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Multi-photon Absorption Photo-polymerization: Unique Technique to build Micro-structures with Nano Resolution

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Abstract: we report on the ability of the Multi-photon absorption (MPA) to build 3D polymeric structures with nano resolution and arbitrary dimension. 100 fs laser pulses were utilized for structuring. Different parameters such as laser power (laser pulse energy) and scanning speed were optimized to build qualitative structures. Using a medium numerical aperture (NA=0.85) microscope objective resolution of 300 nm was achieved.

Keywords Multi-photon absorption, photo-polymerization, micro-nano-structuring, photo-initiator, nonlinear optics

Introduction

Multi-photon absorption (MPA) was predicted in 1931 by Maria Göppert-Mayer [1]. In MPA process, two or more photons are simultaneously absorbed to bridge the ground state to a higher energy state having an energy gap larger than the energies of each photon individually. Such a transition for one-photon absorption is forbidden due to the exclusion rules even if the resonance condition $\Delta E = h\nu$ is fulfilled. MPA is a nonlinear optical process which is different from the sequential linear absorption process, where a real intermediate energy level is involved. Hence, materials used with MPA are transparent show no linear absorption at the wavelength of the utilized laser. Although higher order of MPA leads to higher resolution the two-photon absorption (2PA) is most utilized in practice, since the 2PA coefficient is much higher than that of the 3PA or others. When the laser beam is focused inside the sample, by adjusting the laser power the intensity in the focus exceeds to the threshold for the 2PA process. Therefore, in the small volume around the focal point 2PA occurs resulting in exciting the absorbing species. Since the probability of 2PA scales as the square of the incident light intensity the probability for 2PA drop very rapidly away from the focus leaving a small volume pixel (voxel) of modified material within the sample. This property has led to many 2PA based applications such as two-photon excited fluorescence (2PEF) microscopy [2], two-photon photo-dynamic therapy (PDT) [3], 3D optical data storage [4] and two-photon polymerization (2PP) [5-14].

In 2PP usually a femtosecond laser beam is tightly focused using a high numerical aperture microscope objective inside the resin. The resin is a monomer containing a photoinitiator (PI) to trigger the polymerization process. The irradiated PIs inside the focus volume converted to free radicals which are highly active to cross link to monomer molecule. The produced molecule is still a free radical to attach to another monomer molecule creating longer molecule. In this way the monomer turns to polymer. However, the polymerization process will stop by some self terminating processes keep the dimension of the polymerized structure below a limit. To build a polymeric structure based on 2PP the laser focus is scanned within the resin by a 3D motorized stage. By scanning the focus in one direction a polymeric line can by produced. The line width is considered as the resolution of 2PP based structures. Line width blow 100 nm has been reported by different groups [14-17] thus, 2PP can be classified as a nanostructuring technique.

Materials and Method

The resin used for 2PP is a combination of a monomer and a two-photon initiator (2PI). The photopolymerizable monomer was a 1:1 mixture (wt. %) of ethoxylated (20/3)-trimethylolpropanetriacrylate (ETA, Sartomer 415) and trimethylolpropane triacrylate (TTA, Genomer 1330). B3FL [18] as a 2PI was added to this monomer. B3FL contains fluorenone as acceptor in the central part of the π bridge. The introduction of an aromatic ketone with a stereo rigid carbon frame not only facilitates the intramolecular charge transfer process but also extends the conjugation length of the whole π system, which is critical in enhancing the 2PA cross section. For 2PP, 2PIs with low fluorescence quantum yields are preferred as this is a requirement for producing radicals more efficiently to initiate the polymerization.

Fabrication of the microstructures was done using a standard 2PP setup (Fig. 1). Starting with the Ti-sapphire laser (max. power: 450 mW) creating 100 fs pulses with

76 MHz repetition rate the near-infrared laser beam (λ=793 nm) passes though an acousto-optic-modulator (AOM) in order to make the laser beam On/Off. In order to adjust the laser beam power reaching the sample a set a rotatable λ/2 wave-plate in combination with a polarizing beam-splitter was used. A drop a resin was poured on a microscope slice and then mounted on the z-axes stage. The laser beam was focused inside the resin using a microscope objective (60x, NA=0.85). The focus was scanned inside the resin using a 3D high precision air bearing translation stage. The 3D structure is built in layer by layer fashion. Each layer is created by scanning the focus in x-y plane. After the layer is finished the sample is moved for building the next layer by z-axes stage. A CCD camera was used to live monitoring the polymerization process and find the position of the laser beam focus. In the beginning the focus is adjusted at the bottom of resin a few micron below the surface of the glass slice. The created structure is then stuck to the glass slice not floating in the resin. After the polymerization is finished the created structure was developed in ethanol to remove the residual monomer form the cured polymer.

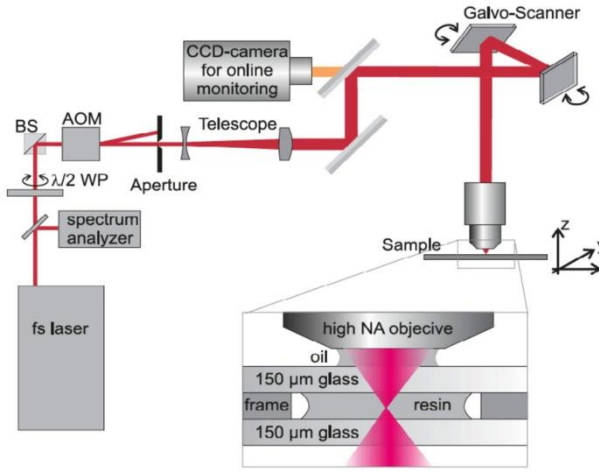

Fig. 1. Schematic of 2PP based 3D structuring

Results and Discussion

In 2PP, in order to build fine structures two parameters should be optimized; laser power and scanning speed. To find the optimal value for these two parameters a matrix of structures with different pulse energy from a few mW to tens of mW and different scanning speed from a few mm/s to tens of mm/s was built.

Figure 2 shows SEM image of some structures as an example to represent the capability of 2PP technique for nano resolution micro size structures. Such a structure can be a photonic crystal, a micro-chip device or a micro machine for drug delivery.

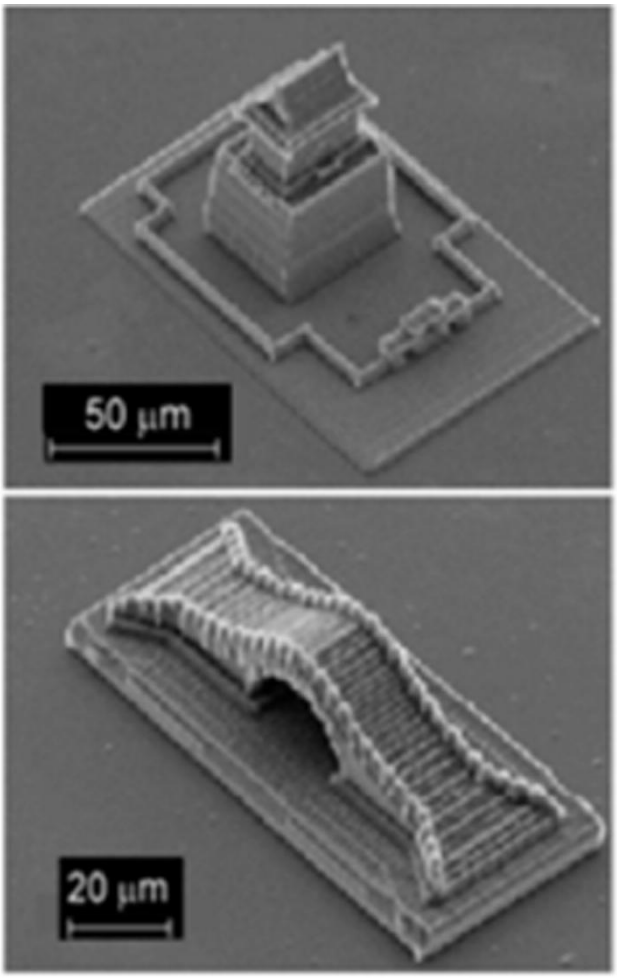

Fig. 3. SEM image of structures build based on 2PP

Figure 3 shows 4 different structures built with the same scanning speed of 10 mm/s but different laser power. The best quality was achieved within the window of 6-12 mW. Sample number 1 shows an example of structures built with laser power of 9 mW. Numbers 2, 3 and 4 were build with powers of 15, 20 and 27 mW respectively. Using powers higher than 22 mW led to burning the structures and creating non resolvable structures.

Polymeric line width defined as the resolution of the structures was estimated to be less than 300 nm in created structures. The resolution can be improved to less than 100 nm using higher numerical aperture (up to NA=1.4), increasing the scanning speed which is off course requires

2PIs having higher 2PA cross section and adding additives which cause faster self terminating process.

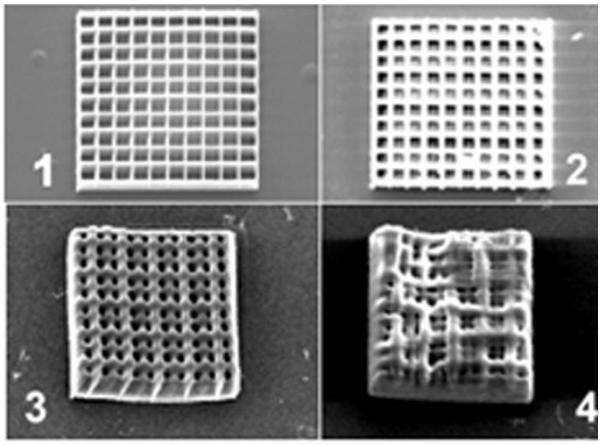

Fig. 3. SEM image of structures built with different laser power. 1 with 9 mW, 2 with 15 mW, 3 with 20 mW and 4 with 27 mW.

Conclusions

3D mico-nano-structures were successfully built based on 2PA photo-polymerization. The resolution of the structures is well beyond the diffraction limit of the optics and laser beam used for structuring. This is a unique technique to reach resolutions which is impossible for common direct photo-polymerization methods based on linear (one-photon) absorption.

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