

1) Maruo S., O. Nakamura, Kawata S.,
**"Three-dimensional microfabrication
with two-photon-absorbed
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134 (1997)

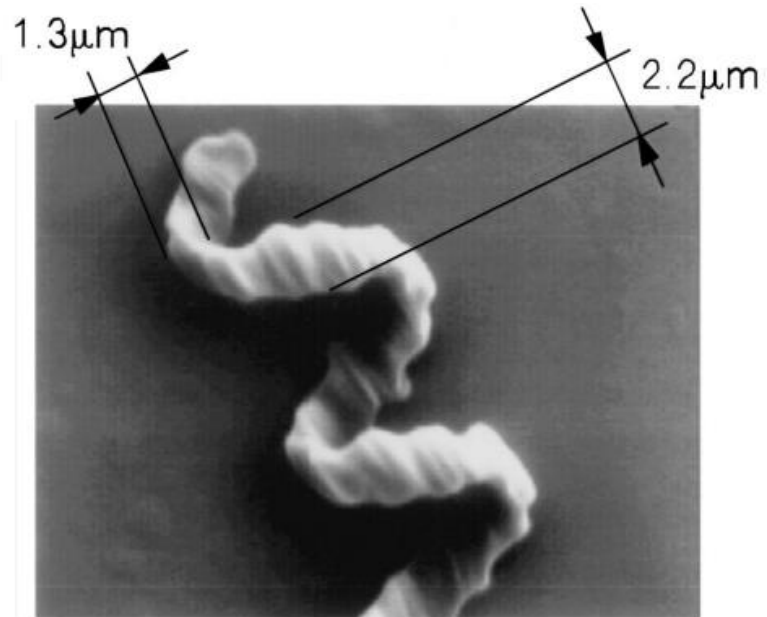
2) Somers P., Liang Z., Johnson J. E.,
Boudouris B. W., Pan L., Xu X.,
**"Rapid, continuous projection multi-
photon 3D printing enabled by
spatiotemporal focusing of
femtosecond pulses,"**
Light: Science & Applications **10**, 199
(2021)

MICRO-722 : 3D Printing with light

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Magnonics



Three-dimensional microfabrication with two-photon-absorbed photopolymerization

Maruo S., O. Nakamura, Kawata S
Opt. Lett. 22, 132-134 (1997)

Objectives of the research

- Three-dimensional microfabrication with photopolymerization stimulated by two-photon absorption with a pulsed IR laser
- Set the spatial resolution attained with photopolymerizing in 3D
- Solve the problem of low spatial resolution in longitudinal direction and light absorption at non focused points with already existing photopolymerization methods

- Two-photon absorption :
 - Near IR laser is focused in an UV photopolymerizing material → material photosolidify in a small volume within the depth of focus
 - Resin transparent to near IR → layer by layer
- Laser : Ti-sapphire laser oscillating wavelength 790 nm and pulse width 200 fs
- Resin : SCR-500 from Japan Synthetic Rubber Company, Ltd

I : photoinitiator

R : free radicals

M : monomers-oligomers

urethane acrylate monomer

urethane acrylate oligomers

M_n : Polymer chain of length n

R-M_n : Growing polymer chain with radical at the end

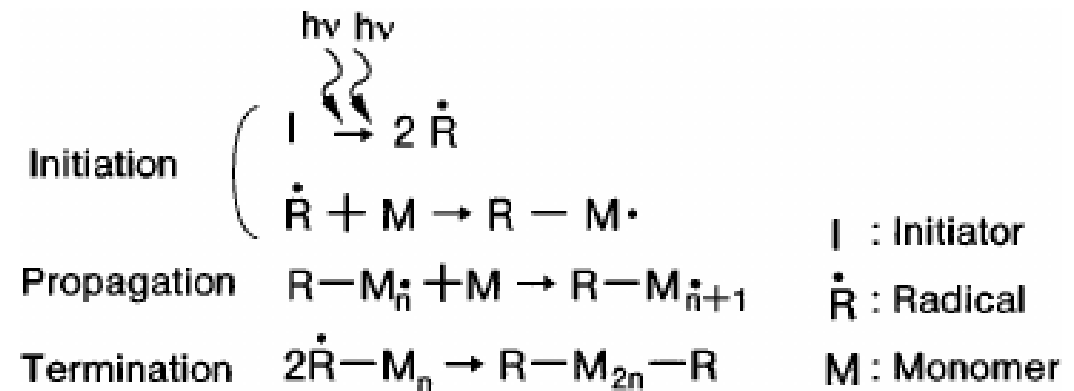


Fig. 1. Photochemical reaction for two-photon micro-fabrication.

Reaction speed \propto square of the photon density at each position in the resin

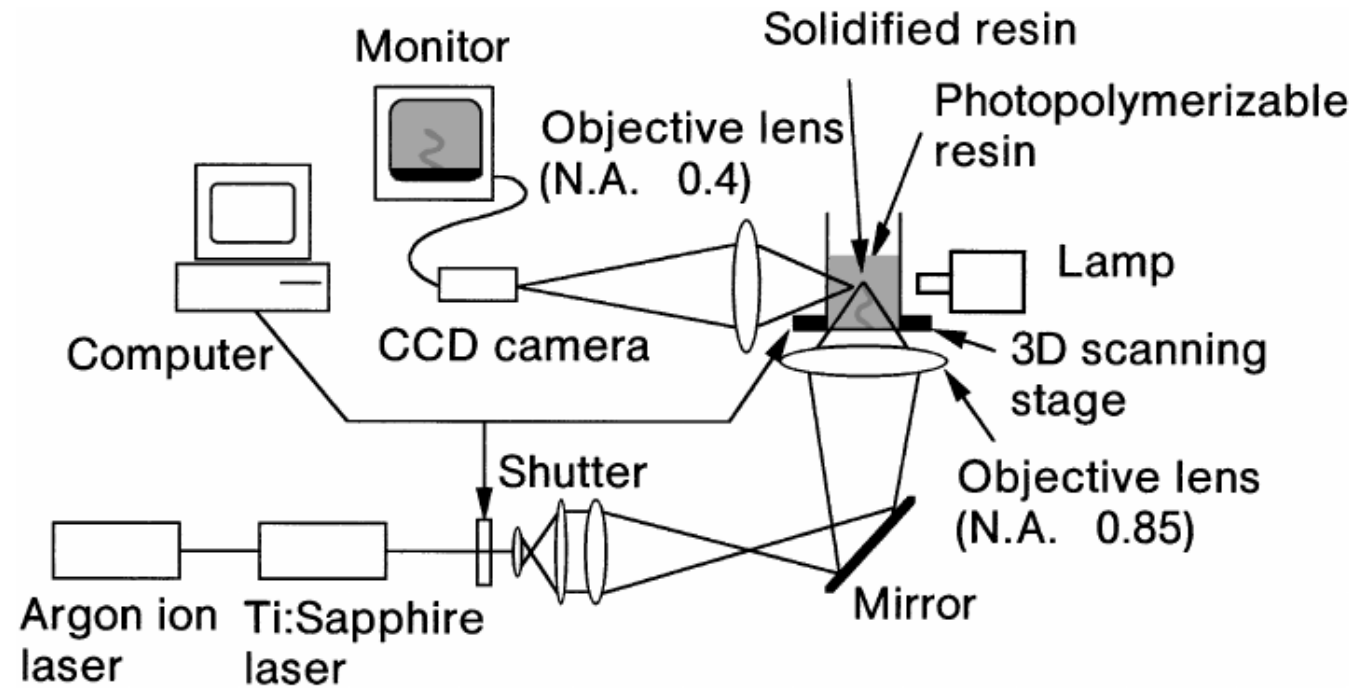
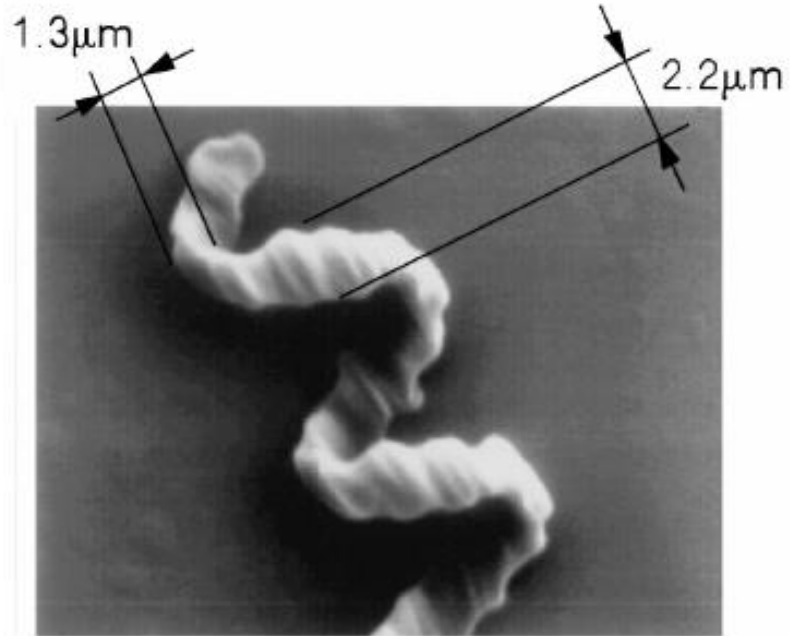
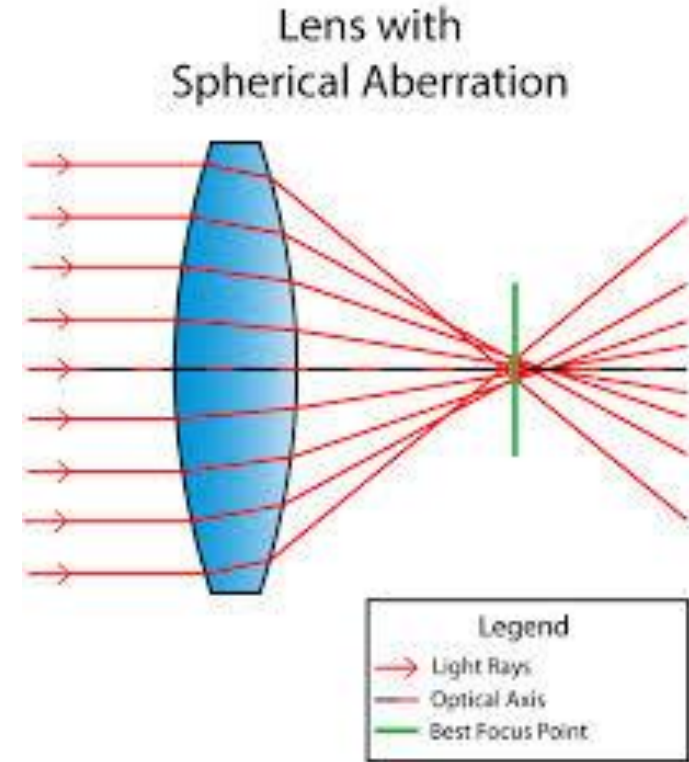


Fig. 2. Optical system for two-photon microfabrication.



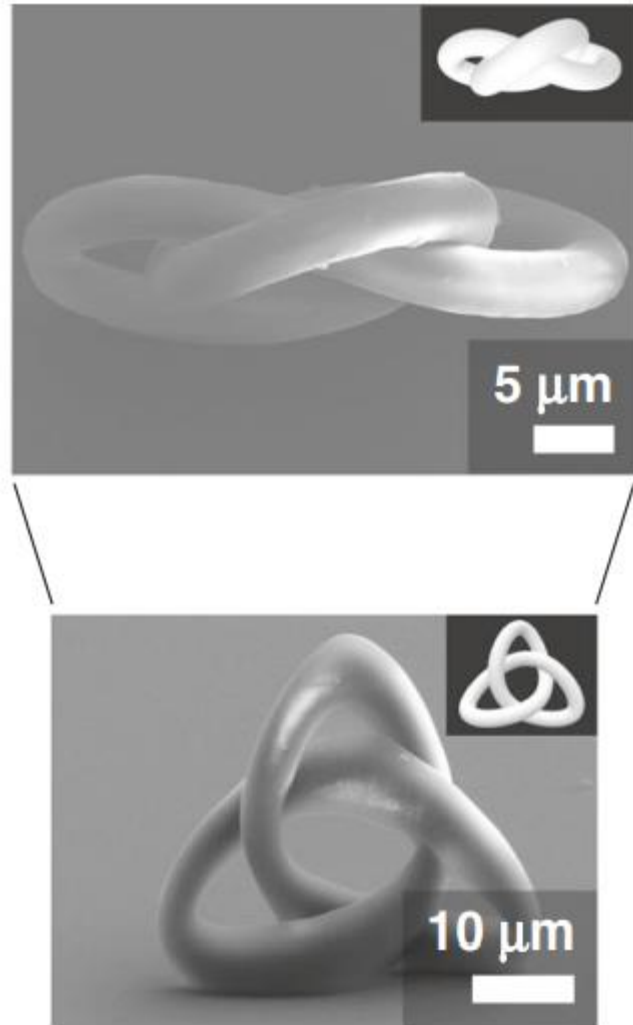
SEM image of the final structure coated with 40 nm gold

Limits



Limit of the length of the structure via spherical aberration

Spatial resolution : limited by radical diffusion and growth of polymer chains outside illuminated regions



Rapid, continuous projection multi-photon 3D printing enabled by spatiotemporal focusing of femtosecond pulses

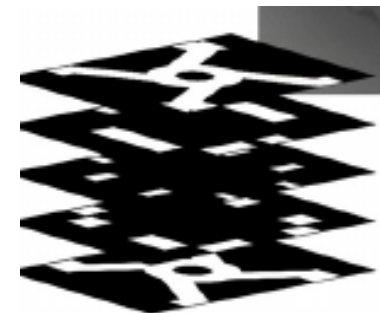
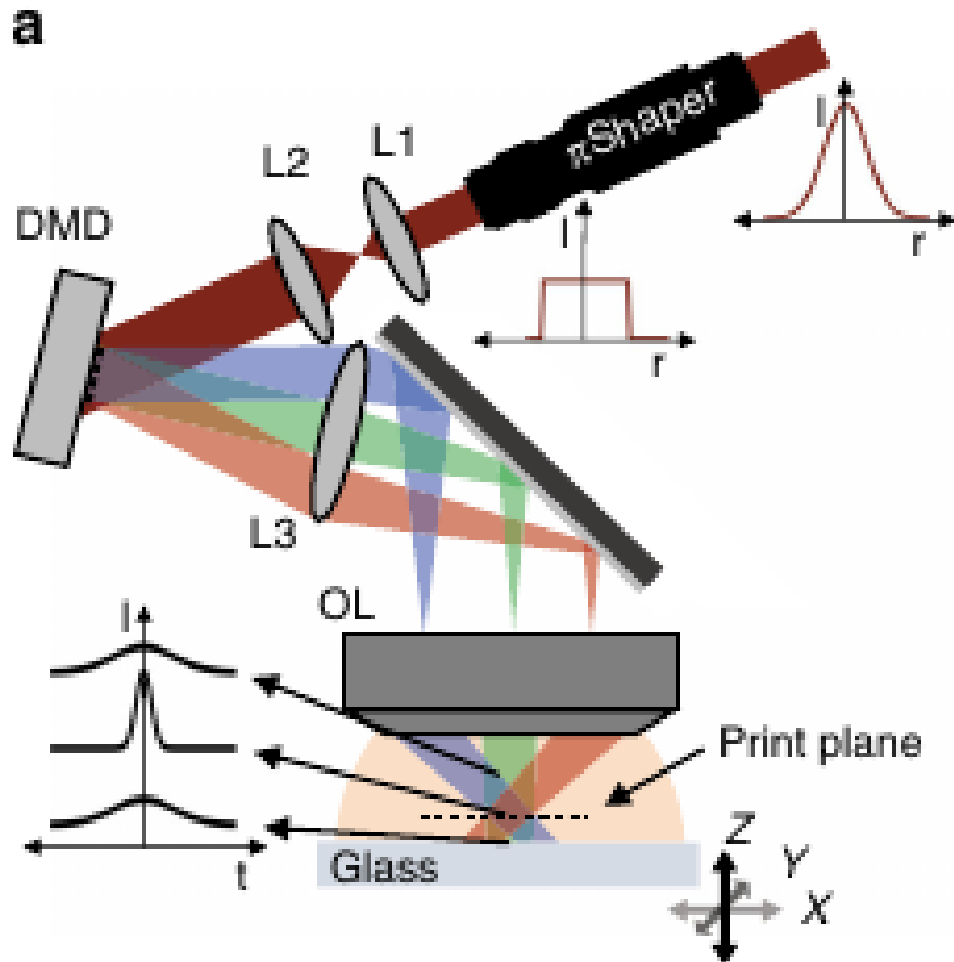
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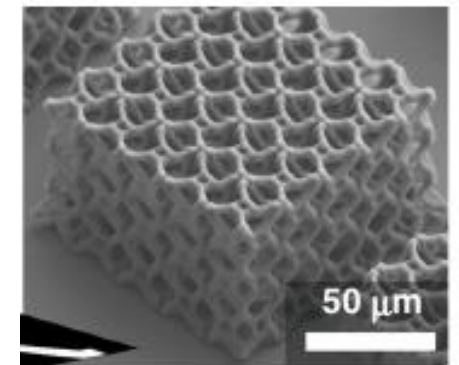
Objectives of the research

- Scaling up 3D printing throughput : High-speed projection multi-photon printing combined with spatiotemporal focusing
- Spatiotemporal focusing confines printing to thin layers : print thickness micron and submicron scale
- Projection of varying patterns with no pause : continuous fabrication process

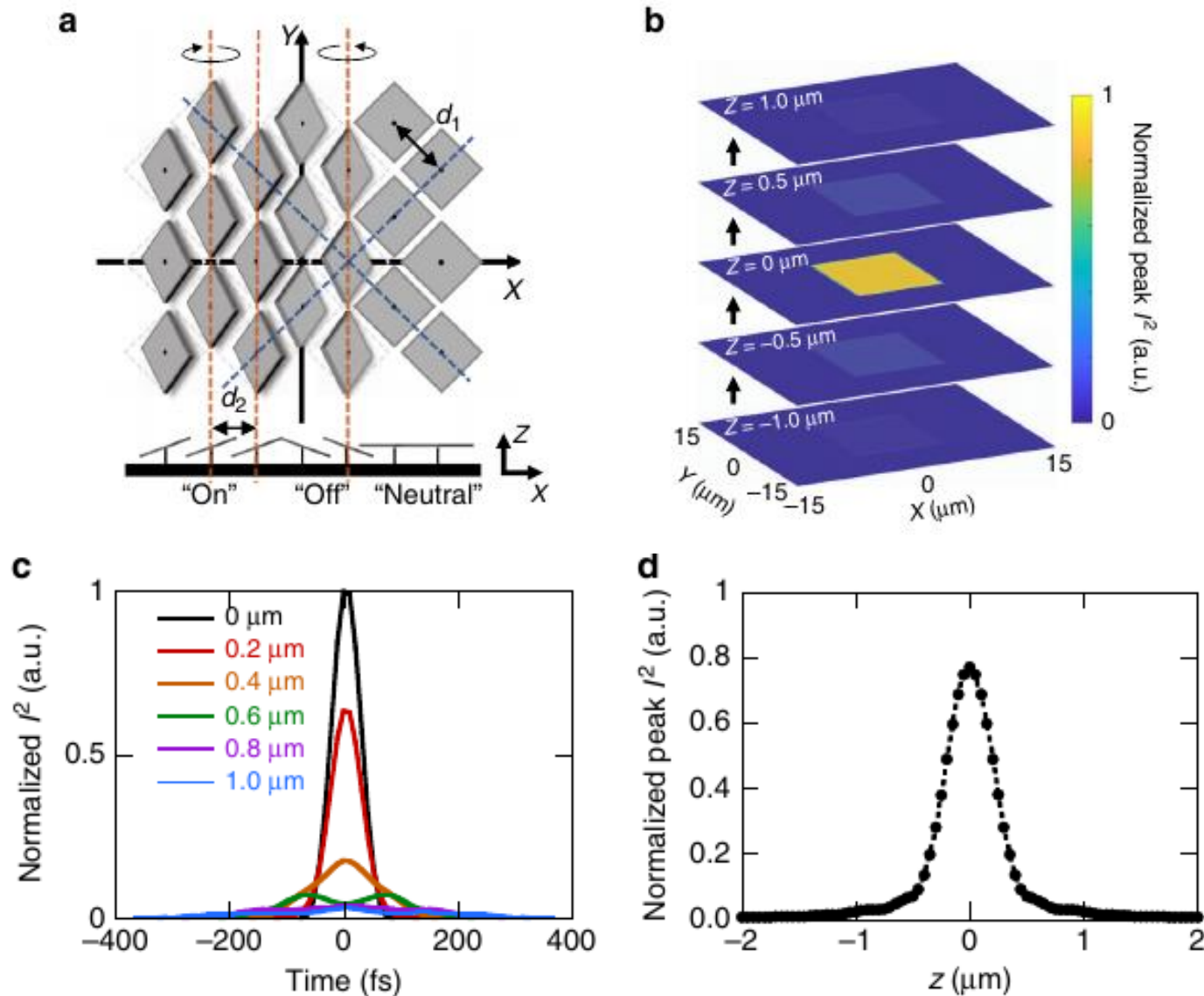
- Implementing temporal focusing :
 - Separating the component wavelengths of a femtosecond laser pulse and recombining them at a single plane
 - Digital micro-mirror device (DMD) + efficient photoinitiator system
 - Laser pulse stretched in time when the component wavelength are separated : pulse intensity reduced
 - Recombination in the pattern plane : shortest and highest intensity pulse



$< 250 \frac{\text{ms}}{\text{unit cell}}$

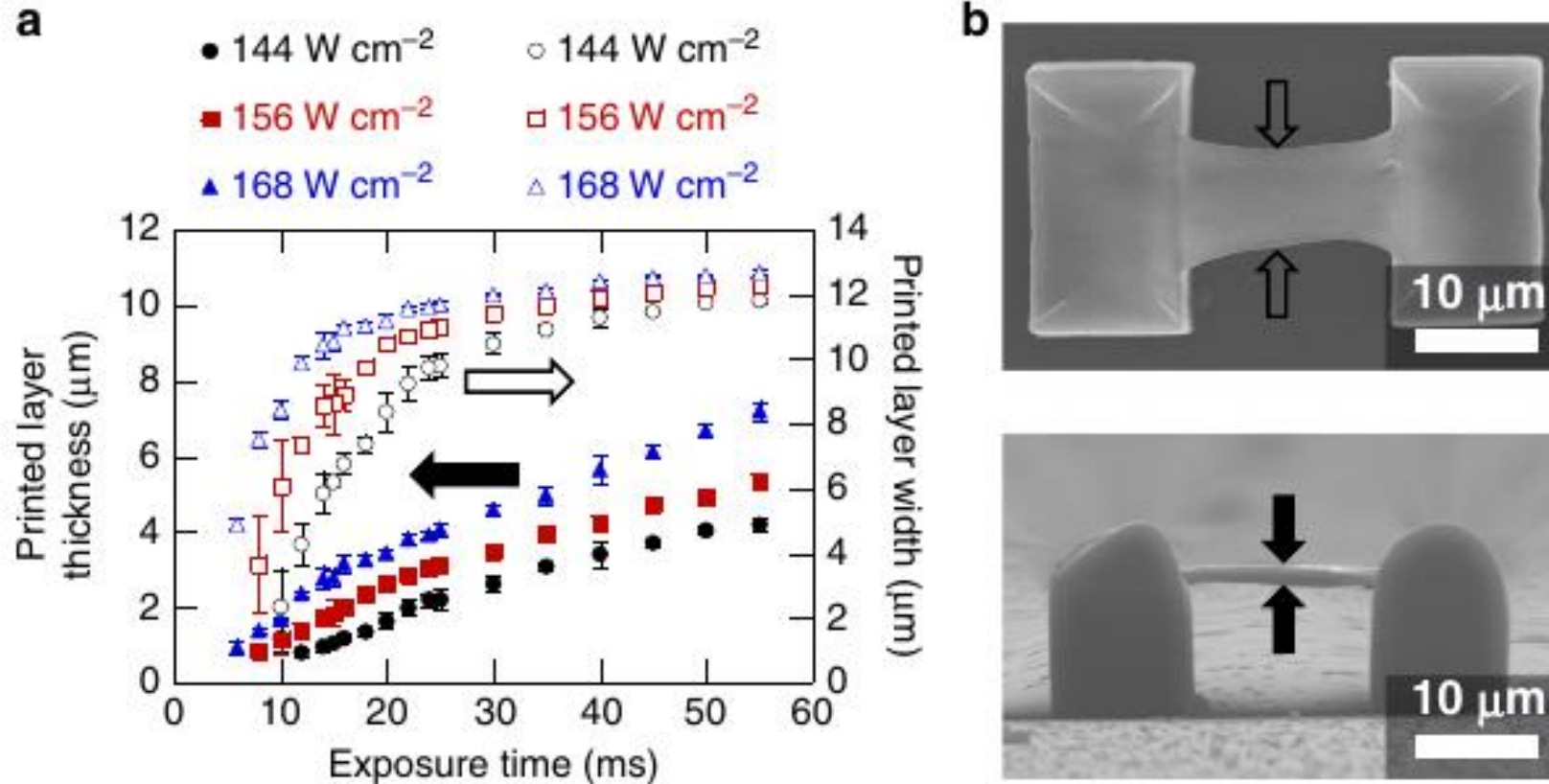


- Laser : 800 nm laser (Spectra-Physics Spitfire) with 22 nm bandwidth and 5 kHz repetition rate (regeneratively amplified femtosecond laser)
- Photoinitiator : (2E,6E)-2,6-Bis (4-(dibutylamino)benzylidene)-4-methylcyclohex-anone (BBK) (0.7% (by weight))
- Monomer : pentaerythritol triacrylate (PETA)
- DMD :
 - (DLP3000) dynamically patternable device, patterning rates up to 4 kHz
 - Acts as grating → adds angular dispersion required for temporal focusing



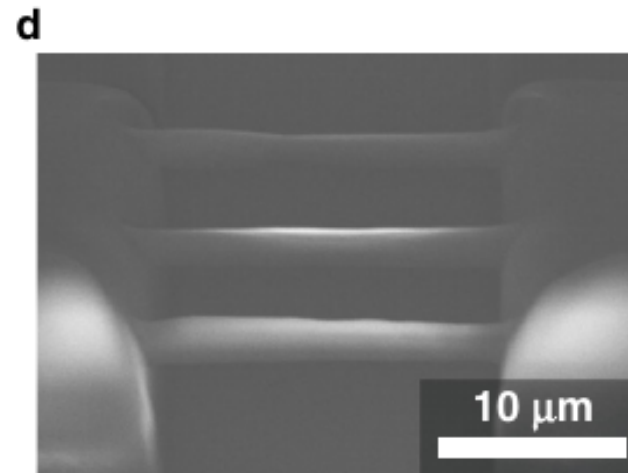
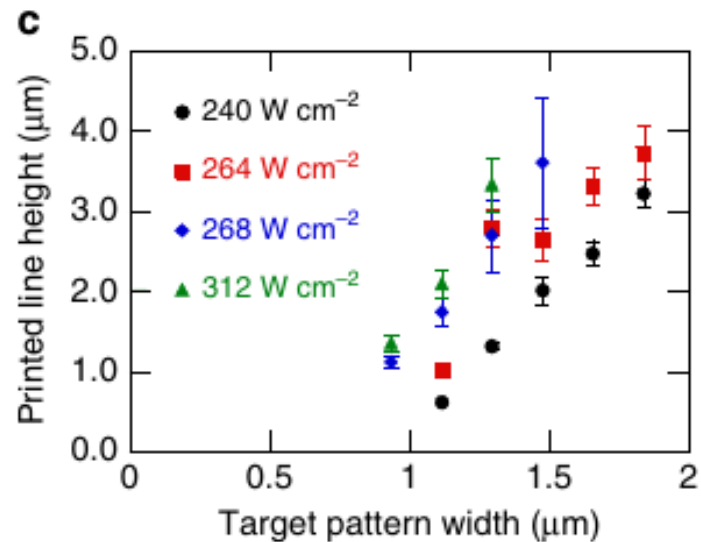
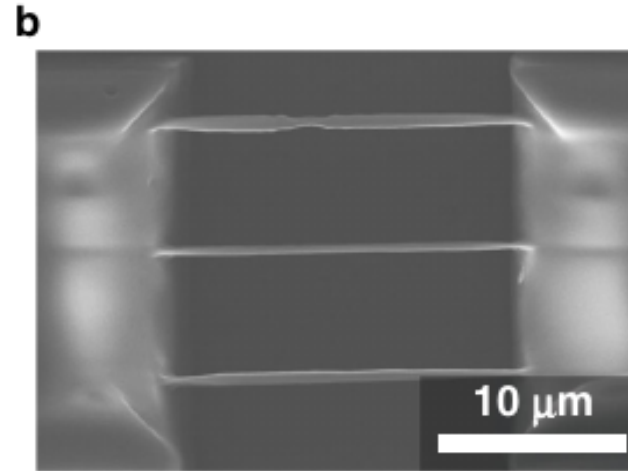
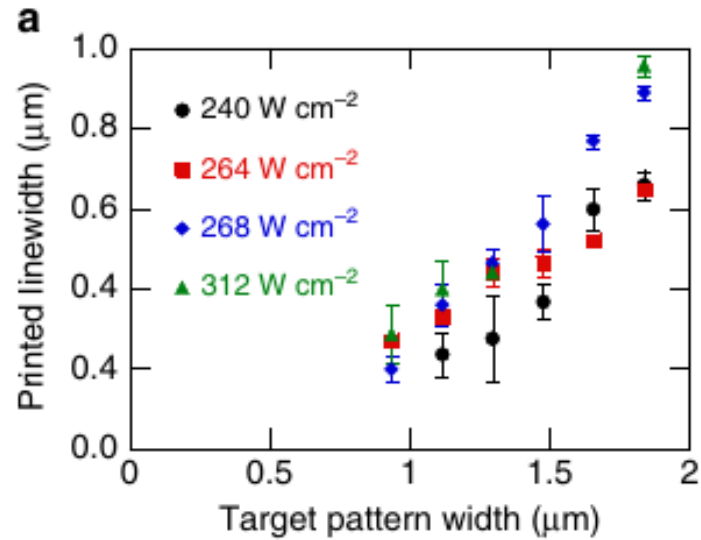
Intensity square : strength of the two-photon absorption that must occur for printing

Analysis of spatiotemporal printing features



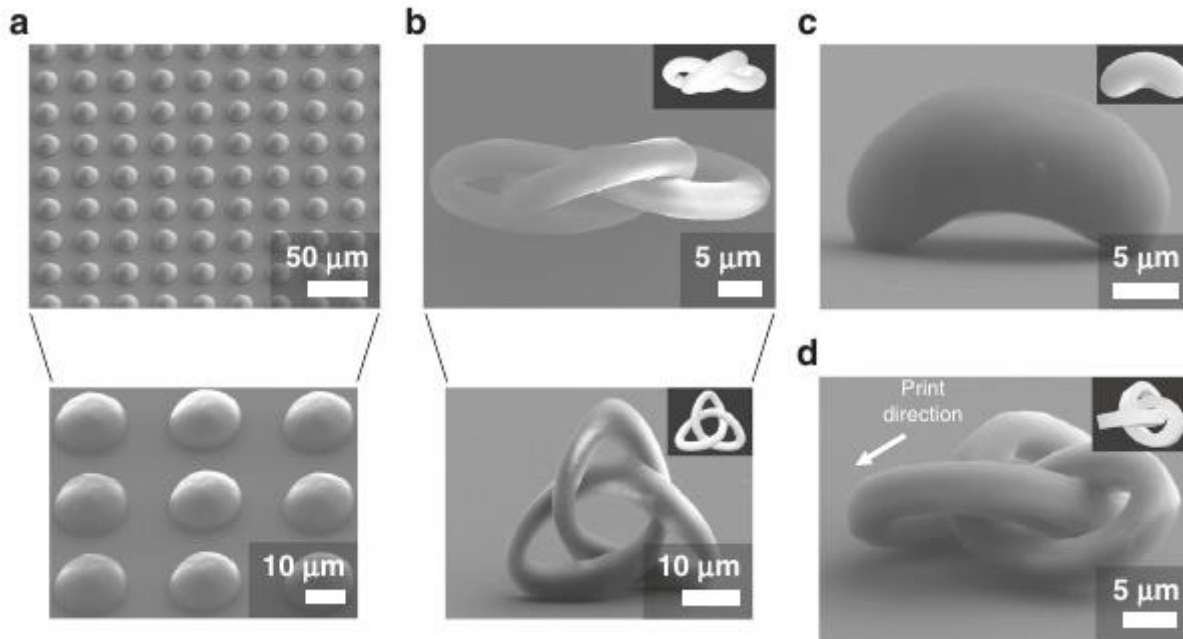
- Growth : Local oxygen depleted in a large volume around the print while laser on : threshold for polymerization reduced
- Plateau : lack of sufficient laser intensity further away from the print plane

Analysis of spatiotemporal printing features

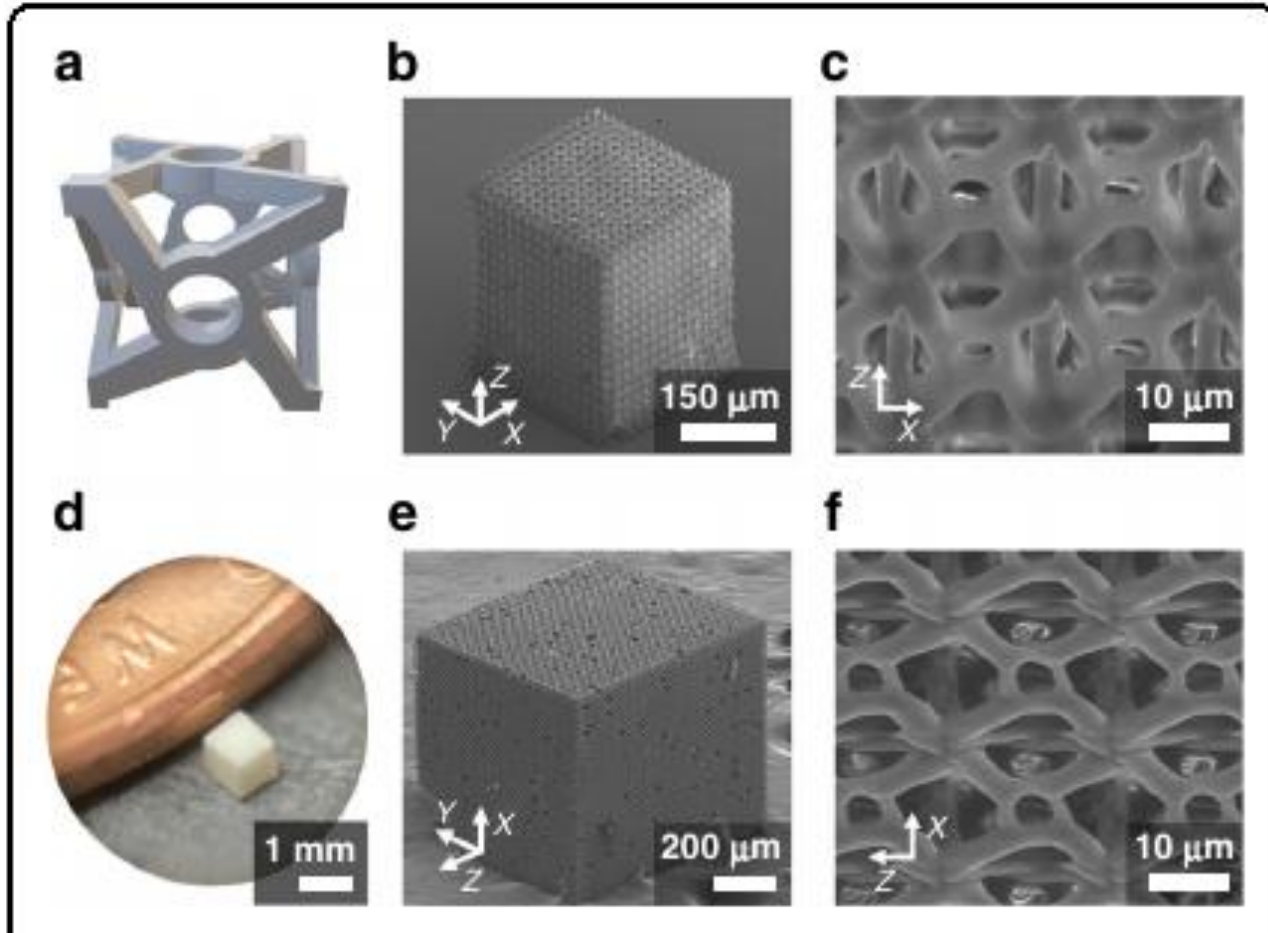


- actual printed width was significantly smaller than the target width
- combination of strong inhibition processes at the edge of the pattern and structure shrinkage
- linewidths of less than 200 nm were achieved

Continuous, layer-by-layer fabrication of complex 3D structures



- DMD pattern slices separations of **125–420 nm**, (much smaller than the $\sim 1 \mu\text{m}$ estimated minimum layer thickness) \rightarrow smooth print
- individual DMD mirrors translated to **$\sim 51 \text{ nm}$ size at the print plane**, which is below the diffraction limit of the system allowing smooth, curved patterns to be printed without being limited by the DMD resolution
- surface with no layering artifacts on the sides



- straight and curved components in all 3 dimensions as well as close separations along the z direction
- vertical stage speed of $400 \mu\text{m s}^{-1}$ for printing
- 1 mm s^{-1} stage translation speed between units
- b) $15 \times 15 \times 15$ unit , laser intensity 216 W cm^{-2} .
- e) $42 \times 42 \times 42$ unit , laser intensity $312 \text{ W cm}^{-2} \rightarrow 2.3$ hours

Structuring potential of projection two-photon lithography

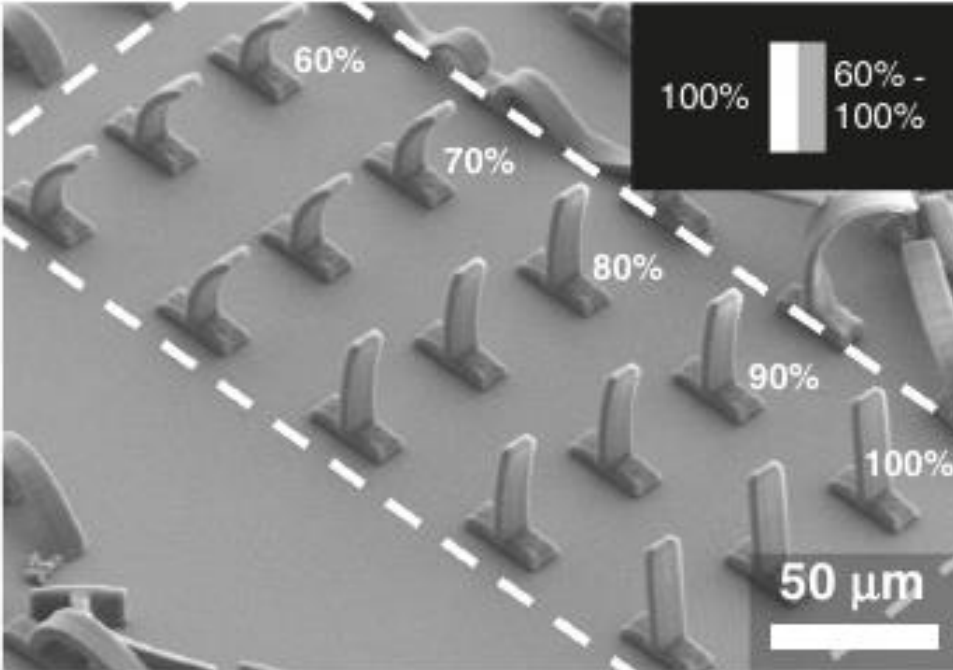


Fig. 7 Tuning structure characteristics using grayscale projection.

Grayscale pattern projection demonstrating tunable material properties in printing of standing pillars. Percentages indicate grayscale level of the pattern shown in the inset. Print speed was $500 \mu\text{m s}^{-1}$ stage speed

- DMD can introduce grayscale patterning : tuning exposure dose
- lower grayscale values : less crosslinking of the photoresist which leads to a larger amount of shrinkage after development.
- amount of curvature is tunable by controlling the grayscale value

- From two-photon lithography single voxel system to continuous layer-by-layer projection two-photon lithography printing system
- High speed fabrication of polymer 3D structures $1.08 \times 10^{-3} \text{ mm}^3 \text{ s}^{-1}$ with arbitrary 3D structures
- Possible to print complex 3D geometries including smooth, curved, surfaces
- The print area \rightarrow print speed, can be increased further by simple changes in the system optics