Recent Progress of Lithographic Microfabrication by the TPA-Induced Photopolymerization

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Several different structures of micro-objects were fabricated by two-photon initiated photopolymerization using newly synthesized chromophore whose structures have been engineered for high two-photon activity. A raster graphics type voxel matrix scanning (VMS) scheme allowed fabrication of two-dimensional (2D) micro-object from a bitmap format figure. Using this technique along with the vacuum pressure discrepancy technique, nano-precision polydimethylsiloxane (PDMS) replica has been fabricated from it original PDMS mold that was originally prepared by two-photon initiated photopolymerization of soft-resin. For better result in photonic crystal fabrication, a quantized-pixel laser writing scheme was employed. A complicated sub-micron 3D photonic lattice was fabricated with high reproducibility. In order to enhance physical/mechanical stability of resulting micro-object, we have tested a new material system which consists of sol-gel precursor and photocrosslinking of soft-resin. The physical/mechanical stability of micro-object was enhanced greatly by introducing the formation of silica glass interpenetrating network with organic polymer resin.

Keywords: Two-photon absorption, Two-photon initiated photopolymerization, 3D microfabrication

1. Introduction

Following the extrasensory theoretical perception in multi-photon process by Göppert Mayer [1], and the pioneering works by Renzepis on optical memory [2], by Webb on confocal imaging and stereo photolithography [3, 4], and by Kawata on photopolymerization for three-dimensional (3D) microfabrication [5], the nonlinear multi-photon process has drawn great deal of attention over the past decay due to the its wide-open possibilities in fields of applications for up-converted fluorescence lasing, two-photon optical power limiting, 3D optical data storage, two-photon excited fluorescence for non-destructive bio-imaging, two-photon photodynamic therapy, and precision high resolution laser microfabrication [2-13]. In particular, 3D microfabrication by two-photon initiated photopolymerization became much attractive because it provides the feasibility on fabrication of future high-integrated micro information engineering devices. These devices evidently require high structural complexity and the conventional photolithography is limited to the

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fabrication of two-dimensional (2D) structures.

The two-photon absorption (TPA) process occurs when the high intensity light is irradiated to a molecule. As the light pass through a molecule, a very short living virtual state may form. Then if the second photon arrives before the decay of this virtual state, the combined energy of the two photons accesses the excited state of the molecule. If the energy of the two photons is identical, the process is referred as degenerate TPA, otherwise, the processes is non-degenerate TPA. The rate of energy absorbed in a degenerated TPA process that is simultaneous absorption of two photons with the same energy, \( \frac{dW}{dt} \), can be written as in Equation 1, where \( I \) is the intensity of light. Because TPA process depends on both a temporal and spatial overlap of the two photons at virtual state, its probability is quadratically proportional to the incident light intensity where as the one-photon absorption probability is linearly depends on the incident light intensity.

\[
\frac{dW}{dt} = \frac{8\pi^2 \omega}{c^2 n^2} I^2 \text{Im}[\chi^{(3)}] 
\]

Eq (1)

- \( c \): light velocity
- \( n \): refractive index
- \( \omega \): optical frequency

By taking advantage of the quadratic power dependency of the two-photon process so that controlling physical and chemical processes within tightly confined volume using focused excitation beam, the TPA induced photopolymerization allows fabricating such devices even with sub-diffraction-limit spatial resolution in three dimensions. The lithographic microfabrications by TPA initiated photopolymerization at first age have been performed with existing UV-photoinitiators whose two-photon absorption cross-sections are very small. In consequence, near damage threshold (structure material) of high incident laser power and long exposure times (another factor for damaging material) are required to induced two-photon event, limiting versatility of TPA initiated photopolymerization for microfabrication. The increased efficiency of two-photon photoinitiator with large TPA cross-section, therefore, would surely be beneficial to overcome those limits and even broadens its scope of applications.

In this contribution, we include our efforts to search for the better two-photon absorbers (chromophores), microfabrication of various micro-objects with high structural complexities, a new material system to enhance physical/mechanical stability of the fabricated microstructures.

2. Two-photon Chromophores

The large TPA cross-section of a molecule may be the most important for wide range of applications including two-photon initiated photopolymerization technology [14-19]. Use of these highly TPA active photoinitiators enables replacing expensive and sophisticated laser system to inexpensive CW laser or nanosecond pulsed laser. Also it would make possible to control incident excitation beam power due to a wide dynamic power range tailoring microstructure dimensions. Some critical molecule design criteria have already been explored in efforts for establishing relationship between molecular structure and TPA activity. Among them, one important effort in molecule design is searching for molecular structure whose change of dipole moment (\( \Delta \mu \)) is potentially larger. Upon excitation, the polar molecules go large change of dipole moment (\( \Delta \mu > 10 \text{ D} \)) between excited state and ground state. Since both the ground state and the excited state will participate in the formation of the virtual state, the two photon transition probability is proportional to \( \Delta \mu^4 \) [16, 23]. The \( \pi \)-conjugated molecular systems particularly those with phenylethyl [14], fluorenyl [16, 24] or polyenyl [25] found to be good candidates. In these molecules electron-donating (D) and/or electron-withdrawing (A) moieties were covalently connected by a conjugated \( \pi \)-electron bridges causing symmetric charge transfer from the ends of a conjugated system to the center or vice versa. In addition to increasing intrinsic molecular TPA cross-section of chromophores, there is another concept to enhance TPA by increasing the chromophore number density without causing aggregation [26, 27].
In our laboratory, we have designed and successfully synthesized a large variety of two-photon chromophores for various applications including optical power limiting and two-photon initiated photopolymerization as shown in Figure 1. In addition to following the suggested basic molecular design criteria, we also have systematically varied electron donors and π-conjugated bridges to investigate effects on the two-photon activity in aspect with the electronic configuration of bridging moiety and the planarity of molecule. The wavelength sensitivity should be concerned as another very important factor when designing two-photon chromophores. Since most suitable femtosecond laser is solid wavelength-tunable Ti:Sapphire laser, of which window of wavelength ranges from 680 nm to 840 nm, the optical transparency of a two-photon chromophore beyond half the wavelength of excitation laser beam is particularly important in order to exclude linear absorption by the chromophore. All the chromophores in our system show the UV-visible absorption peaks at the wavelength of near 400 nm making these chromophores ideal. They are highly two-photon active with large TPA cross-sections (Table 1).
Table 1. Optical data of efficient two-photon absorbing chromophores

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{pl}$ (nm)</th>
<th>$\sigma_z$</th>
<th>excitation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz-EPS-Cz</td>
<td>403$^a$</td>
<td>446$^c$</td>
<td>10.5</td>
<td>z-scan</td>
<td></td>
</tr>
<tr>
<td>TP-EPS-TP</td>
<td>412$^a$</td>
<td>464$^c$</td>
<td>12.5</td>
<td>z-scan</td>
<td></td>
</tr>
<tr>
<td>Cz-Flu-Cz</td>
<td>441$^b$</td>
<td>486$^b$</td>
<td>7.4</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>TP-Flu-TP</td>
<td>411$^b$</td>
<td>452$^b$</td>
<td>9.5</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>NBU2-Flu-NBu2</td>
<td>415$^b$</td>
<td>457$^b$</td>
<td>11.4</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>Cz-DTT-Cz</td>
<td>441$^b$</td>
<td>486$^b$</td>
<td>7.4</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>TP-DTT-TP</td>
<td>453$^b$</td>
<td>503$^b$</td>
<td>11.1</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>NBU2-DTT-NBu2</td>
<td>457$^b$</td>
<td>506$^b$</td>
<td>9.8</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>EA4BPA-VB</td>
<td>423$^d$</td>
<td>475$^d$</td>
<td>18.1</td>
<td>810</td>
<td></td>
</tr>
<tr>
<td>EA2BPA-VB</td>
<td>424$^d$</td>
<td>507$^d$</td>
<td>-</td>
<td>764</td>
<td></td>
</tr>
<tr>
<td>EHHAP-VB</td>
<td>425$^d$</td>
<td>485$^d$</td>
<td>-</td>
<td>770</td>
<td></td>
</tr>
<tr>
<td>EHSEA-VB</td>
<td>423$^d$</td>
<td>480$^d$</td>
<td>-</td>
<td>740</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: solution in CH$_2$Cl$_2$, $^b$: solution in THF
$^c$: $<10^{28}$ cm$^{-4}$-s/photon-molecule
$^d$: for excitation femtosecond laser was used in all measurements

3. Microfabrication Set-up and Material System

For microfabrication, we have used a laser system that was established by Kawata (Figure 2) [28]. The laser beam focusing which mainly governed by microscopic objective lens is of the most importance in the entire microfabrication system and larger the magnification is more advantageous for monitoring fabrication in-situ. The resolution of a targeted micro-object is determined by the wavelength of excitation laser beam and the numerical aperture (NA) of objective lens. Although, a shorter wavelength excitation laser beam will undoubtedly reduce focal spot size, the availability of the short wavelength laser system is limited. Since the size of excited volume (confined volume), voxel depends on $1/(\text{NA})^2$ in 3D fabrication, using larger NA optics is essential for realizing a high fabrication resolution. A 780 nm wavelength mode-locked Ti:sapphire laser with 80 femtosecond pulse width operating at 80 MHz repetition was employed for two-photon photopolymerization. The excitation laser was focused by an objective lens with 1.4 or 1.24 numerical apertures. The border between objective lens and glass substrate was filled with immersion oil (refractive index of 1.5) for higher spatial resolution. The spatial resolution of a micro-object during the fabrication was known to be restricted by spherical aberration that causes the variation of refractive index. As a material system, the SCR-500$^8$ resin which consists of urethane acrylate oligomers with different molecular weight of 480 and 1200, its monomer as a dilutor, and a mixture of carbonyl group containing initiators (benzoyl-cyclohexanol and morpholino phenylaminoketones) was mixed with small portion of a two-photon photoinitiator (typically about 0.1 wt. %). Then, the laser focal spot was scanned in three dimensions by the computer controlled Galvano-scanner for $x$, $y$ and by the piezoelectric stage for $z$ axis. The Galvano shutter was also used to control exposure time. The unpolymerizable resin was removed by washing with appropriate solvent leaving the micro-object behind.

Figure 2. Laser set-up for two-photon initiated microfabrication [28].

4. Two-photon Initiated Microfabrication

Recently, we have fabricated nano-precision PDMS replica by combining two-photon photopolymerization and vacuum pressure discrepancy technique. Using the objective lens with 1.24 NA, the laser was focused into the mixture of the SCR-500$^8$ soft-resin and two-photon photoinitiator (0.1 wt. %). Then, the laser focal spot was scanned in three dimensions by a computer controlled Galvano-scanner with 24 nm resolution and by piezoelectric z stage with 100 nm resolution. A micro structure was fabricated by raster graphics type voxel matrix scanning (VMS) scheme, which is now proposed to produce easily a 2D micro-object from a bitmap format figure [29]. In VMS, a black-and-white bitmap of a figure is transformed into line commands which have the information about precise position and exposure time of each voxels (Figure 3). The first step of the transformation is conversion of a bitmap file into a voxel matrix from that consist of '0's for white pixels and '1' for black pixels. This matrix says where the excitation laser beam should be exposed. The Galvano scanner stops at the position of '1' and the shutter opens for a preprogrammed exposure time, while the scanner passes without
exposing the shutter for ‘0’. In the second step, more fabrication input parameters are given such as exposure time, laser power, vertical positions of a voxel, scanner positions and the shutter on/off. Figure 4b shows the fabricated 2D micro-object along with its original bitmap image (Figure 4a) clearly proving that the VMS technique is capable of transferring a bitmap image into a nearly identical 2D micro-object with 200 nm resolution by two-photon photopolymerization. After the successful fabrication of 2D micro-object we were interested in preparing polydimethylsiloxane (PDMS) mold which is widely used to make microstructures for bio-MEMS. A 10:1 mixture of the PDMS prepolymer, Sylgard 184A® and the curing agent, Sylgard 184B® was placed in a vacuum chamber and degassed for a certain time.

This mixture was poured onto the micro-object substrate while maintaining vacuum then vacuum was released. This later release of vacuum will assure filling the small voids which may present between PDMS and micro-object (Figure 5).

Generally, it is not necessary to perform such a process under the vacuum, if desiring scale is in several micron. Even the smallest void between PDMS and micro-object, however, will deform the resulting PDMS in the process of fabricating molds with higher precision. The PDMS mold was easily peeled-off from micro-object after curing the prepolymer (Figure 4c). Before making the PDMS replica using PDMS mold, a thin layer of gold (30 nm) was deposited on the micro-object to insert surface incompatibility. As shown in Figure 4d, this technique allowed to replicate the identical structure from the micro-object fabricated with two-photon photopolymerization and PDMS mold. Therefore, it should be applicable for fabricating micro- or nano-patterns without any expensive photomask.

A novel optical structure, photonic crystals, is one of the most popular research fields in current optical science and engineering including optoelectronics and optics. This unique structure is capable of precisely controlling, confining, and manipulating photons from emission to propagation due to the photonic bandgap (PBG) effect [30, 31]. The direct laser writing is profitable to fabrication of such a photonic crystal because of the intrinsic 3D processing capability and the compatibility to various functional polymeric materials by means of doping or chemical synthesis [32]. Despite intense efforts, not many photonic crystal structures fabricated by two-photon photopolymerization of soft-resin showed meaningful bandgap effect except for a few. Collaboration with Sun and Kawata’s group in Osaka University, Japan, we have fabricated 3D photonic crystal lattices that show PBG effect [33]. The log-pile structure that is the most used
configuration for photonic crystal is illustrated in Figure 6a. The rod diameters are not uniform when fabrication was performed conventionally by scanning series of lines. They are thicker at two ends due to acceleration and deceleration of the piezo stage, leaving narrower intervals at the four side facets of cubic structure or even sealing them. Furthermore, the rod cross-section in line scanning technique takes the shape of the focal-spot point spread functions as shown in Figure 6b [34]. As a solution for that problem, we have utilized an alternative laser-scanning scheme which has been used for creating nanomachines. At first, the entire 3D space was quantized into uniformly spaced pixels of volume a-b-c (nm³), laser focus passes through all pixels by raster scanning. It resides only at the points those prescribed and exposes for a given duration to define a feature. As a result, both the size of polymerized volume elements, voxel (Figure 6b), and the pixel dimensions of a, b, and c become sufficiently decrease so that the contour of written feature takes the designed shape, which is a fundamental requirement of high-precision depiction. Figure 6c is the scanning electron microscope (SEM) image of the 15-layer photonic crystal fabricated in this study. The structure was designed and prescribed with a horizontal cross-section of 20 µm × 20 µm. The structural features of the fabricated photonic crystal are extremely well-defined as expected. Interestingly, with the layer number increases, however, the layer area of the structure shrinks from 20 µm × 20 µm at the bottom to 17 µm × 17 µm at the top within a vertical span of 7.5 µm. The structural shrinkage is due to the denser molecular composition in solid phase than that in liquid phase and the induced tensile was released gradually from the bottom layer that was adhered to the substrate. Unfortunately, this structural deformation in the transition layer is a detrimental factor for high-precision laser nanofabrication.

In many cases, the microfabrication by two-photon initiated photopolymerization of soft-resin suffers from its lack of physical and/or mechanical stability of the resulting micro-object, primarily due to the weak adhesive strength to substrate and the volume shrinkage after dissolving non-irradiated resin [33, 34]. It is widely realized that organic-inorganic hybrid materials by sol-gel process are very promising for enhancing physical and mechanical properties of organic component as well as chemical and thermal resistance of the materials. Thus, we strongly believed combining the sol-gel process with two-photon photopolymerization for micro-fabrication would be beneficial for improving physical and mechanical stability of the micro-object. This time, the additional component 3-isocyanatopropyltriethoxy-silane (IP-TEOS), the sol-gel precursor, was added to the materials system along with SCR-500® and TPA chromophore. The mixture was stirred vigorously over 2 days at ambient temperature for homogeneous mixing. Then, the laser focal spot was scanned in three dimensions as described above. For comparison, two identical micro-objects were fabricated with the same manner except without a sol-gel precursor. As shown in Figure 7a, the micro-pigeon which was fabricated

![Figure 6.](image1)

![Figure 7.](image2)
without a sol-gel precursor completely collapsed after washing off unsolidified resin due to the weak mechanical/physical strength of organic polymer and the weak adhesive strength between micro-pigeon and glass substrate. On the other hand, the micro-pigeon which was fabricated with new materials system reveals (Figure 7b) the very fine features of micro-pigeon evidently showing the facileness of sol-gel process in photopolymerization. It is obvious that the introducing the sol-gel process into the two-photon photopolymerization of soft-resin is beneficial for enhancing the structural stability of a micro-object as well as strengthening adhesion on glass substrate. The curing was then performed by increasing temperature after washing. The width, length and height of the micro-pigeon were 8.1 \( \mu \text{m} \), 13.2 \( \mu \text{m} \), and 15.6 \( \mu \text{m} \), respectively. The same material system was also employed for fabrication of photonic crystal structure. Over the past years, many photonic crystal micro-structures have been fabricated by the two-photon initiated photopolymerization using soft-resin. The photonic bandgap effect of an organic photonic crystal structure, however, was obstructed from the structural defects of three-dimensional microstructure. These unwanted defects were mainly originated from the intrinsic volume shrinkage of organic polymer and the unsolidified residual resin inside photonic crystals after developing step. Especially, the photonic crystal research by this method was disappointed with an affliction of no such a band-gap effect observed from the microstructure. In addition, due to the densely integrated three-dimensional crystal structure, it is also extremely difficult to clean the photonic crystal. In order to prove versatility of our material system, the 8-layered three-dimensional 23 \( \mu \text{m} \times 24 \mu \text{m} \) photonic crystal structures were fabricated by both the conventional method and the sol-gel photolithographic method using the new materials system as in described above. After the fabrication, two photonic crystal micro-structures were washed with solvent (methanol) using the ultrasonic-wave. The micro-structure obtained by the sol-gel photolithographic method was allowed to be cured by raising the temperature. The resulting micro photonic crystals are shown in Figure 8. Both the structures appeared to be relatively stable and well defined. However, the measured height of the microstructure fabricated by conventional method was 5.1 \( \mu \text{m} \) (Figure 8a), whereas the height of the microstructure fabricated by sol-gel photolitho-

Figure 8. SEM images of (a) the photonic crystal structure fabricated without sol-gel precursor, (b) identical structure fabricated with sol-gel precursor.

graphic method was 7.2 \( \mu \text{m} \) (Figure 8b) showing considerably improved resistance on the structural volume shrinkage (30%). The sol-gel process through hydrolysis-condensation reaction of alkoxy-silanes results in formation of Si-O-Si interpenetrating network-bonds and this network-cohesion certainly can be utilized to improve the mechanical/physical stability of the micro-object in microfabrication by two-photon initiated photopolymerization.

5. Summary and Conclusions

We have designed and synthesized a large variety of chromophores whose TPA cross-sections are fairly high. Using these chromophores as a light sensitizer/initiator, several different structures of micro-objects were fabricated by two-photon initiated photopolymerization. New direct laser writing, raster graphics type voxel matrix scanning (VMS) scheme, allowed fabrication of two-dimensional (2D) micro-object from a bitmap format figure. Using this handy technique along with the vacuum pressure discrepancy technique, nano-precision polydimethylsiloxane (PDMS) replica has been successfully fabricated from it original PDMS mold that was originally prepared by two-photon initiated photopolymerization of soft-resin. For better result in photonic crystal fabrication, a quantized-pixel laser writing scheme was employed. A complex sub-micron 3D photonic lattice was fabricated with high reproducibility. The enhancement of the physical/mechanical stability of resulting micro-object was achieved by using new material system which consists of sol-gel precursor and photo-crosslinking of soft-resin. The physical/mechanical stability of micro-object was enhanced greatly by introducing the formation of silica glass interpenetrating network with organic polymer resin.
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