrication. The experimental setup is similar to the TPP fabrication process, as described in Section 2.2, except significantly higher laser powers than the TPP process (two to seven times higher) are required. Cured (IP-L, a trademark name of a photo-resist from Nanoscribe GmbH) polymers were used as the raw material, which promises a high spatial resolution beyond the diffraction limit. Because of the short pulse duration of the femtosecond laser (120 fs), which is much shorter than the electron-phonon coupling time (∼1 ps) [28], there is limited heat exchange between the irradiated

Figure 9.7 (a, b) Single-spiral, (c, d) overlapped single-spiral, and (e, f) double-spiral structures.
Figure 9.8 Scanning electron micrographs of microlens arrays and optical cavity structures fabricated by three-dimensional lithography. (a) A vertically aligned aspheric lens array. (b) A horizontally aligned aspheric lens array. (c) A vertically aligned biconvex lens array. (d) A horizontally aligned biconvex lens array. (e) A disk-shaped optical cavity for dye laser application. (f) A spherical microlens array.

Figure 9.9 Scanning electron micrographs of some examples of complex three-dimensional (3D) structures fabricated by two-photon polymerization lithography. (a) Side view of a 3D National Science Foundation (NSF) logo. (b) Top view of a 3D NSF logo. (c) 3D logo of the University of Nebraska Cornhuskers.
area and the surroundings during the subtractive MPA process, resulting in stable and reproducible subtractive fabrication with minimized thermal stress and collateral damage. Fig. 9.10(a) shows an array of holes created by MPA in a 200-nm-thick IP-L film. A magnified image of one hole is shown in the inset of Fig. 9.10(a). The diameter of the holes is around 180 nm, far beyond the diffraction limit of the laser beam. In addition, Fig. 9.10(b) shows five interconnected hollow rings resembling the Olympic rings created in a cured IP-L polymer film created by MPA.

9.4 Comprehensive 3D micro-/nanofabrication

Although both additive and subtractive micro-/nanofabrication methods are established separately, they have been largely isolated. Fabricating advanced devices of complex 3D geometries calls for the use of both additive and subtractive processes. For example, a seamless spherical shell is difficult to fabricate using either an additive or subtractive process. In additive processes the solid shell of the sphere prevents the unexposed photoresist from dissolving inside the sphere and producing a void. In subtractive processes, a solid sphere has to be created before subtracting the inner part to make a hollow shell. Therefore, a comprehensive 3D micro-/nanofabrication method possessing both additive and subtractive functionalities is not only desirable but also in demand for advanced device fabrication.

We successfully integrated an additive (TPP) and a subtractive (MPA) process into a single femtosecond laser direct writing system in which process conditions could be precisely controlled. The integrated fabrication method not only inherits the merits of both TPP and MPA, such as writing resolution smaller than the diffraction limit and features with sharp and clean edges, but also offers the possibility to produce novel device structures that are difficult to fabricate using either TPP or MPA alone.
Fig. 9.11 shows a schematic of an integrated 3D micro-/nanofabrication system combining both additive TPP and subtractive MPA processes. The whole fabrication process consists of three steps. First, TPP is used to fabricate solid 3D microstructures inside the negative photoresist of IP-L (Nanoscribe GmbH). Second, the unsolidified IP-L photoresist is washed away by rinsing the sample in isopropyl alcohol (99.5%; BDH Chemicals) for 20 min. Third, a subtractive process based on MPA is carried out in air to tailor the cured IP-L to a desired 3D geometry. Depending on the size of the desired structure, TPP is performed by using average laser powers that vary between 3.5 and 8 mW. Instead, MPA requires an average laser power that is two to seven times higher than that used for TPP. The laser beam is generated by a mode-locked femtosecond-fiber laser (780-nm central wavelength, 100-MHz repetition rate, and 120-fs pulse duration) and is tightly focused within the sample by an oil-immersion objective lens (numerical aperture: 1.4; Magnification: 100). Writing in both additive and subtractive processes is achieved by moving the sample around a fixed laser beam by means of a computer-controlled XYZ piezo stage.

To demonstrate the capabilities of the “TPP + MPA” method in 3D micro-/nanofabrication, we fabricated two kinds of device structures. The first one is shown in Fig. 9.12; it consists of arrays of microstructured polymer fibers with different diameters. The TPP process was used to fabricate these structures with 2-, 1-, and 0.5-μm line widths, as shown in Fig. 9.12(a,c,e), respectively. The average laser power and stage scanning speed used for TPP were 7 mW and 100 μm/s, respectively. And the different line widths of the fibers were achieved by controlling the number of laser passes in fabricating a single polymer fiber. Upon polymerization, the refractive index of IP-L increases to a value of 1.52. Therefore, the polymer fibers could be used as light waveguides for integrated optics [29]. Following TPP, a subtractive MPA process was performed with an average laser power of 26 mW, laser exposure time of 5 ms/spot, and a stage scanning speed of 100 μm/s. Periodic hole patterns with a ~500-nm diameter were fabricated along the polymer fibers to form Bragg grating structures in waveguides, as shown in Fig. 9.12(b,d,f). The diameter and the periodicity of the holes were tunable by adjusting the average laser power, exposure time, and scanning
It is noteworthy that the fiber Bragg gratings shown in Fig. 9.12 are difficult to fabricate using either TPP or MPA alone.

The second type of device structures fabricated by implementing TPP and MPA is shown in Figs. 9.13 and 9.14, where meshed and spiral microfluidic channel systems are represented, respectively. First, polymer cubic structures were fabricated on glass substrates using the additive process of TPP. Then, interconnected microchannels were directly written within the polymer microstructures via the subtractive process of MPA. The average laser power and the scanning speed used to create the channels were 26 mW and 50 μm/s, respectively. Fig. 9.13(a, b) clearly shows the typical microchannels created by MPA. The diameter of a channel is about 1 μm, according to the
SEM characterization. Fig. 9.13(c) shows the meshed microfluidic channel system created inside the IP-L polymer cube. Liquid flowing through the meshed channels can be clearly observed in Fig. 9.13(d,e), which verifies the hollow structure and the connectivity of the microfluidic channels. In addition to the 2D meshed channels, 3D spiral microchannels were also successfully fabricated inside the IP-L polymer. Fig. 9.14(a) shows the schematic structure of a 3D spiral channel inside a polymer cube. The labels of “A” and “B” in Fig. 9.14 refer to two points that are the highest and the lowest in the $z$ direction, respectively. The optical microscopy image of the spiral channel changes as the focal plane of observation shifts from low to high, as shown in Fig. 9.14(b–d), which indicates the 3D characteristics of the spiral microfluidic channel created inside the IP-L polymer. By using the TPP + MPA method, arrays of the spiral microfluidic channels with a user-defined spacing can be readily fabricated, as shown in Fig. 9.14(e). Compared with the mainstream technique of soft lithography for fabricating microfluidic systems [31], the TPP + MPA method holds several advantages. First, it is a mask-free process. It provides an unparalleled convenience and freedom in prototype design using a computer-aided design program, without the need to fabricate replica molds, as is always required by the soft
lithography method. Second, it is a truly 3D fabrication method, in contrast to soft lithography, which is inherently limited to 2D processing because of the requirement of molding. Third, it needs no sealing of microchannels, which is a necessary fabrication step in the soft lithography process.

9.5 Conclusions

Research efforts have been extended to 3D micro-/nanofabrication based on the FsLDW method. A truly 3D laser direct writing platform has been established. Both additive TPP and subtractive MPA techniques for 3D micro-/nanofabrication have been demonstrated separately based on this platform. Process optimization by studying the dependence of the voxel dimension and the surface roughness on various laser scanning parameters has been obtained. Raman spectroscopy has been proven to be a reliable tool for DC characterization in TPP. The successful fabrication of a wide range of 3D micro-/nanostructures by either TPP or MPA processes, including 3D photonic crystals, optical lenses, disk cavities, hole arrays, and embedded channels, have proven the usefulness and efficiency of TPP and MPA in 3D micro-/nanofabrication.

Figure 9.14 Three-dimensional (3D) spiral microfluidic channels inside a IP-L polymer cube fabricated by the “two-photon polymerization + multiphoton ablation” method: (a) schematic of the 3D spiral microfluidic channel. (b), (c), and (d) show the x-y cross-sectional view of a spiral channel under a transmission-mode optical microscope at different focal planes (scale bar: 10 μm). The coil diameter of the spiral channel is 20 μm. (e) An array of spiral microfluidic channels fabricated inside a polymer cube with a coil diameter of 5 μm and an inter-channel spacing of 3 μm [30].
Moreover, a comprehensive and versatile 3D micro-/nanofabrication method has been developed by integrating both additive TPP and subtractive MPA processes into a single FsLDW framework. The nonlinear characteristics of the fabrication processes offer a writing resolution <200 nm, far beyond the optical diffraction limit. In addition, this method also inherits the virtues of MPA in creating sharp and clean processing edges as a result of the minimized thermal stress and collateral damages. Results show that the combination of additive and subtractive fabrication processes enables the fabrication of complex 3D micro-/nanostructures that are difficult for either TPP or MPA alone. It is believed that this new 3D micro-/nanofabrication method paves the way for the development of advanced devices such as integrated optical circuits and lab-on-a-chip devices.

References


