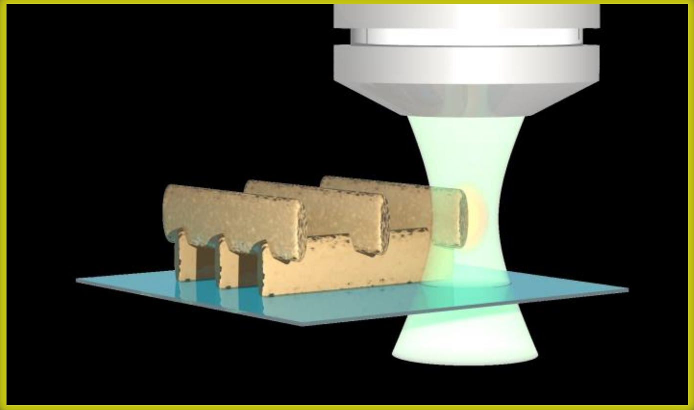
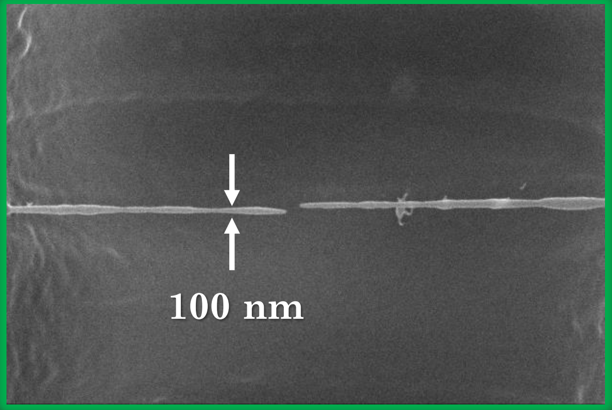
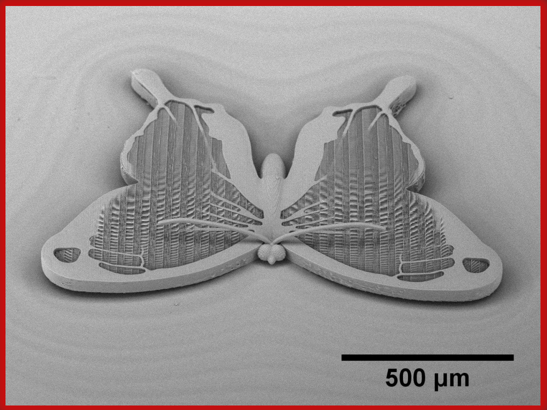
X-Photon 3D Lithography



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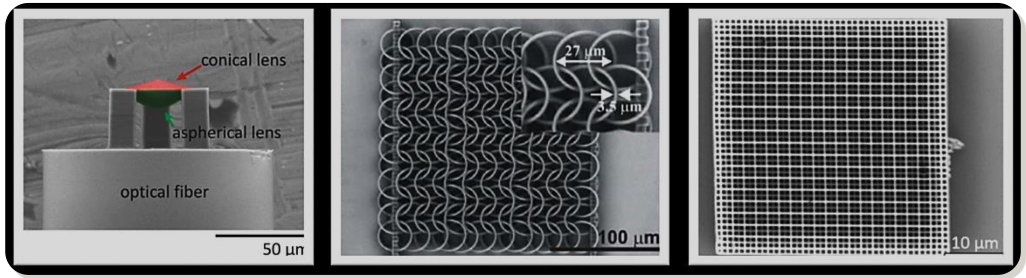
Laser Nanophotonics Group

Laser Research Center, Physics Faculty, Vilnius University

Vilnius University Excellence Center of Advanced Light Technologies

1. **Light-mater interaction at DLW fabrication conditions;**
2. **Multi-functional and micro-optical components for the propagation of light;**
3. **3D microporous scaffolds for biomedical applications;**
4. **Photonic crystals for the spectral and spatial manipulation of light;**
5. **Optical 3D printing of renewable resources based bioresins.**



Ultrafast laser processing of materials: from science to industry, Light: Sci. Appl. **5**, e16133 (2016) [NPG].

Light Science & Applications

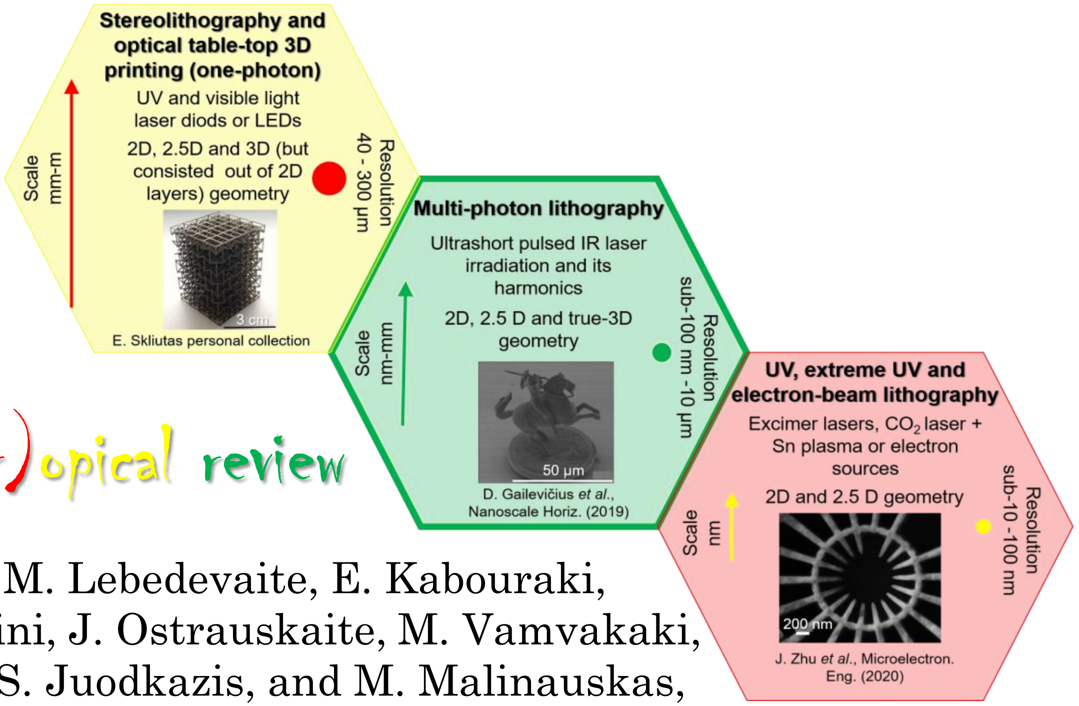
1008 citations!

HIGHLY CITED PAPER

Group Leader: **Prof. Mangirdas Malinauskas**
Researchers: **Dr. Edvinas Skliutas**
Engineer: Mr. Arūnas Čiburys, **Mr. Giedrius Balčas, Mr. Karolis Galvanauskas**
Master students: **Jurga Jeršovaitė,** Eulalia Puig Vilardell,
Bachelor students: **Antanas Butkus,** Saulė Petrauskaitė, Ioanna Petsi Angeliki

Outline of the Talk

- **Exposure and photomodification**
- **Laser mesoscale lithography: maskless, contactless, scalable**
- **Applications: from lab-to-fab**
- **Plant based renewable resins**
- **Ceramic and crystalline inorganics**
- **Summary and outlook**



A fresh t(r)opical review

E. Skliutas, M. Lebedevaite, E. Kabouraki, T. Baldacchini, J. Ostrauskaite, M. Vamvakaki, M. Farsari, S. Juodkazis, and M. Malinauskas, "*Polymerization mechanisms initiated by spatio-temporally confined light*“, Nanophotonics **10**(4), 1211-1242 (2021); https://doi.org/10.1515/nanoph-2020-0551

ADVANCED FUNCTIONAL MATERIALS

Review

Two-Photon Polymerization Lithography for Optics and Photonics: Fundamentals, Materials, Technologies, and Applications

Hao Wang, Wang Zhang, Dimitra Ladika, Haoyi Yu, Darius Gailevičius, Hongtao Wang, Cheng-Feng Pan, Parvathi Nair Suseela Nair, Yujie Ke, Tomohiro Mori, John You En Chan, Qifeng Ruan, Maria Farsari, Mangirdas Malinauskas, Saulius Juodkazis, Min Gu, Joel K. W. Yang ... See fewer authors

First published: 22 March 2023 | https://doi.org/10.1002/adfm.202214211 | Citations: 15

ADVANCED FUNCTIONAL MATERIALS

Perspective | Open Access

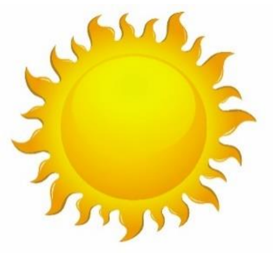
Fabrication of Glass-Ceramic 3D Micro-Optics by Combining Laser Lithography and Calcination

Giedrius Balčas, Mangirdas Malinauskas, Maria Farsari, Saulius Juodkazis

First published: 14 May 2023 | https://doi.org/10.1002/adfm.202215230 | Citations: 4

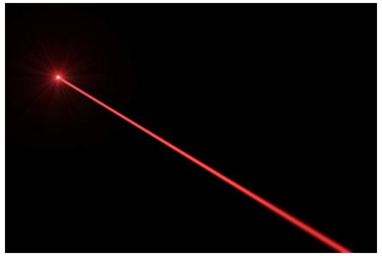
Ultrafast laser 3D lithography* based on non-linear light-matter interaction known as **Two-Photon Polymerization (**2PP**, **TPP**, or **Multi-Photon Lithography** (**MPL**), o **laser 3D nanolithography**).
Now it is a well-established technological field, as a **Laser Direct Writing** (**LDW**) tool it offers unrivaled precision and flexibility in **Rapid Prototyping** (**RP**) and **Additive Manufacturing** (**AM**).

QUANTIZING LIGHT INTO INDEPENDENT PARAMETERS

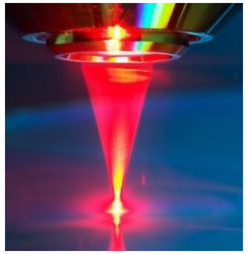


Natural
(sun or fire)

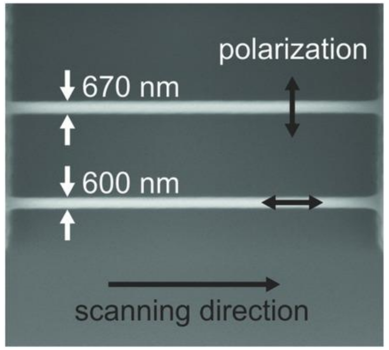
Synthetic
(also thermal)



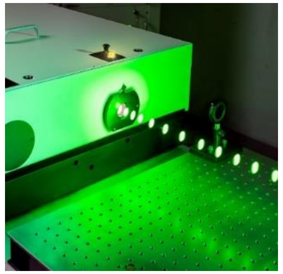
Laser (monochromatic, coherent - λ)



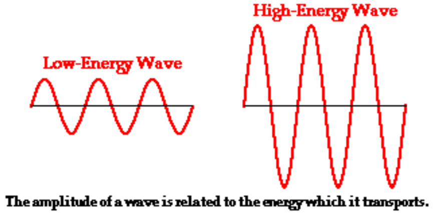
Selective spatial concentration (F)



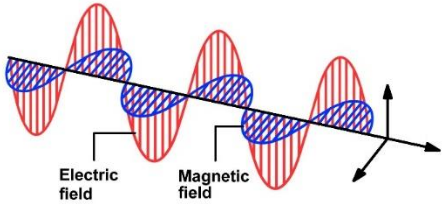
Rekštytė, Adv. Opt. Mater. **4**(8), 1209 (2016)



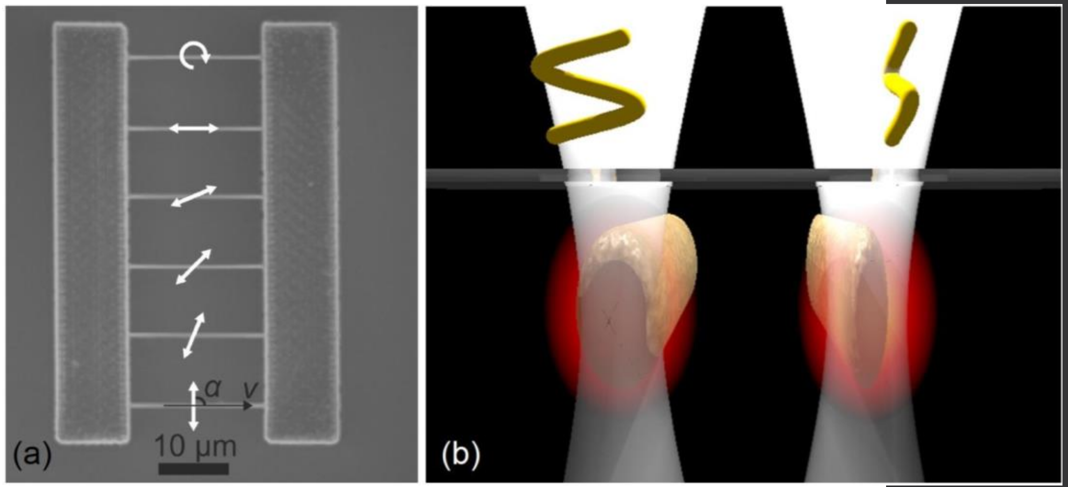
Temporal concentration (type of interaction/ linearity of process)



Already many parameters:
P (P_p, P_a), E (E_p, D), I (I_p & I_p)



But at least one more -
the polarization..



Still enough space for research..

S. Varapnickas and M. Malinauskas, *Processes of Direct Laser Writing 3D Nano Lithography*, Handbook of Laser Micro- and Nano-Engineering, **Springer**, 1-31 (2020).

Tunable LIGHT's parameters on demand

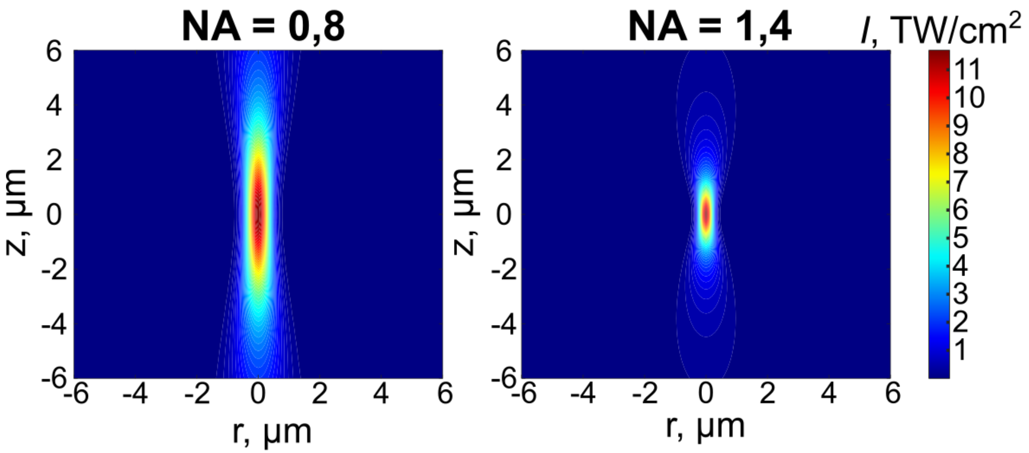
Parameter	Value	Comments and supporting references
λ	515, 800 and 1030 nm	400, 532 and 1064 nm are also possible [2, 3, 4]
τ	10 - 325 fs	ps, ns and CW are also possible [5, 6, 7]
R	1 kHz - 100 MHz	single pulse [8, 9] and GHz [10] reported, too
v	100 μm/s (10 - 10 000 μm/s)	not relevant for projection/interference lithography
t_{exp}	10 μs - 10 ms	0.1 - 10 s exposure can be applied in interference lithography [11]
P_a	0.02-70 mW	more than 100 mW power can be applied in interference lithography [12]
P_p	0.3 - 47 kW	peak power per pulse is more important than the average [13]
E_p	0.1 - 7 nJ	lower than 0.1 nJ [14] and higher than 7 nJ [15] values can be observed
D	20 pJ - 650 μJ	accumulated dose of multiple individual pulses
NA	1.4 (1.35 - 1.45)	only tight focusing or immersion oil objectives (NA > 1.3) are considered [16].
F[1]	3 μJ/cm^2 - 21 kJ/cm^2	accumulated exposure dose per area at the sample
I[1]	0.2 - 7 TW/cm^2	> 20 TW/cm^2 can be calculated, if assuming 100 % objective transmittance
I_v[1]	2 - 150 TW/cm^3	towards considering the energy is absorbed within volume not at the surface
W_{abs}[2]	80 pJ/cm^3 - 0.3 mJ/cm^3	absorbed energy density per single pulse

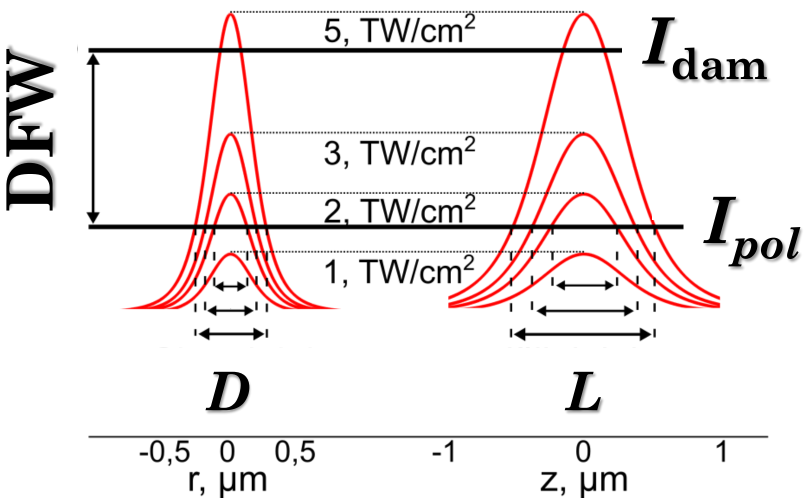
$$I = \frac{2PT}{R\omega_0^2\pi\tau}$$

P – average power, ***T*** – whole optics including objective transmittance,
R – pulse repetition rate, ***ω*** *– radius of the beam waist,* ***τ*** – pulse duration.

E. Skliutas et al., *Polymerization mechanisms initiated by spatio-temporally confined light*, Nanophotonics **10**(4), 1211-1242 (2021).

Assessment nomenclature



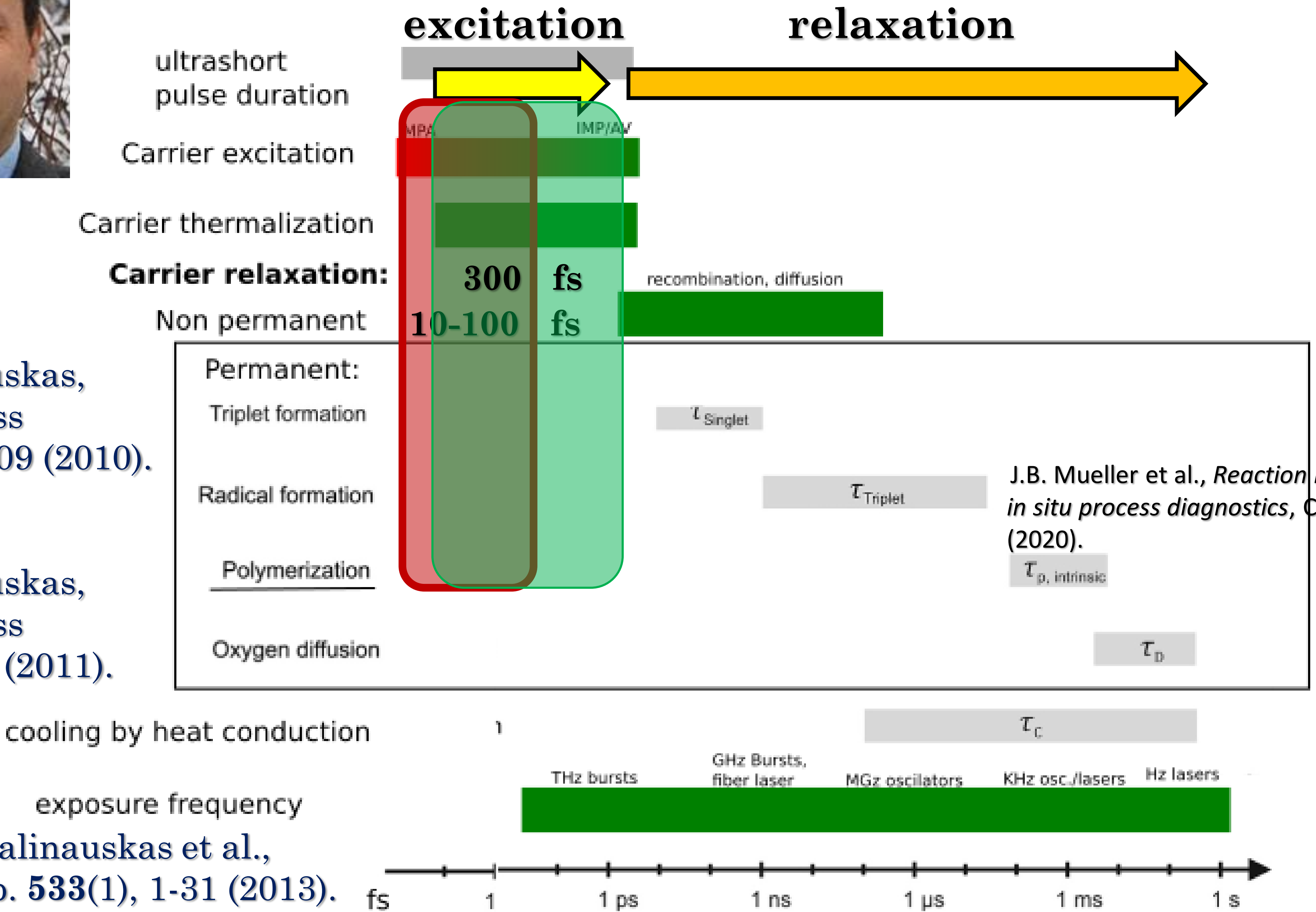


$$\omega_0 = \frac{0{,}61\lambda}{NA} \qquad z_r = \frac{n\pi\omega_0^2}{\lambda} \qquad D = 2\omega_0\sqrt{\frac{2}{n_{ef}}\ln\frac{I}{I_{pol}}} \qquad L = 2z_r\sqrt{\sqrt[n_{ef}]{\frac{I}{I_{pol}}} - 1} \qquad DFW = \frac{I_{dam} - I_{pol}}{I_{pol}}$$

ω_0 – Airy radius, z_r – Rayleigh lenght, n – refractive index, n_{ef} – effective order of absorption.

S. Juodkazis, Nanotechnology **16**(6), 846-849 (2005)

Controlled Energy *via* fs-pulses Delivery



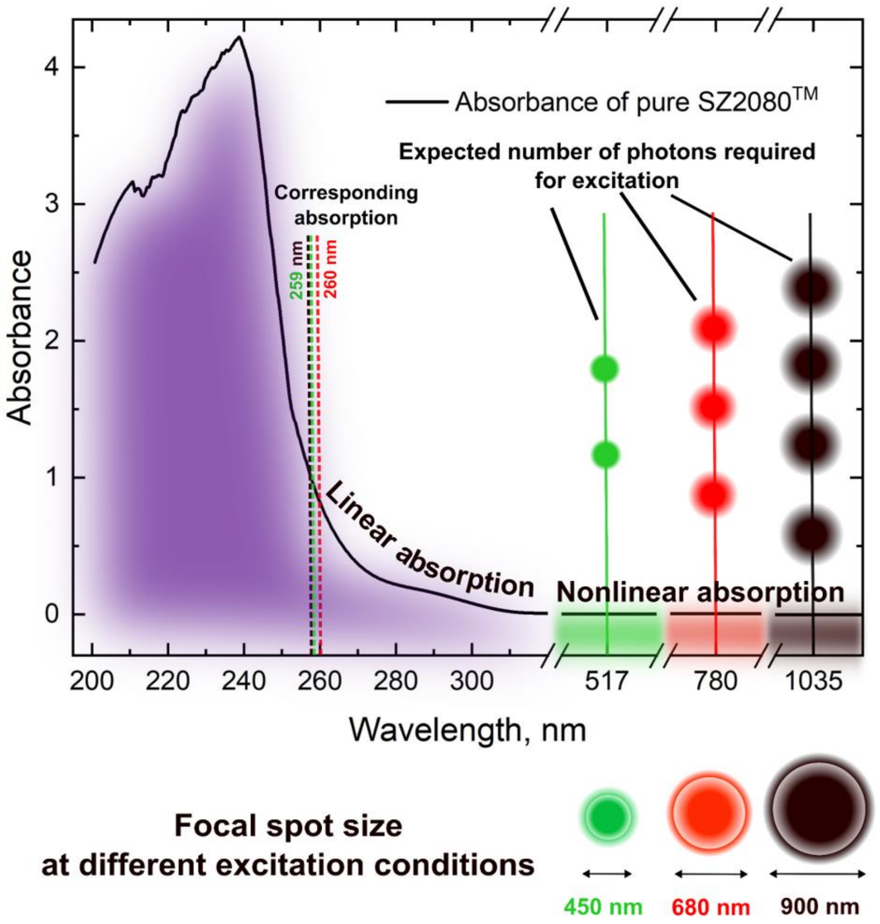
J.B. Mueller et al., *Reaction mechanisms and in situ process diagnostics*, Ch. 3.1, Elsevier (2020).

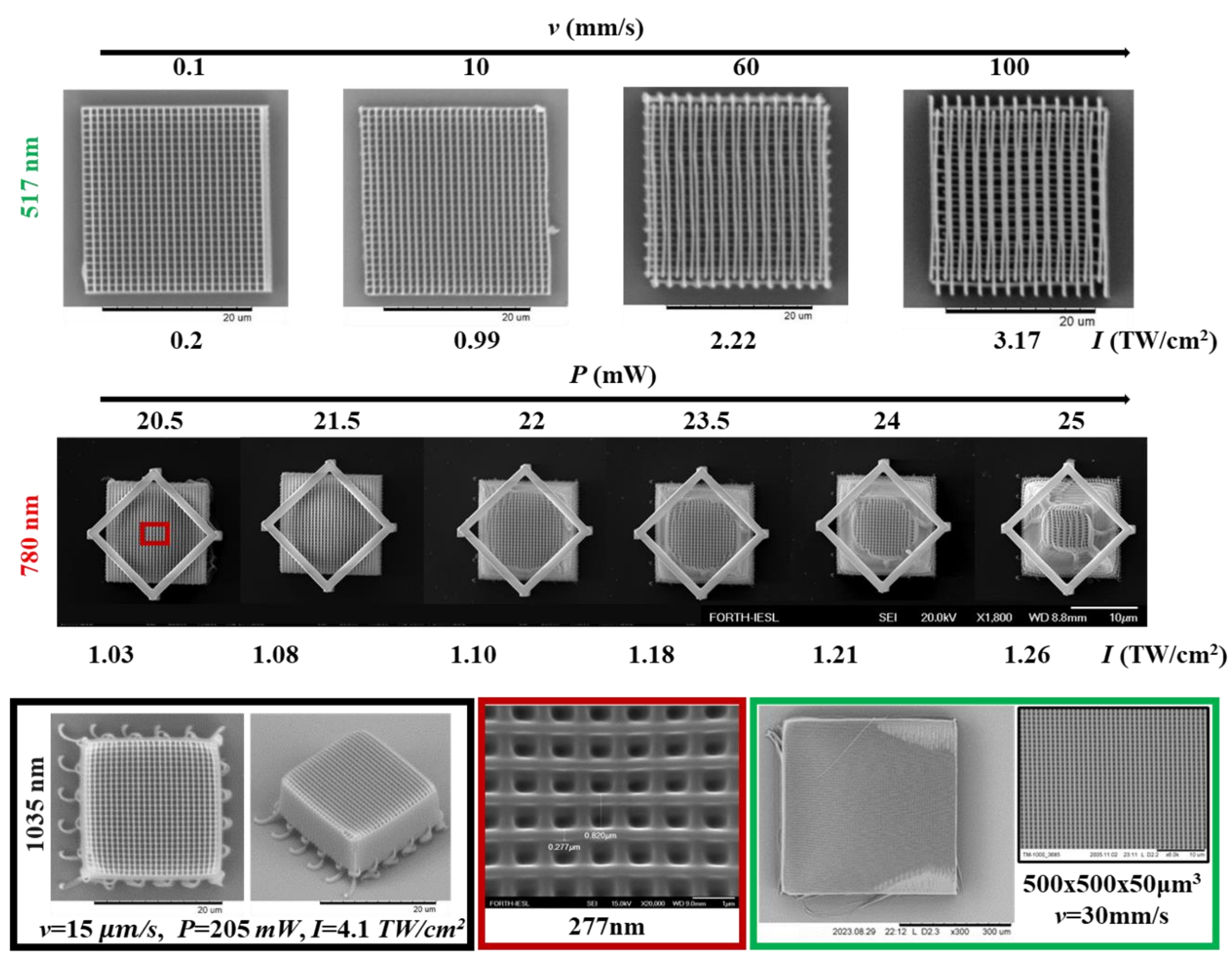
M. Malinauskas, Opt. Express **18**(10), 10209 (2010).
No PI!

M. Malinauskas, Opt. Express **19**(6), 5602 (2011).
ps-LDW!

M. Malinauskas et al., Phys. Rep. **533**(1), 1-31 (2013).

Updated absorption figure
– *two-photon polymerization extended*

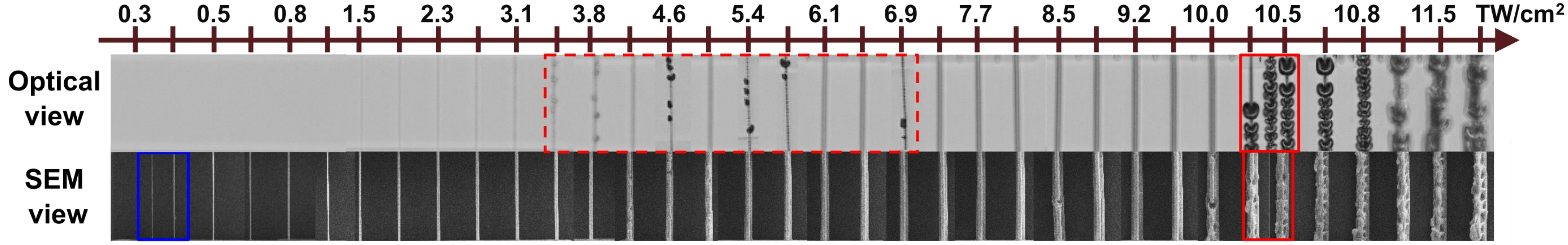


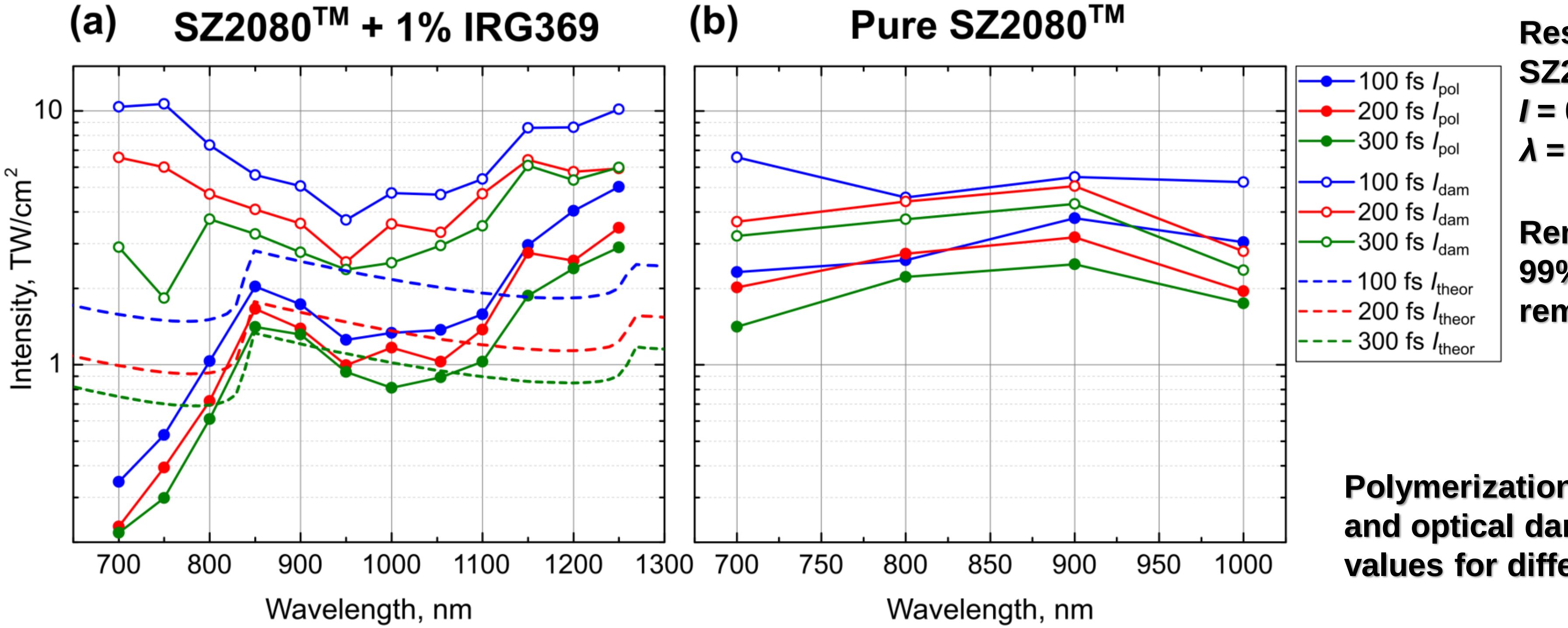


Dimitra Ladika, Antanas Butkus, V. Melissinaki, E. Skliutas, E. Kabouraki,
S. Juodkazis, M. Farsari, and M. Malinauskas, Light: Adv. Manuf., *to be submitted* (SOON).

X-photon evaluation of thresholds via OM and SEM

700 nm, 100 fs, SZ2080^{TM} + 1% IRG369





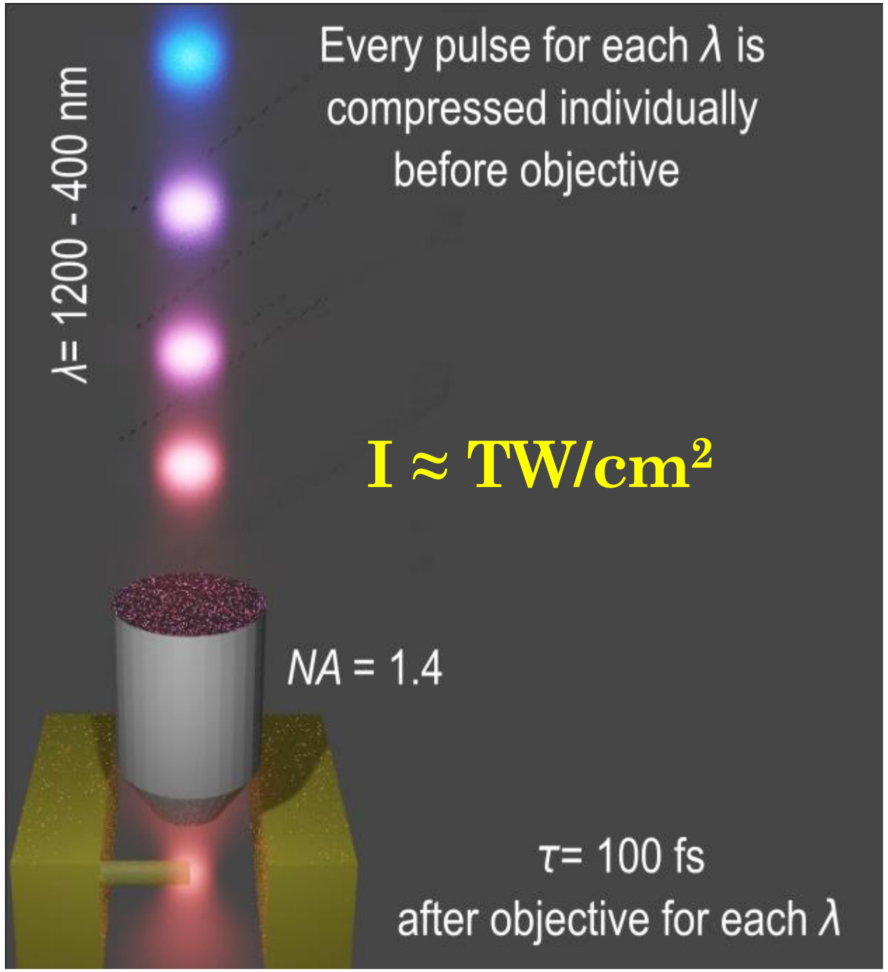
Resolution bridges in SZ2080^{TM} + 1% IRG when I = 0,3-12 TW/cm^2 and λ = 700 nm at τ = 100 fs.

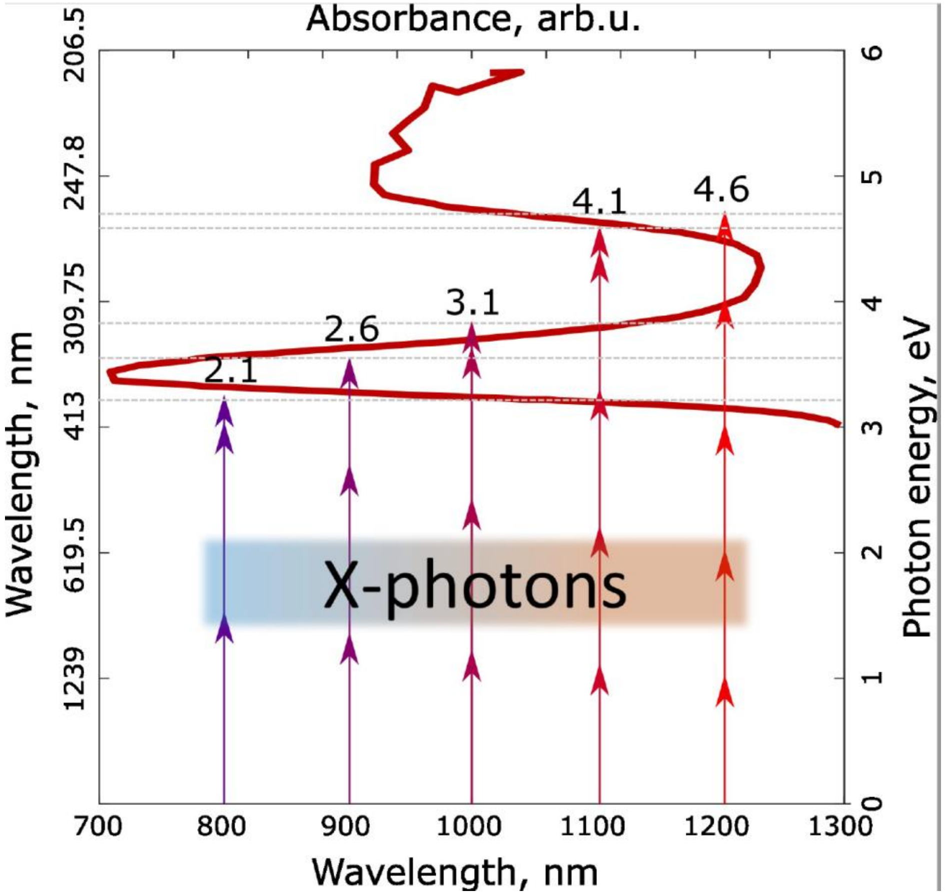
Removing 1% of PI, 99% of material remains the same.

Polymerization threshold (I_{pol}) and optical damage (I_{dam}) values for different λ and τ.

E. Skliutas et al., X-photon laser direct write 3D nanolithography, *Virtual. Phys. Prototyp.* **18**(1), e2228324 (2023); https://doi.org/10.1080/17452759.2023.2228324.

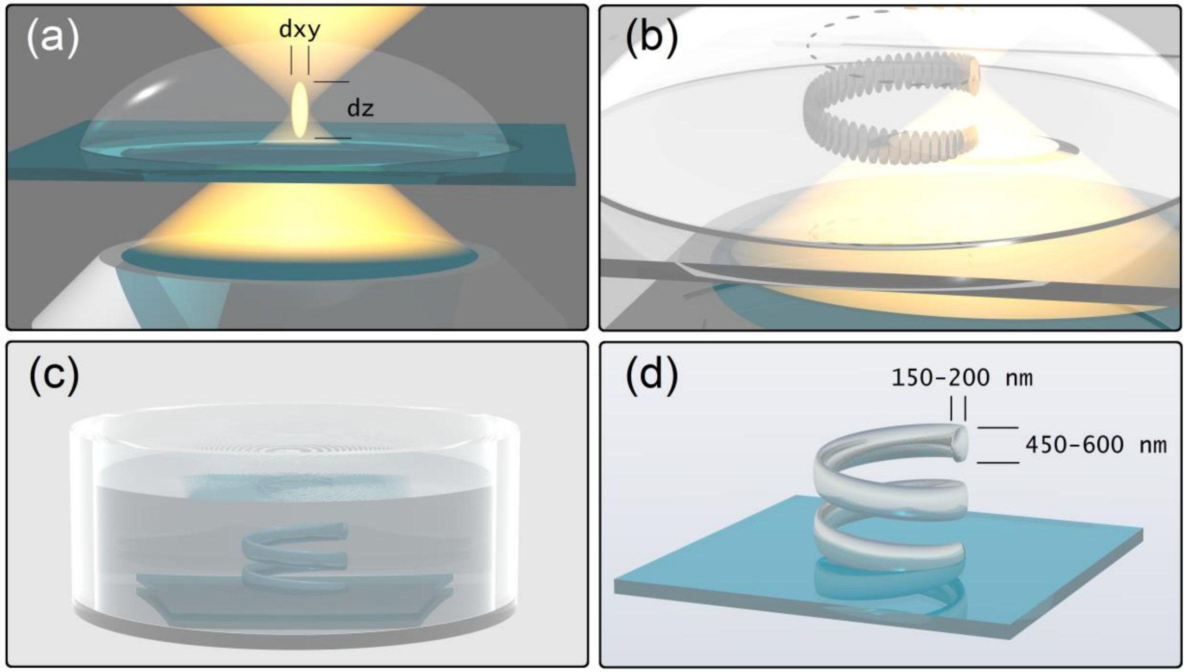
Conclusion : TPP* achieved



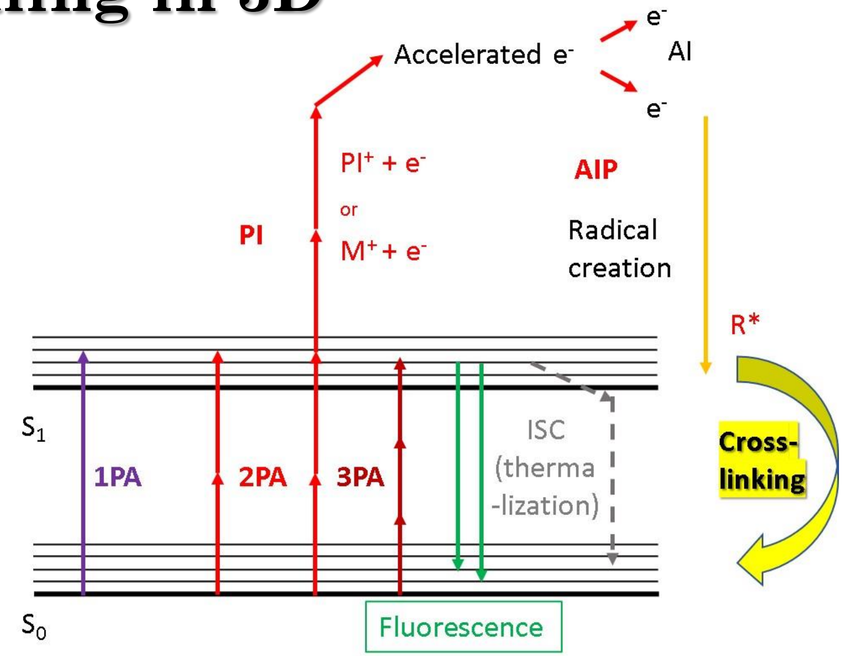


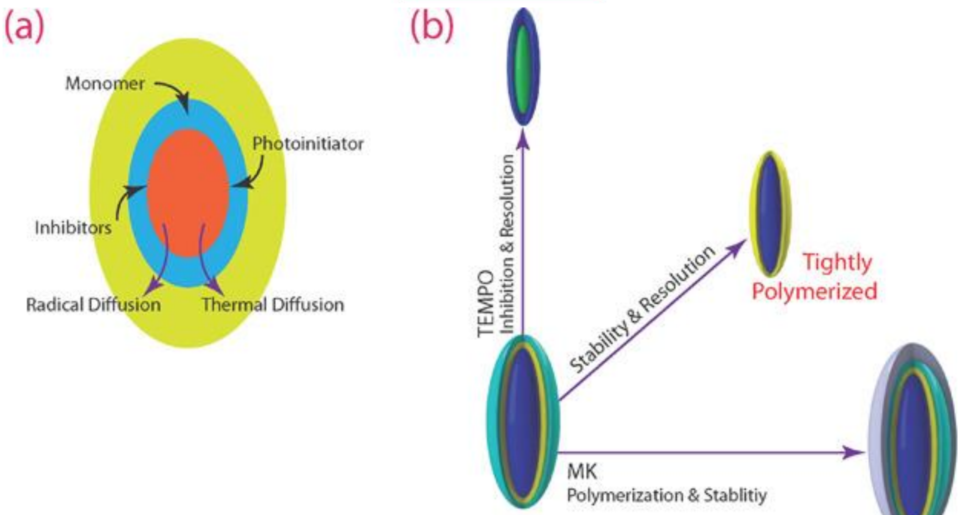
TPP* – Towards Perfect Polymerization

Thresholding and scaling in 3D



S. Varapnickas and M. Malinauskas, *Processes of Direct Laser Writing 3D Nano Lithography*, Handbook of Laser Micro- and Nano-Engineering, **Springer**, 1-31 (2020).





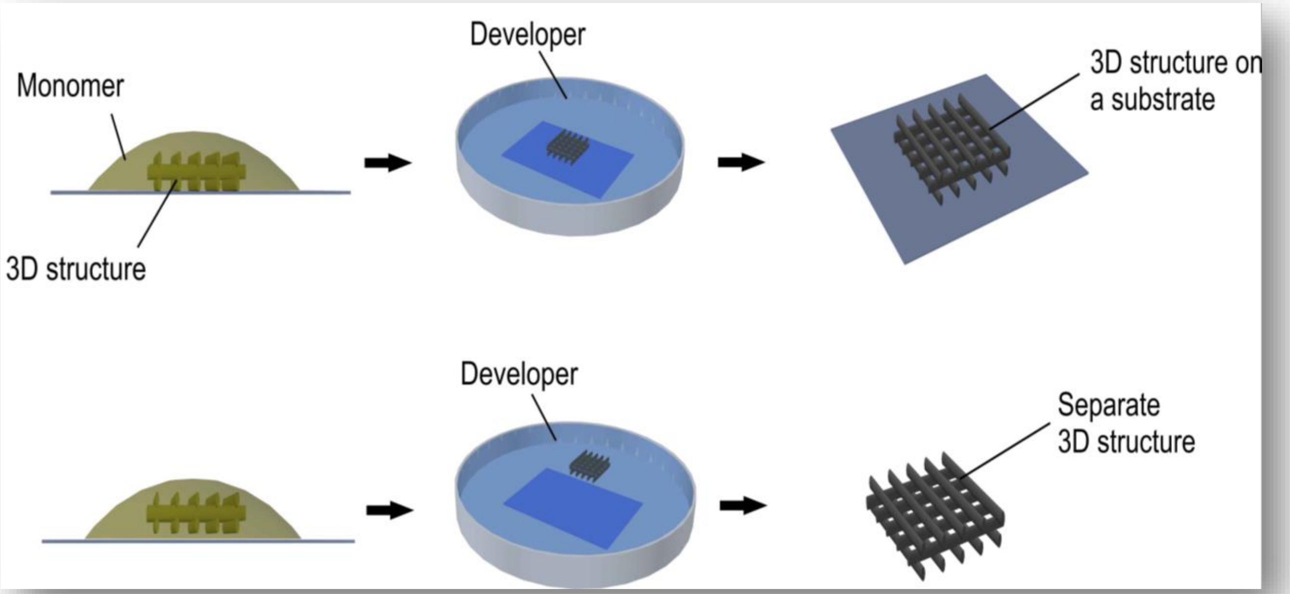
Controlled photo-physical-chemical mechanisms for unlimited freedom in 3D nanotechnology

P. Prabhakaran, Y. Son, C.-W. Ha, J.-J. Park, S. Jeon, K.-S. Lee, *Optical Materials Forming Tightly Polymerized Voxels during Laser Direct Writing*, Adv. Eng. Mater. **20**(10), 1800320 (2018).

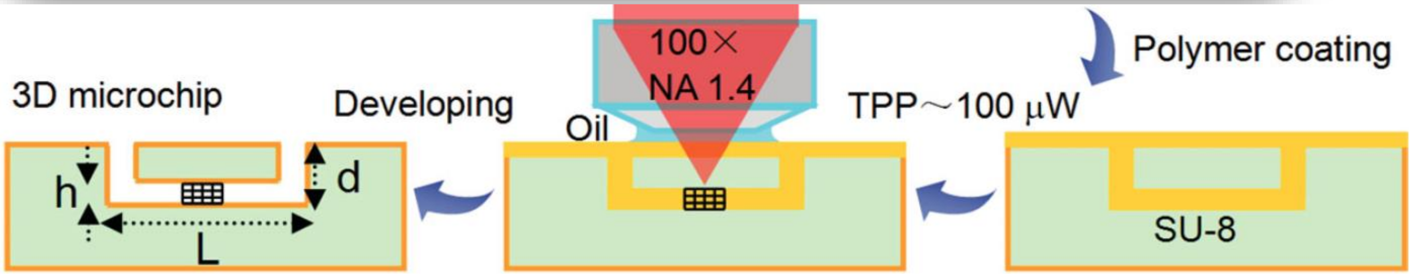
ON any substrate, with NO substrate, or IN substrate

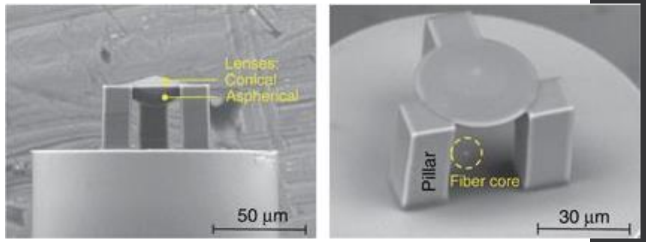
ON substrate

NO substrate

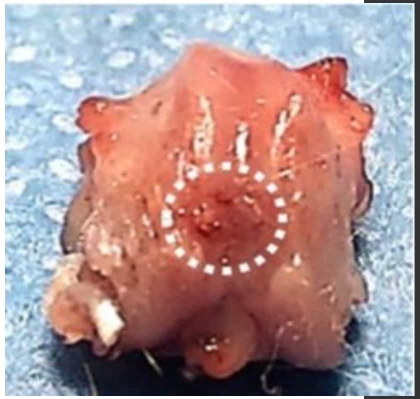


IN substrate

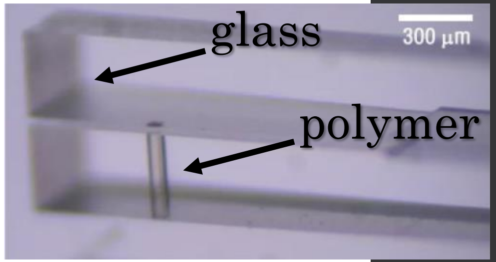




Žukauskas, *J. Laser. Micro. Nanoeng.* **9**, 68 (2014)



Mačiulaitis, *Appl. Surf. Sci.* **487**, 692 (2019)



Tičkūnas, *Opt. Express* **25**, 26280 (2017)

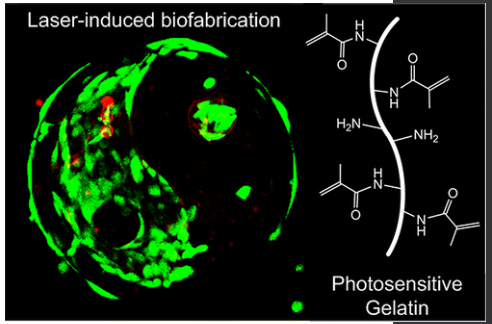
3D laser mesoscale lithography offers flexible materialization of objects on particular substrates or without them as well as in them.

This might look trivial, yet sometimes become critical for practical applications.

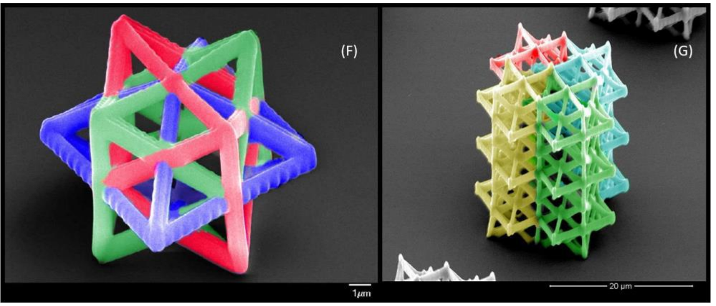
[ON, NO] – S. Rekštytė et al., *Direct Laser Writing of 3D Polymer Micro/Nanostructures on Metallic Surfaces*, Appl Surf Sci **270**, 382 (2013).
[IN] – D. Wu et al., *Hybrid femtosecond laser microfabrication for true 3D ship-in-a-bottle biochip*, Laser Photon. Rev. **8**, 458 (2014).

Laser Two-Photon / Multi-Photon / Non-Linear / Lithography as a precise Additive μ-Manufacturing tool

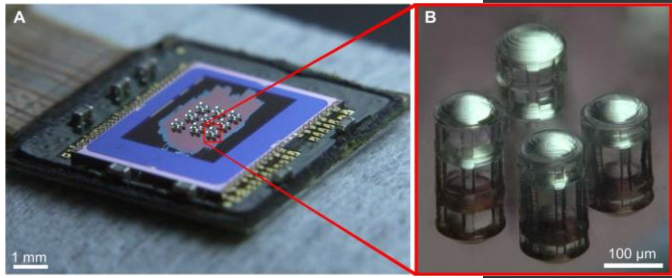
Free-standing microring resonator and the coupling waveguide
Osellame et al., Lab Chip ***19****, 1985-1990 (2019)*



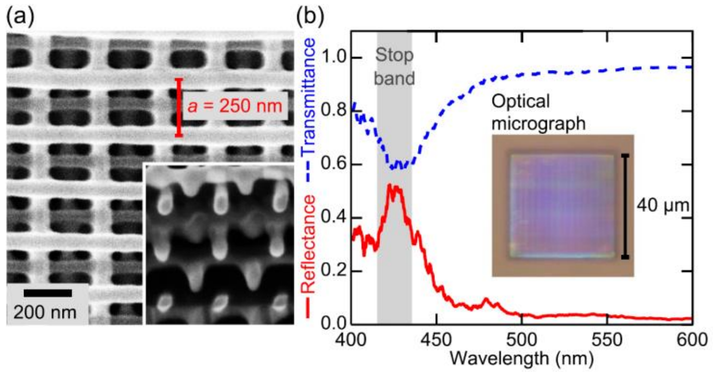
Cell-Containing Hydrogel Constructs
Ovsianikov et al., Langmuir ***30****, 3787 (2014)*



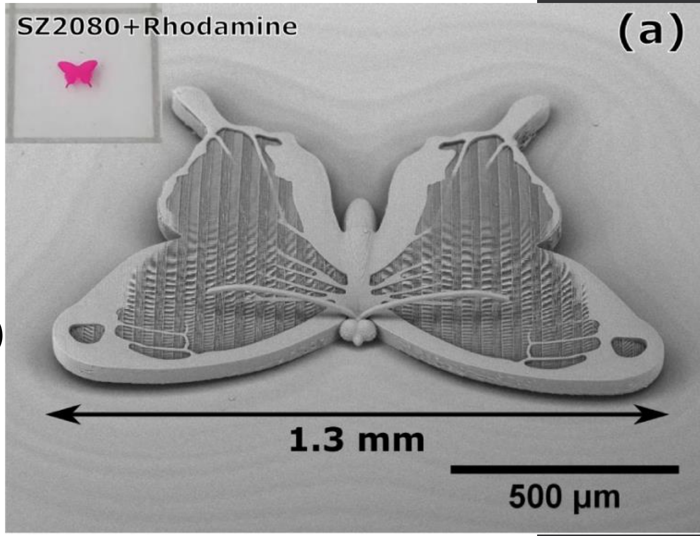
Intertwined microlattices for enhanced metamaterials *Farsari et al., Math. Mech. Sol.* ***24****, 2636 (2019)*



Compound lenses directly printed onto a CMOS
Giessen et al., Sci. Adv. ***3****, e1602655 (2017)*

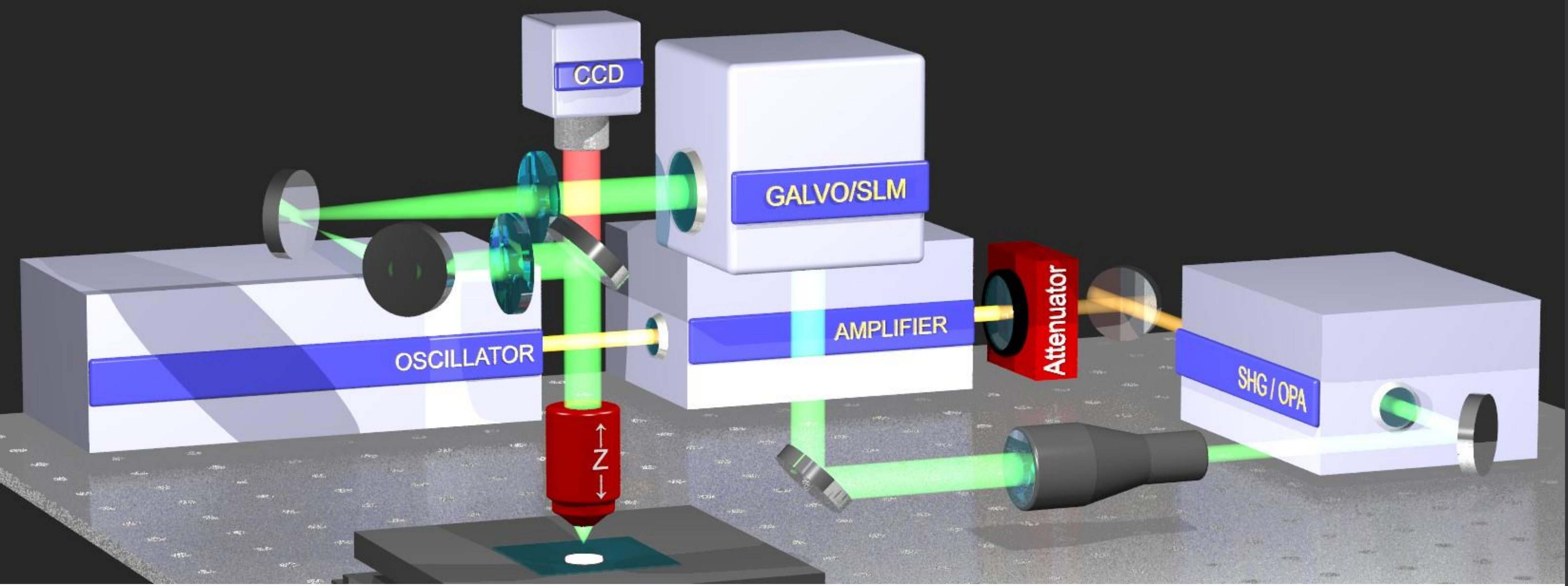


Woodpile photonic crystal with a period of a 250 nm *Wegener et al., Opt. Lett.* ***39****, 6847 (2014)*



A universal mesoscale optical 3D printer
Jonušauskas et al., Opt. Express ***27****,15205 (2019)*

<u>Just a few benchmarking examples out of the established field!</u>



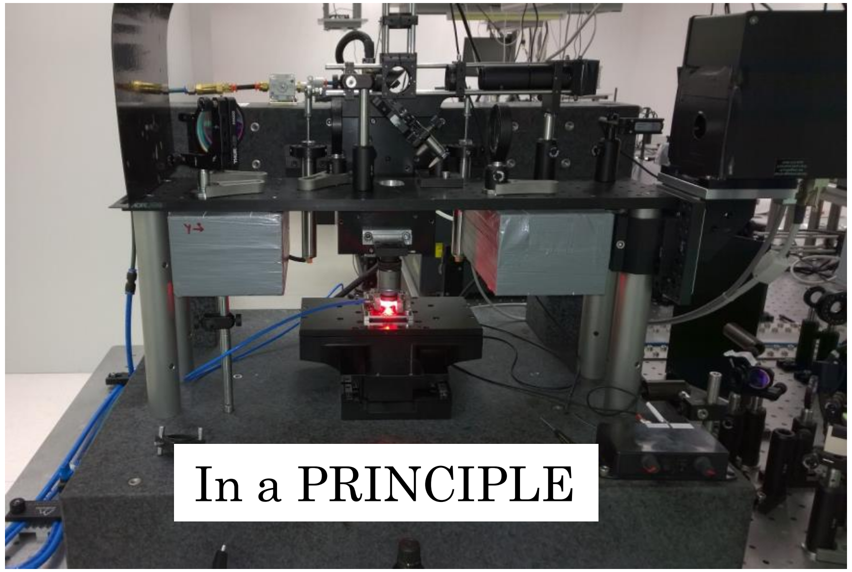
A Typical/Custom Laser 3D-micro/nano-Fabrication Setup

S. Varapnickas and M. Malinauskas, *Processes of Direct Laser Writing 3D Nano Lithography*, Handbook of Laser Micro- and Nano-Engineering, **Springer**, 1-31 (2020).

Direct fs-Laser Writing Setup:
integration of laser, stages and software

Workshop of Photonics

LIGHT CONVERSION



(I) Yb:KGW laser (200 fs – 20 ps, 1 kHz – 1 MHz, 300 - 2700 nm), includes pulse picker for pulse-on-demand operation Pharos (Light Conversion Ltd.).

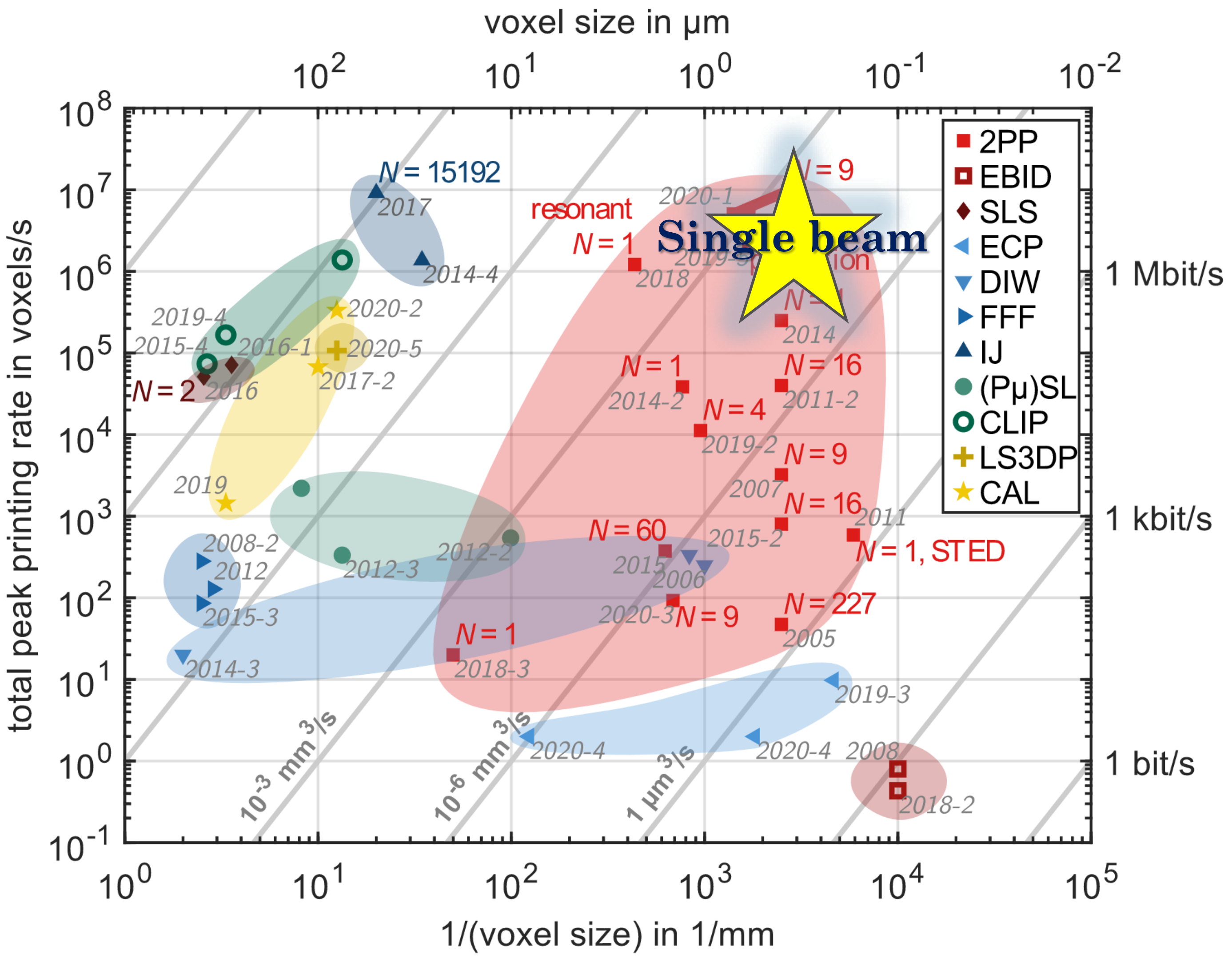
(II) Positioning systems:

- (a) Aerotech linear stages combined with galvanometer scanner (up to 300 mm/s scanning velocity, 10 nm resolution, 11x11x6 cm^3 working field)
- (b) piezo nanopositioner + step motor stages (~100 µm/s with 1 nm scanning precision).

(III) Focussing: 100x NA = 1.4 – 4x NA = 0.1 objective lenses.

(IV) Full process automatization via commercially available „3D Poli“ (Femtika) or “AltSca” (Altechna R&D) software. Input files: .stl, .bmp or directly programmed code.

Continuous 3D laser direct writing



3D Printing (3DP): **rapid prototyping** *vs* **additive manufacturing**

Rapid Prototyping is a fast fabrication of a physical part, model or assembly using 3D Computer Aided Design (CAD).

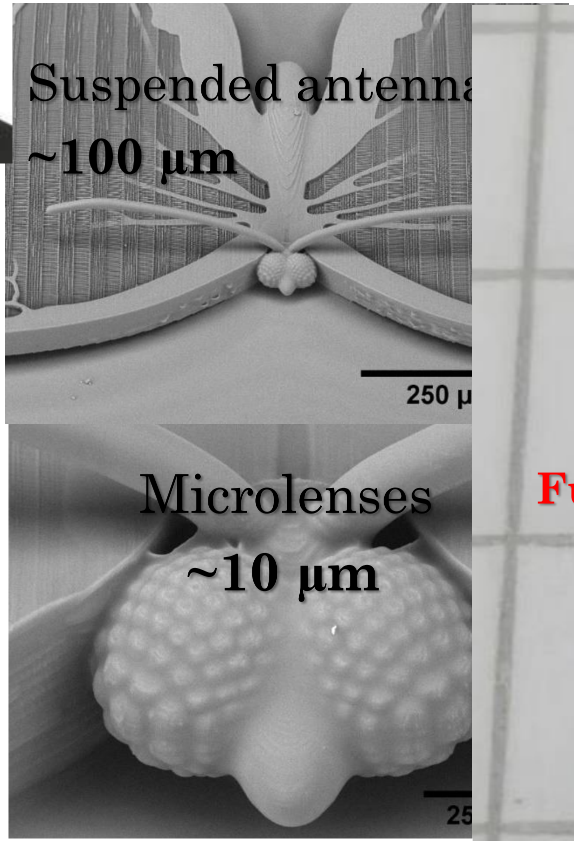
Additive manufacturing (AM) is the industrial production name for 3D printing, a Computer Aided Manufacturing (CAM) process that creates objects in an additive manner.

3D printing : CAD-CAM technique.

3Dprintingspeed.com

V. Hahn, P. Kiefer, T. Frenzel, J. Qu, E. Blasco, C. Barner-Kowollik, M. Wegener,
Rapid Assembly of Small Materials Building Blocks (Voxels) into Large Functional 3D Metamaterials.
Adv. Funct. Mater. ***30****(26),1907795 (2020); doi.org/10.1002/adfm.201907795.*

Putting it all together: meso-butterfly

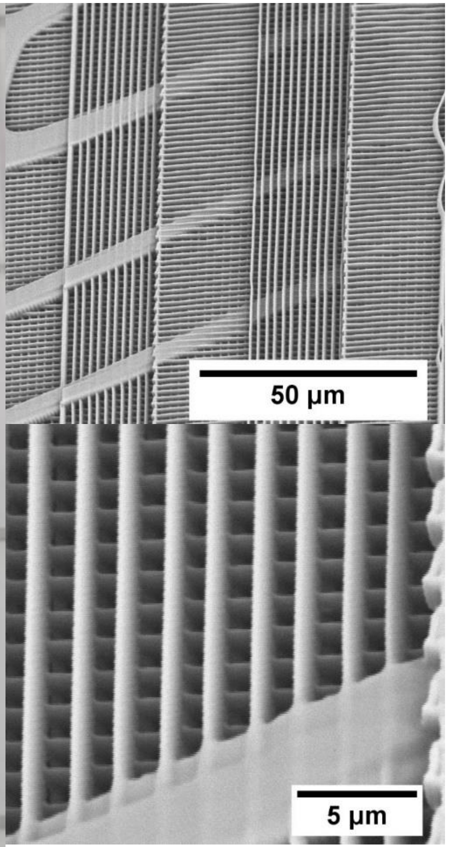


Made in: 2.5 hours

Additive manufacturing:
1.9×10^{-3} mm^3/min

NA = 1.4
3.2×10^5 voxels/s

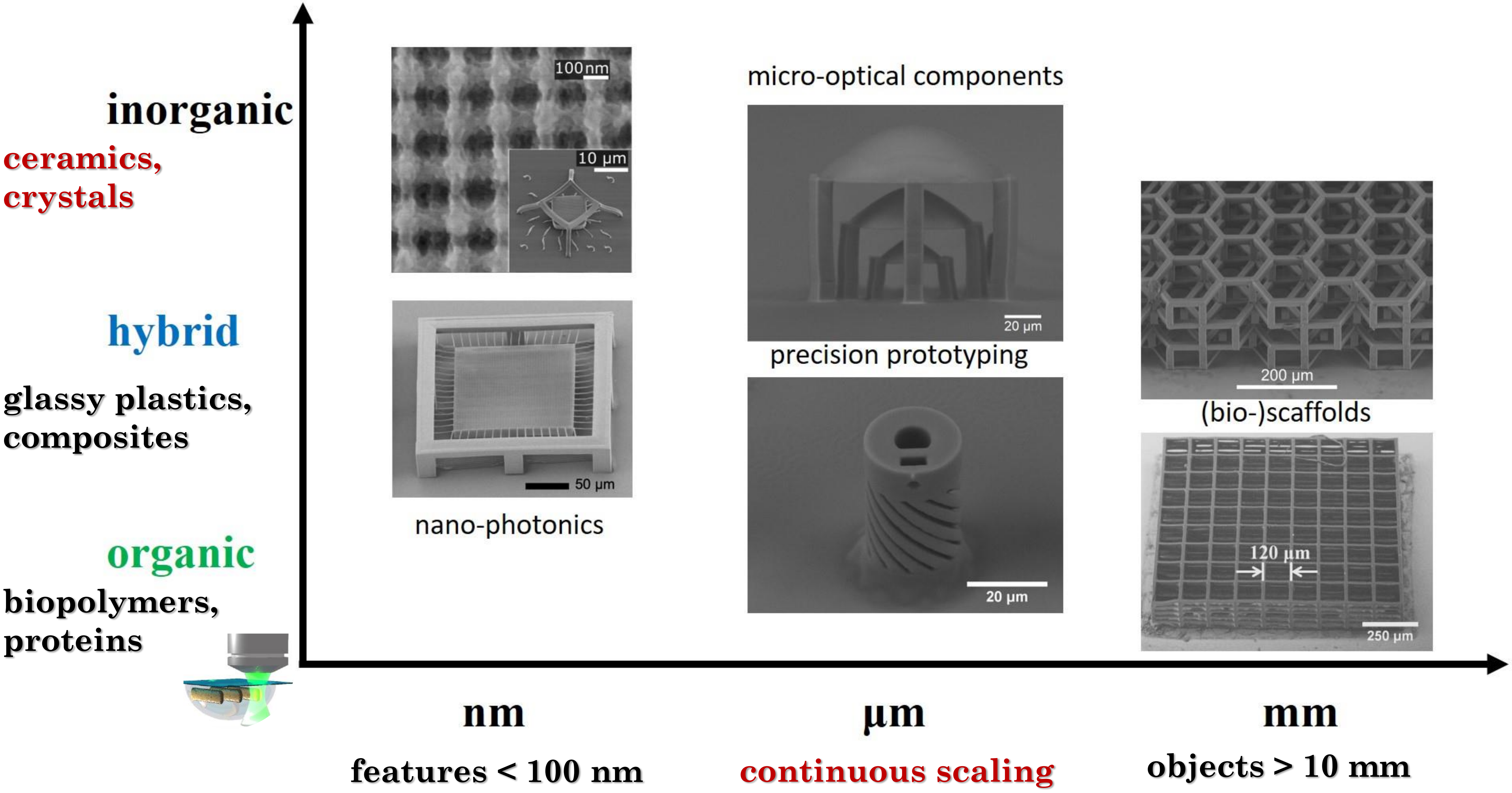
Embedded nanolattice



Line width ~650 nm

Jonušauskas, *Opt. Express* **27**, 15205 (2019)

True 3D printing: multi-scale and multi-color



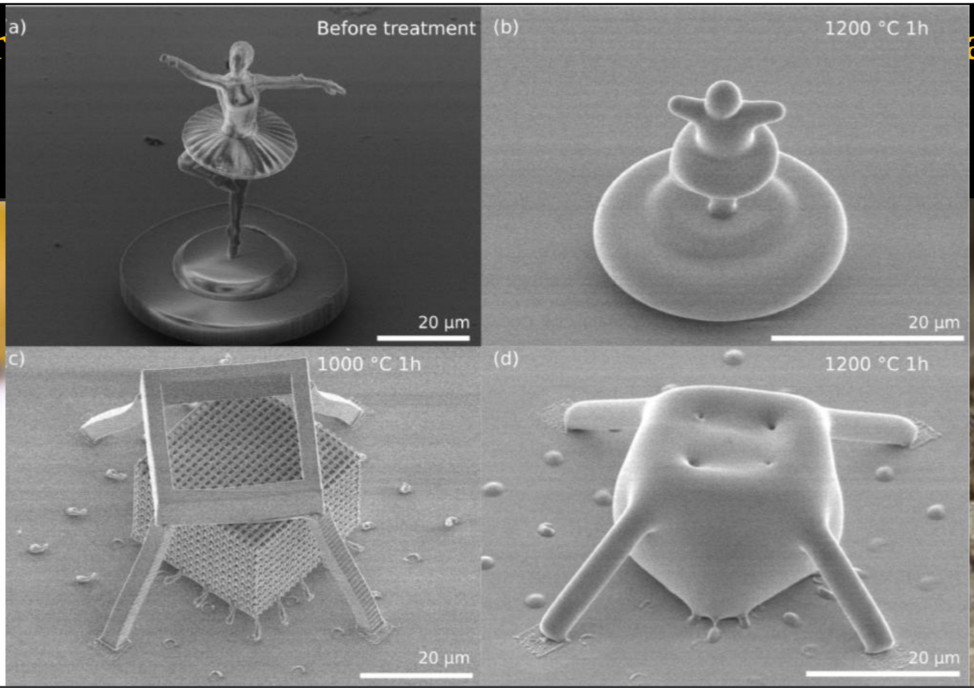
Is mesoscale 3D printer black & white, grayscale or colorful (material sense)?

Materials' spectrum:

Ranges from natural biodegradable/biocompatible to synthetic tunable properties composites towards inorganics.

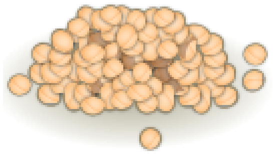
Proteins – Biopolymers – Hydrogels – Acr

asses-Ceramics-Crystals



Motivation: plant-based resins as renewable materials for sustainable O3DP

- Direct laser writing (DLW) 3D nonlinear lithography (NLL) allows precise manufacturing of microscale objects out of polymers reaching nm-scale resolution.



Zhu, Nature, **540**(7633), 354 (2016).

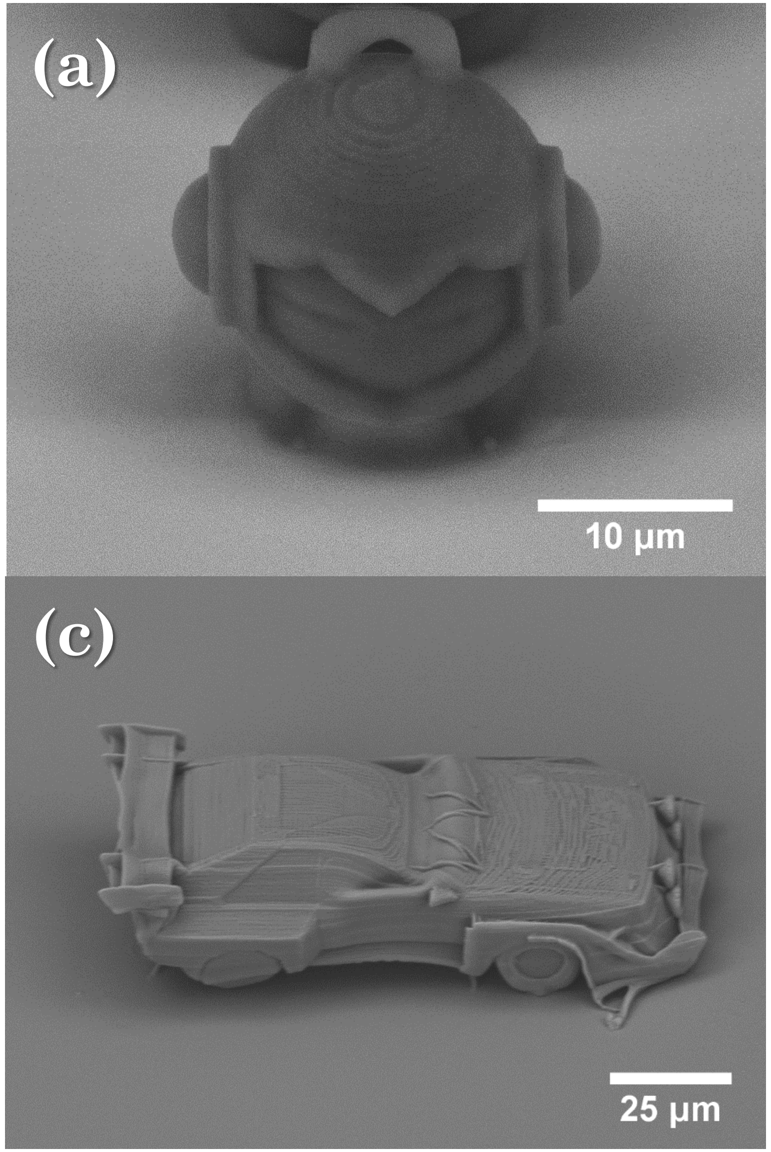
- Material selection is one of the key factors as it determines mechanical, chemical, thermal, optical and other properties of the fabricated objects.

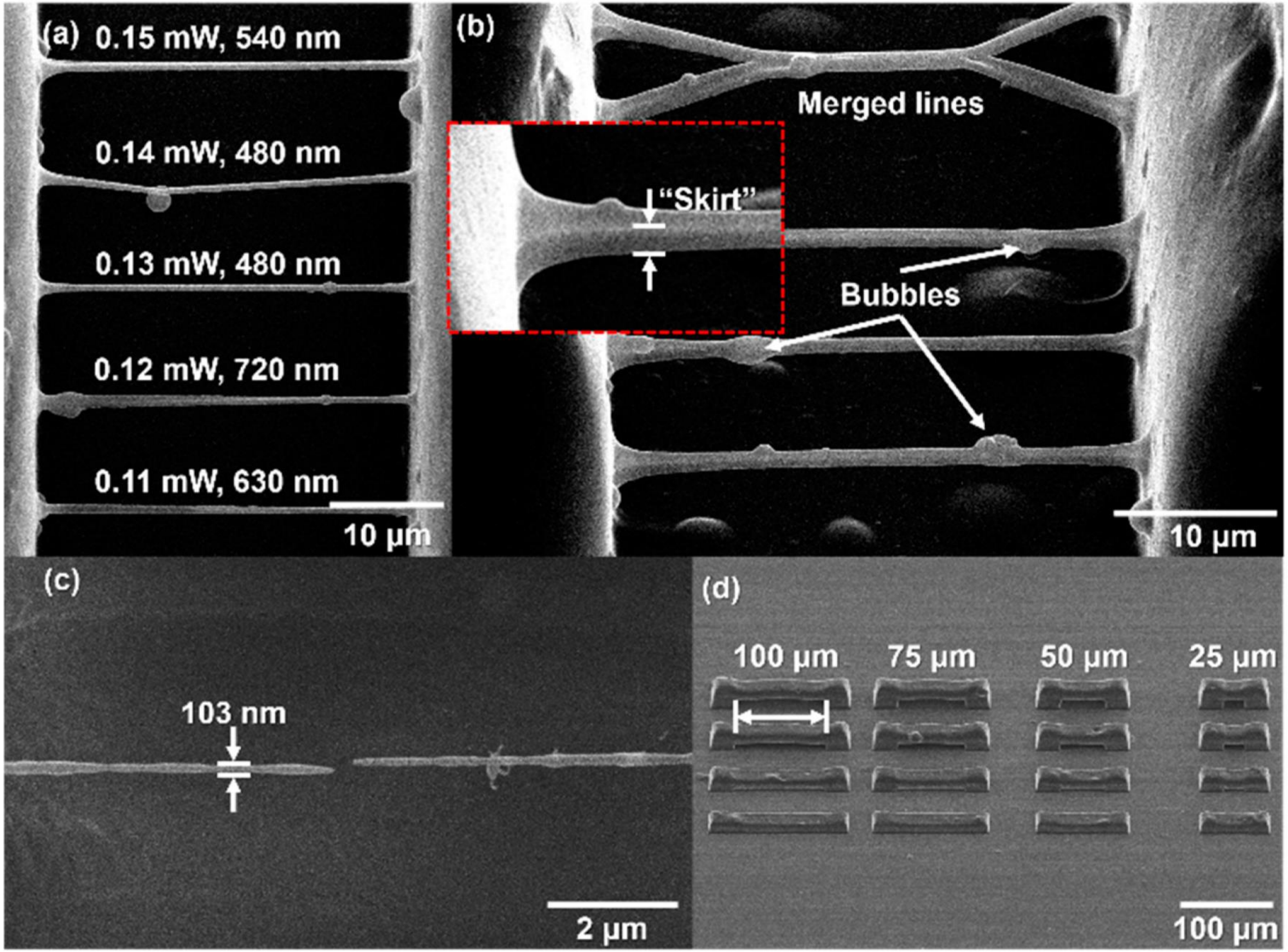
- Plant-based oils offer biodegradability and renewability, thus such substances recently became a popular target of researchers to replace common petroleum-derived plastics.

- **Research aim** – investigate acrylated epoxidized soybean oil (AESO) photostructuring suitability for the DLW 3D NLL.

*E. Skliutas et al., "Photosensitive naturally derived resins toward optical 3-D printing," Opt. Eng. **57**(4), 041412 (2018).*

Fabrication of 3D solid μ-objects



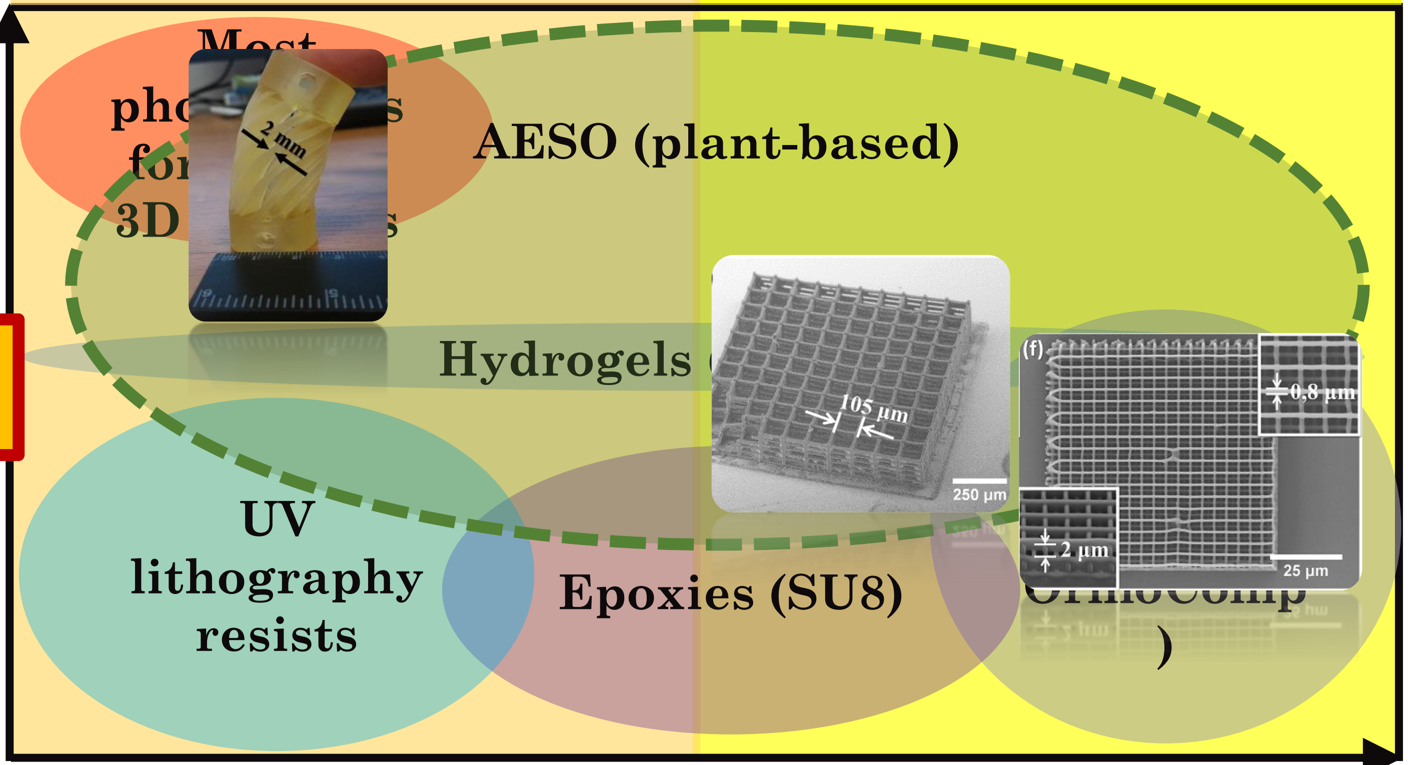


Renewable resins

Optical 3D lithography

Continuous exposure: Digital light processing Stereolithography	Pulsed laser exposure: Direct laser writing
LED, diode laser	Pico-, nano-, femtosecond pulsed laser

Spatial resolution nm – m



mW/cm^2 – TW/cm^2

Light intensity

Applications

- Manufacturing
- Prototyping
- Tissue engineering
- Micro-fluidics
- Micro-optics
- Photonics

Prof. J. Ostrauskaitė, Polymer Technology

Lebedevaitė et al., **Polymers** 11(1), 116 **(2019)**.
Navaruckienė et al., **Polymers** 12(2), 397 **(2020)**.
Grauželienė et al., **Polymers** 13(6), 872 **(2021)**.
Jaras et al., **Polymers** 14(12), 2460 **(2022)**.
Sereikaite et al, **Polymers** 14(24), 5361 **(2022)**

Skliutas, *A Bio-Based Resin for a Multi-Scale Optical 3D Printing*, Sci. Rep. **10**, 9758 (2020).

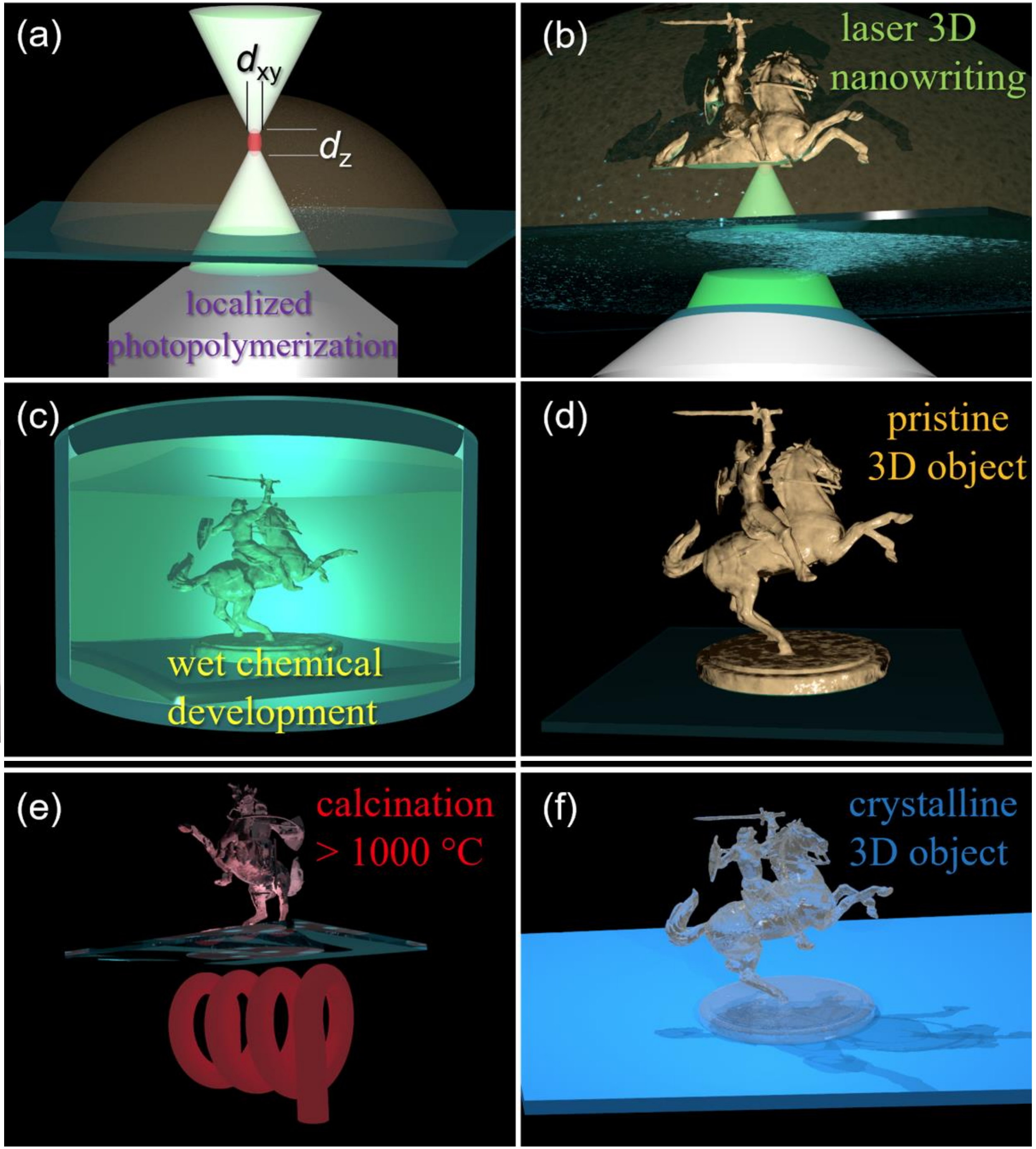
Editor's pick & Top 100

And Now for Something Completely Different..

(*Monty Python 1971*)

[1] E. Skliutas et al., Photopolymerization mechanisms at spatio-temporally ultra-confined light, Nanophotonics, **10**(4), 1211-1242 (2021); 10.1515/nanoph-2020-0551.

[2] G. Merkininkaite et al., Laser additive manufacturing of Si/ZrO_2 tunable crystalline phase 3D nanostructures, Opto-Electron. Adv. **5**, 210077 (2022); 10.29026/oea.2022.210077.



Typical LDW 3D MPL
(two photon, non-linear)
polymerization technique.

Freeform micro-/nano-
Structures of diverse materials.

High-temperature post-treatment
of hybrid materials:
removes inorganics and converts
into glass-ceramic substance

Isotropic downscaling!

MATERIAL

SZ2080™
Hybrid organic-inorganic

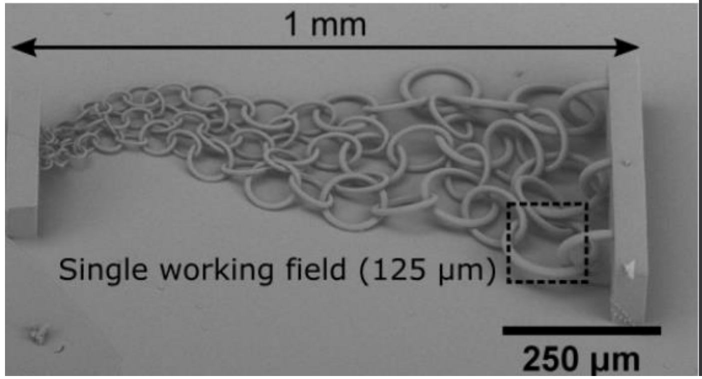
$C_4H_{12}SiZrO_2$

Widely use in microfabrication by TPL

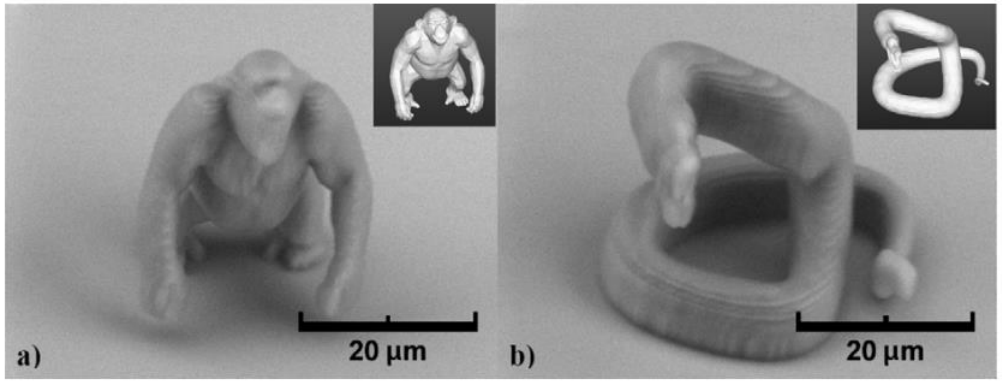
FORTH
INSTITUTE OF ELECTRONIC STRUCTURE AND LASER

Dr. Maria Farsari
NonLinear Lithography Group

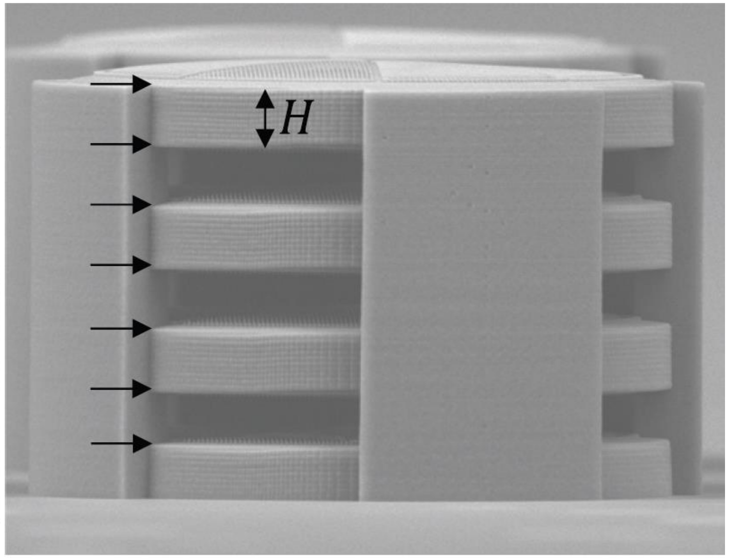
Low shrinkage and **high mechanical stability**



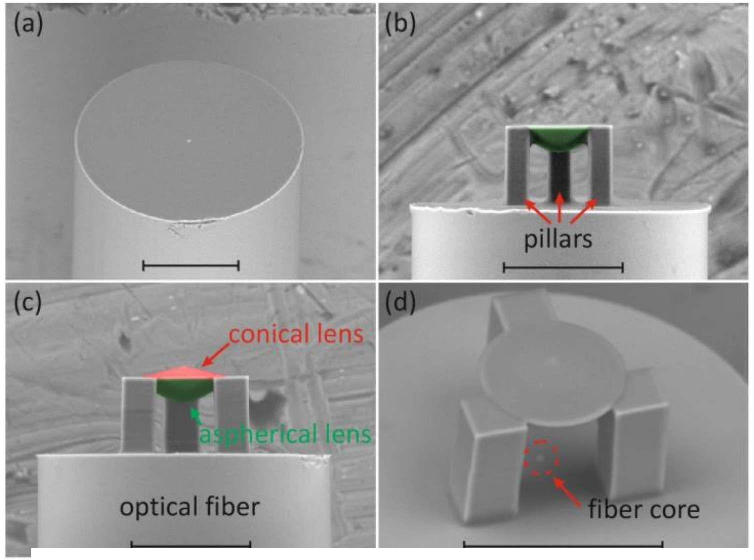
Gradient chain-mail 1 mm long (with support walls).
L. Jonušauskas et al., Opt. Express. ***27****(11), 15205 (2019).*



Microanimals fabricated by two-photon lithography.
M. Malinauskas et al., J. Opt. ***12****(3), 8 (2010).*

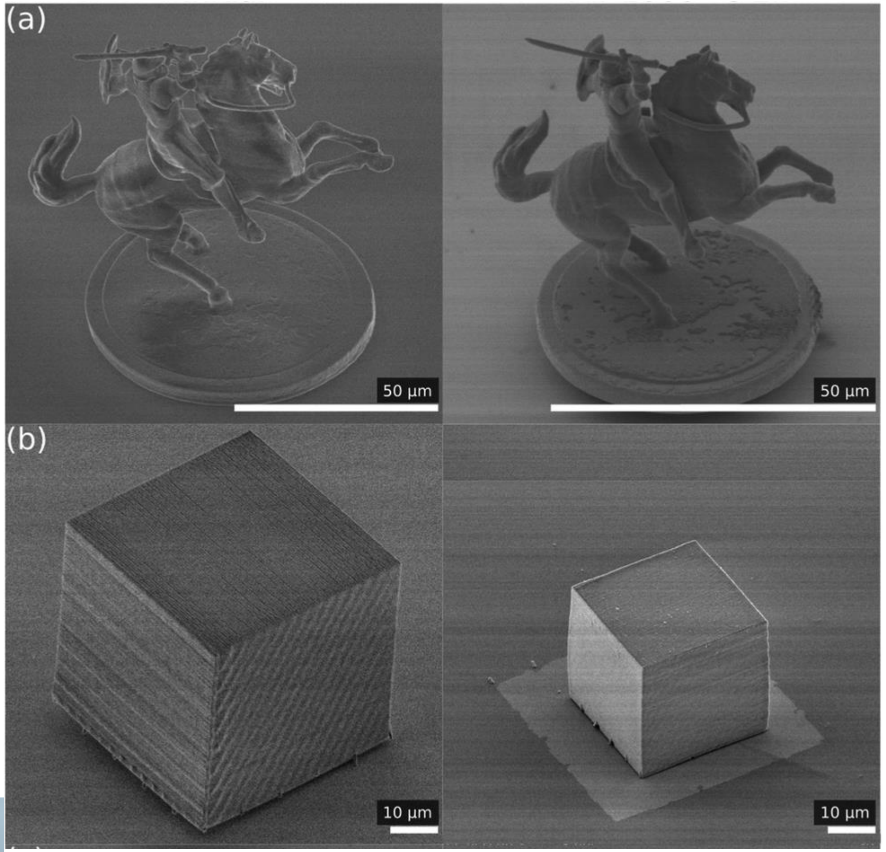


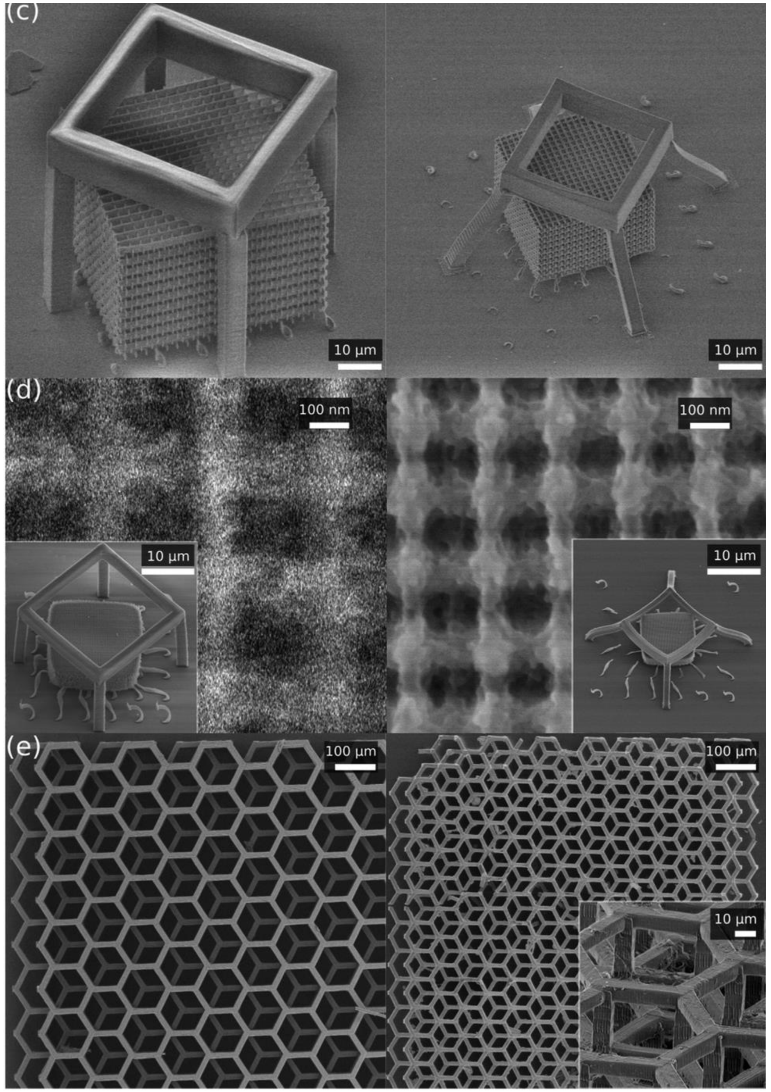
30 µm 3D metasurfaces. *S. Varapnickas et al., Appl. Phys. Lett.* ***118****, 151104 (2021).*



Micro optical components on top of a fiber.
A. Zukauskas et al., JLMN, ***9****(1), 68 (2014).*

Geometry and size independent isotropic downscaling

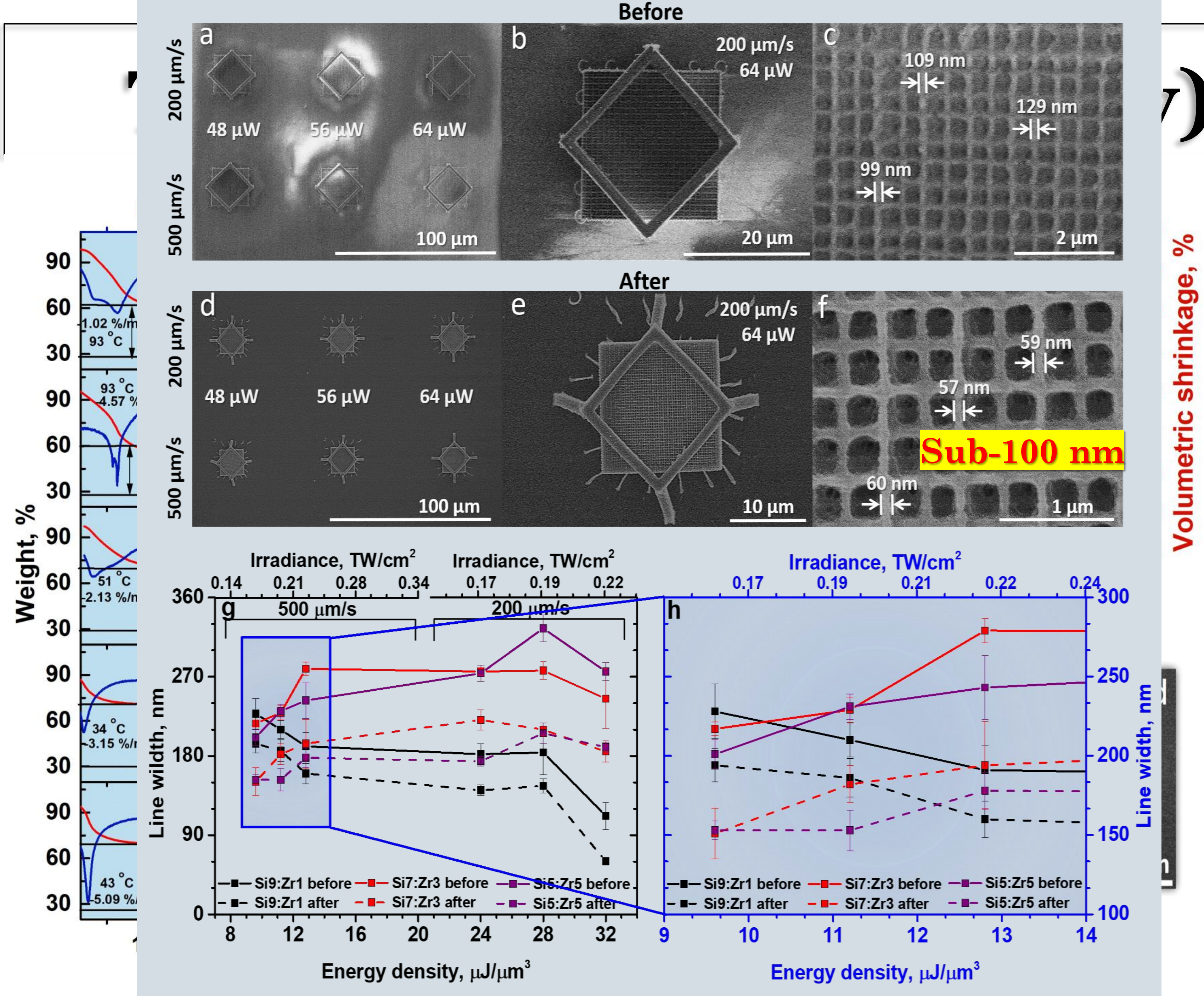




Reached volume change 40–50% *(dependent on the annealing protocol)*

- Free-form structures
- Bulky structures
- 3D periodic structures
- Sub-100 nm features
- Super-5 mm sizes

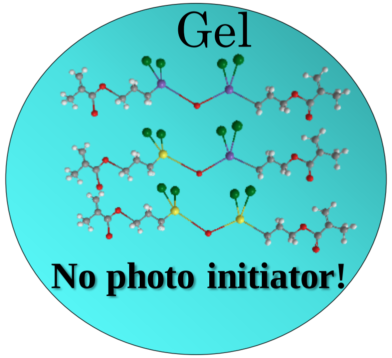
D. Gailevičius, *Nanoscale Horiz.* 4, 647 (2019)



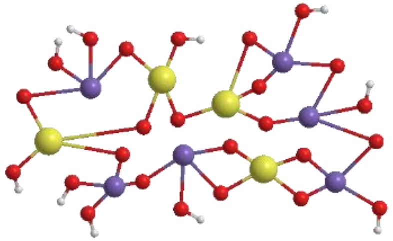
G. Merkininkaitė et al., *Opto-Electron Adv* 5, 210077 (2022); doi: 10.29026/oea.2022.210077

TECHNOLOGY

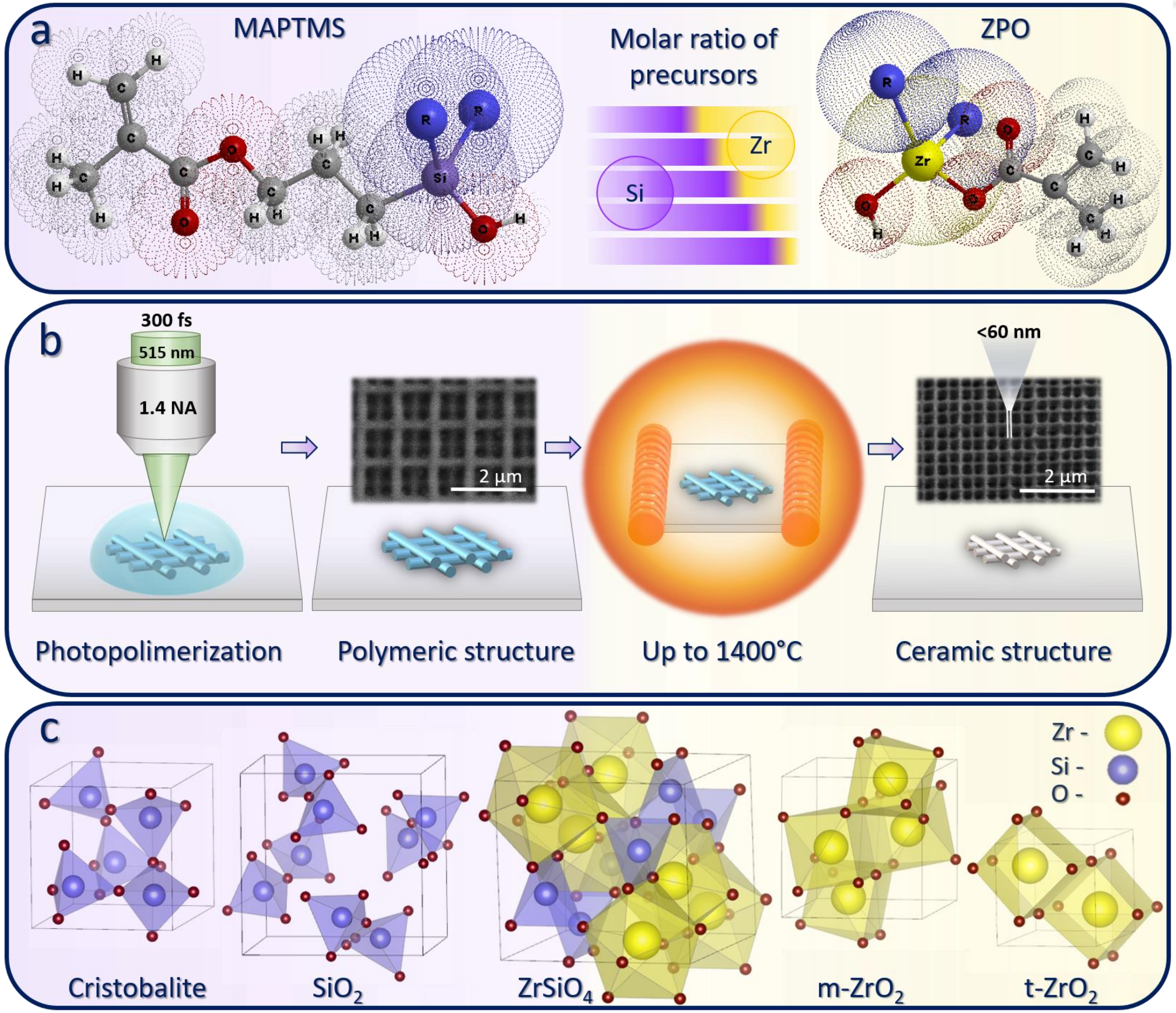
Synthesis



Laser Writing



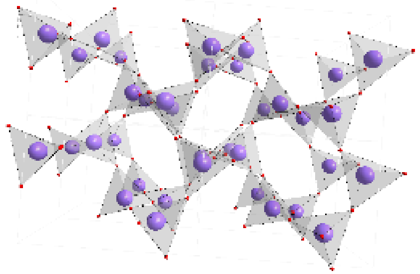
Heat Treatment

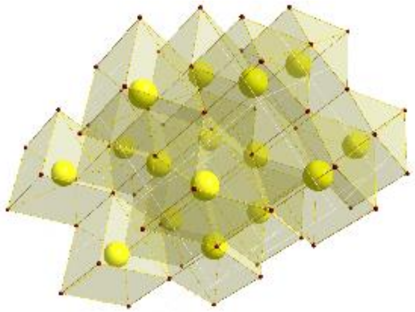


G. Merkininkaitė, Opto-Electron. Adv. **5**, 210077 (2022); 10.29026/oea.2022.210077

Cristabolite – exotic material;
$ZrSiO_4$ – diamond like (hard);
t-ZrO_2 – abrasion resistant;
m-ZrO_2 – biomaterial.

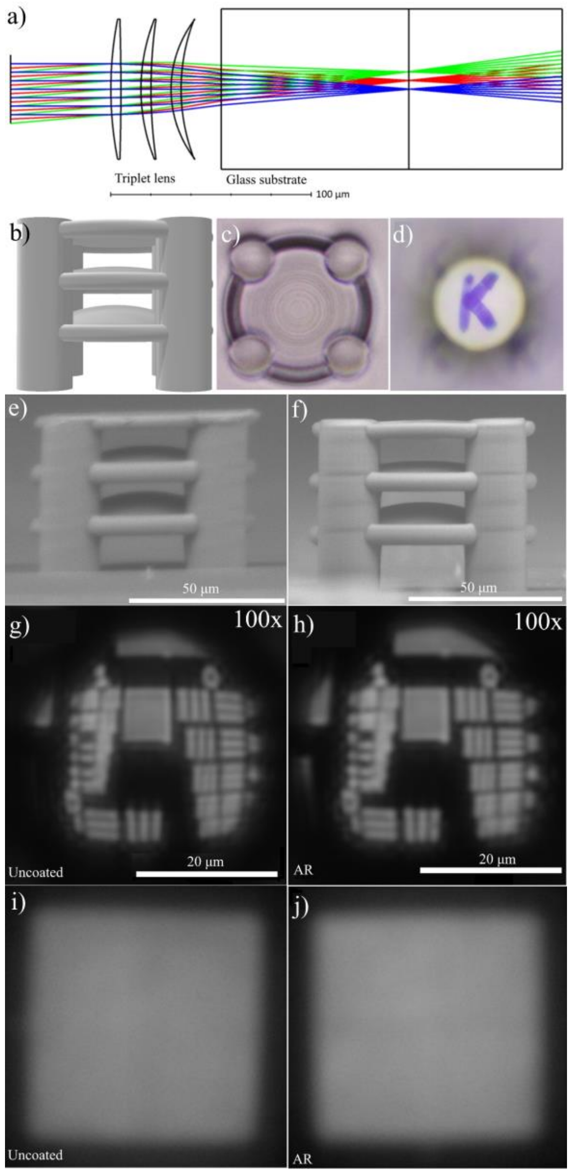
Amorphous glass



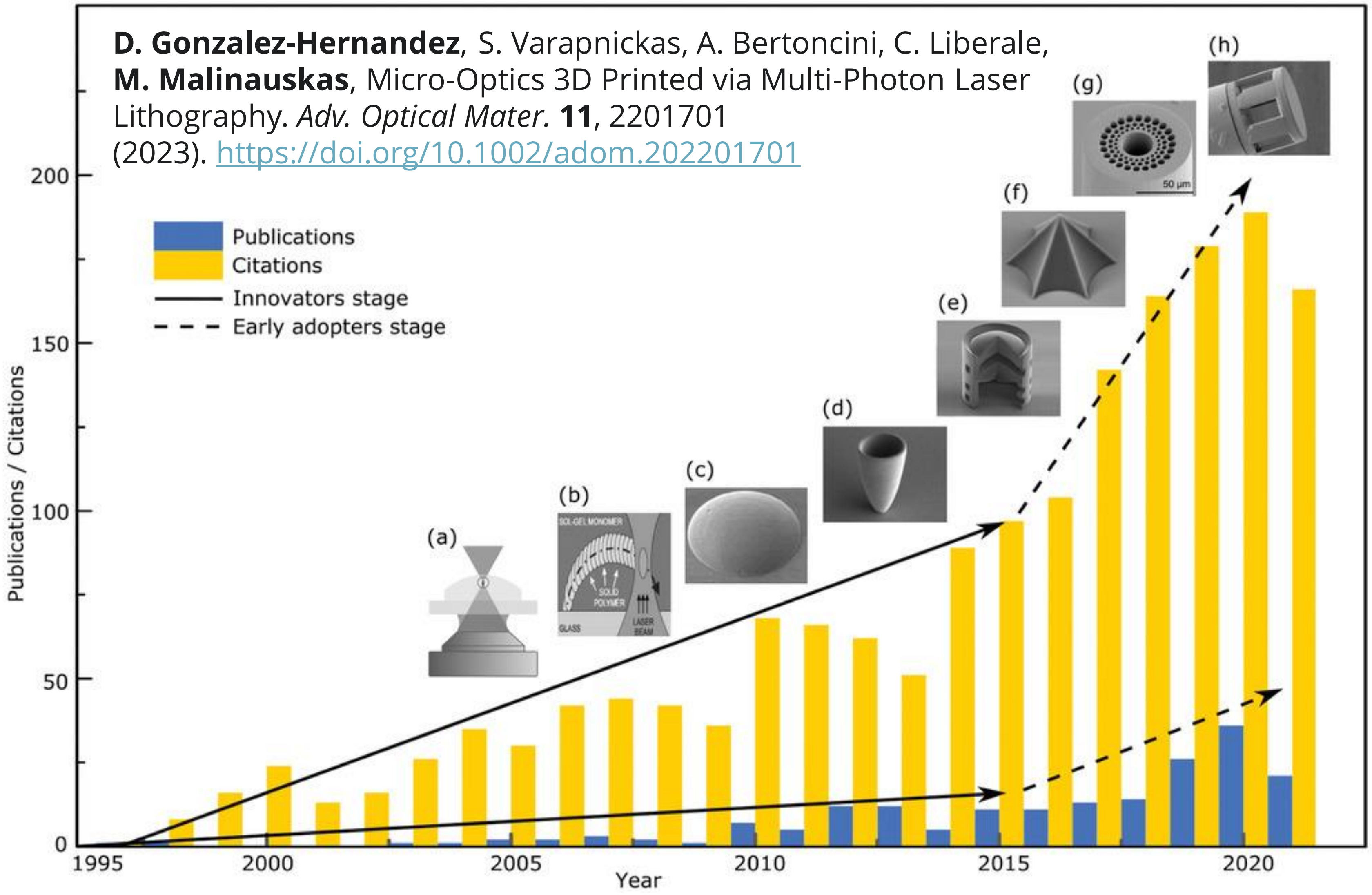


Crystalline ceramic

Micro-Optics as immediate application



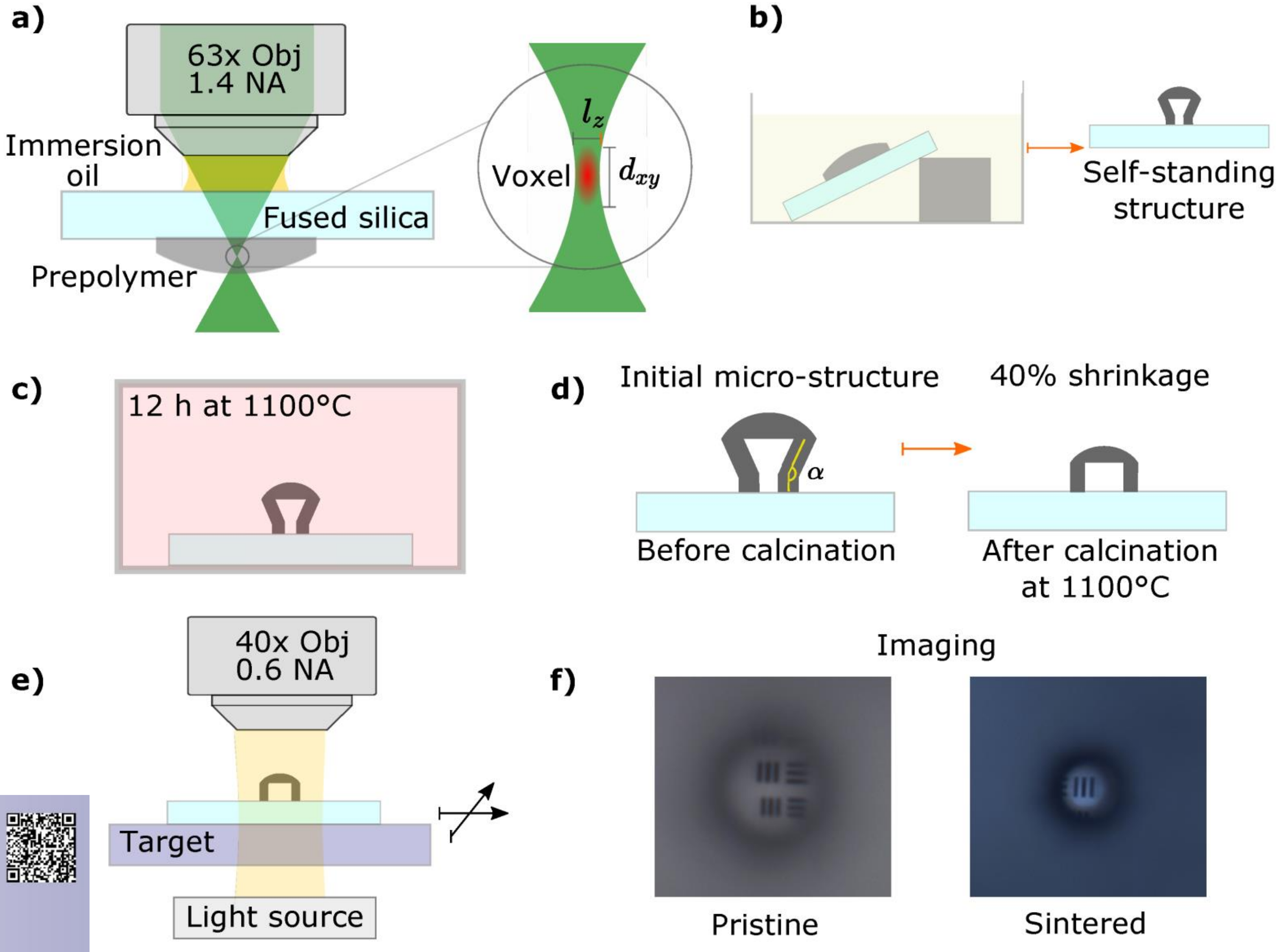
D. Gonzalez-Hernandez, S. Varapnickas, A. Bertoncini, C. Liberale, **M. Malinauskas**, Micro-Optics 3D Printed via Multi-Photon Laser Lithography. *Adv. Optical Mater.* **11**, 2201701 (2023). https://doi.org/10.1002/adom.202201701



τ = 300 fs
λ = 515 nm
ν = 200 kHz

Microscope objective: 63x 1.4 NA (oil immersion)
v = 500 µm/s
I = from 0.23 to 0.37 TW/cm^2

T = 1100 °C
t = 12 h.



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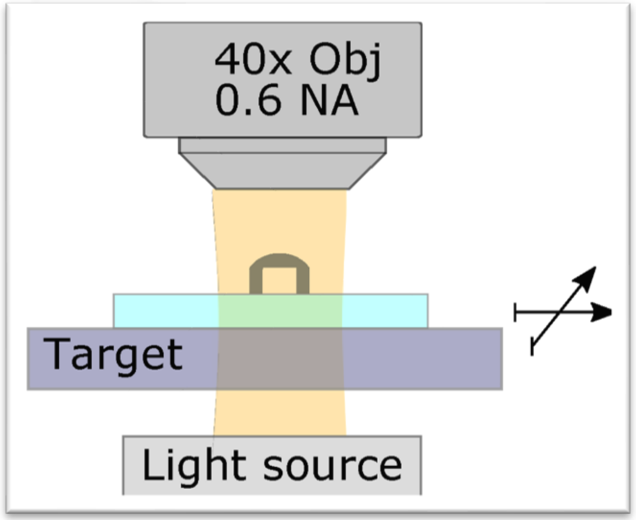
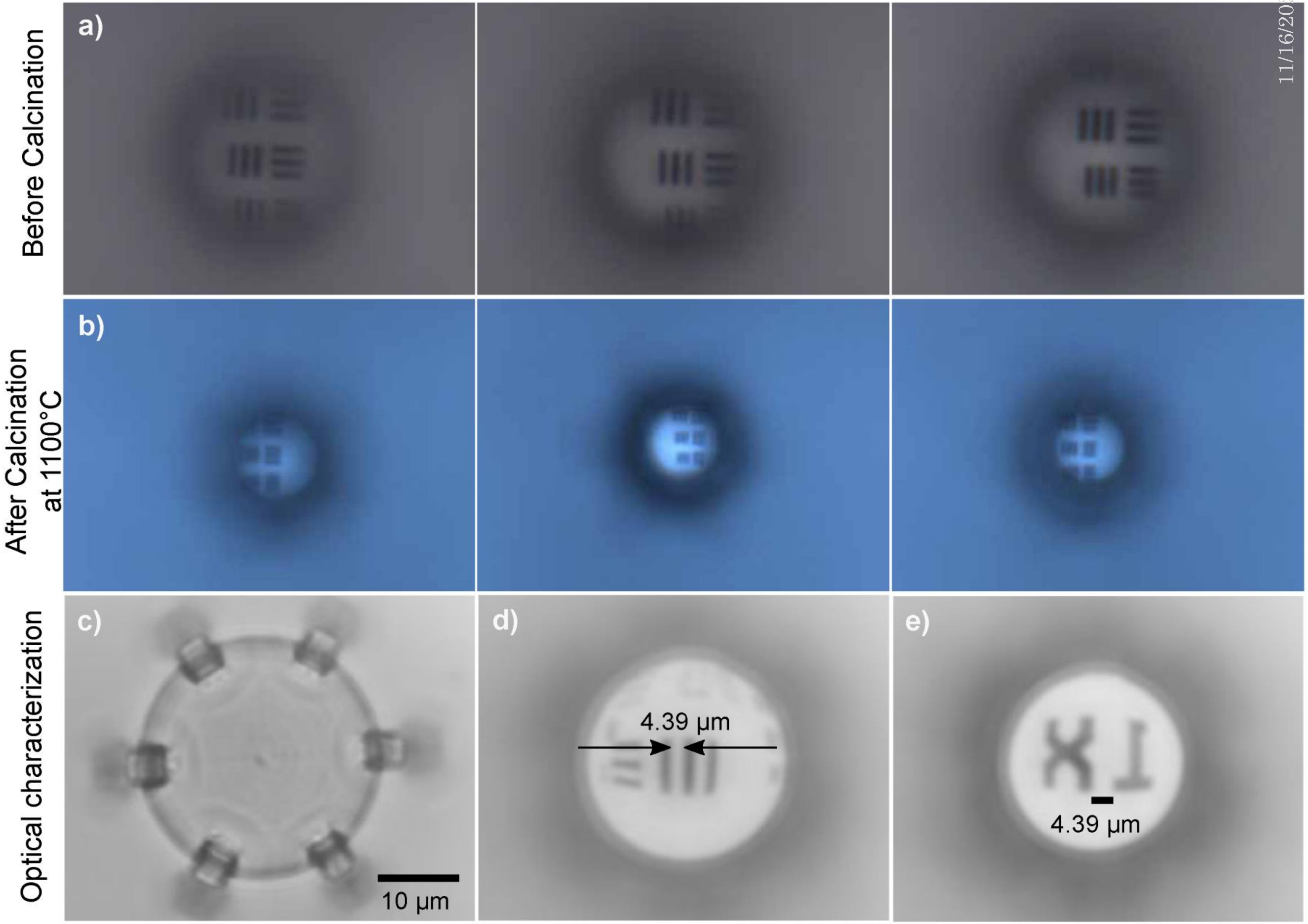
Laser 3D Printing of Inorganic Free-Form Micro-Optics

Diana Gonzalez-Hernandez; Simonas Varapnickas; Greta Merkininkaitė; Arūnas Čiburys; Darius Gailevičius; Simas Šakirzanovas; Saulius Juodkazis; Mangirdas Malinauskas

Photonics 2021, Volume 8, Issue 12, 577

Imaging performance

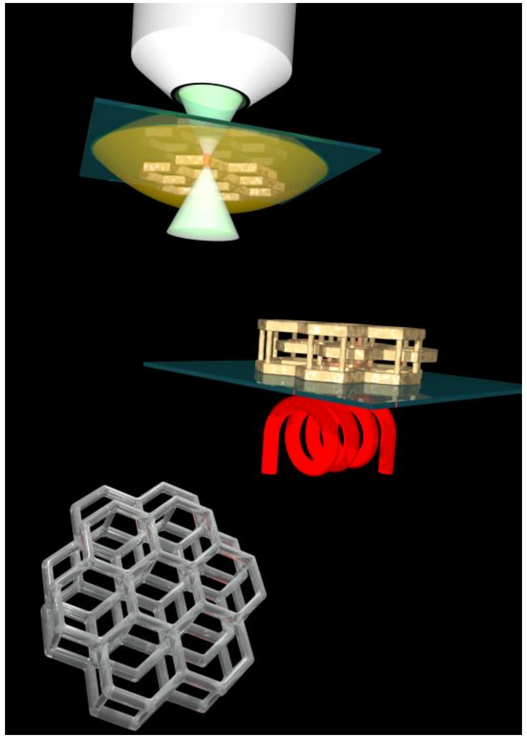


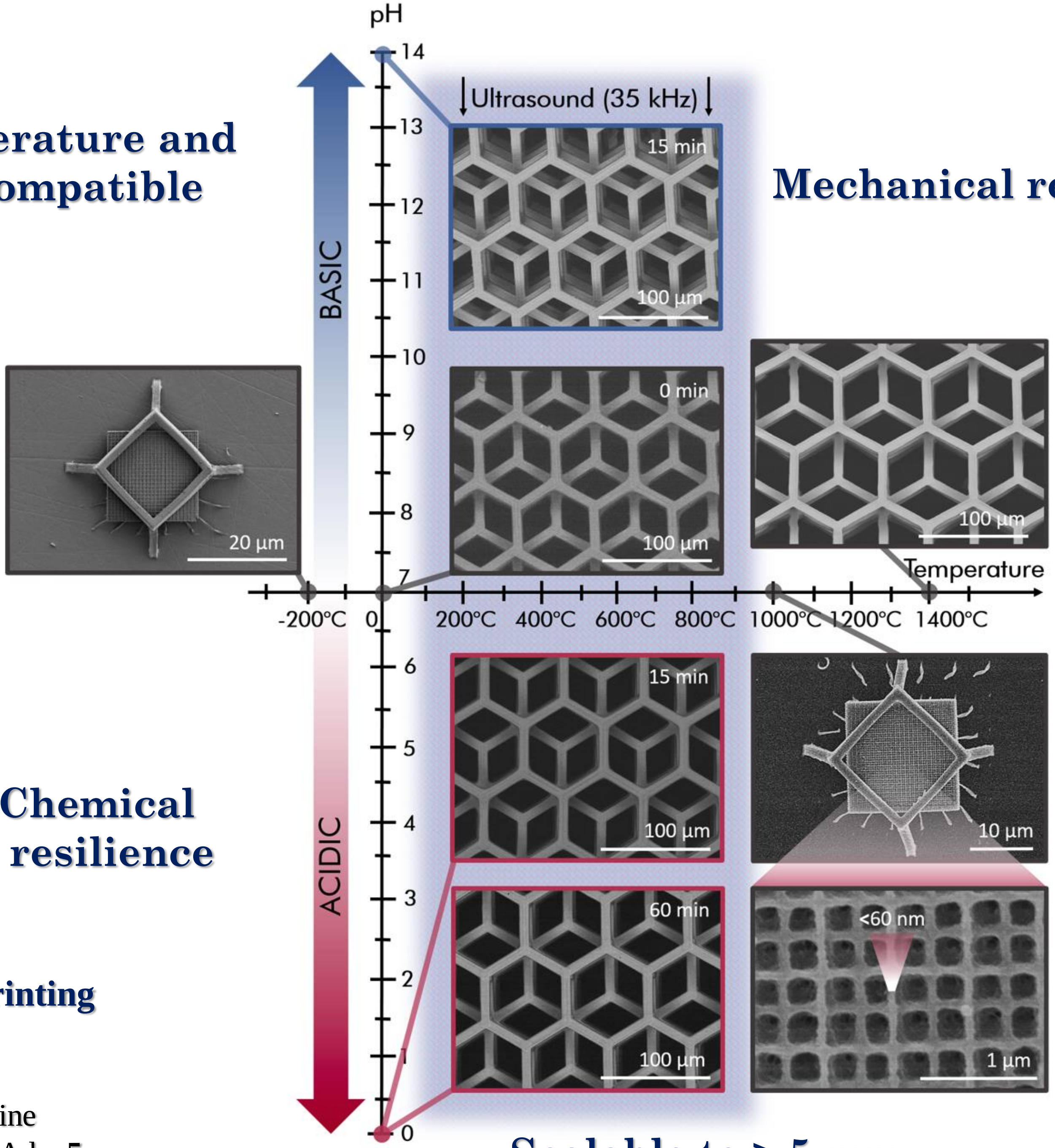


Low temperature and vacuum compatible

Mechanical resilience

Temperature resistant to > 1000 – 1400 °C





Chemical resilience

Ultra-high precision: Features of 60 nm

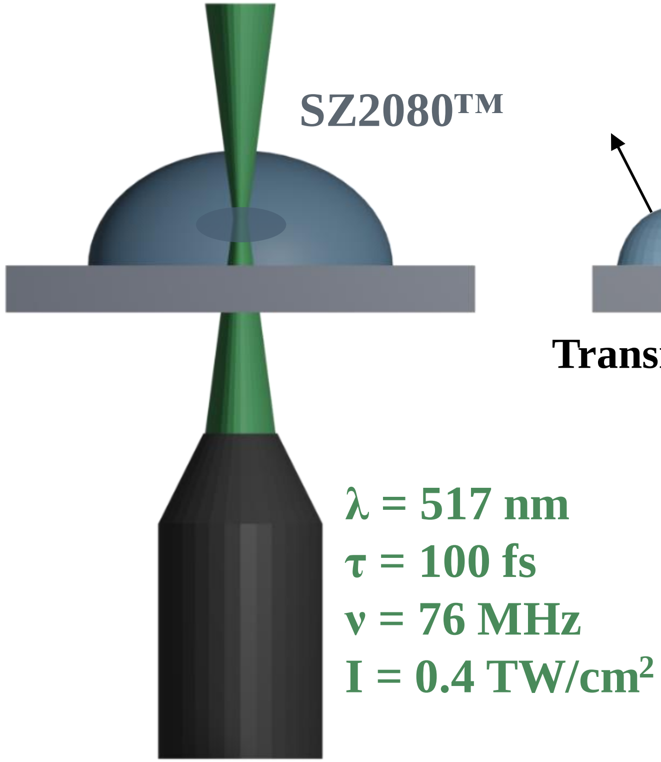
Scalable to > 5 mm

2PP super-powered for 3D nanoprinting of diverse inorganics:
G. Merkininkaite et al., Laser additive manufacturing of Si/ZrO_2 tunable crystalline phase 3D nanostructures, Opto-Electron. Adv. **5**, 210077 (2022); 10.29026/oea.2022.210077

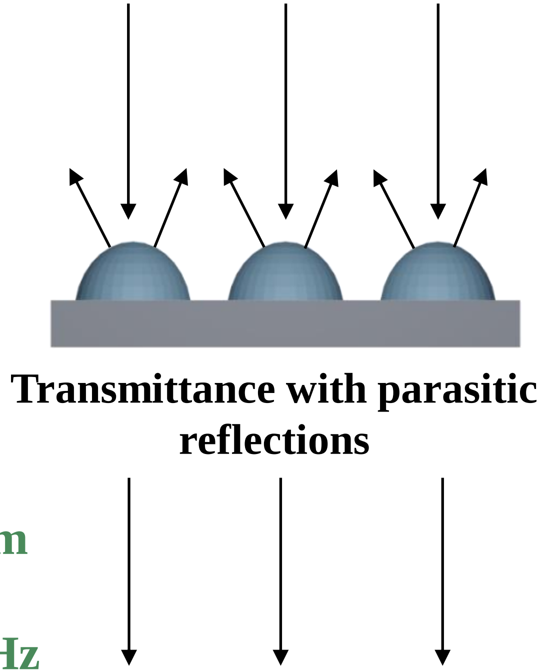
Deposition of antireflective coating on micro-lenses

CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

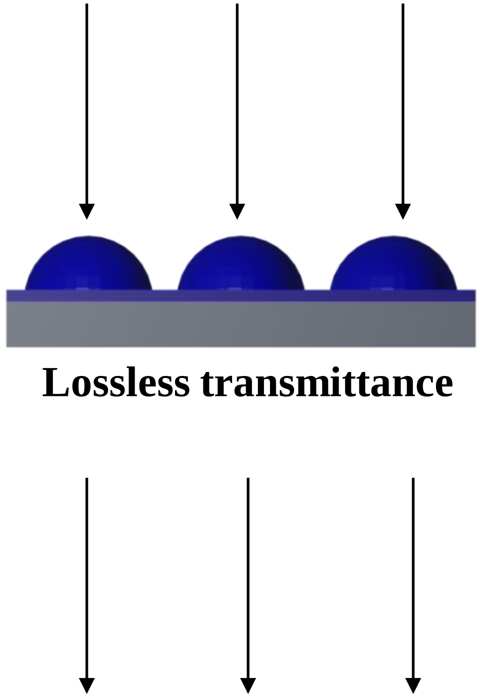
i. Laser direct writing (LDW)



ii. Polymerized micro-lenses



iii. Micro-lenses with ALD AR coating



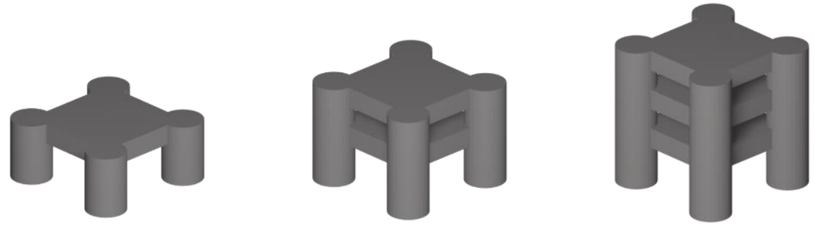
Vilnius University

K. Galvanauskas,
Dr. D. Gailevičius,
Prof. M. Malinauskas

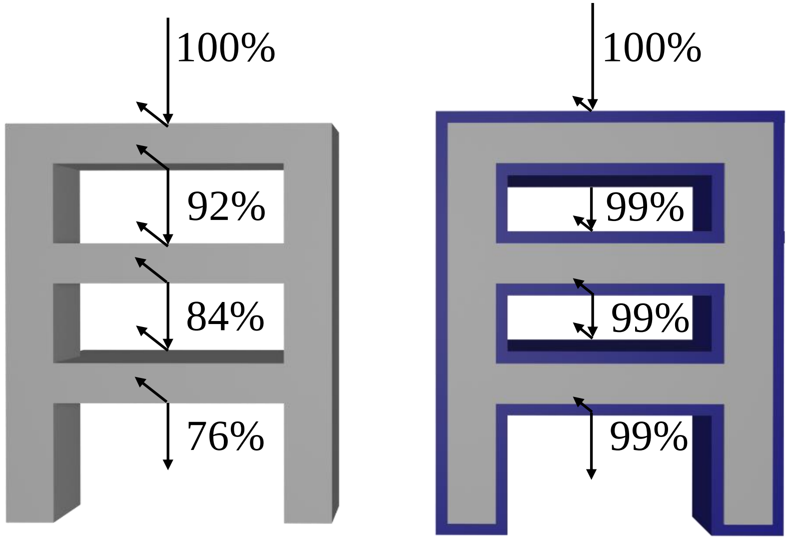
Fabrication of highly transparent micro-optics combining LDW and ALD.

Darija Astrauskytė, … **Dr. Lina Grinevičiūtė**,
"Anti-Reflective Coatings Produced via Atomic Layer Deposition for Hybrid Polymer 3D Micro-Optics." *Nanomaterials* **13**(16), 2281 (2023).

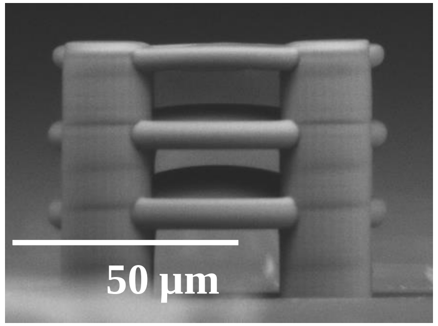
Transmittance of the stacked microstructures

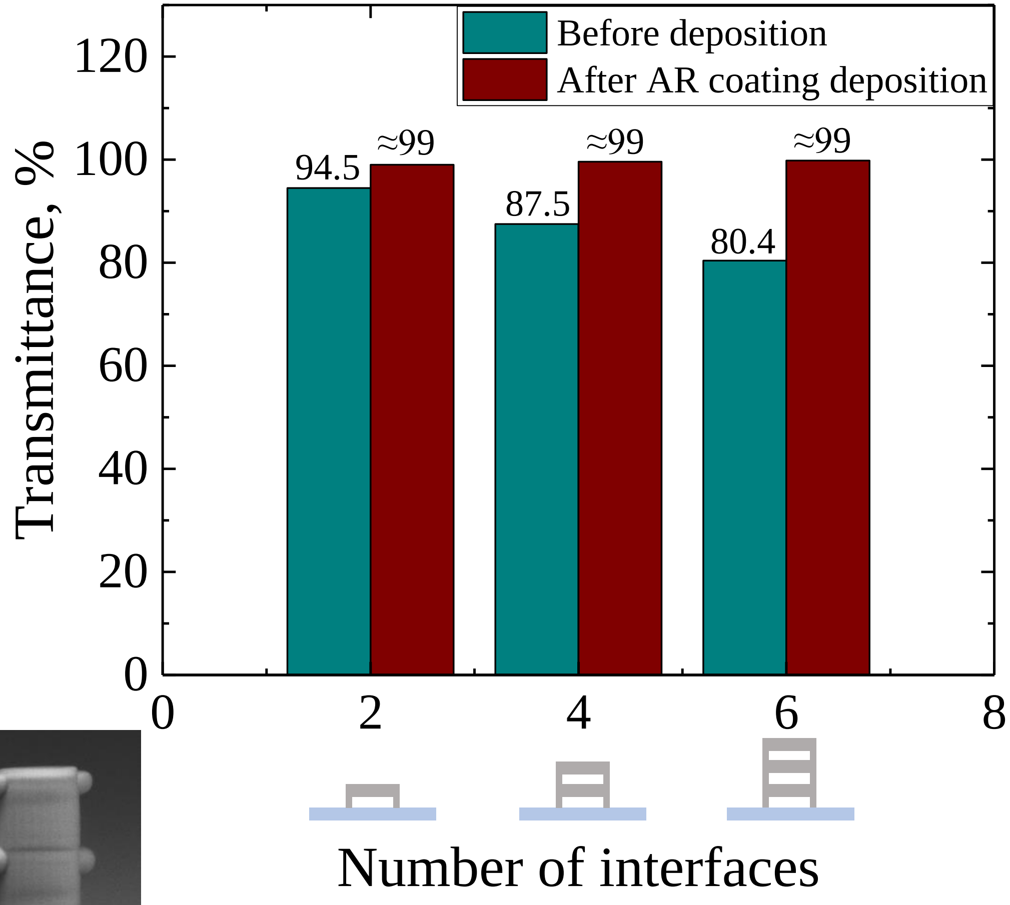


Two surface microstructure | Four surface microstructure | Six surface microstructure



A comparison between uncoated and AR-coated stacked microstructures.



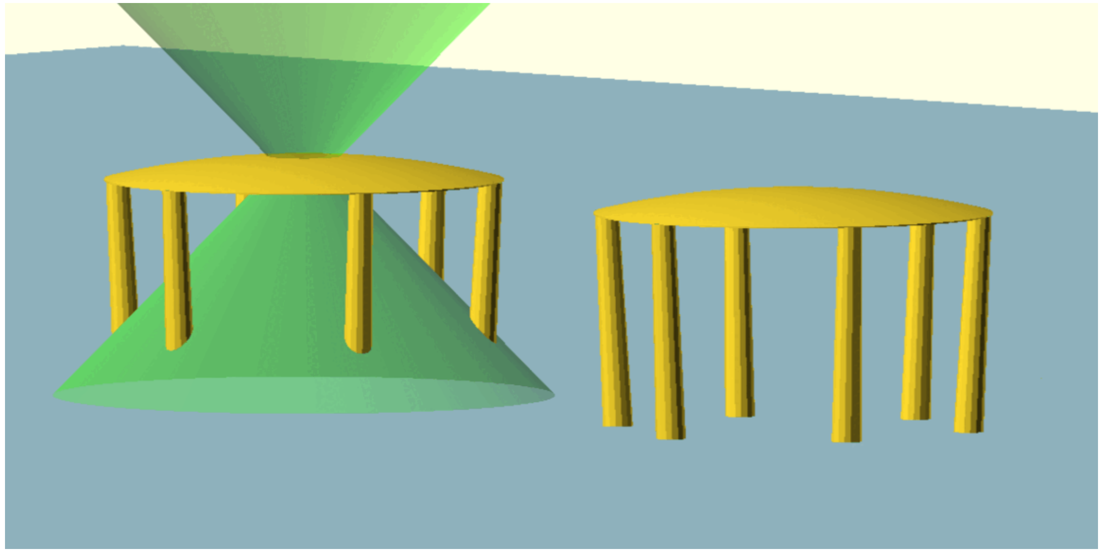


Transmittance of the stacked microstructures at the wavelength of 633 nm.

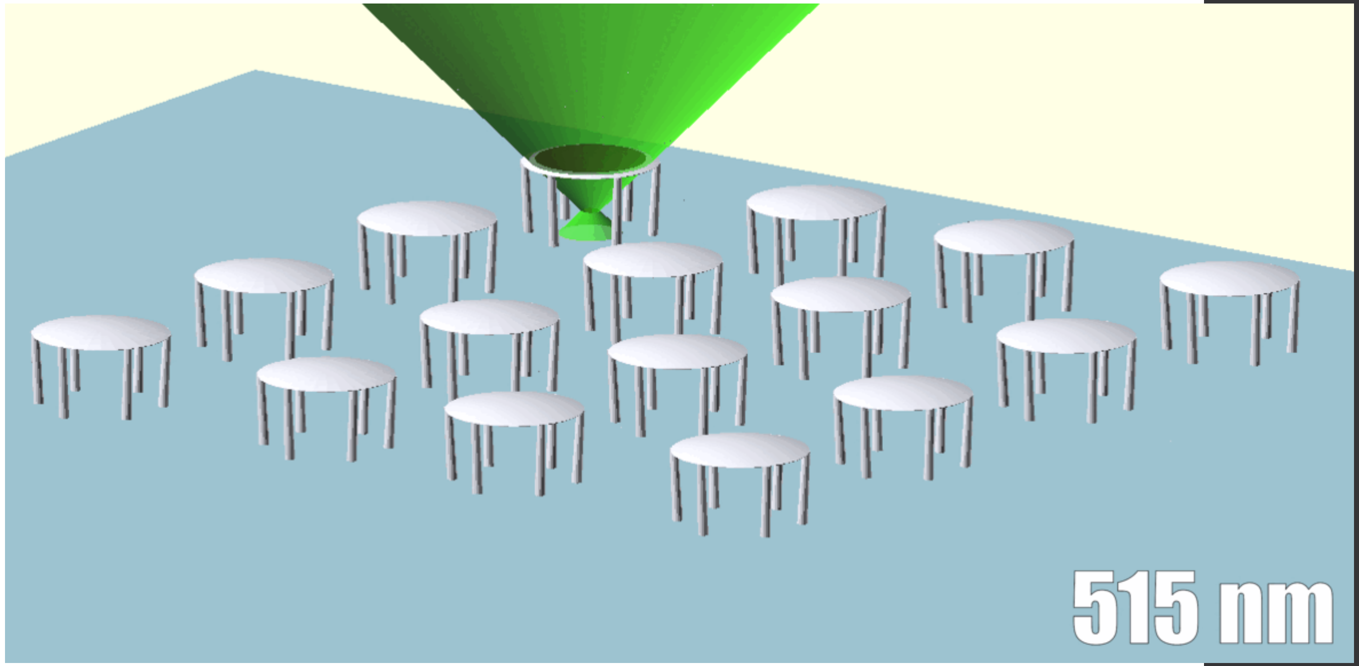
K. Galvanauskas et al. “High-transparency 3D micro-optics of hybrid-polymer SZ2080™ made via Ultrafast Laser Nanolithography and atomic layer deposition,” *Opt. Open* 104228 (2023).

Laser-induced damage threshold tests

- Localized damage (4 µm);
- Non-localized damage (up to 20 µm);



Optical damage experiment principle



S-on-1 Laser damage setup

$$\lambda = 1030, 515\ nm$$
$$f = 200\ kHz$$
$$t = 300\ fs$$
$$Objective\ 20x\ NA = 0.8$$
$$50\ ms - 5\ s\ exposure$$
$$Localized\ - 4\ \mu m\ diameter\ 1/e^2$$
$$Nonlocalized\ - 20\ \mu m\ diameter\ 1/e^2$$

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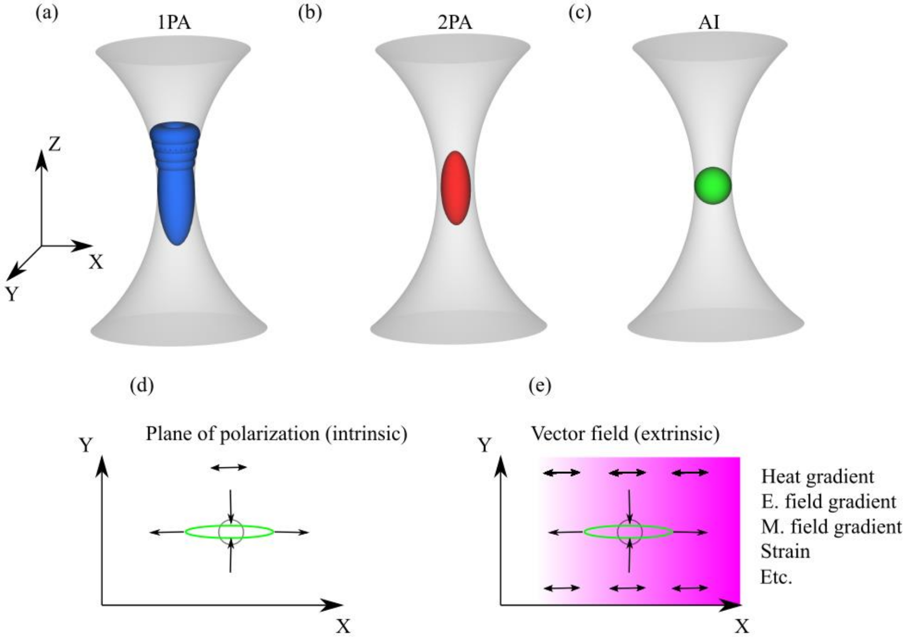
Calcination-Enhanced Laser-Induced Damage Threshold of 3D Micro-Optics Made with Laser Multi-Photon Lithography

Darius Gailevicius; Rokas Zvirblis; Karolis Galvanauskas; Gintare Bataviciute; Mangirdas Malinauskas

Photonics **2023**, Volume 10, Issue 5, 597

My time is over, but not Yours ;-)

- Questions?
- Comments!
- Discussions..



mangirdas.malinauskas@ff.vu.lt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Shelton PhotoWorks