

# Sculpturing with light: advanced processing of materials for optical and biological applications

Prof. Dr. Cleber R. Mendonca

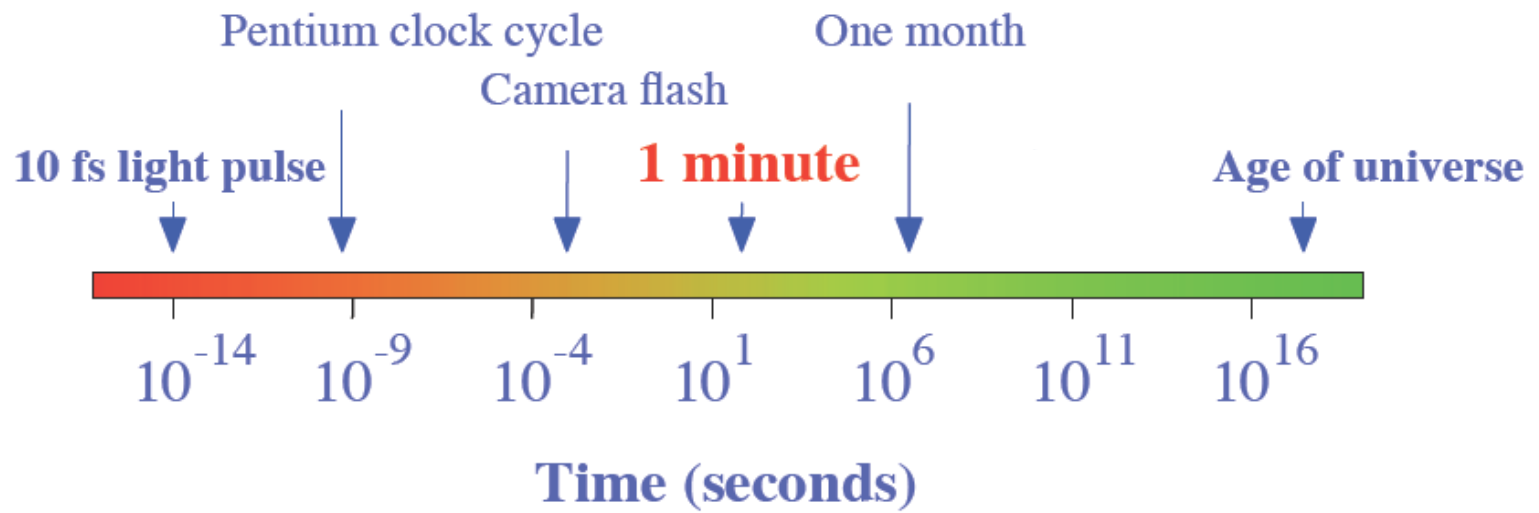


# Microfabrication

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

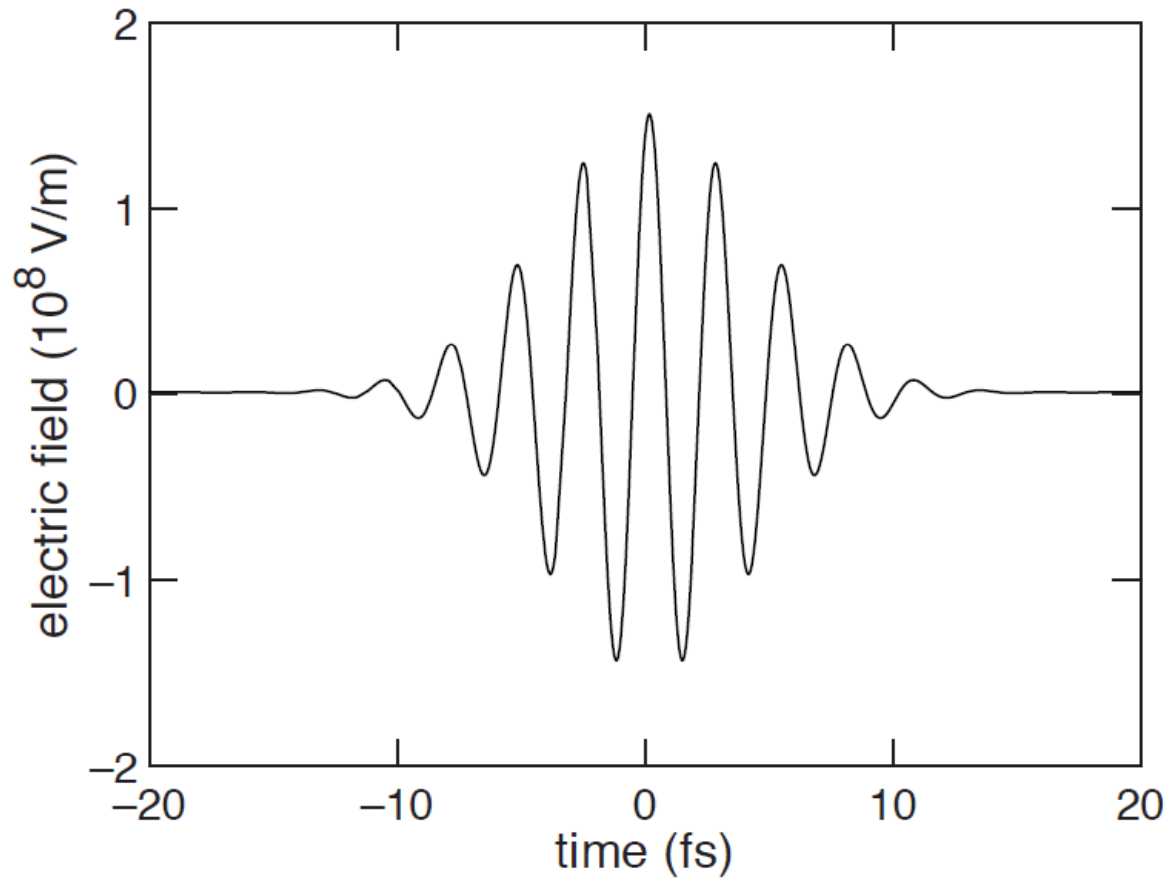
# Microfabrication

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



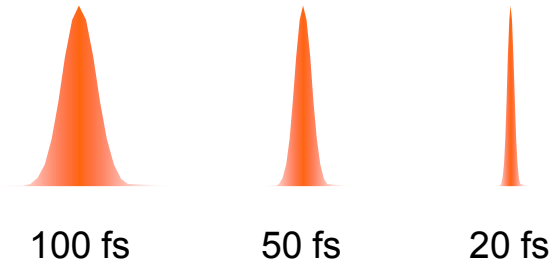
# introduction

how short is a femtosecond pulse ?



# Microfabrication

Ti:Sapphire lasers



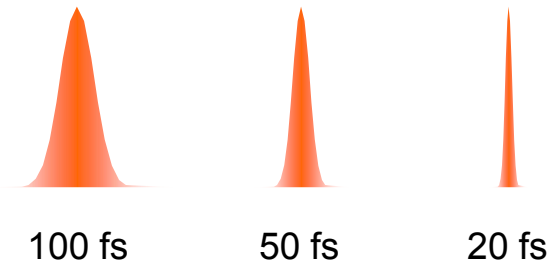
Very intense light

*Laser intensities* ~ 100 GW/cm<sup>2</sup>  
1 x 10<sup>11</sup>W/cm<sup>2</sup>

Laser pointer: 1 mW/cm<sup>2</sup> (1 x 10<sup>-3</sup> W/ cm<sup>2</sup>)

# fs-laser micromachining

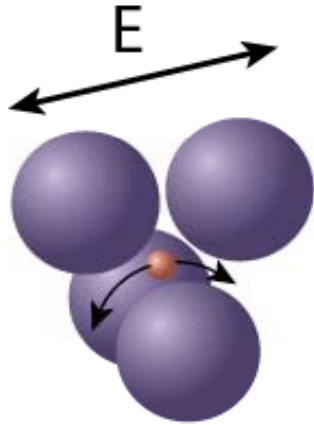
Ti:Sapphire lasers



Very intense light

***Nonlinear Optical Phenomena***

# Nonlinear Optics



anharmonic oscillator

high light intensity

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

nonlinear polarization response

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

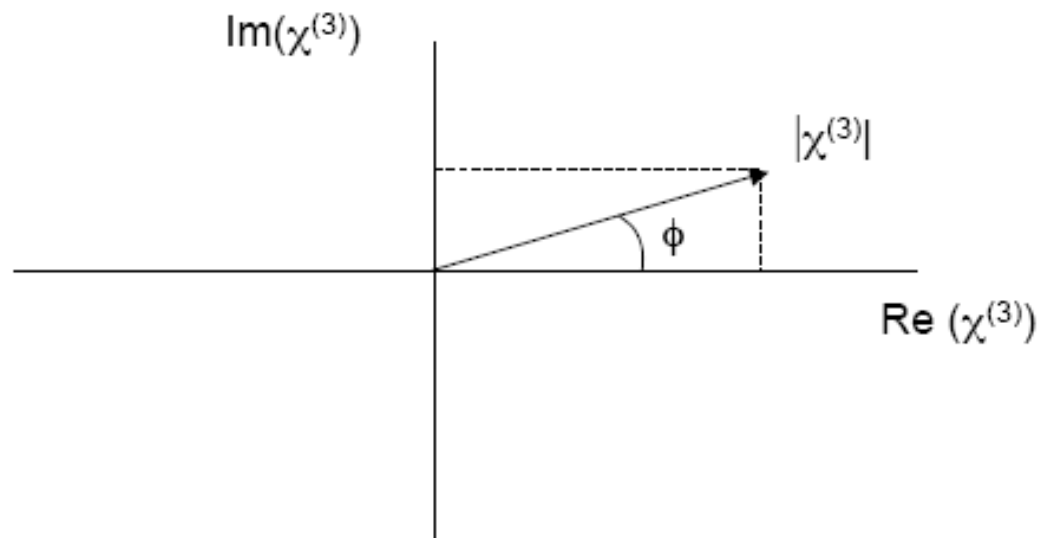
# Nonlinear Optics

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

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

Related to intensity  
dependent refractive index

Related to two-photon  
absorption



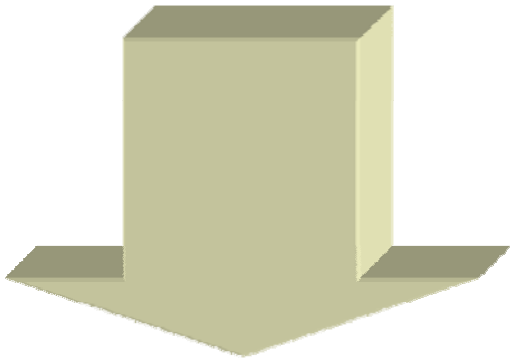


# Nonlinear Optics

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

Refractive process:

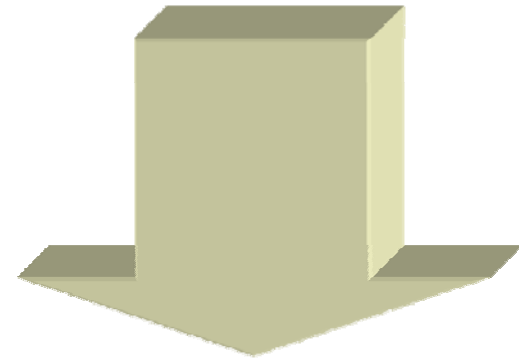
$$n = n_0 + n_2 I$$



- self-phase modulation
- lens-like effect

Absorptive process:

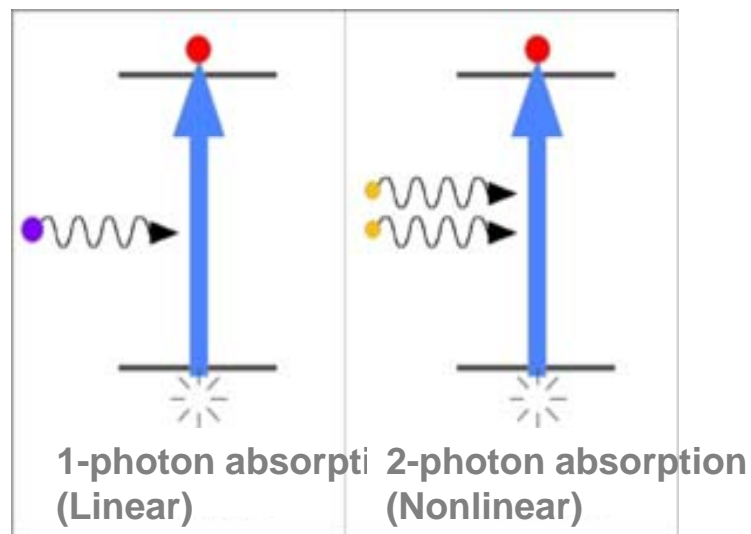
$$\alpha = \alpha_0 + \beta I$$



- nonlinear absorption
- two-photon absorption

# Two-photon absorption

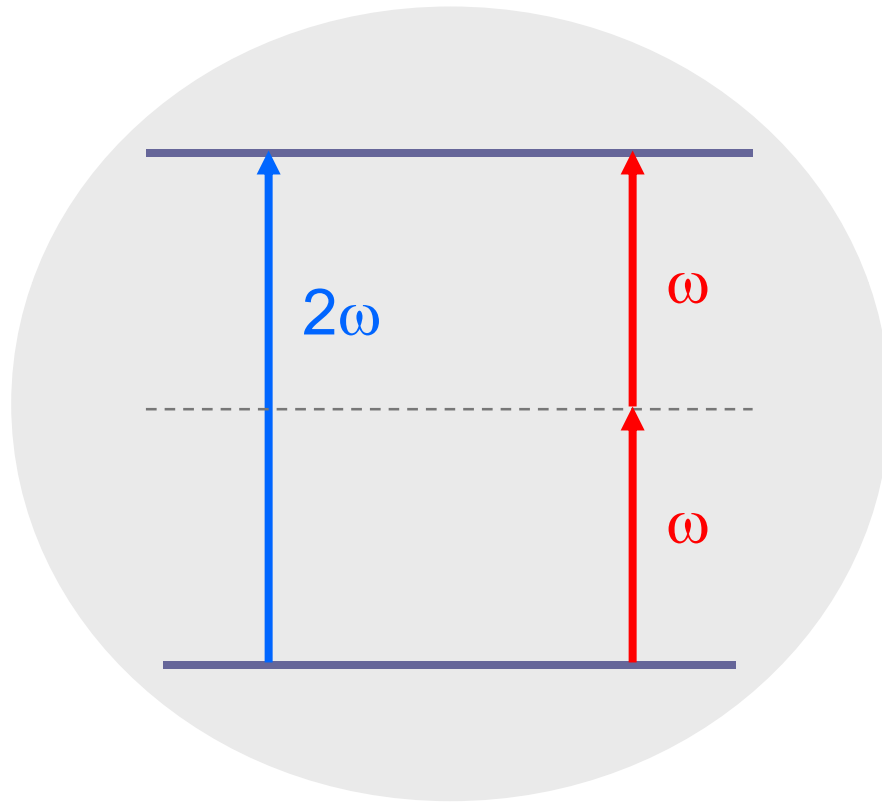
Phenomenon does not described for the Classical Physics and **does not observed until the development of the Laser.**



Theoretical model: Maria Göppert-Mayer, 1931

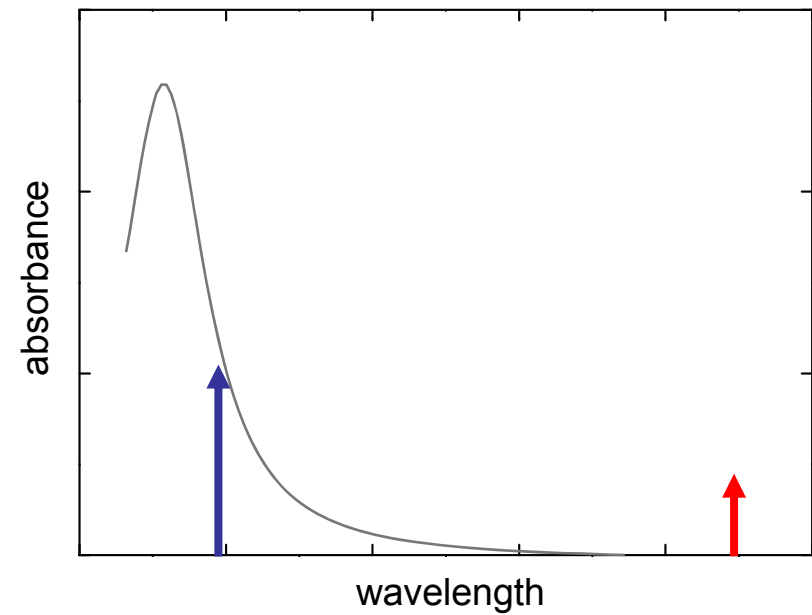
Two photons from an intense laser light beam are simultaneously absorbed in the same “quantum act”, leading the molecule to some excited state with energy equivalent to the absorbed two photons.

# Two-photon absorption



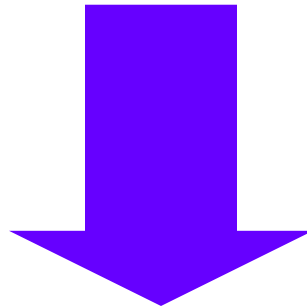
$$\alpha = \alpha_0 + \beta I$$

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



# fs-laser microfabrication

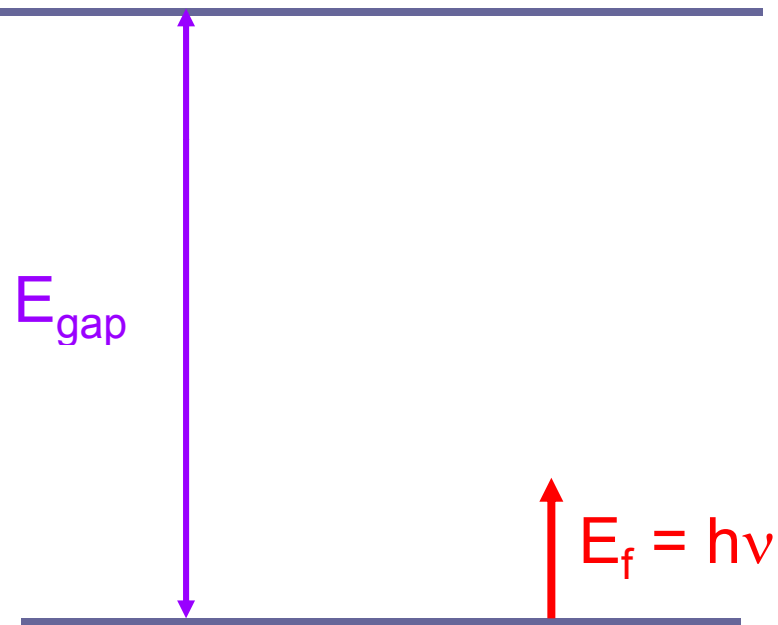
photon energy  $<$  bandgap



nonlinear interaction

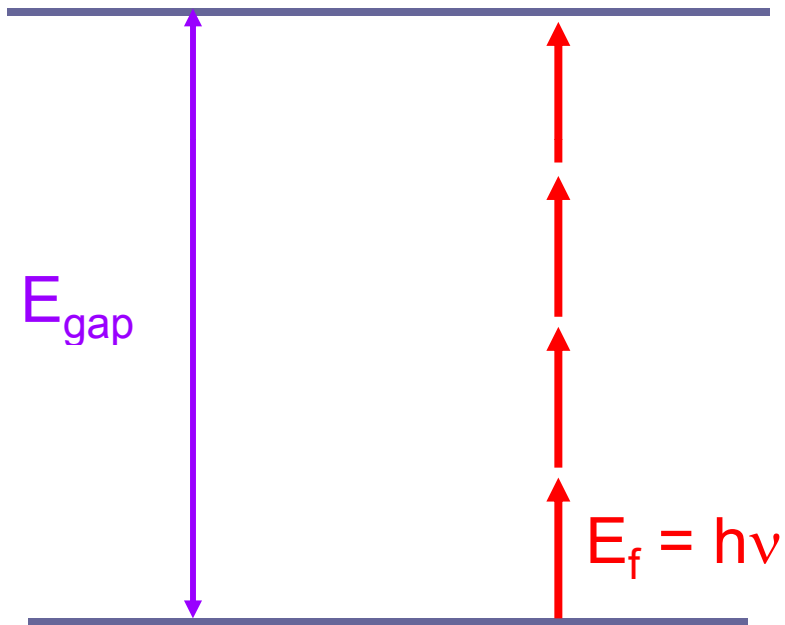
# fs-laser microfabrication

nonlinear interaction



# fs-laser microfabrication

nonlinear interaction



multiphoton absorption

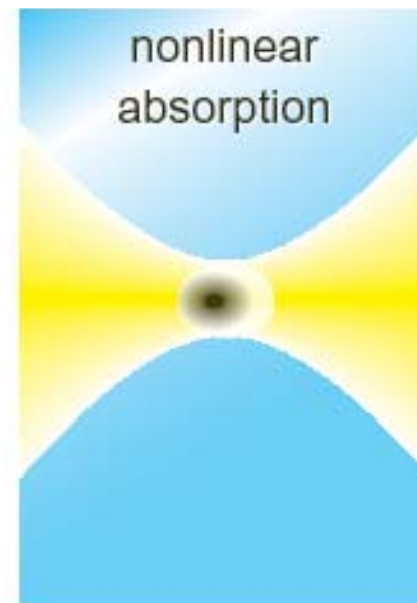
# Multi-photon absorption

Nonlinear interaction provides spatial confinement of the excitation

fs-microfabrication



$$\alpha = \alpha_0$$



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

# Two-photon absorption

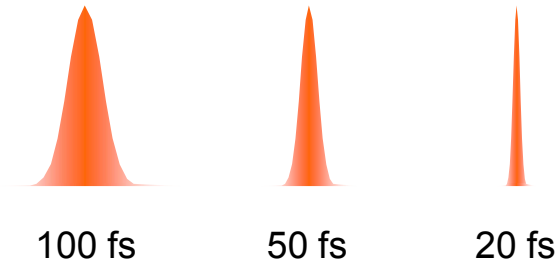


spatial confinement of excitation



# femtosecond pulses

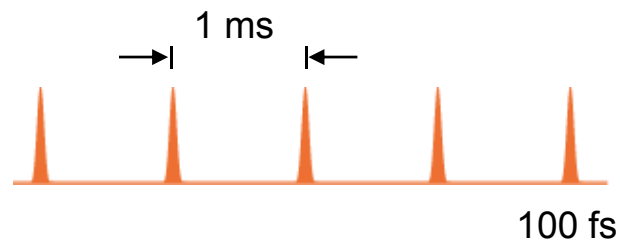
Ti:Sapphire lasers



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

Repetition rate

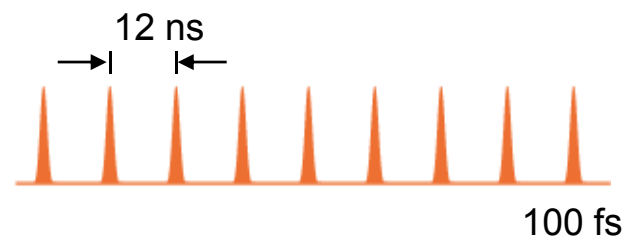
1 KHz



Energy

mJ

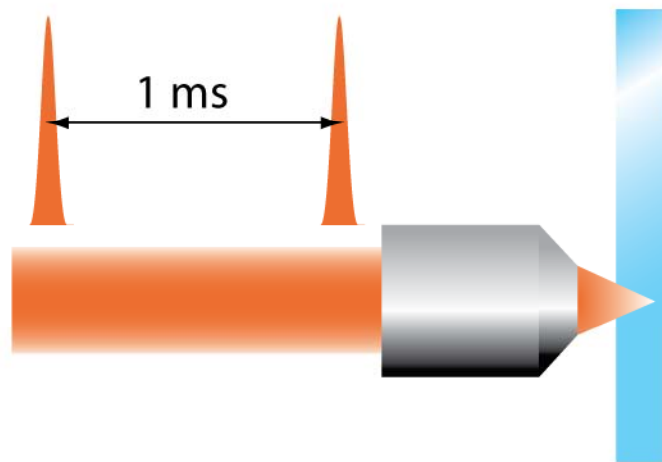
86 MHz



nJ

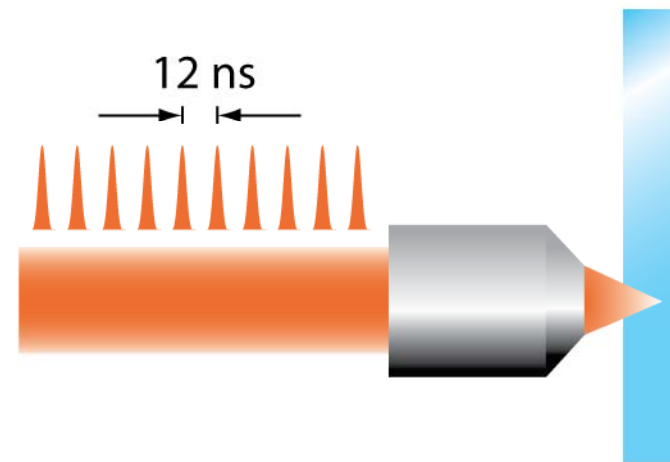
# femtosecond pulses

amplified laser



repetitive

oscillator

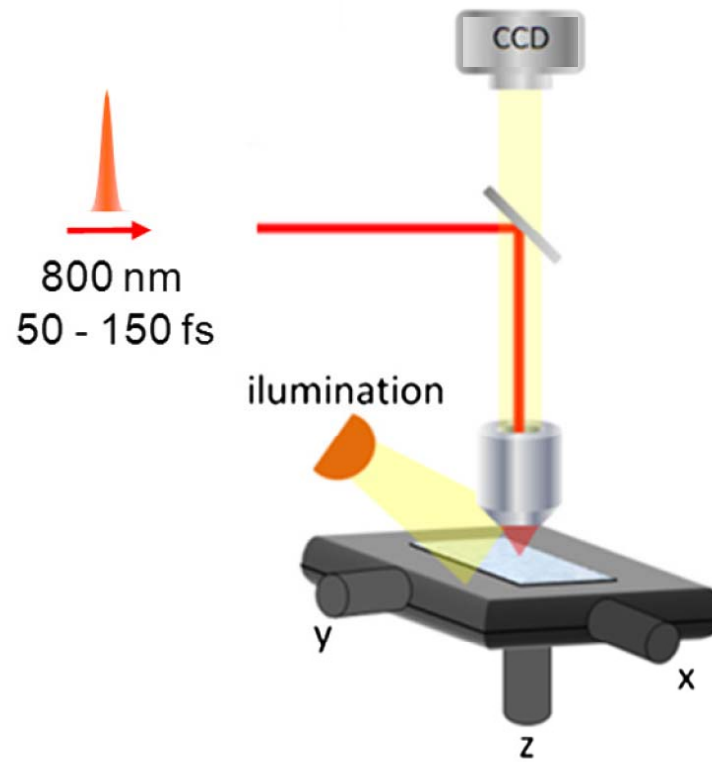


cumulative

## two main techniques

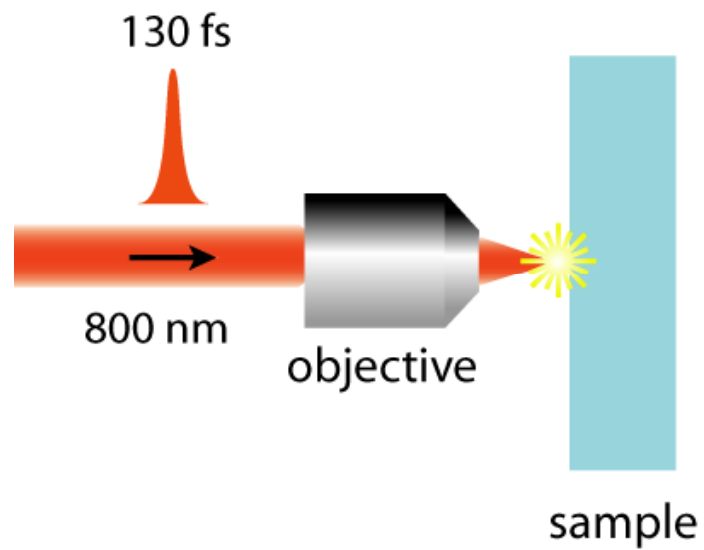
- fs-laser micromachining/microstructuring
- microfabrication via two-photon polymerization

# fs-laser microstructuring experimental setup

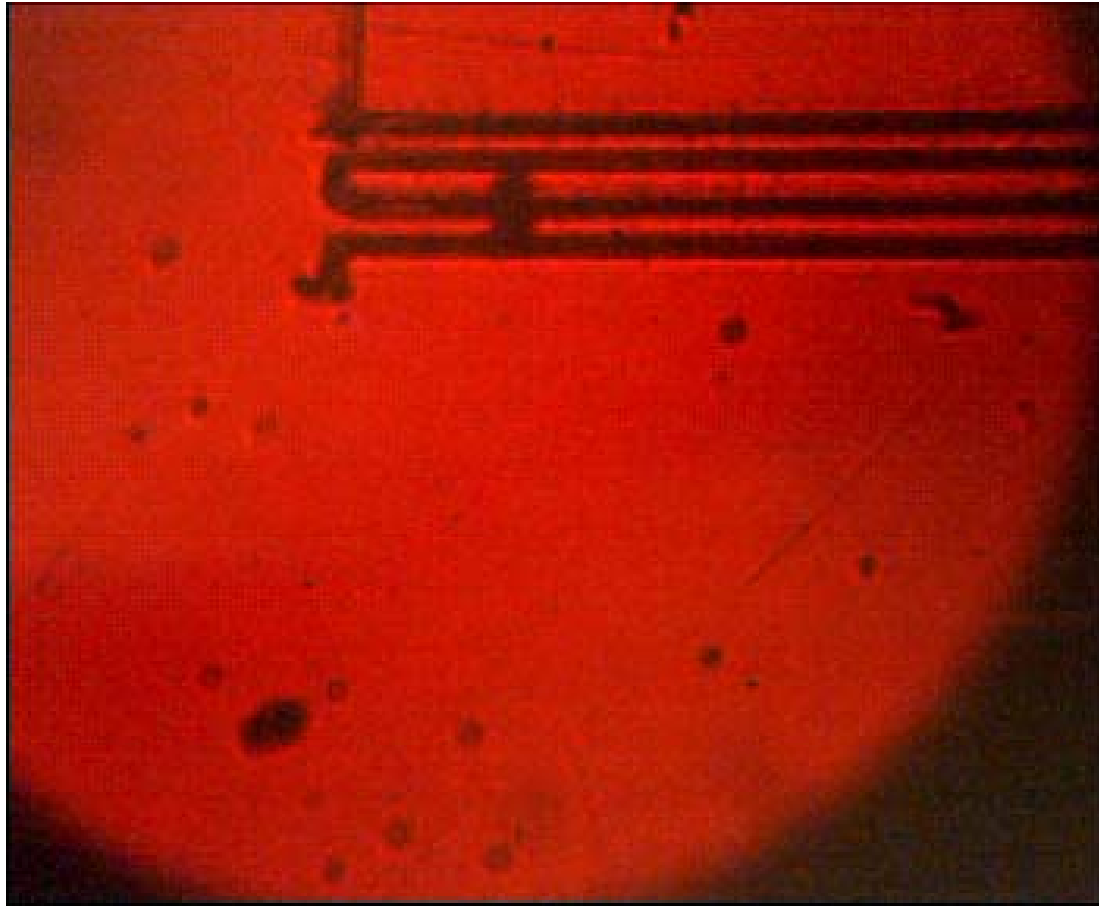


# fs-laser micromachining

Surface

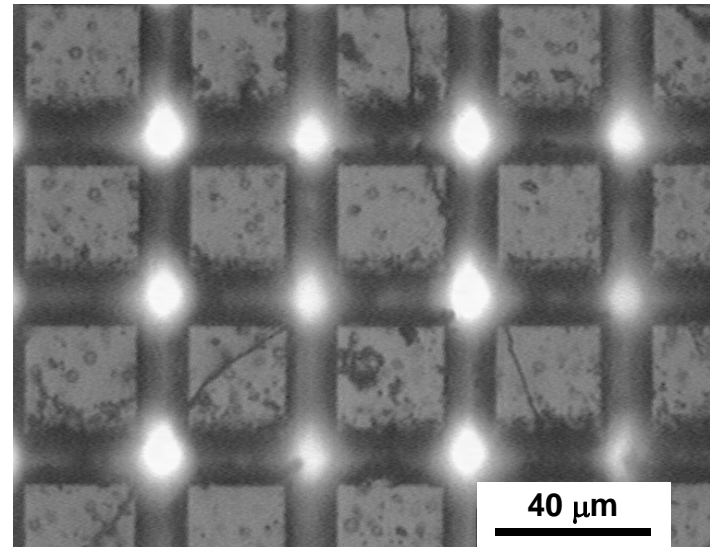
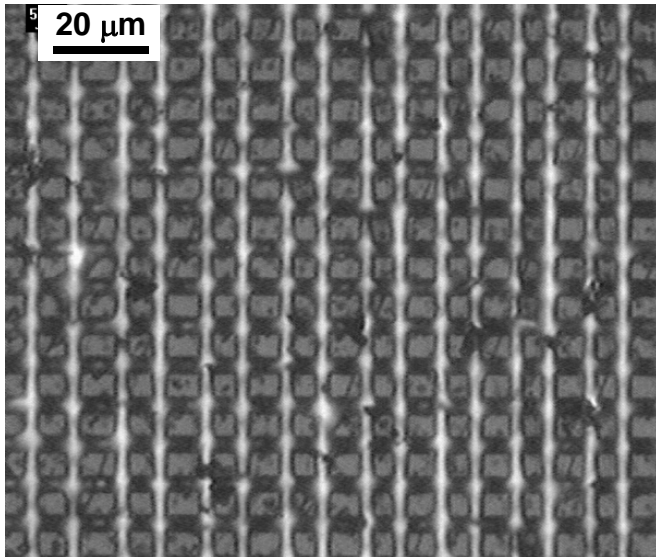


microstructuring polymer: super hydrophobic surface



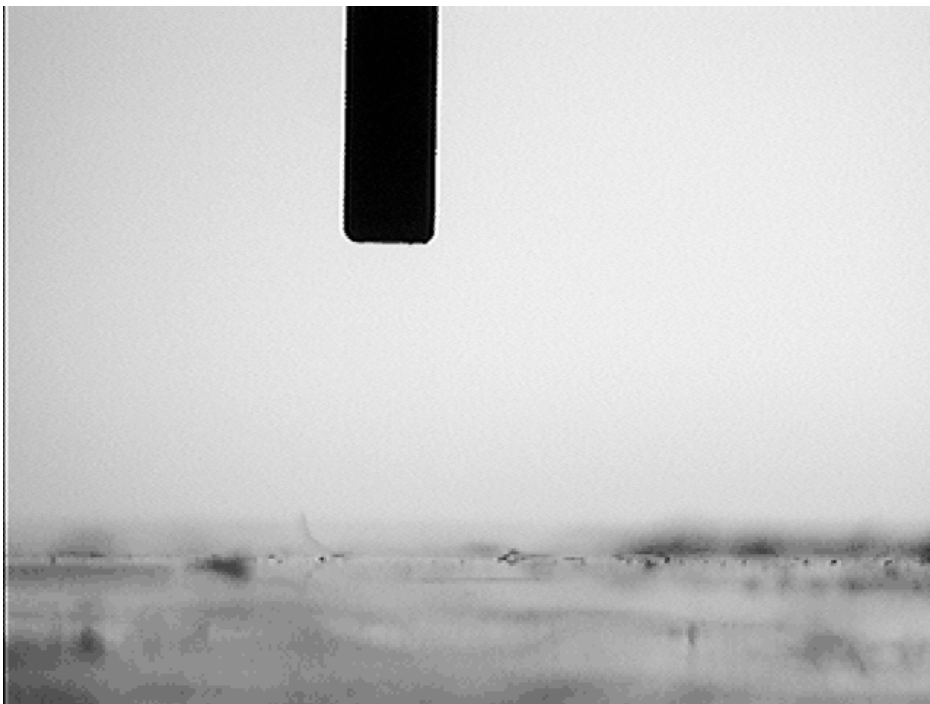
# laser microfabrication: super hydrophobic surface

examples of fabricated surfaces

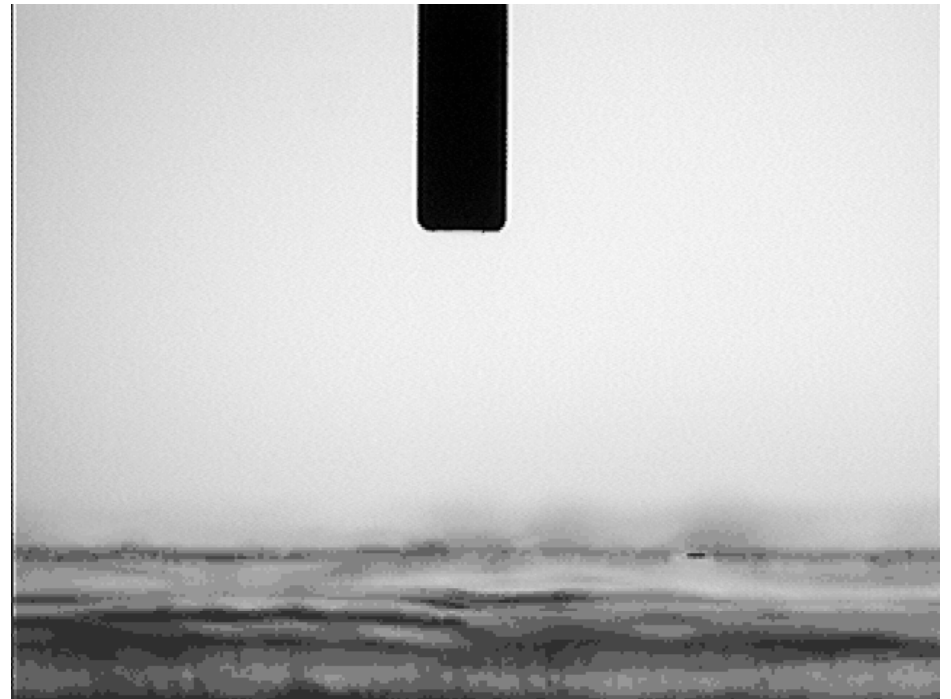


# laser microfabrication: super hydrophobic surface

## Superhydrophobic surfaces



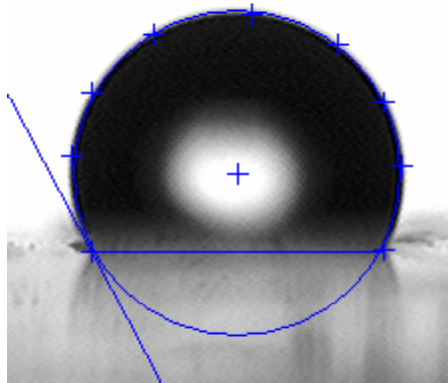
flat surface



microstructured surface

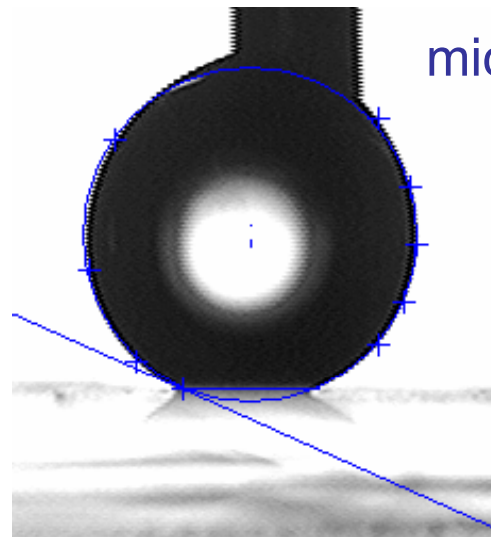


# microstructuring polymer



flat surface

$$\theta = 118^\circ$$

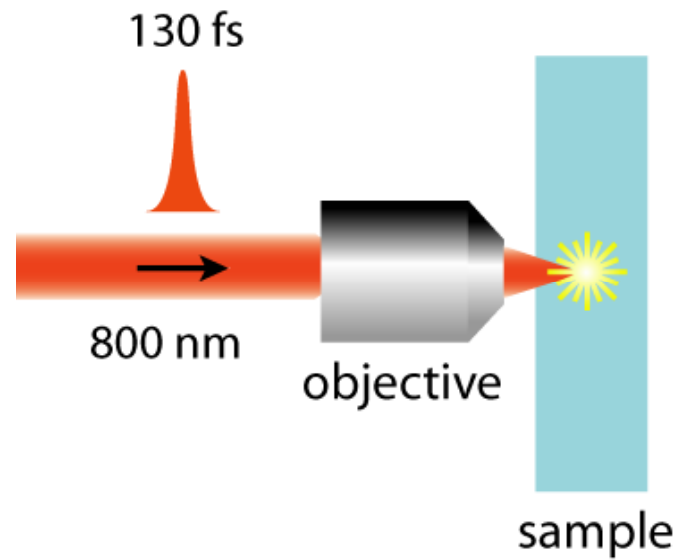


microstructured surface

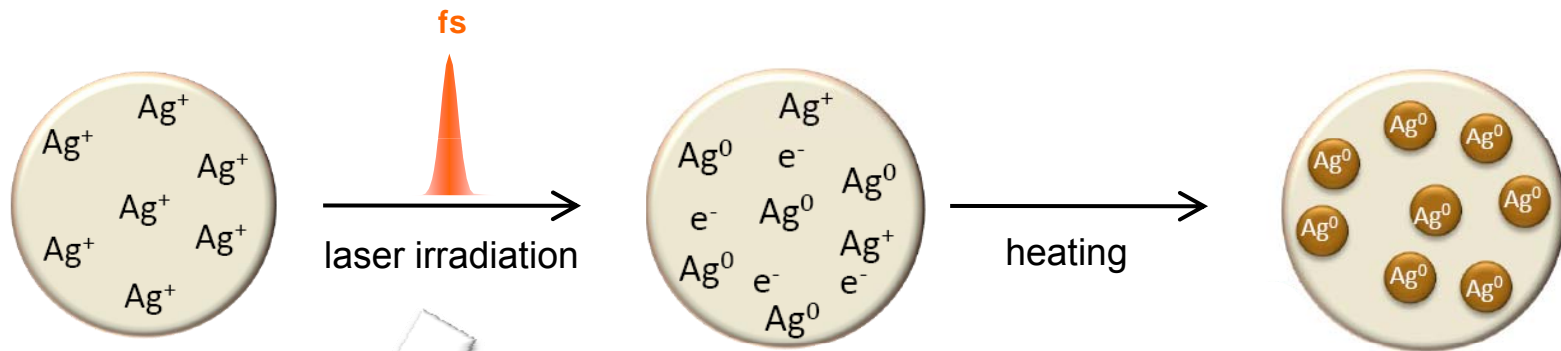
$$\theta = 160^\circ$$

# fs-laser micromachining

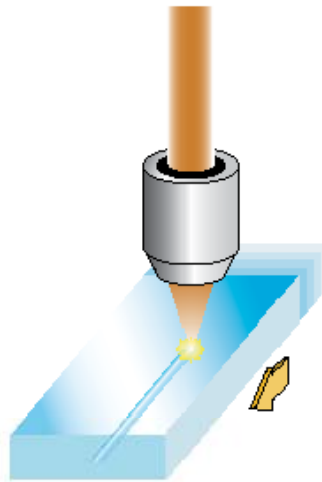
Volume



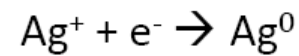
# Generation of Ag nanoparticles



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



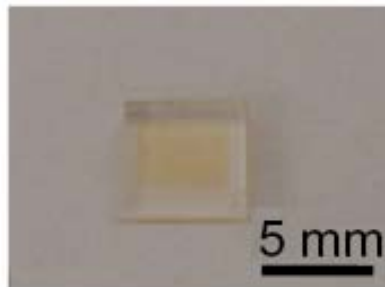
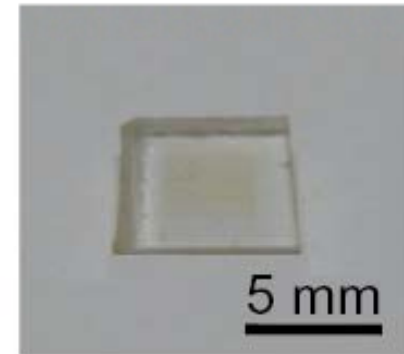
Free electron generation  
Photoreduction reaction



# *Generation of Ag nanoparticles*

Silver doped barium borate glass (Ag:BBO)

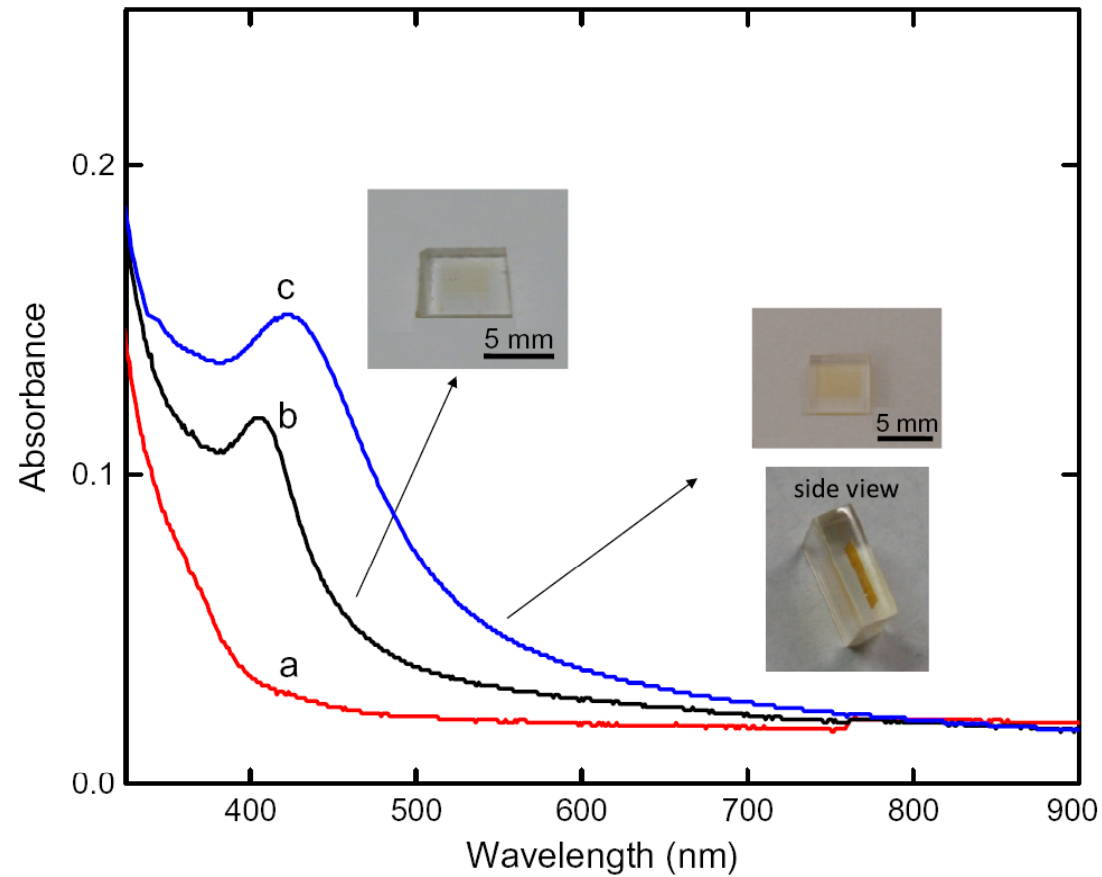
Sample after irradiation with the amplified fs-laser (1 kHz) and subsequent thermal treatment at 400 C for 1 h



Sample after irradiation with the 5 MHz fs-laser

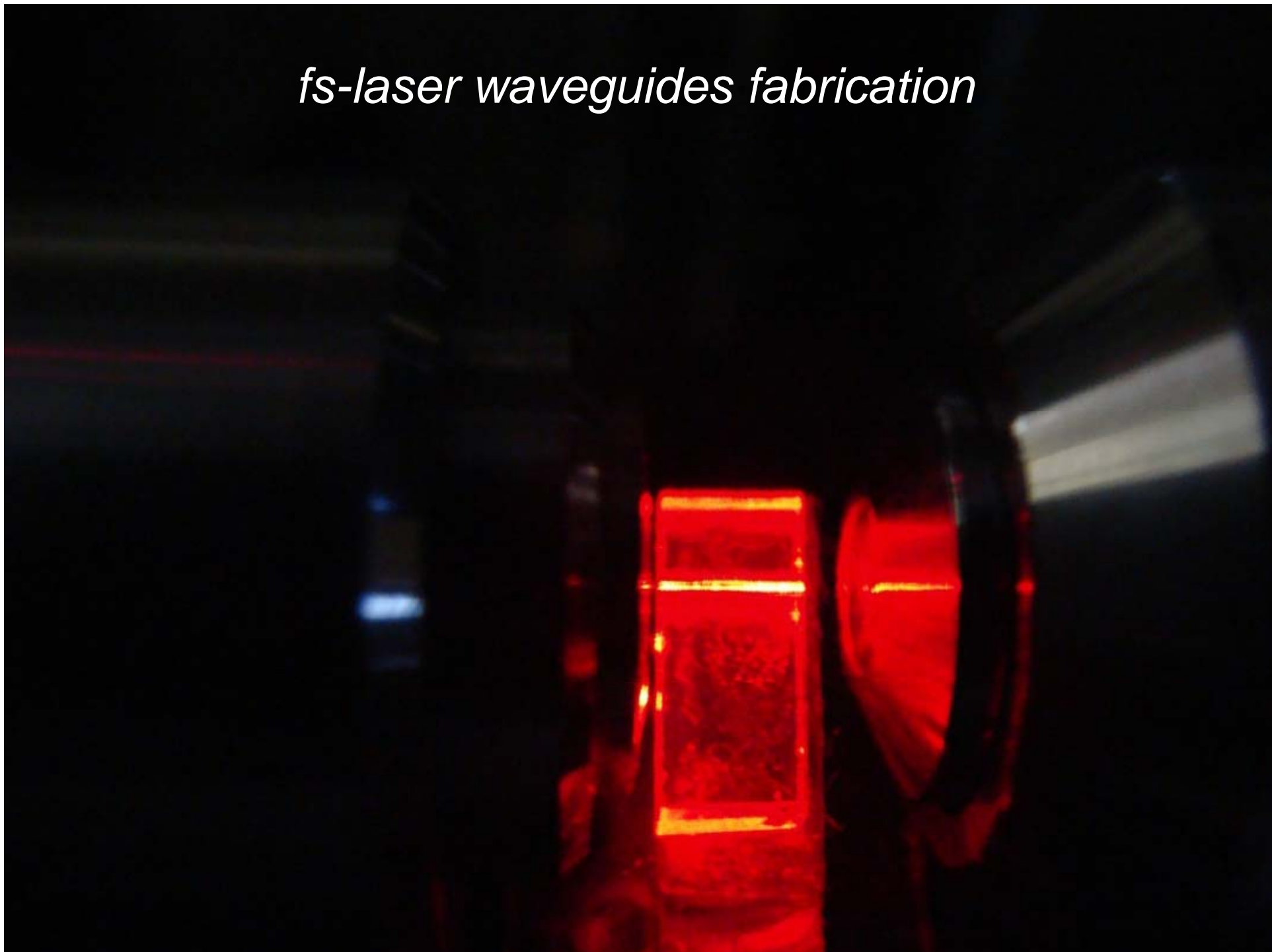


# Generation of Ag nanoparticles



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 -  $(70\text{Pb}_2\text{P}_2\text{O}_7-30\text{WO}_3):1\text{AgCl}$  (%mol)*

Waveguides fabricated using the 5-MHz laser system (50 fs) with 37 nJ/pulse and  $v = 10 \mu\text{m/s}$



Top view



Cross-section  
view

# Waveguides fabrication

Coupling light into the waveguides

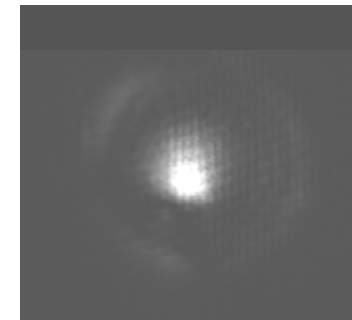
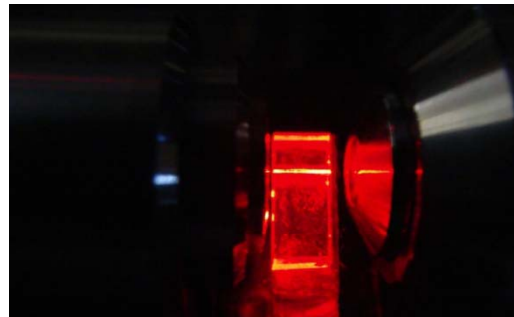
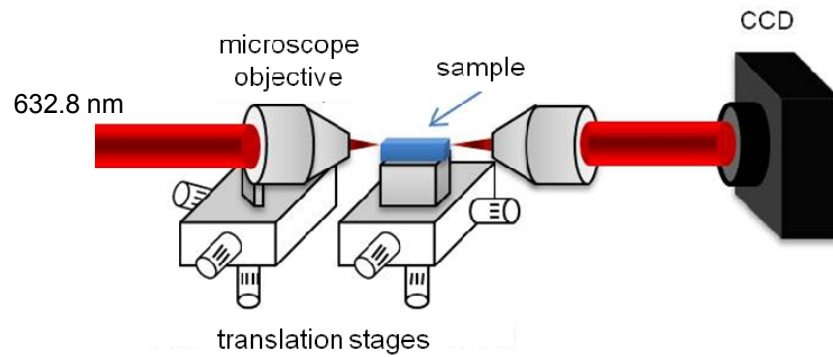
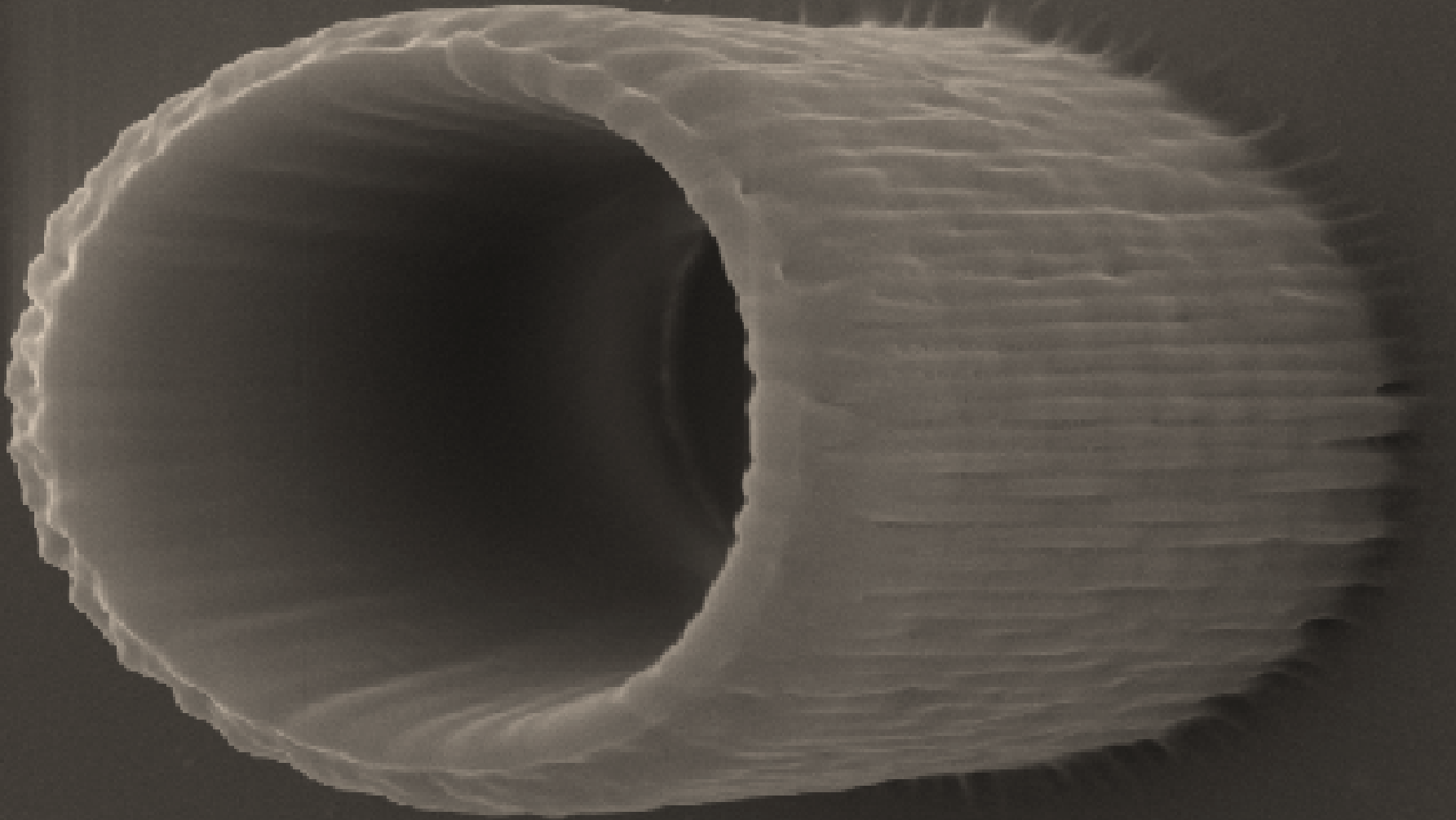


image of the waveguide output

measured waveguide loss  $L = 1.3 \text{ dB/mm}$



## fs-laser microfabrication



fabrication of microstructure using fs-laser  
and nonlinear optical processes

# Two-photon polymerization

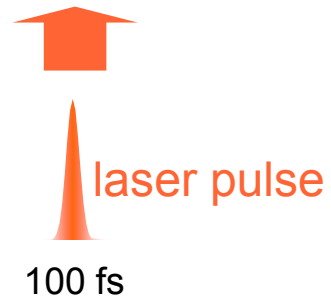
## Photopolymerization

*Monomer + Photoinitiator* → *Polymer*

↑  
light



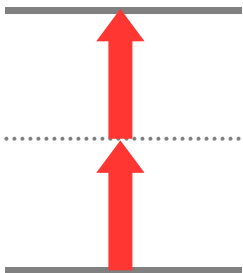
# Two-photon polymerization



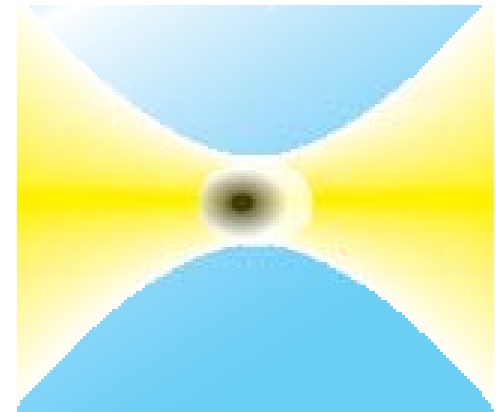
Photoinitiator is excited by **two-photon absorption**

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

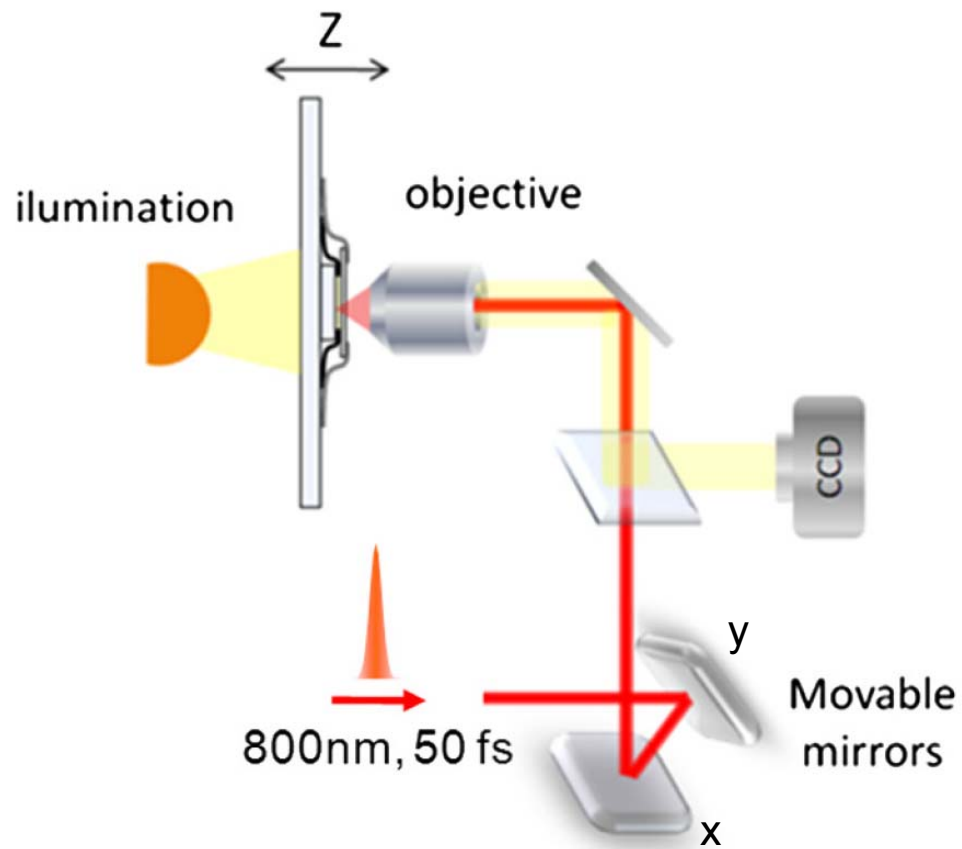
The polymerization is confined to the focal volume.



High spatial resolution



# Two-photon polymerization setup



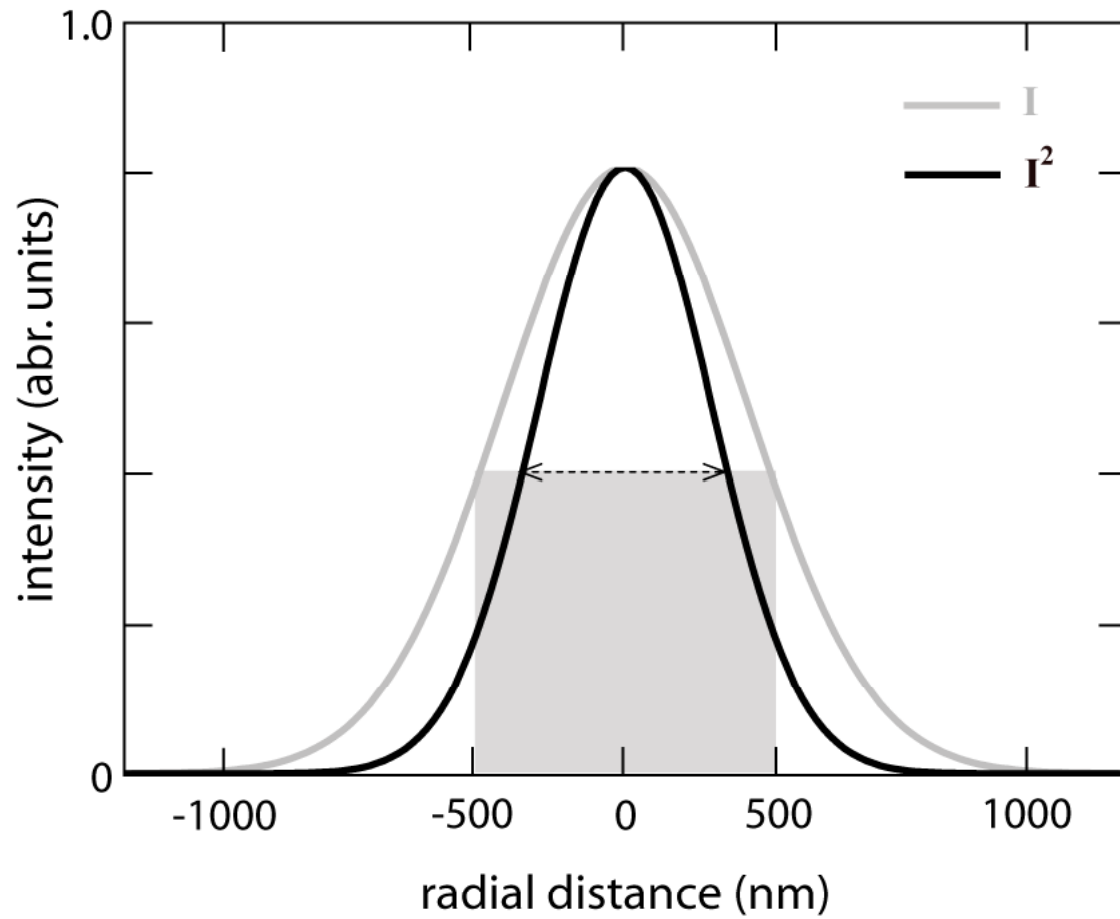
Ti:sapphire laser oscillator

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

Objective

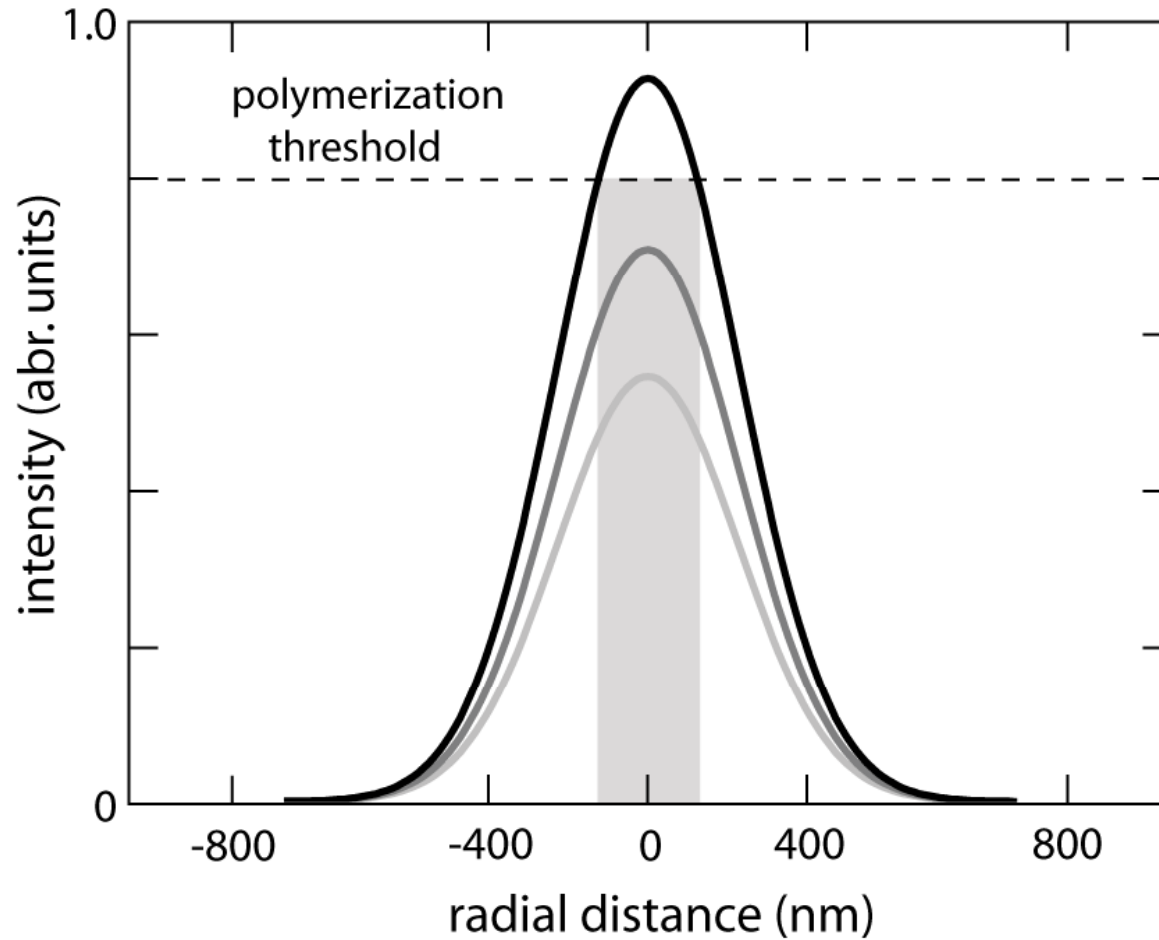
40 x  
0.65 NA

# Two-photon polymerization



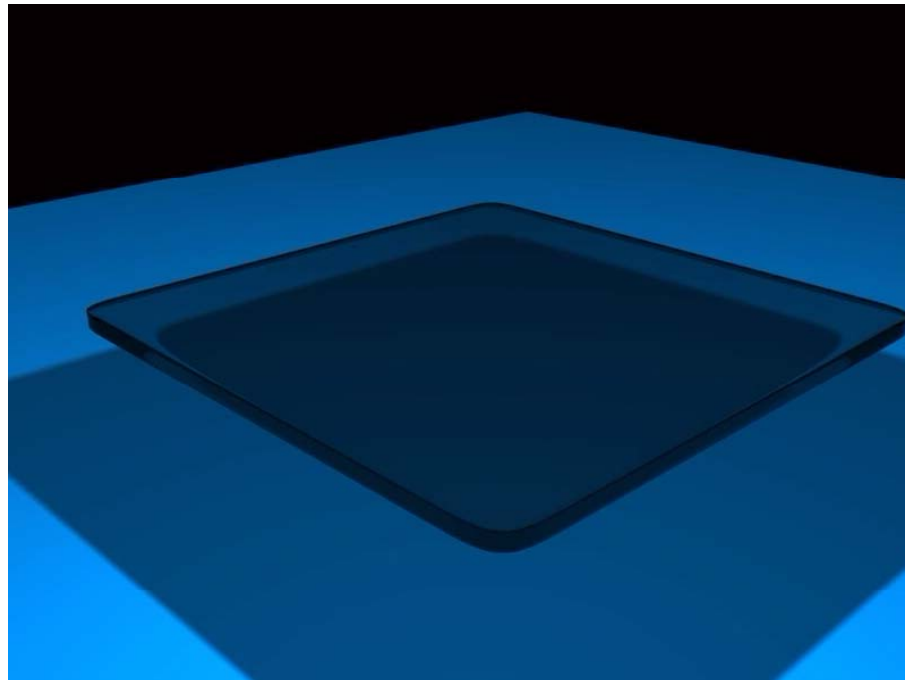
bellow the diffraction limit

# Two-photon polymerization

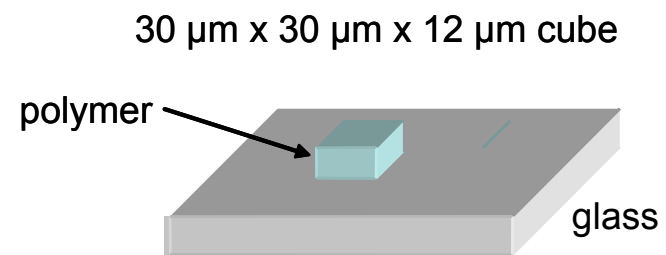
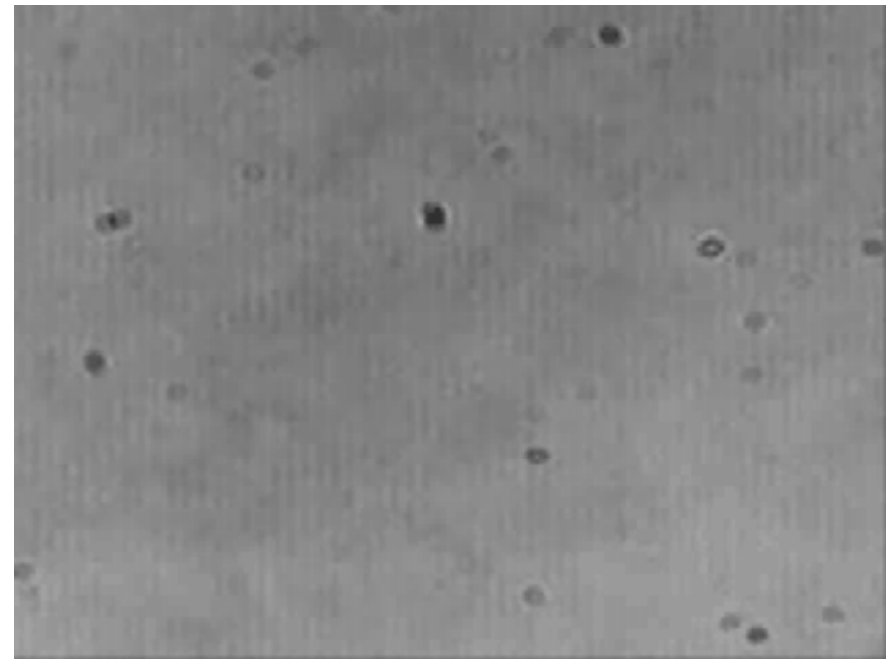
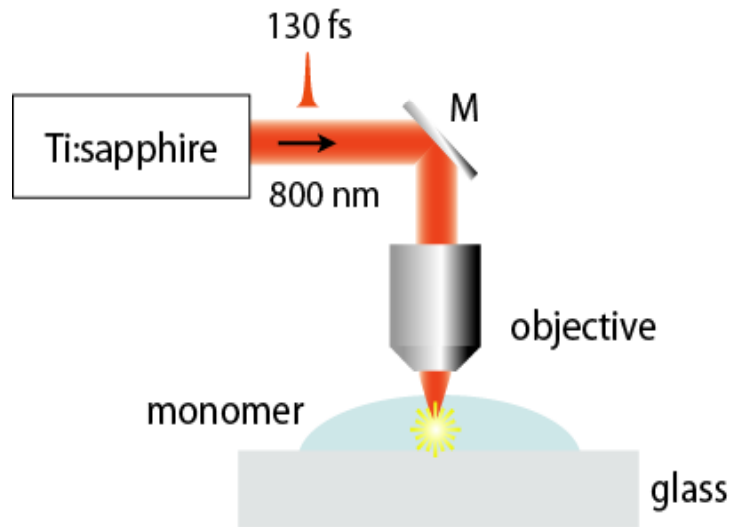


even higher spatial resolution

# Two-photon polymerization

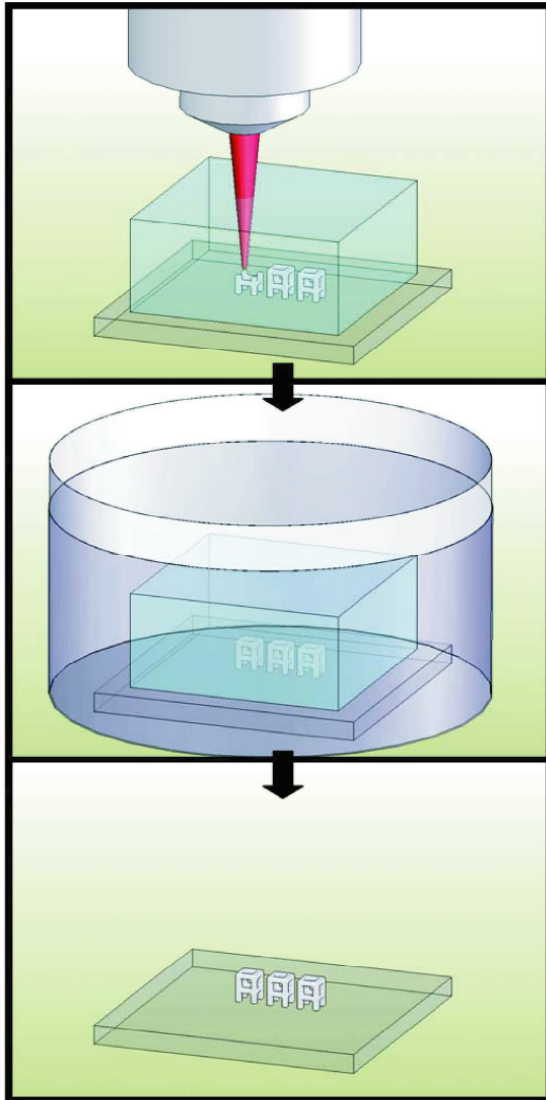


# Two-photon polymerization





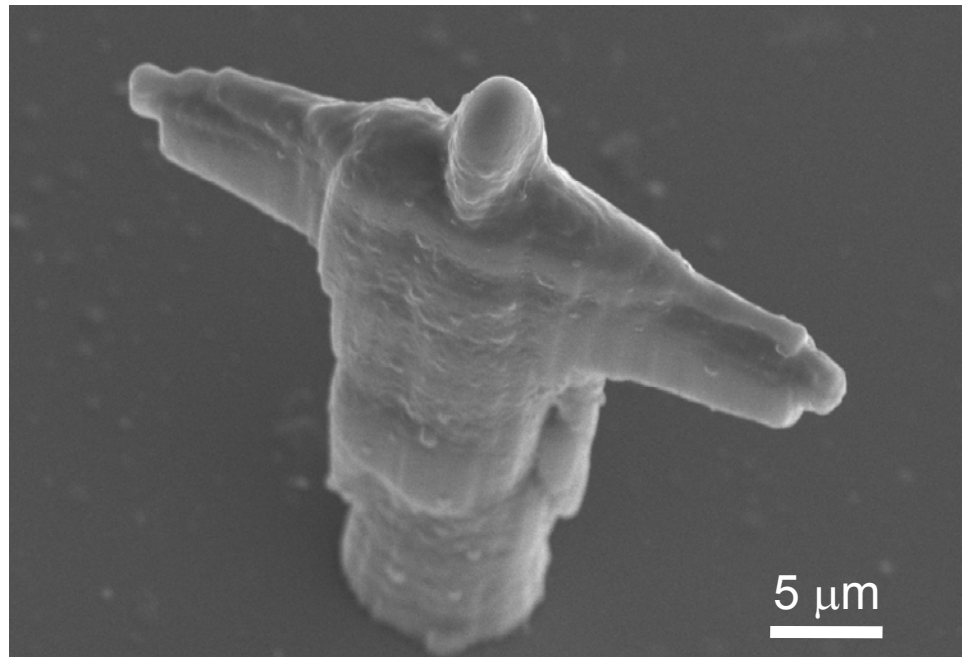
# Two-photon polymerization



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

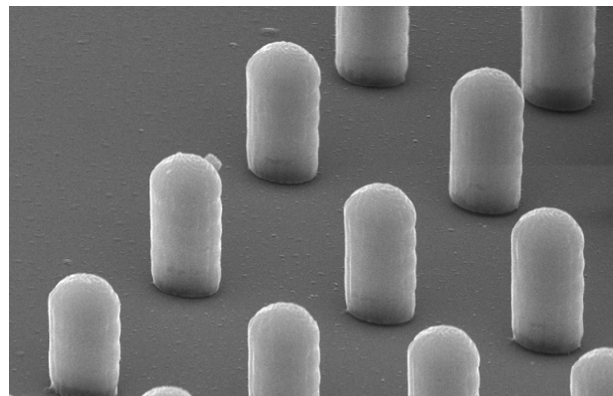
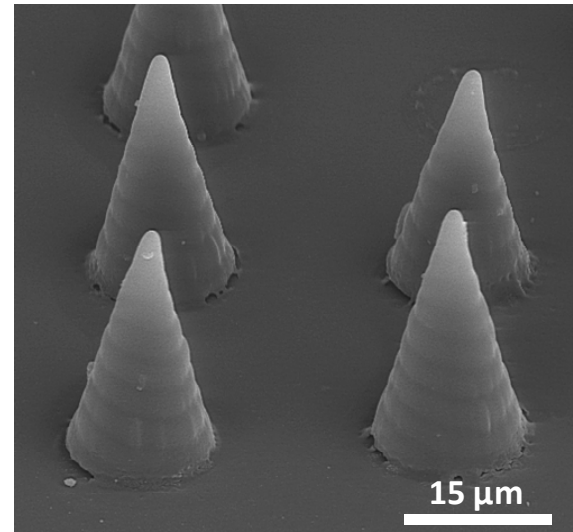
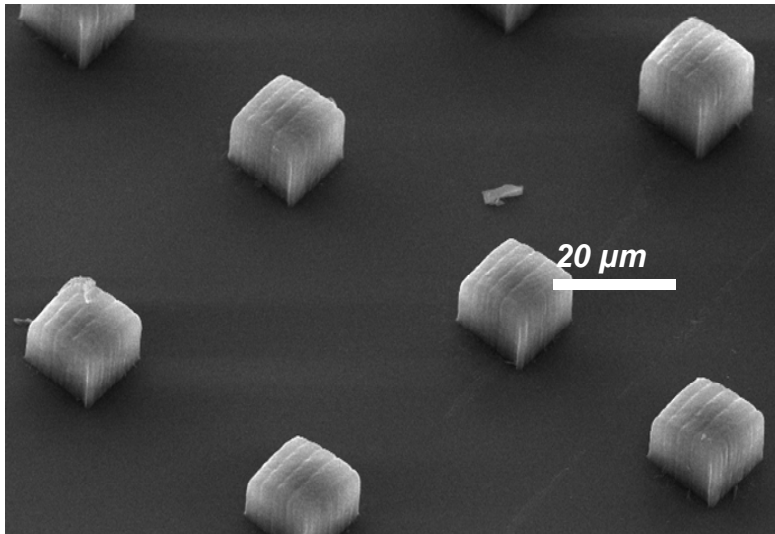
# two-photon polymerization

Microstructure fabricated by two-photon polymerization



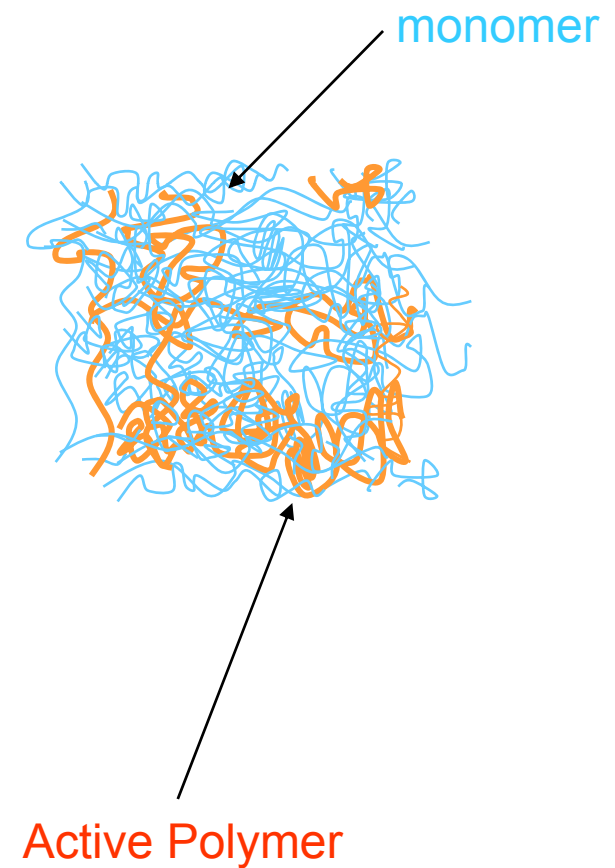
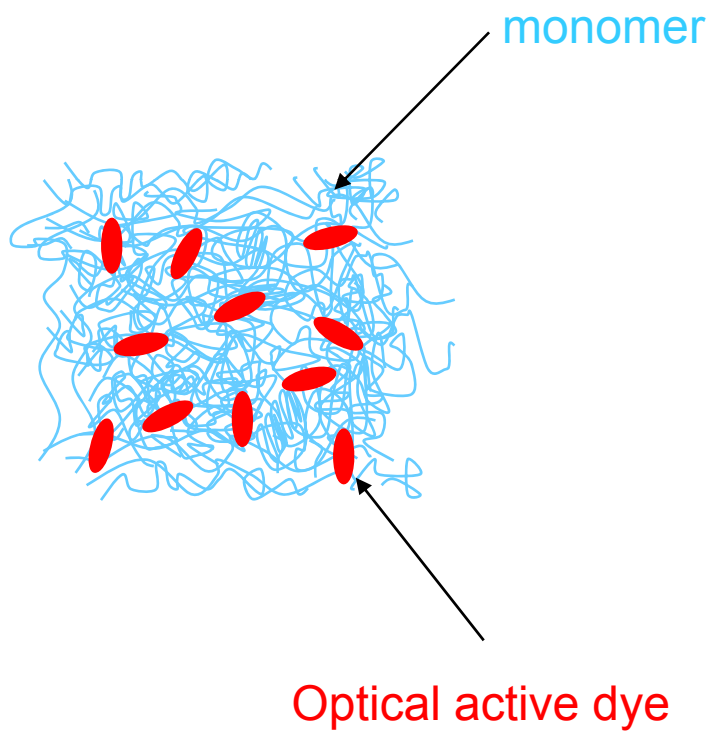
# Two-photon polymerization

Microstructures fabricated by two-photon polymerization



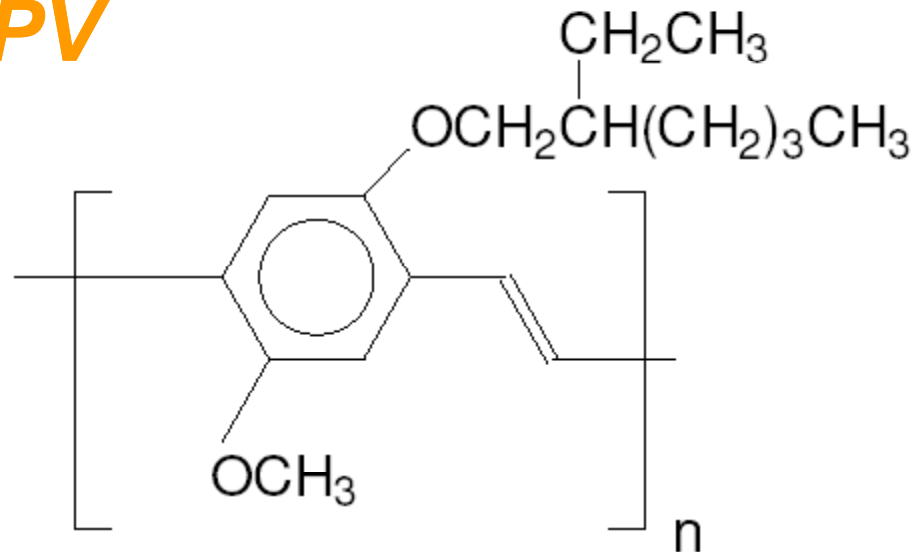
# Doping microstructures

Microstructures containing active compounds



# Microstructure containing MEH-PPV

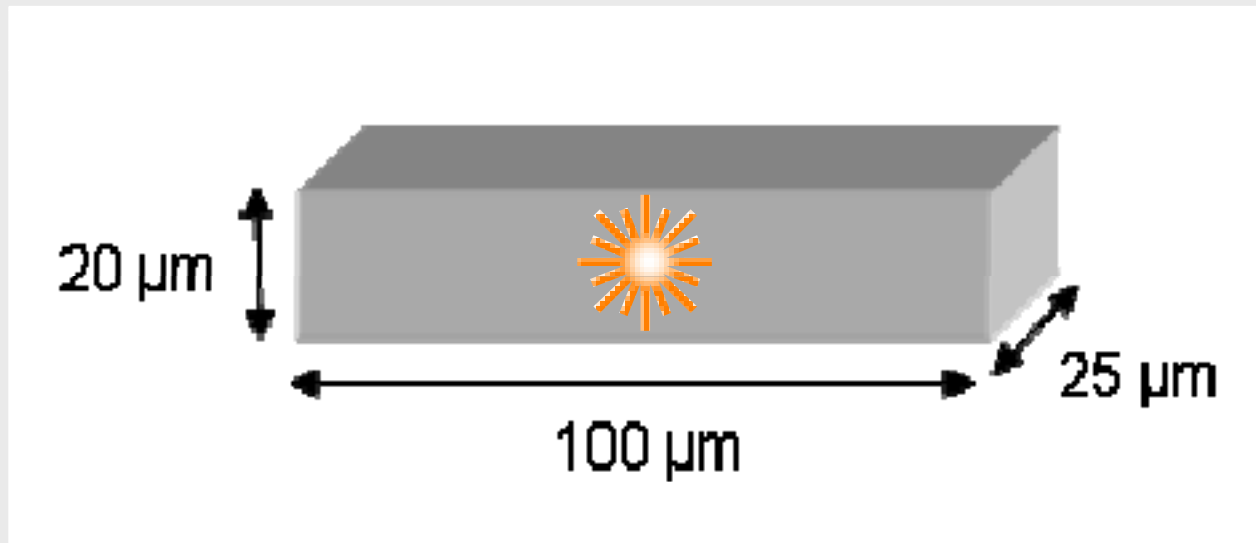
## MEH-PPV



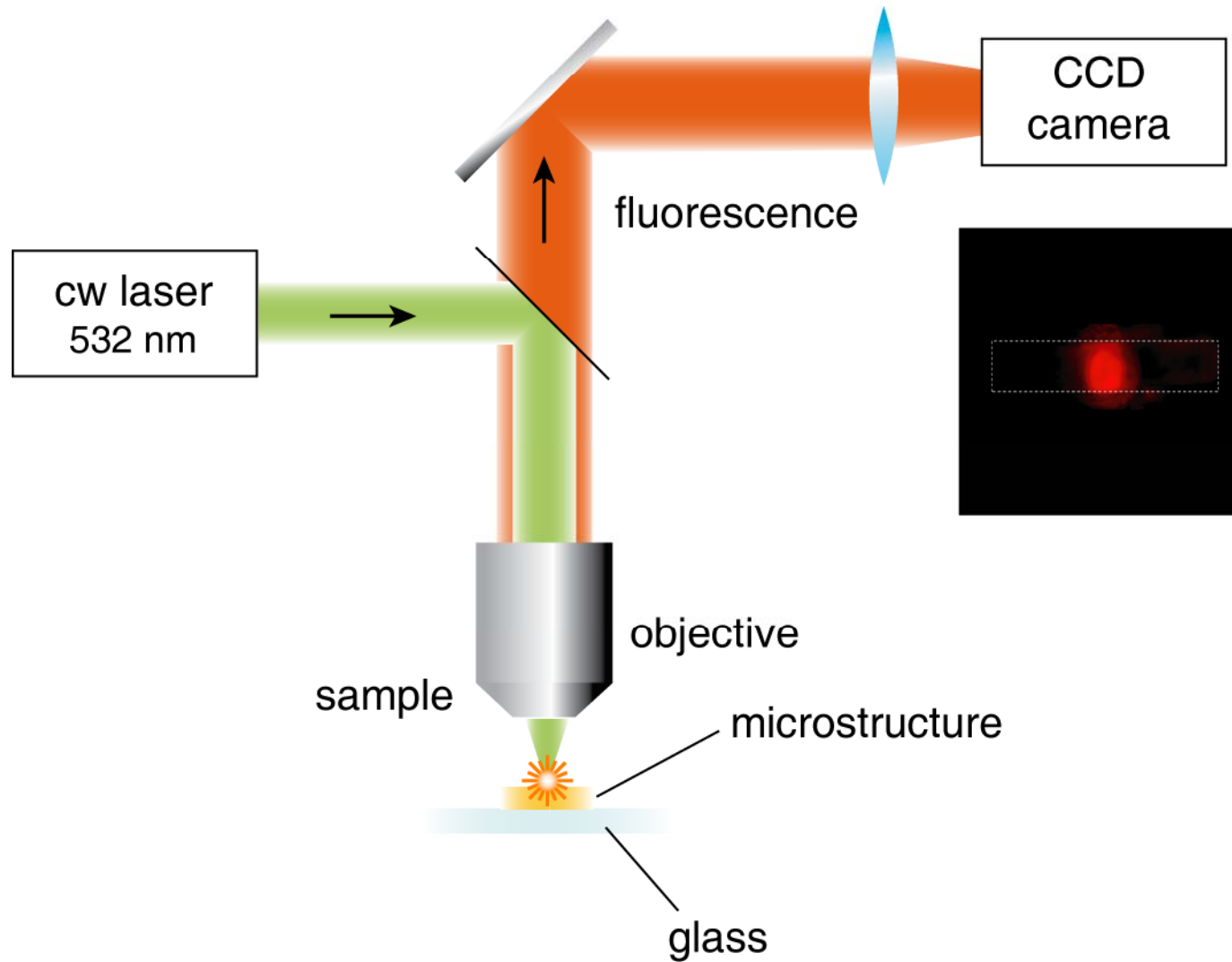
- Fluorescence
- Electro Luminescent
- Conductive

## Microstructure containing MEH-PPV

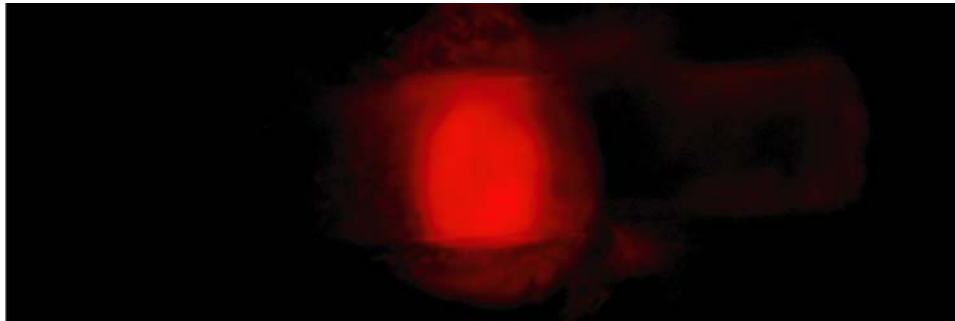
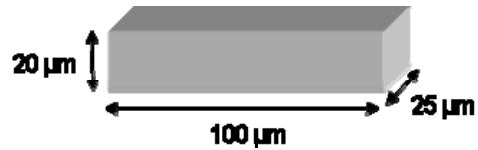
Do we have waveguiding in the microstructure ?



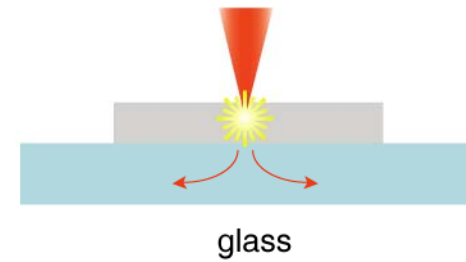
# Microstructure containing MEH-PPV



# Microstructure containing MEH-PPV

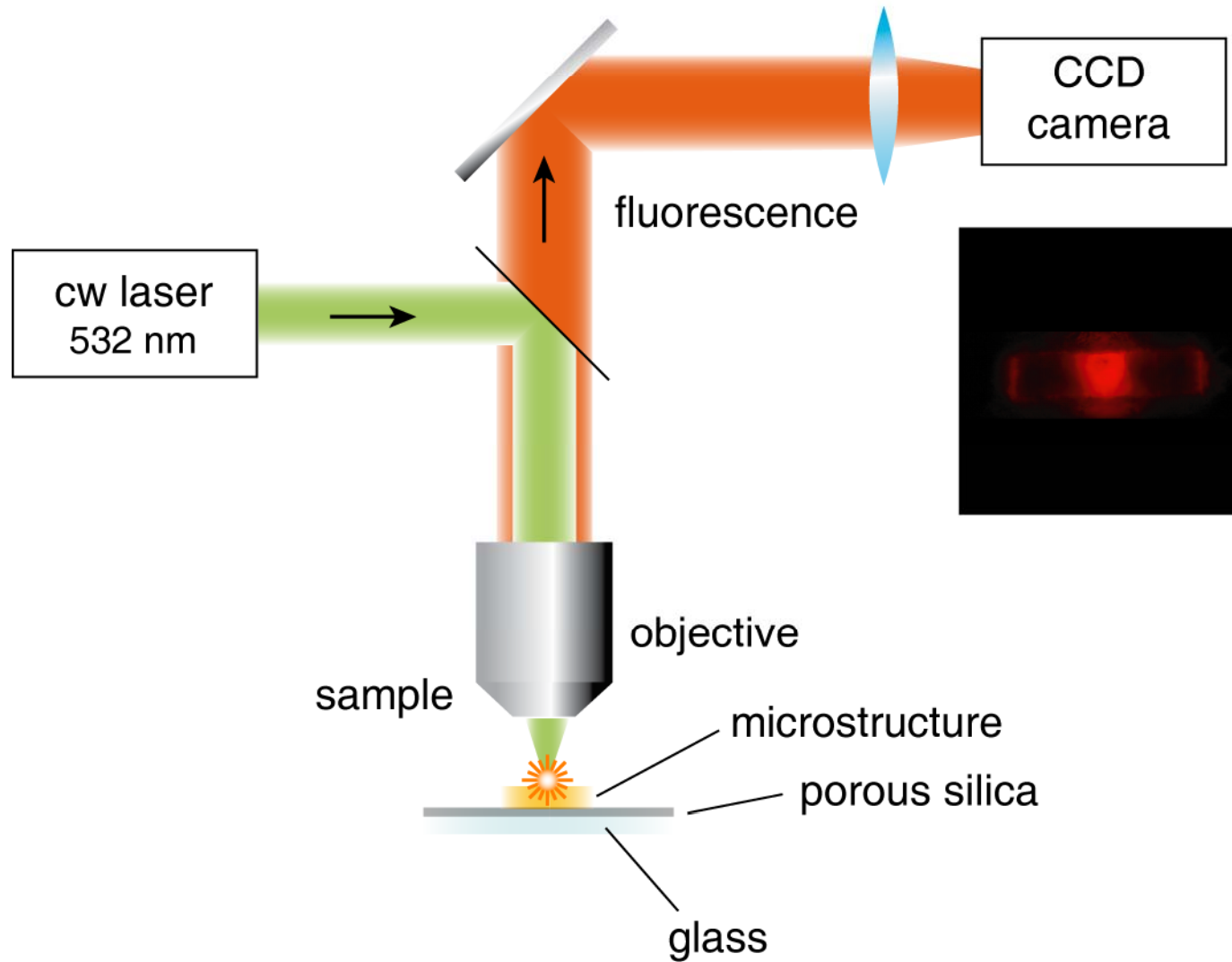


$20\ \mu\text{m}$  

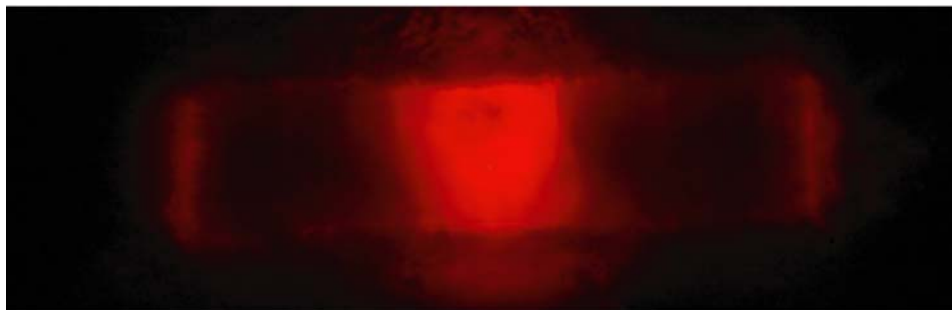
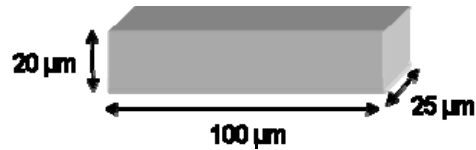




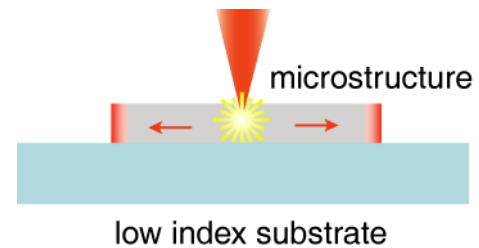
# Microstructure containing MEH-PPV



# Microstructure containing MEH-PPV



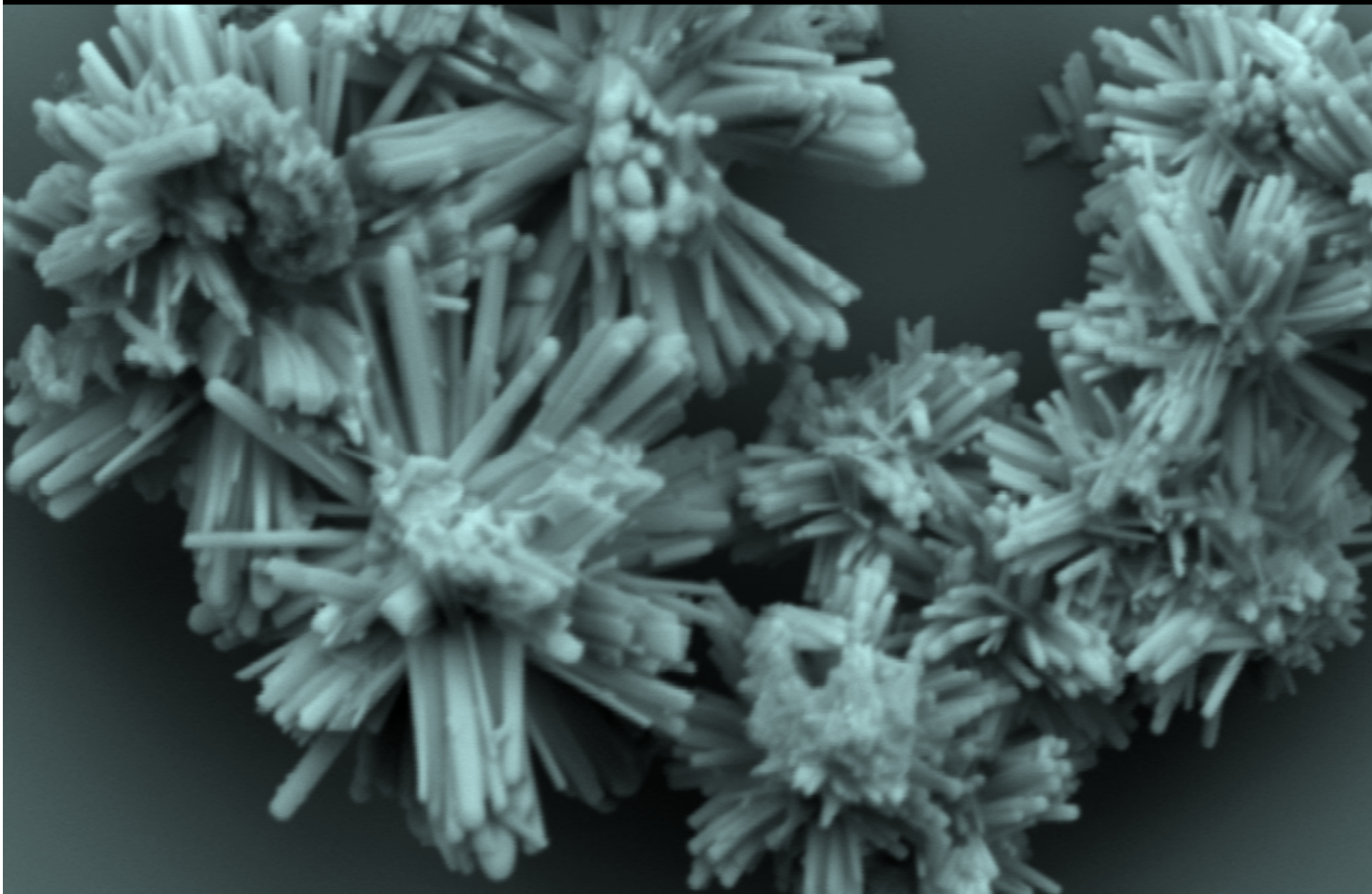
20 μm



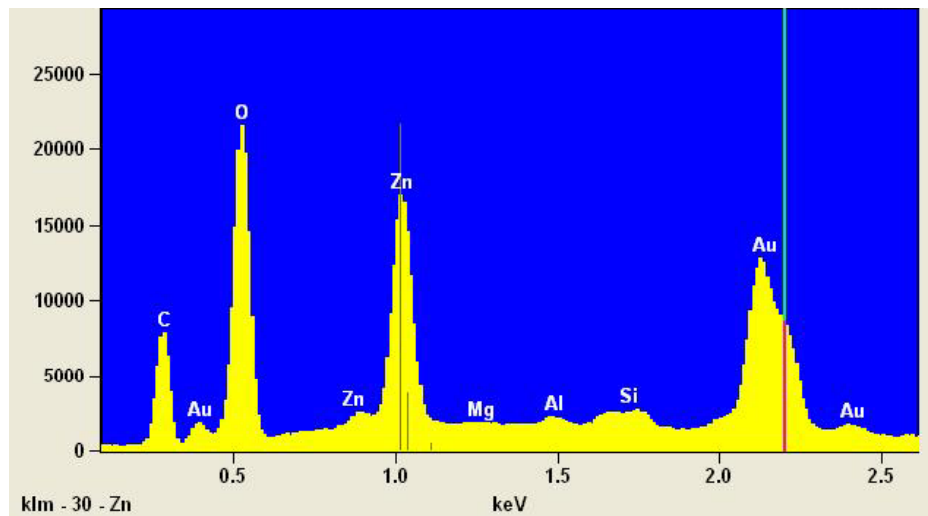
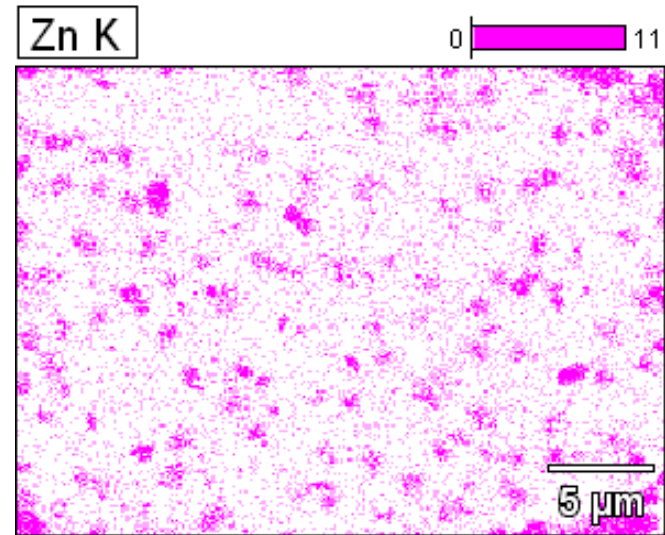
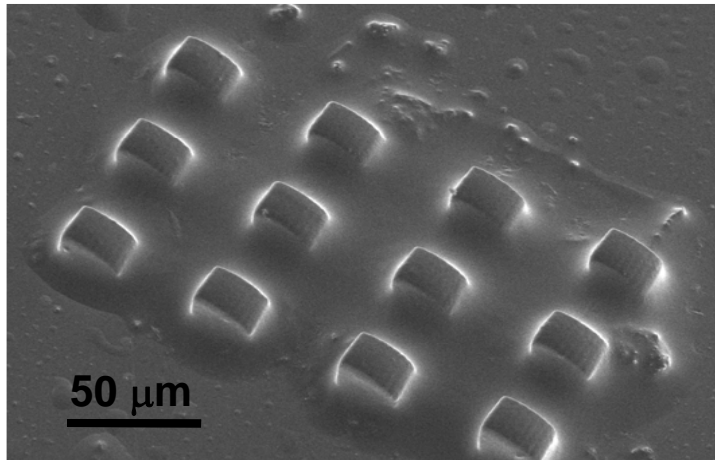
waveguiding of the microstructure fabricated on porous silica substrate ( $n= 1.185$ )

*Applications:* micro-laser; fluorescent microstructures; conductive microstructures

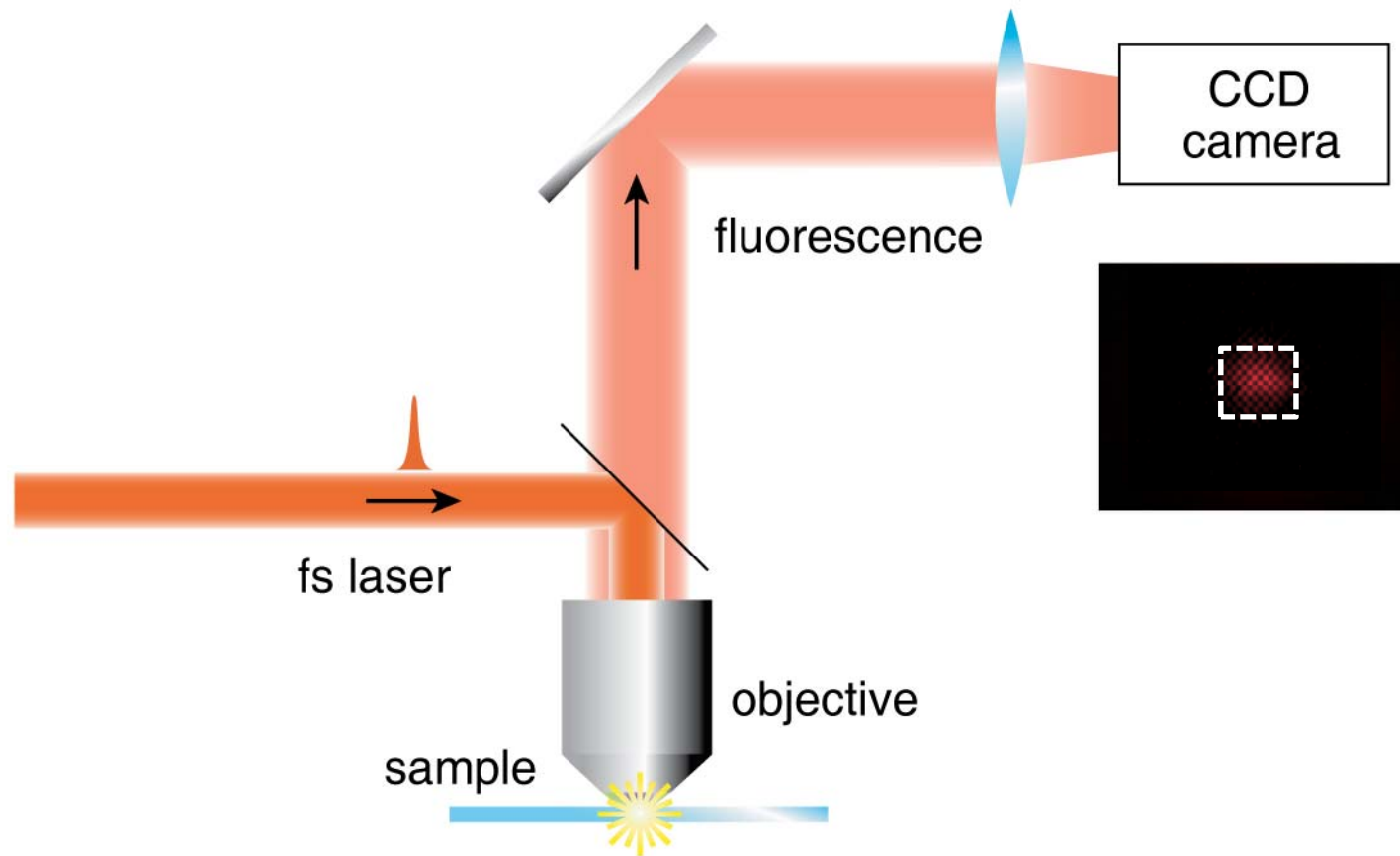
## Microstructures with ZnO nanowires



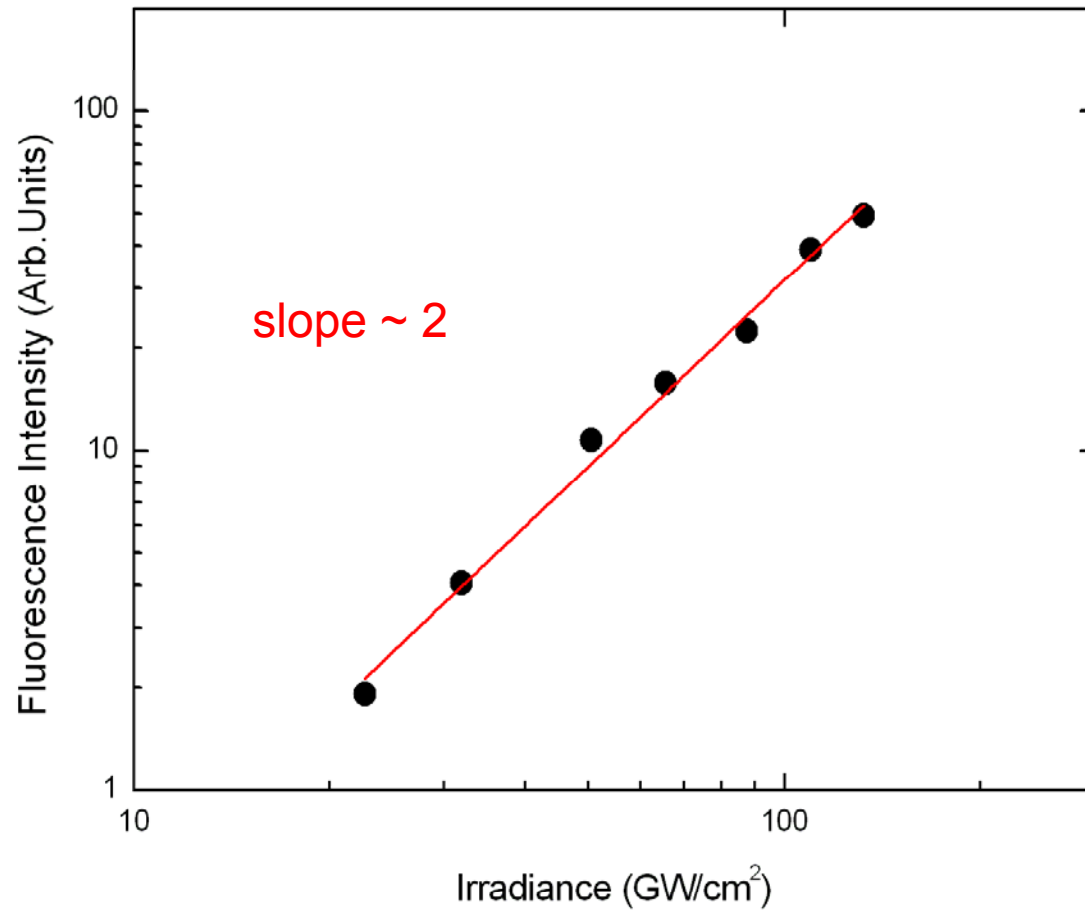
# Microstructures with ZnO nanowires



# Microstructures with ZnO nanowires

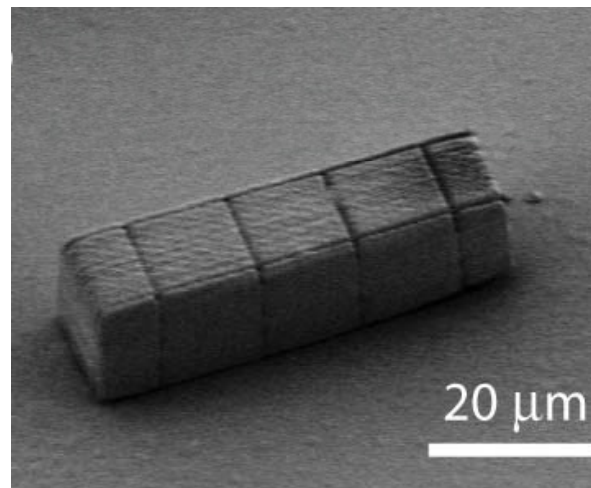
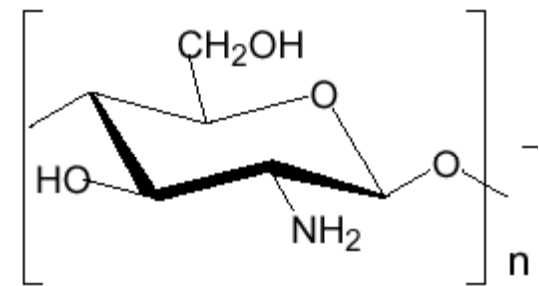
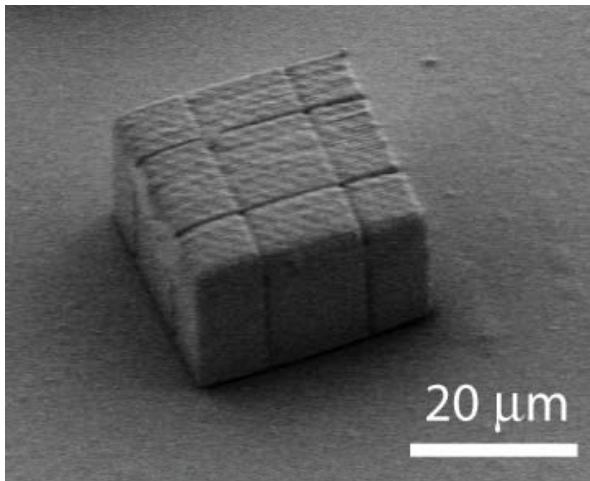


# Microstructures with ZnO nanowires



# Doping microstructures

- microstructures containing biopolymer - chitosan



micro-environment to study cells and bacteria

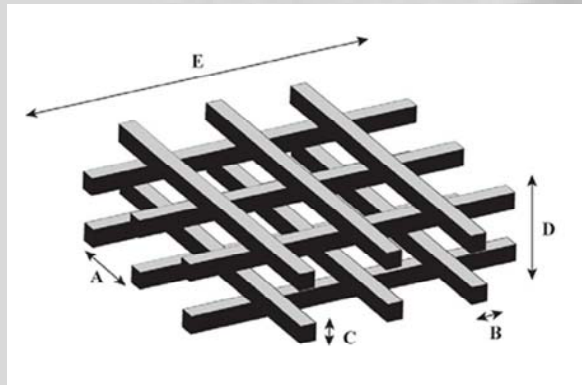
microfabrication of special  
microstructures to biology



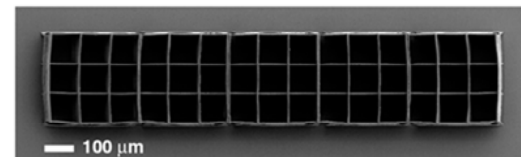


# 3D cell migration

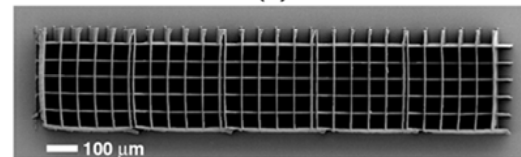
- 3D cell migration studies in micro-scaffolds



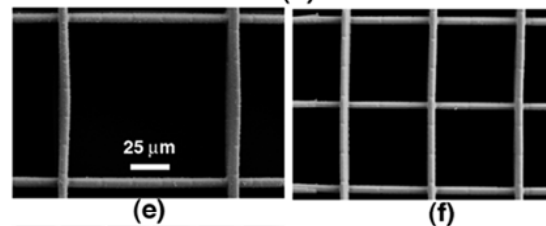
*SEM of the scaffolds*



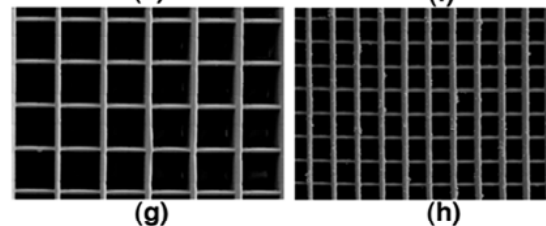
*110  $\mu\text{m}$  pore size*



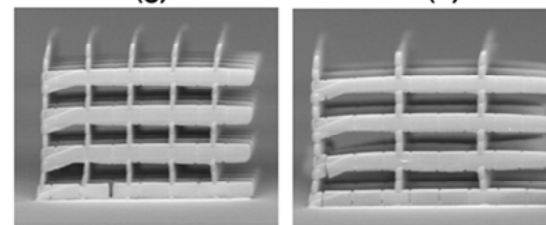
*52  $\mu\text{m}$  pore size*



*Top view*



*110, 52, 25, 12  $\mu\text{m}$  pore size*



*Side view*

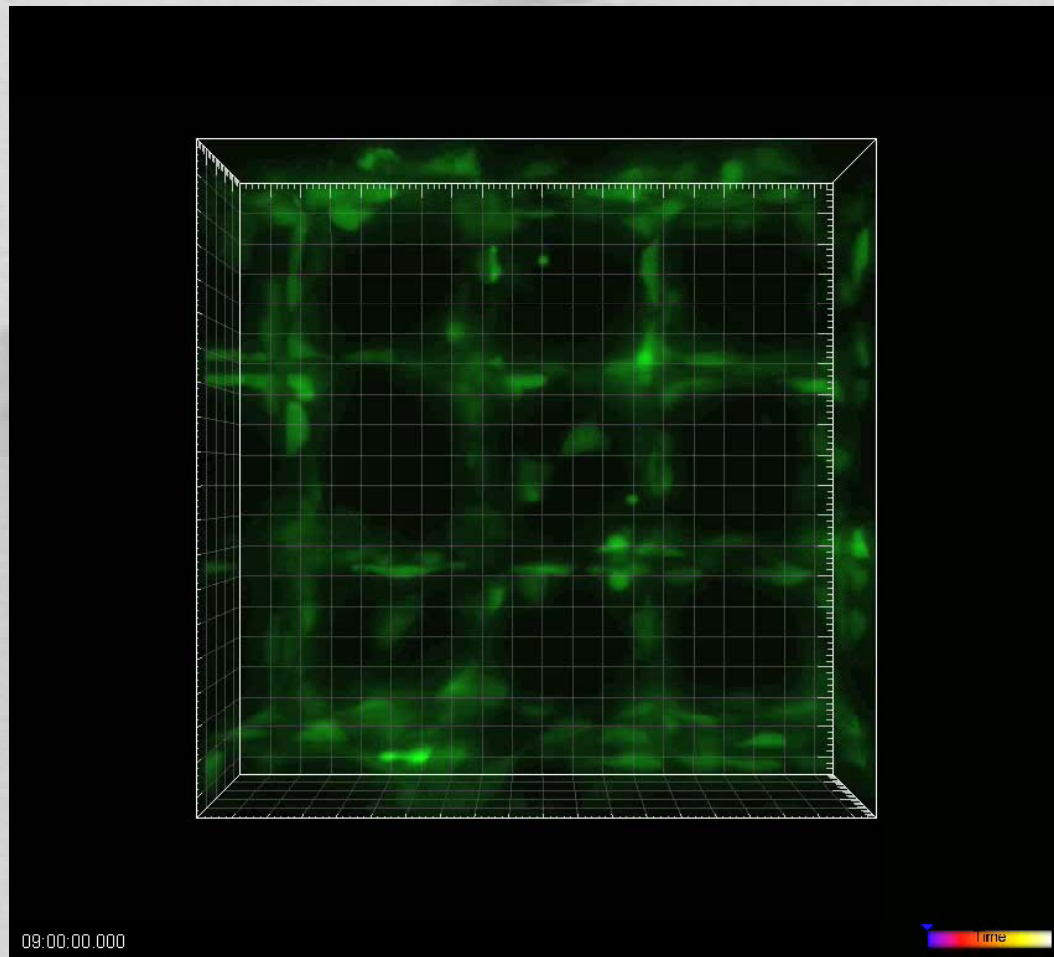
*25, 52  $\mu\text{m}$  pore size*

# 3D cell migration

50  $\mu\text{m}$  pore size

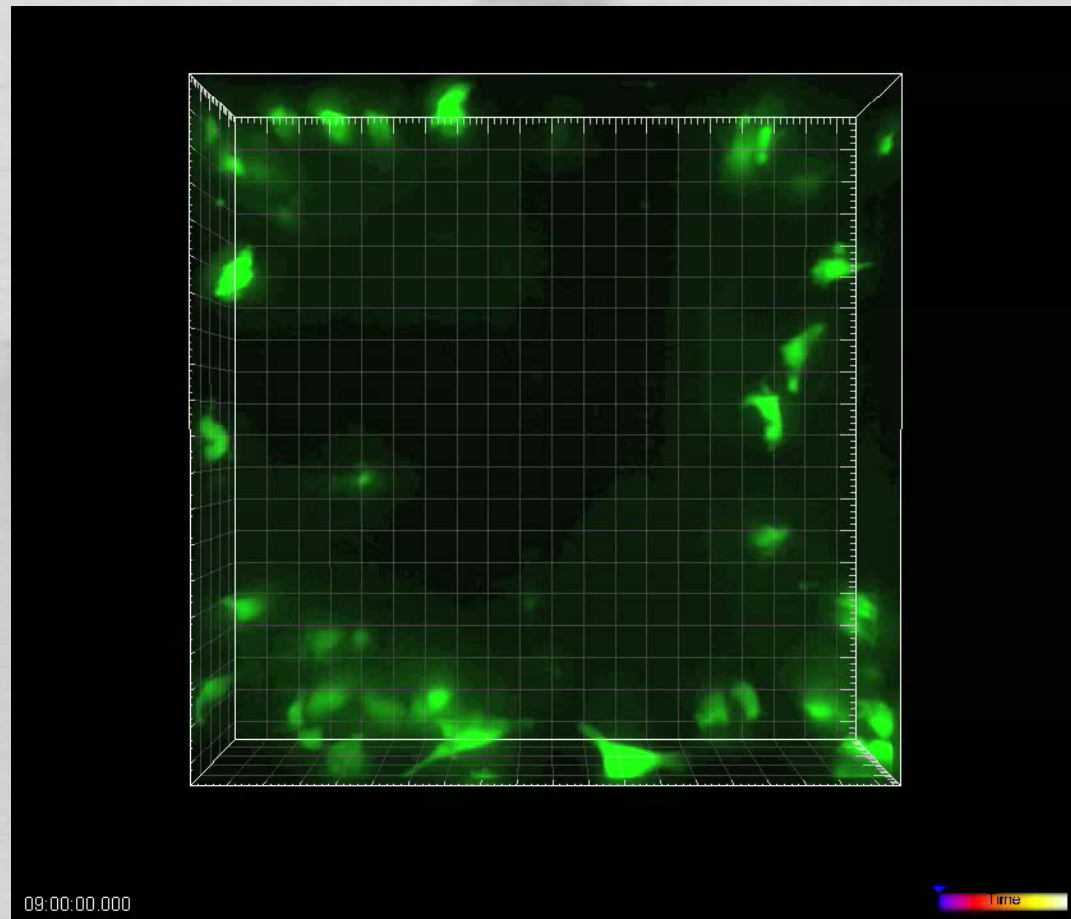


# 3D cell migration



110  $\mu\text{m}$  pore size

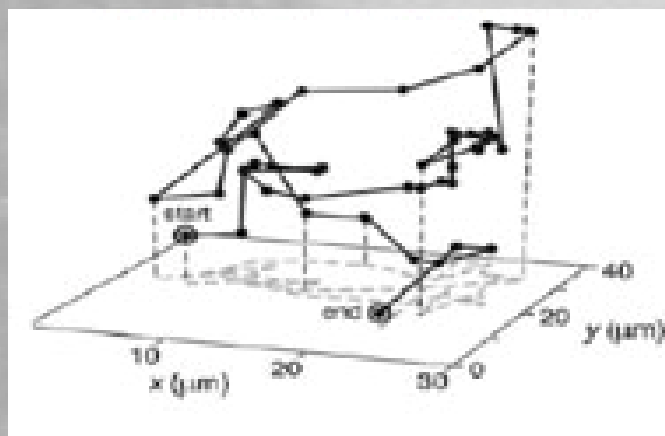
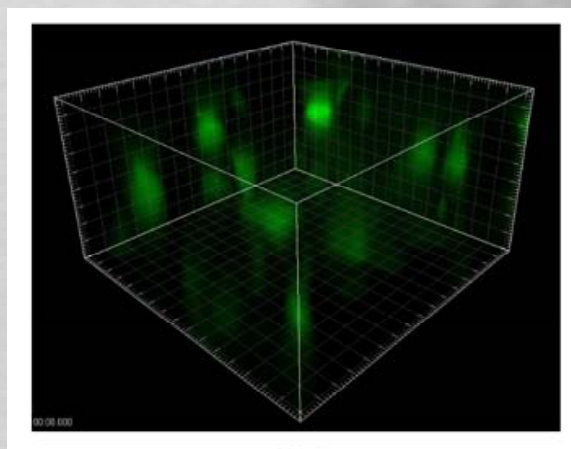
# 3D cell migration



12  $\mu\text{m}$  pore size

# 3D cell migration

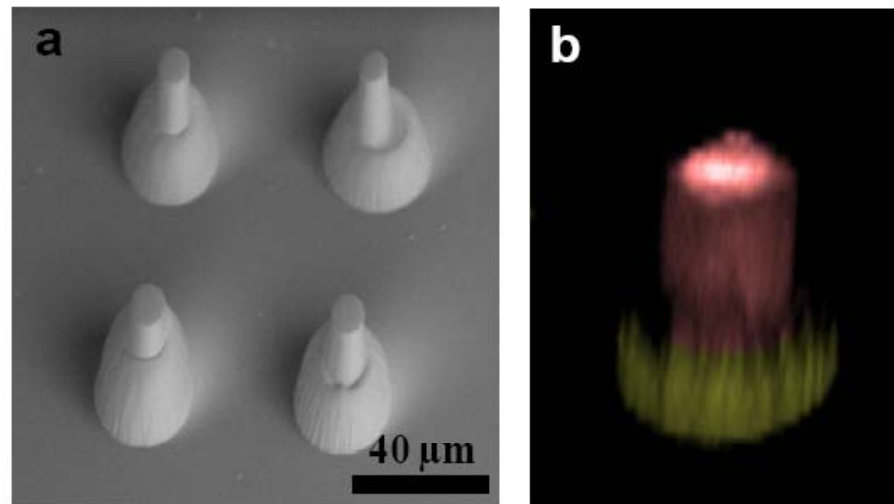
- 3D cell migration studies in micro-scaffolds



# Guiding bacterial growth in a micro-environment

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

microstructure containing Fluorescein and Rhodamine

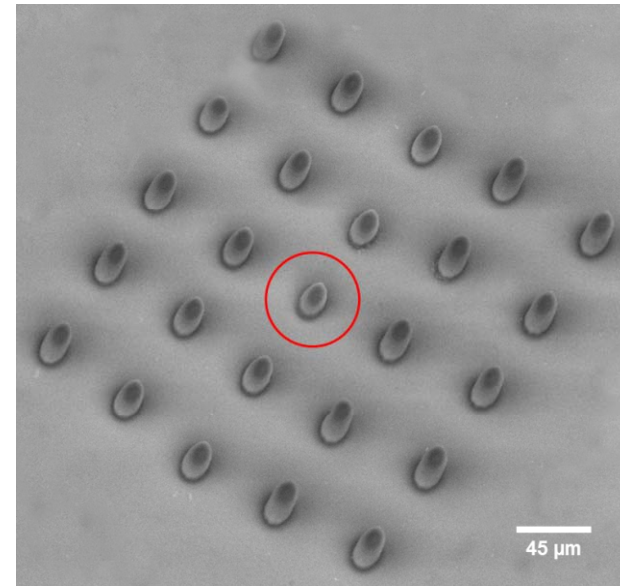
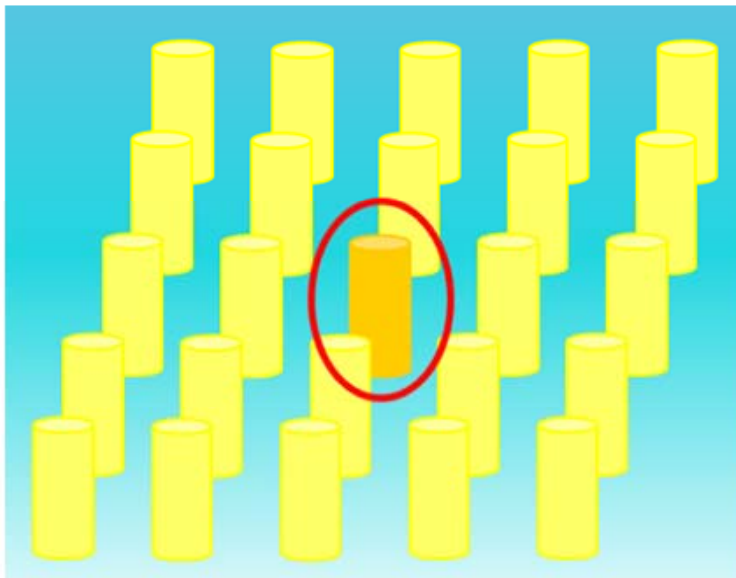


(a) SEM of a double-doped microstructure (top view).

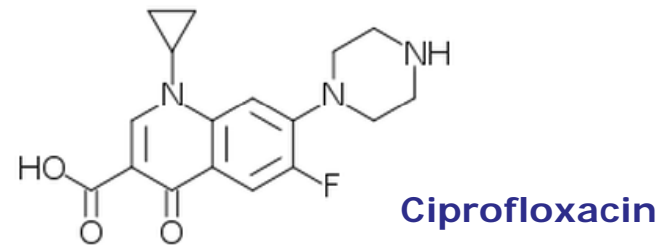
(b) Confocal fluorescent microscopy image of the same microstructure.

# Guiding bacterial growth in a micro-environment

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

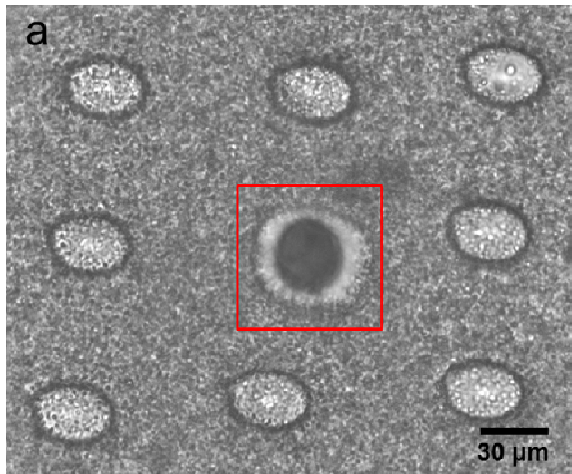


micro-environment in which the central structure contains antibiotic.

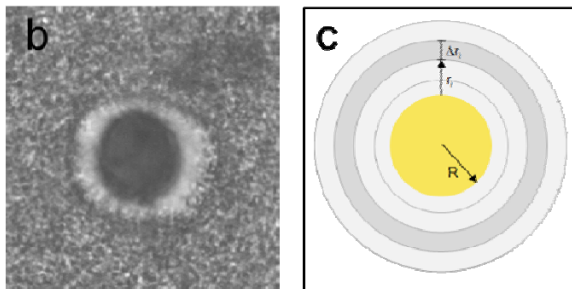


# Guiding bacterial growth in a micro-environment

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



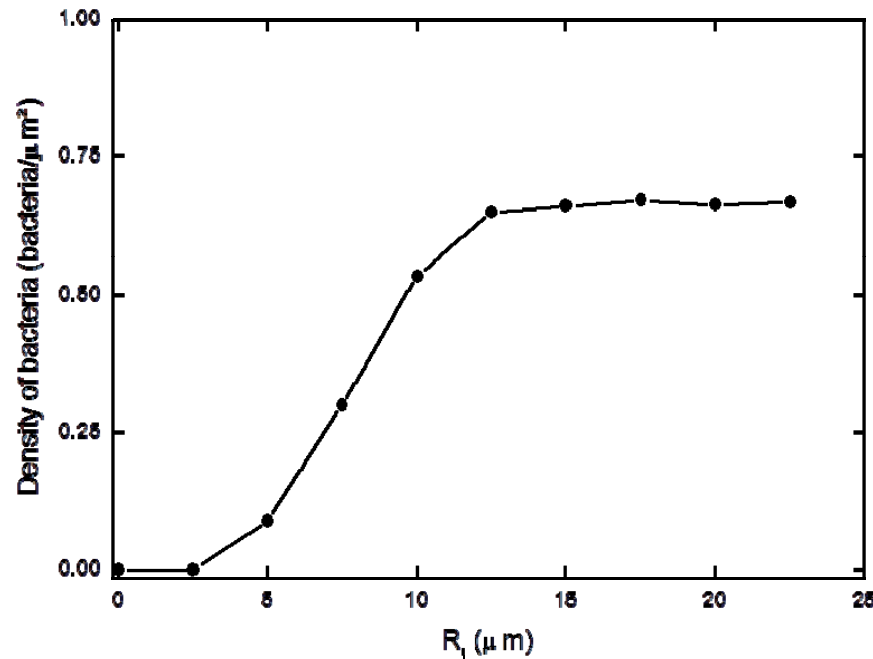
after 3 hours, we observed that a small region around the doped structure does not show bacterial growth.



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



# Guiding bacterial growth in a micro-environment



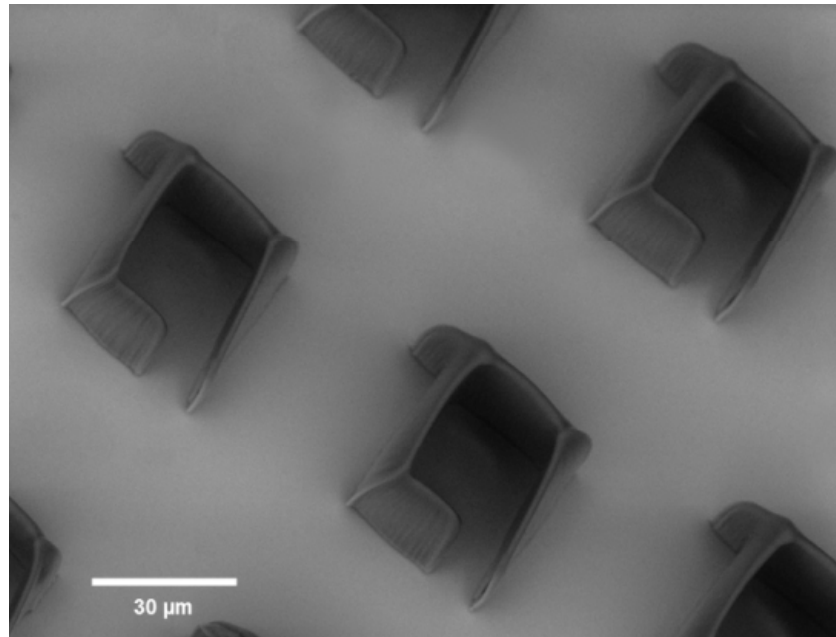
the density of bacteria grows monotonically with  $r_i$

saturating when  $r_i$  reaches approximately 12 μm in about 0.7 bacteria/μm<sup>2</sup>

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

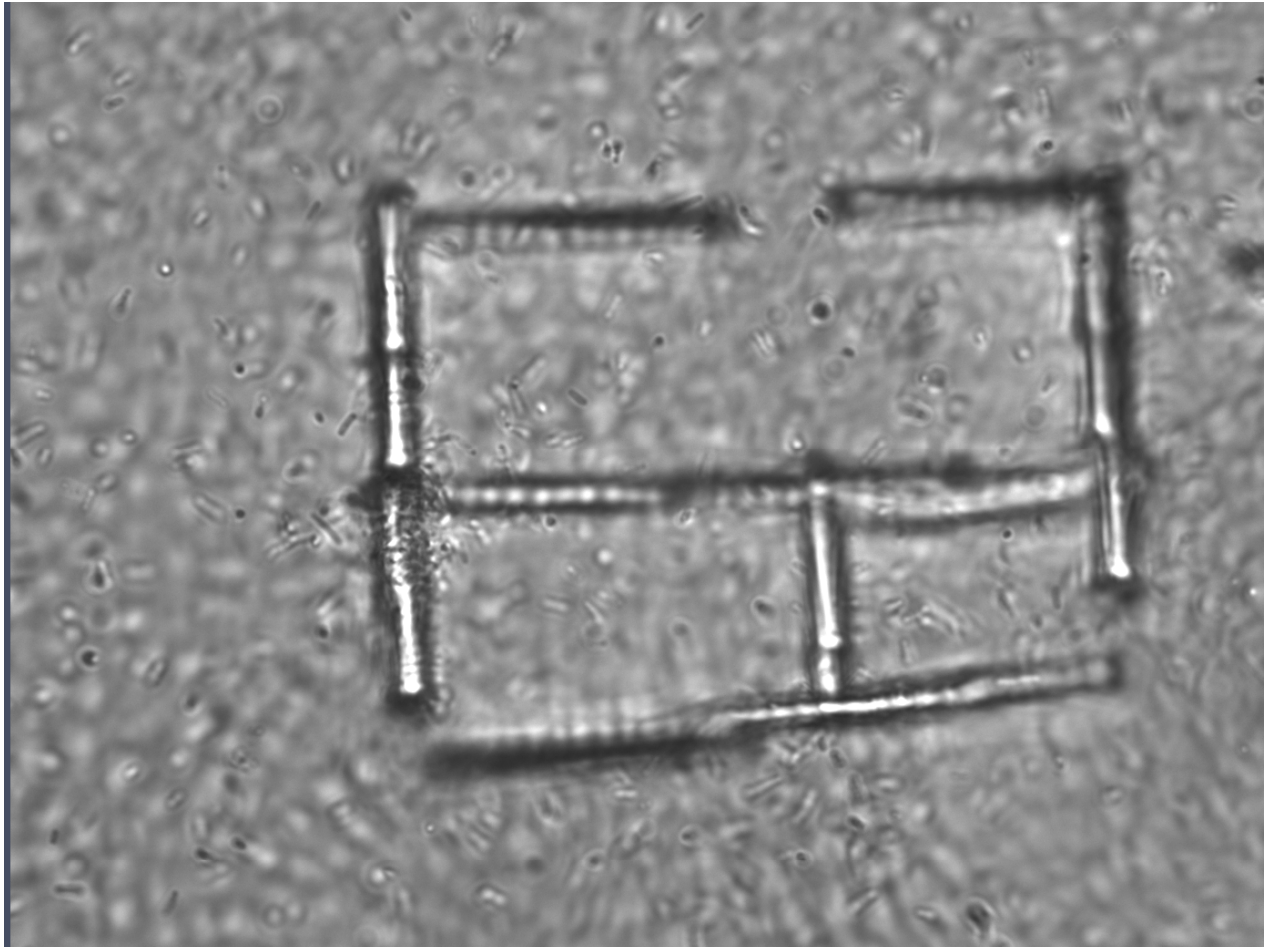
## Bacteria microtraps



using micro-environments to study the dynamics of bacterial migration

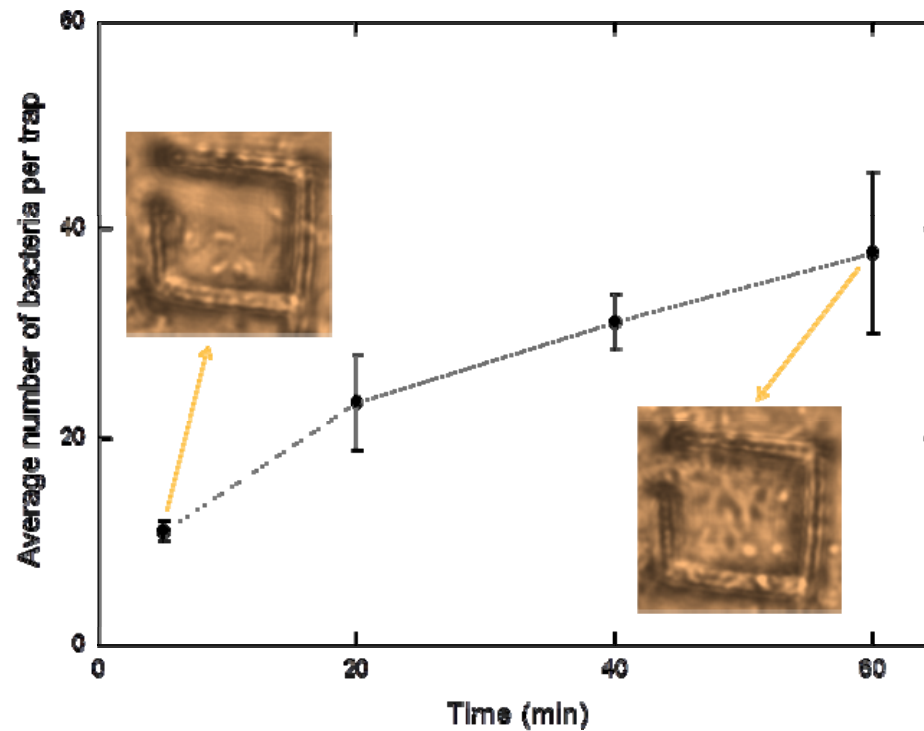
# Guiding bacterial growth in a micro-environment

## Bacteria microtraps



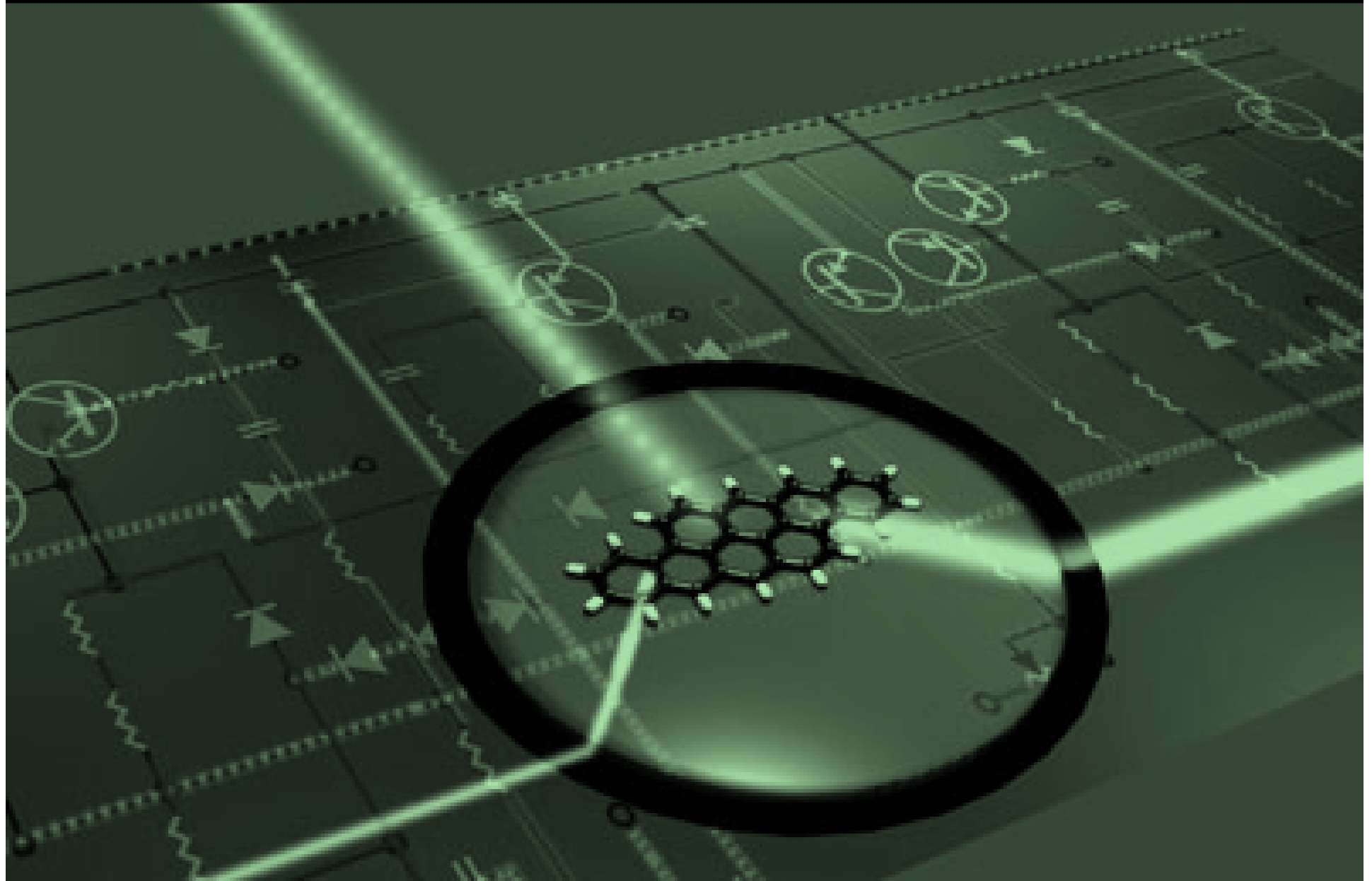
# Guiding bacterial growth in a micro-environment

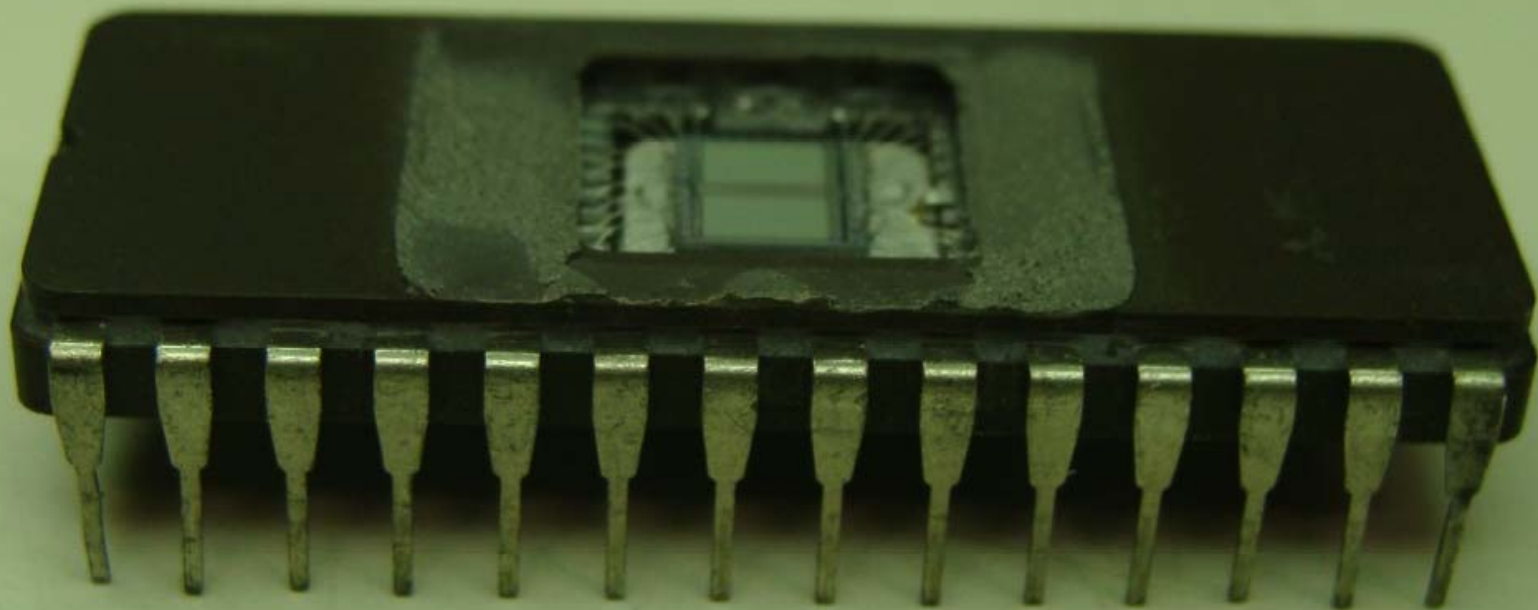
## Bacteria microtraps

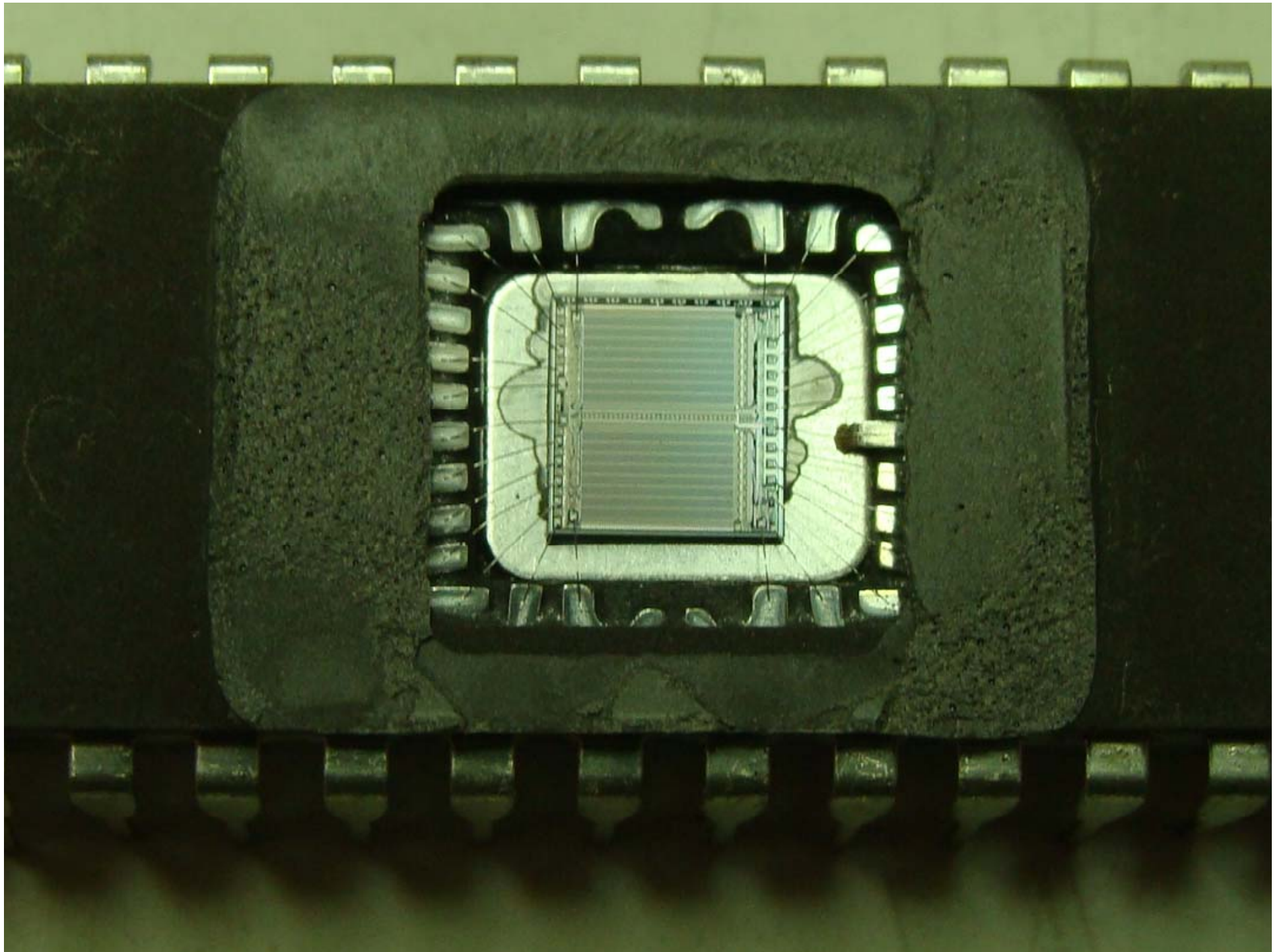


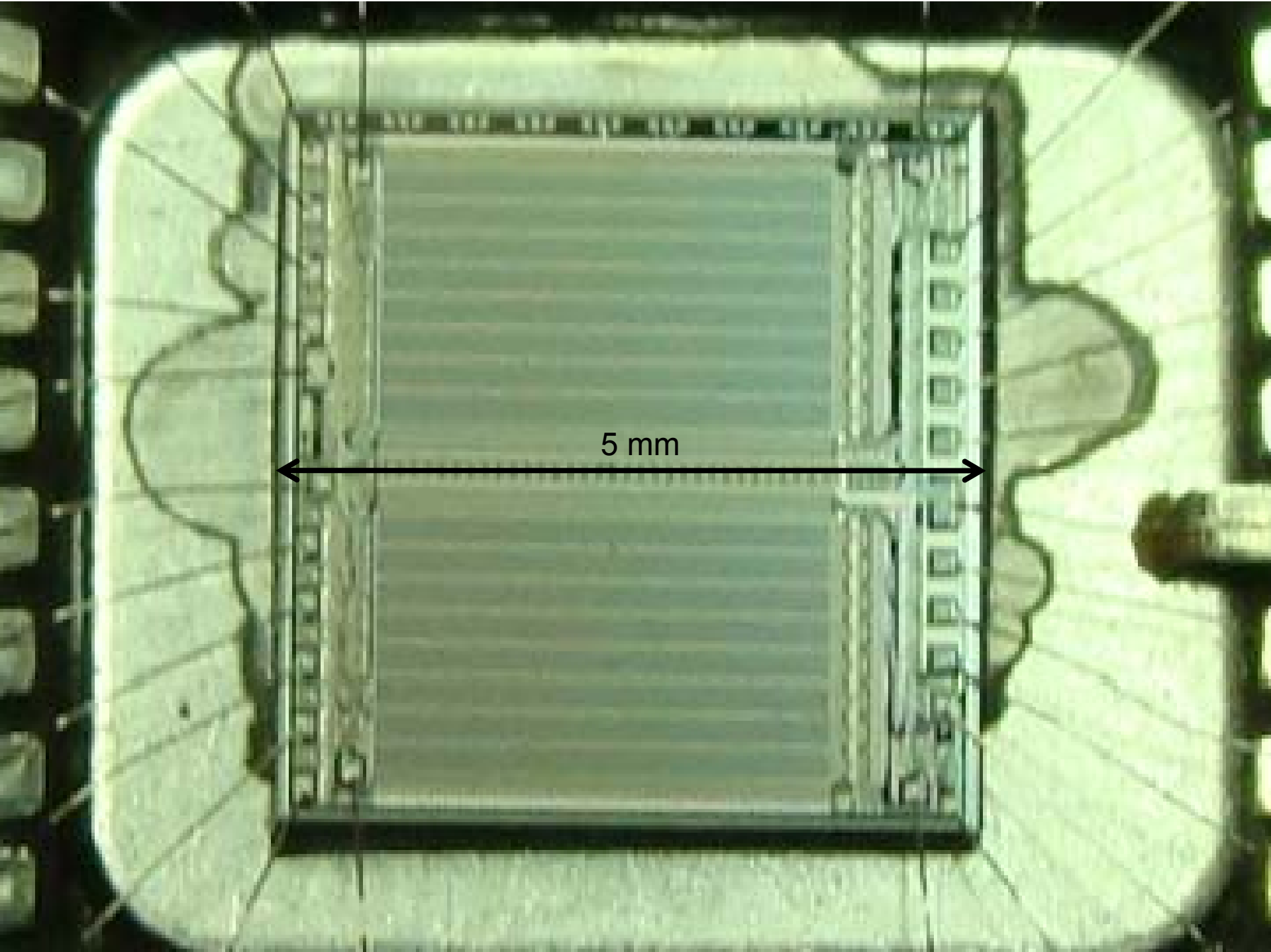
using micro-environments to study the dynamics of bacterial migration

# Optical circuit

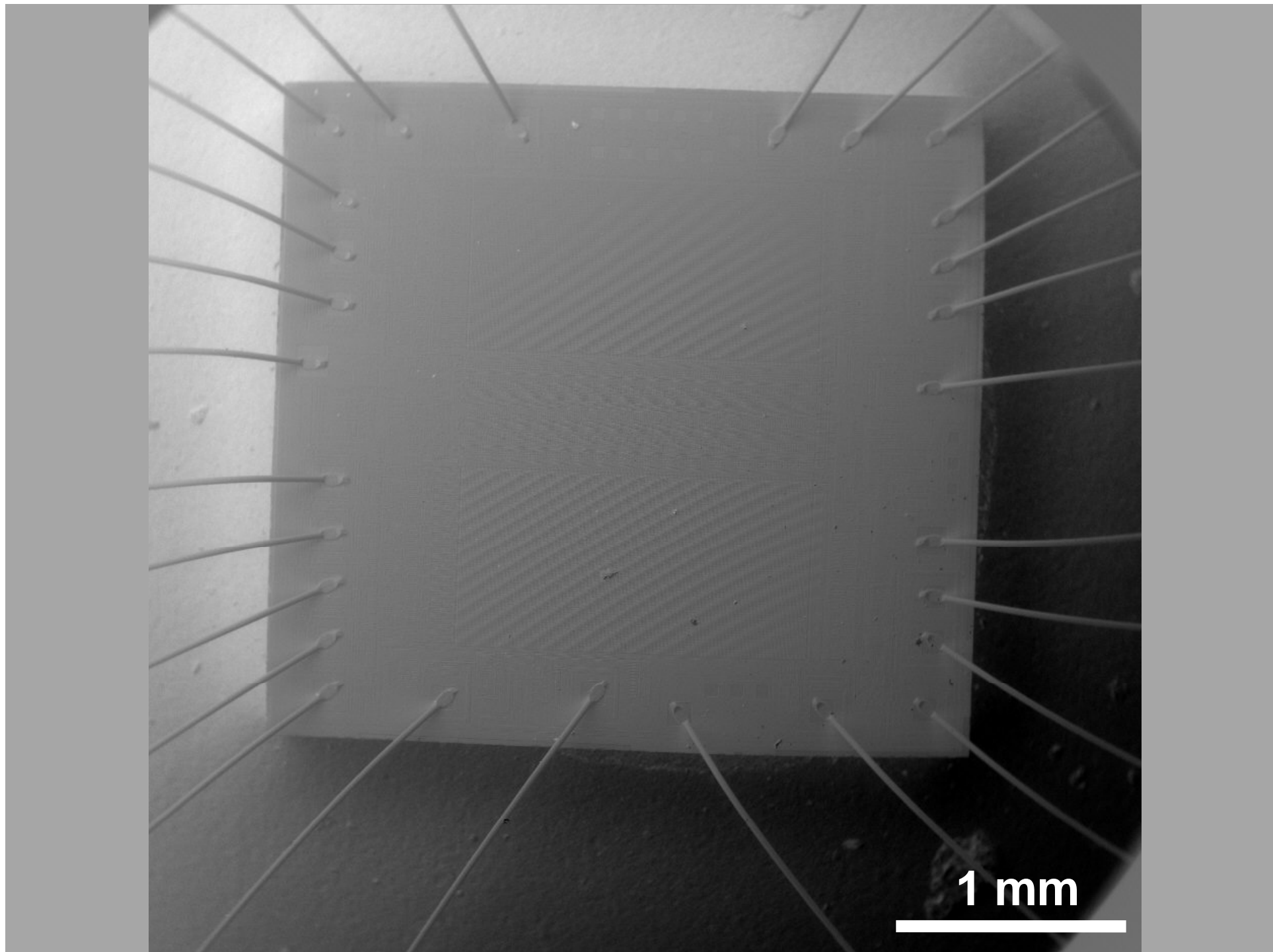




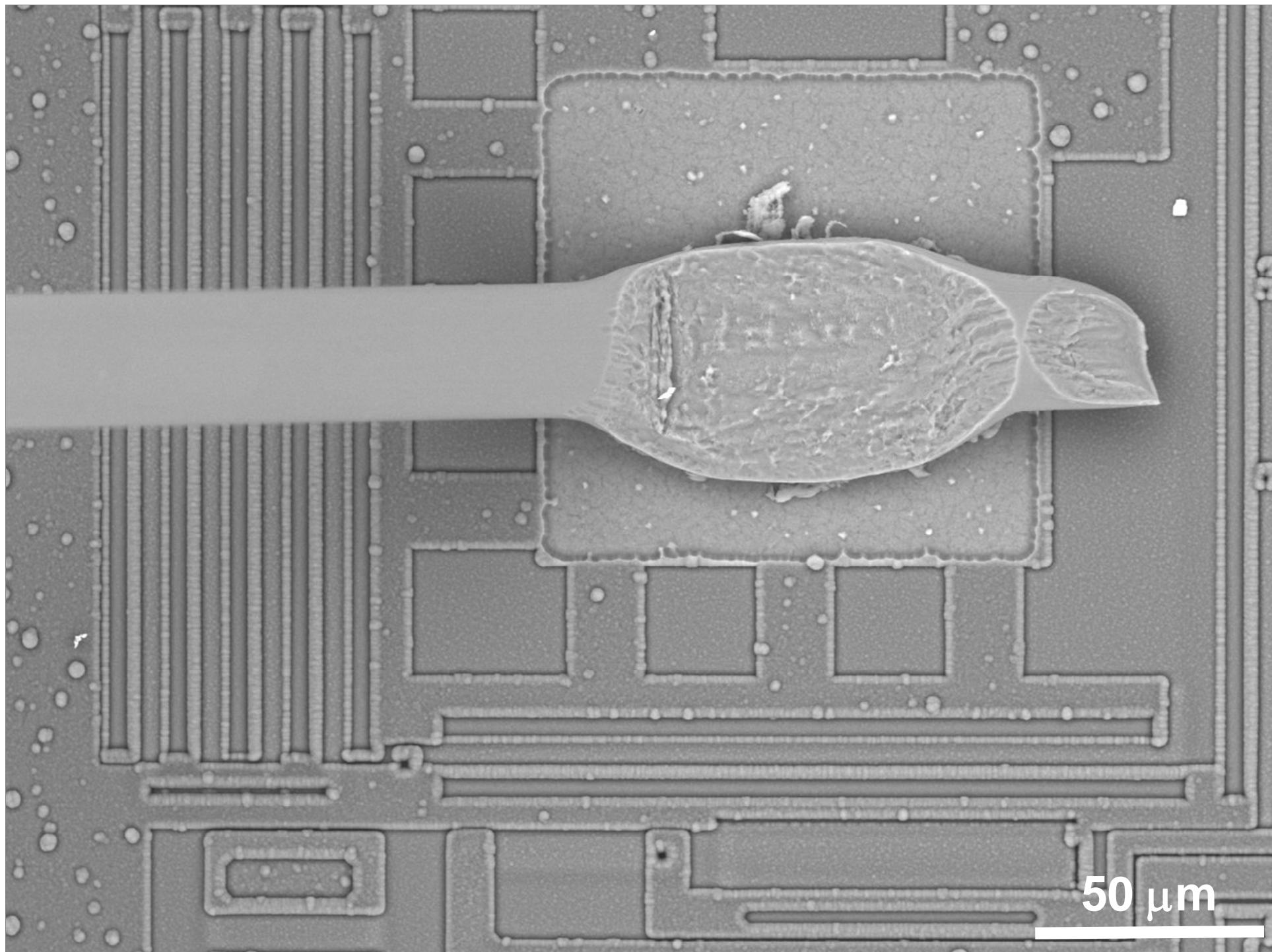








1 mm



# Optical circuit

- microfabrication
- silica nanowires
- coupling microstructures

50  $\mu\text{m}$



# Silica nanowires

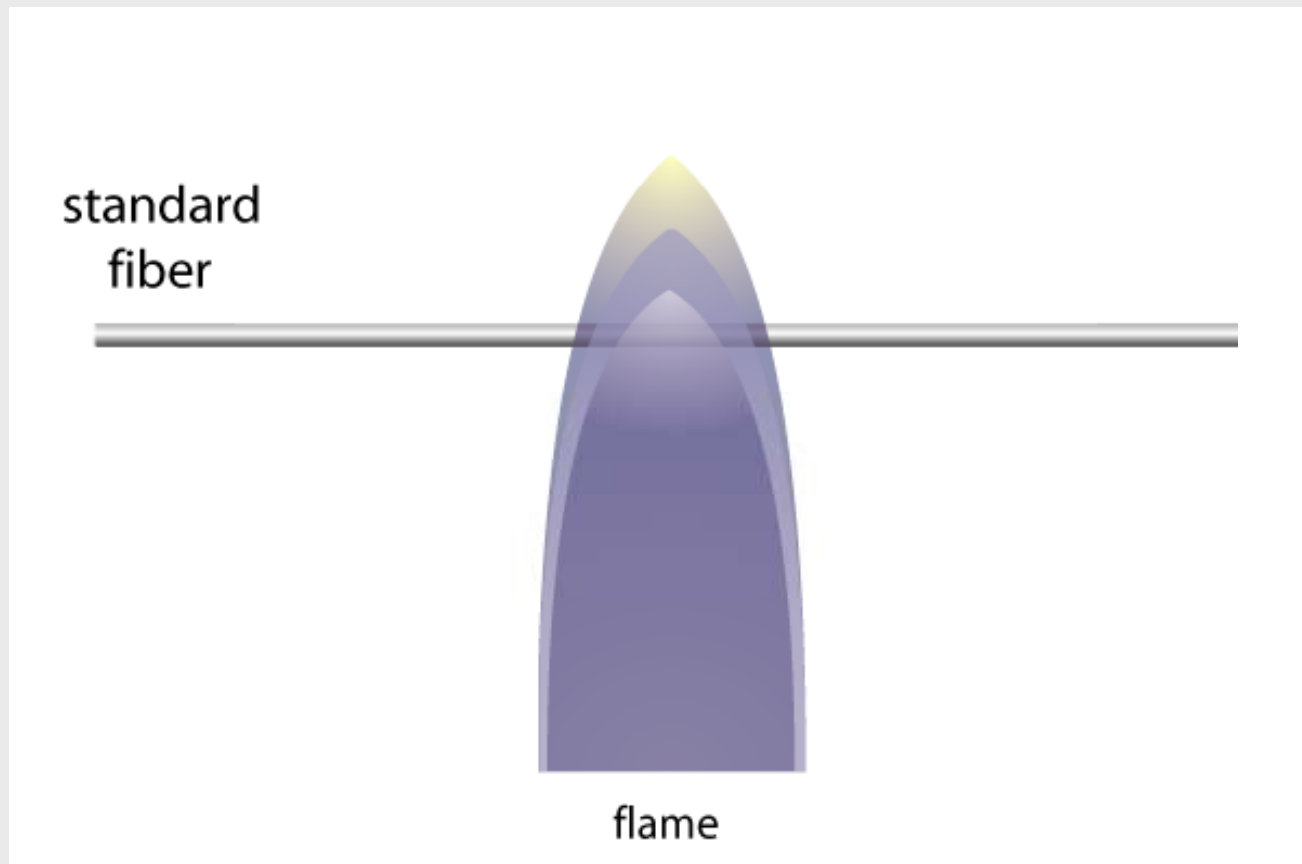
nanowires fabrication process

standard  
fiber



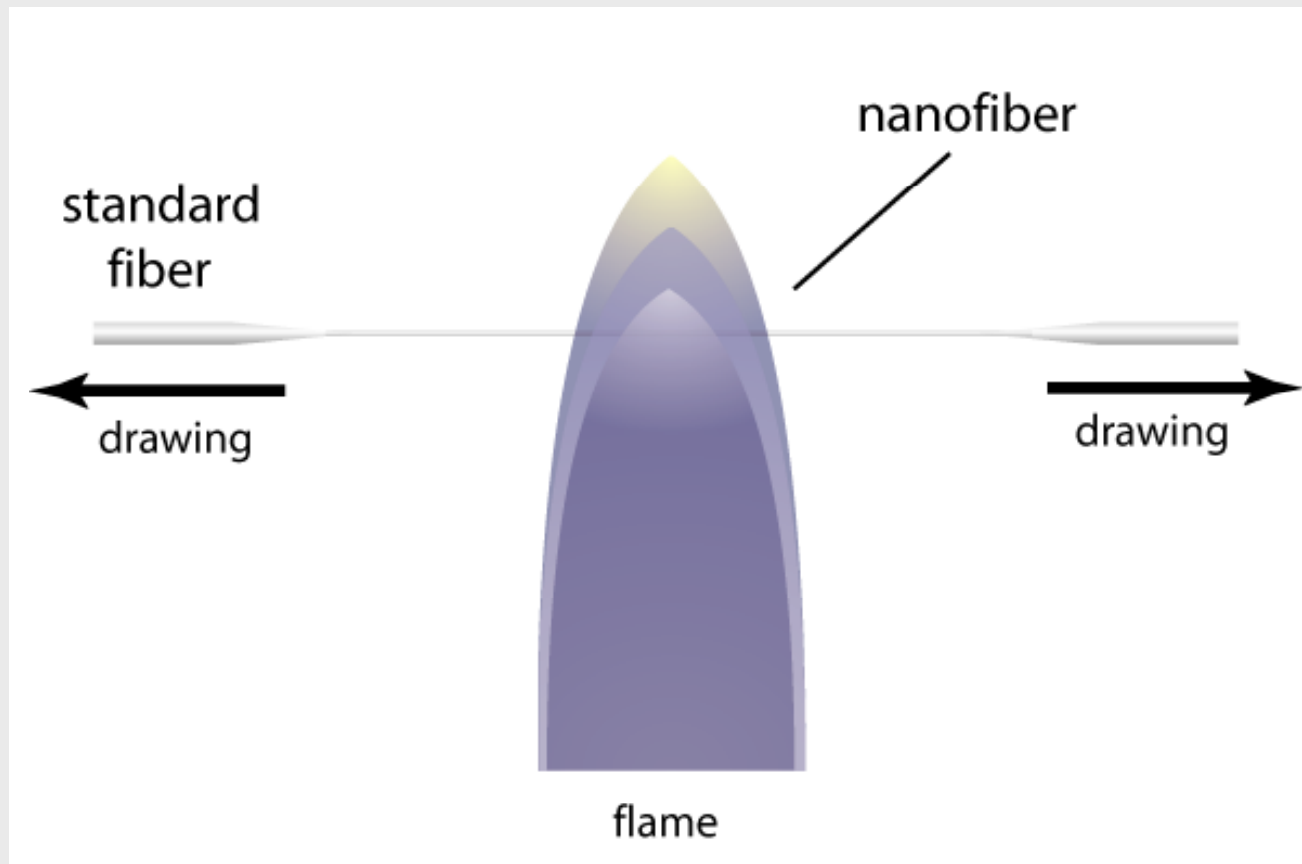
# Silica nanowires

nanowires fabrication process

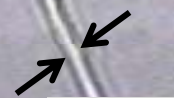


# Silica nanowires

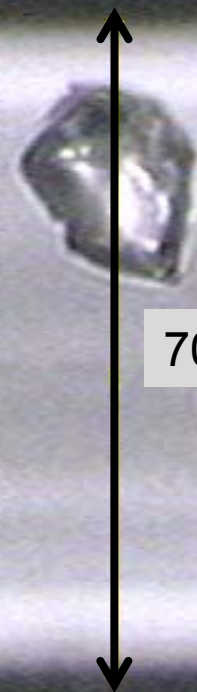
nanowires fabrication process



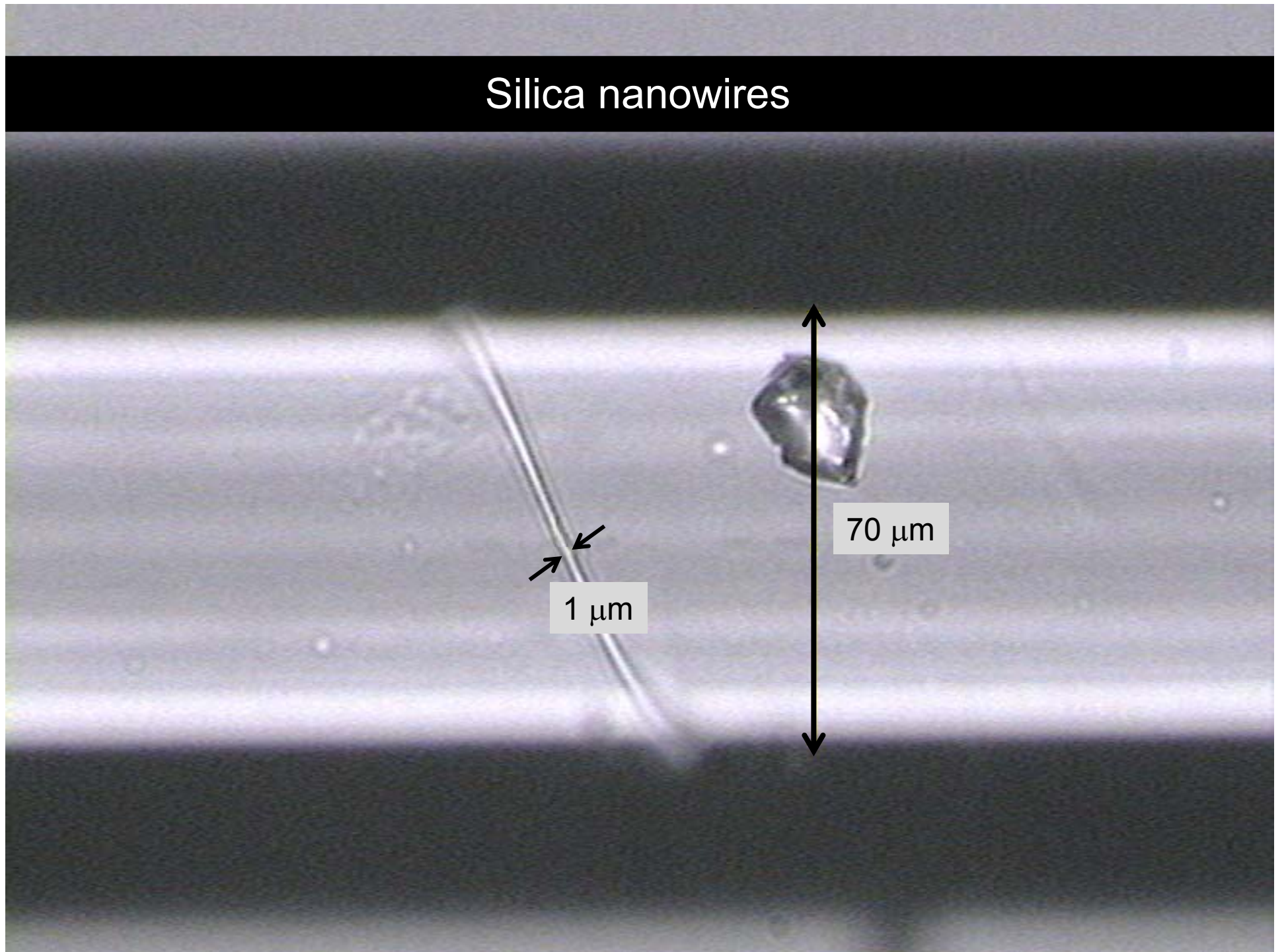
# Silica nanowires



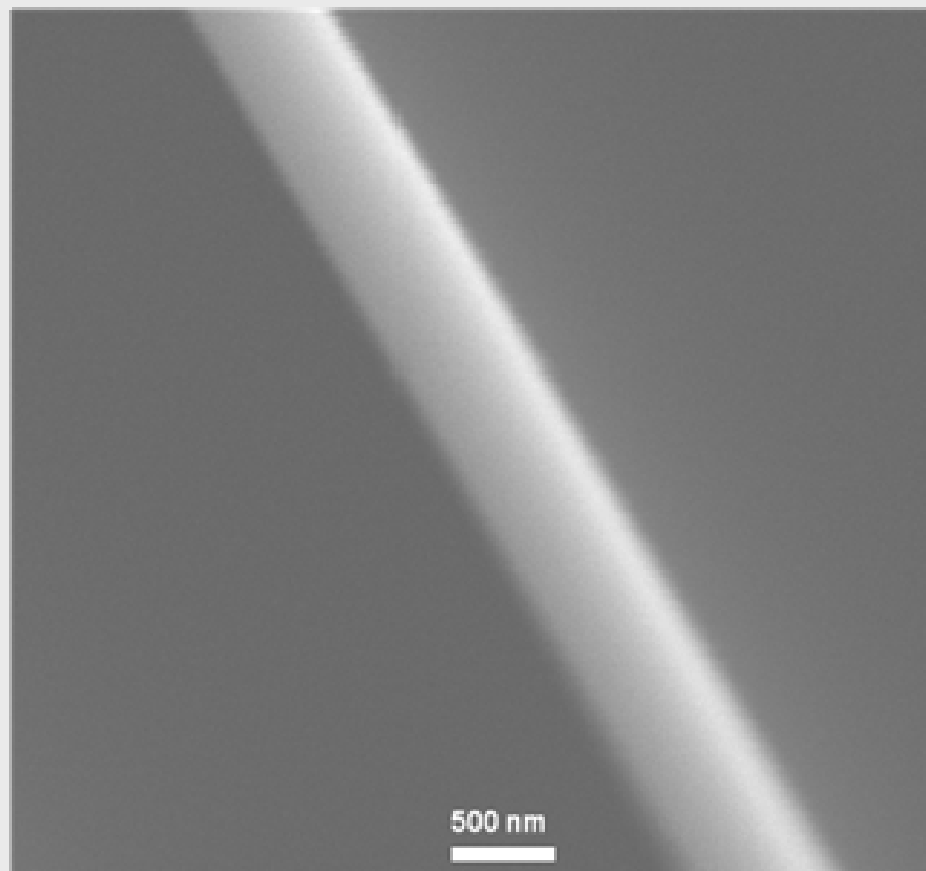
1  $\mu\text{m}$



70  $\mu\text{m}$

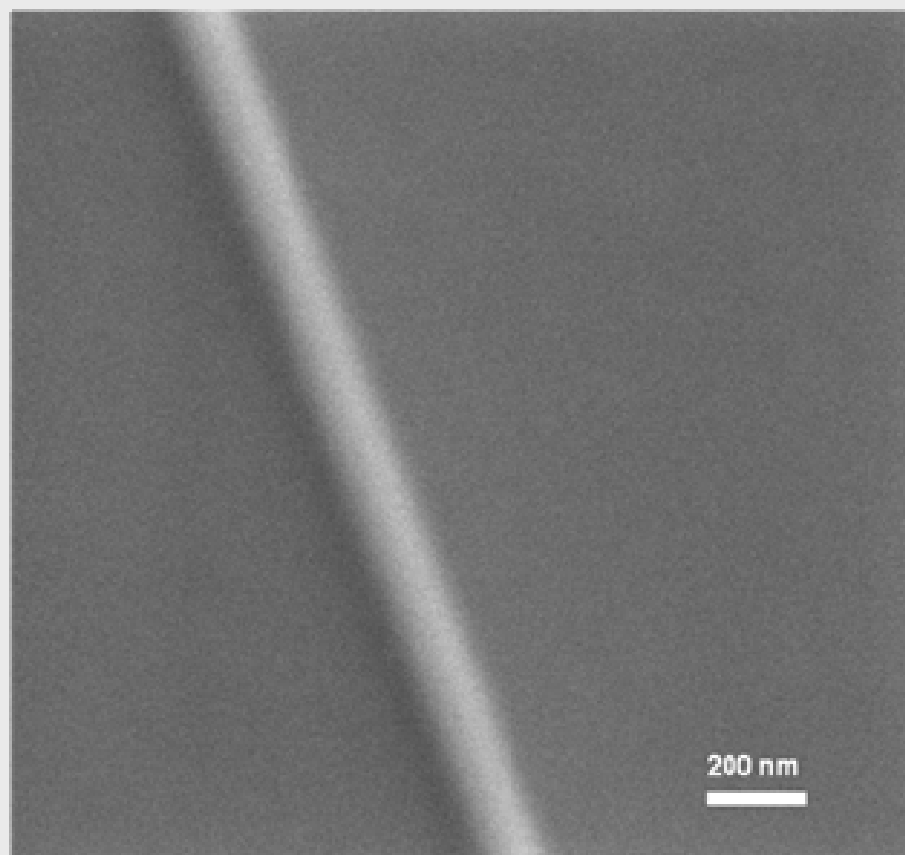


# Silica nanowires



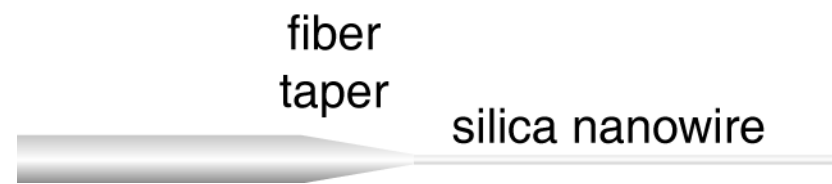


# Silica nanowires



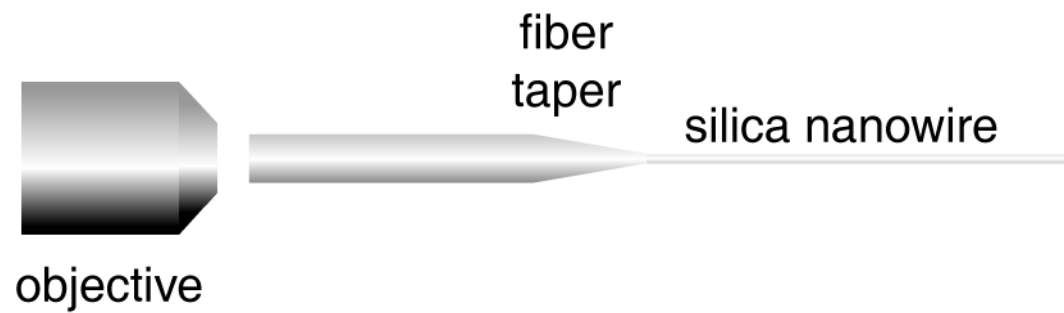
# Silica nanowires

coupling light into nanowires



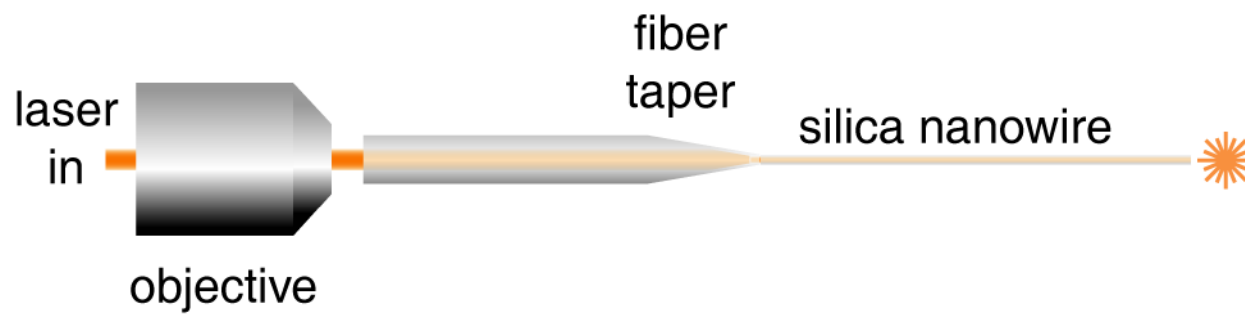
# Silica nanowires

coupling light into nanowires



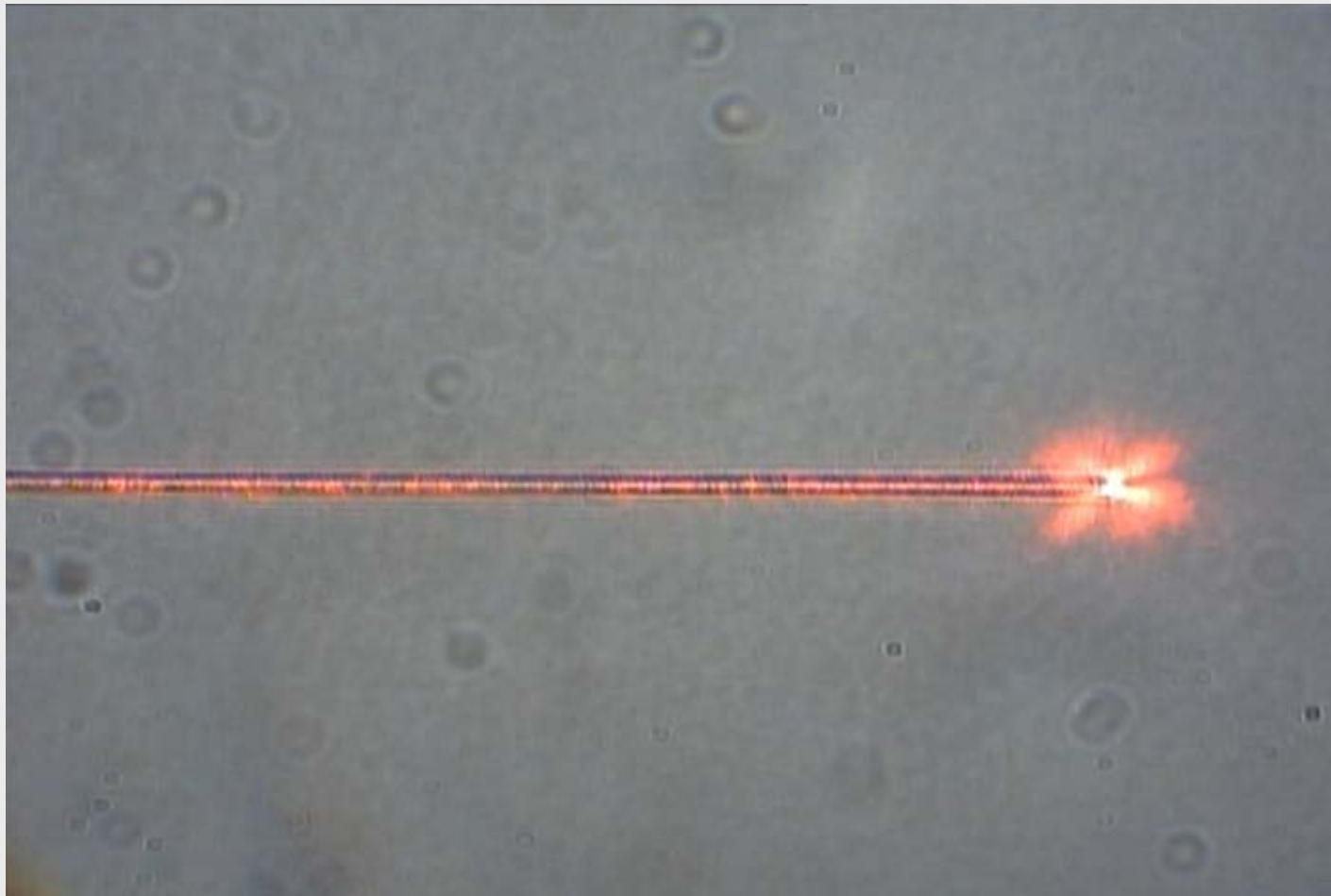
# Silica nanowires

coupling light into nanowires



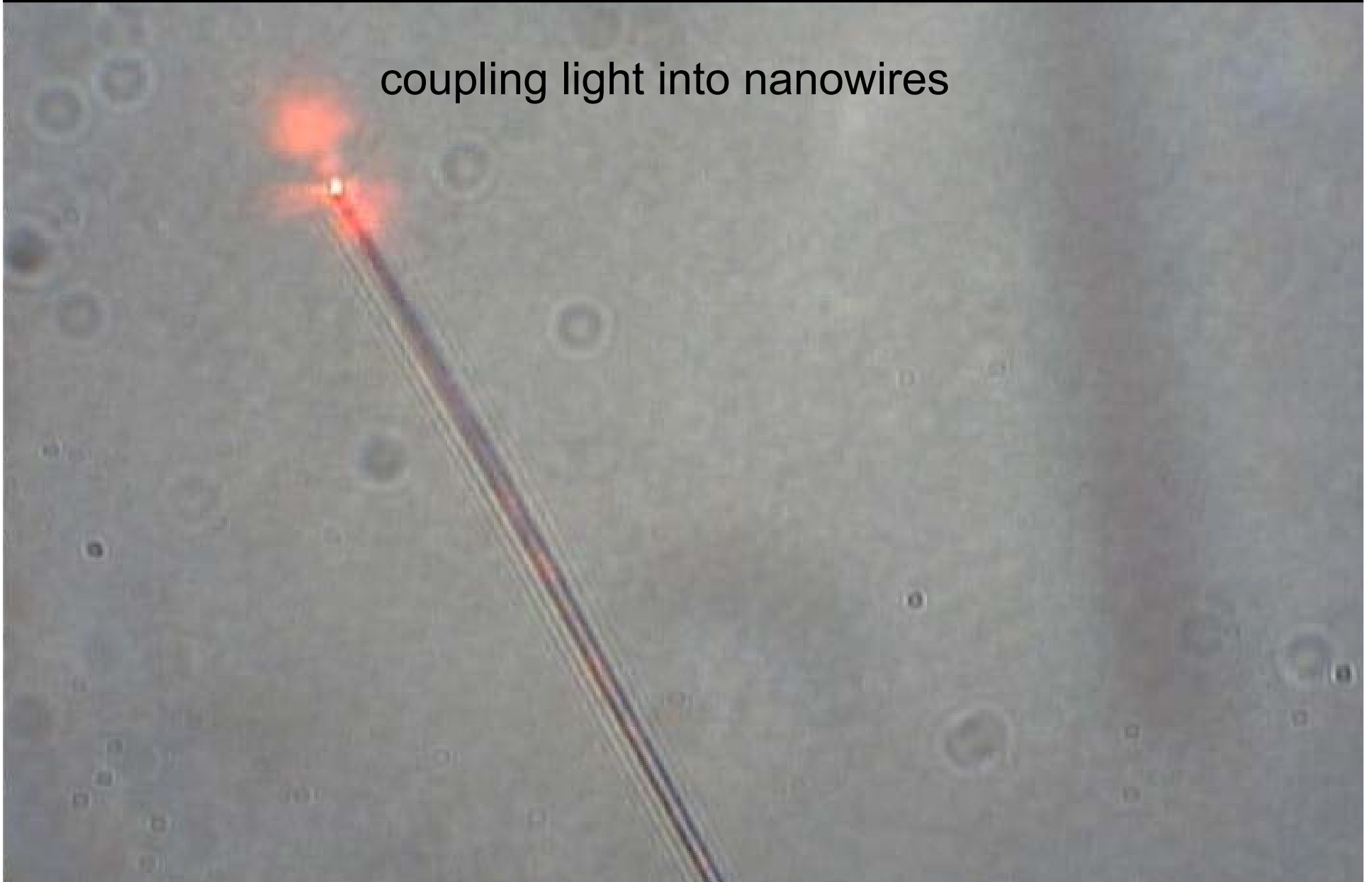
# Silica nanowires

coupling light into nanowires



## Silica nanowires

coupling light into nanowires



## Silica nanowires

coupling light into nanowires

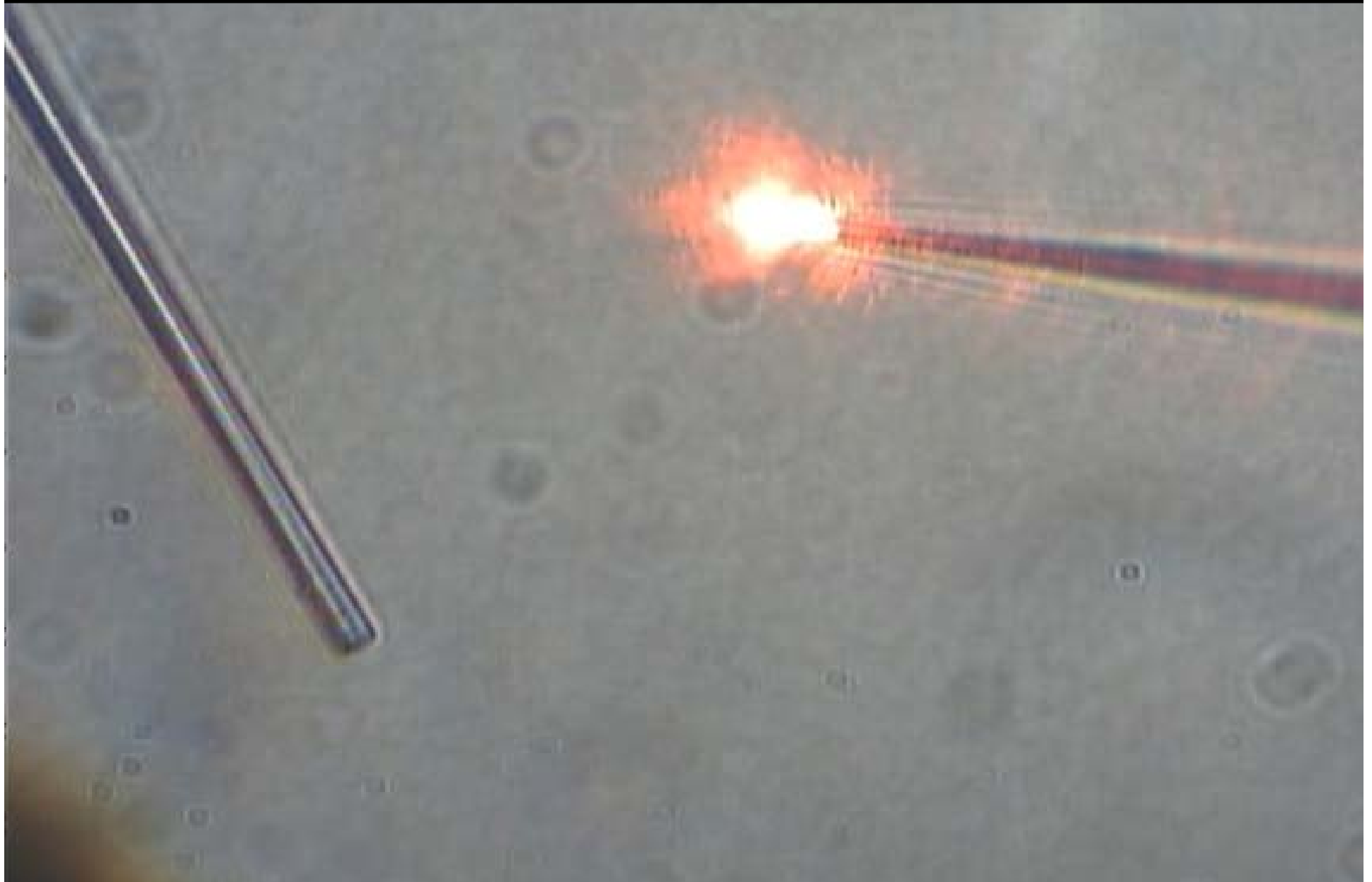


# Silica nanowires

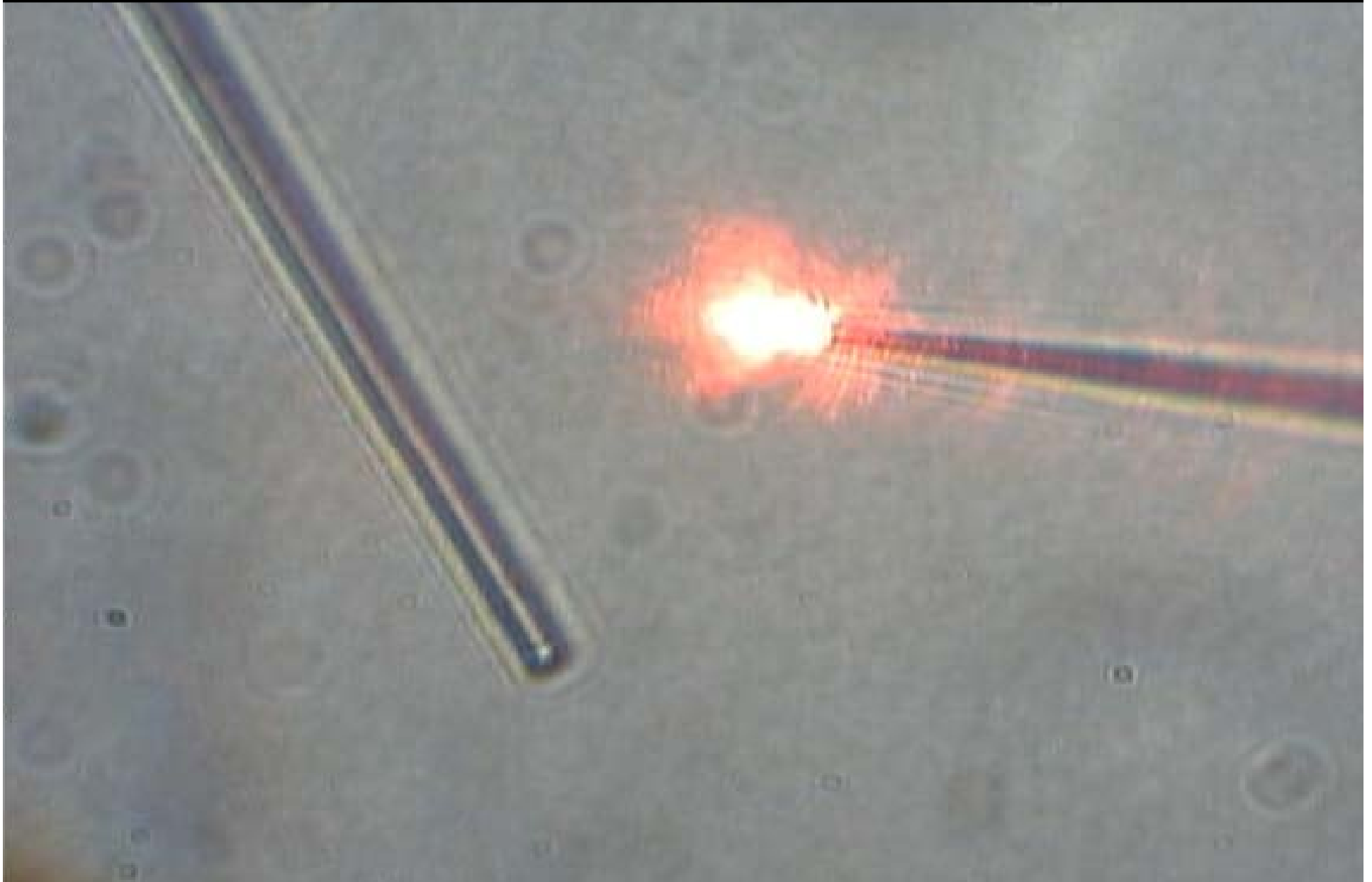
Manipulating the nanowires



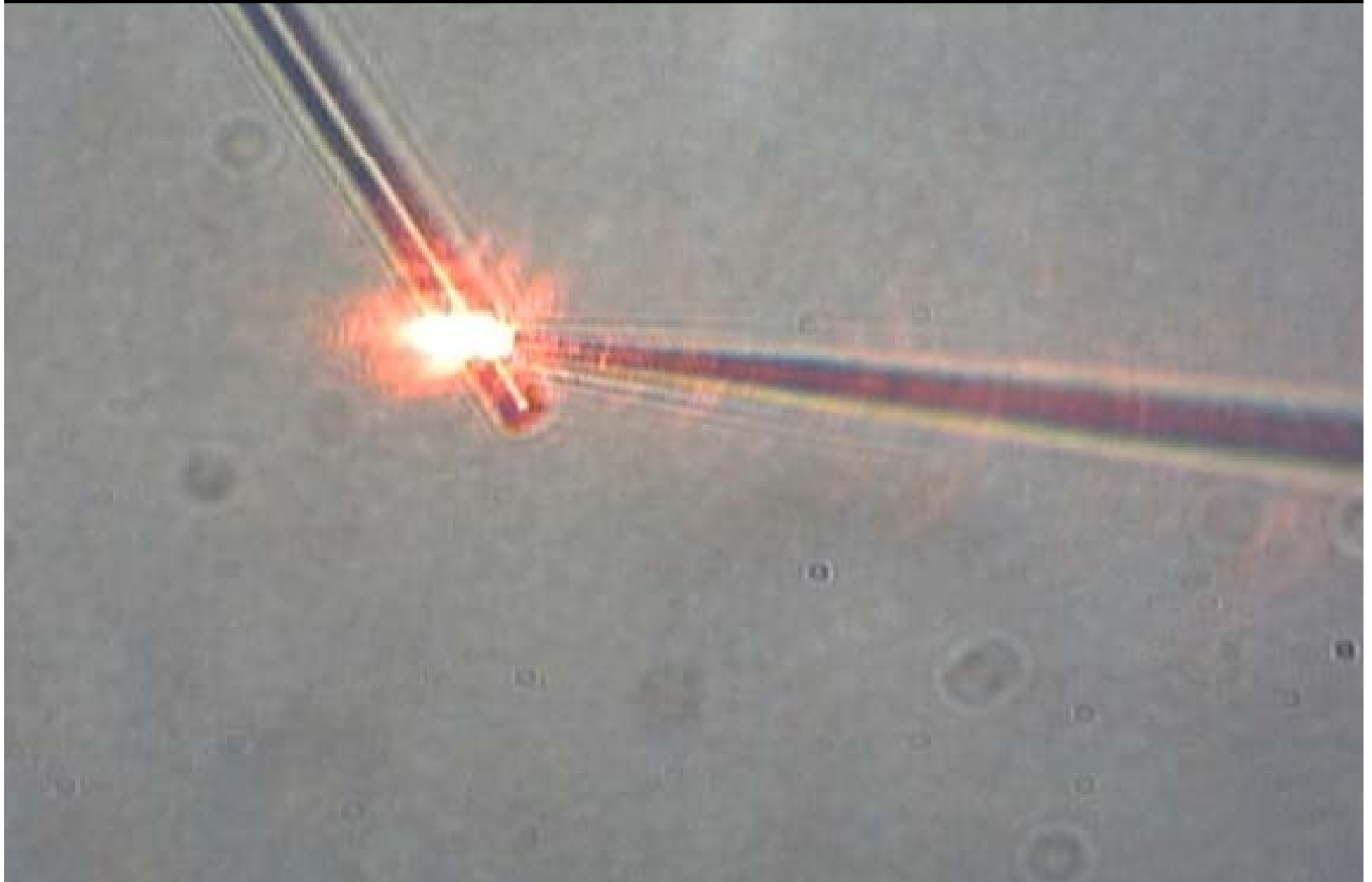
# Silica nanowires



# Silica nanowires

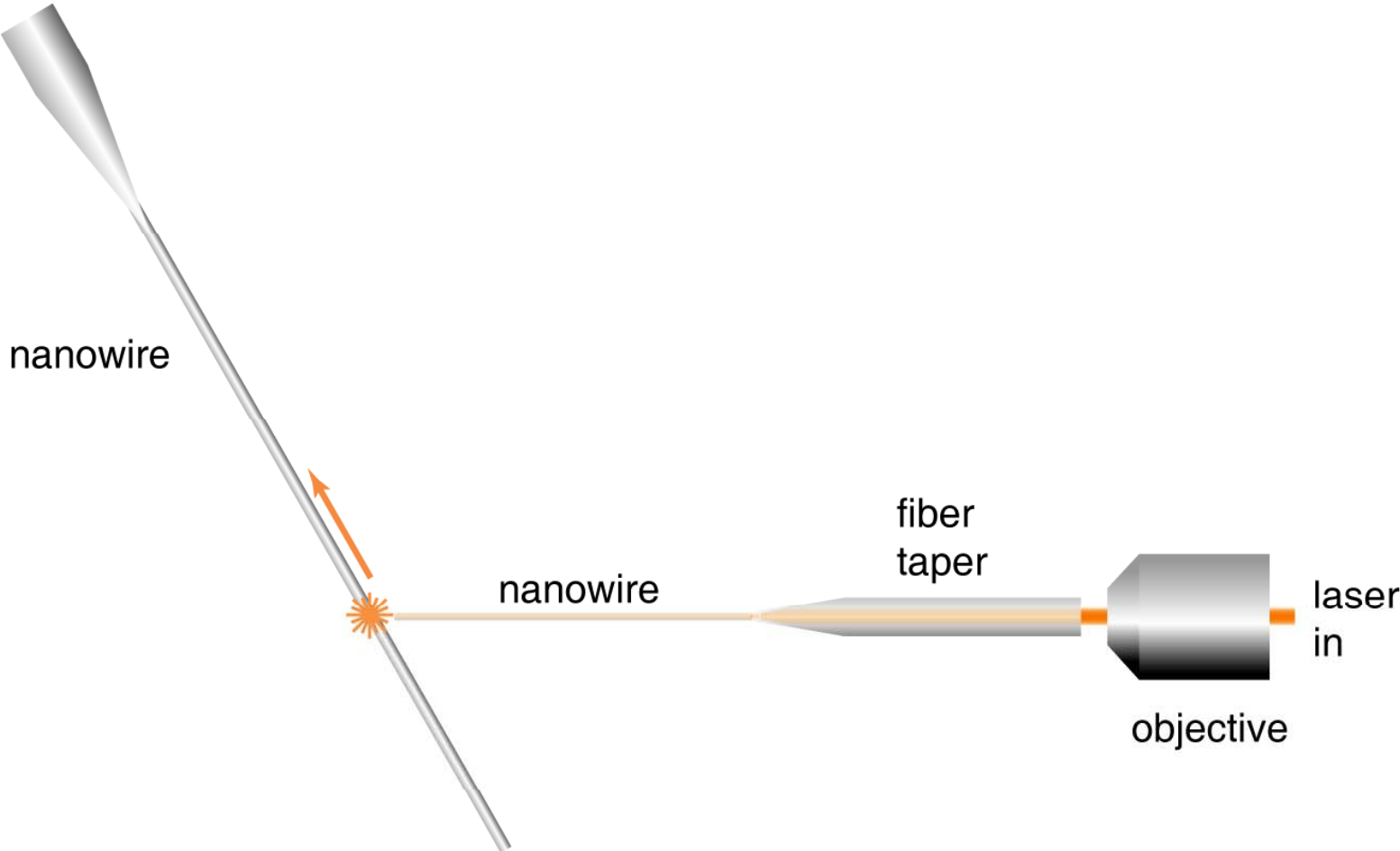


# Silica nanowires



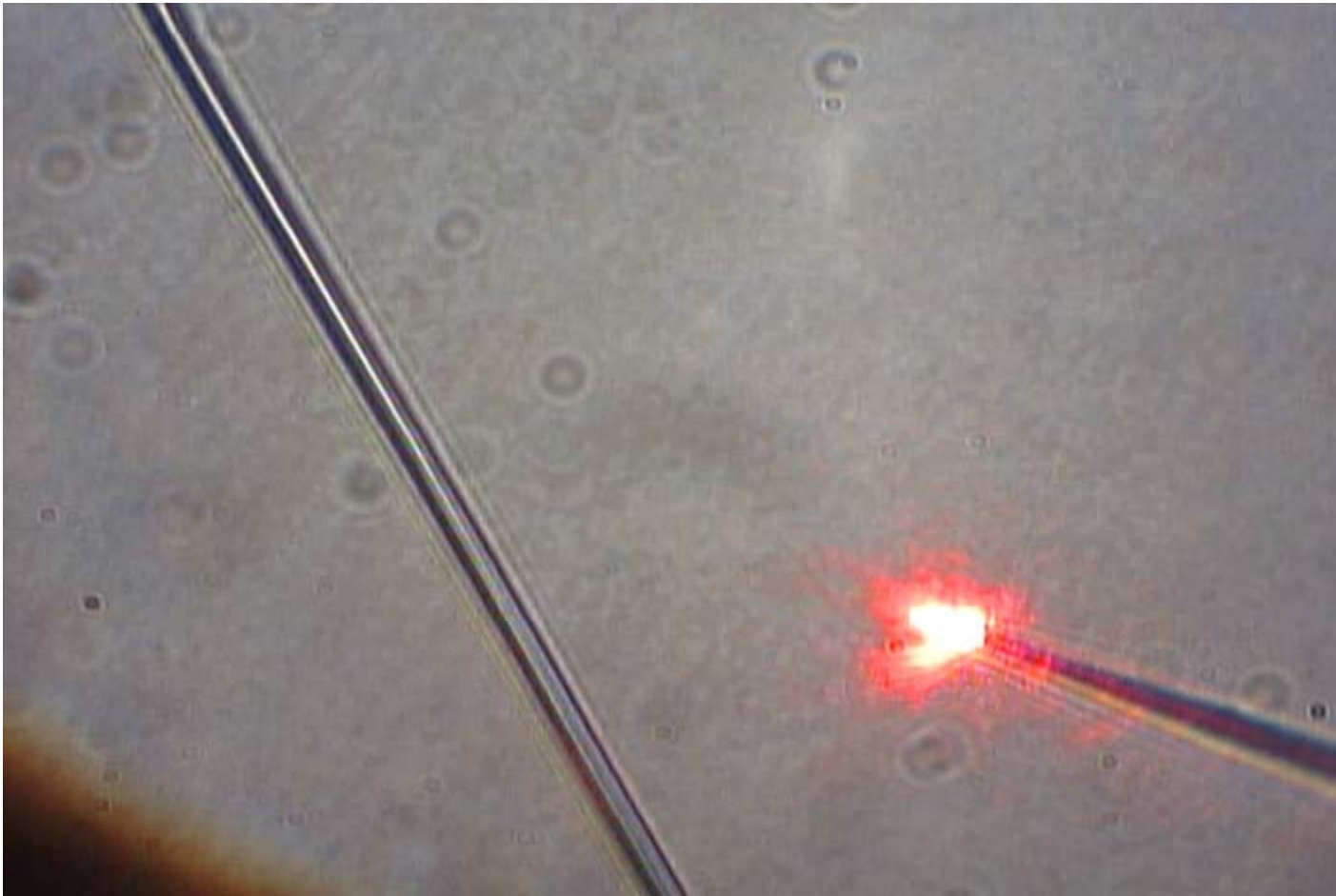
# Silica nanowires

coupling light into nanowires



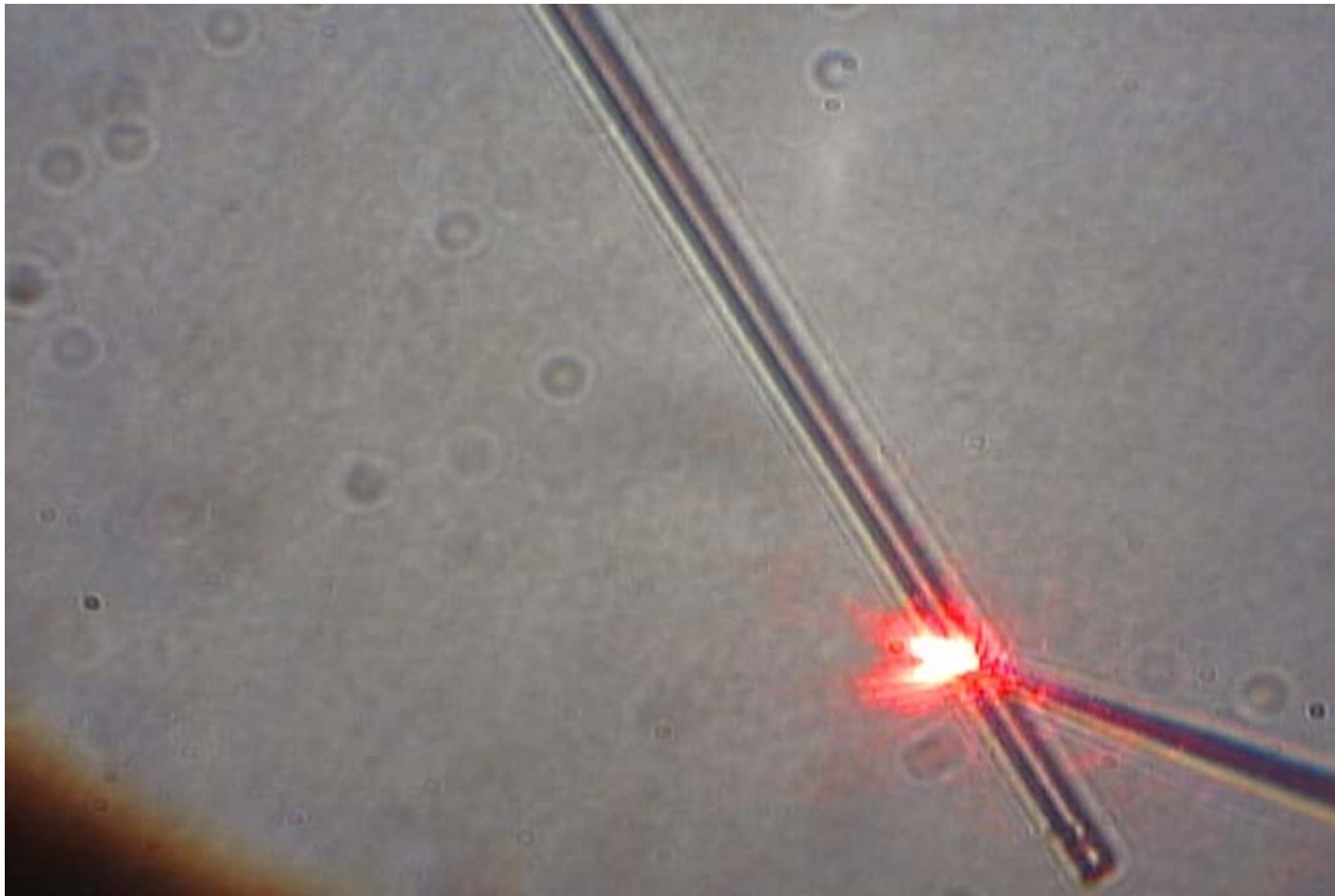
# Silica nanowires

coupling light into nanowires

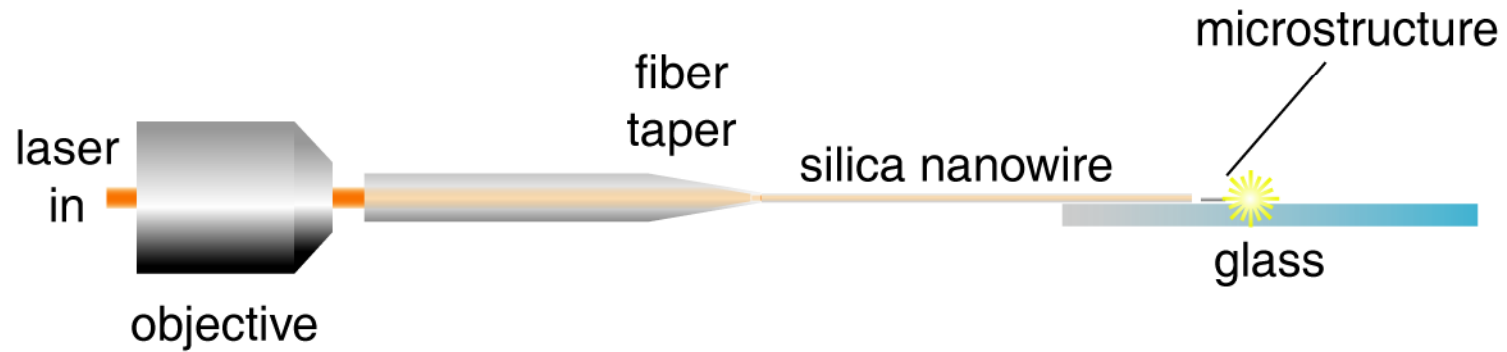


# Silica nanowires

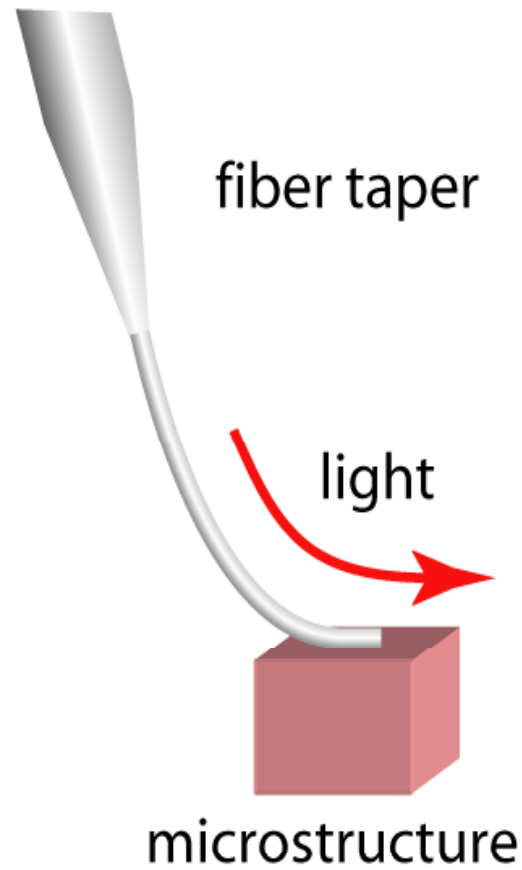
coupling light into nanowires



# Coupling microstructures



# Coupling microstructures





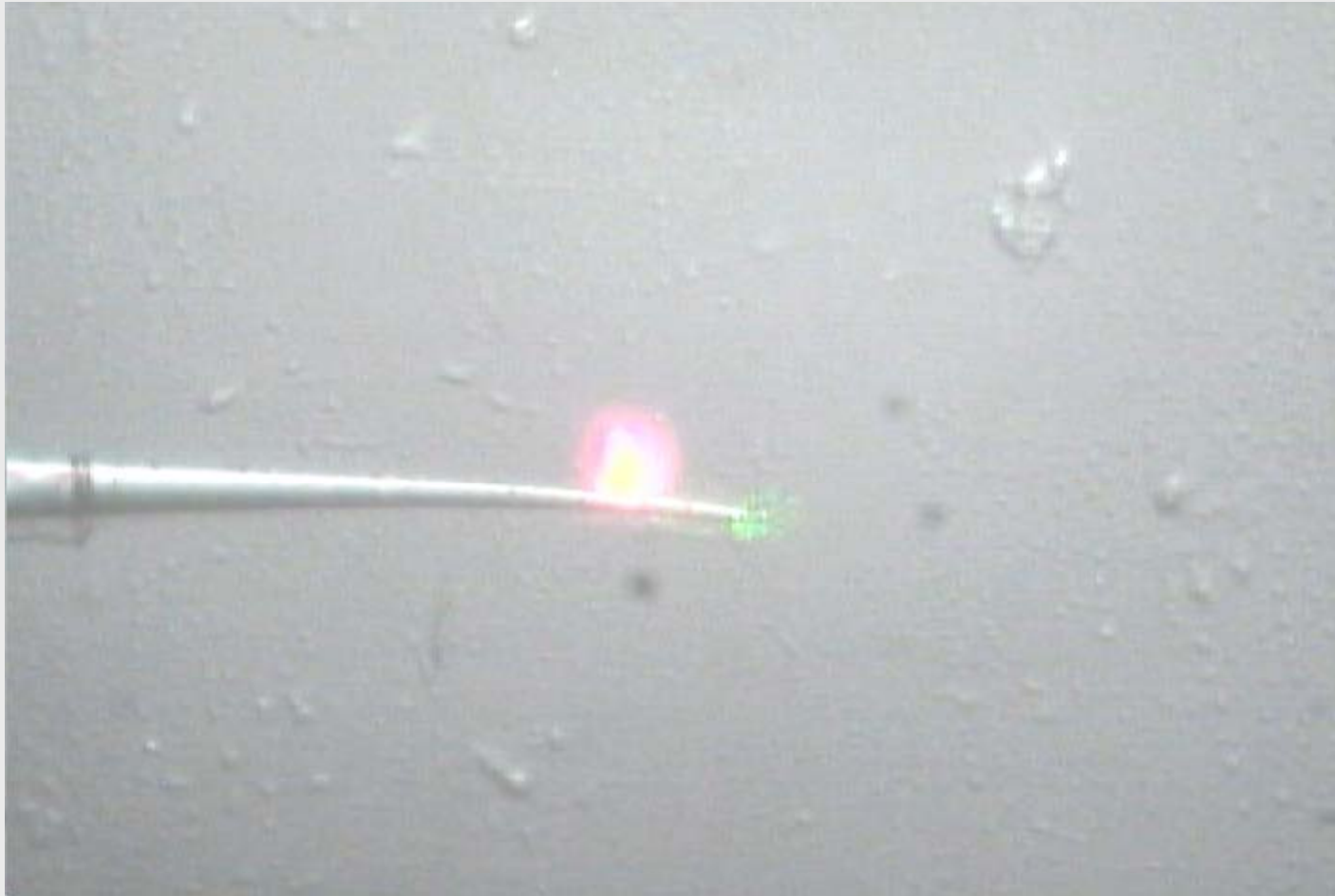
# Coupling microstructures



# Coupling microstructures



# Coupling microstructures



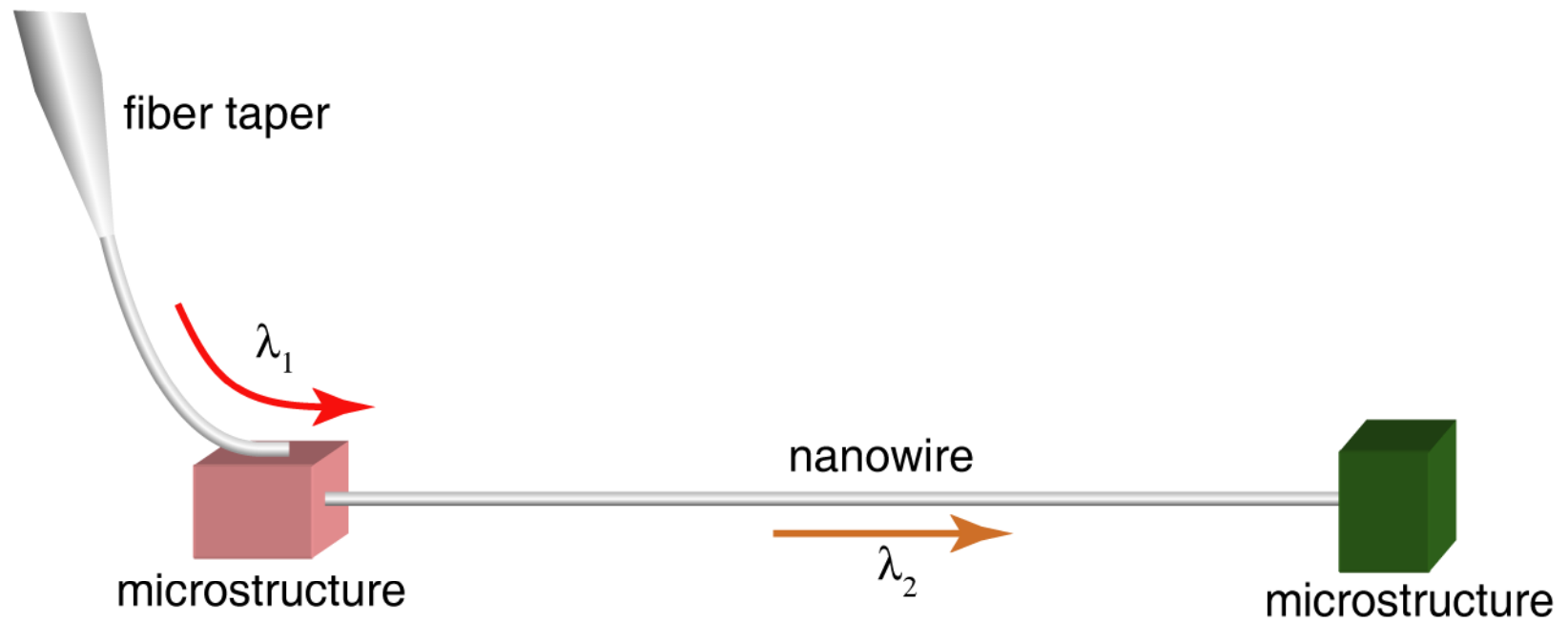
# Coupling microstructures



# Coupling microstructures



# Coupling microstructures



# Coupling microstructures



# Acknowledgments

## *Team*

Juliana Almeida

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*Gustavo Almeida*

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