

Microfabricação em materiais poliméricos usando laser de femtossegundos

Prof. Cleber R. Mendonça



<http://www.fotonica.ifsc.usp.br>

University of Sao Paulo - Brazil



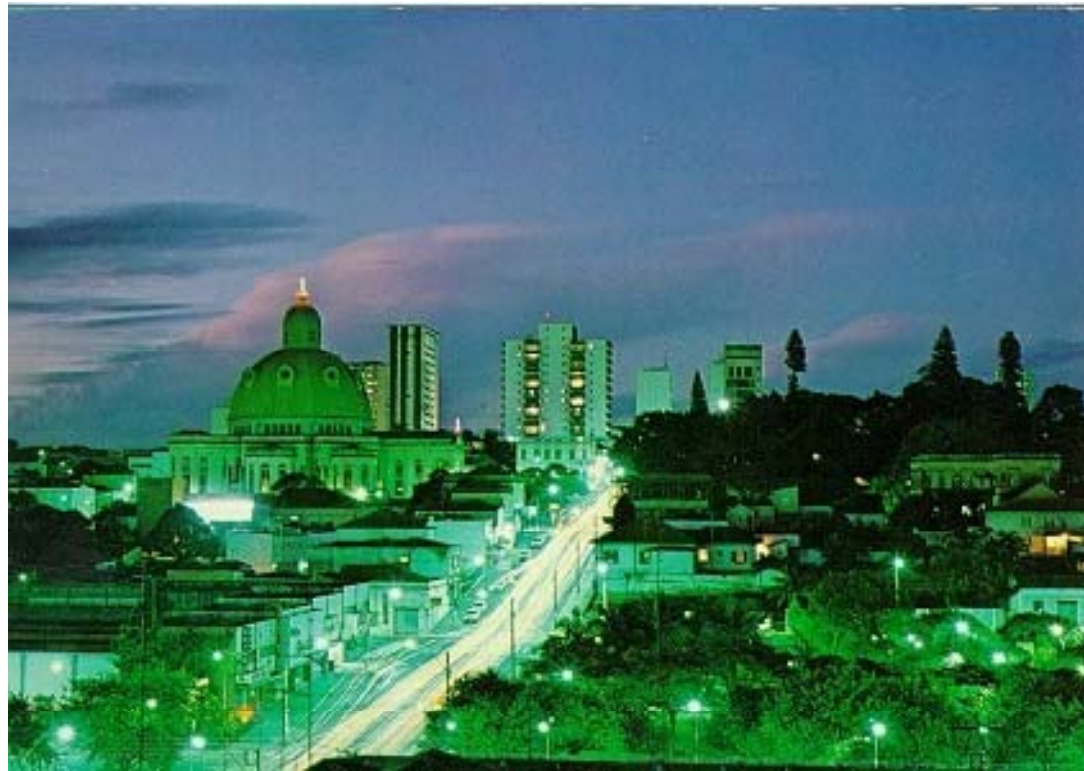
students 77.000
52.000 undergrad.
25.000 grad.
employers 15.000
professors 6.000

- Sao Paulo
- **Sao Carlos** (9.000)
- Ribeirao Preto





University of Sao Paulo – in Sao Carlos

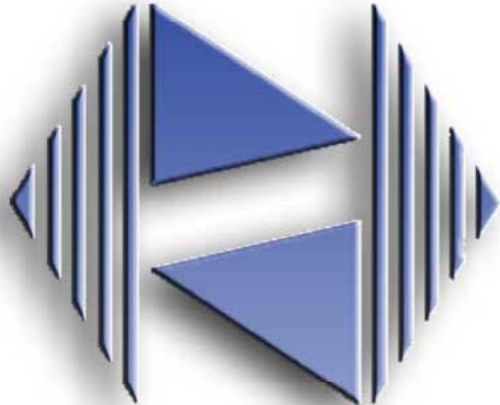




University of Sao Paulo – in Sao Carlos



Instituto de Física de São Carlos



Professors: 80

Employers: 180
(technical and administration)

Students: 450 (undergrad)
100 (master)
140 (phD)

Several research areas in Physics
and Material Sciences



Photonics Groups



The purpose of the Photonics Group is to develop fundamental science and applied technology *in Optics and Photonics* (founded in 2003)

4 – Professor
2 – Researchers
1 – Technician
1 – Administrative

2 – Post docs
10 – PhD students
6 – Master students
5 – Undergrad students

Some of the research areas

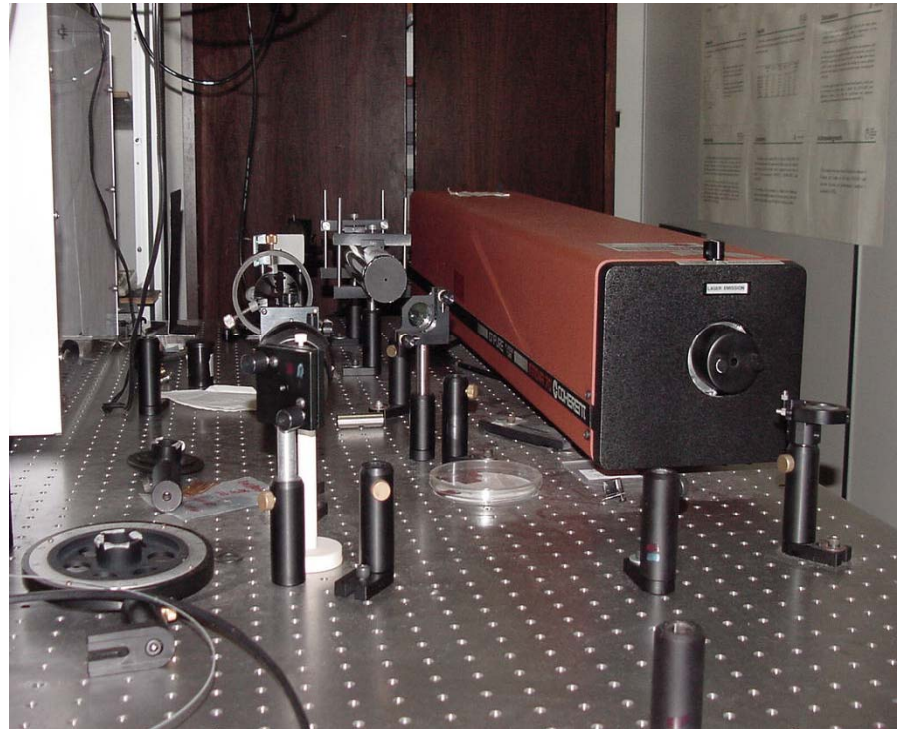
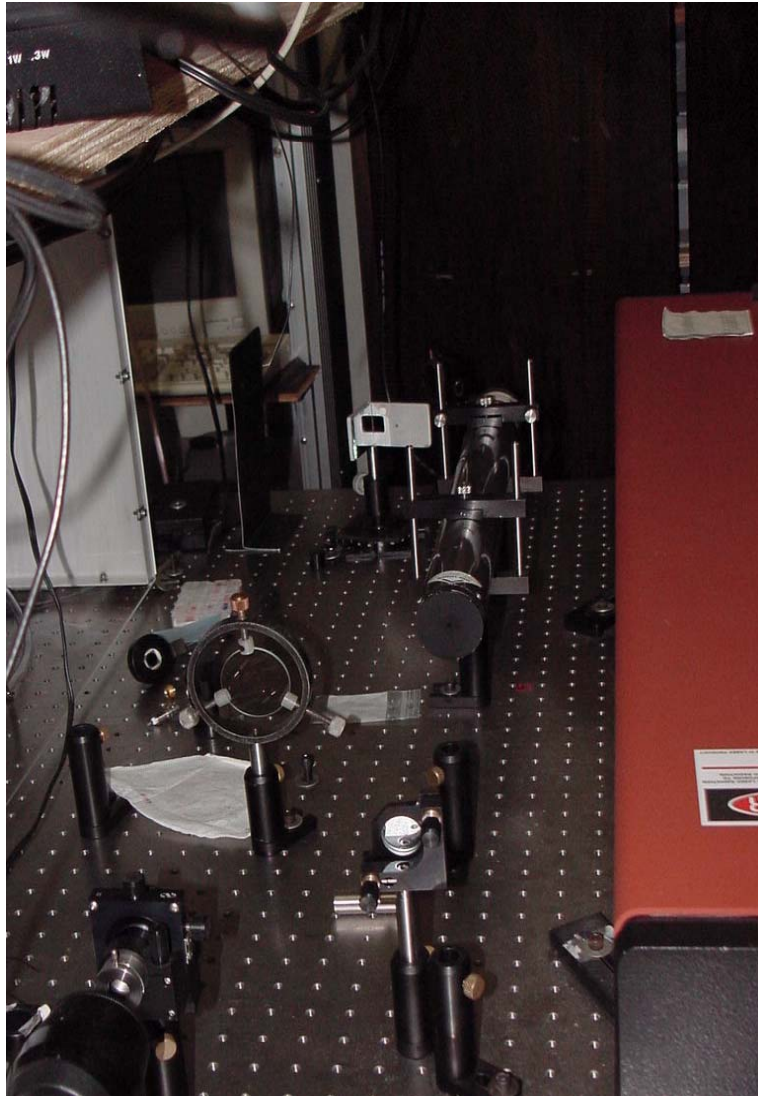
- Nonlinear optics
- Coherent control of light matter interaction
- fs-laser microfabrication and micromachining
- Optical spectroscopy
- Optical storage

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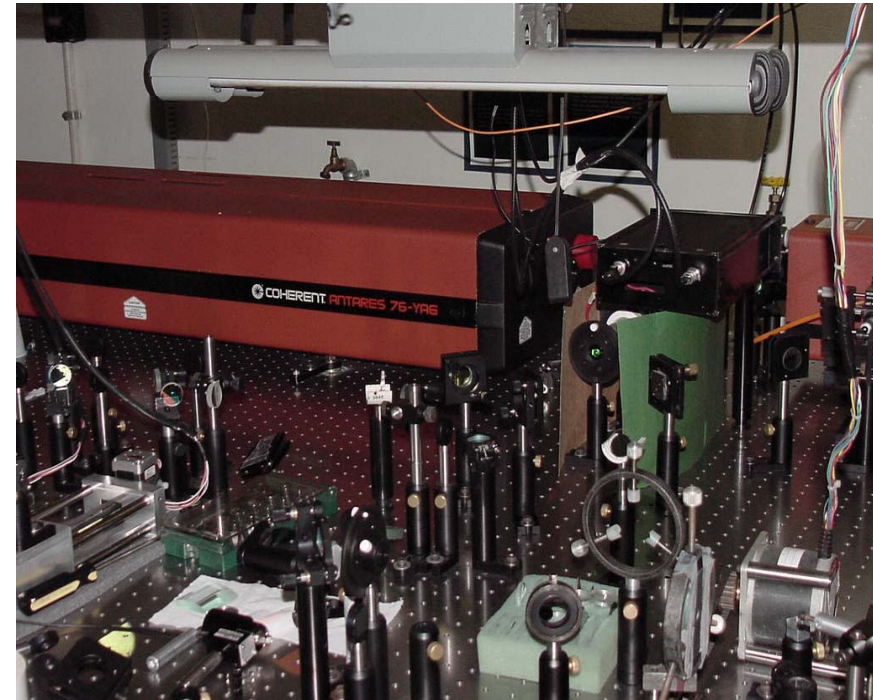
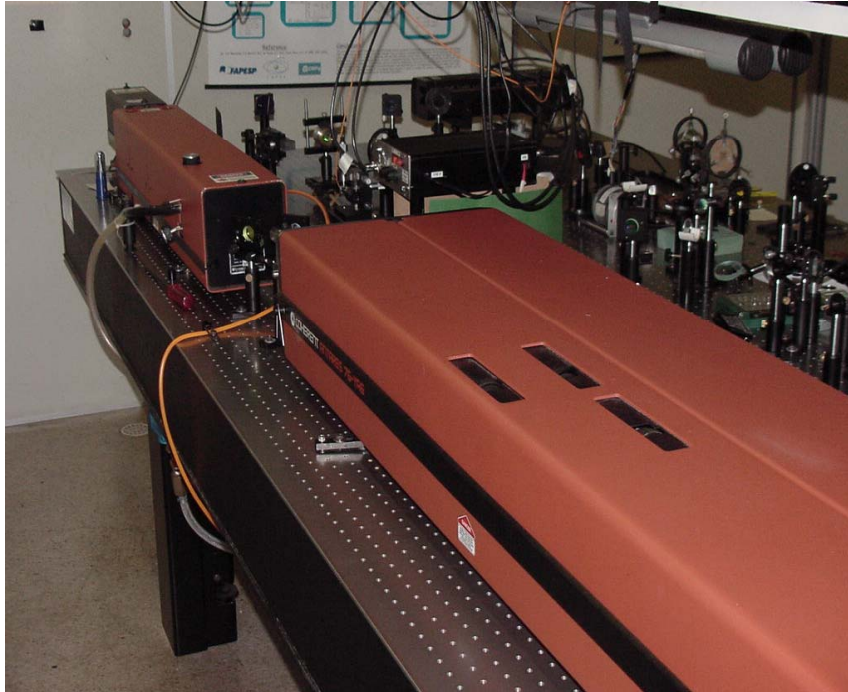
research areas

- study of optical nonlinearities in organic materials
- optical storage and surface relief gratings in azopolymers
- coherent control of light matter interaction
- fs-laser microfabrication

cw laser



Picosecond laser



- ✓ Laser Nd:YAG
- Qswitched/modelocked
 - ✓ 532nm and 1064 nm
 - ✓ 100 ps

150-fs amplified laser system



- ✓ Amplifier
Ti:safira
- ✓ 775 nm
- ✓ 150 fs
- ✓ 800 μ J

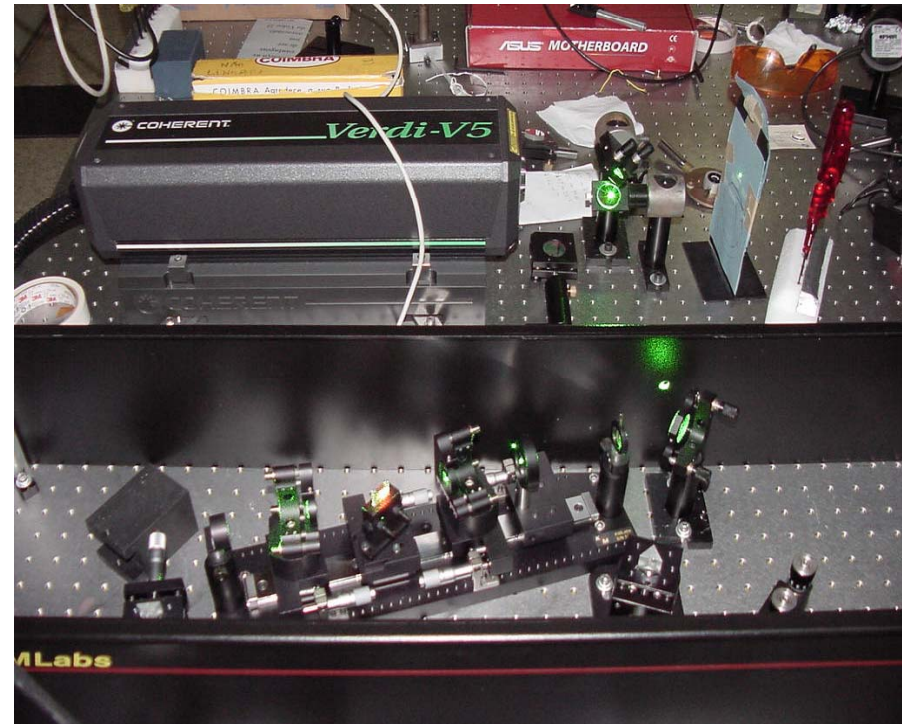
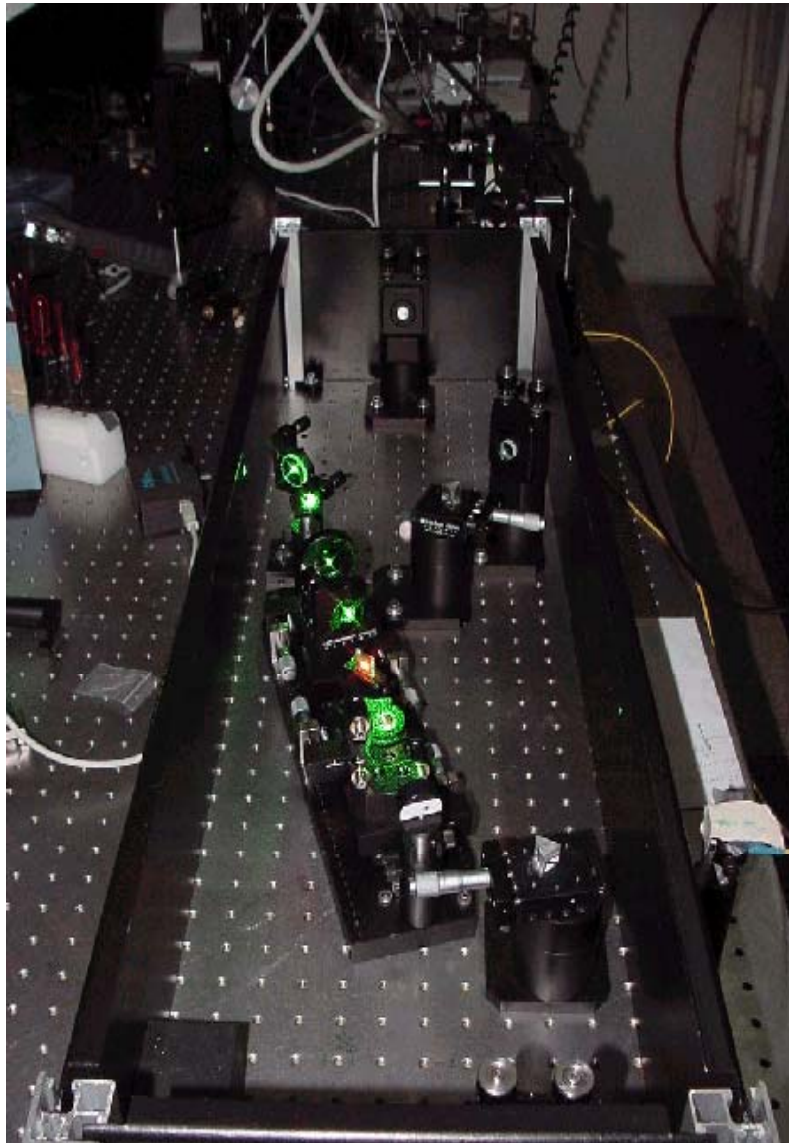
Optical Parametric Amplifier



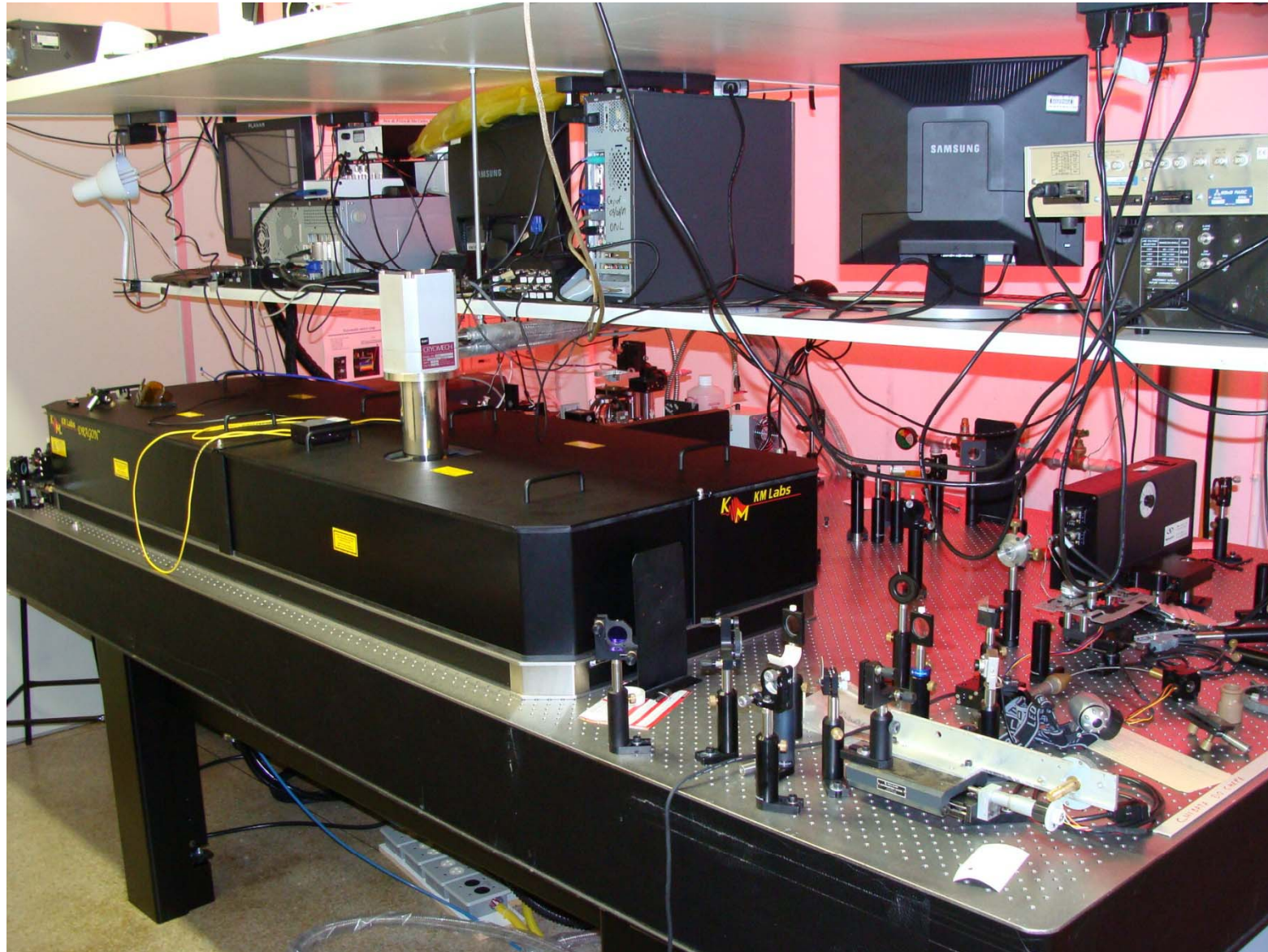
TOPAS

- ✓ *pumped - Laser Clark*
- ✓ *460 - 2600 nm*
- ✓ *≈ 120 fs*
- ✓ *20-60 μ J*

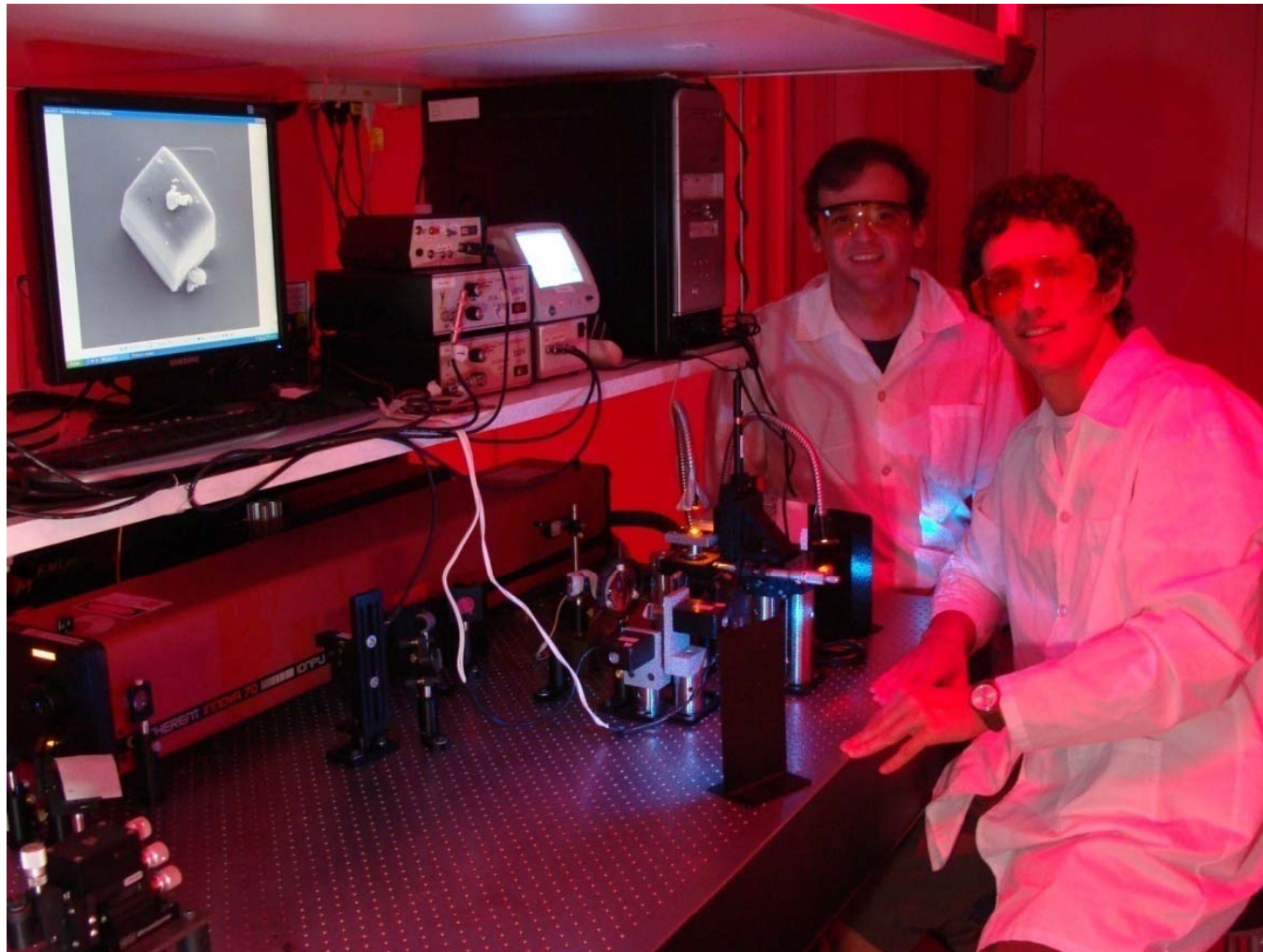
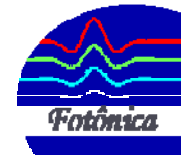
15-fs laser



40-fs amplified laser system



microfabrication lab



research areas

- study of optical nonlinearities in organic materials
- optical storage and surface relief gratings in azopolymers
- coherent control of light matter interaction
- fs-laser microfabrication

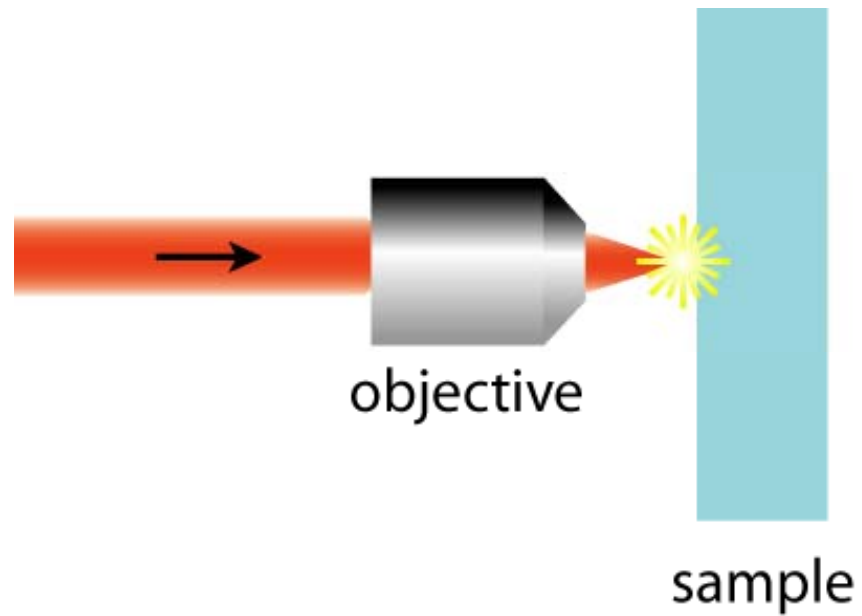
fs-laser microfabrication

Prof. Dr. Cleber R. Mendonca

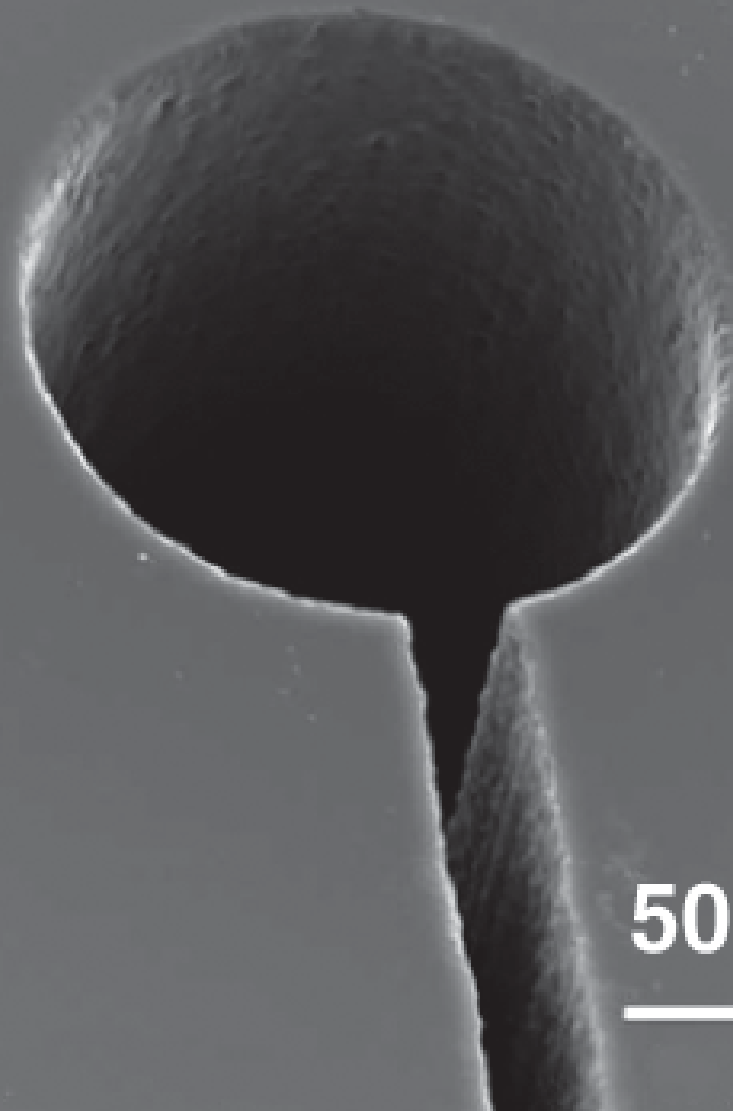


laser microfabrication

focus laser beam on material's surface



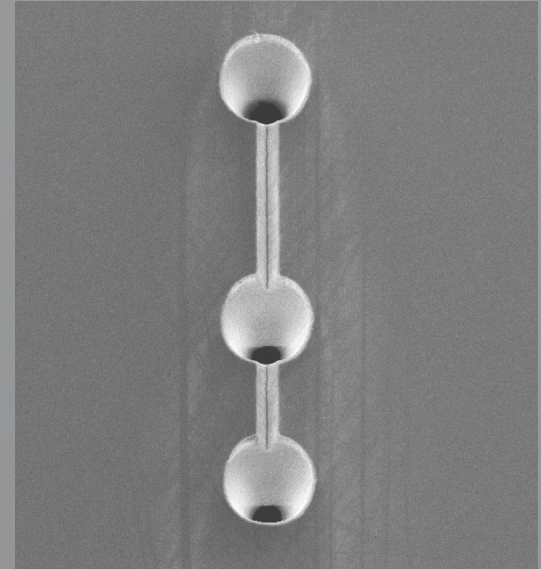
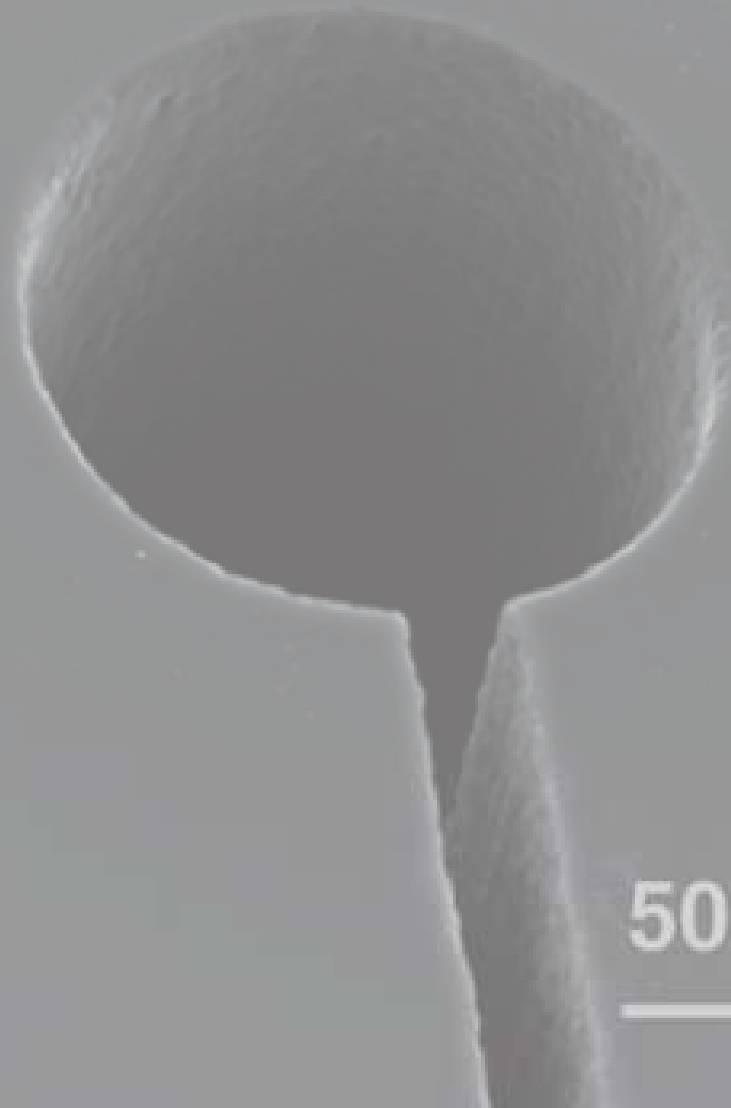
laser microfabrication



50 μm



laser microfabrication

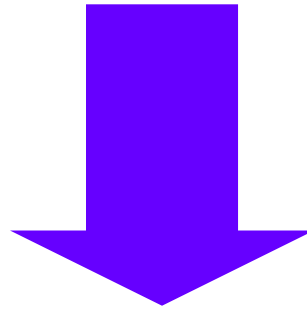


laser microfabrication

surface microstructuring

fs-micromachining

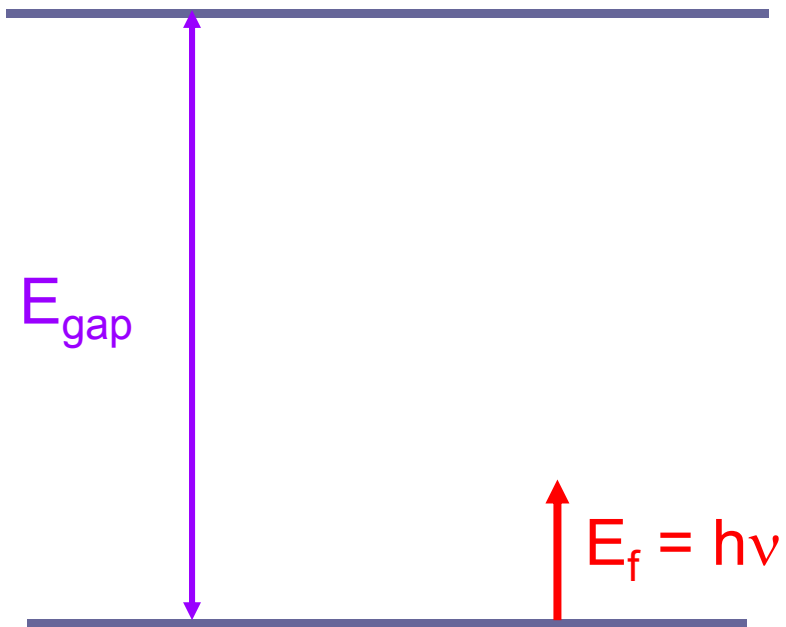
photon energy < bandgap



nonlinear interaction

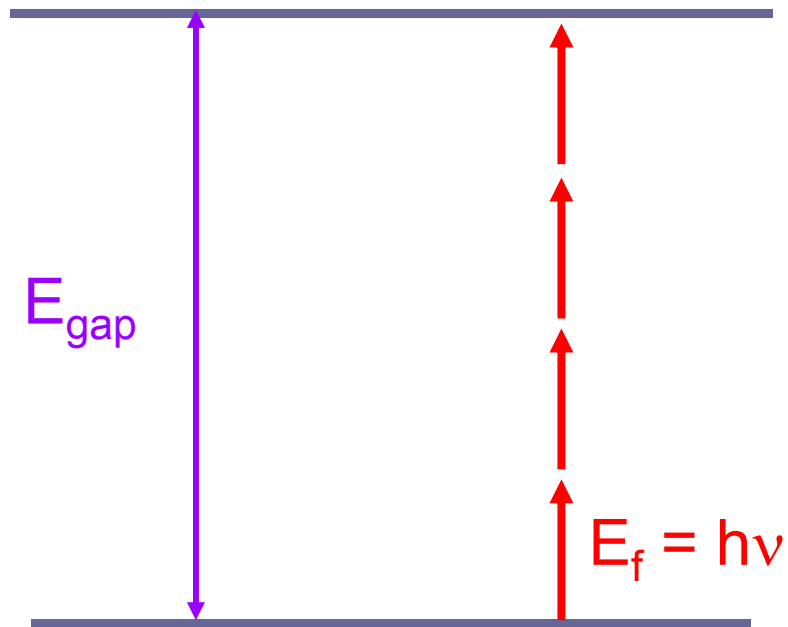
fs-micromachining

nonlinear interaction



fs-micromachining

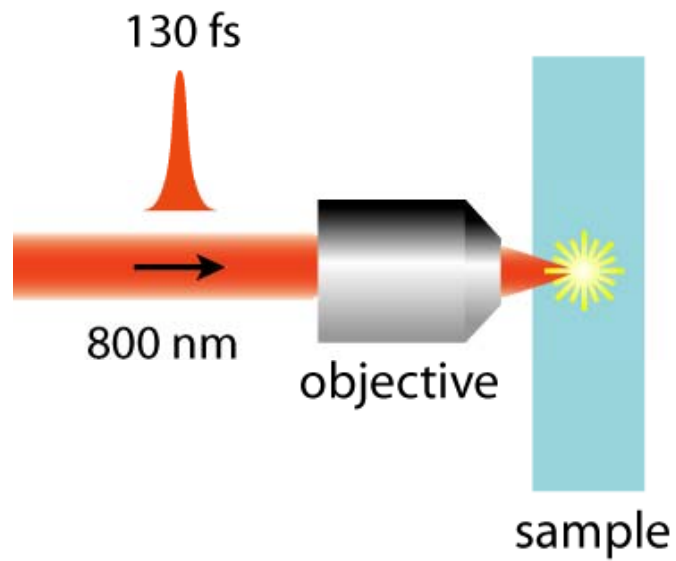
nonlinear interaction



multiphoton absorption

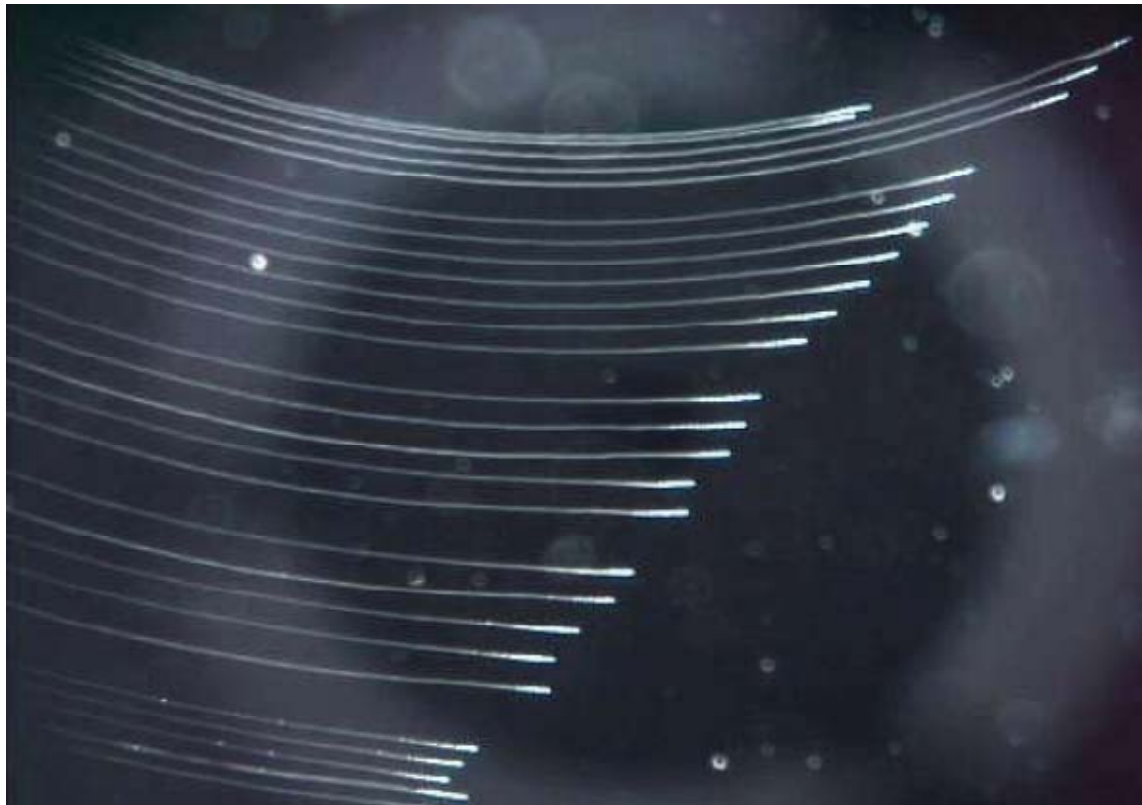
fs-laser microfabrication

focus laser beam inside material



fs-laser microfabrication

curved waveguides inside glass



fs-micromachining

it is important to understand the nonlinear interaction, as well as the nonlinear response of materials

Outline

Introduction to microfabrication/micromachining

fs-micromachining

- microstructuring MEH-PPV

- waveguides in azopolymers

- superhydrophobic surfaces

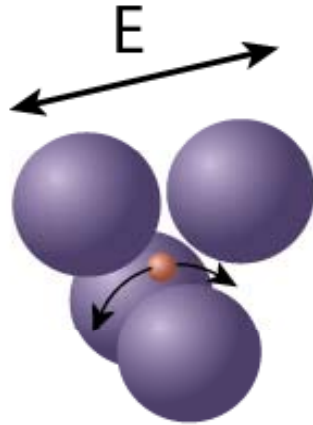
two-photon polymerization

- birefringent microstructures

- fluorescent microstructures

- biocompatible microstructures

Nonlinear optics



anharmonic oscillator

high light intensity

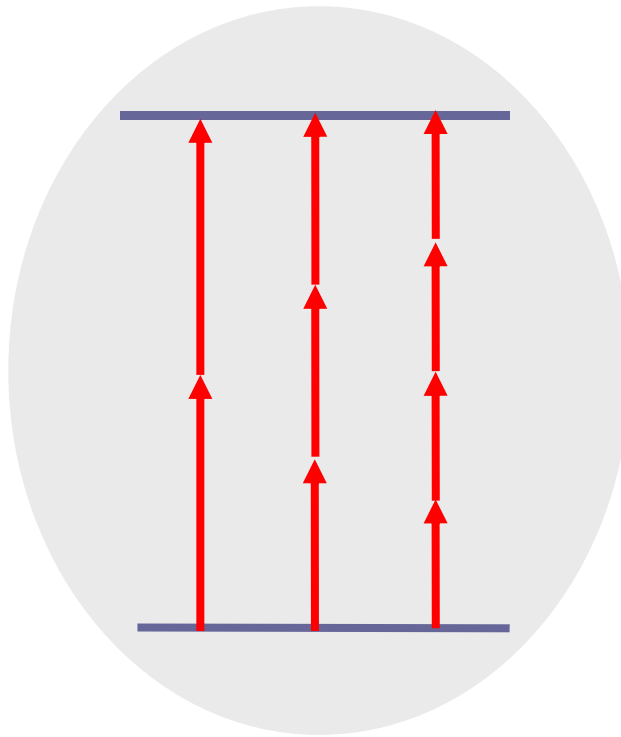
$$E_{\text{rad.}} \sim E_{\text{inter.}}$$

nonlinear polarization response

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$$

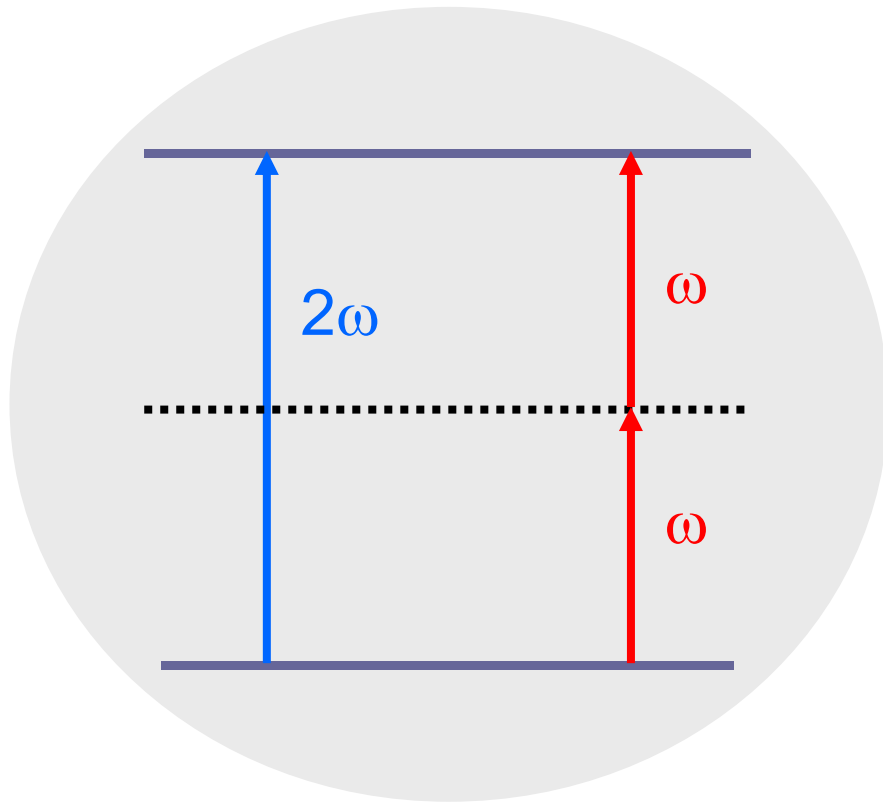
multi-photon absorption

$$\chi^{(3)}, \chi^{(5)}, \chi^{(7)}, \dots$$



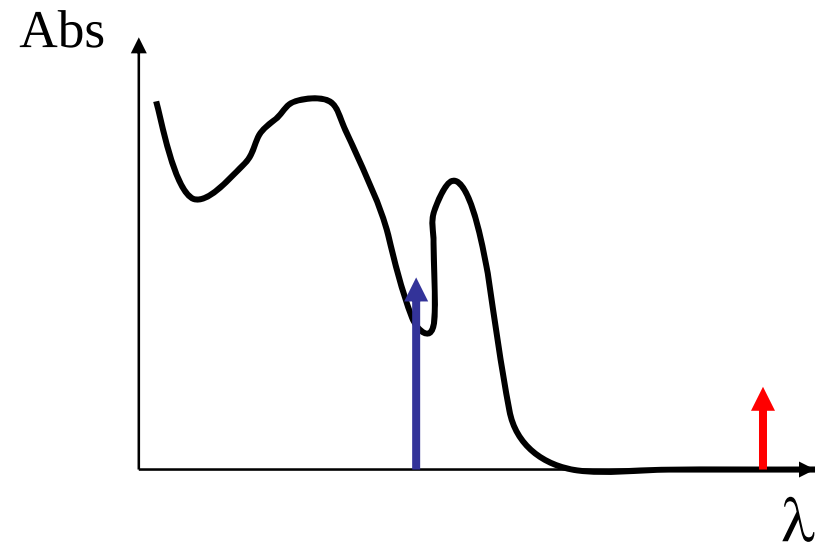
$$\alpha = \alpha_0 + \beta I + \alpha_3 I^2 + \alpha_4 I^3 + \alpha_5 I^4 + \dots$$

two-photon absorption



$$\alpha = \alpha_0 + \beta I$$

Third order processes $\chi^{(3)}$



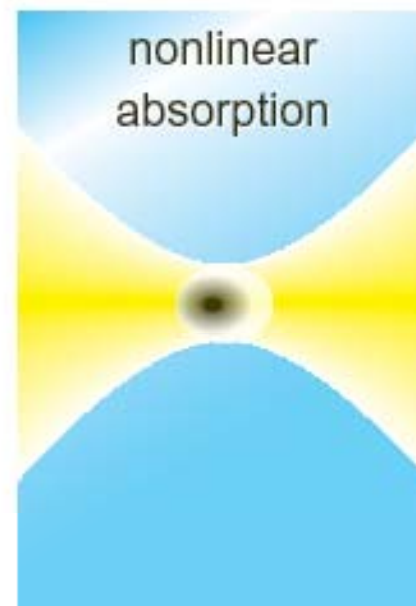
two-photon absorption

Nonlinear interaction provides spatial confinement of the excitation

fs-microfabrication



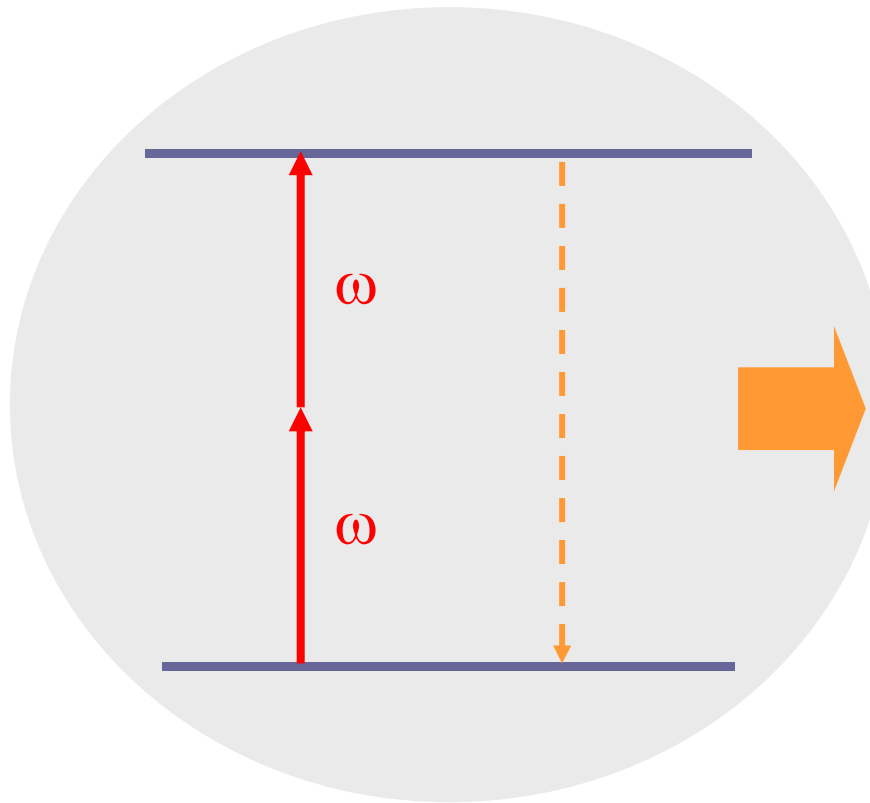
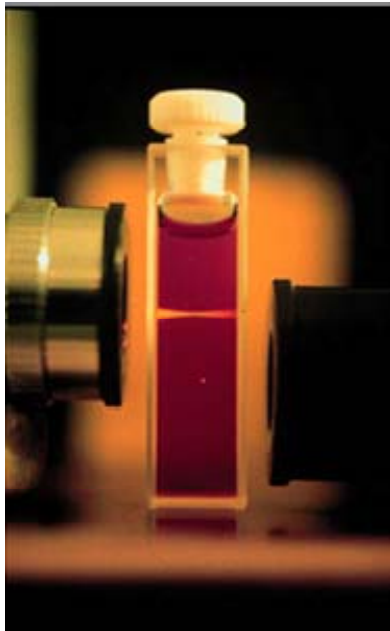
$$\alpha = \alpha_0$$



$$\alpha = \alpha_0 + \beta I$$

two-photon fluorescence

$$\alpha = \alpha_0 + \beta I$$

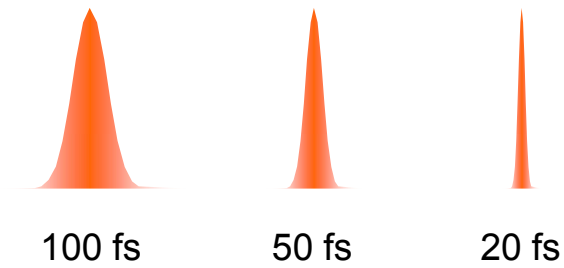


light emission
fluorescence

spatial confinement of excitation

femtosecond pulses

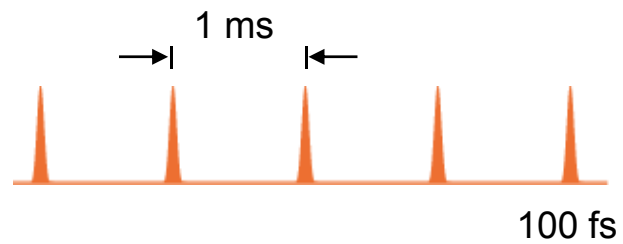
Ti:Sapphire lasers



$1 \text{ fs} = 10^{-15} \text{ s}$

Repetition rate

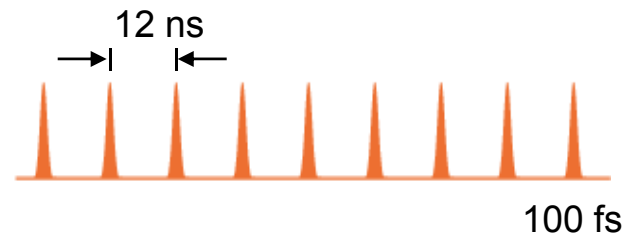
1 KHz



Energy

mJ

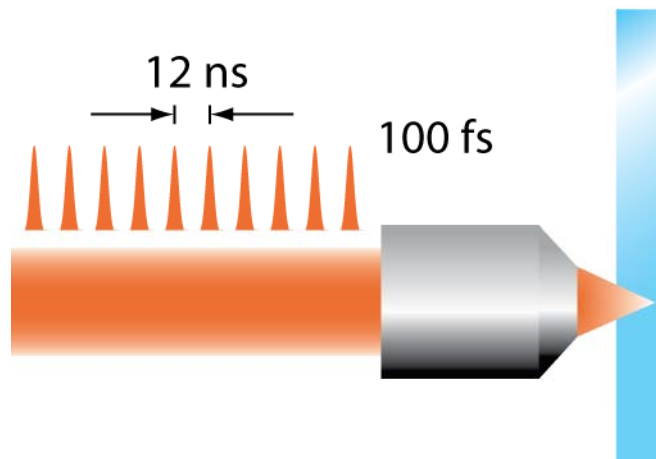
86 MHz



nJ

fs-pulses for micromachining polymers

Oscillator: 80 MHz, 5 nJ

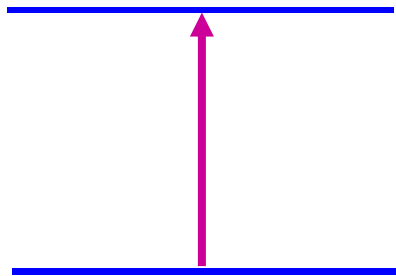


heat diffusion time: $t_{\text{diff}} \sim 1 \mu\text{s}$

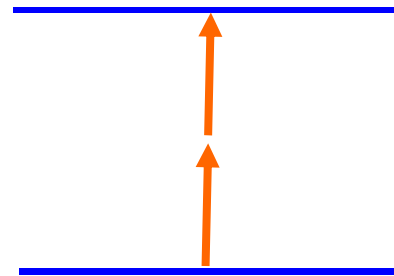
cumulative

fs-microfabrication

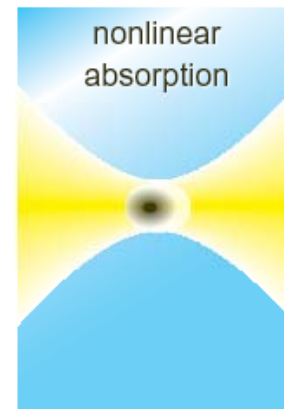
linear *versus* nonlinear absorption



$$\alpha = \alpha_0$$



$$\alpha = \alpha_0 + \beta I$$



two main techniques

1

fs-laser micromachining

ablation

structural modification

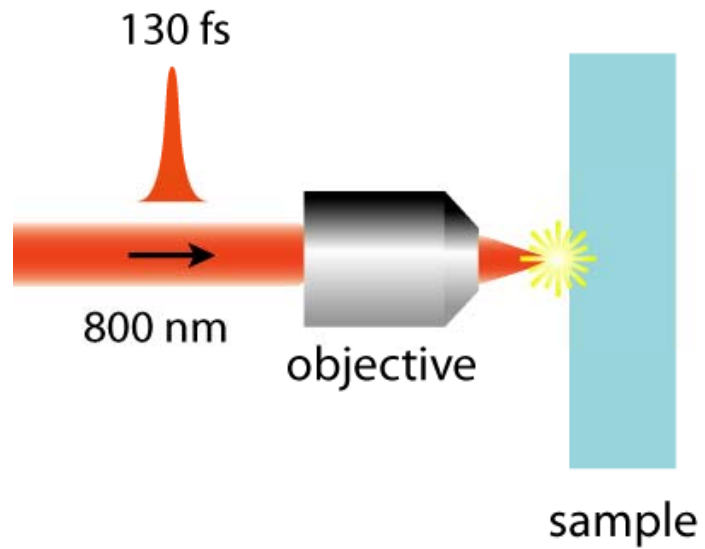
2

microfabrication via
two-photon polymerization

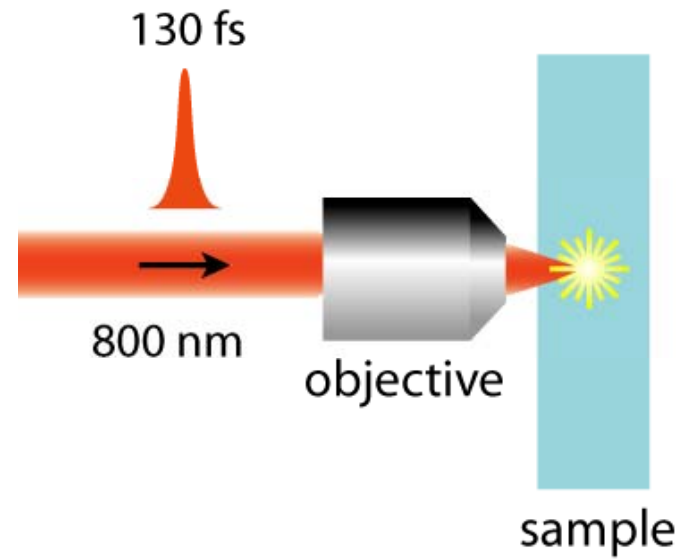
1

fs-laser micromachining

Surface

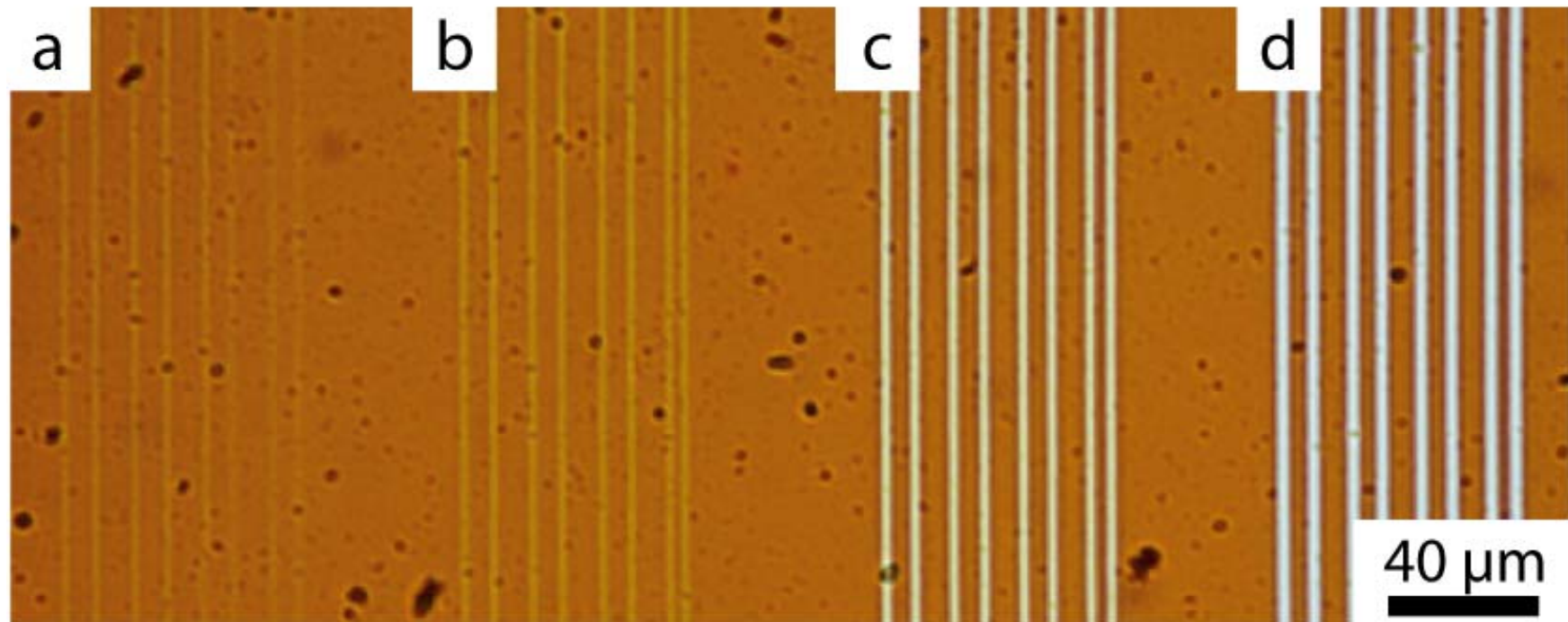


Volume



Micromachining the conductive polymer MEH-PPV

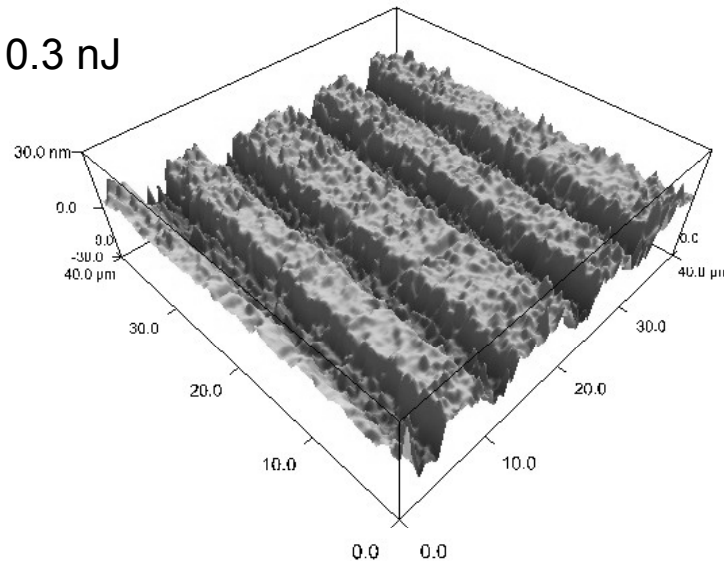
optical microscopy



a: 0.07 nJ
b: 0.14 nJ
c: 0.34 nJ
d: 0.68 nJ

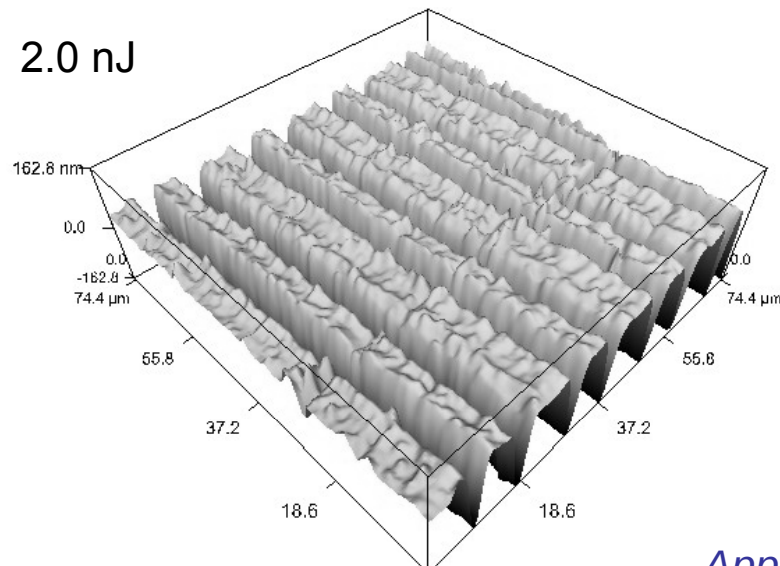
Micromachining the conductive polymer MEH-PPV

a 0.3 nJ

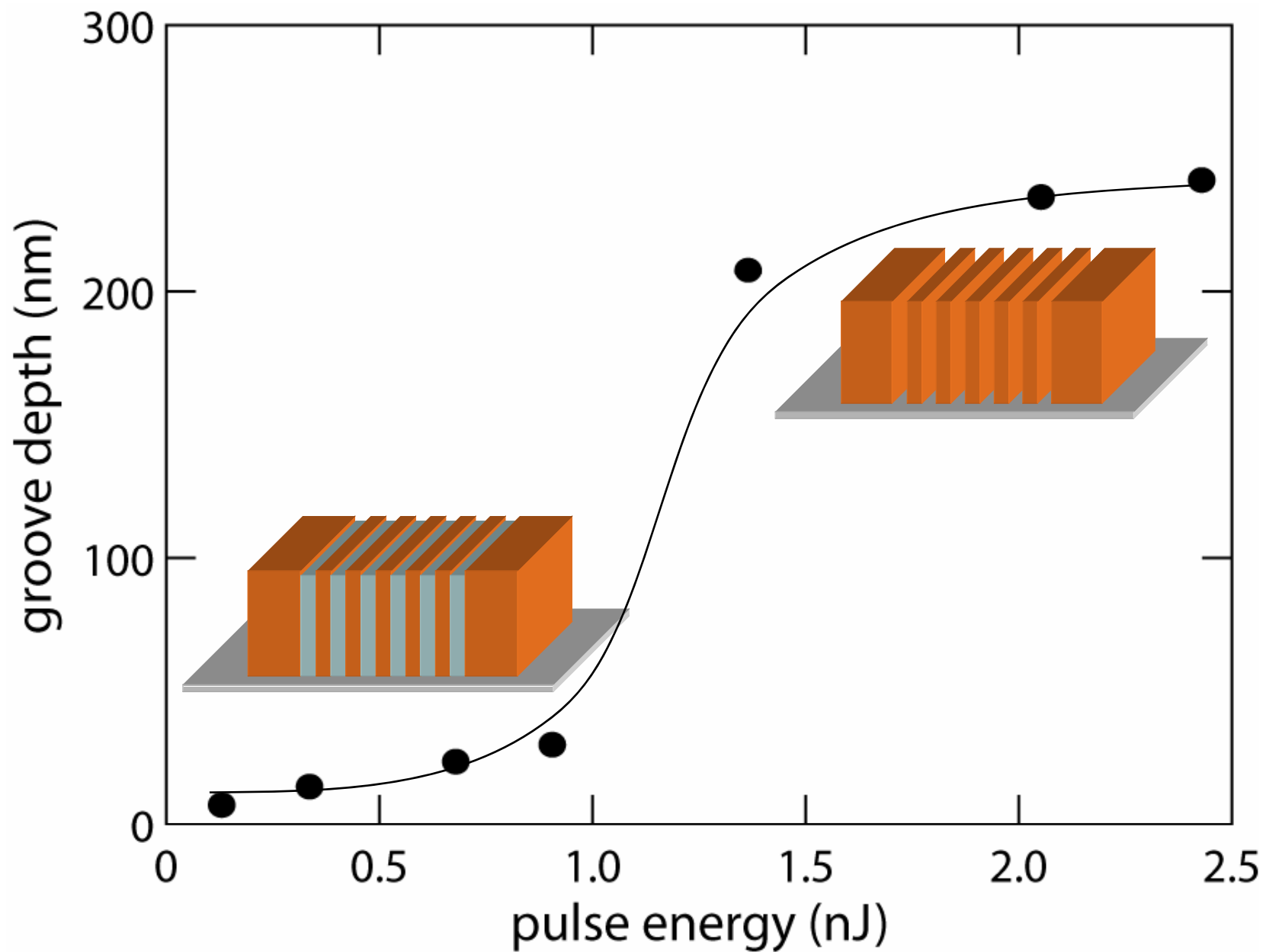


atomic force microscopy

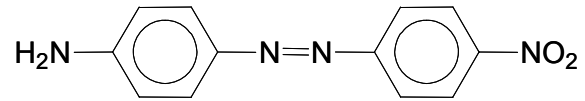
b 2.0 nJ



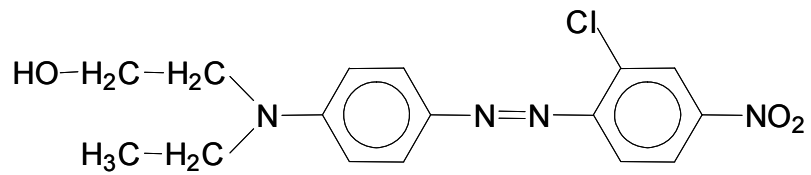
Micromachining the conductive polymer MEH-PPV



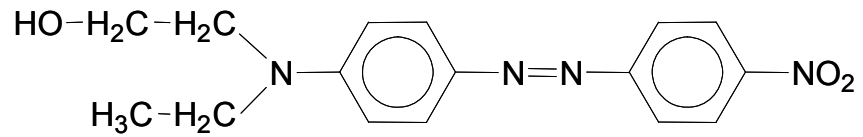
Waveguides in azo-polymers



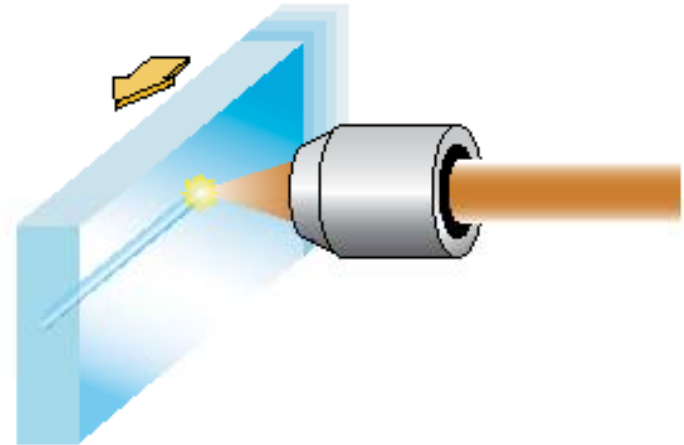
DO3



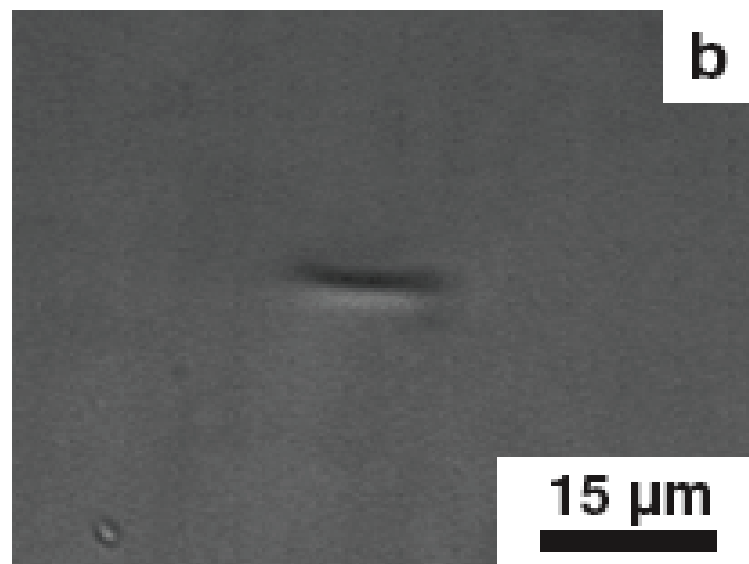
DR13



DR1

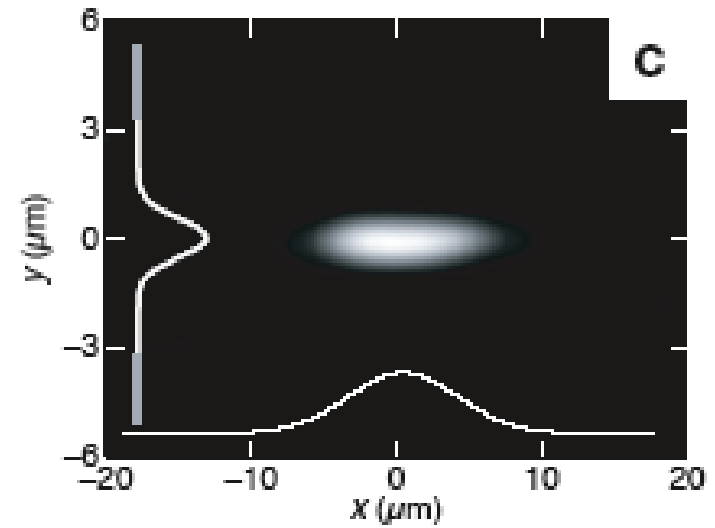
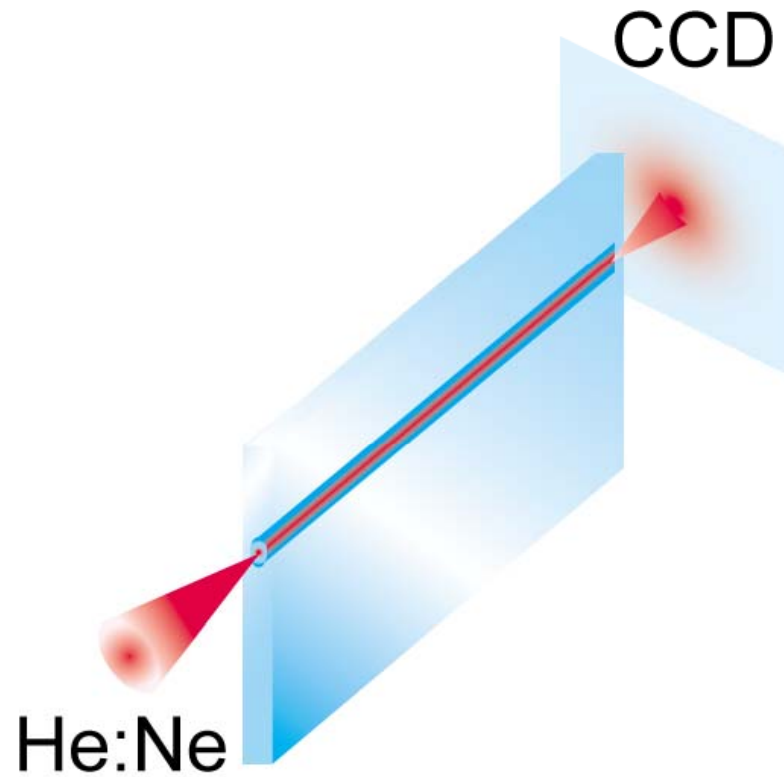


Waveguides in azo-polymers



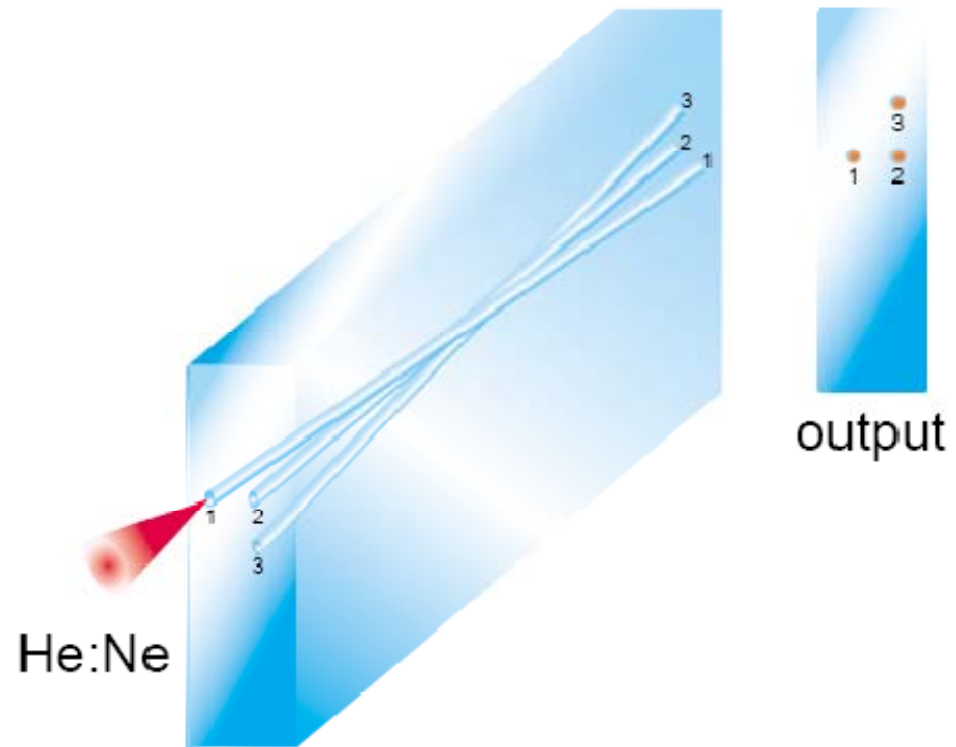
- (a) Optical microscope image of the waveguides micromachined (PMMA/DR1)
- (b) Cross-sectional view of the waveguides

waveguides in azo-polymers

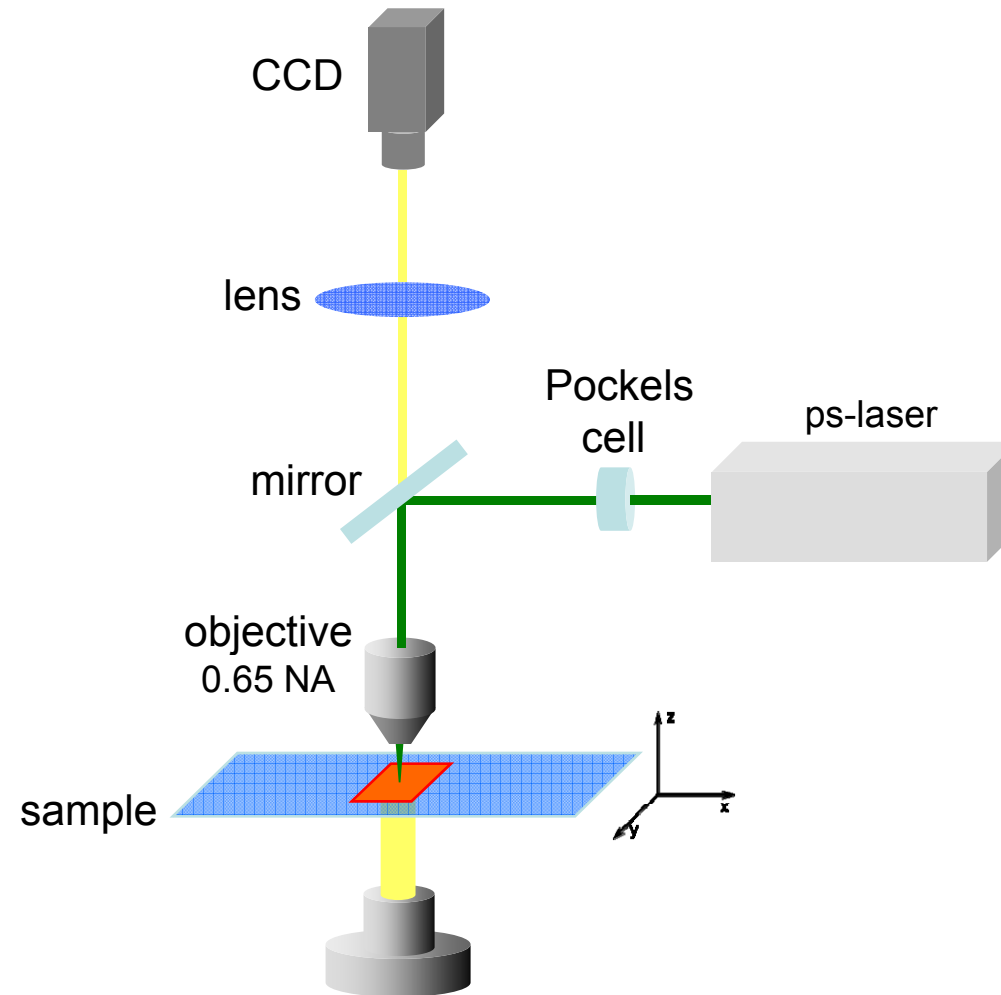


(c) Output image of the mode profile of 632.8-nm light coupled through the waveguide

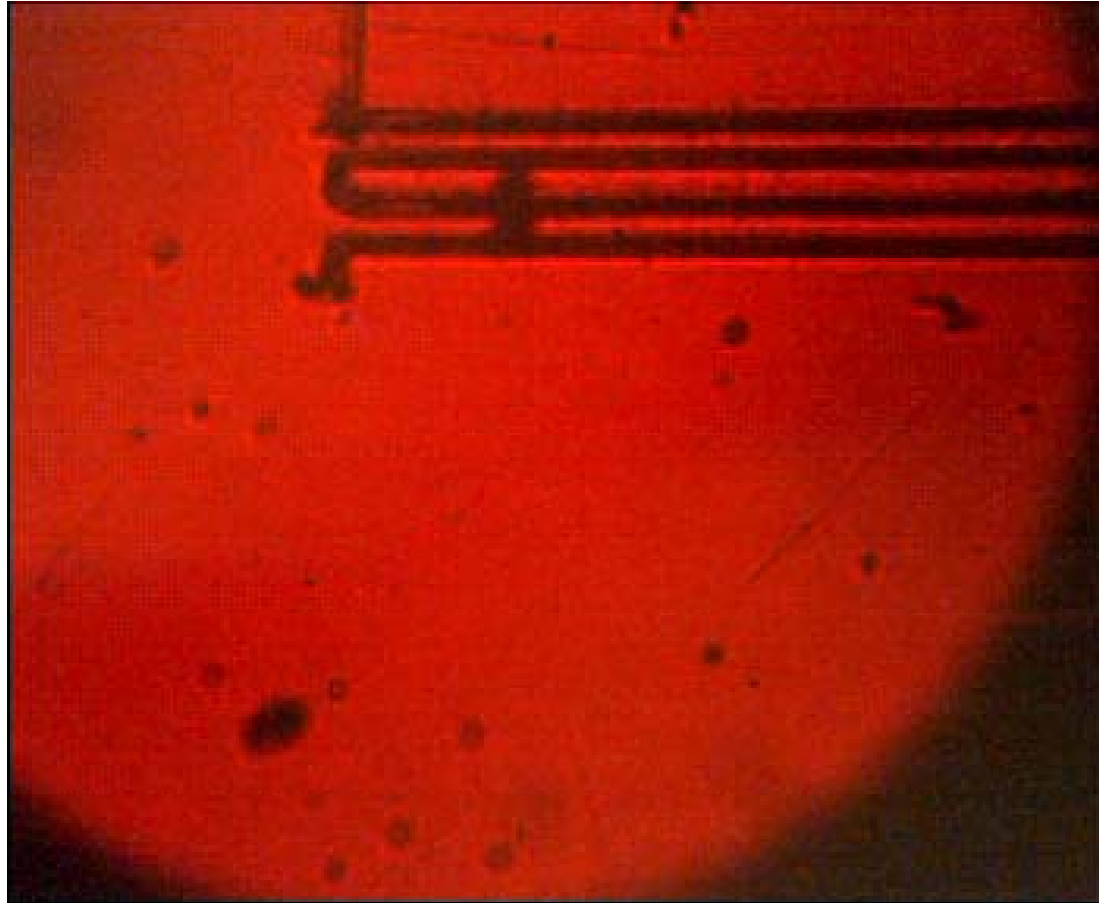
3D wave splitter



microstructuring polymer: super hydrophobic surface

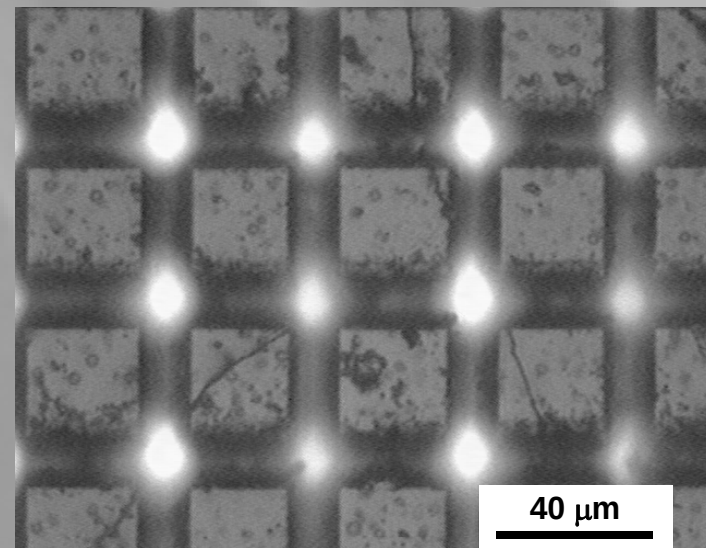
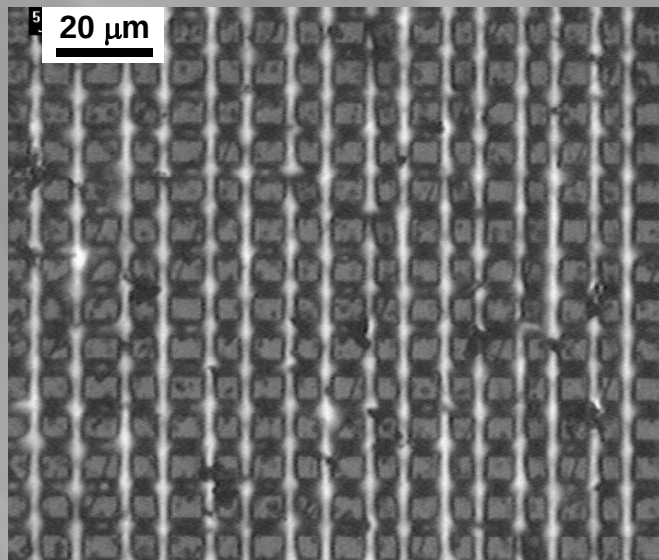


microstructuring polymer: super hydrophobic surface

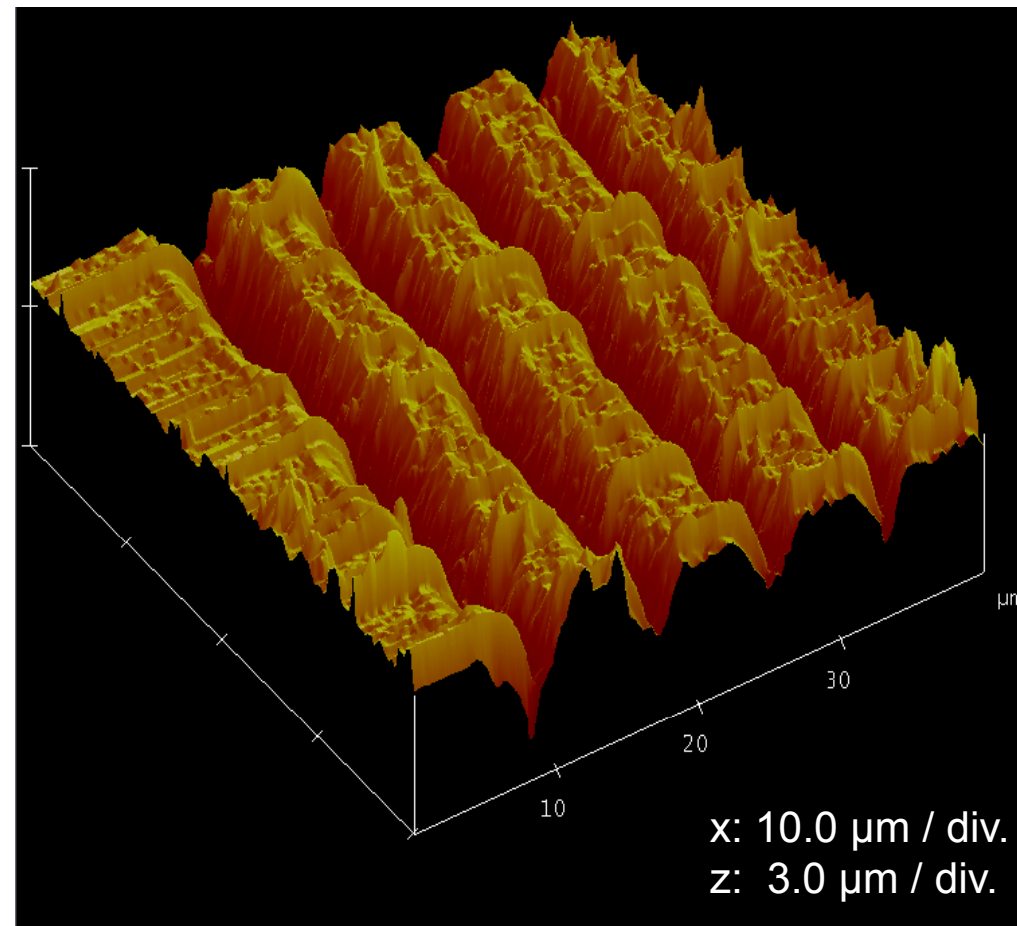


laser microfabrication

examples of fabricated surfaces



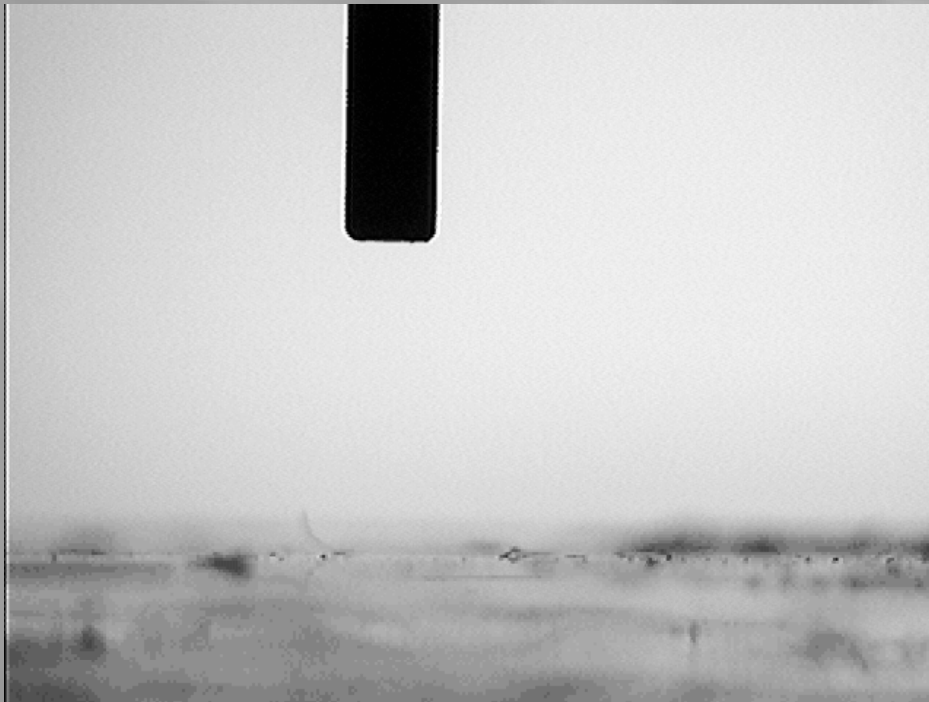
microstructuring polymer



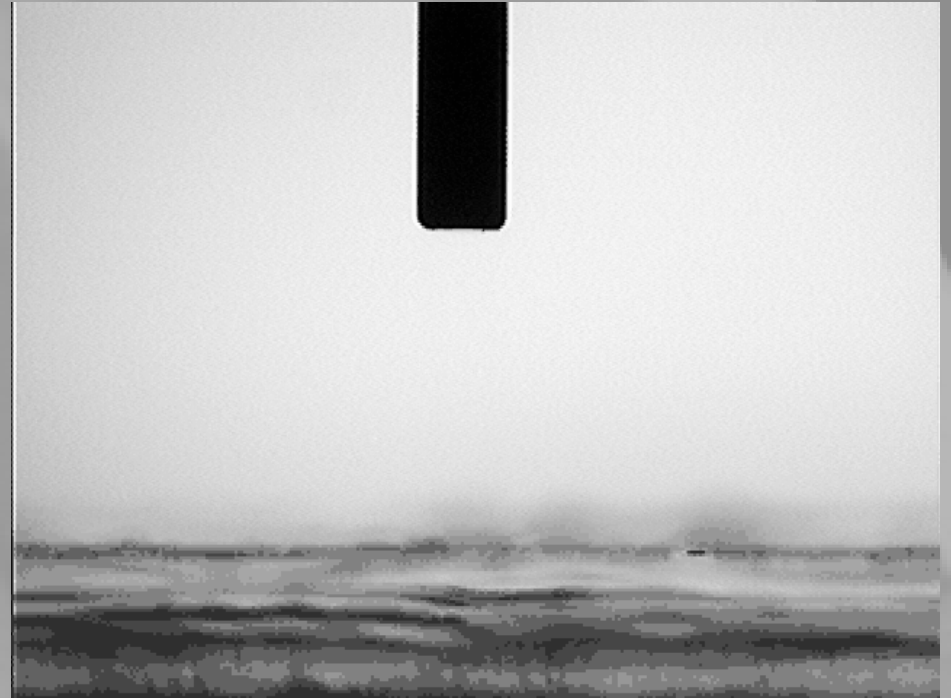
width and depth control

laser microfabrication

Superhydrophobic surfaces

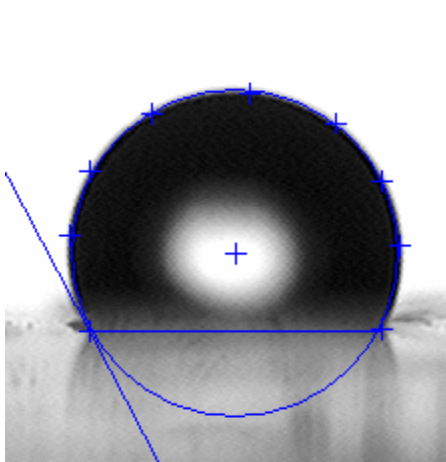


flat surface



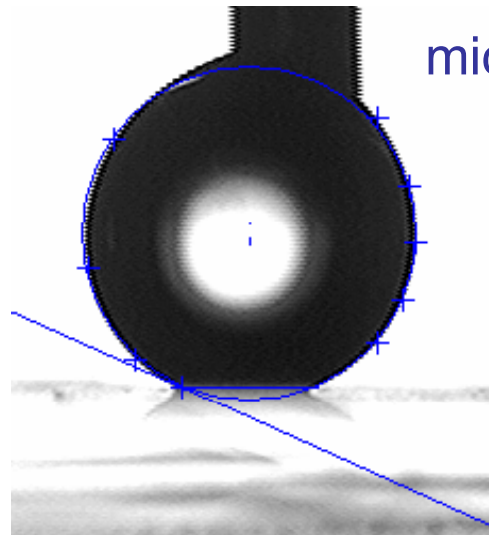
microstructured surface

microstructuring polymer



flat surface

$$\theta = 118^\circ$$



microstructured surface

$$\theta = 160^\circ$$

fs-laser microfabrication

Novel concept:

build a microstructure using fs-laser and nonlinear optical processes

two-photon polymerization

applications

- micromechanics
- waveguides
- microfluidics
- biology
- optical devices

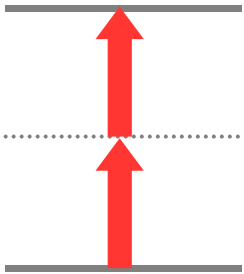
2

Two-photon polymerization

Monomer + Photoinitiator $\rightarrow$ Polymer

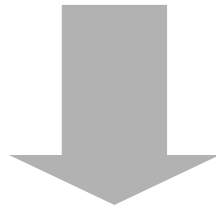


Photoinitiator is excited by ***two-photon absorption***

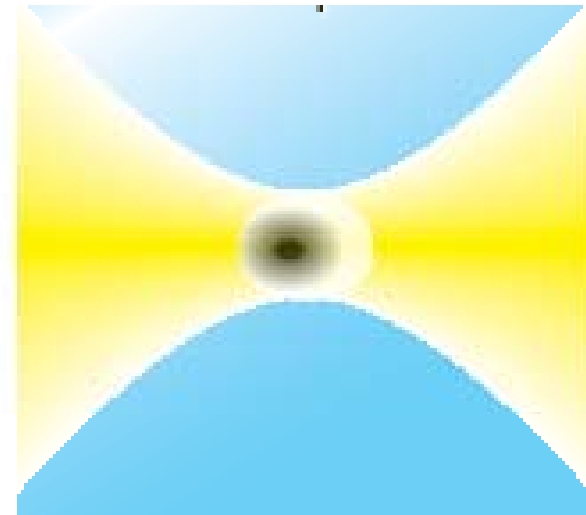


$$R_{2PA} \propto I^2$$

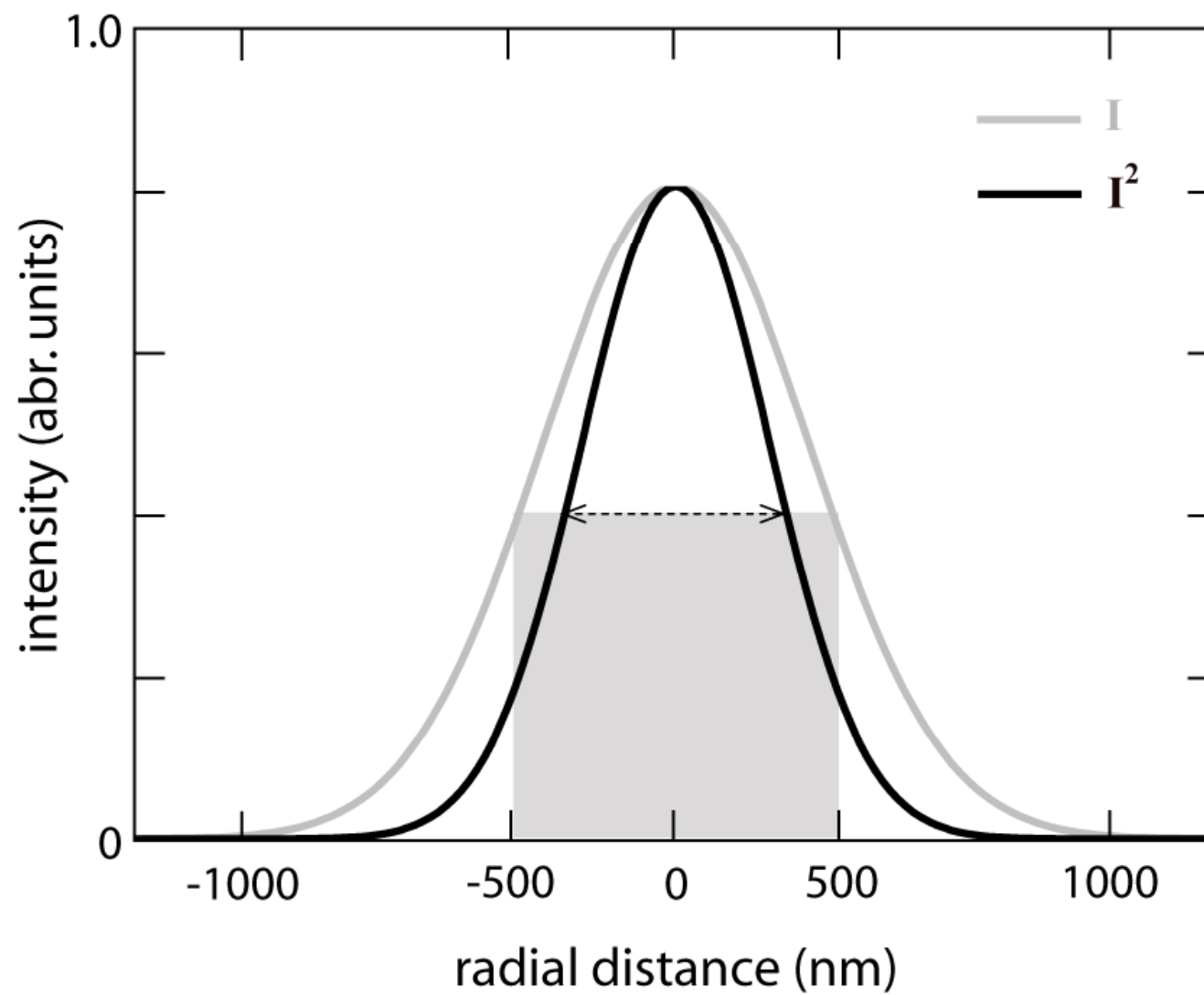
The polymerization is confined to the focal volume.



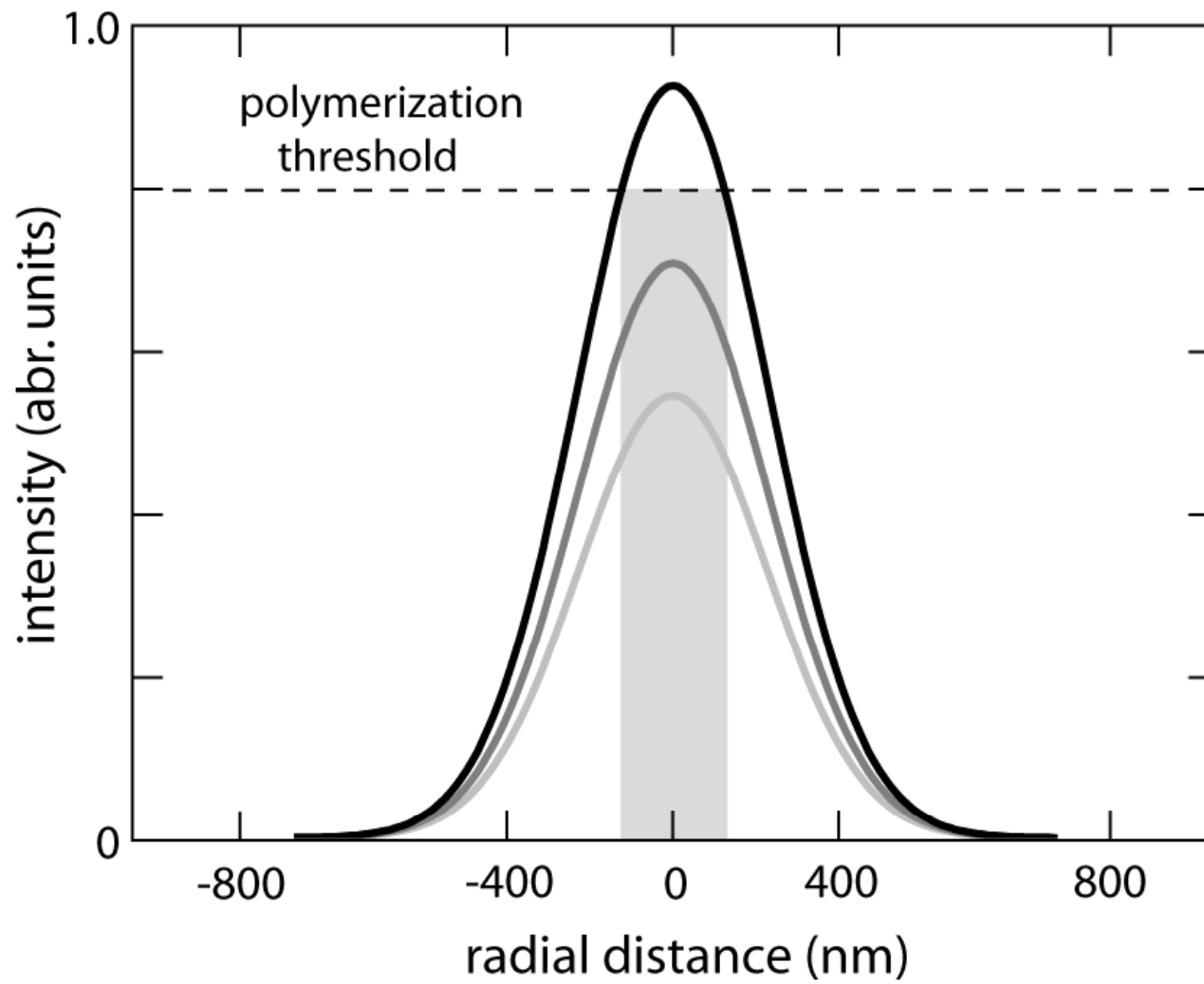
High spatial resolution



Two-photon polymerization

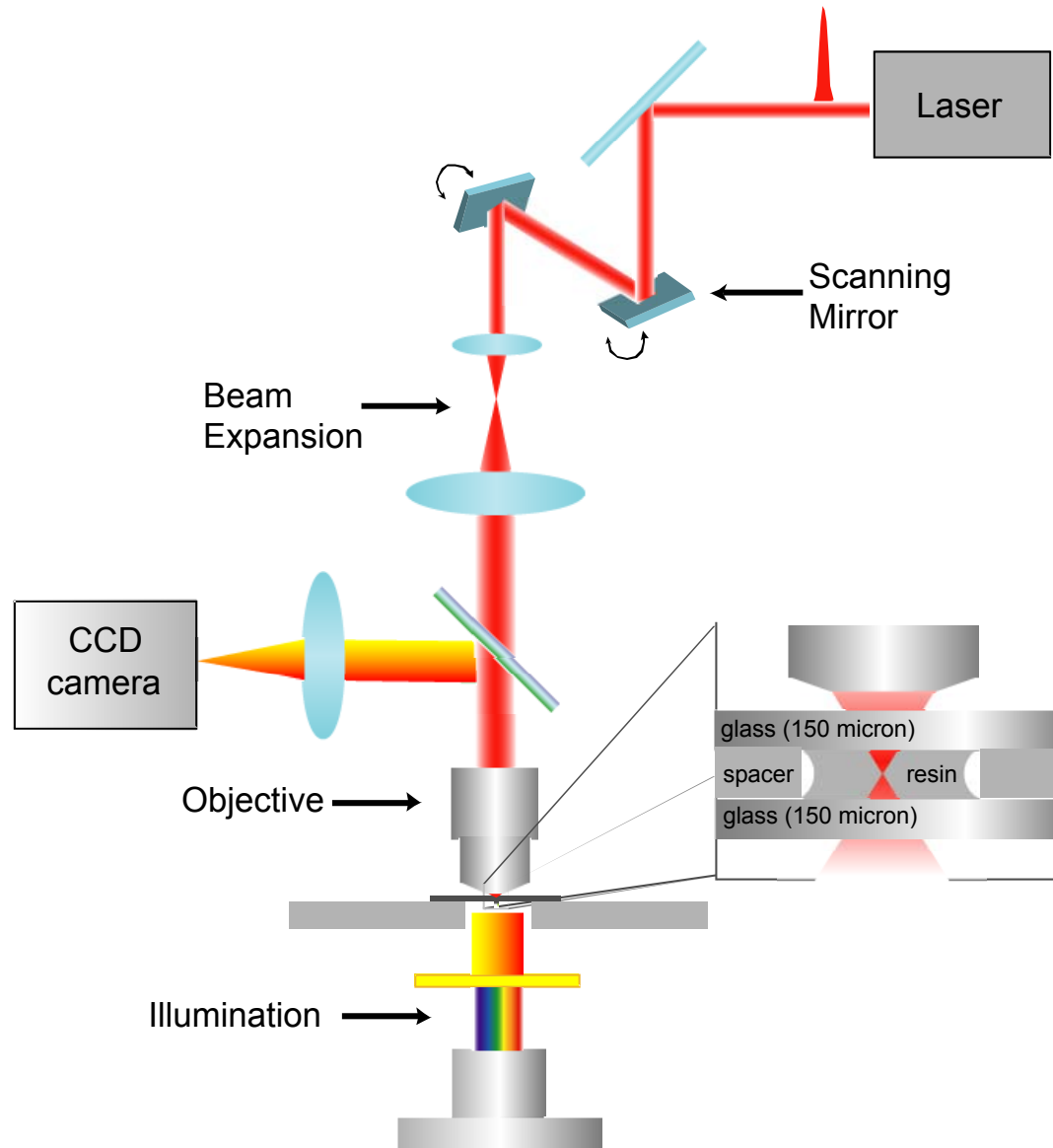


Two-photon polymerization



even higher spatial resolution

Two-photon polymerization setup



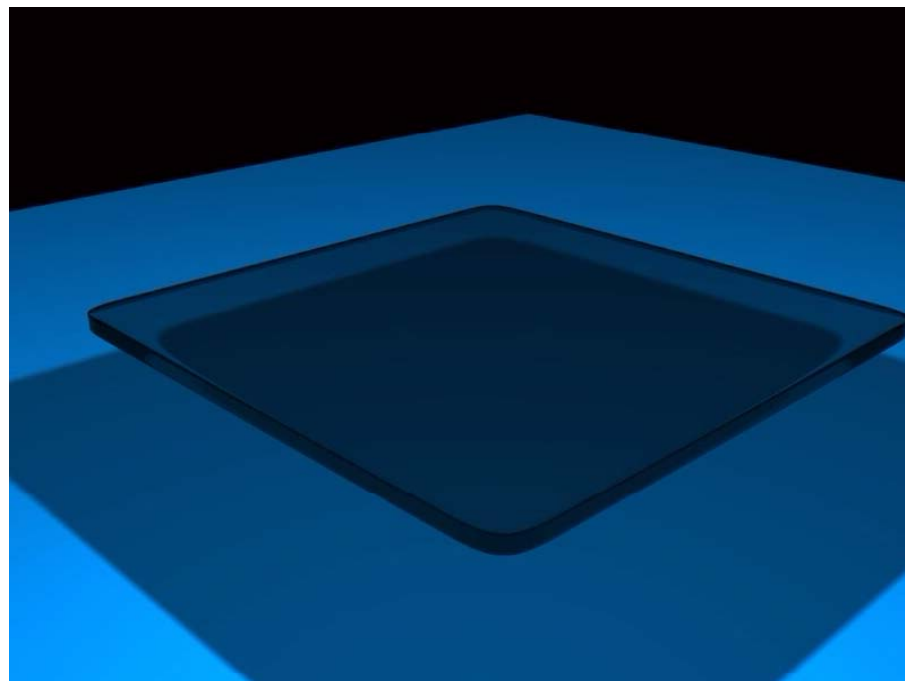
Ti:sapphire laser oscillator

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

Objective

40 x
0.65 NA

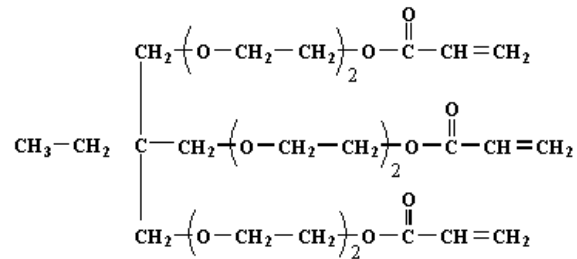
Two-photon polymerization



Resin Preparation

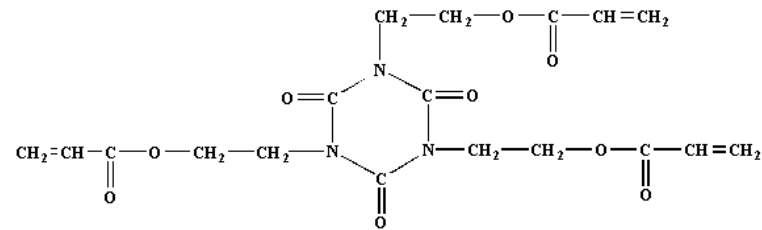
Monomers

Monomer A



reduces the shrinkage upon polymerization

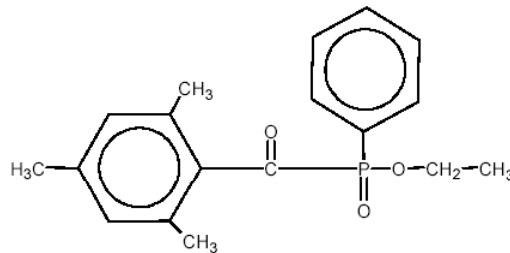
Monomer B



gives hardness to the polymeric structure

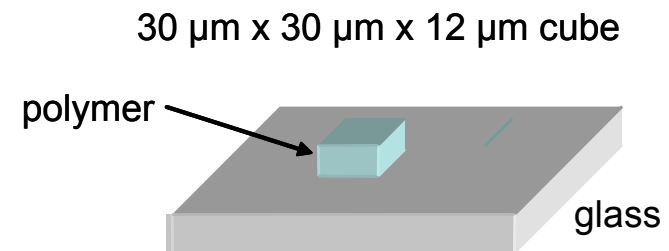
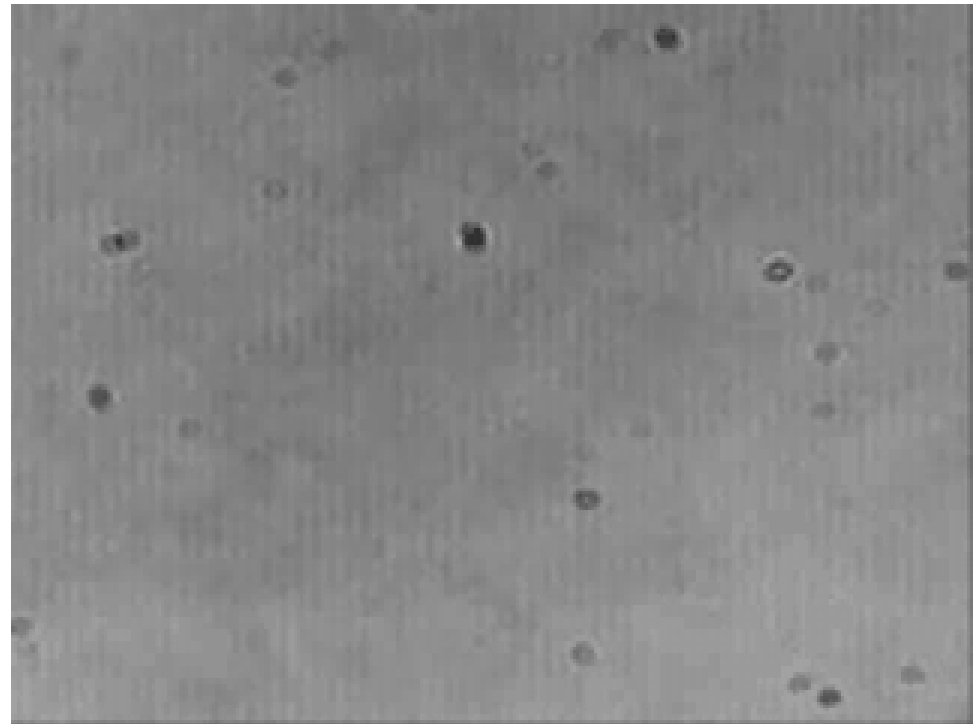
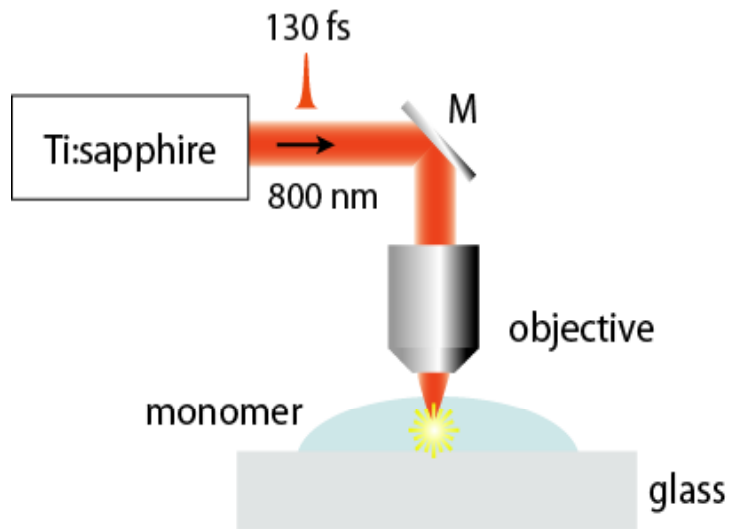
Photoinitiator

Lucirin

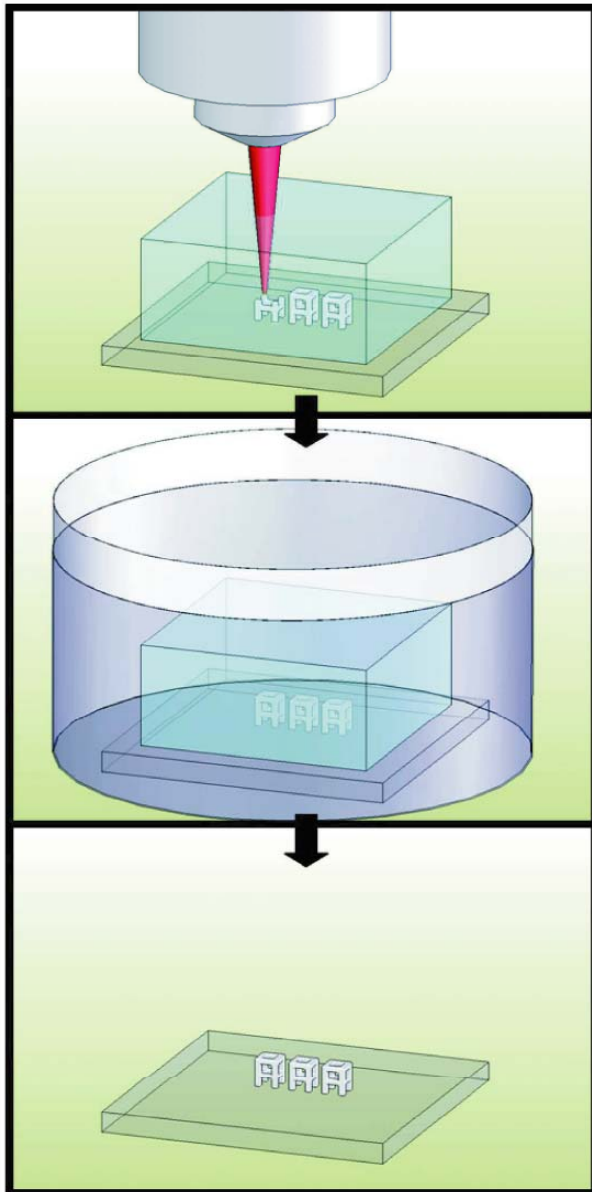


Appl. Phys. A, 90, 633–636 (2008)

Two-photon polymerization

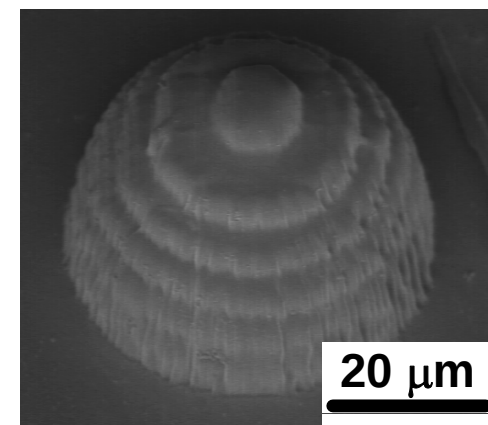
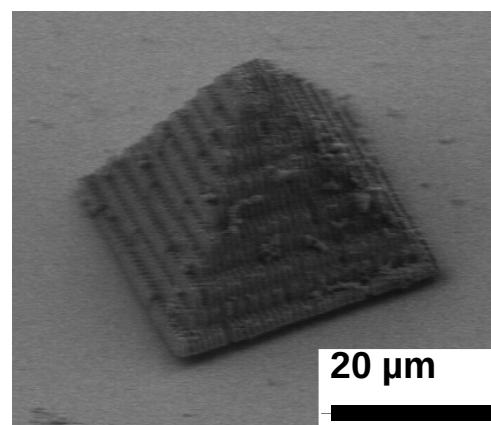
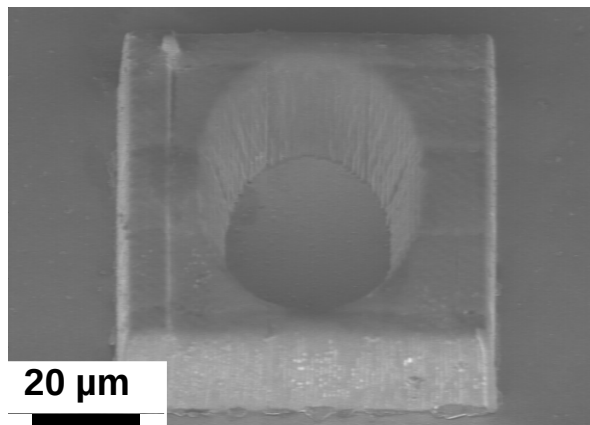
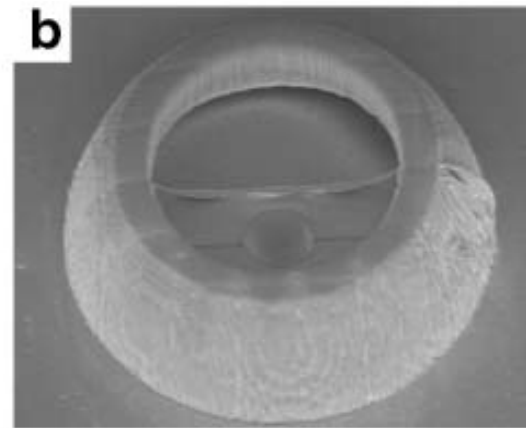
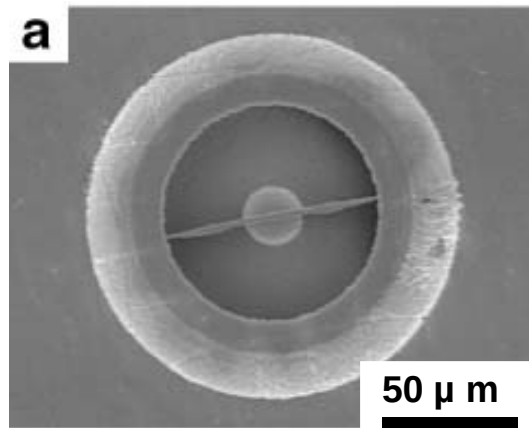


Two-photon polymerization

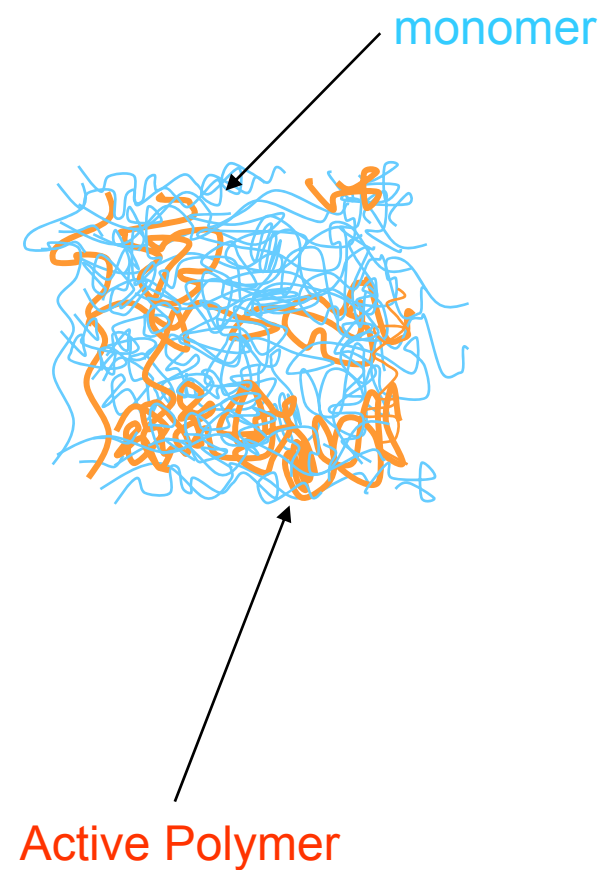
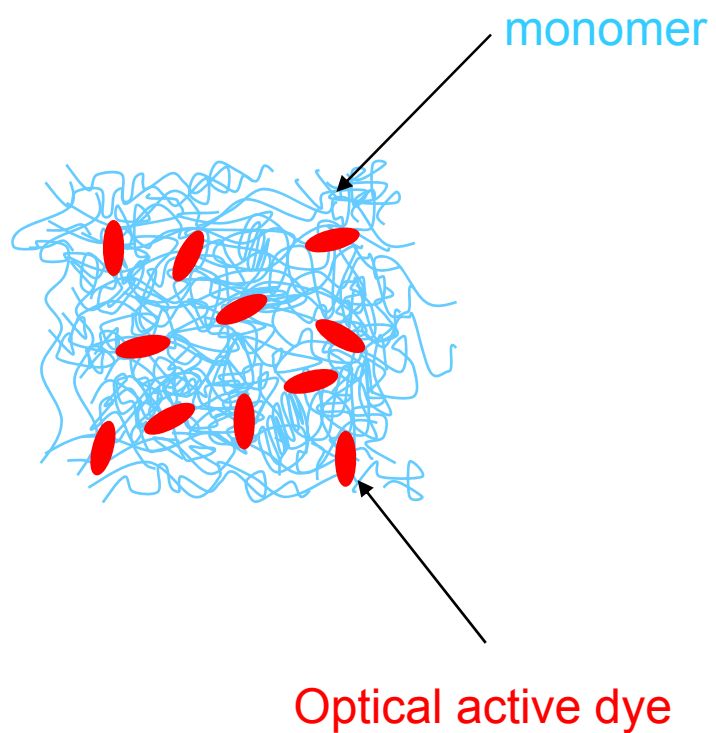


After the fabrication, the sample is immersed in ethanol to wash away any unsolidified resin and then dried

Microstructures fabricated by two-photon polymerization



Microstructures containing active compounds



Applications of two-photon polymerization

Optics and Photonics

Doping microstructures with organic molecules and metals

- fluorescence
- birefringence
- conductivity

Bio-applications

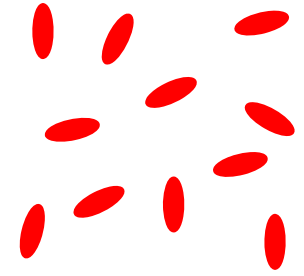
Fabrication using bio-compatible resins to biological applications

- tissue engineering scaffolds
- fabrication of microneedle
- cell study

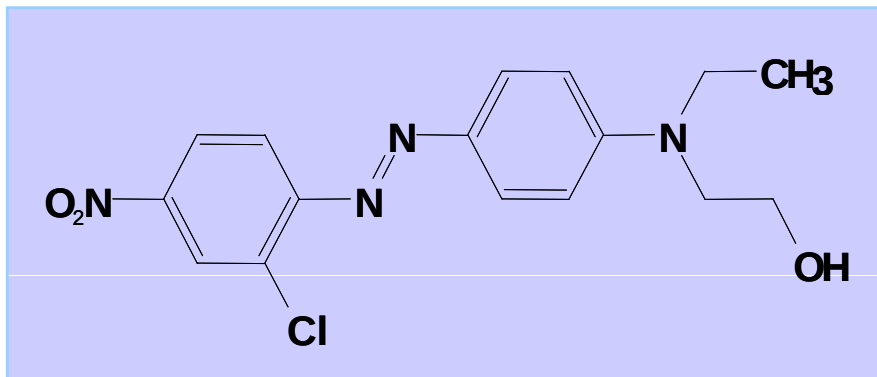
Applications

- 1) Optically induced birefringence
- 2) Emission and conduction
- 3) Biocompatible microstructure

Birefringent microstructures

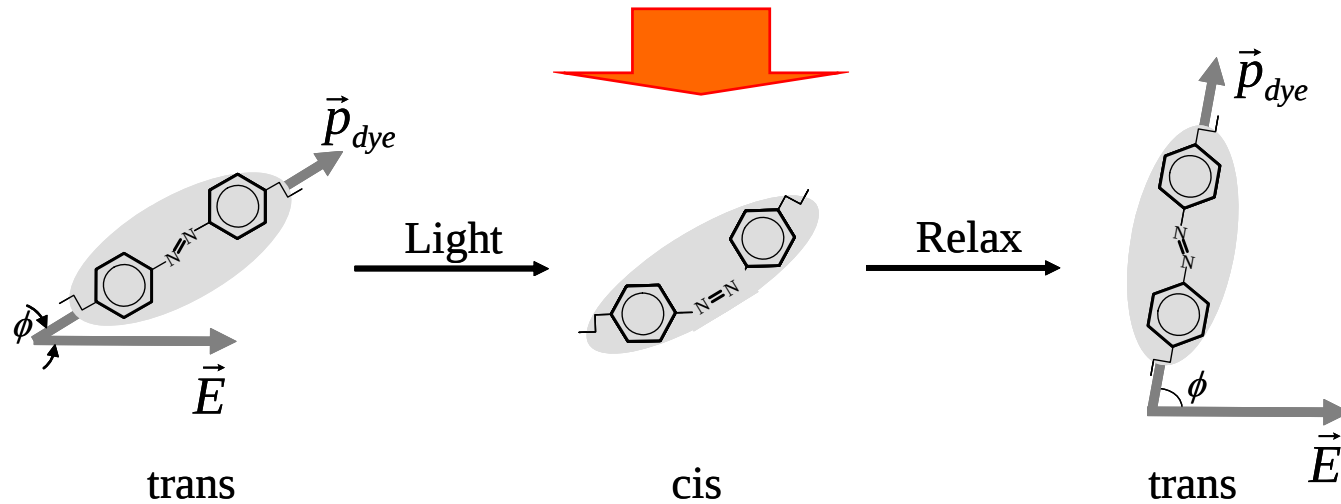
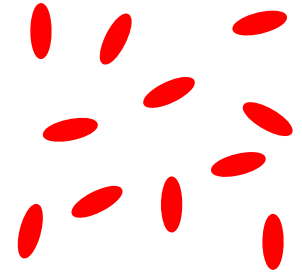


Incorporating the azodye DR13 into the microstructure

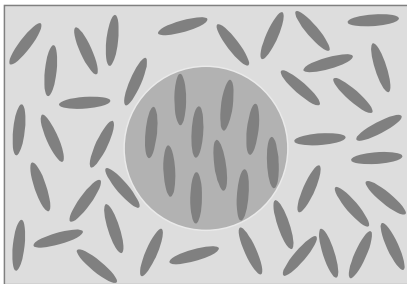


Birefringent microstructures

Molecular orientation by excitation with linearly polarized light



After alignment



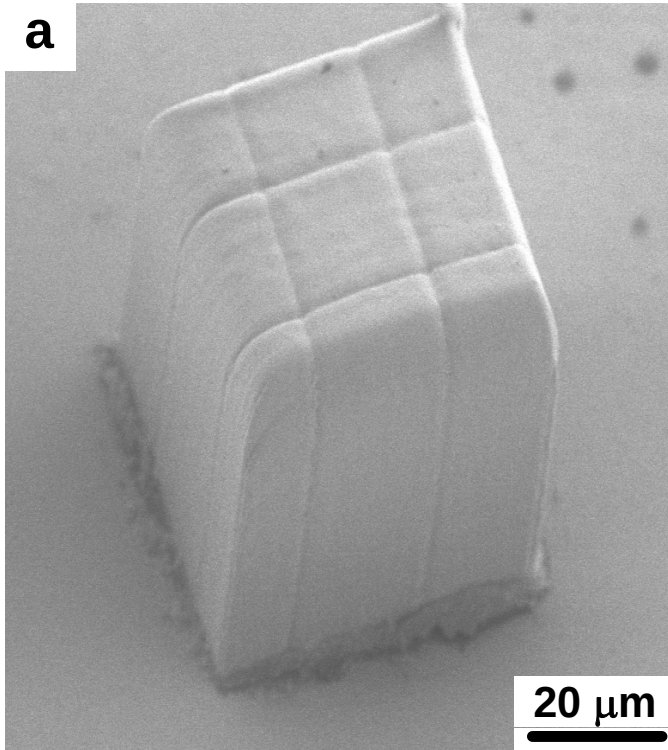
Optically Induced birefringence

n_y

n_x

$n_y > n_x$

Birefringent microstructures

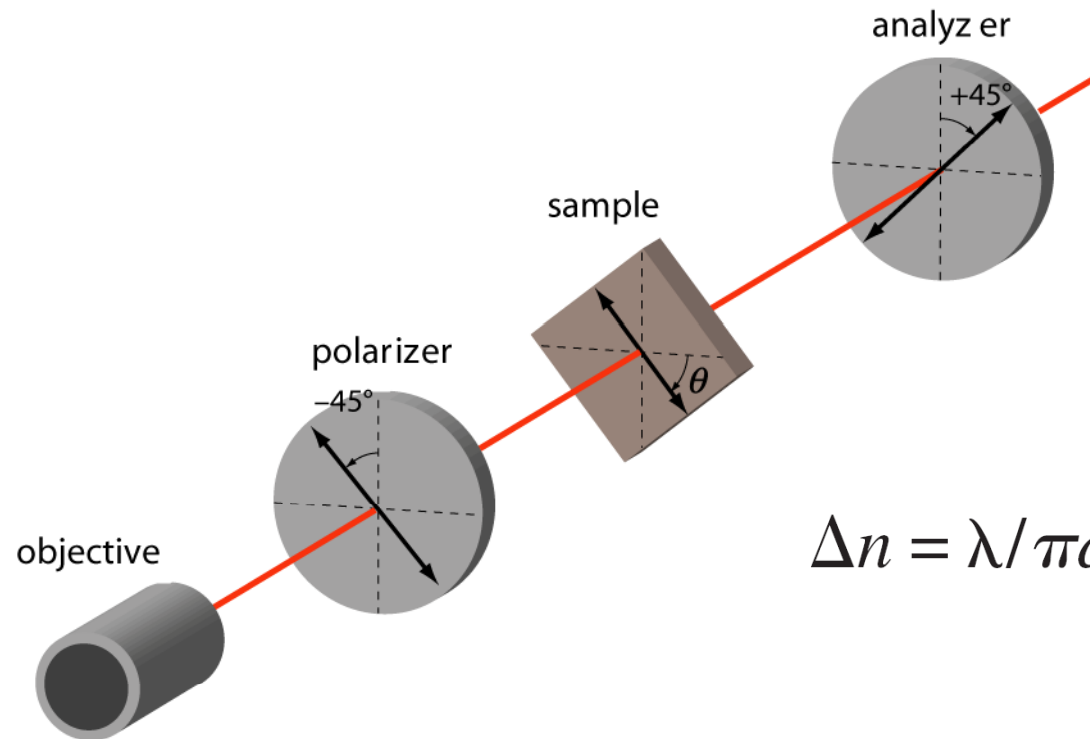


Ar⁺ ion laser irradiation

- 514.5 nm
- one minute
- intensity of 600 mW/cm²

Birefringent microstructures

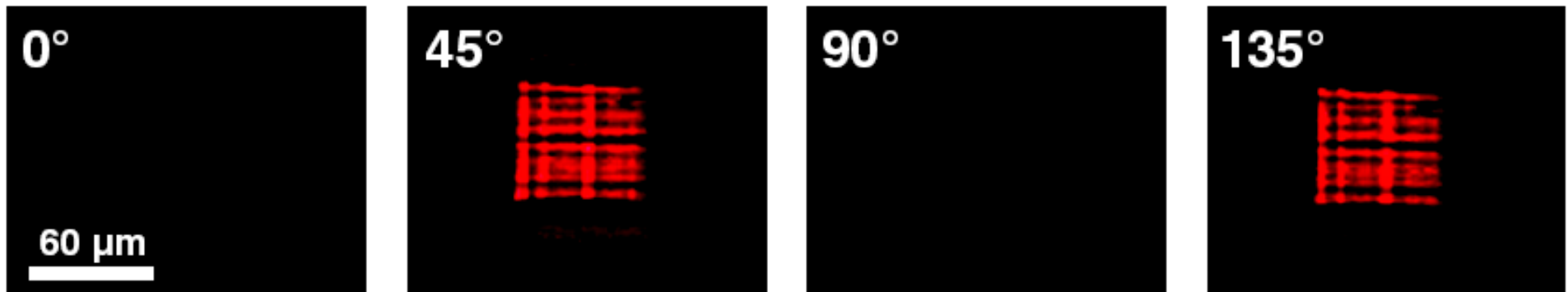
The sample was placed under an optical microscope between crossed polarizers and its angle was varied with respect to the polarizer angle



$$\Delta n = \lambda / \pi d \sin^{-1} \sqrt{T}$$

Birefringent microstructures

The structure is visible when the angle between the birefringence axis and the polarizer is an odd multiple of 45°



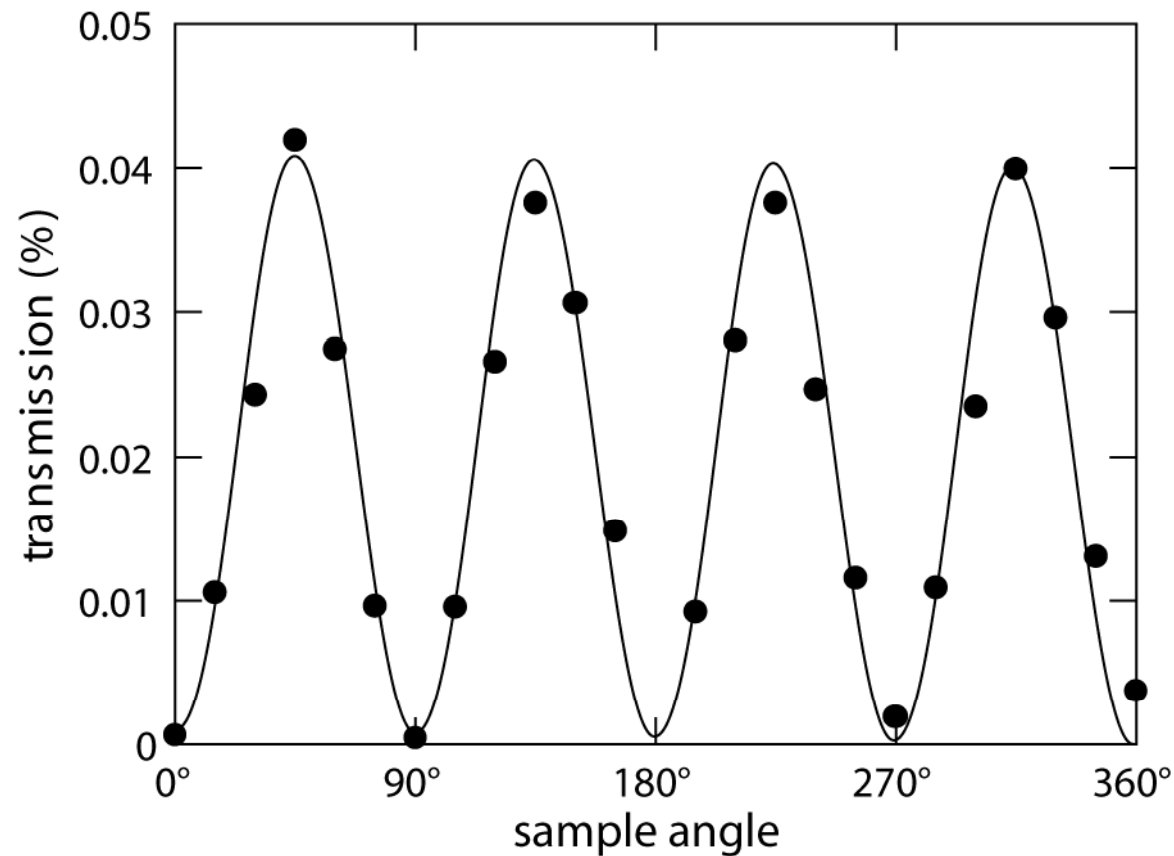
$$\Delta n = 5 \times 10^{-5}$$

This birefringence can be completely erased by irradiating the sample with circularly polarized light.

Applications: micro-optical switch, micro-optical storage

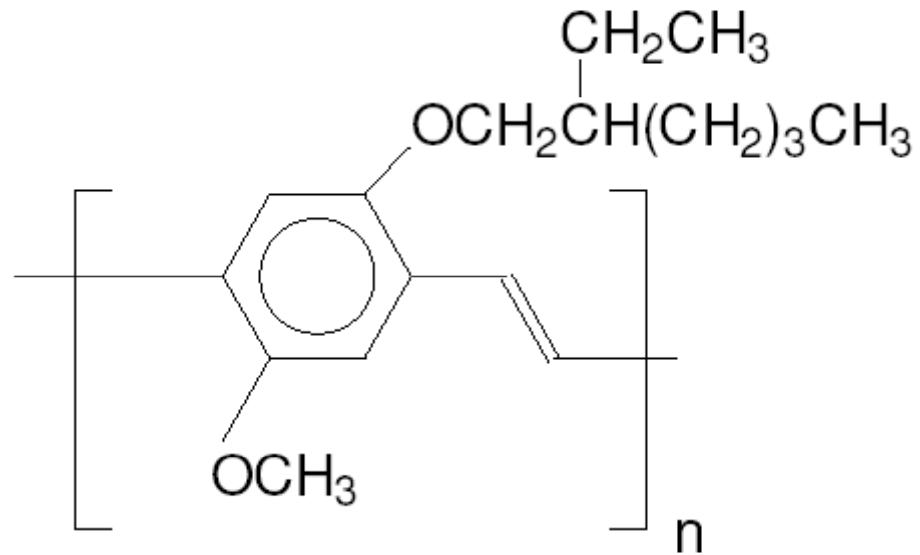
Birefringent microstructures

The structure is visible when the angle between the birefringence axis and the polarizer is an odd multiple of 45°



This birefringence can be completely erased by irradiating the sample with circularly polarized light.

microstructure containing MEH-PPV

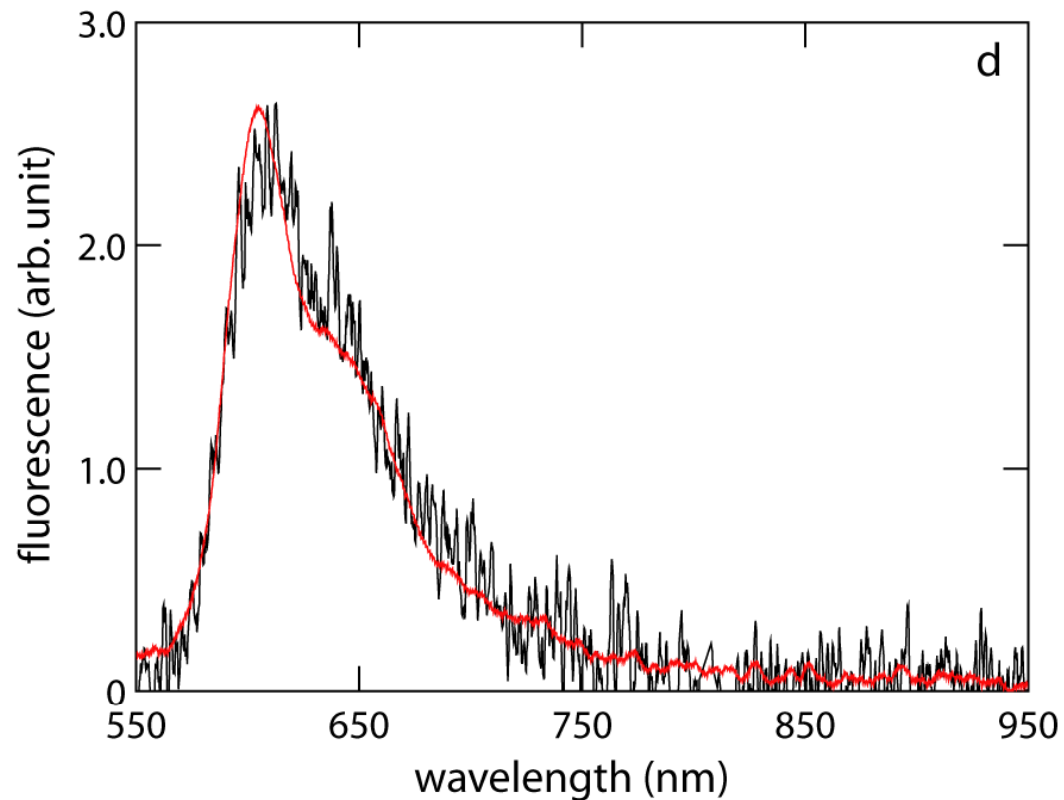
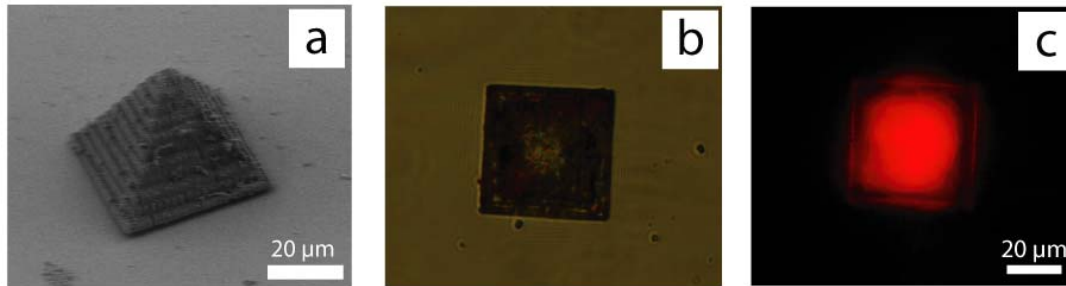


MEH-PPV



Fluorescence
Electro Luminescent
Conductive

microstructure containing MEH-PPV

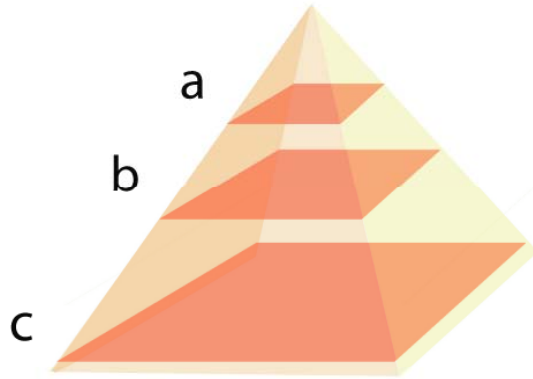


(a) Scanning electron microscopy

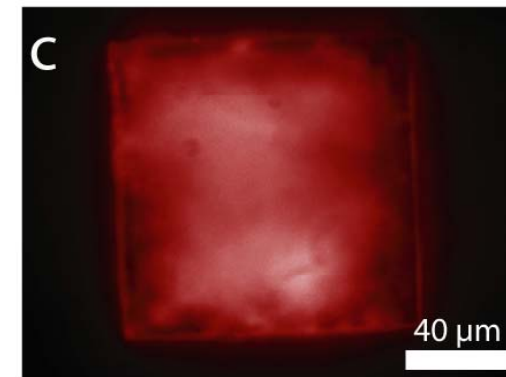
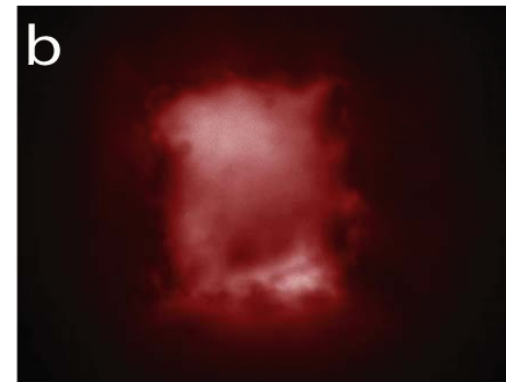
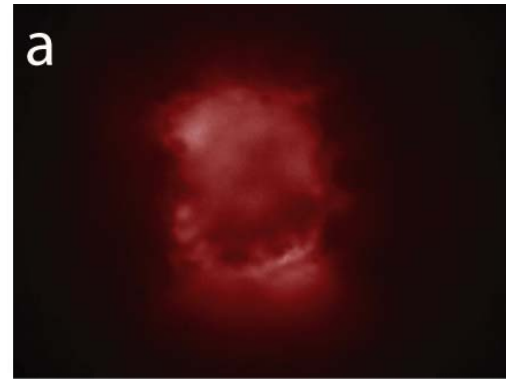
(b,c) Fluorescence microscopy of the microstructure with the excitation OFF (b) and ON (c)

(d) Emission of the microstructure (black line) and of a film with the same composition (red line)

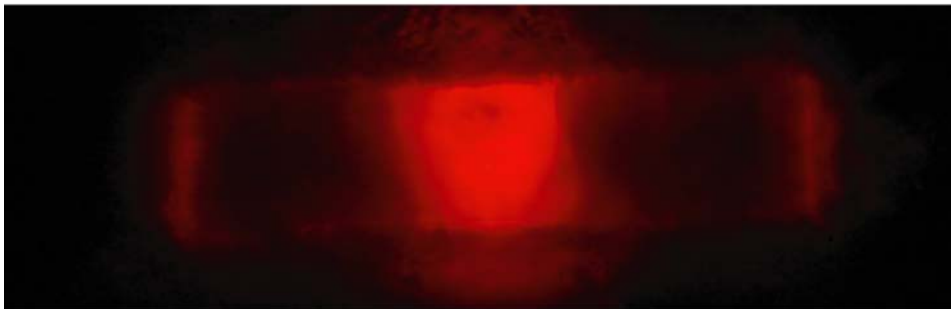
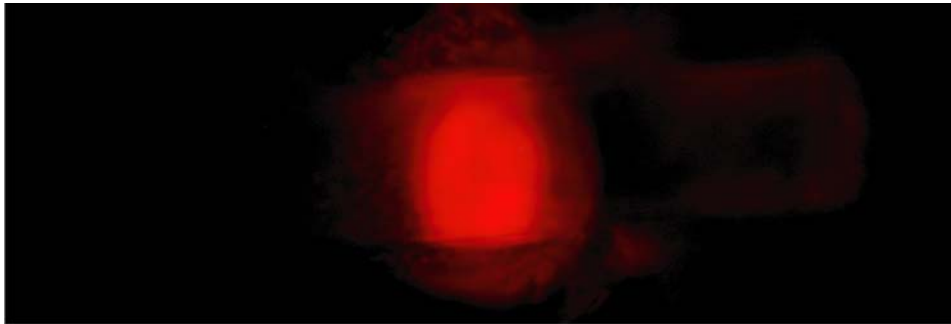
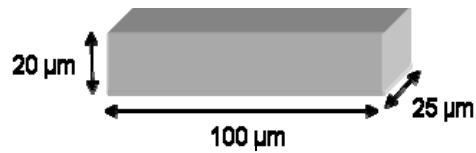
microstructure containing MEH-PPV



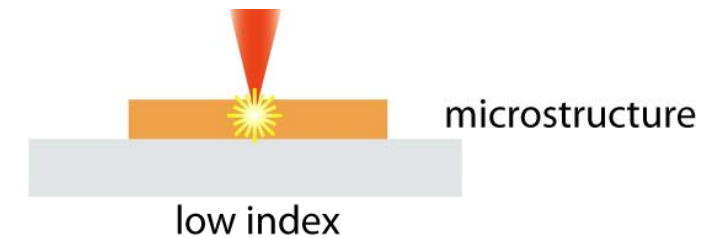
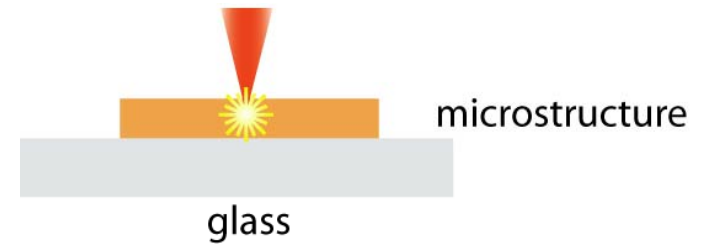
Fluorescent confocal microscopy images in planes separated by 16 μm in the pyramidal microstructure.



microstructure containing MEH-PPV



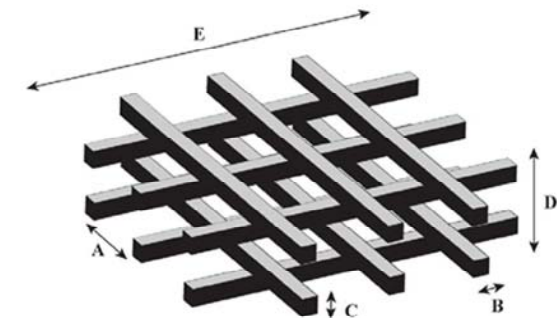
$20\ \mu\text{m}$ 



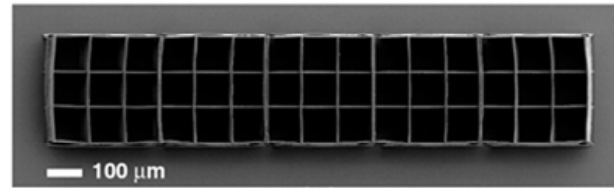
waveguiding of the microstructure fabricated on porous silica substrate ($n=1.185$)

Applications: micro-laser; fluorescent microstructures; conductive microstructures

3D cell migration studies in micro-scaffolds



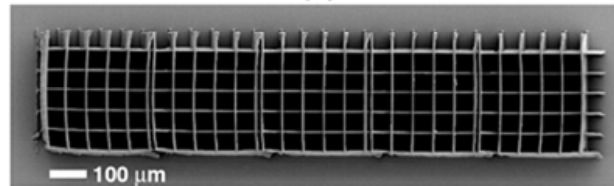
schematic of the scaffold



(c)

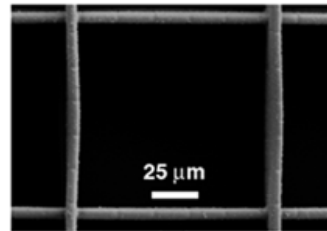
SEM of the scaffolds

110 μm pore size



(d)

52 μm pore size



(e)



(f)

Top view

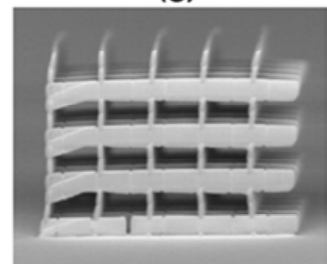
110, 52, 25, 12 μm
pore size



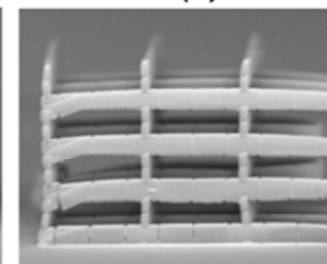
(g)



(h)



(i)



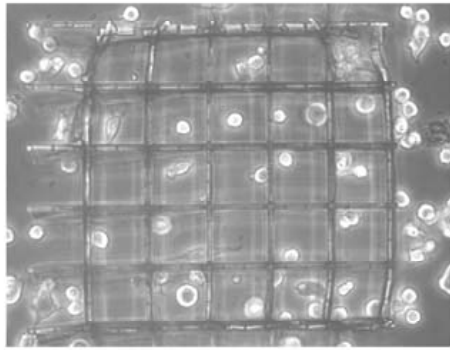
(j)

Side view

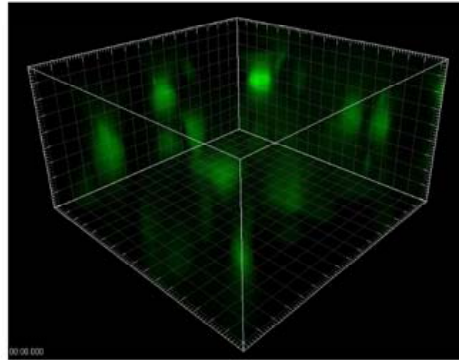
25, 52 μm
pore size

cell migration

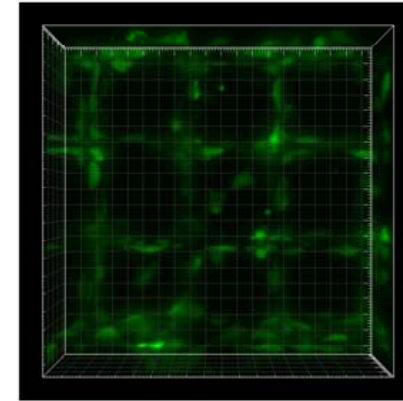
50 μm pore size after 5 hours



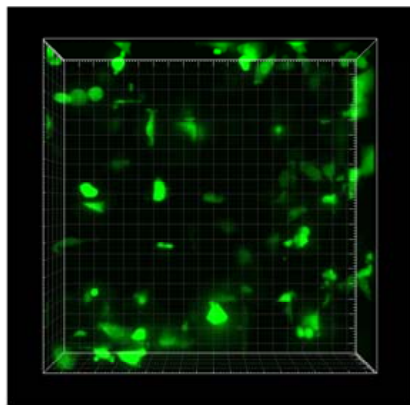
(a)



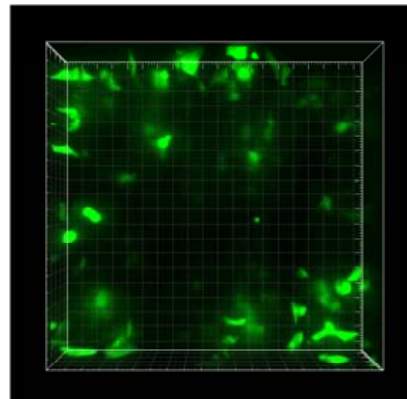
(b)



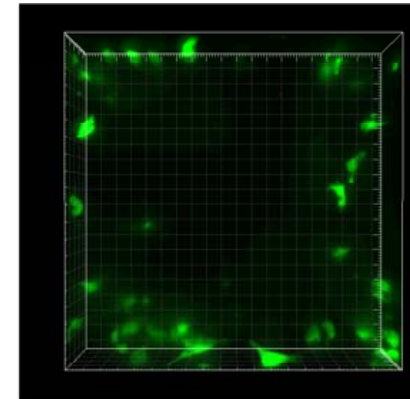
(c)



(d)



(e)



(f)

c-d: 110, 52, 25 and 12 μm

Acknowledgments

FAPESP
CAPES
CNPq

NSF
ARO

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Obrigado!

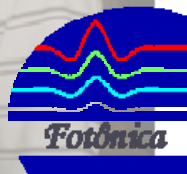


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