Complex microstructures fabricated via two-photon absorption polymerization

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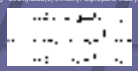
Abstract

Two-photon absorption (2PA) processes have attracted much interest due to their potential applications in different fields of science. The quadratic dependence of the two-photon absorption rate on laser irradiance allows spatial confinement of the excitation, a feature that can be exploited in applications ranging from three-dimensional optical storage, two-photon fluorescence imaging, two-photon photodynamic therapy, and microfabrication via two-photon induced polymerization. Two-photon initiated polymerization allows the fabrication of sophisticated microstructures for optical circuitry, optical data storage, three-dimensional micromechanical actuators and photonic crystals. Typically, molecules of low molecular weight, called photoinitiators, are added to the monomer to start the photopolymerization process. Here we study the 2PA cross-section of Lucirin TPO-L, which has recently been shown to be a very efficient polymerization initiator under two-photon excitation. We fabricated complex microstructures using Lucirin TPO-L and acrylate resin. Finally, we performed molecular orbital calculations using semi-empirical methods to relate the nonlinear optical properties of this compound to its molecular structure.

Resin composition for 2PA polymerization

SR499 ethoxylated(6) trimethyl-lolpropane triacrylate



• reduces structural shrinkage

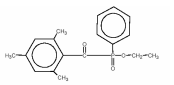
SR368 tris(2-hydroxyethyl) isocyanurate triacrylate

• confers hardness to the structure

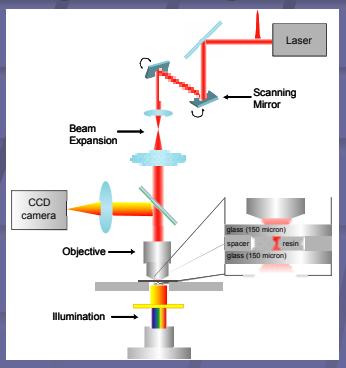
Photoinitiator

Lucirin TPO-L

ethyl-2,4,6-Trimethylbenzoylphenylphosphinate



Experimental setup for 2PP micro-fabrication

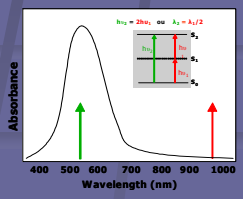


Ti:sapphire laser oscillator

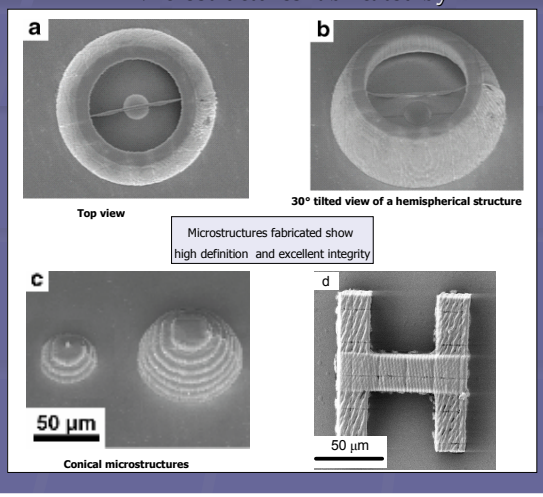
- 130 fs
- 800 nm
- 76 MHz
- 20 mW

Objective

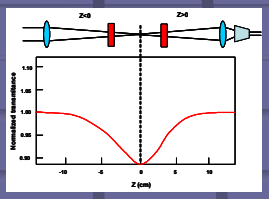
40 x
0.65 NA



Microstructures fabricated by 2PP



Z-scan technique for nonlinear optical characterization



Typical curve of 2PA. Curve is fitted by:

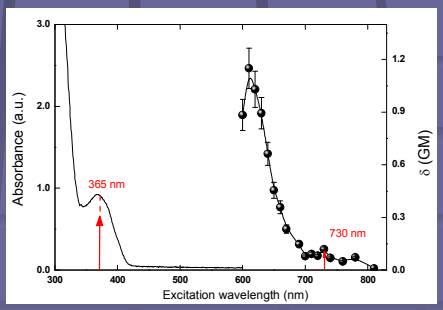
$$TN(z)=\frac{T(z)}{LT}=\frac{1}{\sqrt{\pi}q_0(z,0)}\int_{-\infty}^{\infty}\ln\left[1+q_0(z,0)e^{-\tau^2}\right]d\tau$$

Normalized Transmittance:

$$q_0(z,t)=\beta I_0(t)L\left(1+z^2/z_0^2\right)^{-1}$$

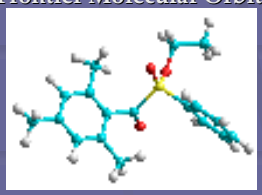
$$\delta=h\nu\beta/N$$

Two-photon absorption (2PA) espectrum of Lucirin T-POL at several λ´s



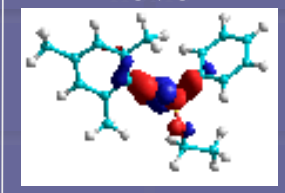
- Data obtainde by plotting the NT of the Z-scan curves for the distinct excitation wavelengths.
- Nonlinearity increases dramatically in regions closer to the linear absorption – Resonant Enhancement
- A subtle feature at 730 nm in the 2PA espectra can be observed, which is reprsents the same one observed in the linear absorption (given by selection rules).

Molecular structure and Frontier Molecular Orbitals of Lucirin T-POL

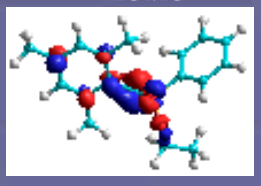


The molecular geometry was optimized with *ab initio* method using a medium basis set (6-31G*)

HOMO



LUMO



Frontier molecular orbitals were calculated using ZINDO/1 (HiperChem 7.5). Configuration interaction (CI) calculations included single excited configurations – 40 (occupied) x 40 (unoccupied)

Conclusions

In conclusion, we measured the two-photon absorption cross-section of the photoinitiator Lucirin TPO-L and established a relation between the molecular structure of this photoinitiator and its nonlinear optical properties. We fabricated microstructures with excellent structural integrity and definition, demonstrating the potential of Lucirin TPO-L for two-photon polymerization microfabrication. This work was carried out with the financial support from FAPESP (Brazil), the National Science Foundation under contract DMI-0334984 and the Army Research Office under contract W911NF-05-1-0471.