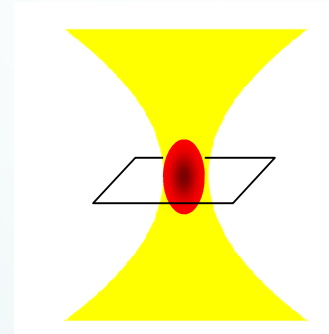
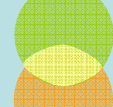
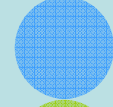
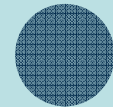
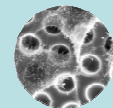
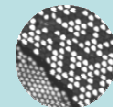
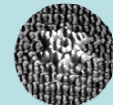


Two Photon Stereolithography (TPS)

Advantage

- sub-100 nm Resolution
- energy threshold in polymerization (inhibitor: oxygene, amine)



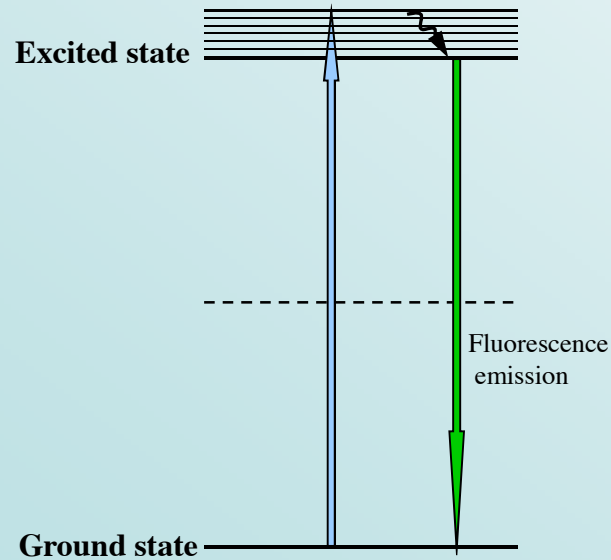


Two Photon Stereolithography (TPS)

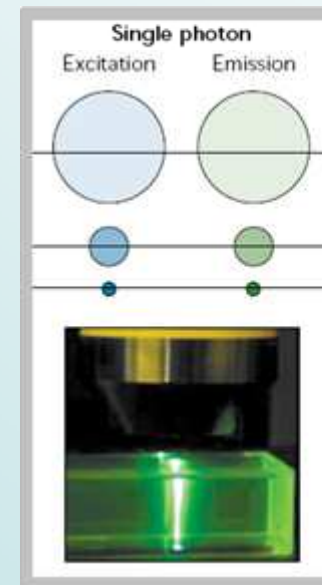
Advantage

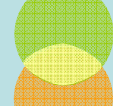
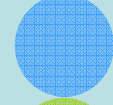
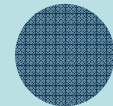
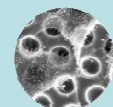
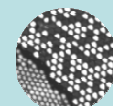
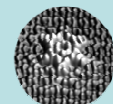
- sub-100 nm Resolution
- energy threshold in polymerization (inhibitor: oxygene, amine)
- non linear effect due to multiphoton absorption

excitation by one photon absorption
(OPA)



Type of excitation
OPA



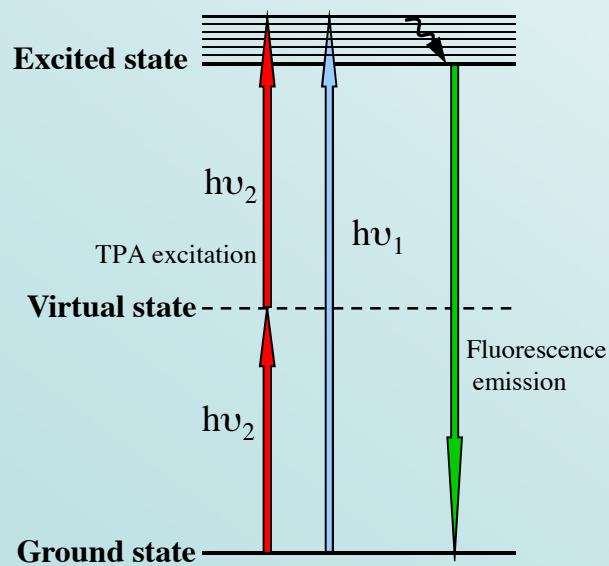


Two Photon Stereolithography (TPS)

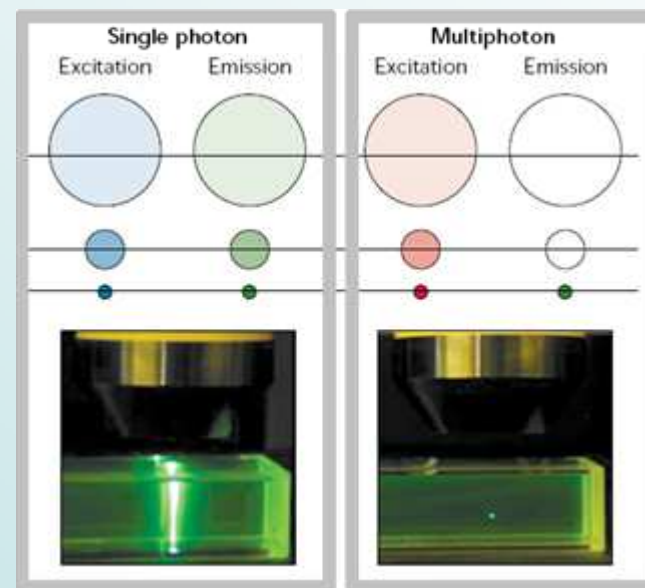
Advantage

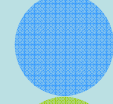
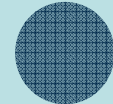
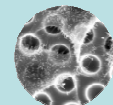
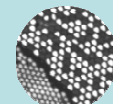
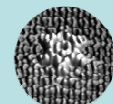
- sub-100 nm Resolution
- energy threshold in polymerization (inhibitor: oxygene, amine)
- non linear effect due to multiphoton absorption

Simultaneous excitation by two photon absorption (TPA)



Type of excitation
OPA TPA



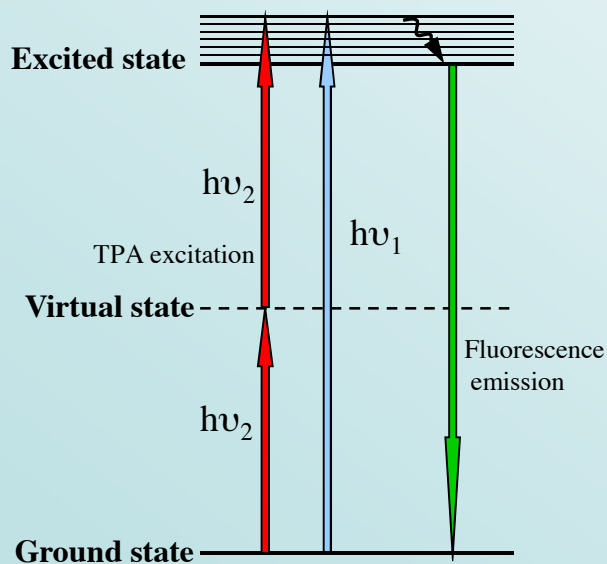


Two Photon Stereolithography (TPS)

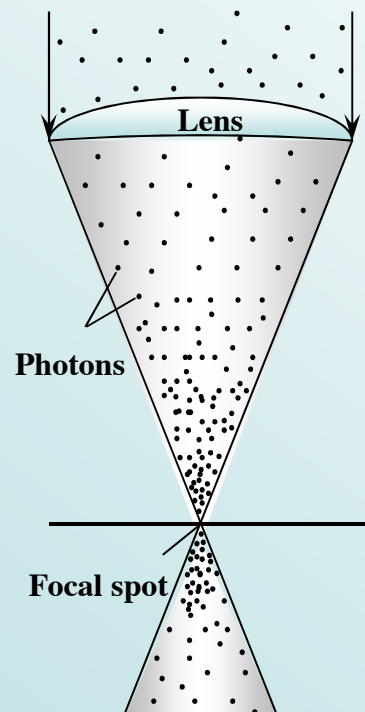
Advantage

- sub-100 nm Resolution
- energy threshold in polymerization (inhibitor: oxygene, amine)
- non linear effect due to multiphoton absorption

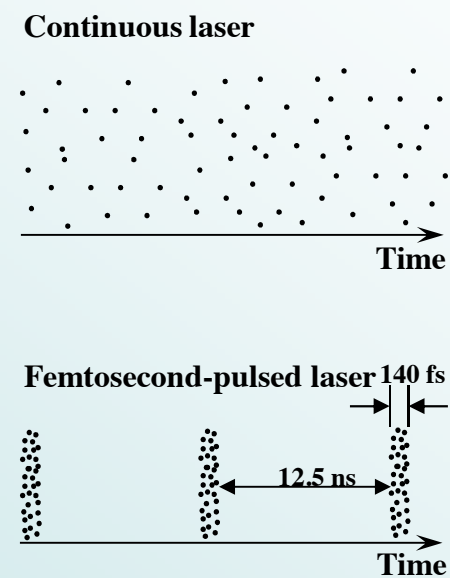
Simultaneous excitation by TPA

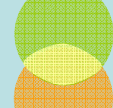
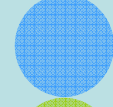
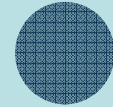
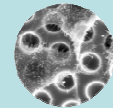
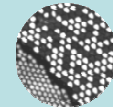
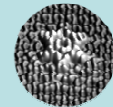


Spatial compression of photons by objective lens



Temporal compression of photons

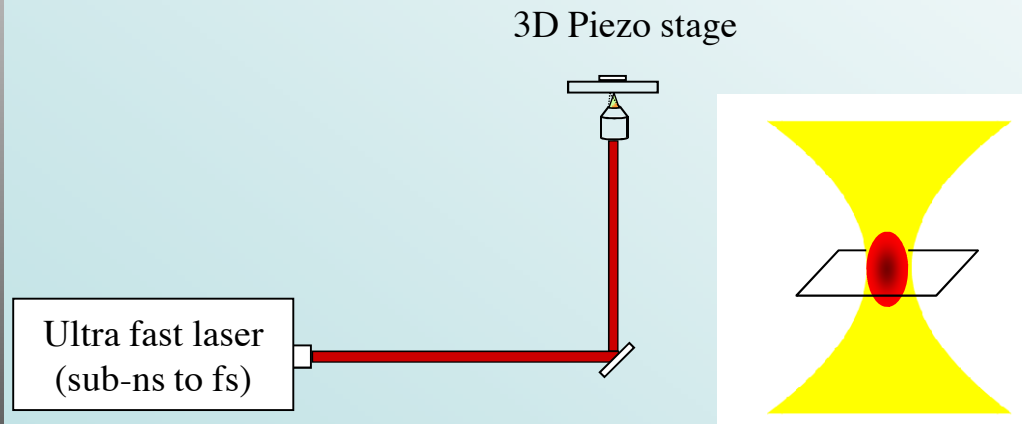




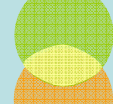
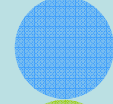
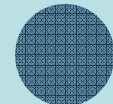
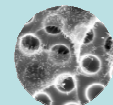
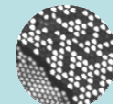
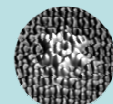
Two Photon Stereolithography (TPS)

Advantage

- sub-100 nm Resolution
- energy threshold in polymerization (inhibitor: oxygene, amine)
- non linear effect due to multiphoton absorption

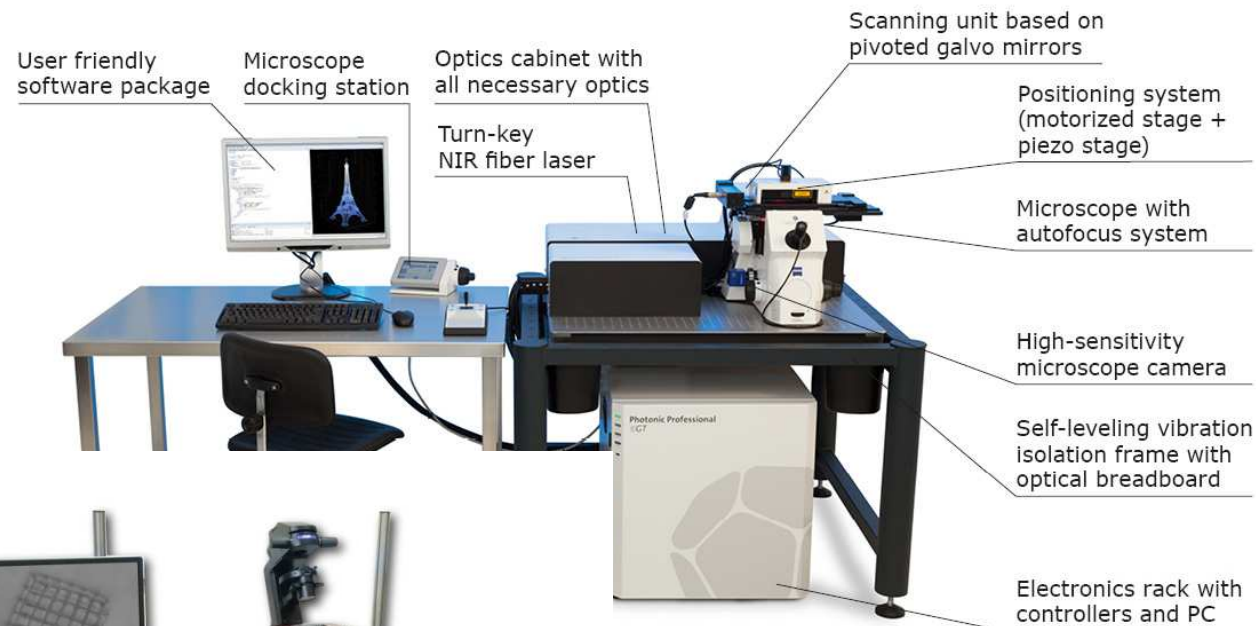


- ➔ confinement of the polymerization to the focal point / voxel (resolution $\lambda/10$)



Two Photon Stereolithography (TPS)

Commercial set-ups

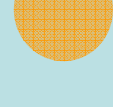
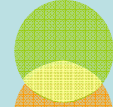
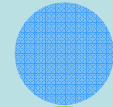
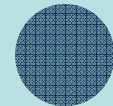
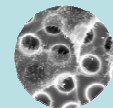
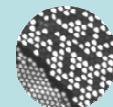
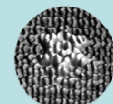


Nanoscribe

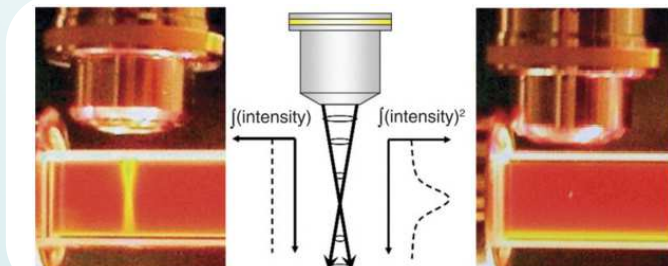


Microlight3D

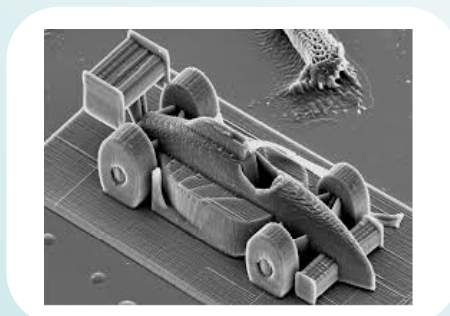
Outline



1

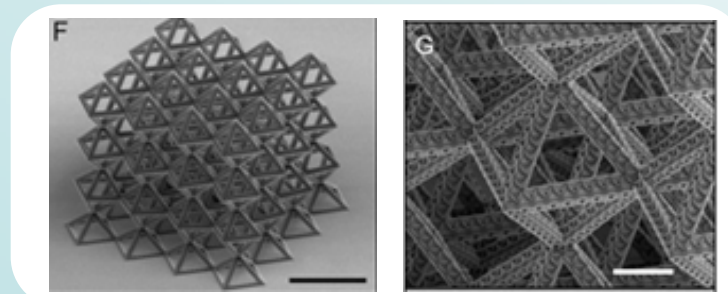


2



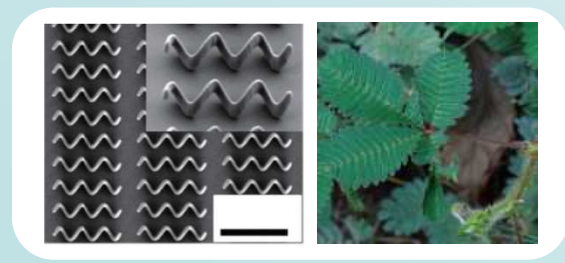
Writing speed & resolution

3

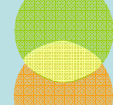
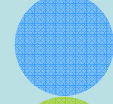
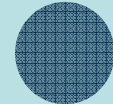
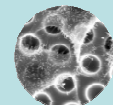
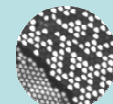
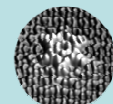


Applications
Medecine & Robotics

4



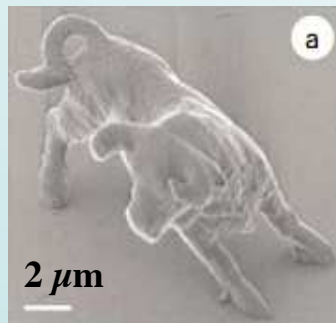
Advanced Functional
Materials



TPS Resolution

State of the art:

● Resolution



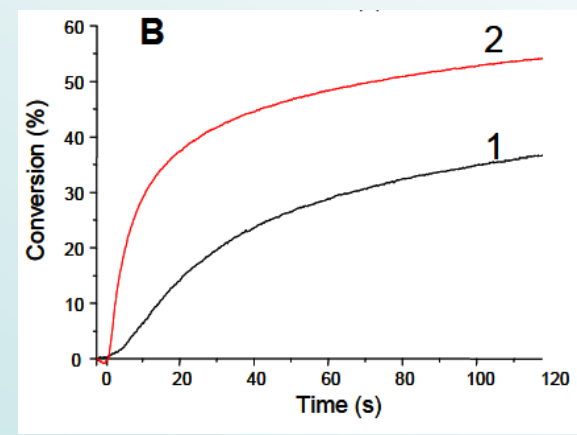
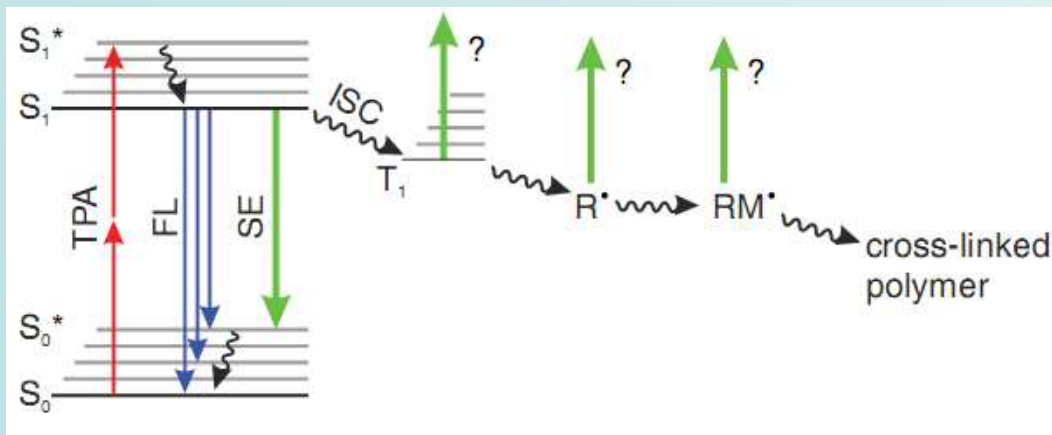
S. Kawata, *Nature* **2001**, 412, 697-698.

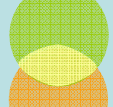
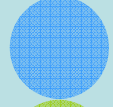
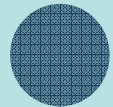
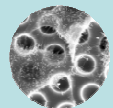
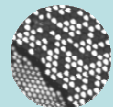
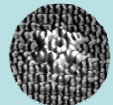
Rés: abs. biphoton. $R_{x,y} = 120$ nm

$\lambda = 780$ nm, $\lambda / 6.5$

→ Resolution due to optical and chemical confinement of the photoreaction

Key role of chemistry → *Nanophotochemistry* (inhibition of radical polymerization by oxygene, diffusion controlled reaction)

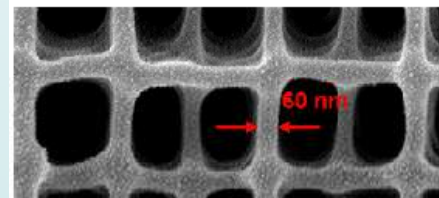
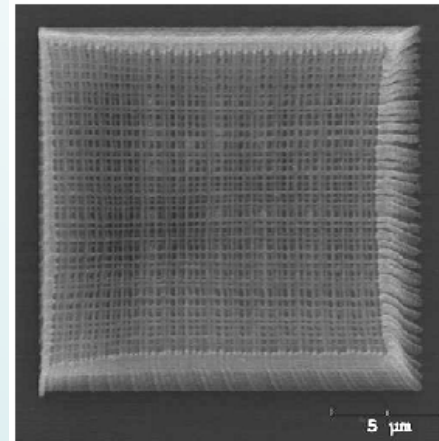
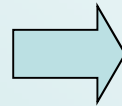
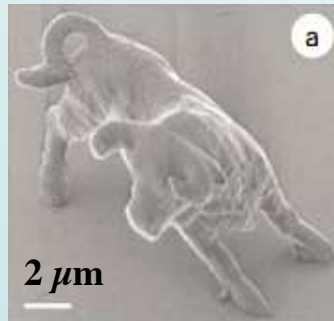




TPS Resolution

State of the art:

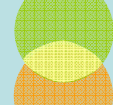
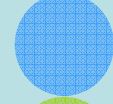
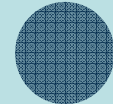
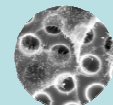
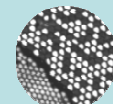
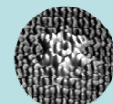
● Resolution



S. Kawata, *Nature* **2001**, *412*, 697-698.
Rés: abs. biphoton. $R_{x,y} = 120 \text{ nm}$
 $\lambda = 780 \text{ nm}, \lambda / 6.5$

Perry, Marder, *Opt. Exp.* **2007**, *15*, 3426-3436.
Rés: abs. biphoton. $R_{x,y} = 65 \text{ nm}$
 $\lambda = 520 \text{ nm}, \lambda / 8$

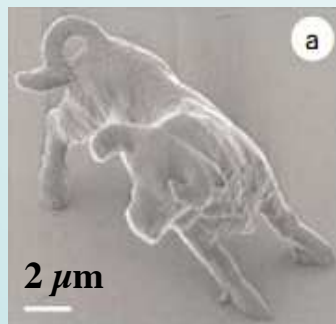
→ Lower resolution due to optical (irradiation wavelength) and chemical strategies
Key role of chemistry → *Molecular engineering* (design & photophysical characterization of photoinitiator)



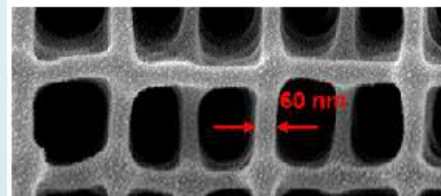
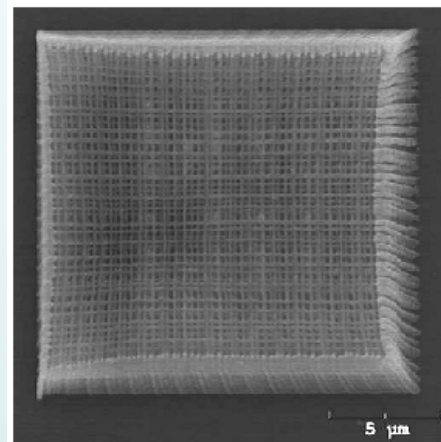
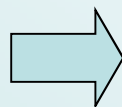
Two-photon Polymerization

State of the art:

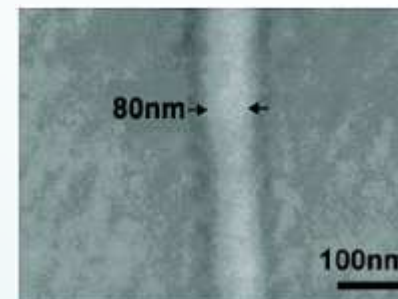
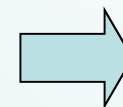
● Resolution



S. Kawata, *Nature* **2001**, *412*, 697-698.
Rés: abs. biphoton. $R_{x,y} = 120 \text{ nm}$
 $\lambda = 780 \text{ nm}$, $\lambda / 6.5$



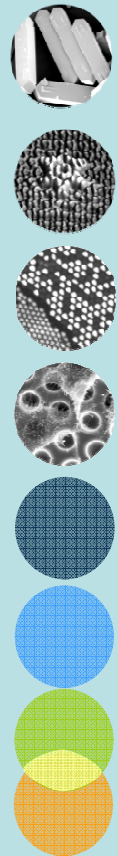
Perry, Marder, *Opt. Exp.* **2007**, *15*, 3426-3436.
Rés: abs. biphoton. $R_{x,y} = 65 \text{ nm}$
 $\lambda = 520 \text{ nm}$, $\lambda / 8$



S. Kawata, *Appl. Phys. Lett.* **2007**, *90*,
Rés: abs. biphoton. $R_{x,y} = 80 \text{ nm}$
 $\lambda = 800 \text{ nm}$, $\lambda / 10$

→ Resolution due to optical and chemical confinement of the photoreaction

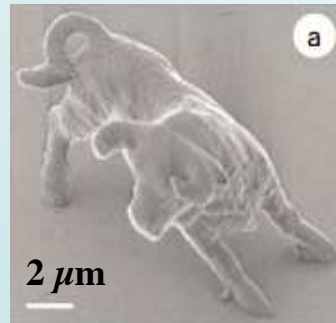
Key role of chemistry → *Nanophotchemistry* (inhibition of radical polymerization by additive, diffusion controlled reaction)



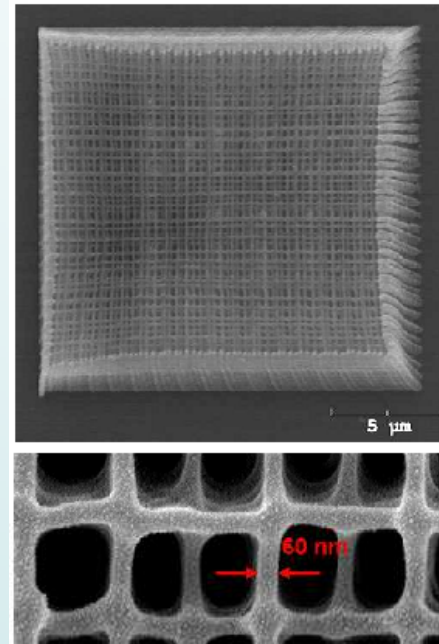
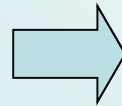
Two-photon Polymerization

State of the art:

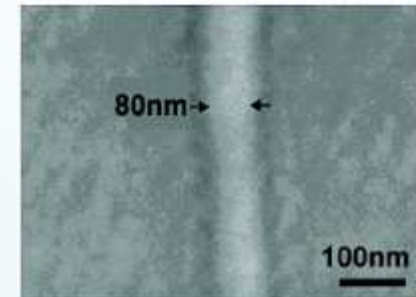
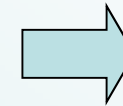
● Resolution



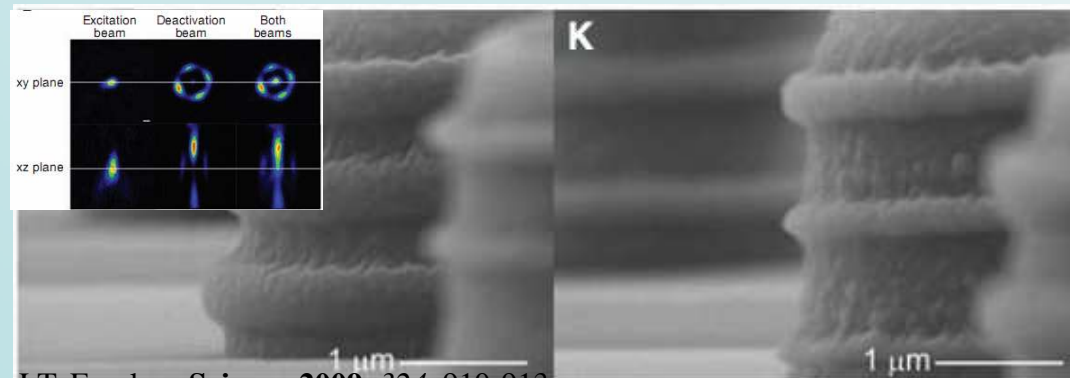
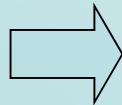
S. Kawata, *Nature* **2001**, *412*, 697-698.
Rés: abs. biphoton. $R_{x,y} = 120 \text{ nm}$
 $\lambda = 780 \text{ nm}$, $\lambda / 6.5$



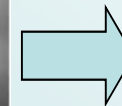
Perry, Marder, *Opt. Exp.* **2007**, *15*, 3426-3436.
Rés: abs. biphoton. $R_{x,y} = 65 \text{ nm}$
 $\lambda = 520 \text{ nm}$, $\lambda / 8$



S. Kawata, *Appl. Phys. Lett.* **2007**, *90*,
Rés: abs. biphoton. $R_{x,y} = 80 \text{ nm}$
 $\lambda = 800 \text{ nm}$, $\lambda / 10$



J.T. Fourkas, *Science* **2009**, *324*, 910-913.
Rés: abs. biphoton. $R_{x,y} = 40 \text{ nm}$
 $R_z = 40 \text{ nm} \rightarrow \lambda = 800 \text{ nm}$, $\lambda / 20$



< 10 nm ?

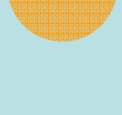
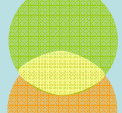
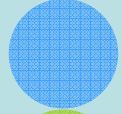
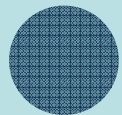
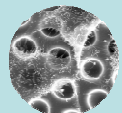
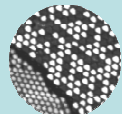
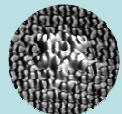
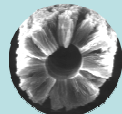
Two-photon Polymerization

- Resolution sub-100 nm

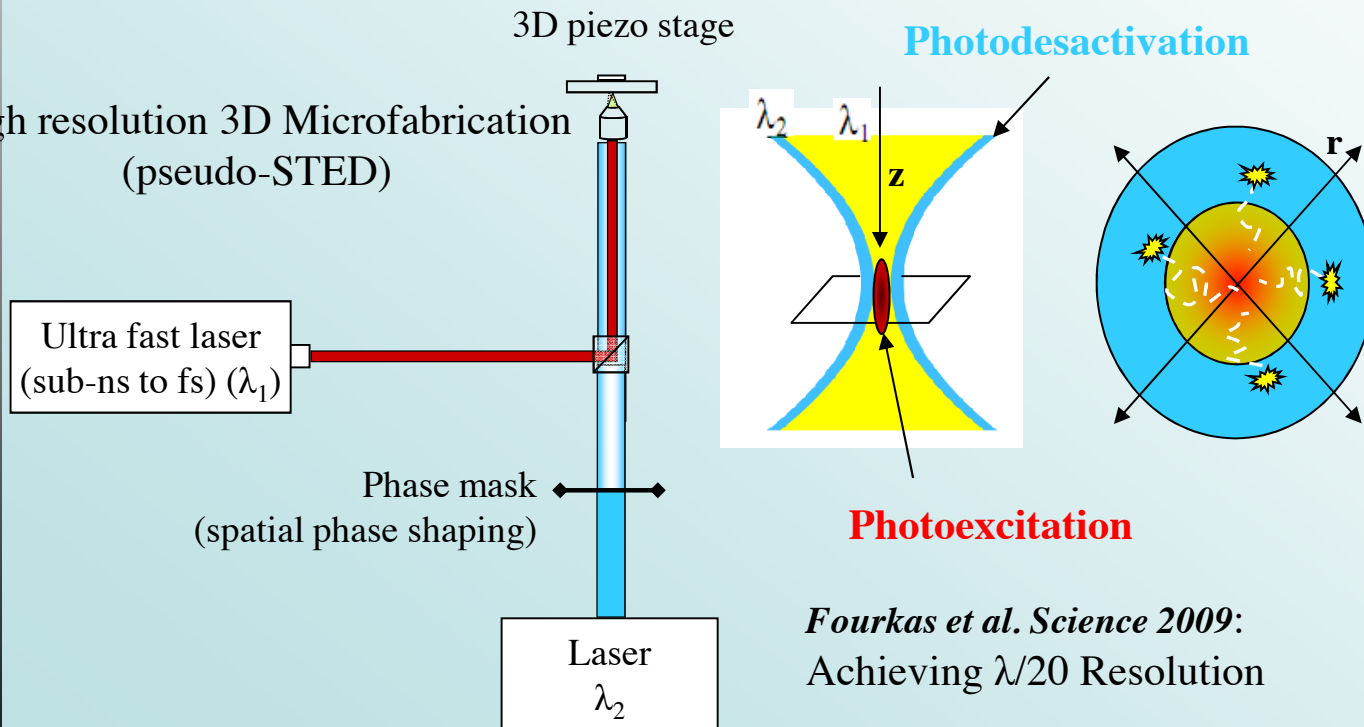
3D Microfabrication by two-photon absorption = two-photon stereolithography (TPS)

- non linear effect due to multiphoton absorption
- energy threshold in polymerization
(inhibitor: oxygene, amine)

→ confinement of the polymerization
to the focal point / voxel
(resolution $\lambda/10$)



High resolution 3D Microfabrication
(pseudo-STED)



Fourkas et al. Science 2009:
Achieving $\lambda/20$ Resolution

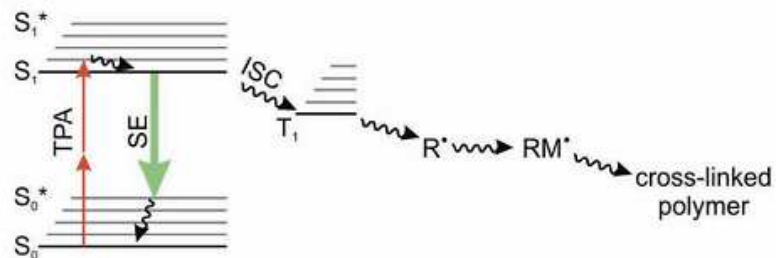
→ Axial resolution of voxel : 600 nm à 40 nm

STED Lithography and derivatives

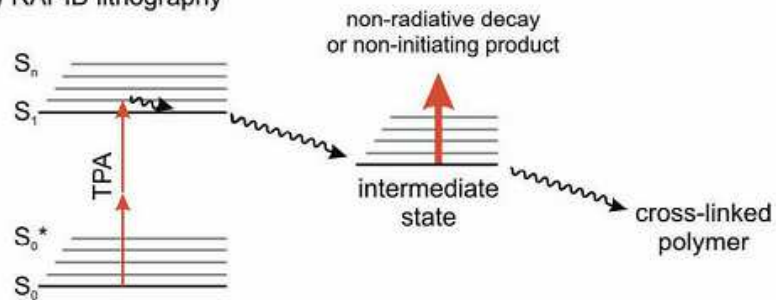
Recent Achievements:

- **Resolution** →
- New concepts (STED, RAPID, 2PII...)

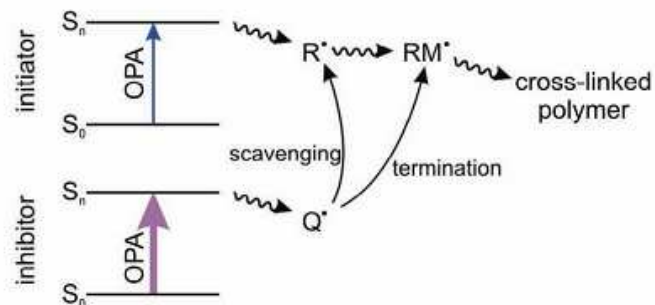
(a) STED lithography



(b) RAPID lithography



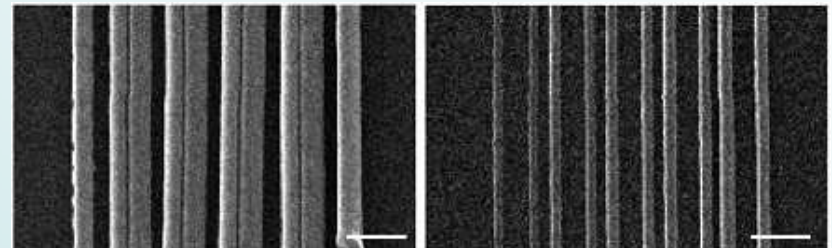
(c) 2PII lithography (photoinhibitor)



- Polymerization involves T_1
- Control of the population of intermediate state

Current challenges:

- Instrumentation issues



- Memory Photoresist → consumption of species between 2 adjacent lines
- Unravelling the photophisic & photochemistry behind TPS & STED-like lithography