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میکرو-نانو ساختارهای سه بعدی تولید شده به روش فوتوپلیمریزاسیون بر پایه جذب دو فوتونی

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چکیده- تولید ساختارهای میکرونی به روش فوتوپلیمریزاسیون با استفاده از لیزر دارای محدودیت رزولوشن به علت پدیده پراش است که توسط طول موج لیزر و اپتیک مورد استفاده تعیین می شود. برای رسیدن به رزولوشن بهتر در حد کسری از طول موج تنها روش استفاده از جذب چند فوتونی مثل جذب دو فوتونی می باشد. در این کار نتایج اندازه گیری سطح مقطع جذب دو فوتونی برای یک آغازگر دو فوتونی با استفاده از تکنیک زی-اسکن باز ارائه شده و سپس از این آغازگر برای تولید میکرو ساختار پلیمری بر پایه جذب دو فوتونی استفاده شده. ساختارهای تولید شده دارای رزولوشن چند صد نانو متر می باشند که بسیار بهتر از حد تحمیل شده توسط پراش برای چیدمان استفاده شده برای فرایند فوتوپلیمریزاسیون دو فوتونی می باشد.

کلید واژه- اپتیک غیر خطی، جذب چند فوتونی، فوتوپلیمریزاسیون، میکروساختارهای سه بعدی

Micro-nano 3D structuring based on two-photon photopolymerization

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Abstract- Based on linear absorption photopolymerization it is not possible to create 3D microstructure with resolution below the diffraction limit which depends on the wavelength of the laser beam used for photopolymerization as well as the optics used for focusing the laser beam. Using high intense laser beam with wavelength beyond the linear absorption spectrum it is possible to create structures based on two-photon photopolymerization (2PP) with resolutions below the diffraction limit. In this work we determined the two-photon absorption (2PA) cross section of a two-photon initiator (2PI) using an open-aperture Z-scan. Then we utilized the examined 2PI for creating 3D microstructures based on 2PP. The realized structures illustrate the resolution of a few 100 nm which is well below the diffraction limit of the setup used for the structuring.

Keywords: Multi-photon absorption, Nonlinear optics, Photo-polymerization, 3D microstructures

1. Introduction

Two-photon absorption (2PA) is a third-order nonlinear resonance process in which two photons are simultaneously absorbed to excite the molecule/atom from ground energy level to a higher state [1]. Since 2PA is proportional to intensity square the absorption is dramatically decreased with distance from the focal point therefore, the material modification can be confined in a very small volume around the focus by controlling the laser beam intensity. 2PA in molecular systems using near infrared ultrashort pulsed laser radiation has attracted much attention of researchers due to its potential applicability in various fields such as two-photon photopolymerization (2PP) [2-8], three-dimensional (3D) optical data storage [9-11], photonic crystals [12], [13, 14] and two-photon [15].

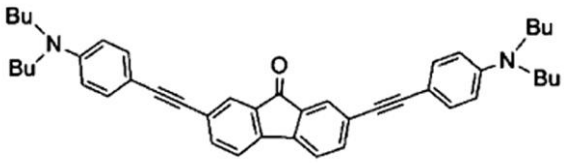
2PP is an additive manufacturing technology (AMT) where a 2PA by a photoinitiator induces photochemical reaction resulting in a resin cured inside the focal point of a pulsed laser beam leading to create a polymerized volume pixel (voxel). By scanning the focal point of the laser beam inside the resin in three dimension it is possible to produce complex 3D polymerized structures with feature sizes below the diffraction limit of the utilized optics and light source. The interest in two-photon polymerization has highly increased during the last years because of its various potential applications such as in the field of mechanical, electronic, and optical microdevices, polymer based optical waveguides, optical data storage, biomedical applications, and the like.

In this work the 2PA cross section of the different two-photon initiators (2PIs) has been measured using open-aperture Z-scan and then they have been used for creating 3D microstructures based on 2PP in order to compare their 2P activities and optimize the writing parameters of the 2PP structuring.

2. Experiments

2.1. Z-scan measurements

A novel 2PI comprising of a cross-conjugated D-π-A-π-D system (Fig. 1), which contains aromatic ketone as acceptor, synthesized in Applied Synthetic chemistry in Vienna University of Technology was chosen for investigation.



B3FL

Fig. 1: molecular structure of the examined 2PI

An open-aperture Z-scan setup [16] was used to determine the 2PA cross section of the examined compounds. In this setup an ultrashort laser system (FEMTOPOWER Compact PRO) was used. This system delivers ultrashort laser pulses with a maximum average power of approximately 800 mW (800 μJ per pulse) at a repetition rate of 1 kHz. The minimum pulse duration, estimated as the full width at half-maximum (FWHM) of a Gaussian temporal profile, is typically 25 fs. The bandwidth, estimated as the FWHM of the spectrum profile, is 41 nm and the spectrum is centered at 796 nm. The incident laser power was measured using a digital power meter prior to each measurement before the sample.

Figure 2 shows Sevaral Z-scan performed at different pulse energies to investigate the pure 2PA cross section. By fitting Eq. 1 to the mesured data the effective 2PA cross section was extracted 440 GM for this compounds showing high 2PA activity at 800 nm.

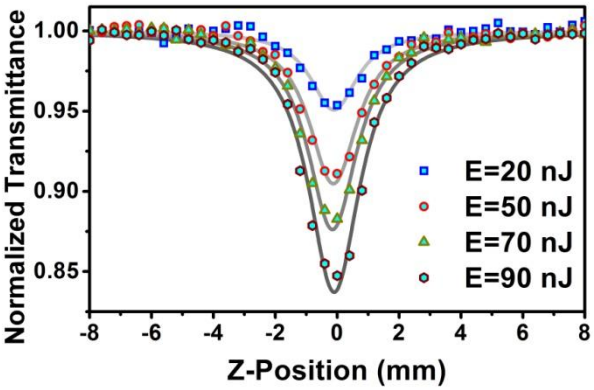
$$T(z)=\sum_{n=0}^{\infty}\frac{\left(-\left(\sigma_2\,\lambda\,N_A\,\rho\times10^{-3}/hc\right)LI_0\right)^n}{(n+1)^{3/2}\left(1+\frac{z^2}{z_R^2}\right)^n} \quad (1)$$

where, T is the normalized transmittance, L is the sample thickness, Z_R is the Rayleigh range,

z is the sample position measured with respect to the focal plane, h is the Plank constant, c is the light speed in free space, N_A is the Avogadro constant, ρ is the concentration of the examined solution in mole/lit, λ is the wavelength, σ_2 is the 2PA cross section and I_0 is the peak on-axis intensity at the focal plane given by Eq.2.

$$I_0 = 4\sqrt{\frac{\ln 2}{\pi}}\,\frac{E}{M^2 \lambda z_0 \tau} \qquad (2)$$

Where E is the pulse energy, M_2 the beam quality factor and τ is the pulse duration.



2.2. two-photon polymerization (2PP)

For the experiments, the photopolymerizable monomer was a 1:1 mixture (wt. %) of ethoxylated (20/3)-trimethylolpropanetriacrylate (ETA, Sartomer 415) and trimethylolpropane triacrylate (TTA, Genomer 1330). This monomer was added to B3FL as a 2PI. B3FL contains fluorenone as acceptor in the central part of the p 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 TPA cross section. For 2PA, photoinitiators with low fluorescence quantum yields are preferred as this is a requirement for a high population of the triplet state (triplet quantum yield), which is usually the active state of the initiators producing radicals or ions for initiating the polymerization.

Fabrication of the microstructures was done using a standard 2PP setup. Starting with the Ti-sapphire laser (max. power: 450 mW) creating 73 fs pulses with 80 MHz repetition rate the near-infrared laser beam (λ=793 nm) passes though an acousto-optic-modulator (AOM) in order the laser beam On/Off. In order to adjust the laser beam power reaching the sample a set a rotatable λ/2 waveplate in combination with a polarizing beam-splitter was used. The laser beam focus was scanned inside the resin using a three high precision air bearing translation stages. A CCD camera was uses to live monitoring the polymerization process. After the polymerization is finished the created structure was developed in ethanol to remove the residual monomer form the cured polymer.

Figure 3 show two microstructures created based on 2PA. These models reveal the capability of such a technique illustrating the submicron resolution.

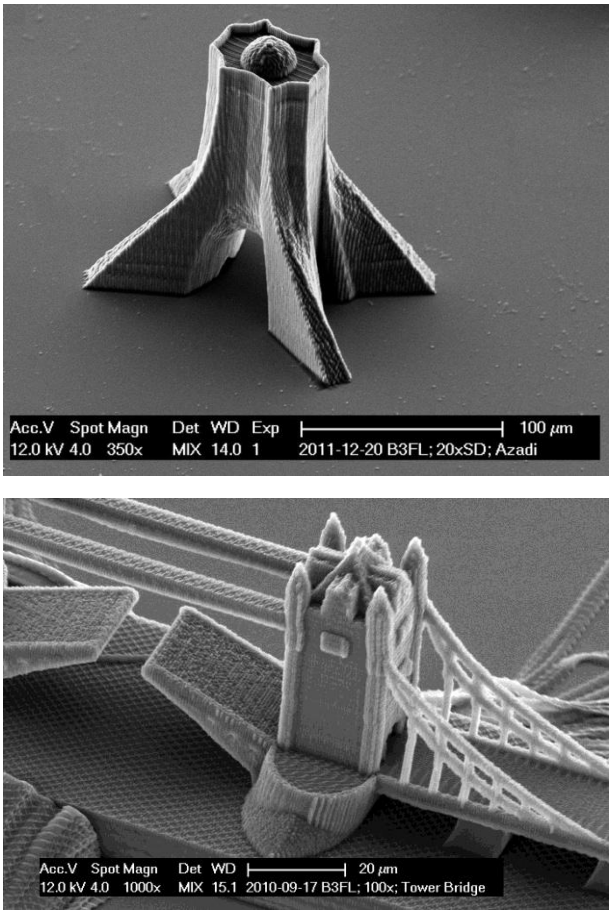


Fig. 3. 3D polymeric microstructures. The width of polymeric lines is in the order of few 100 nm.

3. Conclusion

Using the open-aperture Z-scan technique we determined the 2PA cross section of B3FL which showed a high cross section of 440 GM. Utilizing this high active 2PI we managed to perform two-photon photopolimerization to create 3D microstructures with resolution well below the diffraction limit.

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