Femtosecond pulses applied to nonlinear spectroscopy and microfabrication

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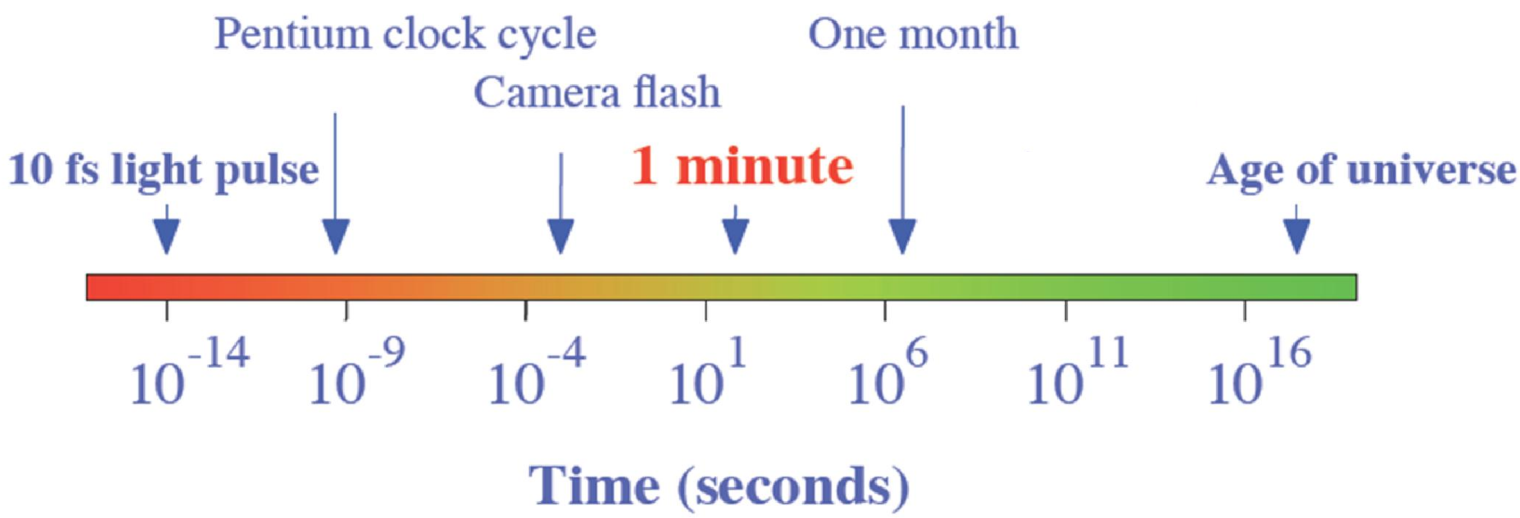
Outline

- introduction to nonlinear optics
- nonlinear spectroscopy of materials
- fs-laser microfabrication

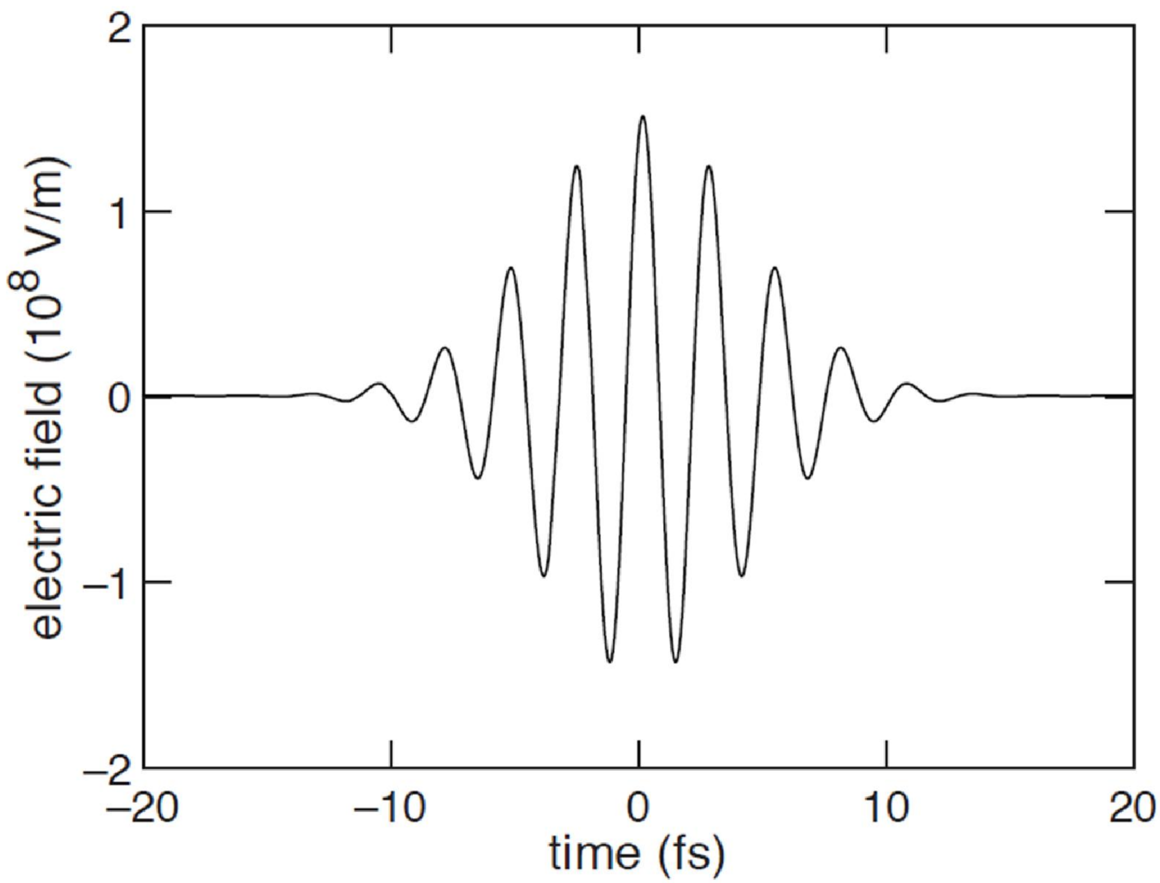
Microfabrication

1 fs = 10^{-15} s



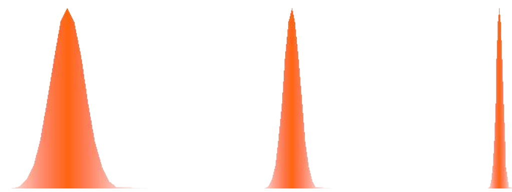
introduction

how short is a femtosecond pulse ?



Microfabrication

Ti:Sapphire lasers



100 fs   50 fs   20 fs

Very intense light

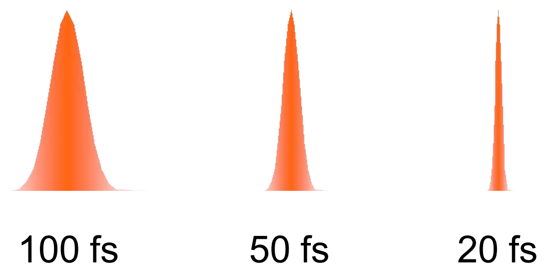
Laser intensities ~ 100 GW/cm^2

1×10^{11} W/cm^2

Laser pointer: 1 mW/cm^2 (1×10^{-3} W/ cm^2)

fs-laser micromachining

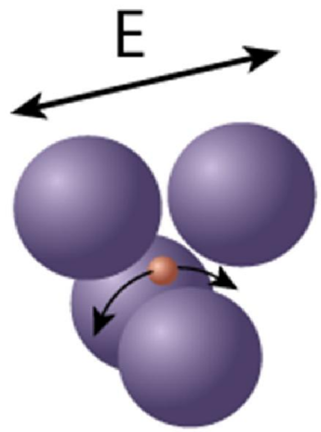
Ti:Sapphire lasers



Very intense light

Nonlinear Optical Phenomena

Nonlinear Optics



anharmonic oscillator

high light intensity

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

nonlinear polarization response

$$P = \varepsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)$$

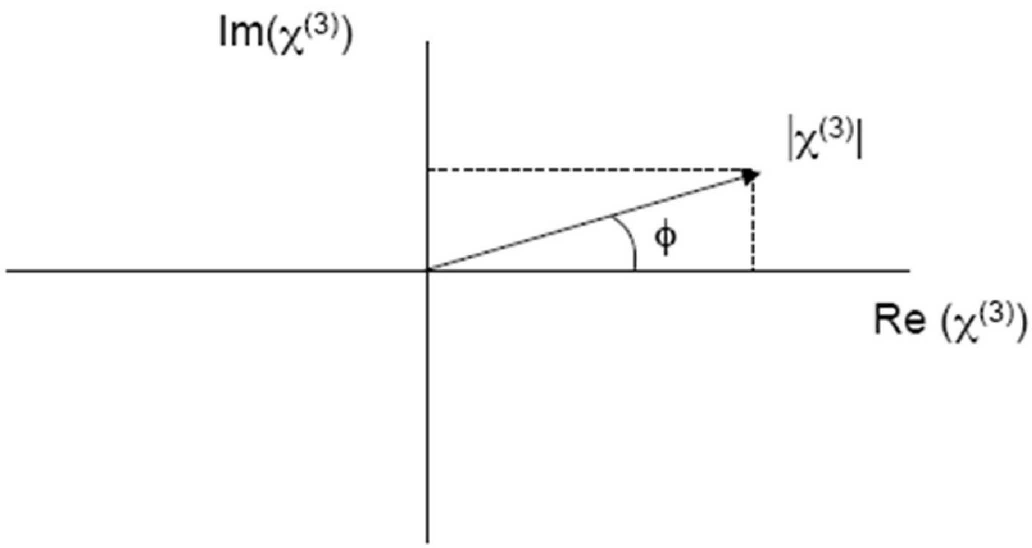
Nonlinear Optics

$\chi^{(3)}$ is a complex quantity

$$\chi^{(3)} = \mathrm{Re}\,(\chi^{(3)}) + i\,\mathrm{Im}(\chi^{(3)})$$

Related to intensity dependent refractive index

Related to two-photon absorption



Nonlinear Optics

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

Refractive process:

$$n = n_0 + n_2 I$$

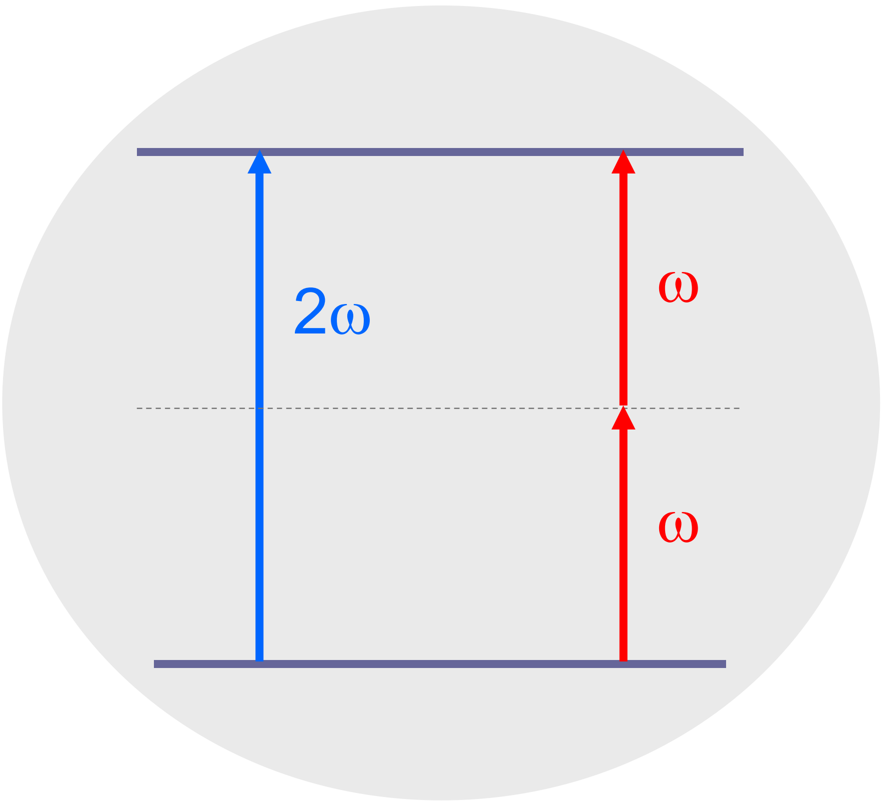
- self-phase modulation
- lens-like effect

Absorptive process:

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

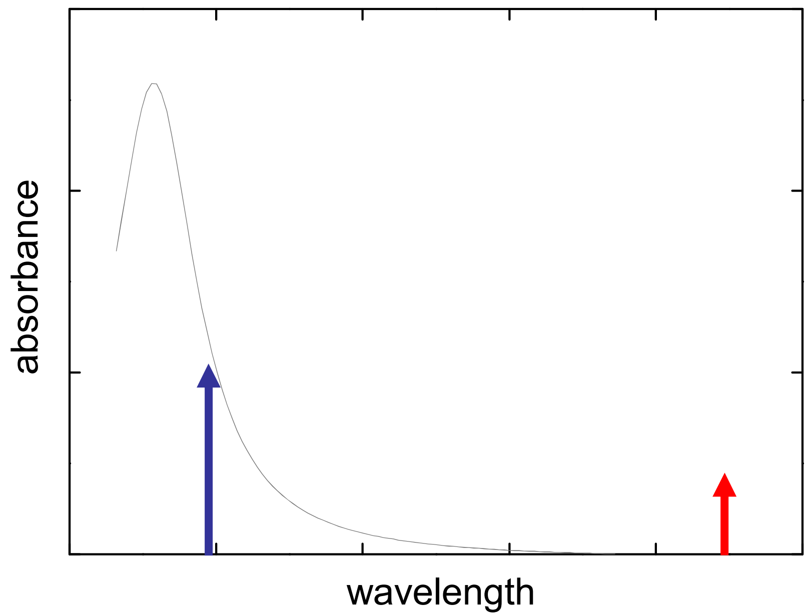
- nonlinear absorption
- two-photon absorption

Two-photon absorption



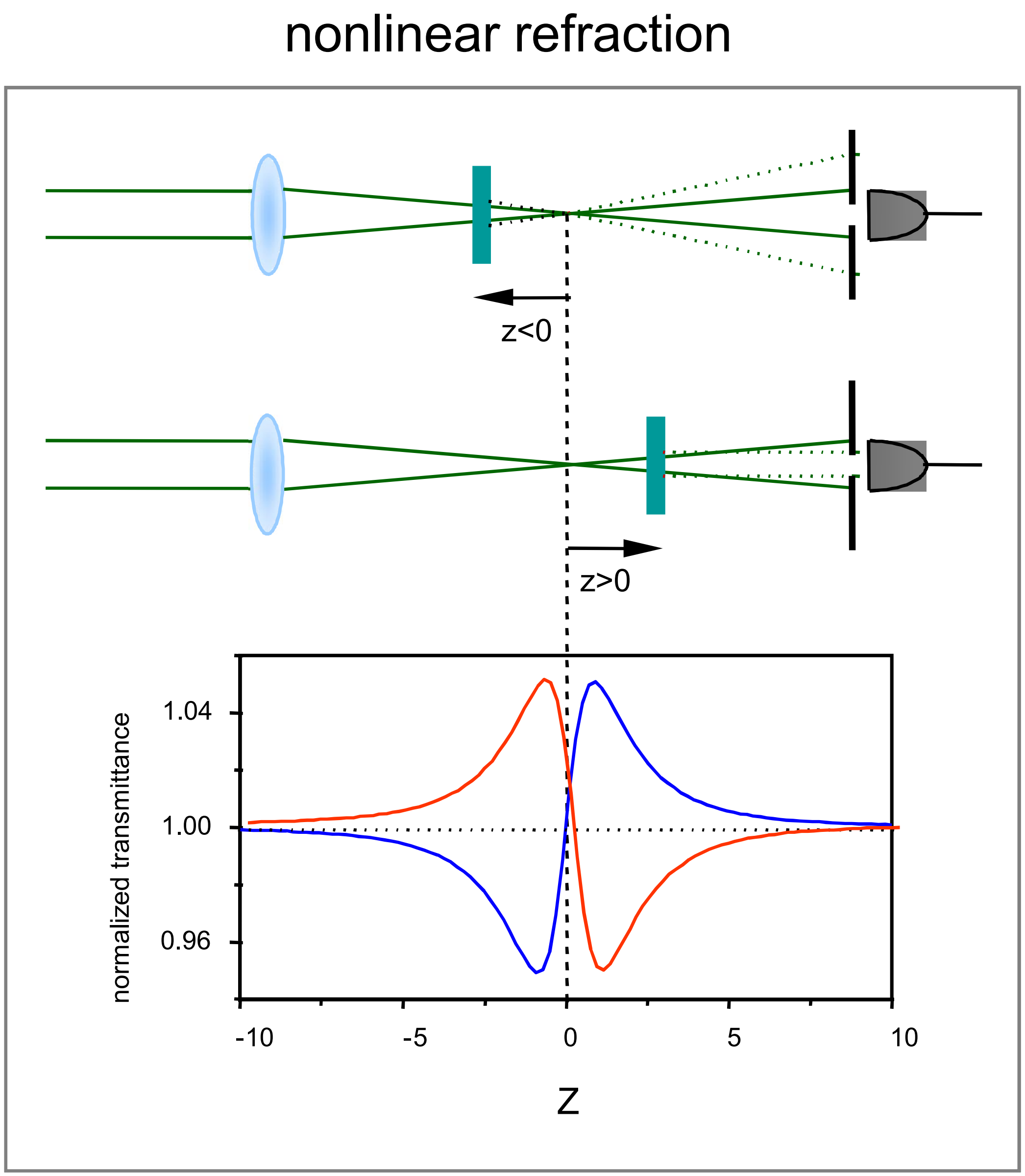
$$\alpha = \alpha_0 + \beta I$$

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



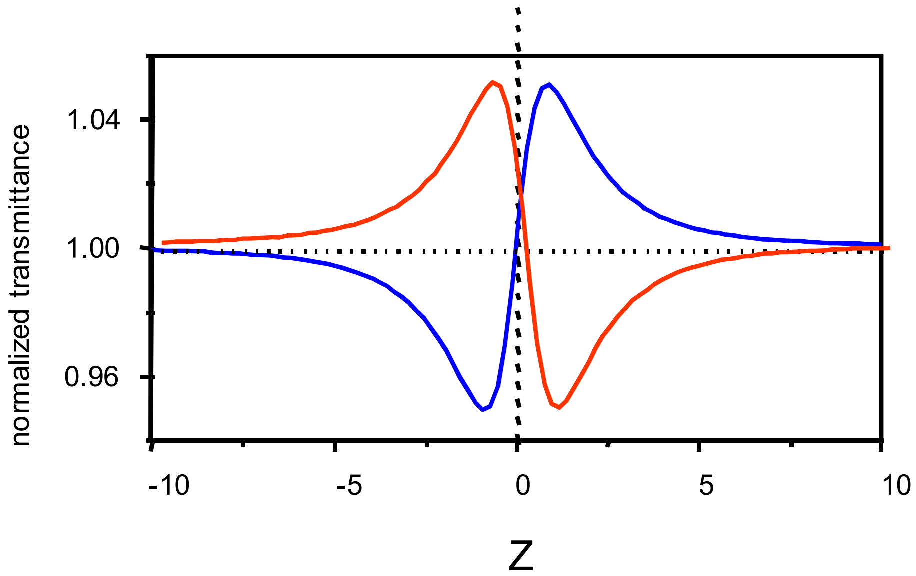
Z-scan: close aperture

$$n = n_0 + n_2 I$$



close aperture Z-scan

Summary



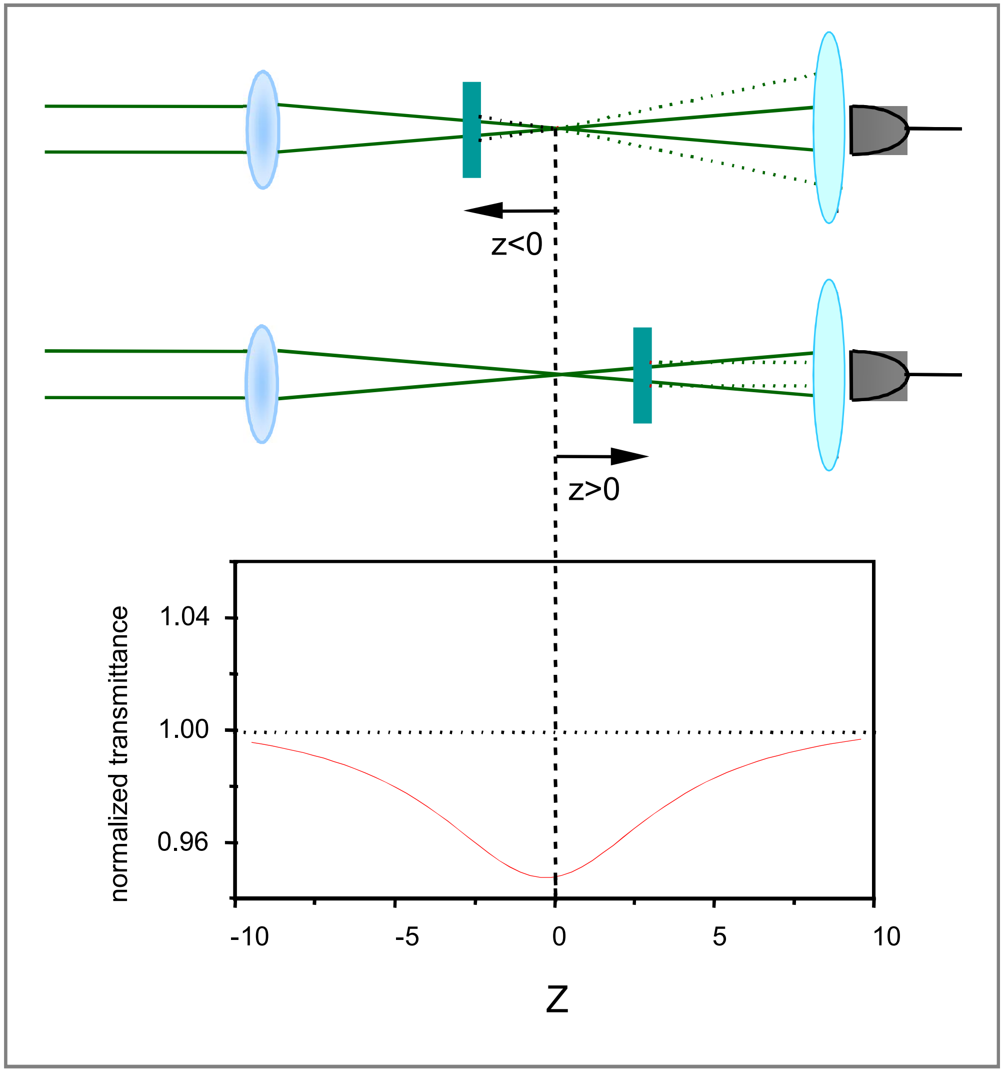
$$\left|\Delta Z_{pv}\right| \approx 1.7 Z_0$$

$$\Delta T_{pv} \cong 0.406(1-S)^{0.27}\left|\Delta\Phi_0\right|$$

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff}$$

Z-scan (two-photon absorption)

Summary



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

$$\Delta T \propto \beta I$$

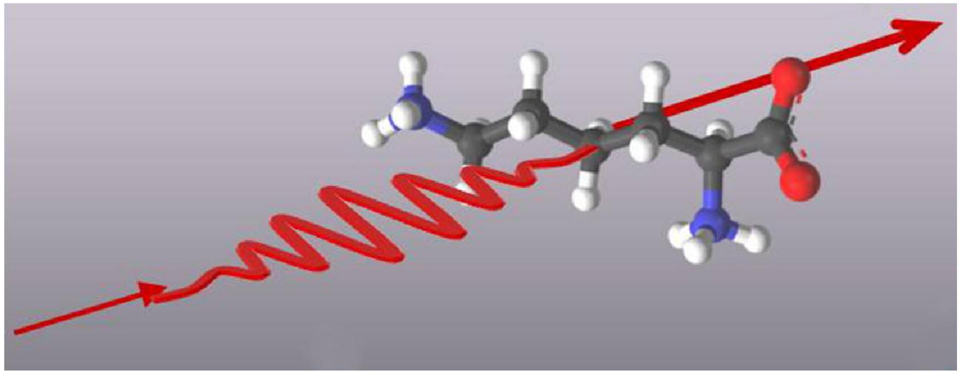
$$T(z) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}}$$

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

Research

- Establish a relationship between the molecular structure and the optical nonlinearities

Molecular engineering of nonlinear materials



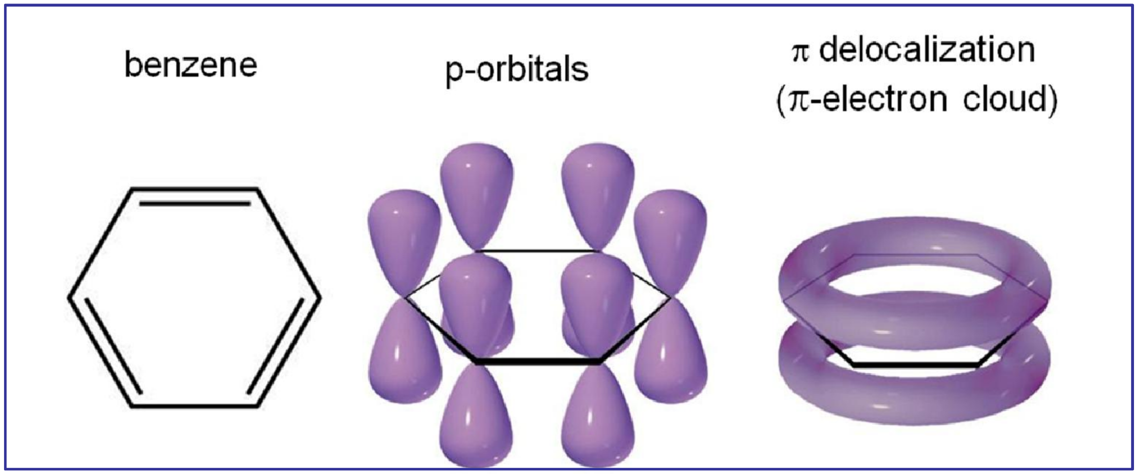
- Development of materials with high nonlinearities

Applications

Organic Materals

Flexibility to tune the material´s nonlinear response by manipulating its molecular structure

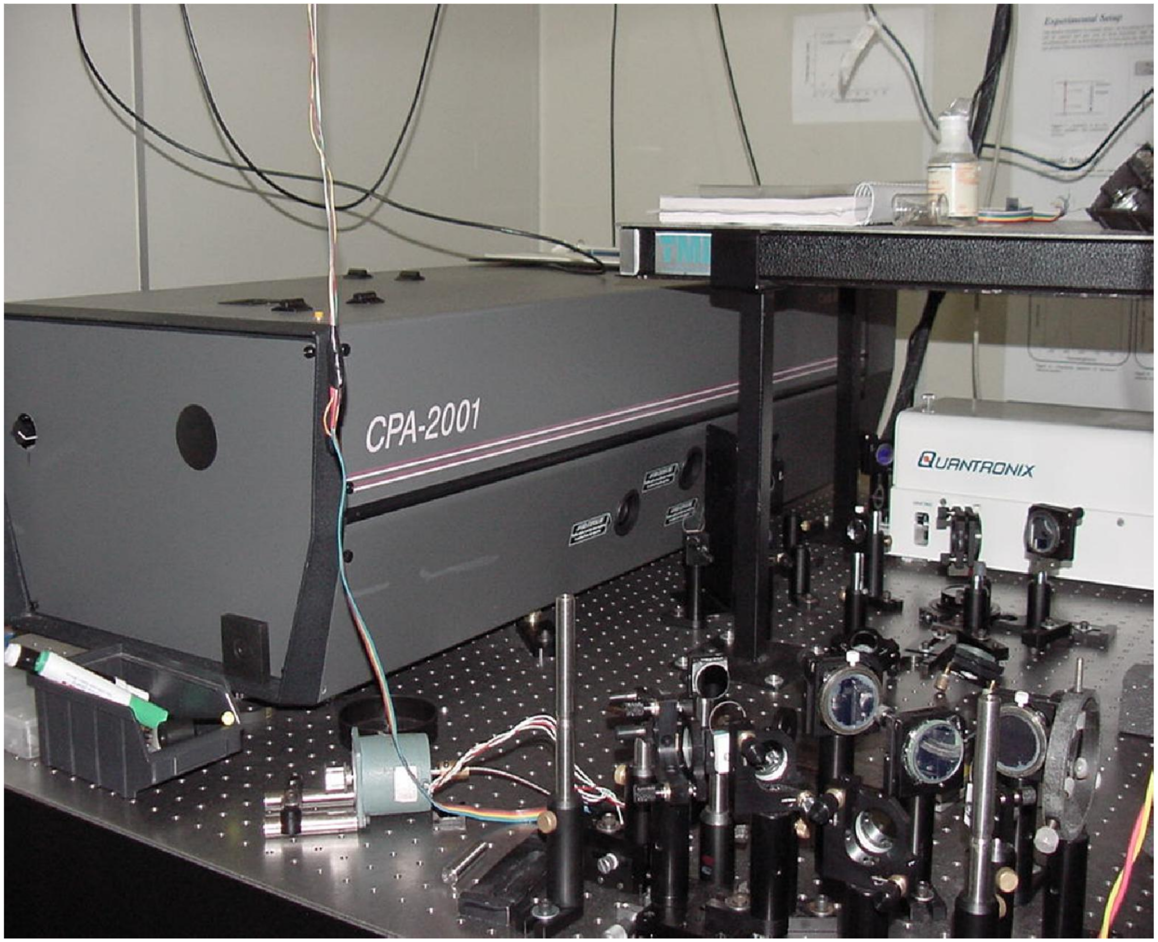
π conjugated structures



high optical nonlinearities

$\uparrow \chi^{(3)}$

Nonlinear refraction – 150 fs laser system



Ti:Sapphire amplifier

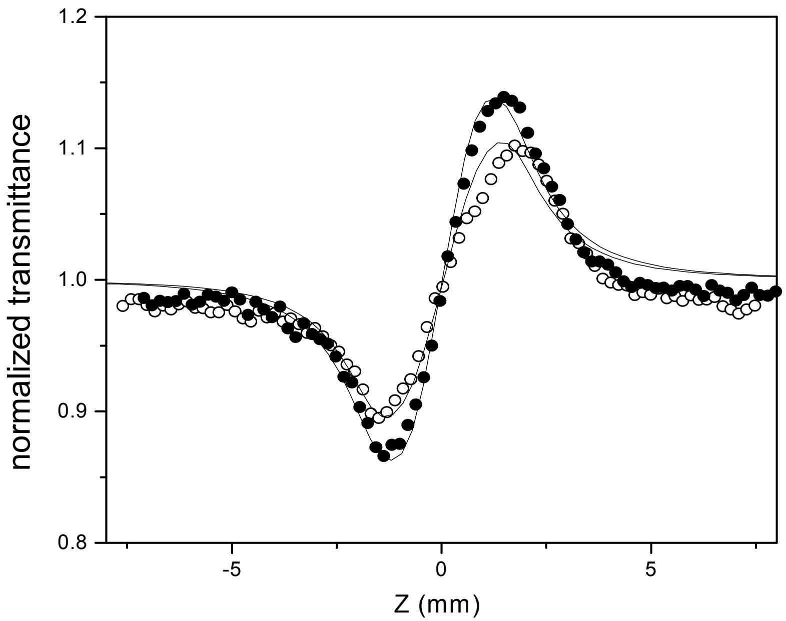
775 nm

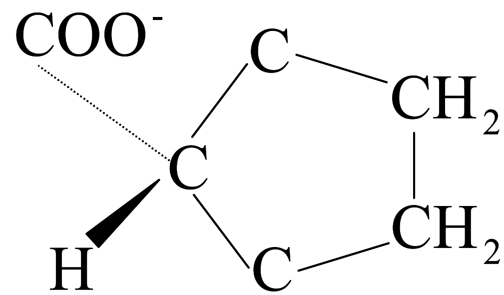
150 fs

800 μJ

Nonlinear refraction

Aminoacids





L-Proline

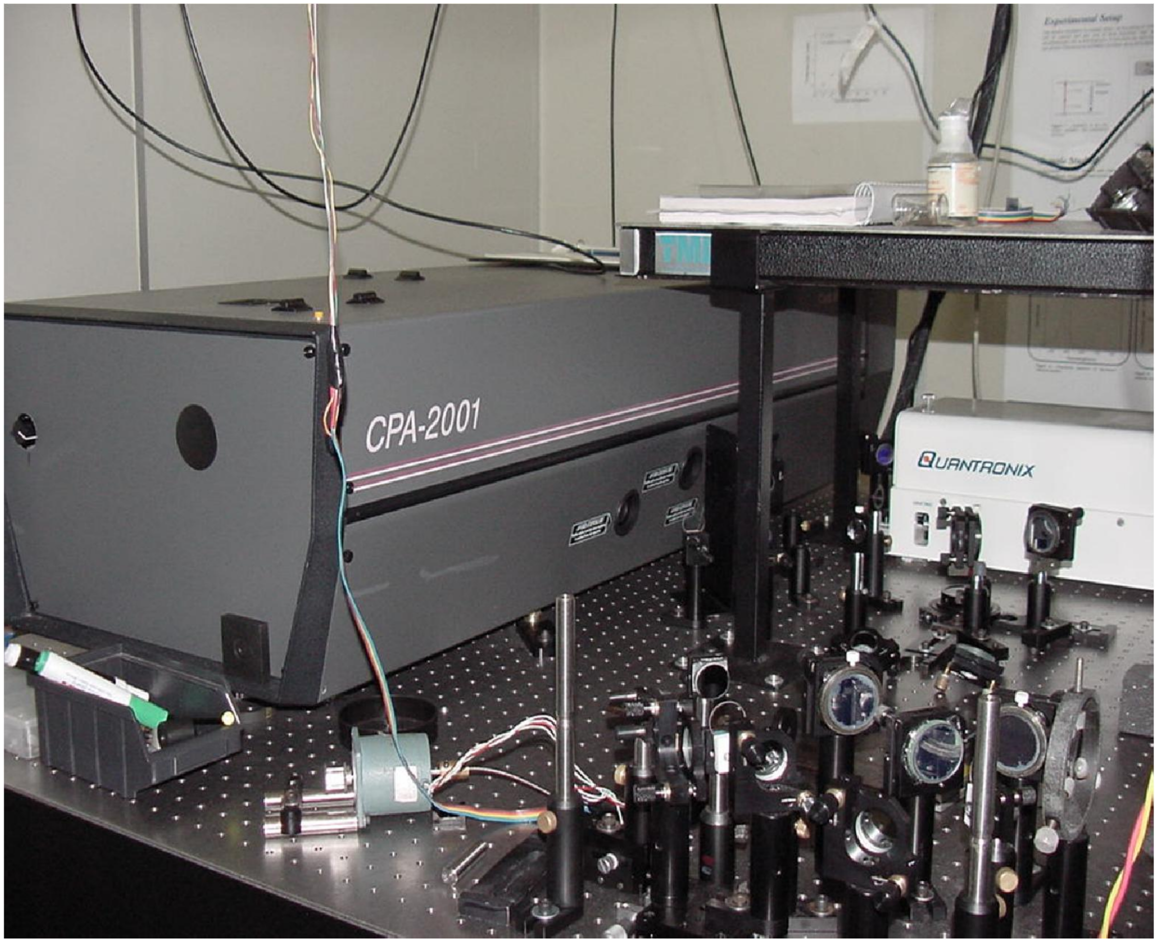
$$\Delta T_{pv} = 0.406\Delta\Phi_0 = 0.406\left(\frac{2\pi}{\lambda}n_2 I_0 L\right)$$

150 fs 100 GW/cm²

775 nm

$$n_2 \propto \chi^{(3)}$$

Nonlinear absorption – 150 fs laser system



Ti:Sapphire amplifier

775 nm

150 fs

800 μJ

Nonlinear absorption spectrum

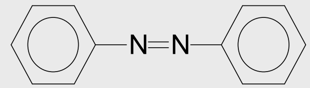
Optical parametric amplifier

460 - 2600 nm

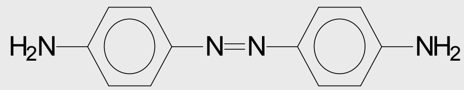
$\approx$ *120 fs*

20-60 μJ

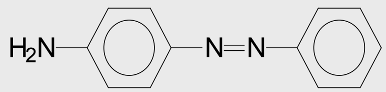
Azoaromatic samples



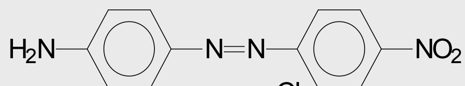
AZO



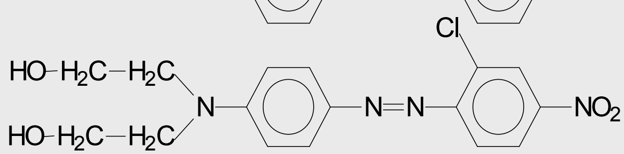
DIAMINO



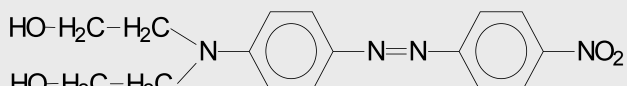
p-AMINO



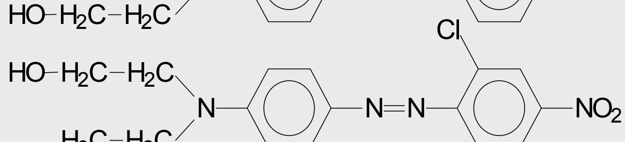
DO3



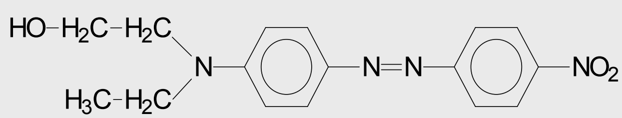
DR19Cl



DR19

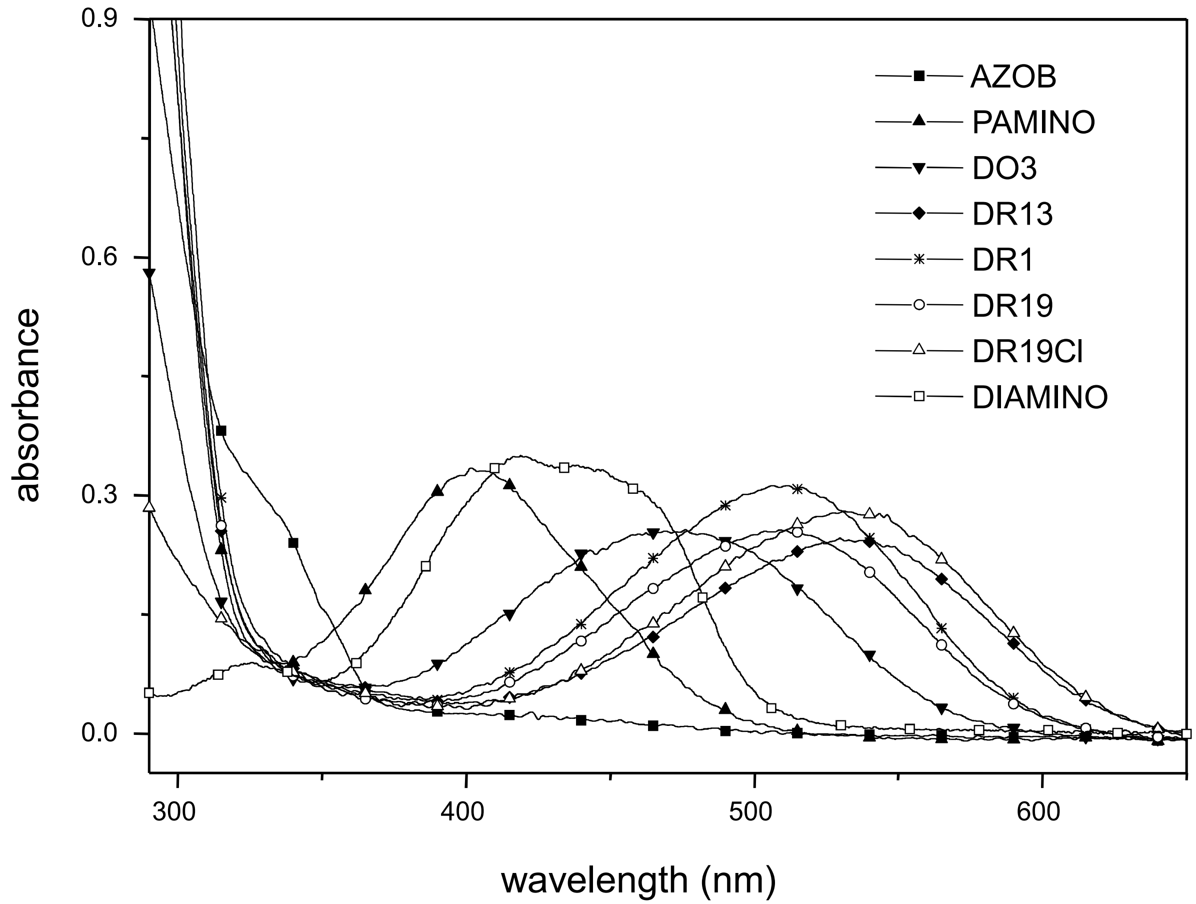


DR13

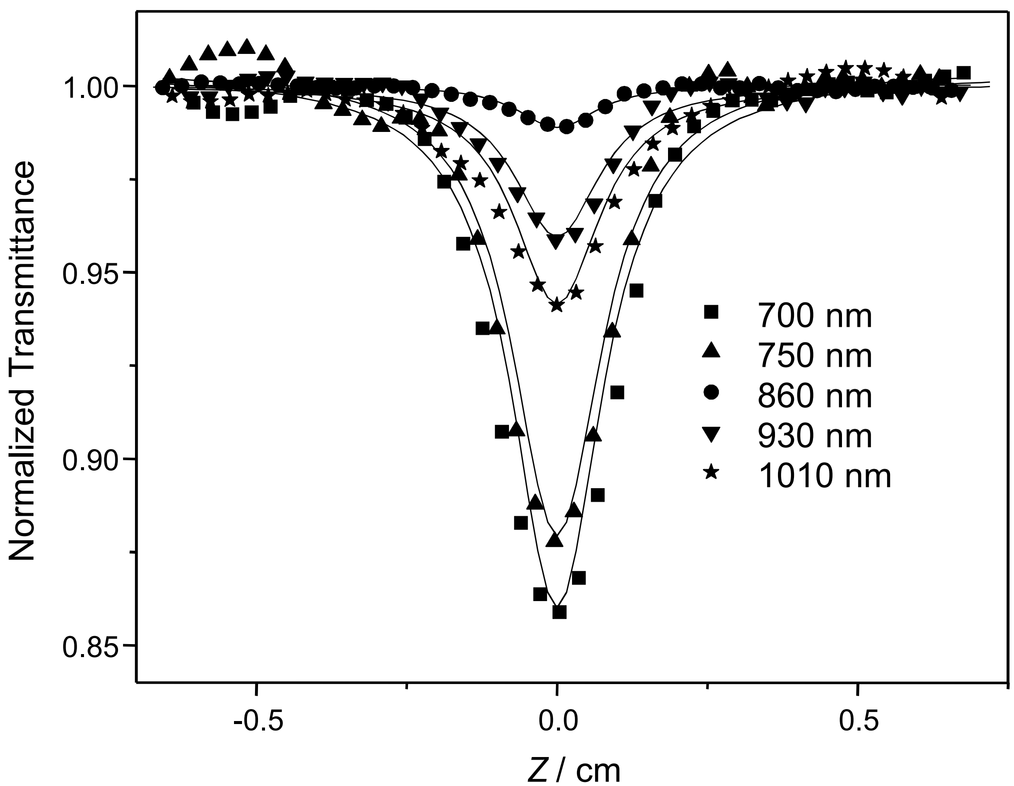


DR1

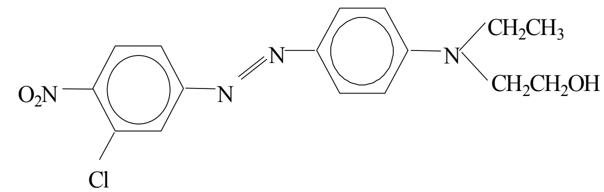
Linear absorption of azoaromatic compounds



Two-photon absorption



DR13

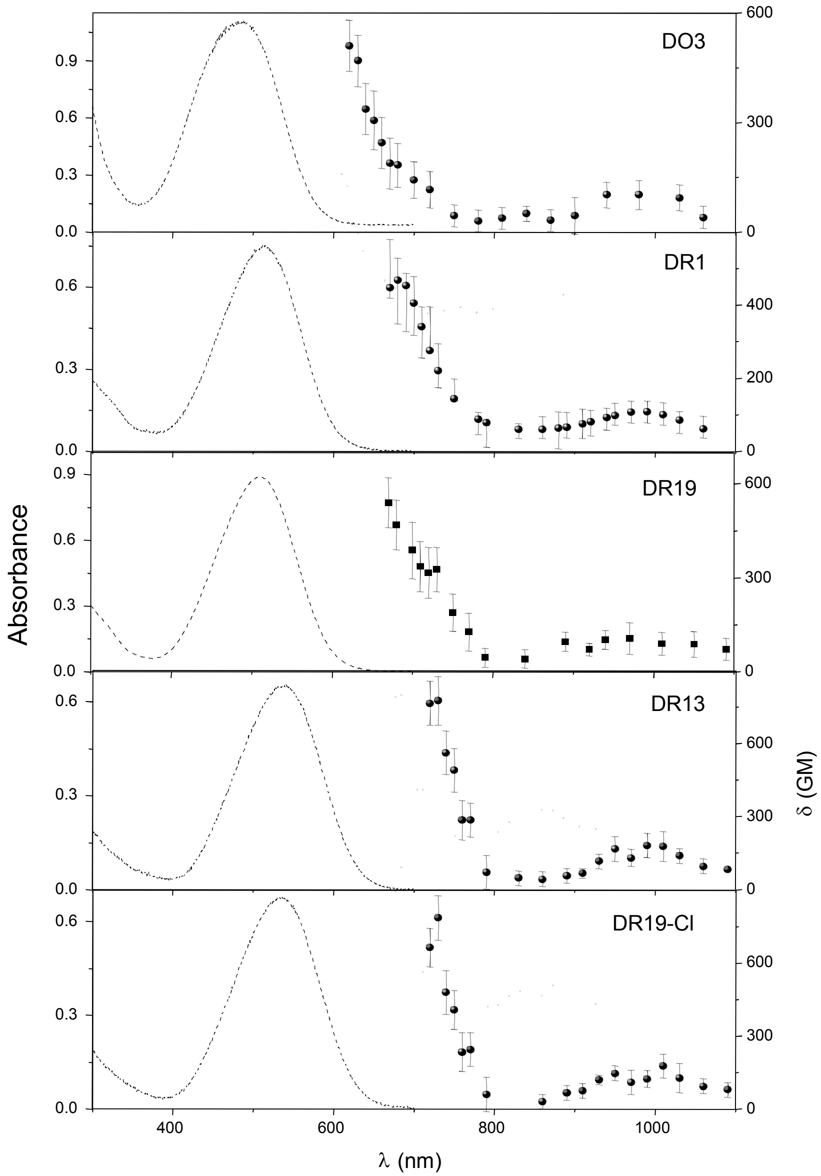


$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

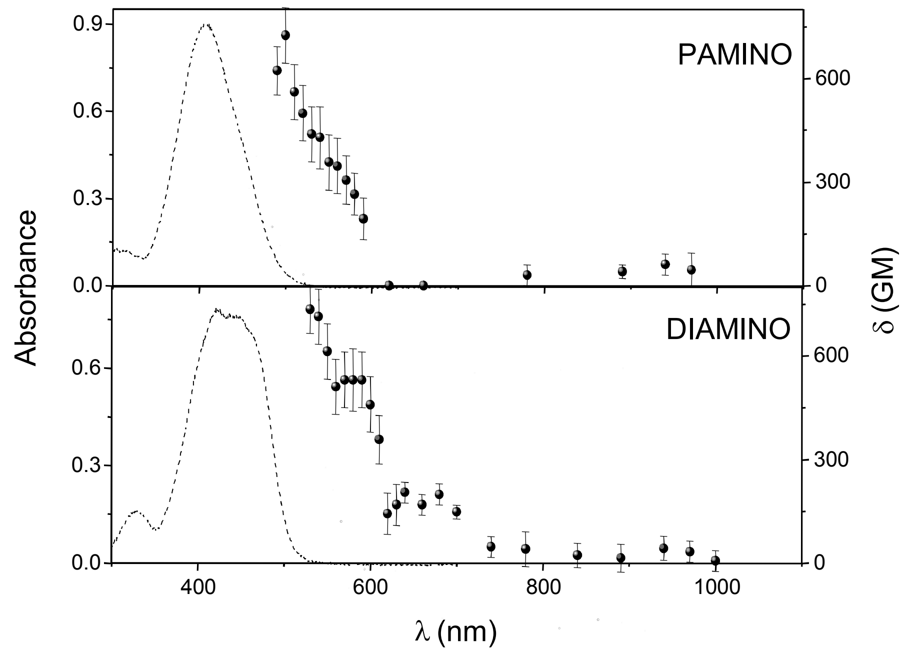
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

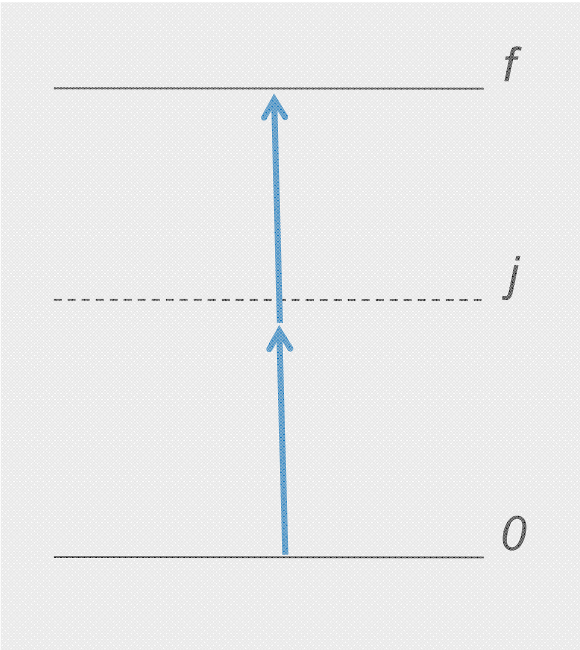
Pseudostilbenes



Aminoazobenzenes



Sum-over-states model



2PA cross-section at the laser frequency ν_p

$$\sigma^{(2)}(\nu_p) = \frac{(2\pi)^4 \nu_p^2}{(ch)^2} g(2\nu_p)|S_{f0}|^2$$

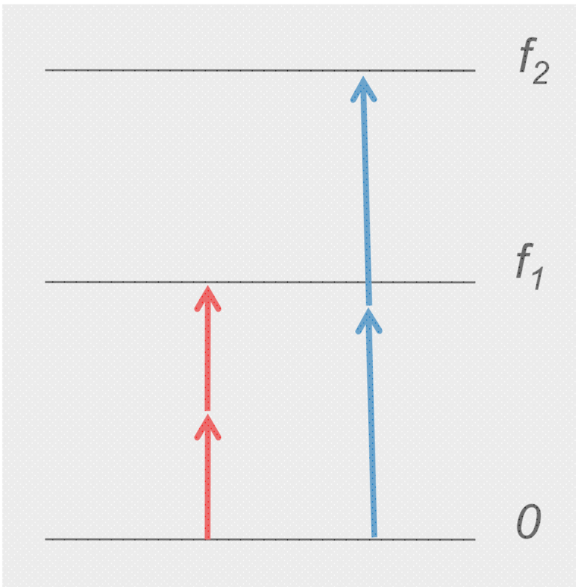
two-photon transition line-shape

$$g(2\nu_p) = \frac{1}{\pi} \frac{\Gamma_{f0}}{(\nu_{f0} - 2\nu_p)^2 + \Gamma_{f0}^2}$$

resonance enhance factor

$$|S_{f0}|^2 = \frac{4}{5} \frac{|\boldsymbol{\mu}_{j0}|^2 |\boldsymbol{\mu}_{fj}|^2}{(\nu_{j0} - \nu_p)^2 + \Gamma_{j0}^2}$$

Sum-over-states model

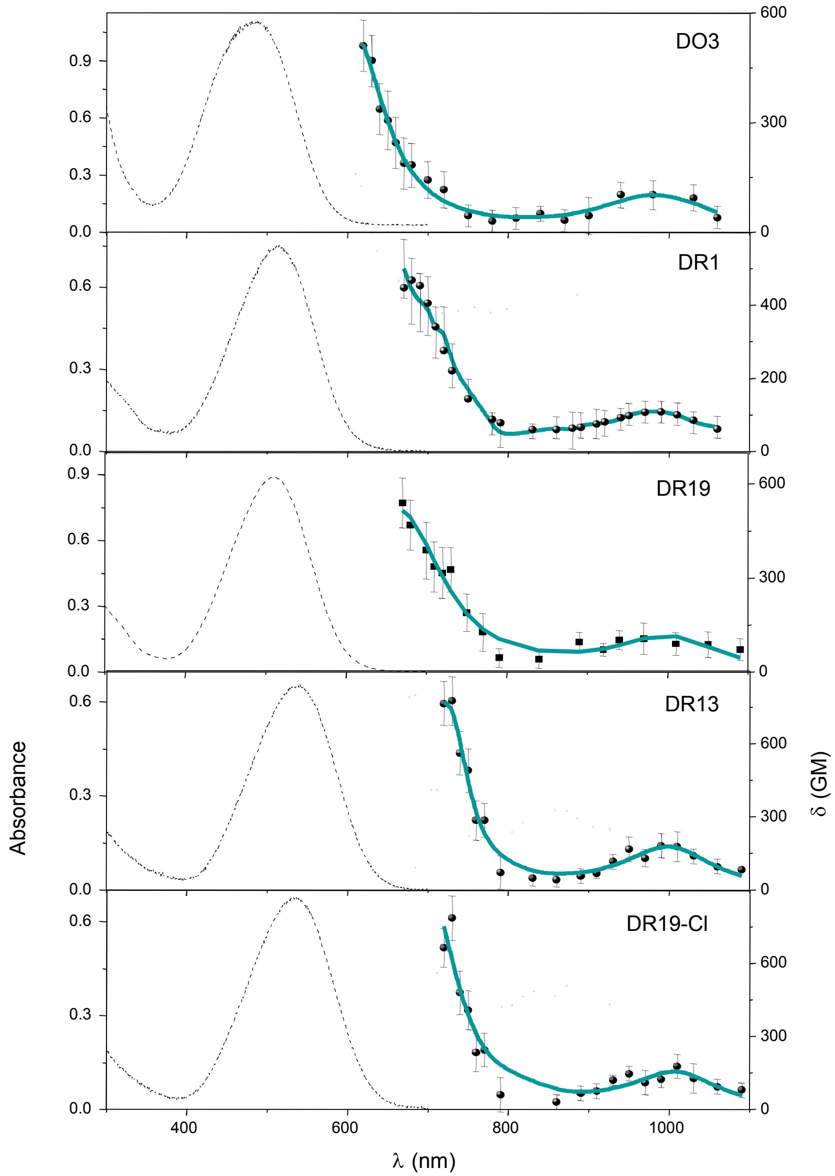


for the azoaromatic compounds there are two final states (f_1 and f_2)

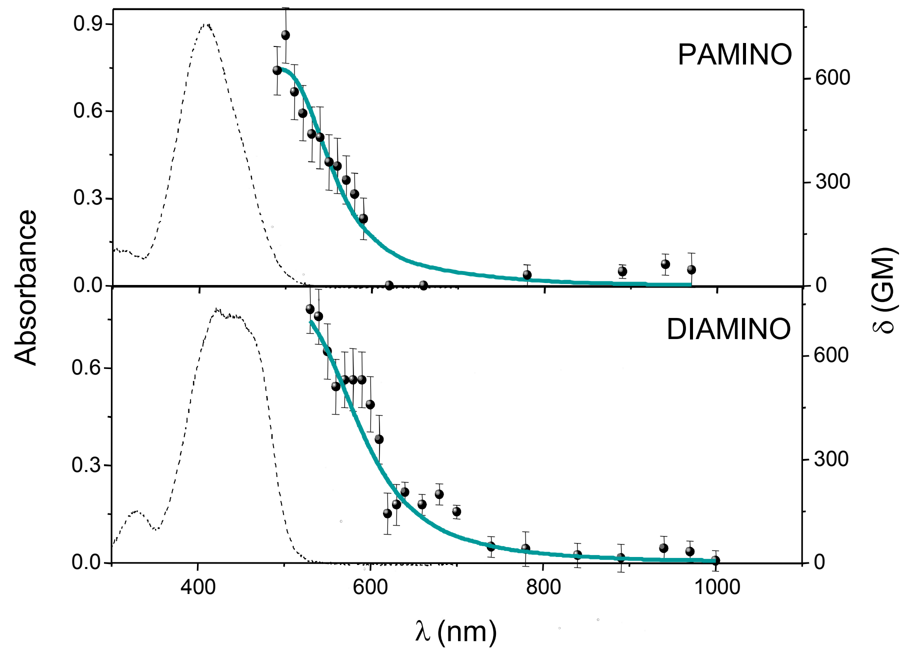
2PA cross-section at the laser frequency ν_p

$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0} - \nu)^2 + \Gamma_{i0}^2} \left[\frac{A_1}{(\nu_{f_1 0} - 2\nu)^2 + \Gamma_{f_1 0}^2} + \frac{A_2}{(\nu_{f_2 0} - 2\nu)^2 + \Gamma_{f_2 0}^2} \right]$$

Pseudostilbenes



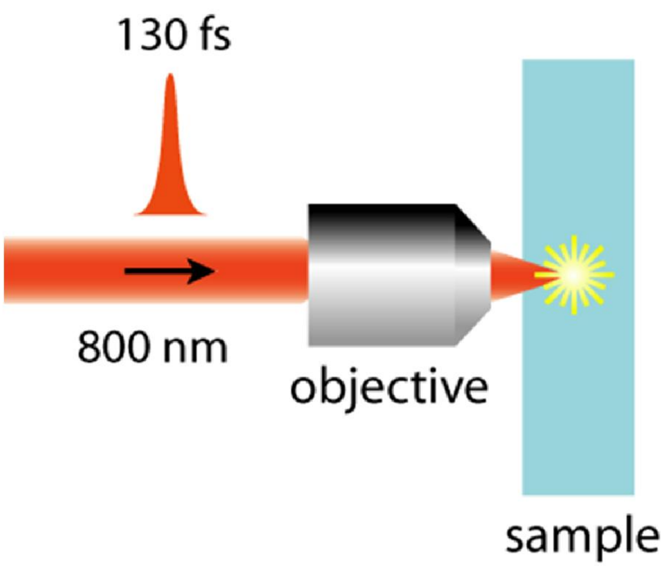
Aminoazobenzenes



$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0}-\nu)^2+\Gamma_{i0}^2}\left[\frac{A_1}{(\nu_{f_1 0}-2\nu)^2+\Gamma_{f_1 0}^2}+\frac{A_2}{(\nu_{f_2 0}-2\nu)^2+\Gamma_{f_2 0}^2}\right]$$

Microfabrication

Microfabricate and microstructure materials using fs-laser and nonlinear optical processes



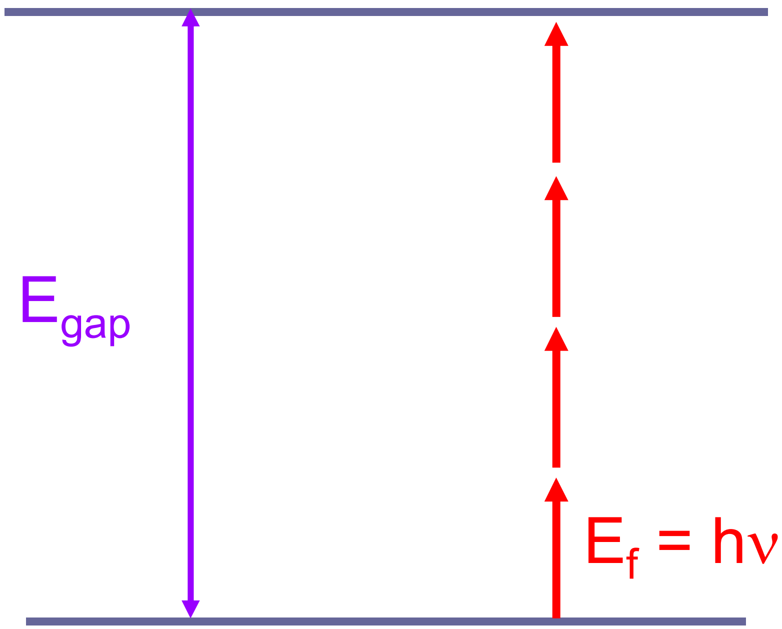
fs-laser microfabrication

photon energy < bandgap

nonlinear interaction

fs-laser microfabrication

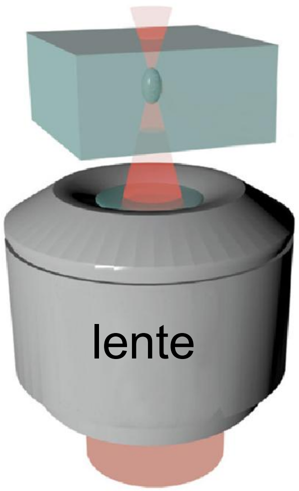
nonlinear interaction



multiphoton absorption

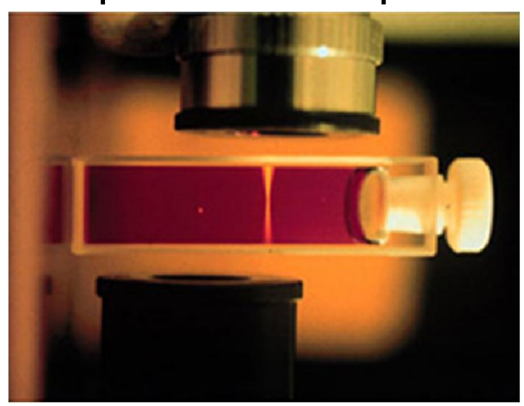
multiphoton absorption

nonlinear interaction



spatial confinement of excitation

two-photon absorption

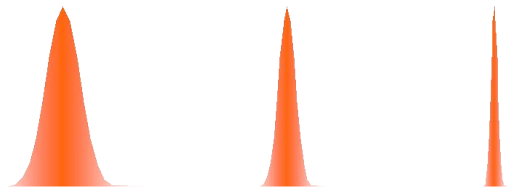


$$\alpha = \alpha_0 + \beta I$$
$$R \propto I^2$$

feature exploited for microfabrication

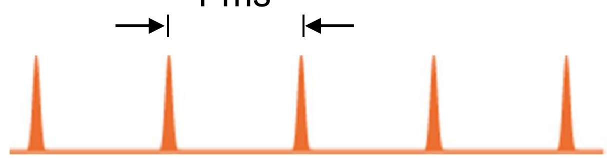
femtosecond pulses

Ti:Sapphire lasers

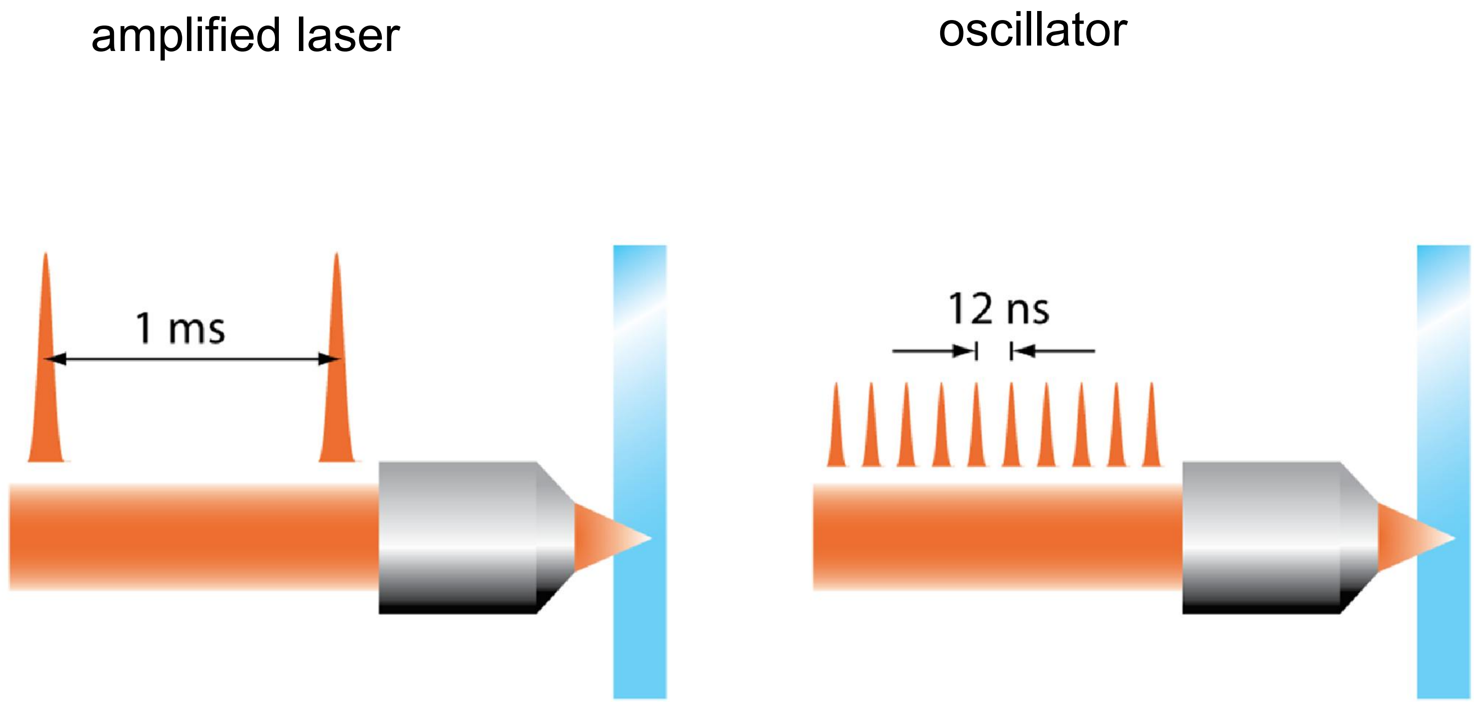


100 fs 50 fs 20 fs

1 fs = 10^{-15} s

Repetition rate		Energy
1 KHz	1 ms  100 fs	mJ
86 MHz	12 ns  100 fs	nJ

fs-micromachining



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

fs-micromachining

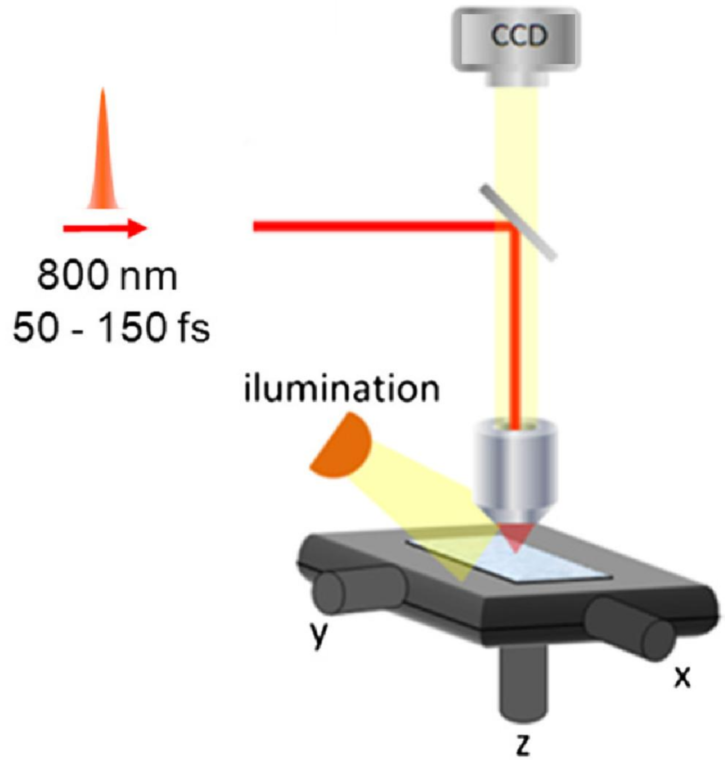
microfabrication can be controlled by

- objective NA
- number of pulses – scanning speed
- pulse energy

two main techniques

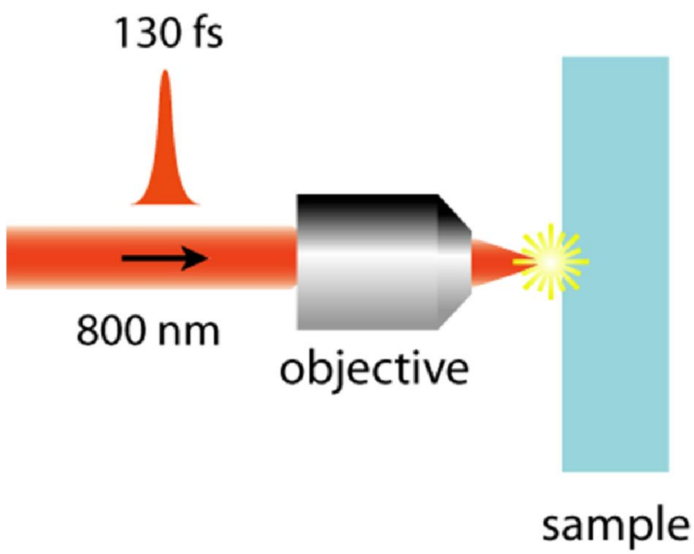
- fs-laser micromachining/microstructuring
- microfabrication via two-photon polymerization

fs-laser microstructuring experimental setup



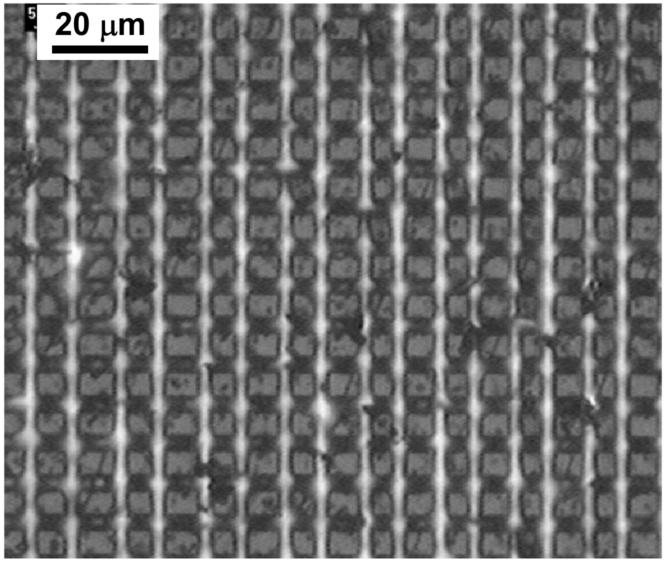
fs-laser micromachining

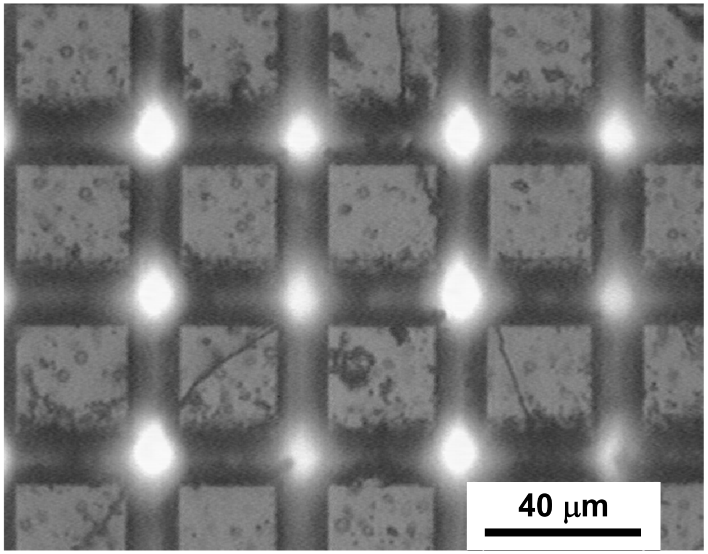
Surface



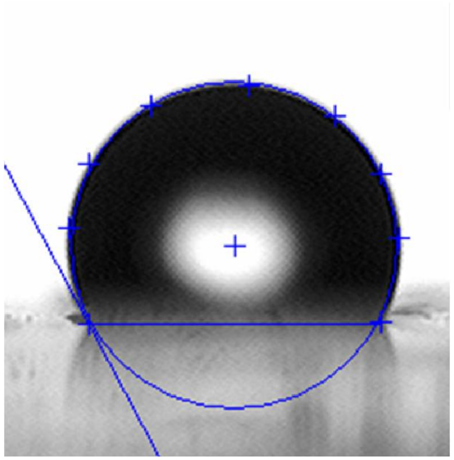
laser microfabrication: super hydrophobic surface

examples of fabricated surfaces



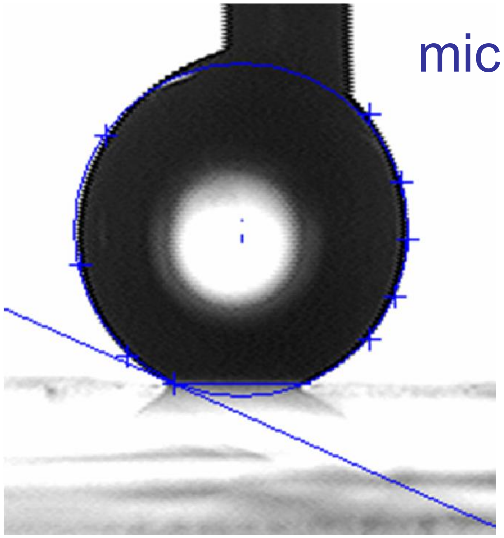


microstructuring polymer



flat surface

θ = 118º

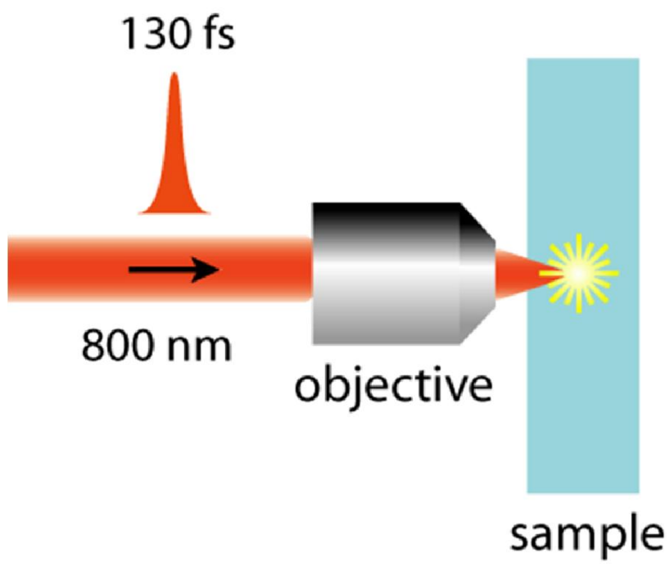


microstructured surface

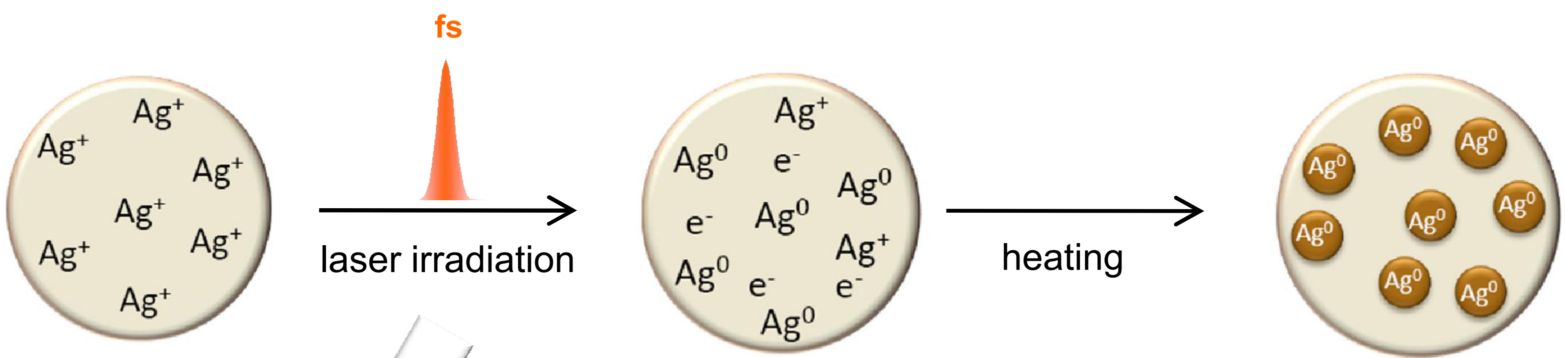
θ = 160º

fs-laser micromachining

Volume



Generation of Ag nanoparticles



Ag nanoparticles are generated only in the irradiated area due to the **fs-laser induced photoreduction**

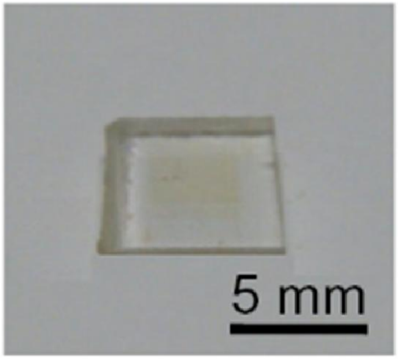
Free electron generation
Photoreduction reaction

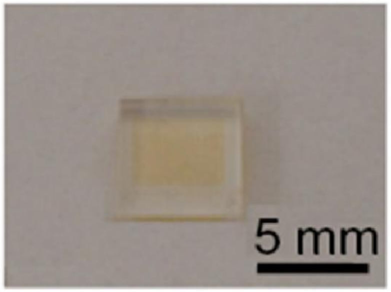
$$Ag^{+} + e^{-} \rightarrow Ag^{0}$$

Generation of Ag nanoparticles

Silver doped barium borate glass (Ag:BBO)

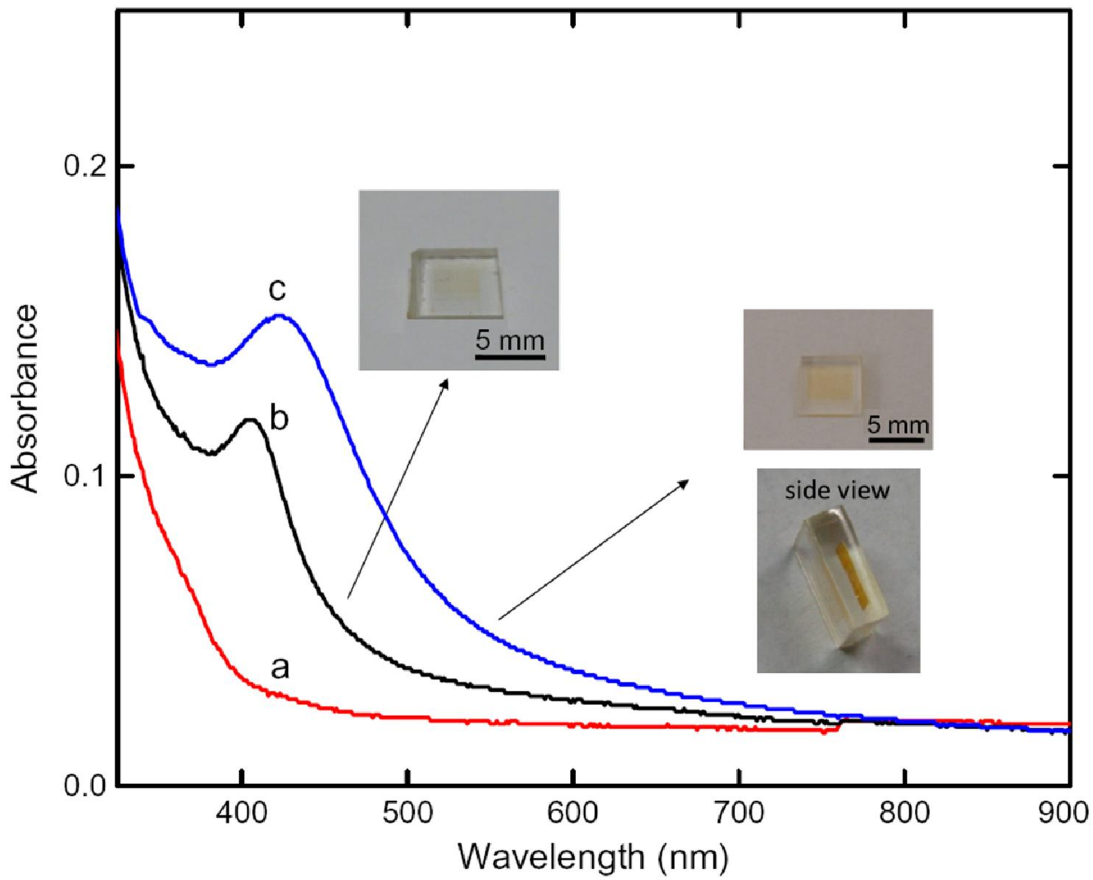
Sample after irradiation with the amplified fs-laser (1 kHz) and subsequent thermal treatment at 400 C for 1 h





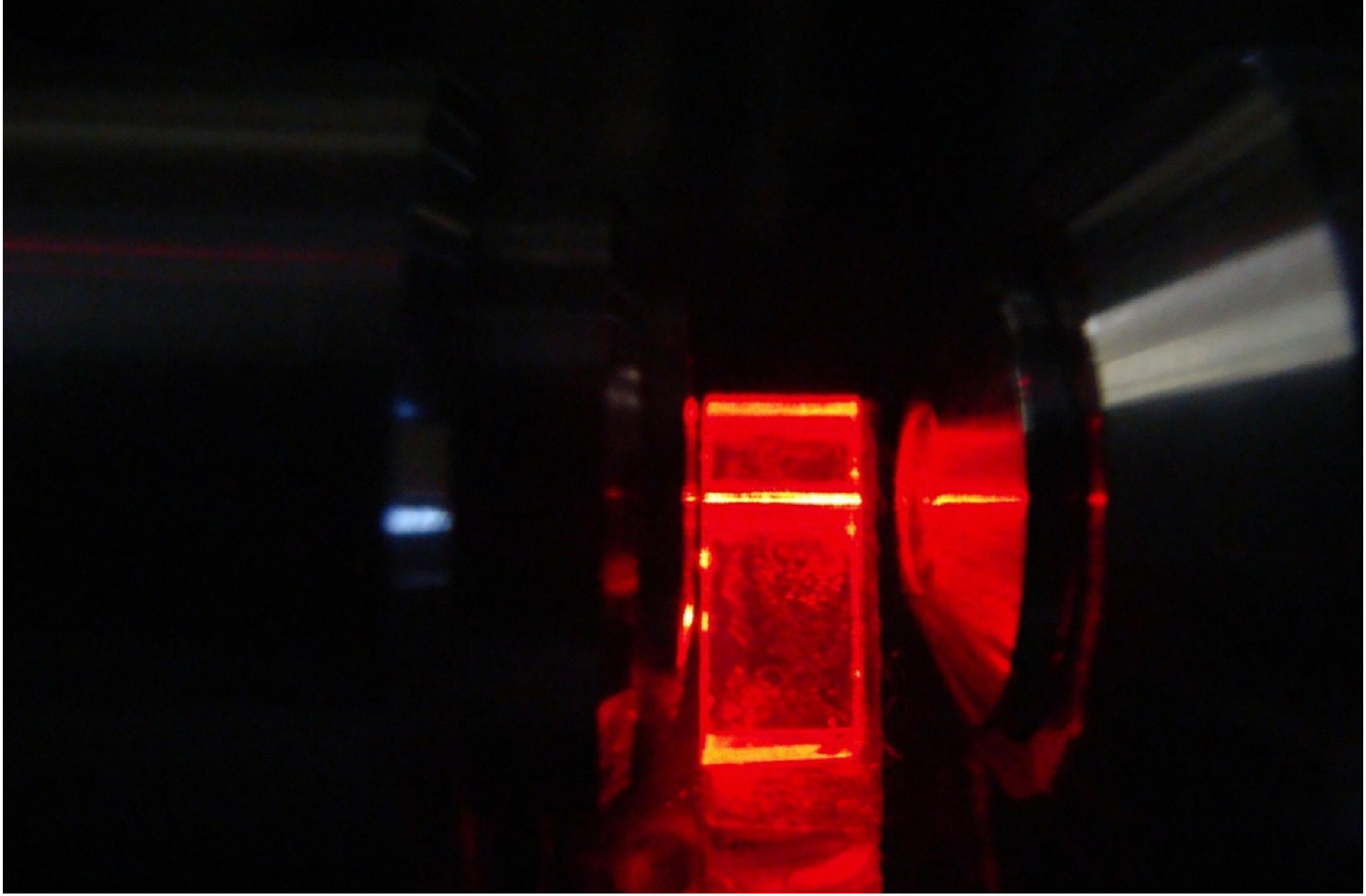
Sample after irradiation with the 5 MHz fs-laser

Generation of Ag nanoparticles



Absorption spectrum of the Ag:BBO sample as prepared (a), after irradiation with the 5 MHz fs-laser (b) and after irradiation with the amplified fs-laser (1 kHz) and subsequent thermal treatment.

fs-laser waveguides fabrication



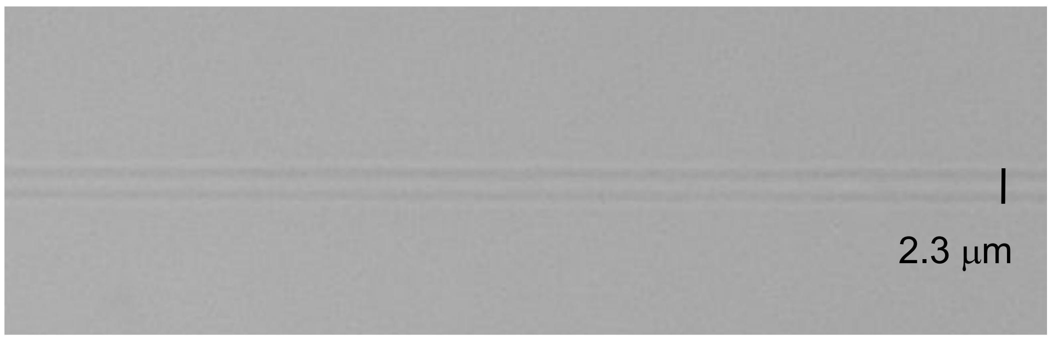
Waveguides fabrication

Sample:

Ag:P7W3

Tungsten lead pyrophosphate glass - ($70Pb_2P_2O_7$-$30WO_3$):1AgCl (%mol)

Waveguides fabricated using the 5-MHz laser system (50 fs) with 37 nJ/pulse and v = 10 µm/s

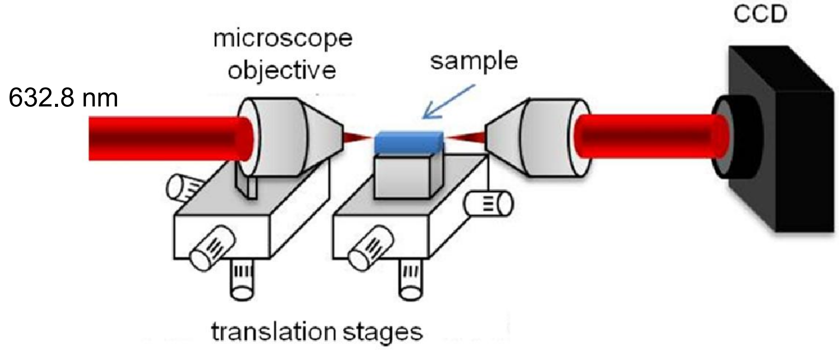


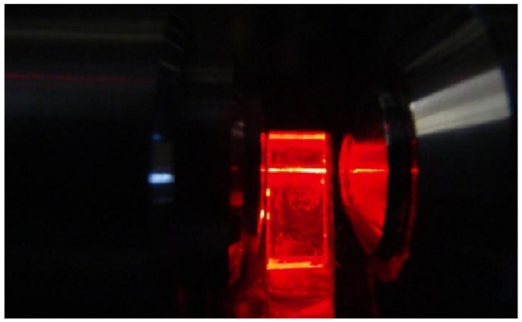
Top view

Cross-section view

Waveguides fabrication

Coupling light into the waveguides





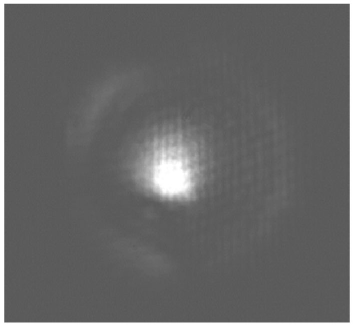
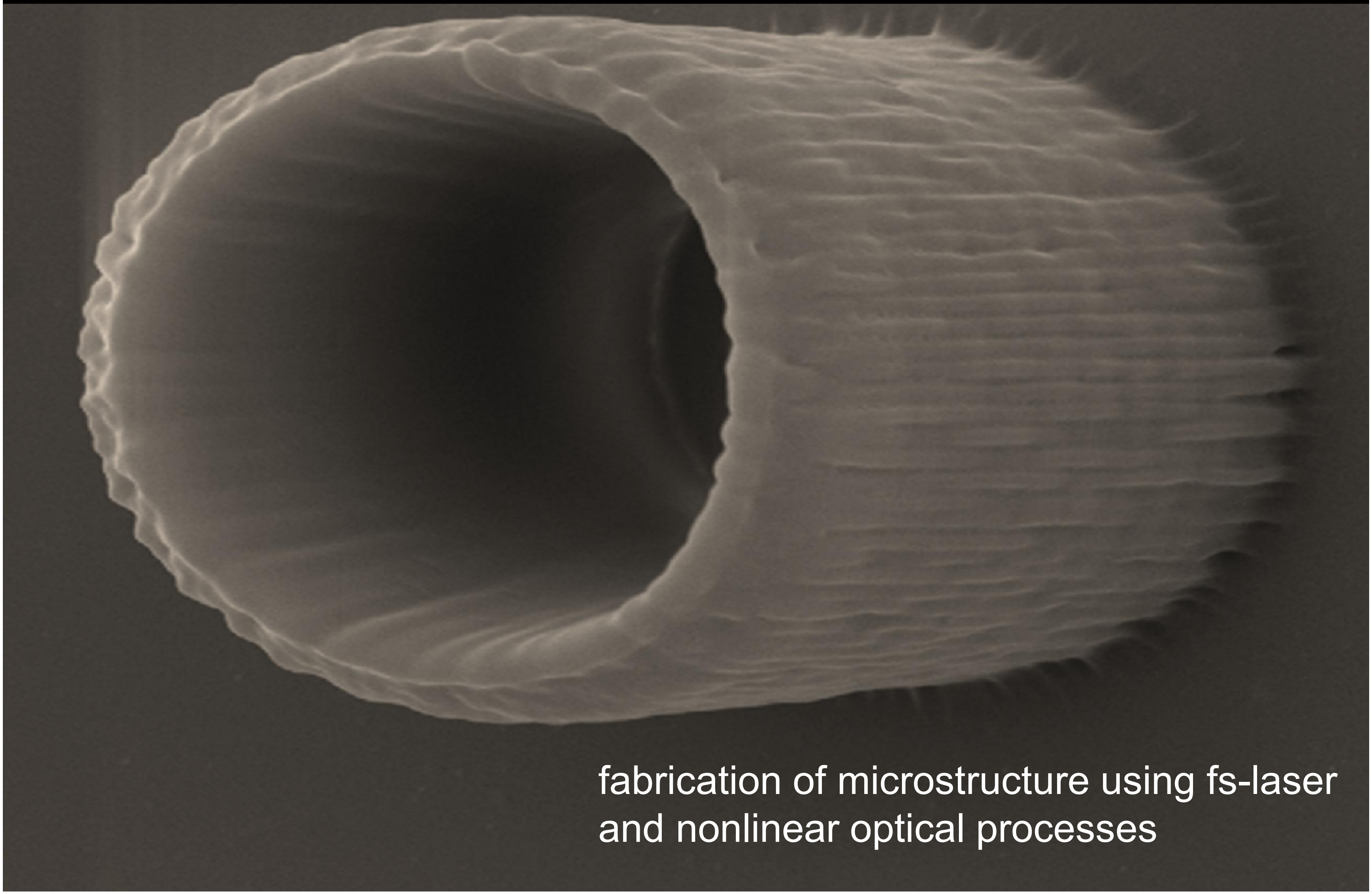


image of the waveguide output

measured waveguide loss L = 1.3 dB/mm

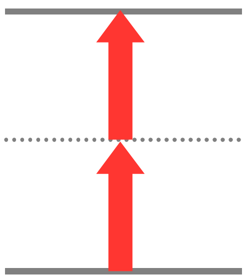
fs-laser microfabrication



Two-photon polymerization

Monomer + Photoinitiator → Polymer

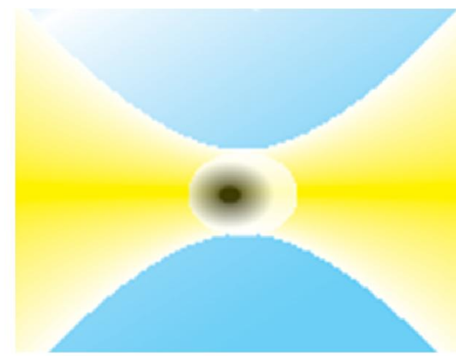
Photoinitiator is excited by ***two-photon absorption***

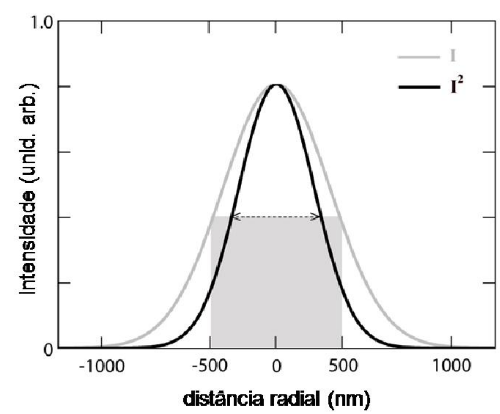


$$R \propto I^2$$

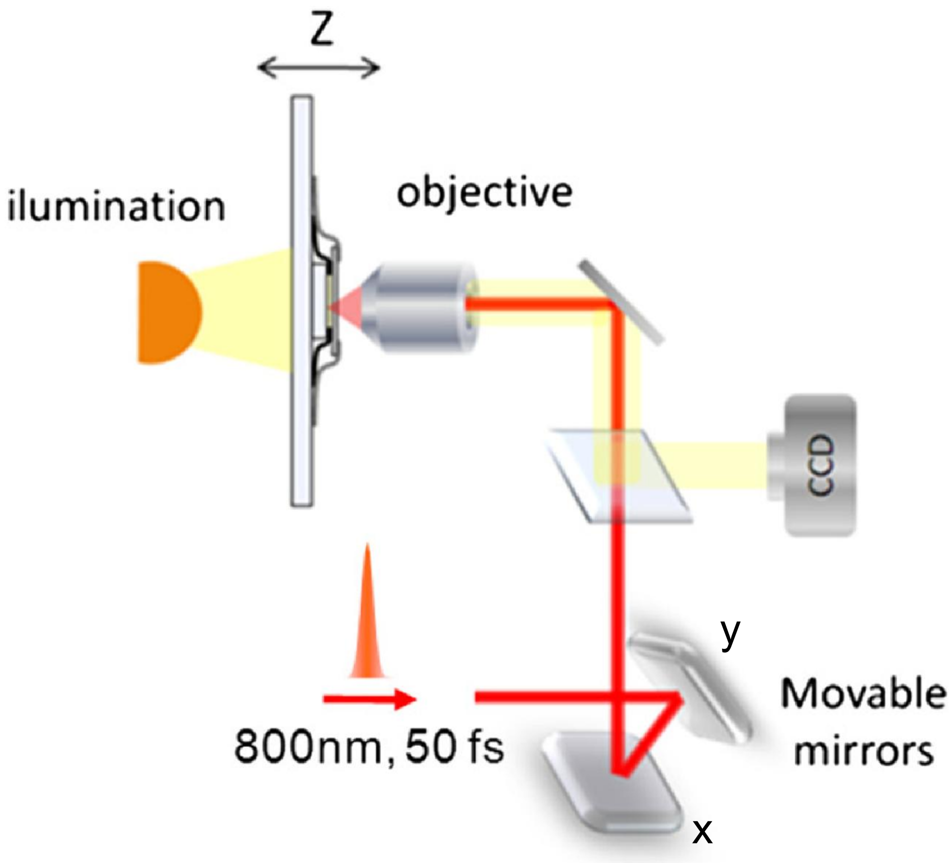
The polymerization is confined to the focal volume.

High spatial resolution





Two-photon polymerization setup



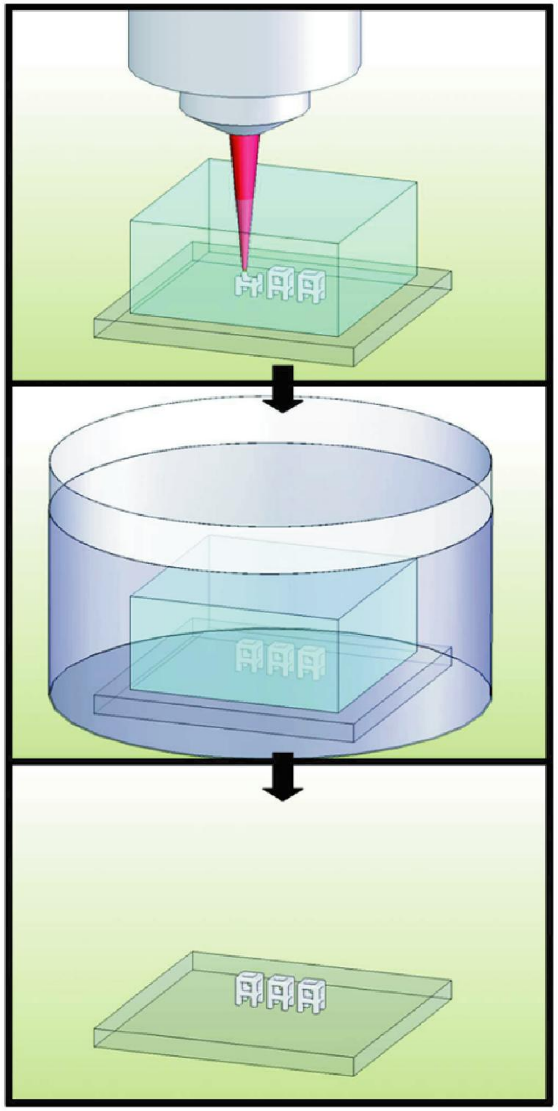
Ti:sapphire laser oscillator

- 50 fs
- 800 nm
- 80 MHz
- 20 mW

Objective

40 x
0.65 NA

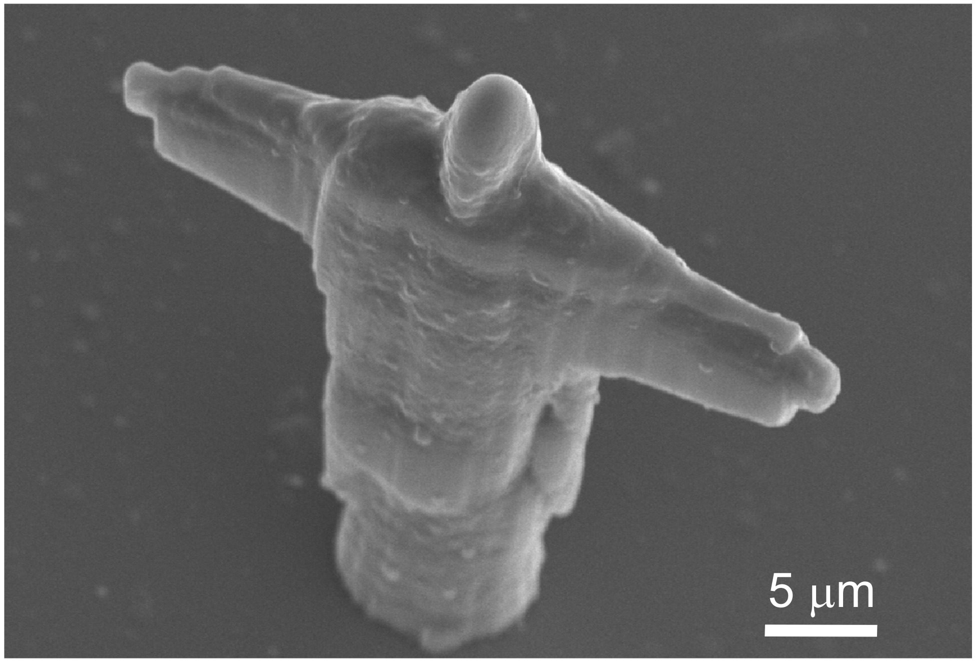
Two-photon polymerization



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

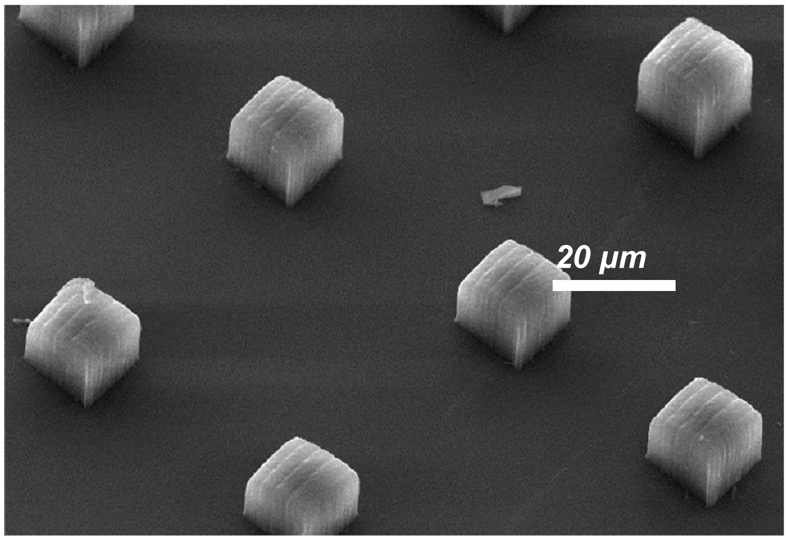
two-photon polymerization

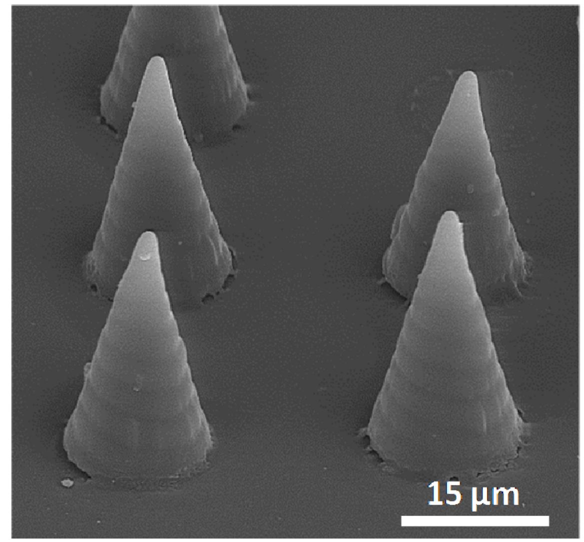
Microstructure fabricated by two-photon polymerization

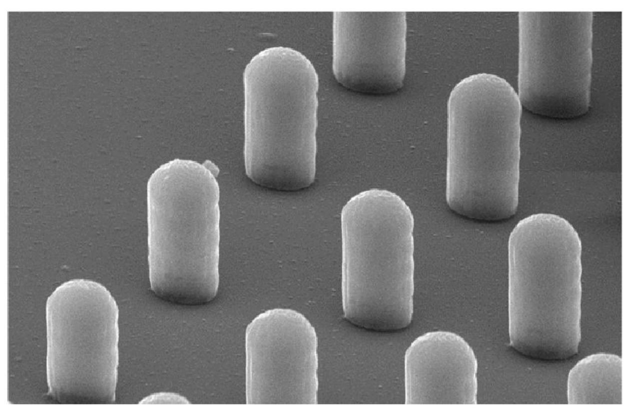


Two-photon polymerization

Microstructures fabricated by two-photon polymerization

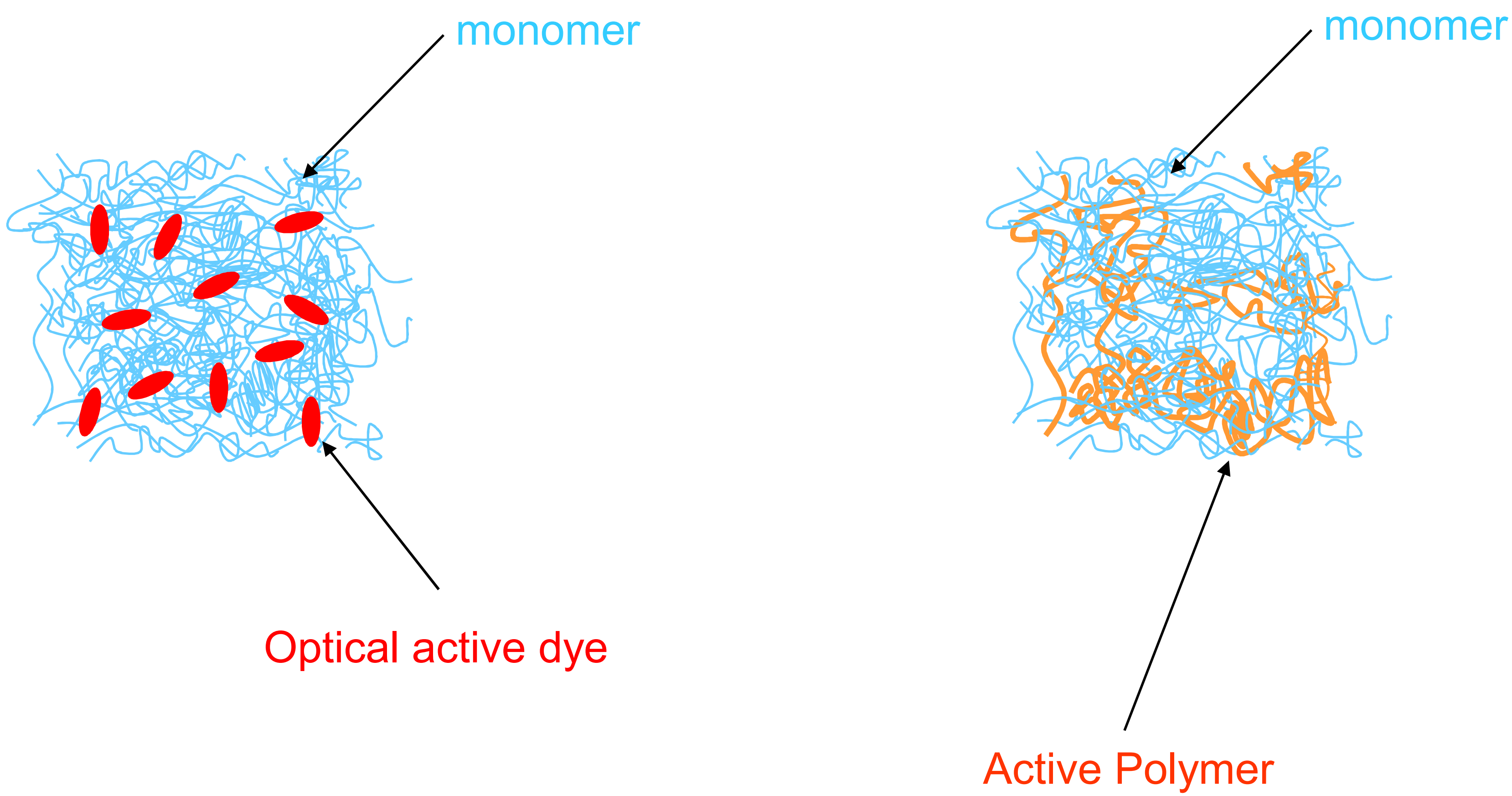






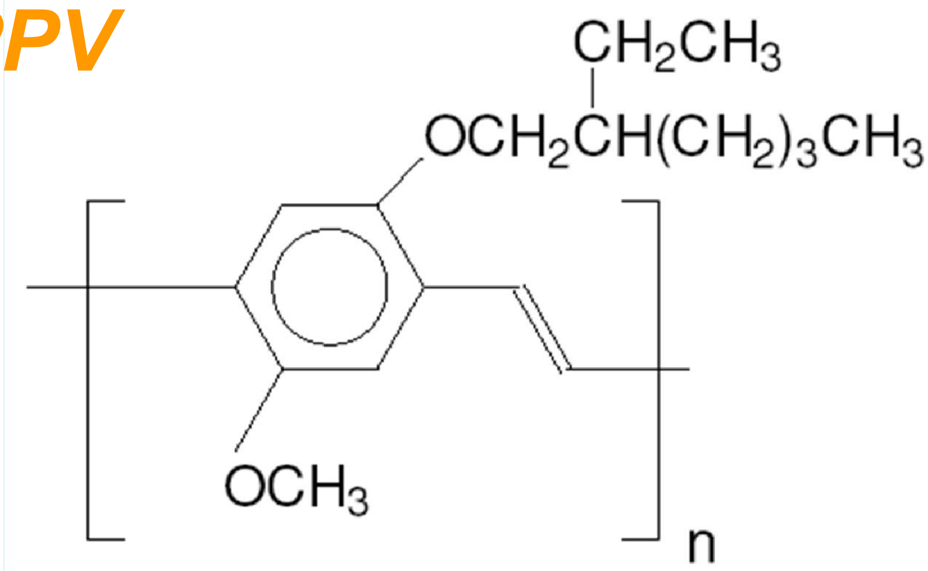
Doping microstructures

Microstructures containing active compounds



Microstructure containing MEH-PPV

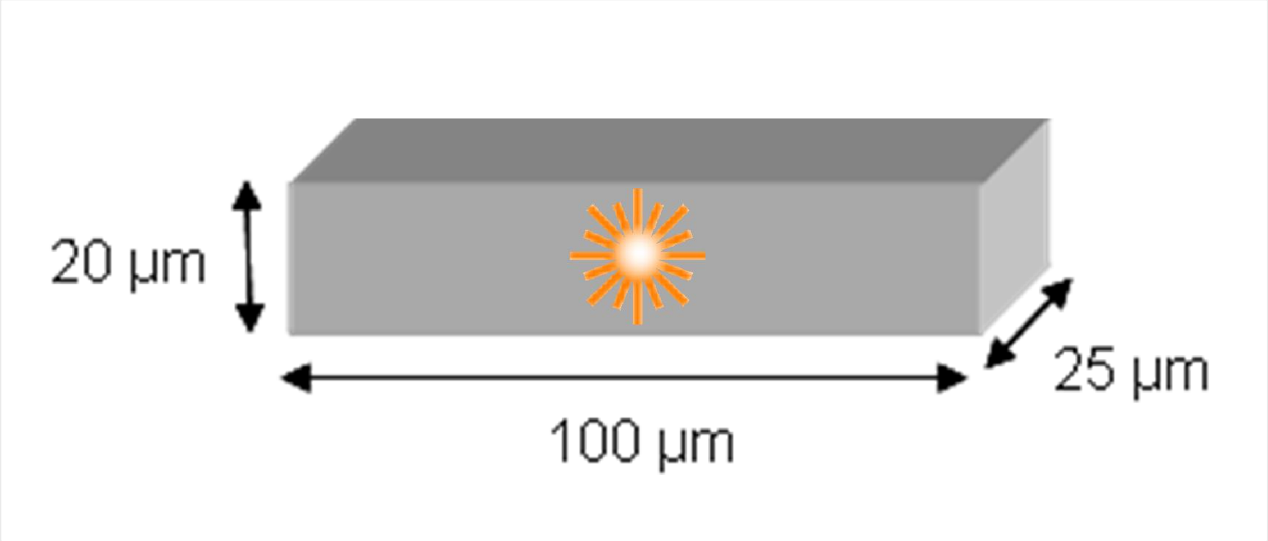
MEH-PPV



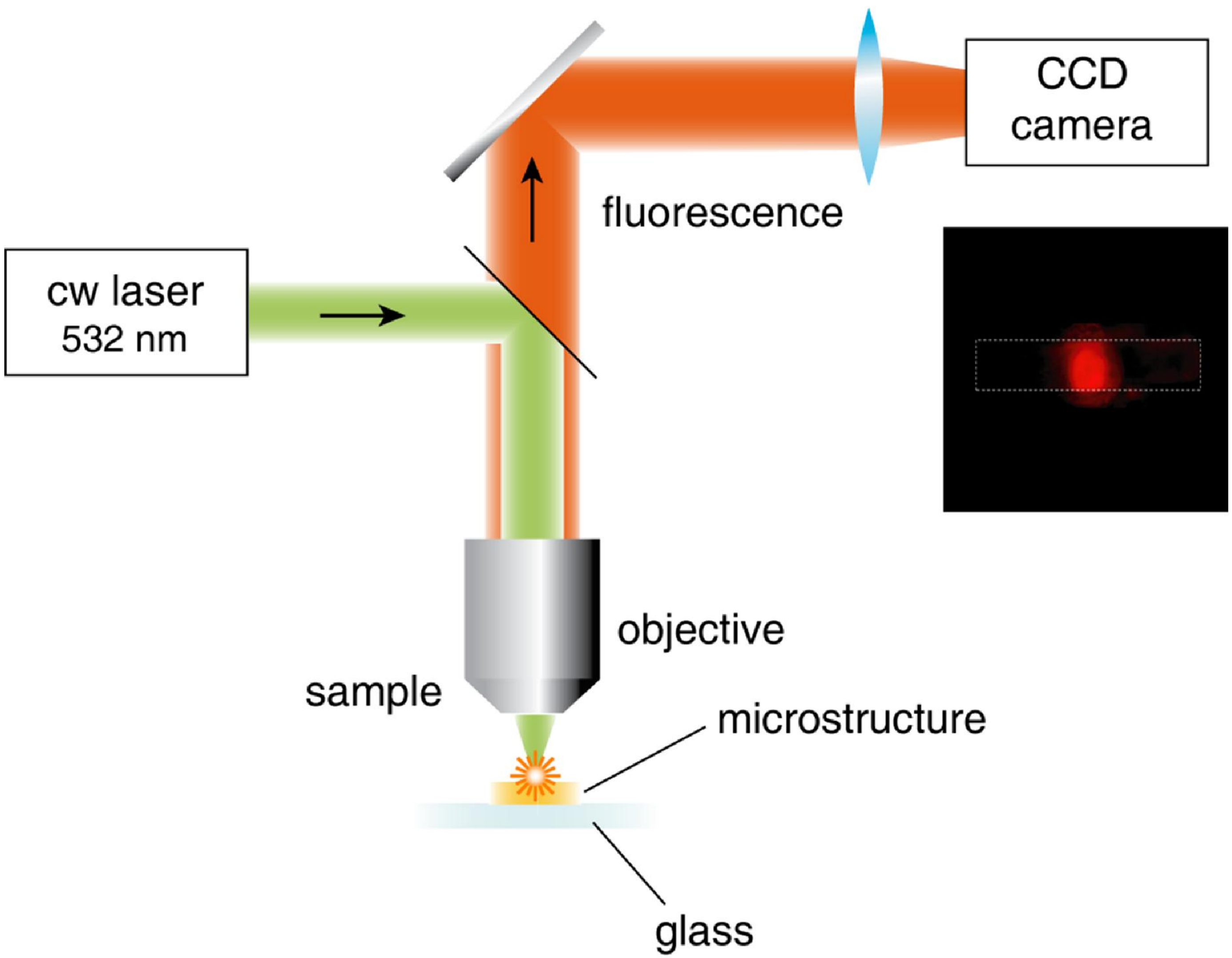
- Fluorescence
- Electro Luminescent
- Conductive

Microstructure containing MEH-PPV

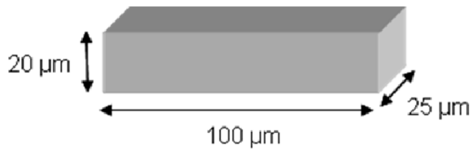
Do we have waveguiding in the microstructure ?

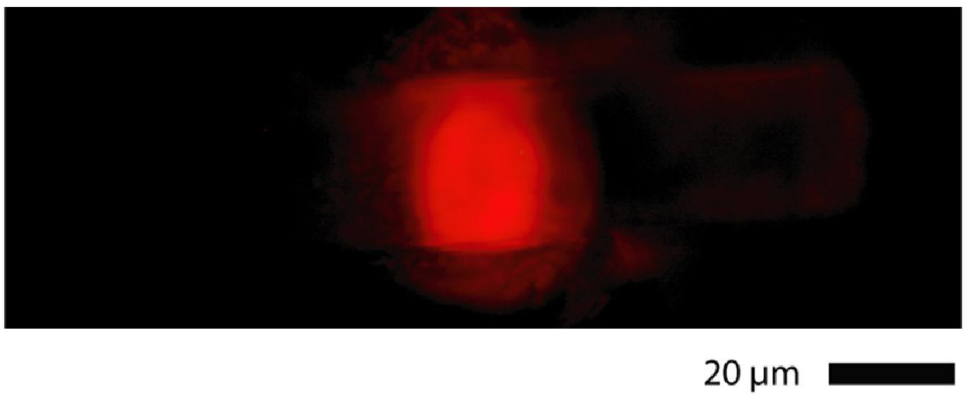


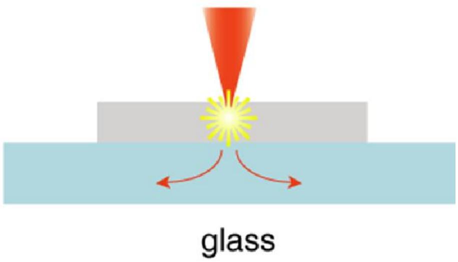
Microstructure containing MEH-PPV



Microstructure containing MEH-PPV

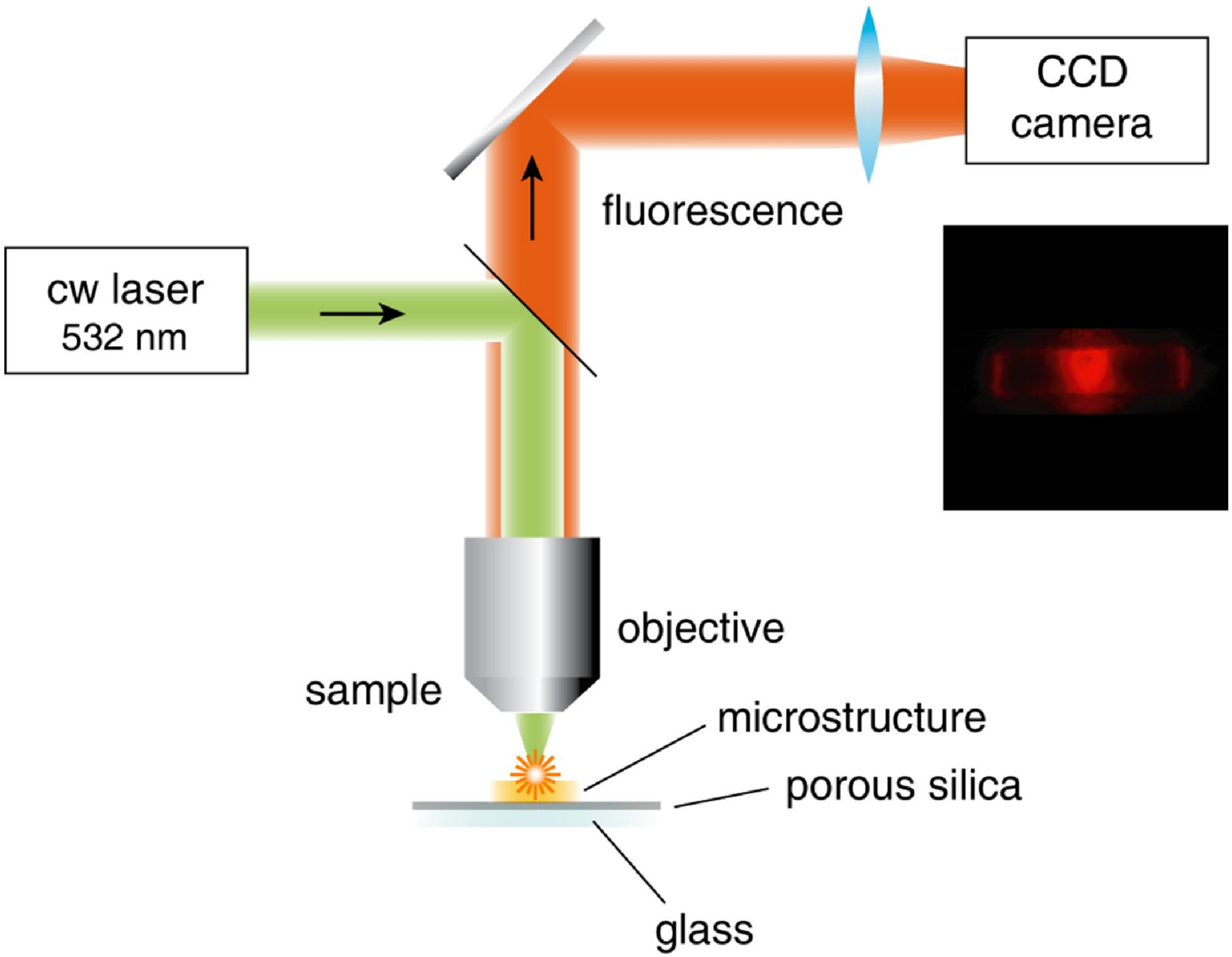




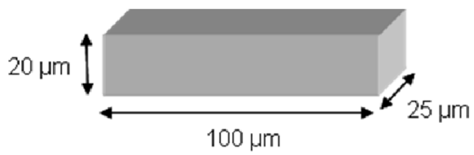


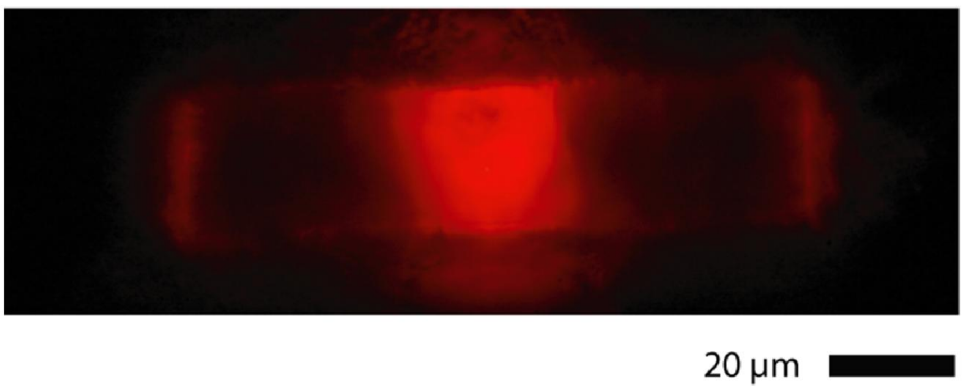
Appl. Phys. Lett., 95 1133091-3 (2009)

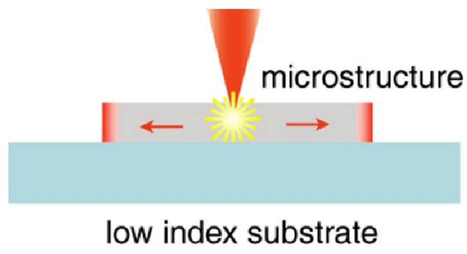
Microstructure containing MEH-PPV



Microstructure containing MEH-PPV







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

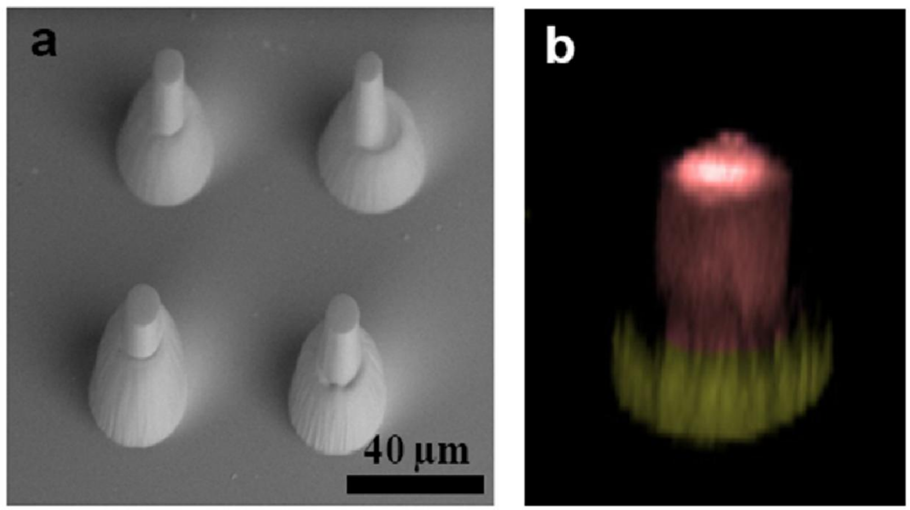
Applications: micro-laser; fluorescent microstructures; conductive microstructures

micro-environment to study cells and bacteria

Guiding bacterial growth in a micro-environment

to study bacterial growth it was needed to develop
double doped microstructures

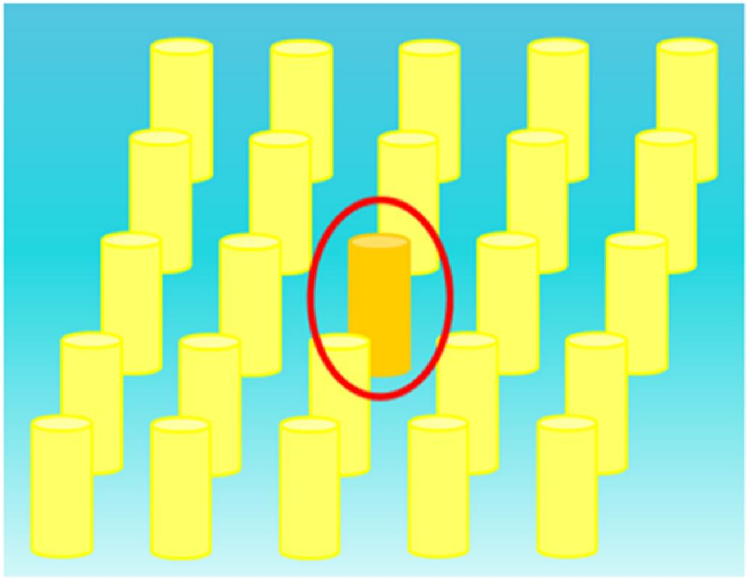
microstructure containing Fluorescein and Rhodamine

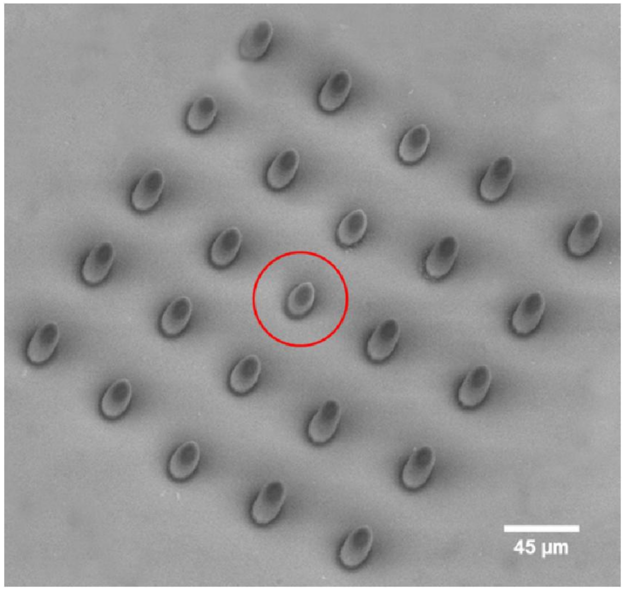


(a) SEM of a double-doped microstructure (top view).
(b) Confocal fluorescent microscopy image of the same microstructure.

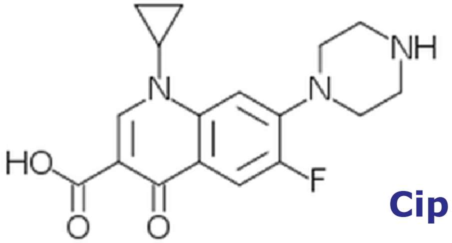
Guiding bacterial growth in a micro-environment

Study the development of E. coli in micro-environments:





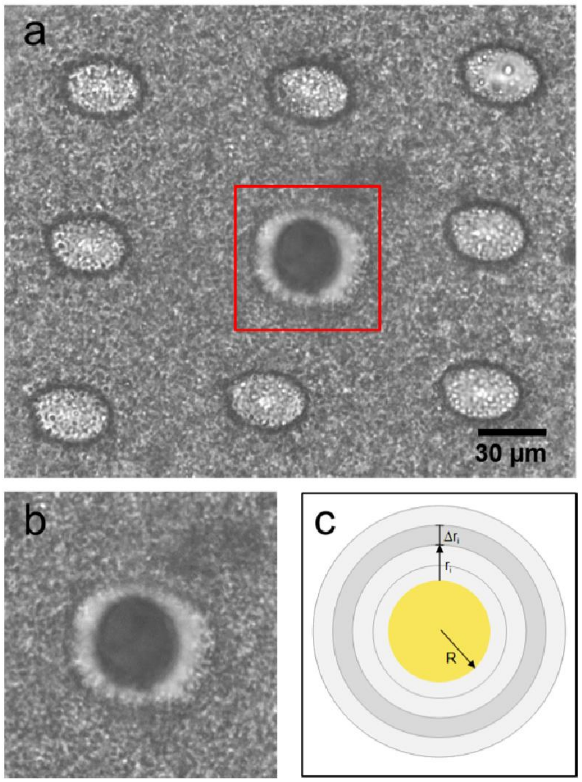
micro-environment in which the central structure contains antibiotic.



Ciprofloxacin

Guiding bacterial growth in a micro-environment

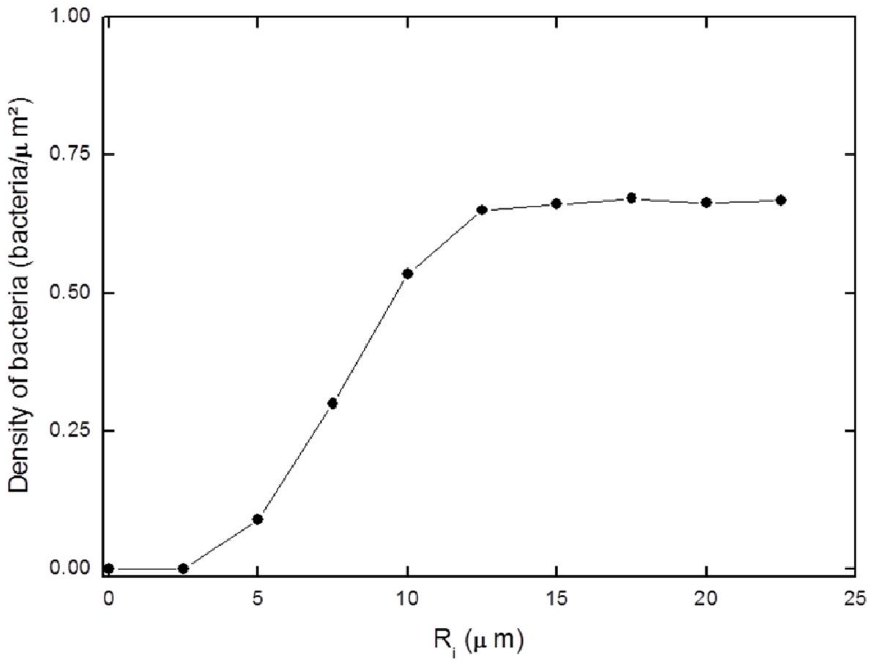
Study the development of E. coli in micro-environments:



after 3 hours, we observed that a small region around the doped structure does not show bacterial growth.

such inhibition zone was analyzed by determining the bacterial density in concentric rings

Guiding bacterial growth in a micro-environment



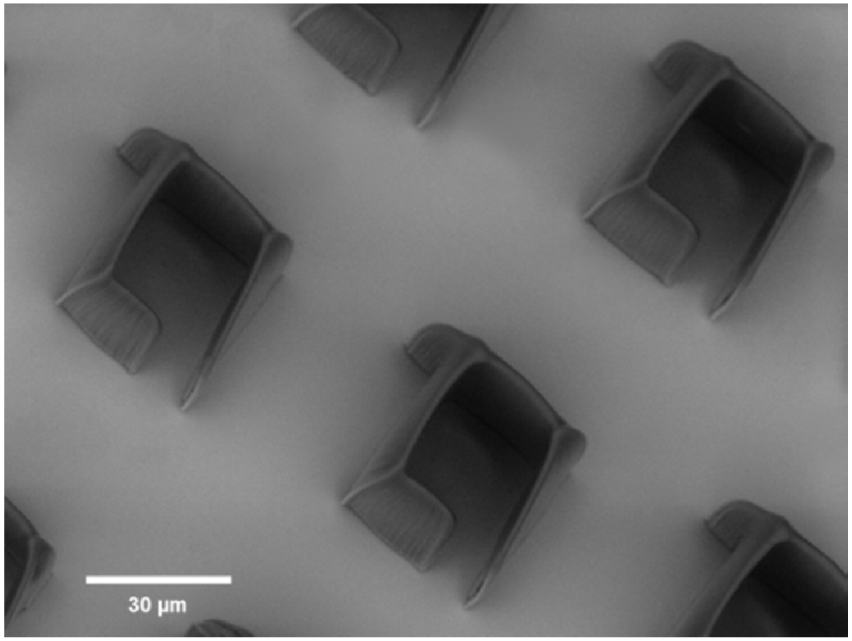
the density of bacteria grows monotonically with r_i

saturating when r_i reaches approximately 12 μm in about 0.7 bacteria/μm^2

the inhibition zone has a maximum range of approximately 10 μm, being more effective as one gets closer to the microstructure impregnated with ciprofloxacin

Guiding bacterial growth in a micro-environment

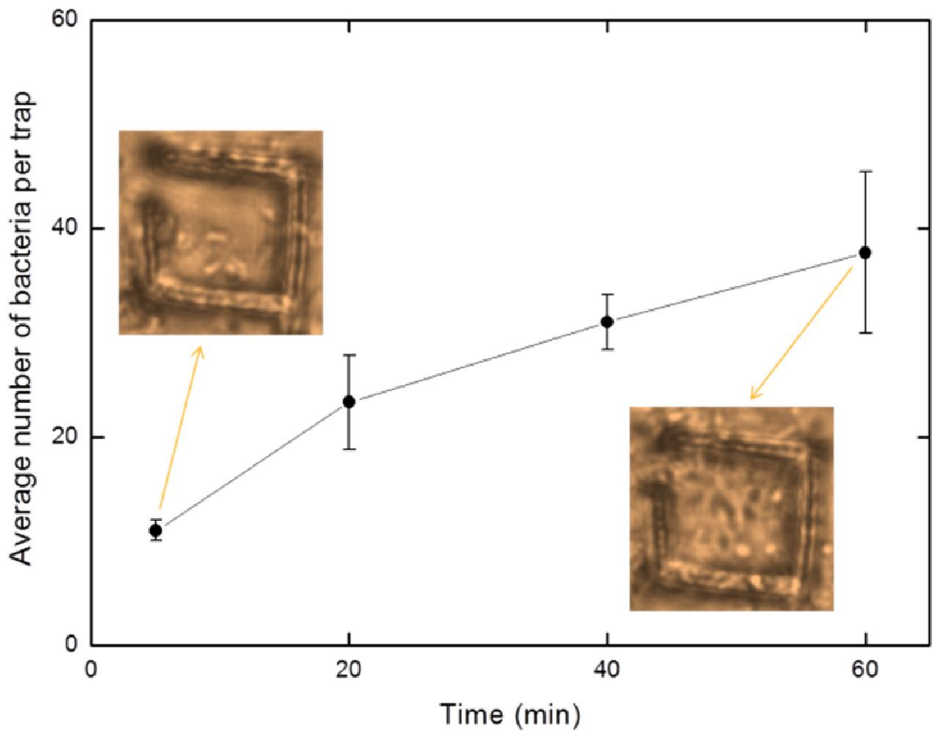
Bacteria microtraps



using micro-environments to study the dynamics of bacterial migration

Guiding bacterial growth in a micro-environment

Bacteria microtraps



using micro-environments to study the dynamics of bacterial migration

Acknowledgments

Team

Daniel S Correa
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Juliana Almeida
Adriano Otuka
Gustavo Almeida
Vinicius Tribuzi
Ruben Fonseca
Renato Martins
Paulo H. D. Ferreira

FAPESP

CNPq

CAPES

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UNITED STATES AIR FORCE

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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, Sao Carlos

Instituto de Física de São Carlos

IFSC

Professors: 92

Employers: 186
(technical and administration)

Students: 600 (undergrad)
105 (master)
170 (phD)

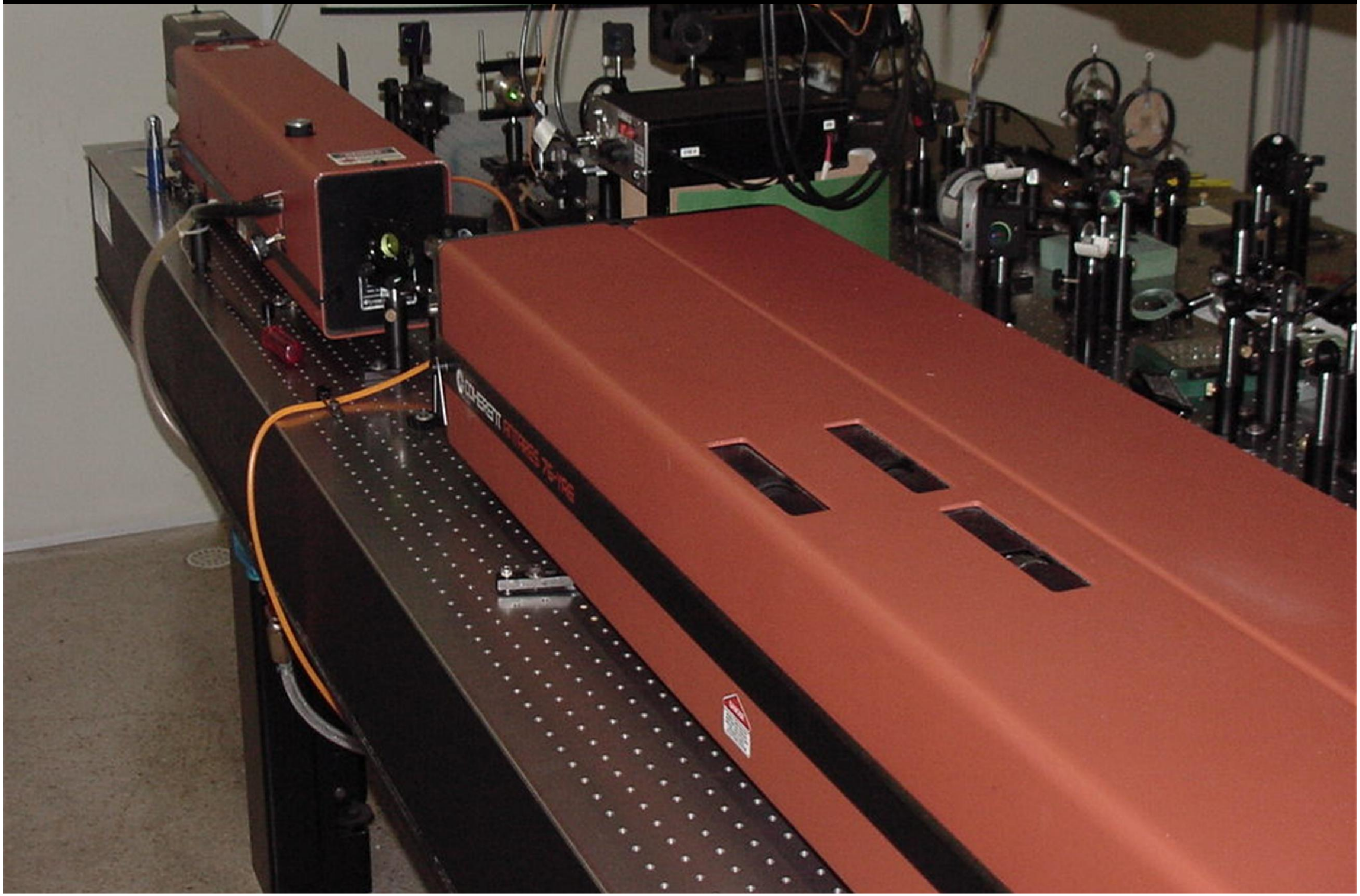
Several research areas in Physics and Material Sciences

Photonics Groups

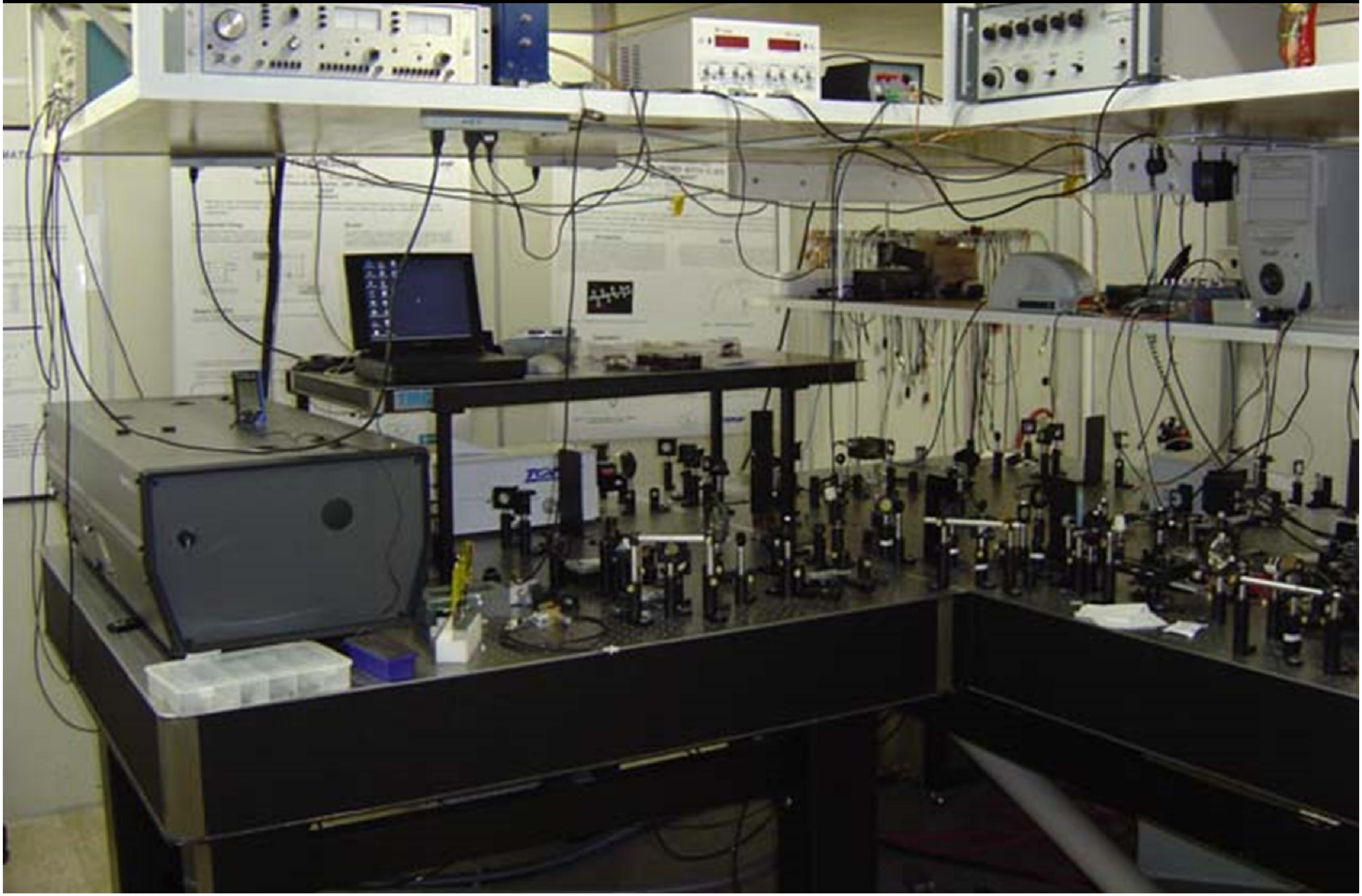
research areas

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

70 ps Q-switch/modelocked laser (532/1064 nm)



150 fs Ti:sapphire amplifier



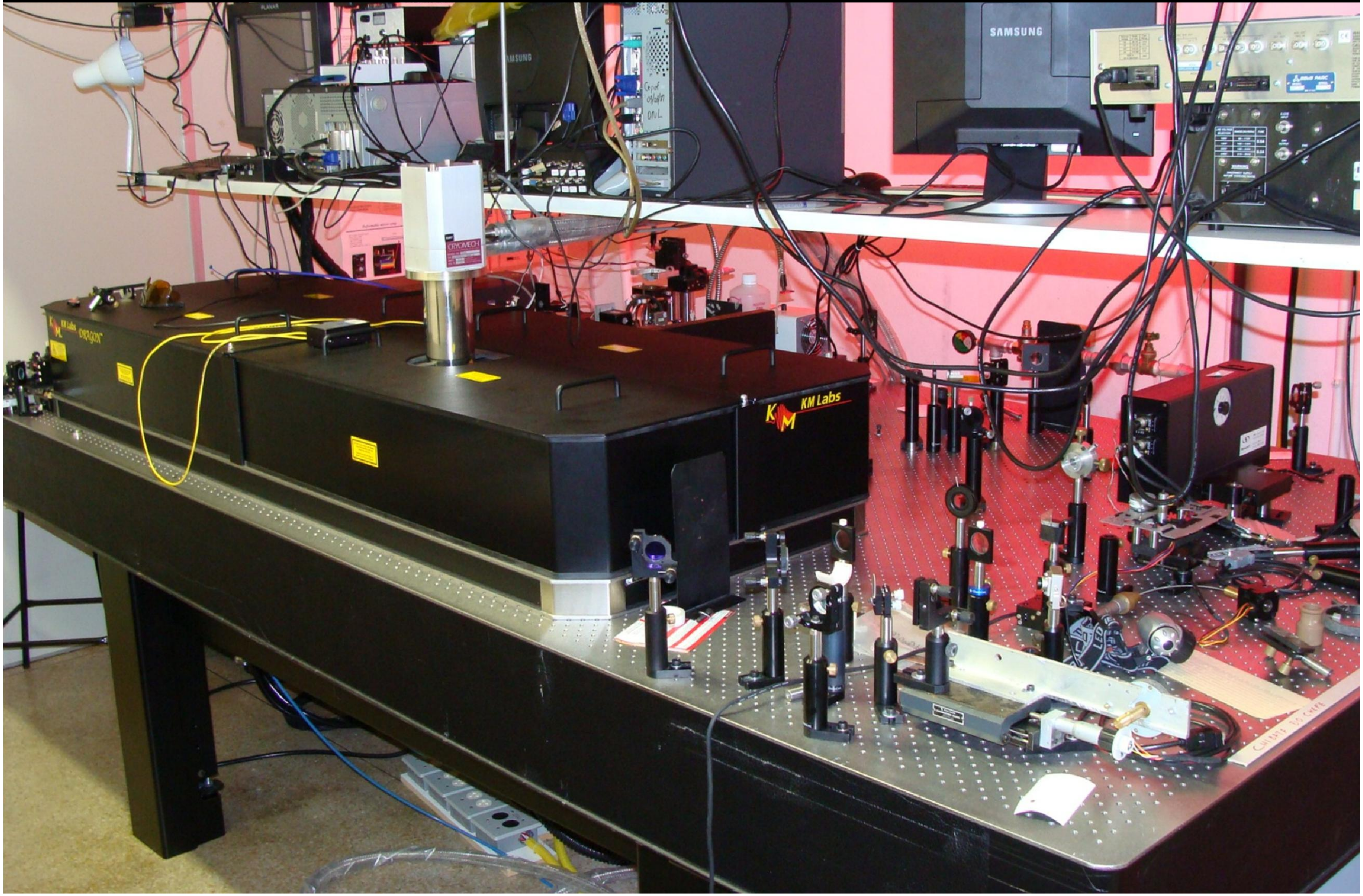
Optical Parametric Amplifier

460 - 2600 nm

≈ 120 fs

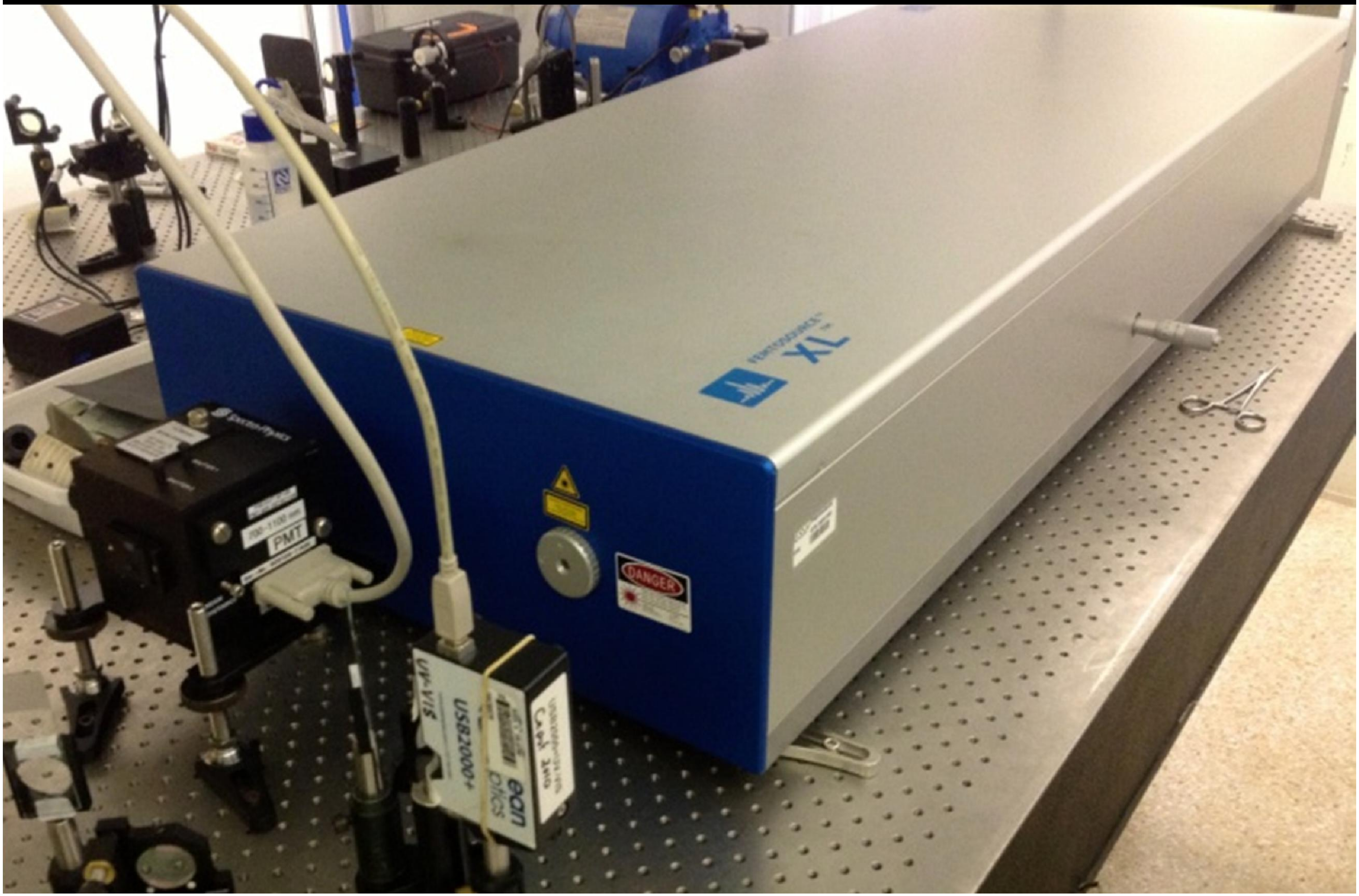
20-60 μJ

40 fs Ti:sapphire amplifier

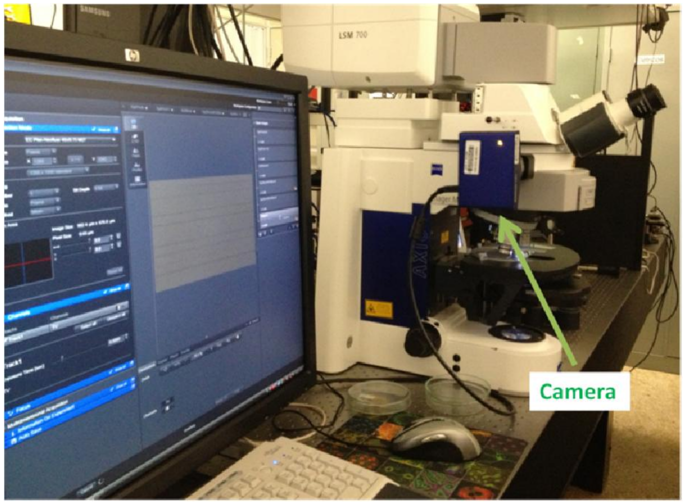


Optical Parametric Amplifier

50 fs Ti:Sapphire Oscillator 5 MHz

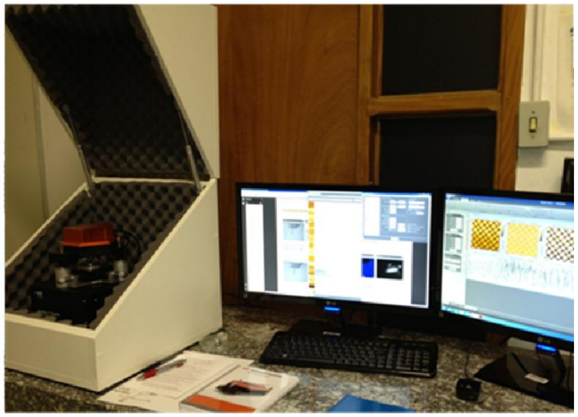


Microscopy infrastructure



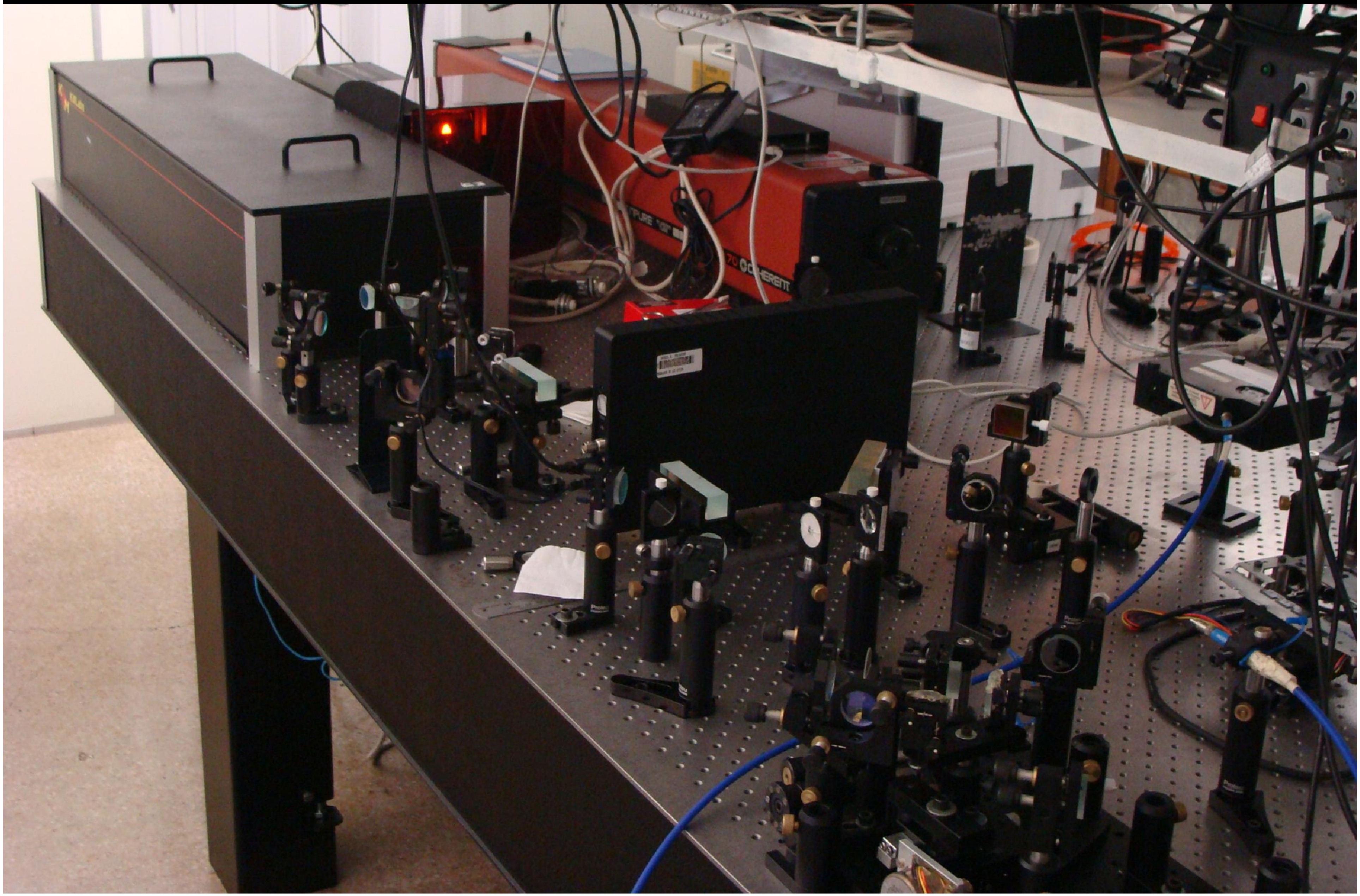
Confocal

SEM



AFM

20 fs laser oscillator



microfabrication laboratory