3D Fabrication via Two-Photon Lithography Direct Laser Writing

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Institut Català de Nanociència i Nanotecnologia
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Brief History of 3D Printing/Additive Manufacturing (AM)

Pre 1970s
Beginnings of AM
Talks of additive layering

1981
Hideo Kodama Patent
Layer by layer UV printing in photoresins

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2000s
Modern Day
Widespread conventional printers

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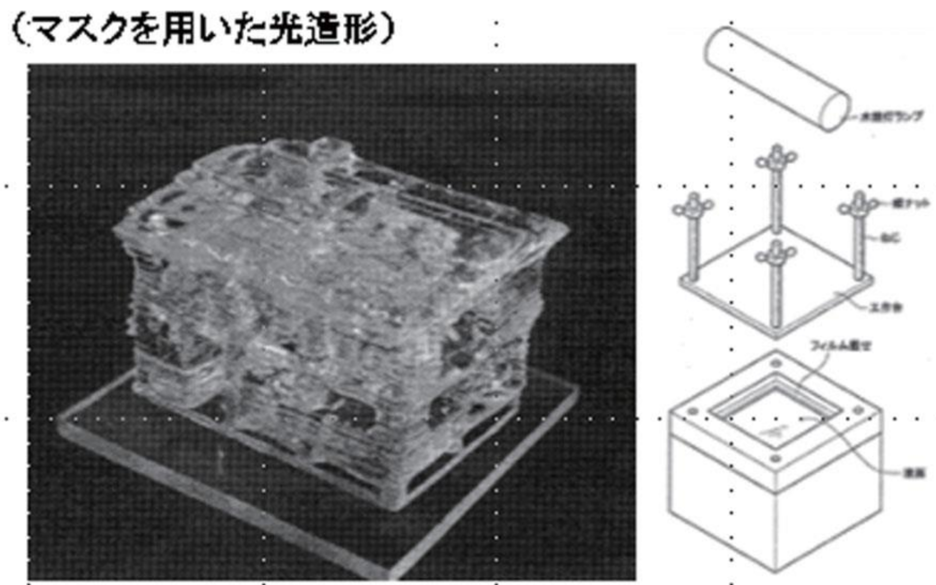
- UV light to harden photoreactive polymers for rapid prototyping
- Creation of STL file type, used today
- At this time, even 2D printers were very expensive!



Kodama, H. JPS56144478A (1981)

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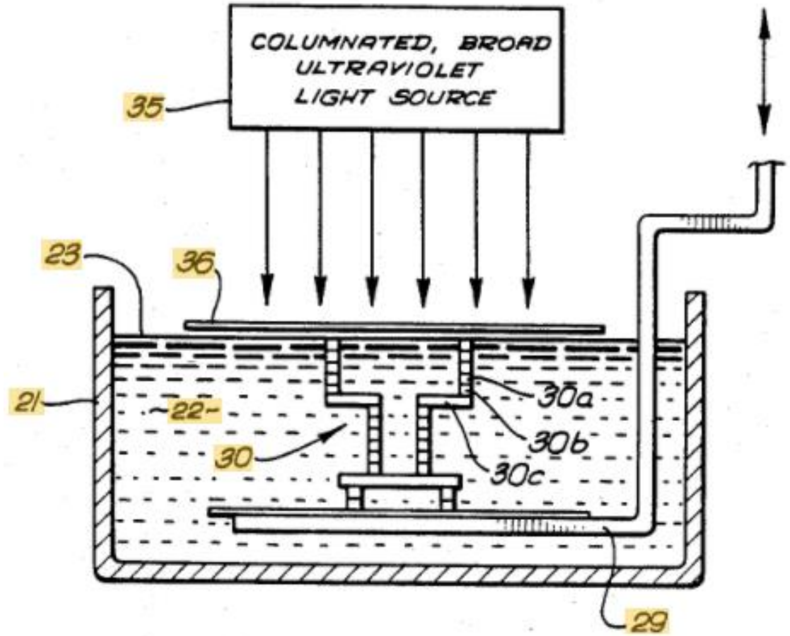
- Stereolithography: Computer controlled focused laser beam is drawn layer by layer in a liquid vat of photopolymer and crosslinked, elevator lowers each solidified layer
- Filed 3 weeks after French inventors



Hull, C. US4575330A (1986)

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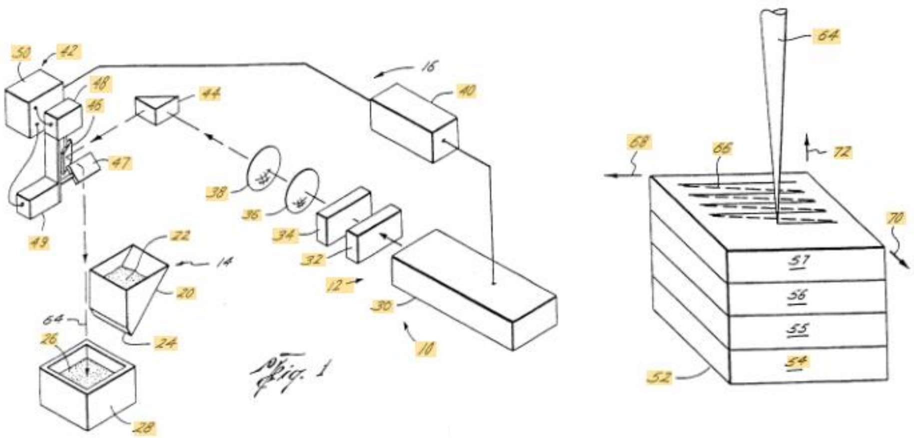
- Selective Laser Sintering (SLS): High power laser used to sinter (fuse) powdered material together, powder bed then lowered
- SLS today is applied to plastic, metal, ceramic, or glass (originally in polymers)



Deckard, C. US5597589A (1988)

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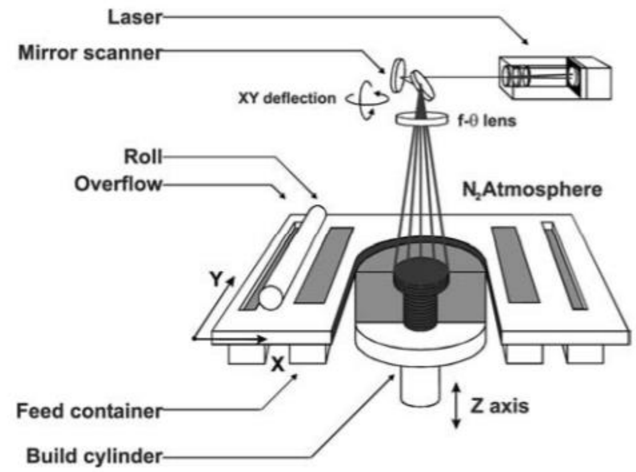
- Direct Metal Laser Sintering (DMLS): Extension of SLS to metals and other materials via partnership with Deckard
- Similar to SLS, using metal powders



Kruth, J-P., et al. *Rapid Prototyping Journal* 11 (1), 26-36 (2005)

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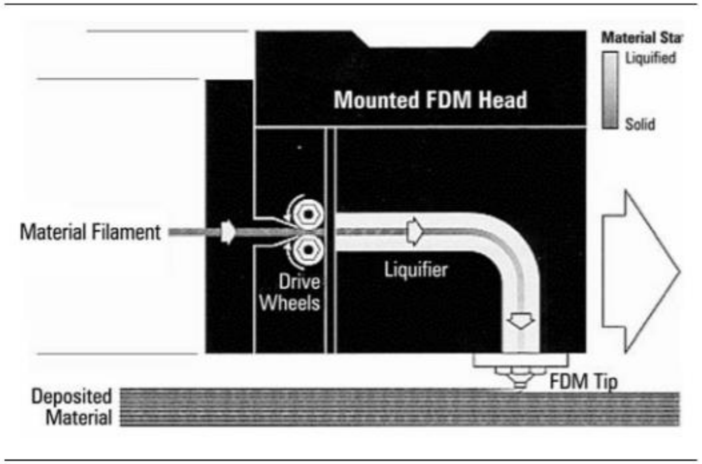
2000s — **Modern Day**: Widespread conventional printers

- Fused Deposition Modeling (FDM): Moving nozzle additively deposits hot liquid thermoplastic



Sung-Hoon, A., et al. *Rapid Prototyping* 8 (4), 248-257 (2002)

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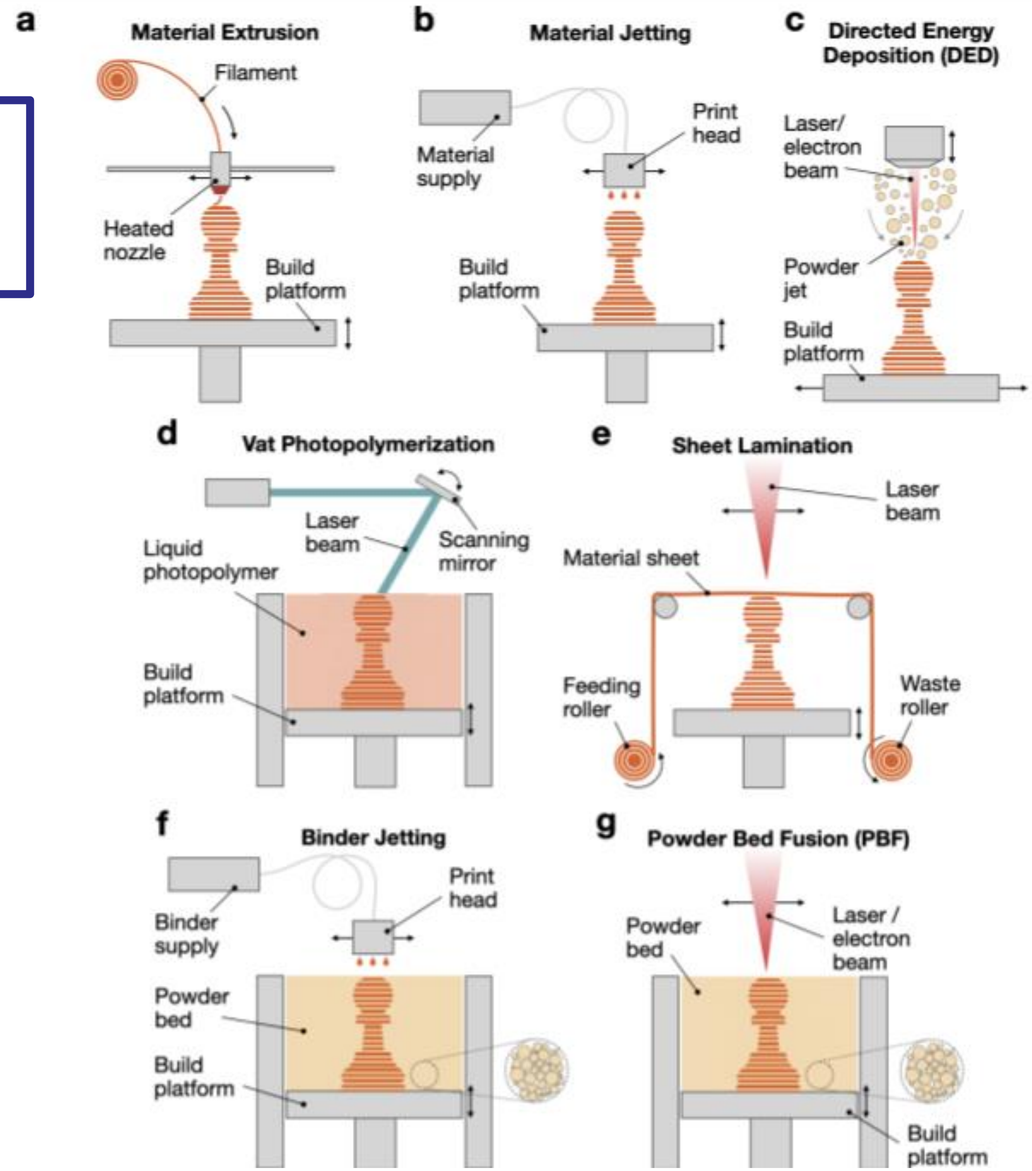
All of these inventions form the foundation of 3D printing/AM today!

Sung-Hoon, A., et al. *Rapid Prototyping* 8 (4), 248-257 (2002)

Crump, S., US5121329A (1989)

<u>Goal</u>: layer by layer fabrication of complex 3D structures with a large suite of different materials

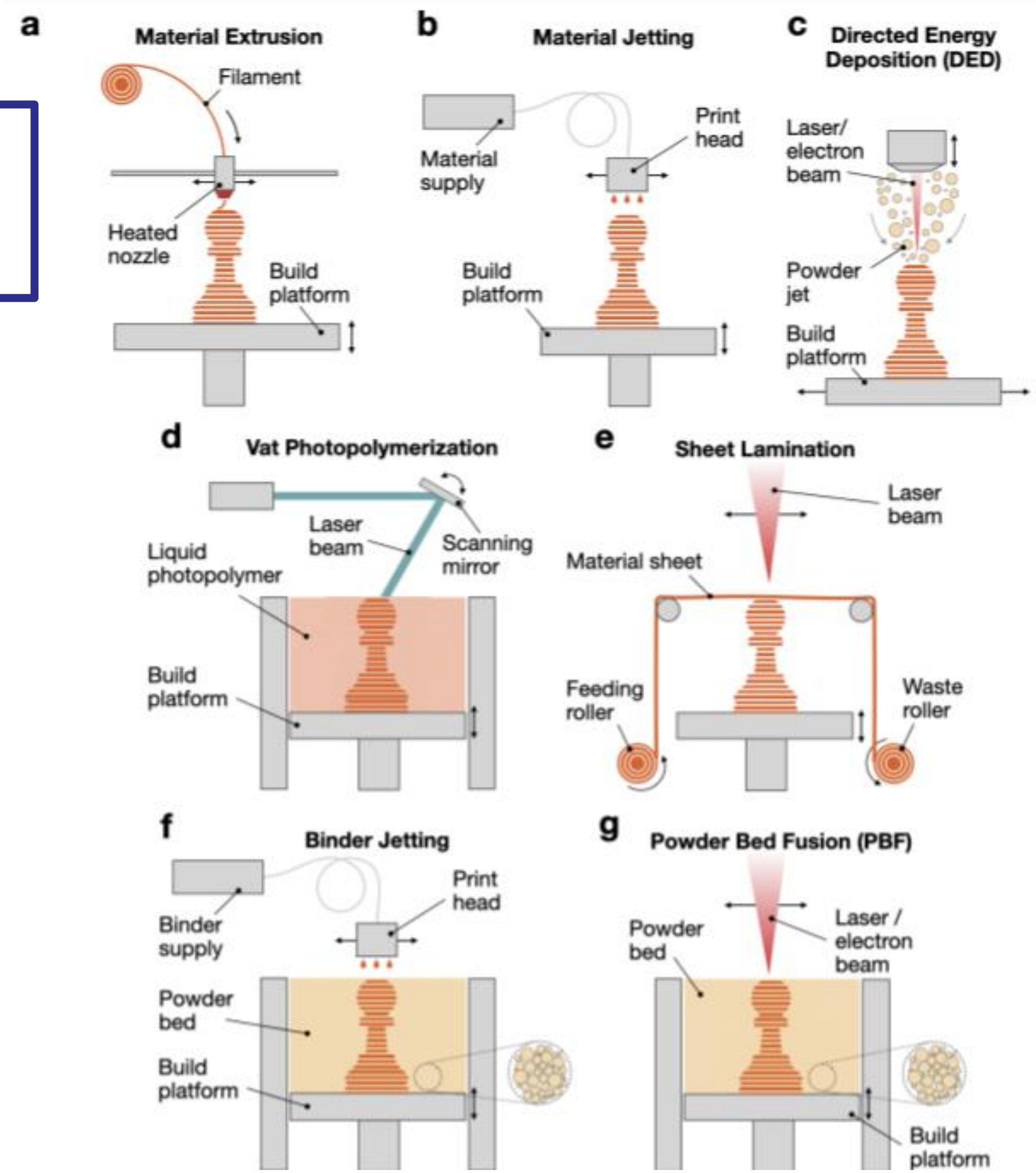


Vyatskikh, A., *Additive Manufacturing of 3D Nano-Architected Metals and Ceramics*. Thesis, Caltech. (2020)

AM Techniques Today

<u>Goal</u>: layer by layer fabrication of complex 3D structures with a large suite of different materials

- Traditionally enables fab in polymers/plastics



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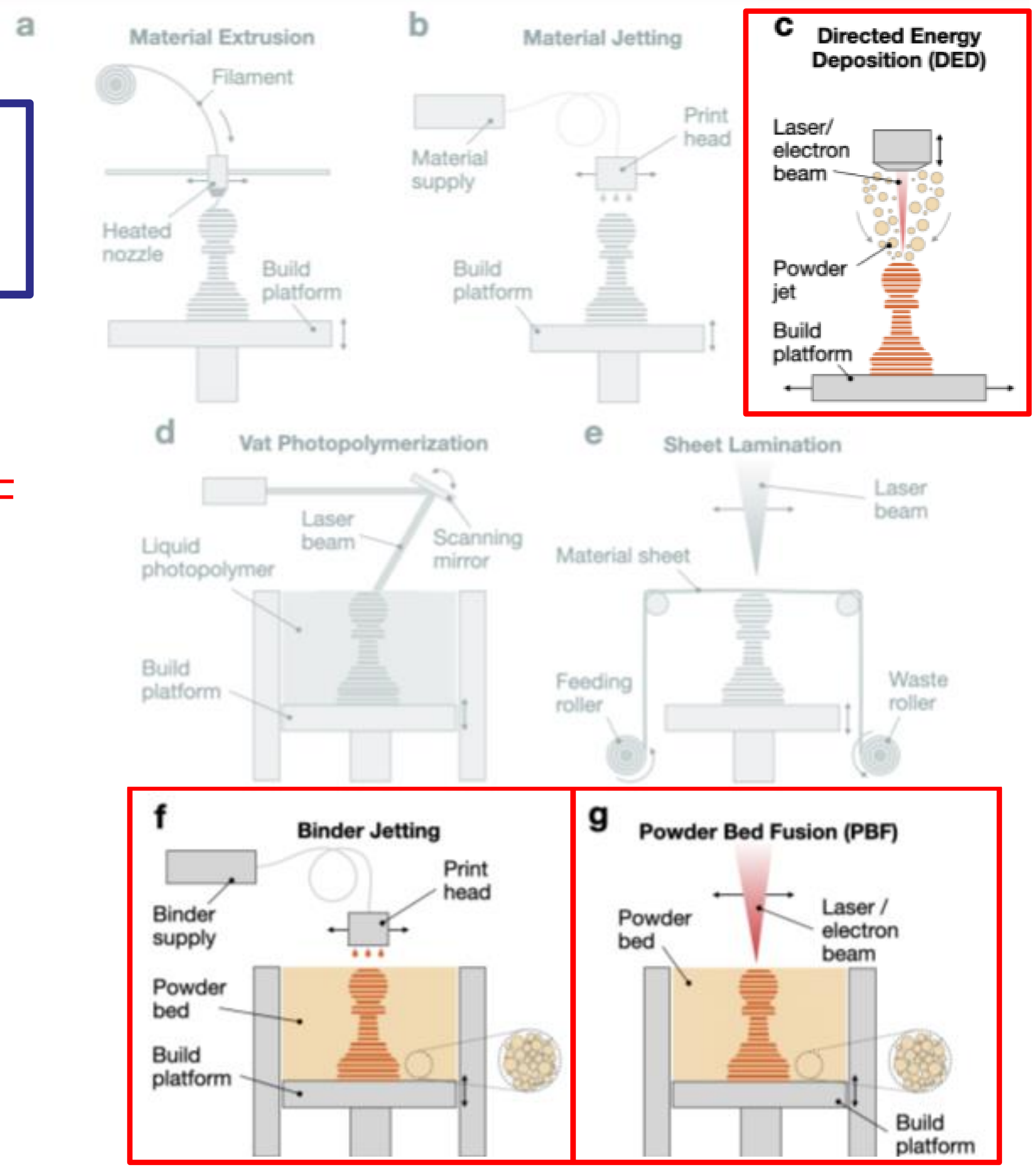
<u>Goal</u>: layer by layer fabrication of complex 3D structures with a large suite of different materials

- Traditionally enables fab in polymers/plastics
- Only DED, binder jetting, and PBF could make metal/ceramic parts



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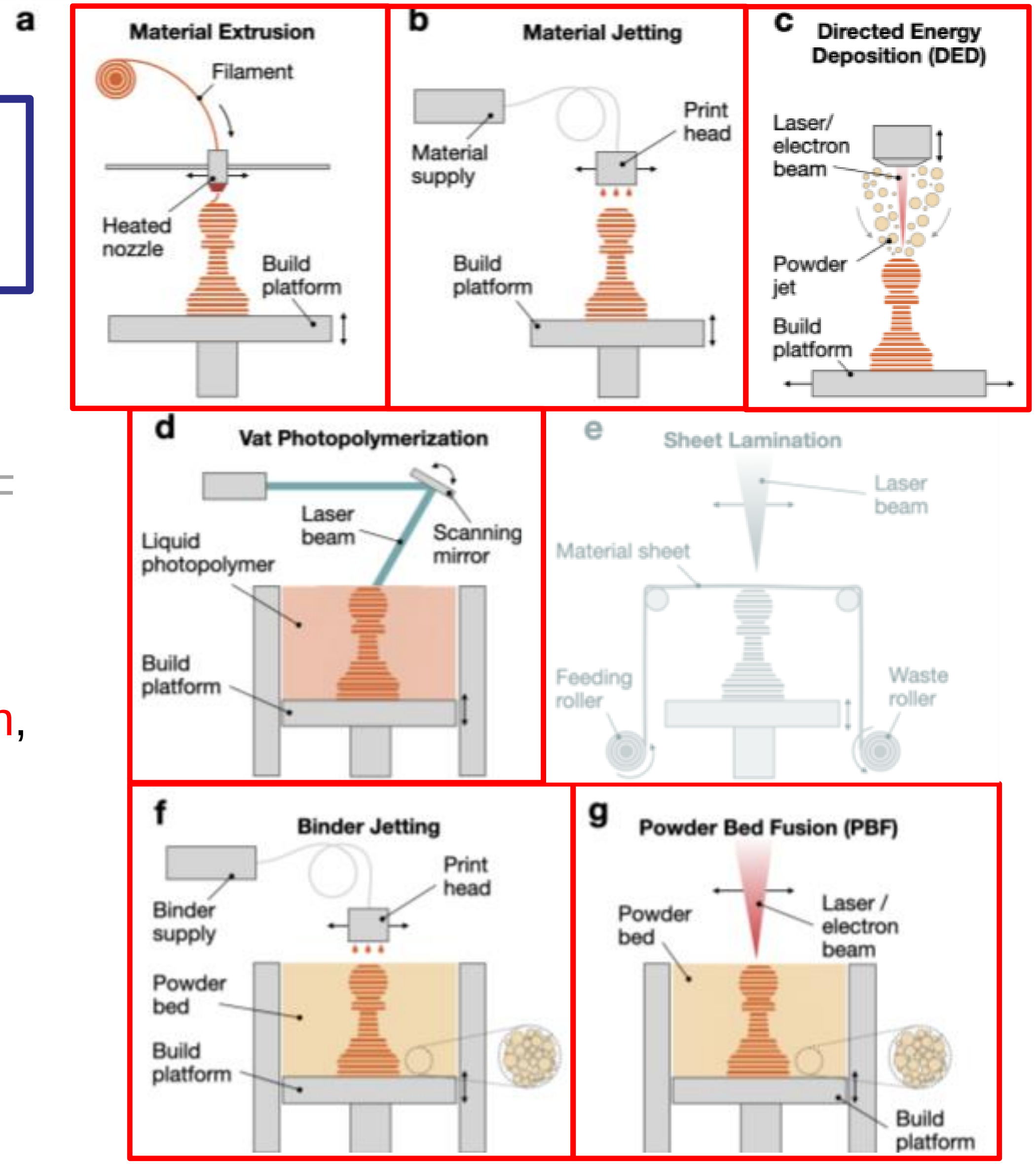
Goal: layer by layer fabrication of complex 3D structures with a large suite of different materials

- Traditionally enables fab in polymers/plastics
- Only DED, binder jetting, and PBF could make metal/ceramic parts
- Recent advances in AM have extended metal/ceramics to extrusion, vat photopolymerization, and material jetting

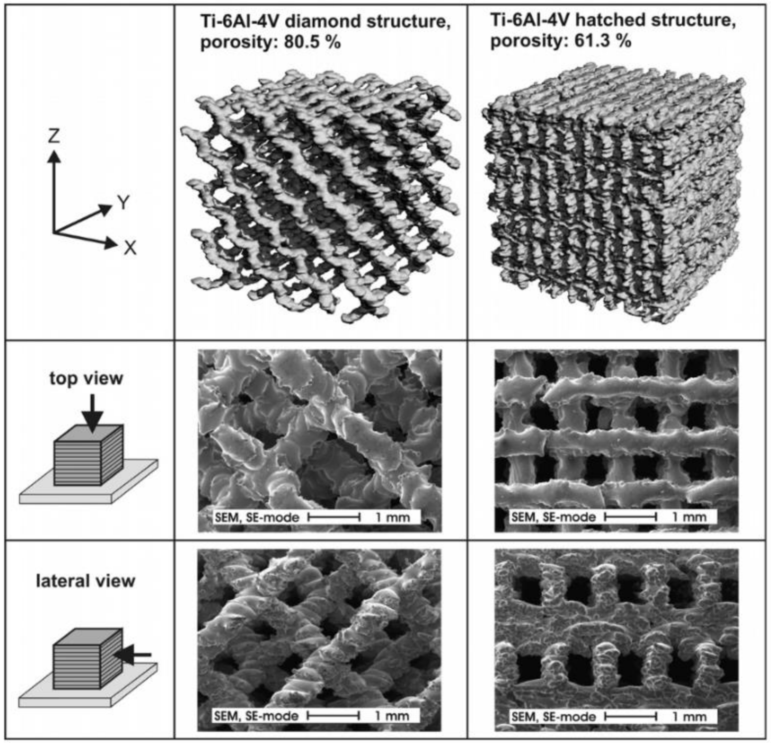


Vyatskikh, A., *Additive Manufacturing of 3D Nano-Architected Metals and Ceramics*. Thesis, Caltech. (2020)

Where is AM already used today?

- Rapid prototyping/manufacturing of parts in various materials (automotive, aerospace, medical industries, etc)
- Freedom of design (parts may not exist)
- Time and cost advantage, less material wasted

Kumar, L. J., et al. *Adv. in 3D Printing & Additive Manufacturing Technologies*, 39-54 (2016)



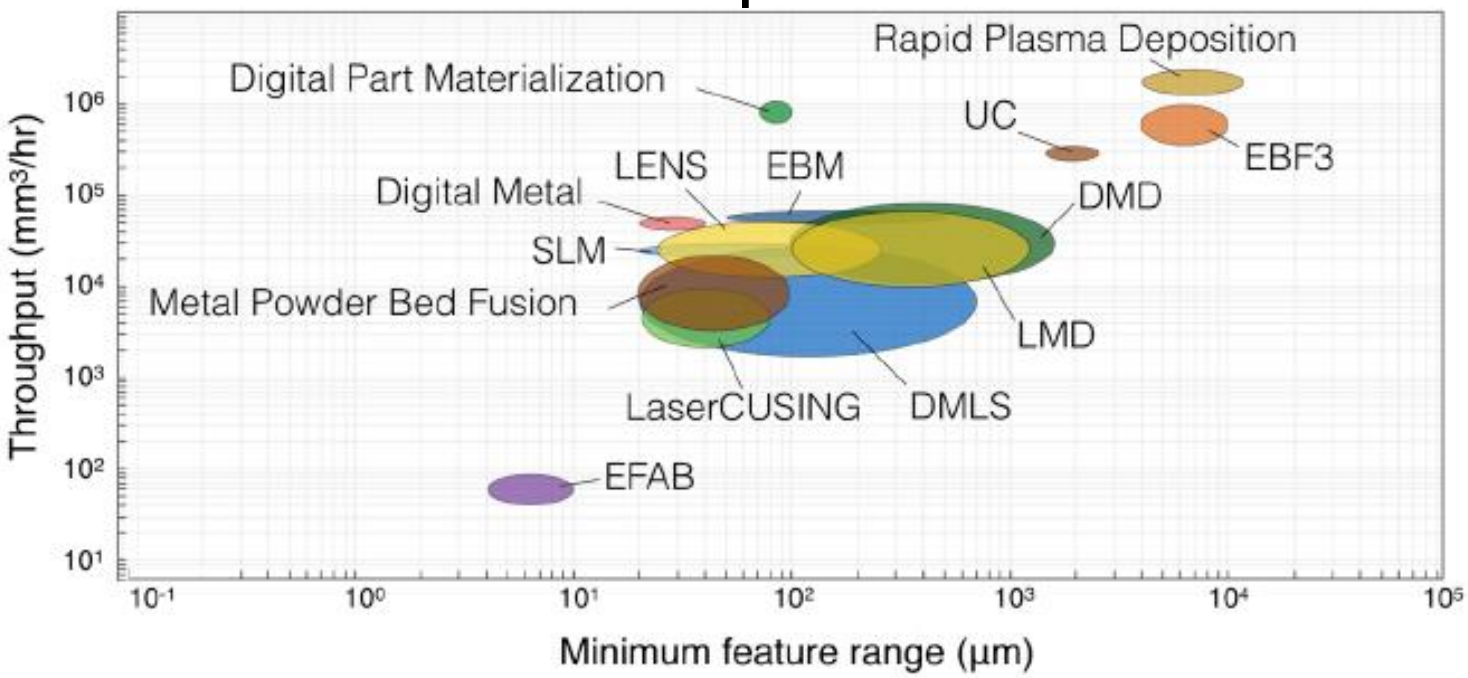
Heinl, P., et al. *Acta Biomaterialia* 4, 1536-1544 (2008)

www.metal-am.com

Limitations of AM as it stands

- Specific application requires specific materials/properties
- Often we are limited by the **resolution** or **throughput**
- For metals/ceramics, most commercial processes limited to ~20-50 um
- Highest resolution processes in polymers only

Metal processes



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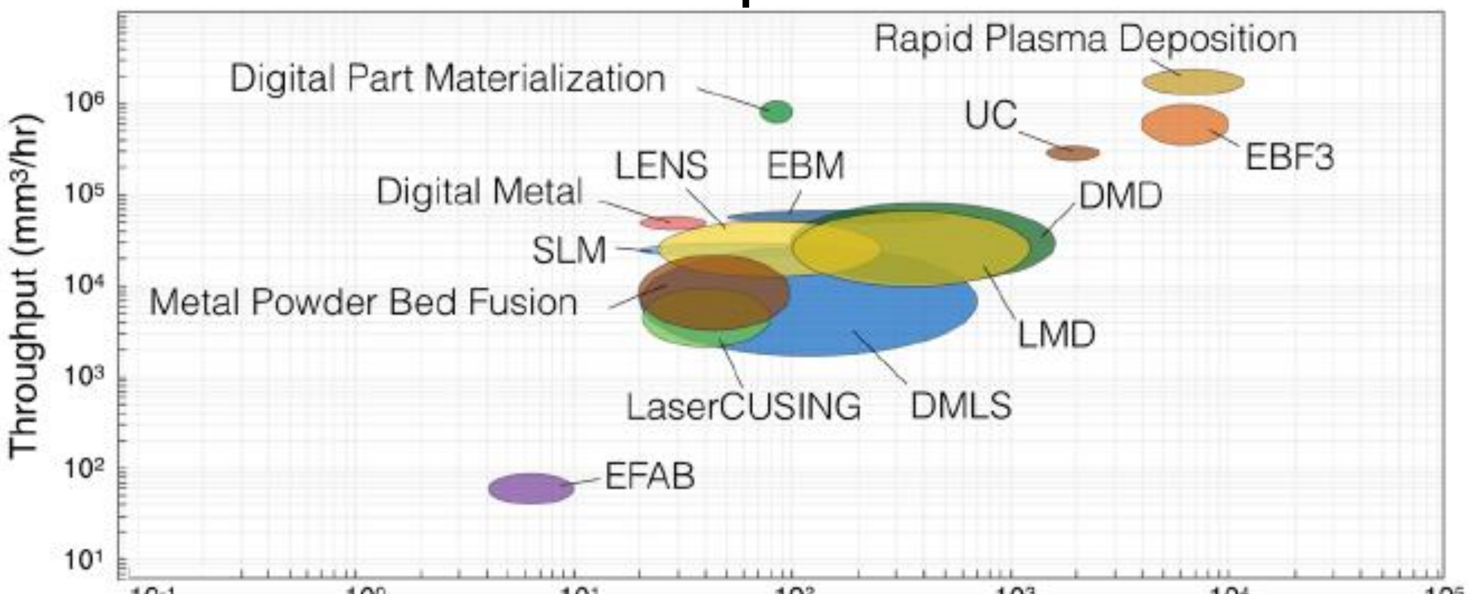
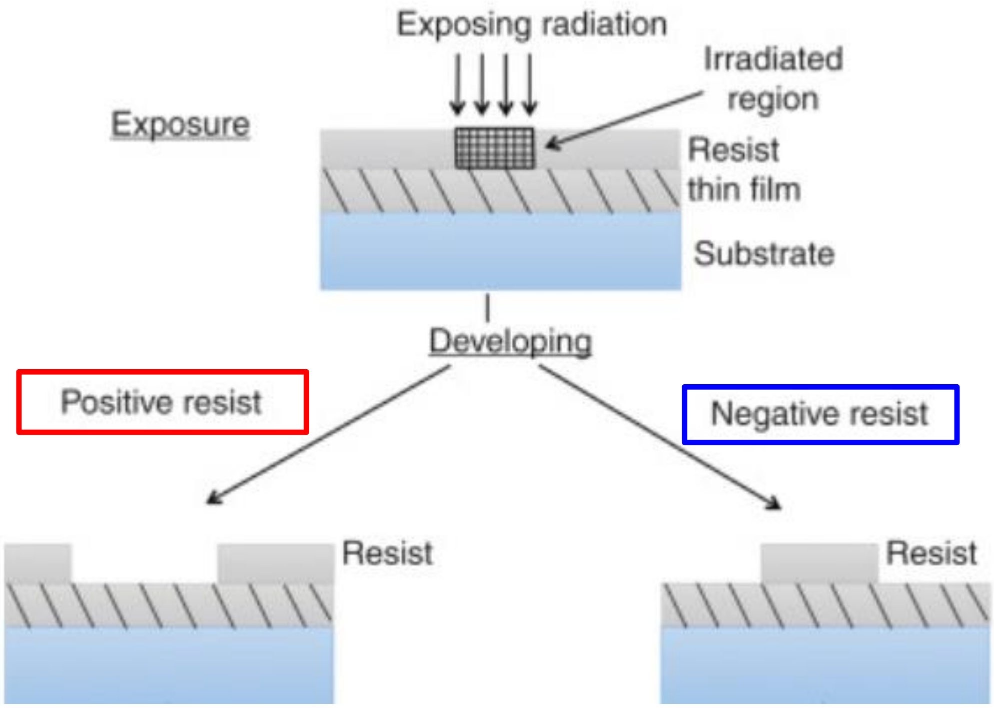


Here, we'll focus on a technique with better **resolution**. How do we bring AM to the nano/microscale?

Vyatskikh, A., *Additive Manufacturing of 3D Nano-Architected Metals and Ceramics*. Thesis, Caltech. (2020)

Photolithography

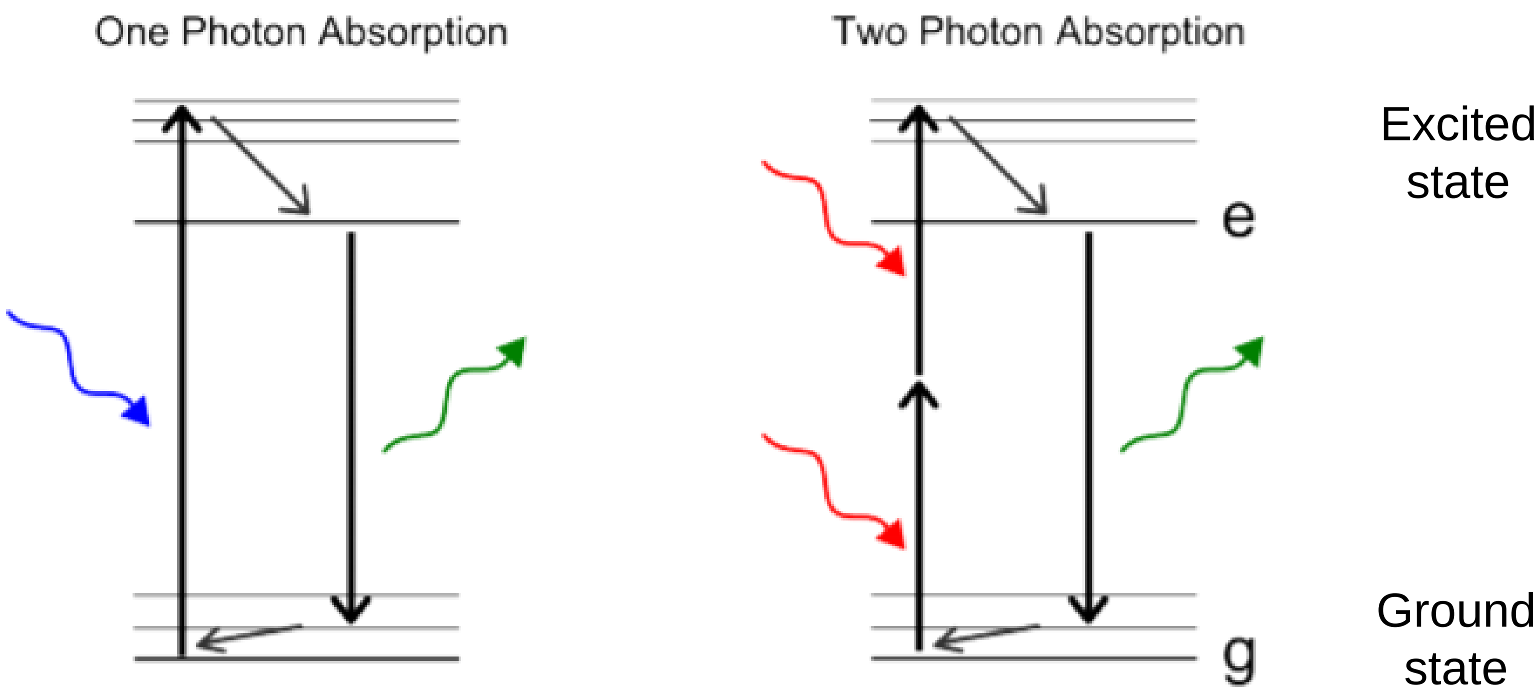
- Photosensitive polymer is exposed with light (often UV)
- Positive resist: exposed region chemically changes to become more soluble in developer and is removed
- Negative resist: exposed region crosslinks and is harder to remove



Thompson, L.F., *An Introduction to* lithography. ACS Symposium Series, Washington DC (1983)

Two-Photon Absorption (TPA)

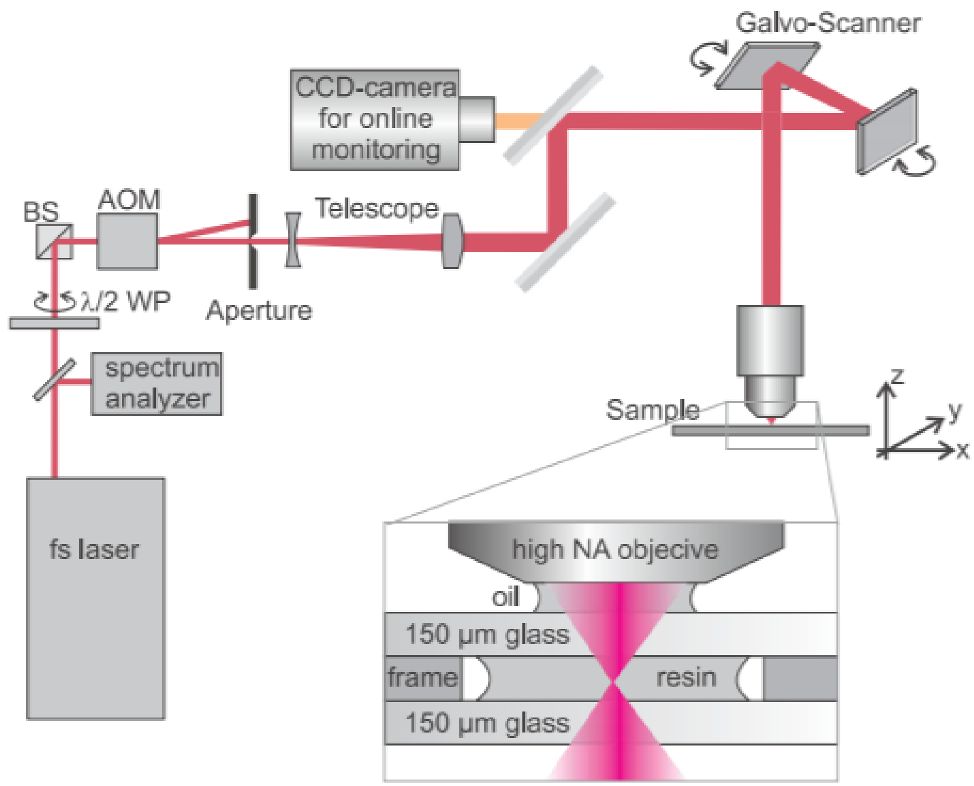
- Excitation from ground → excited state via absorption equal to energy between these states
- Multiphoton absorption can occur at other wavelengths if their energies sum up to the same energy



Lavocat, J.-C., *Active Photonic Devices Based on Liquid Crystal Elastomers*. Thesis, ICFO. (2013)

Two-Photon Lithography (TPL)
Direct Laser Writing (DLW)

- Introduced in Literature in early ~2000s, commercially available as nanoscribe
- Fabrication of Complex 3D Structures on the Nano/Micro-scale
- Uses a longer wavelength (e.g. NIR) laser to expose a shorter wavelength (e.g. UV) sensitive resist



Serbin, J., et al. *Optics Express* 12 (21), 5221-5228 (2004)

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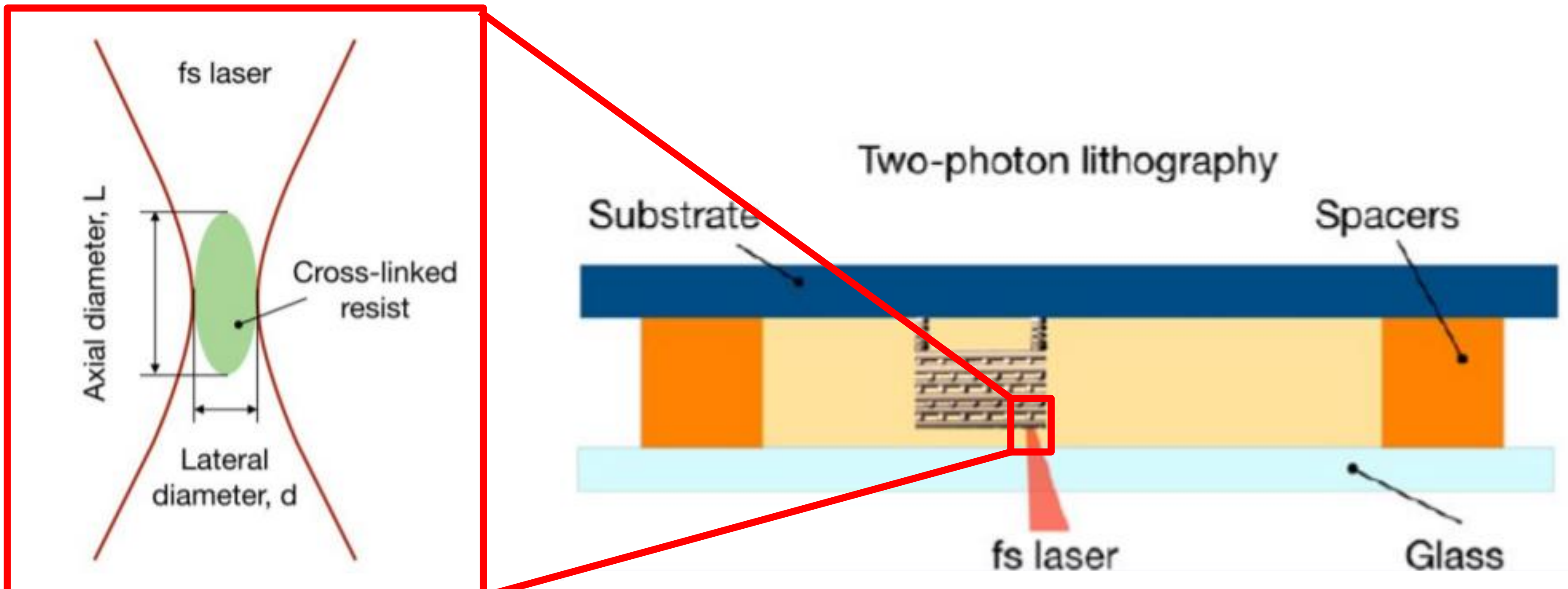
voxel



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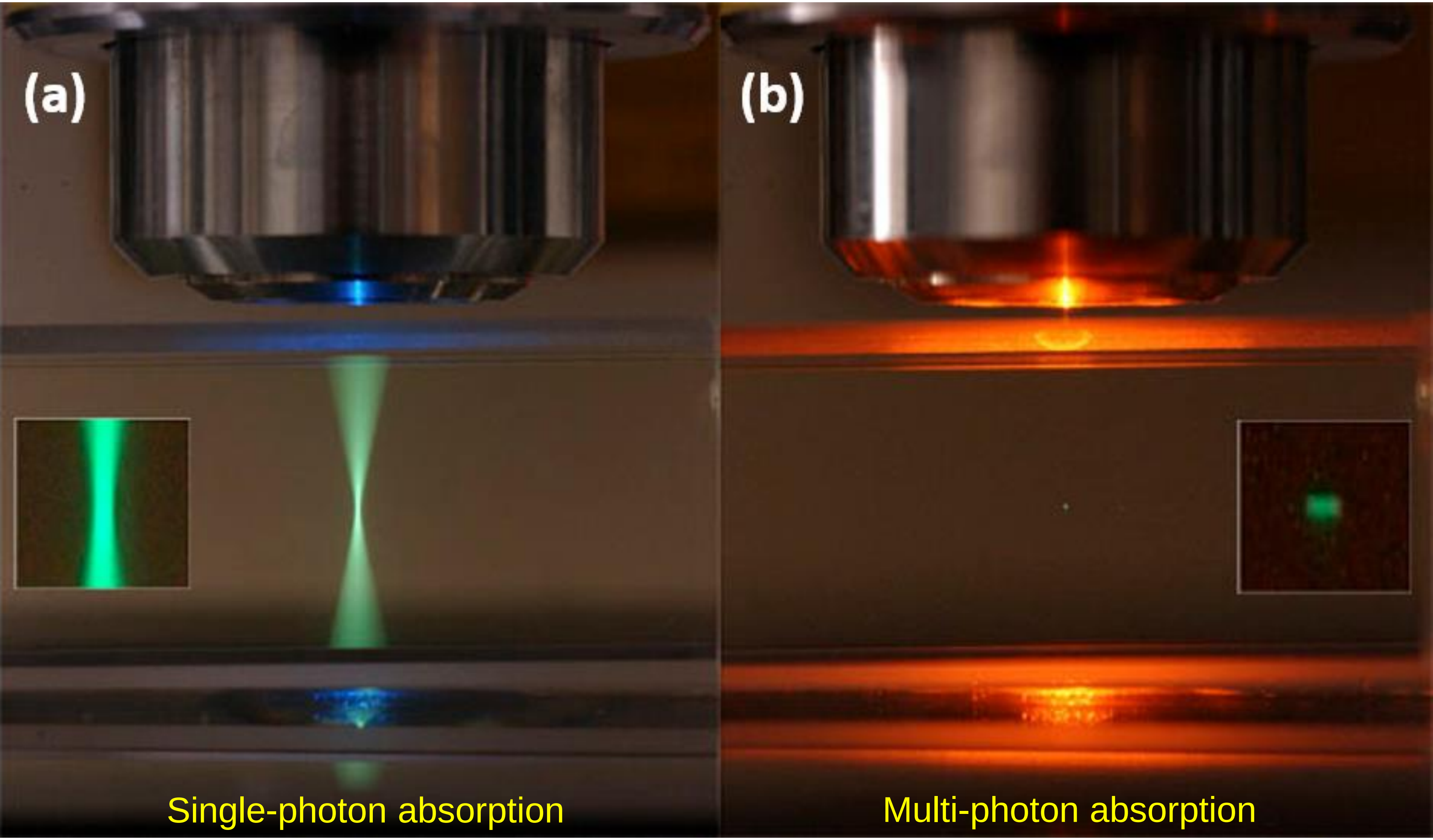

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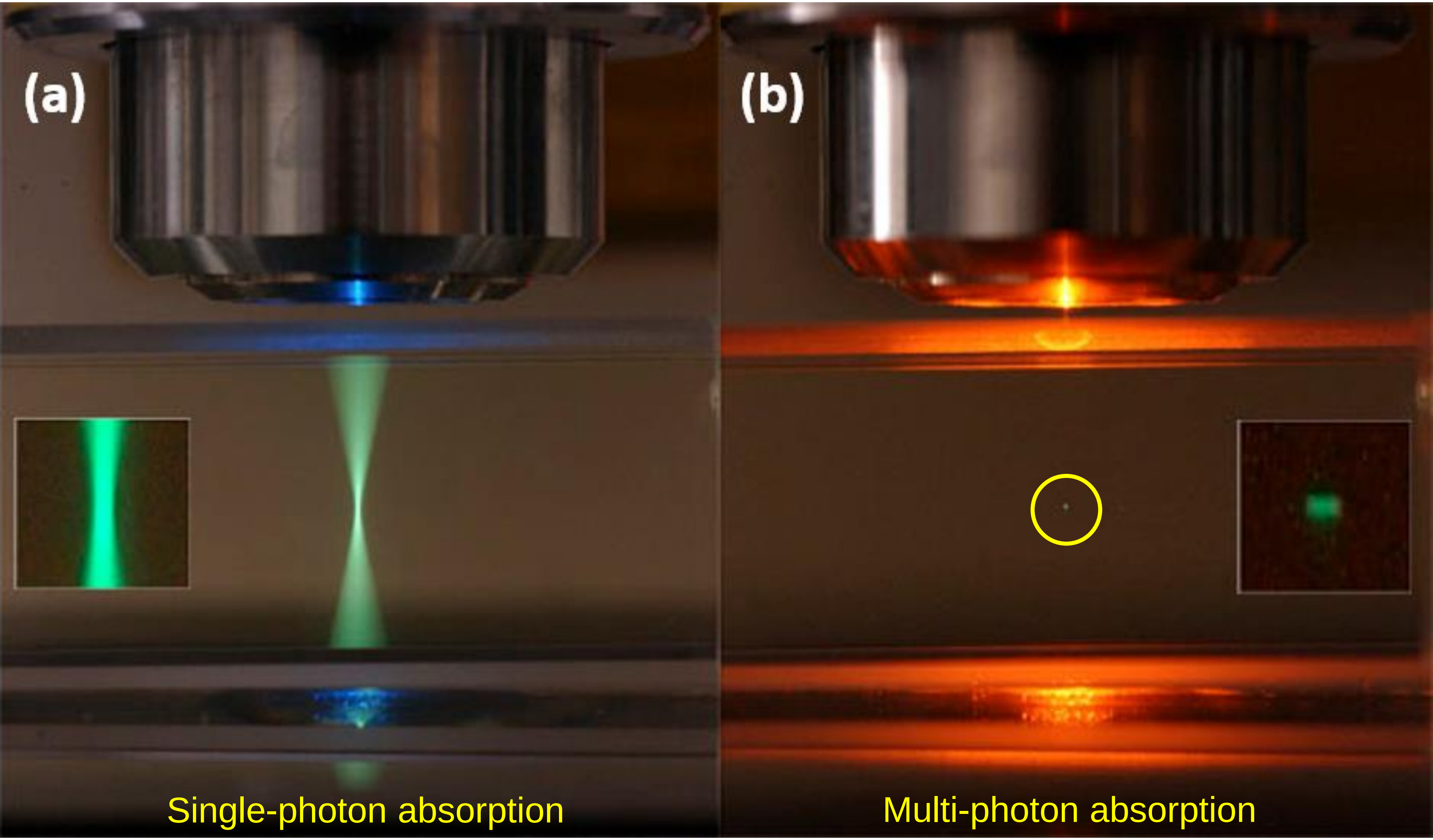

Single-photon absorption

Multi-photon absorption

Two-Photon Lithography (TPL)
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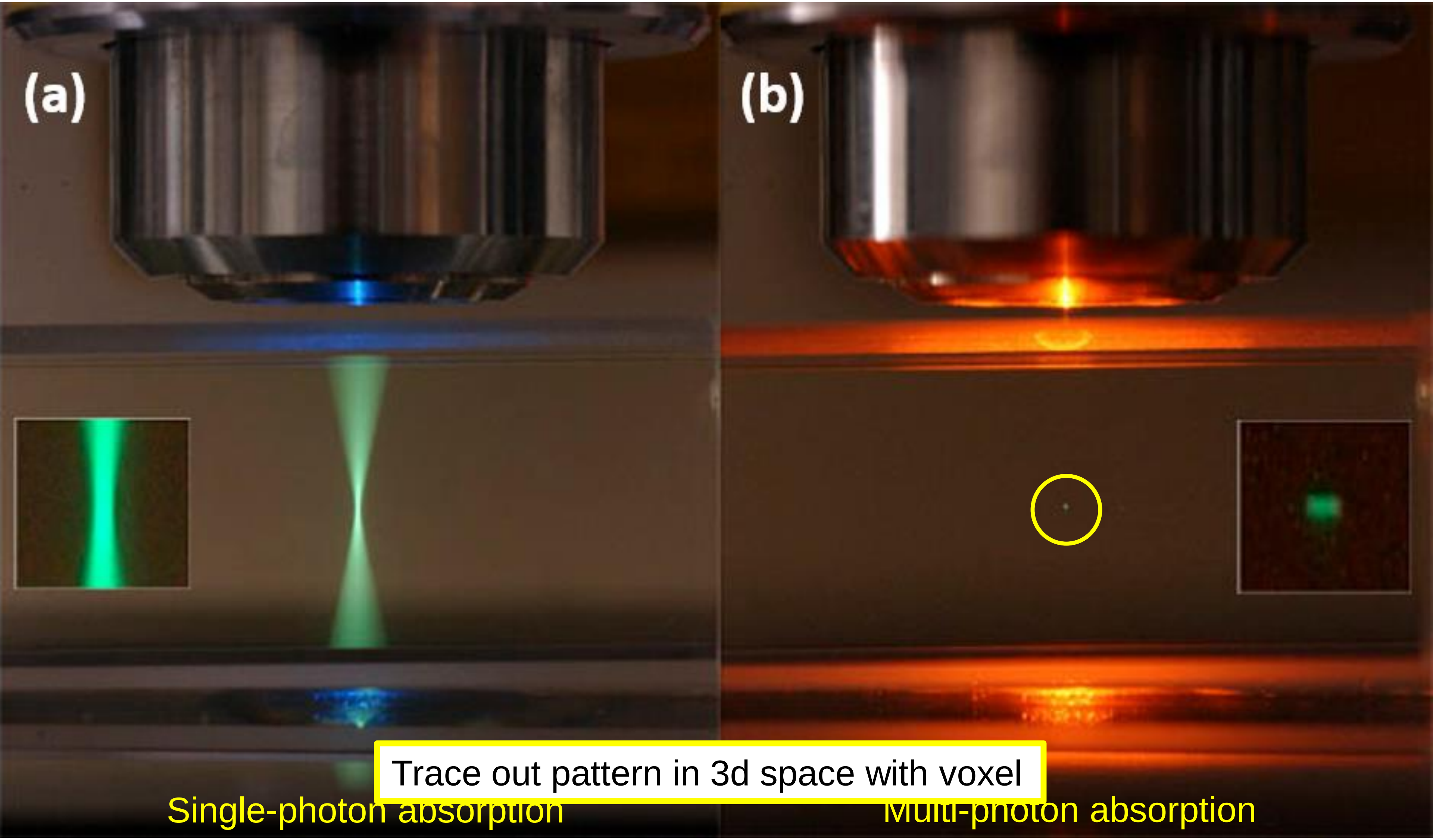

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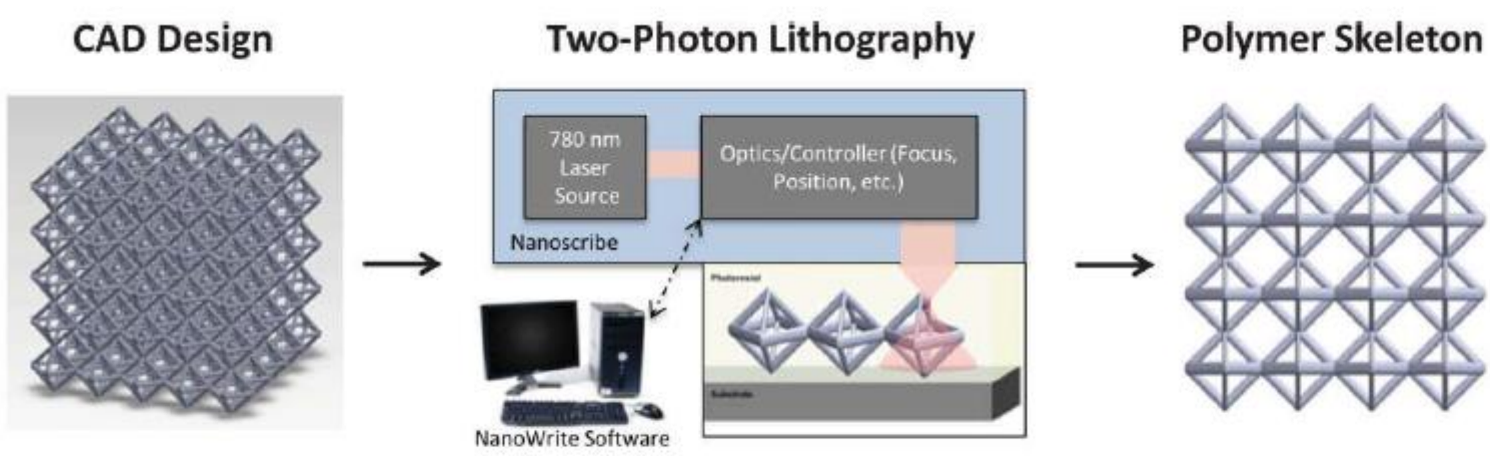

Montemayor, L., et al. *Advanced Engineering Materials* 16 (2), 184-189 (2014)

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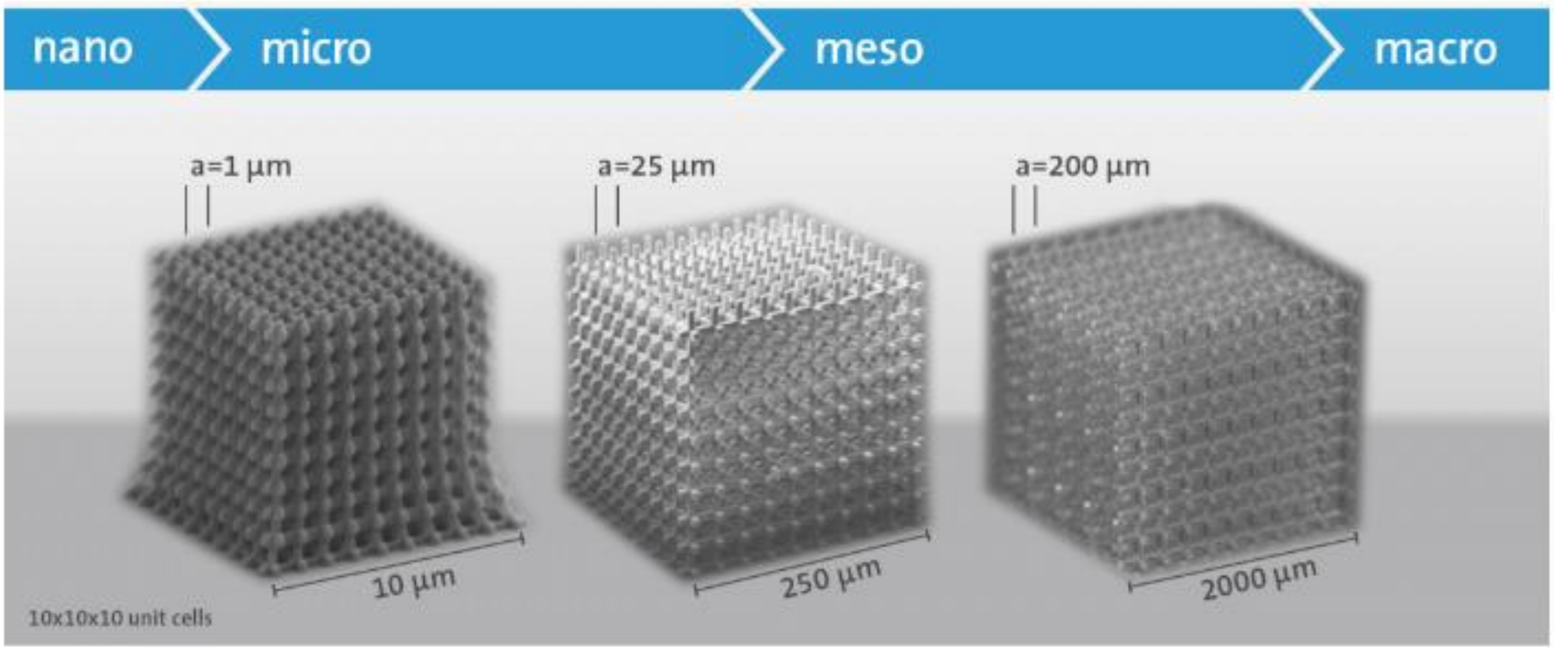
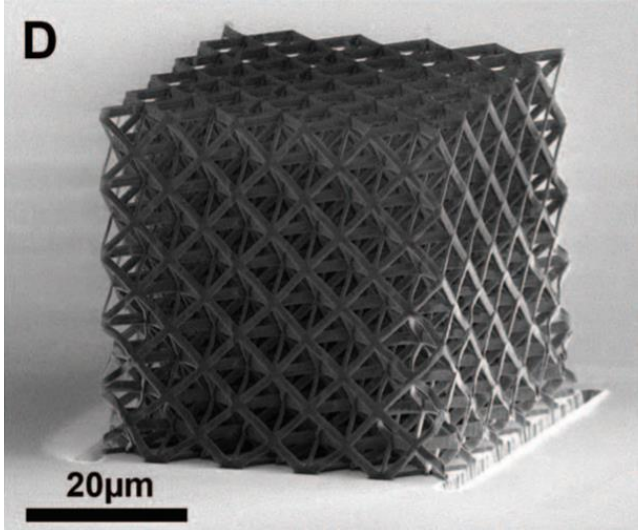
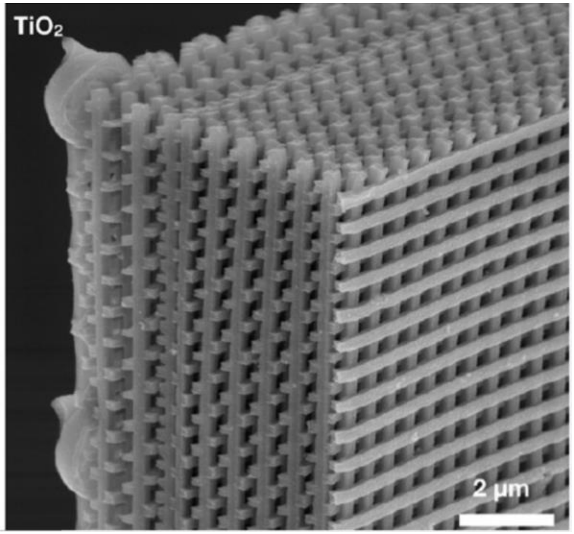


Nanoscribe User Manual. Germany: Nanoscribe GmbH (2015)



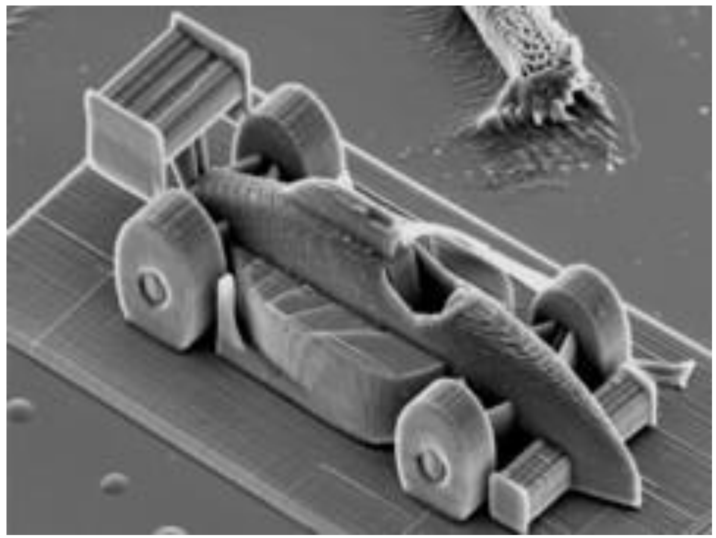
L. Meza, et al. *Science* 345 (6202), 1322-1326 (2014)



Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

HRL Laboratories
Schaedler, T. A., et al. *Science* 334 (6058), 962-965 (2011)

Complex 3D Architectures in TPL



Stampfl, J., Vienna University of Technology

Hastings, T., University of Louisville

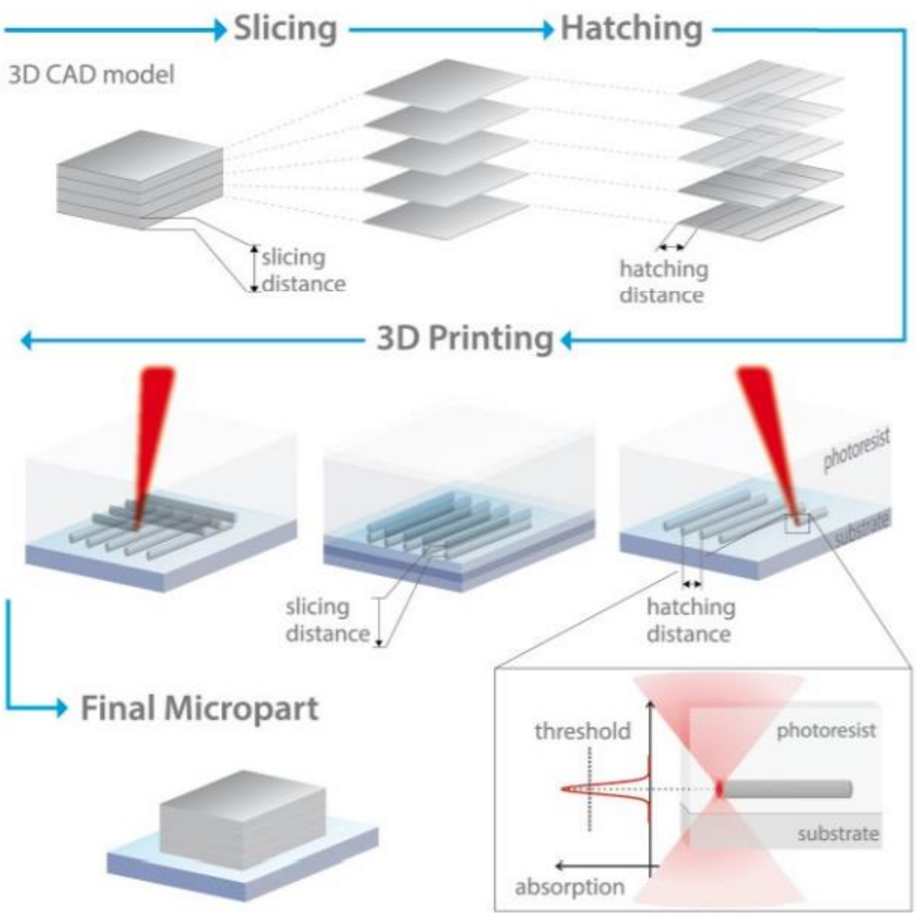
Process Flow

1. Design STL/GWL file
2. Prepare substrate/resist
3. Spin/Drop-Cast Resist
4. Find Substrate-Resist Interface
5. Writing (Dosage, Scan Speed)
6. Development

The short version/quick-start guide

Preparing a GWL File - Parameters

- Following design of pattern, must decide **slicing** and **hatching**



Niesler, F. et al. *Laser Technik Journal*, 16-18 (2014)

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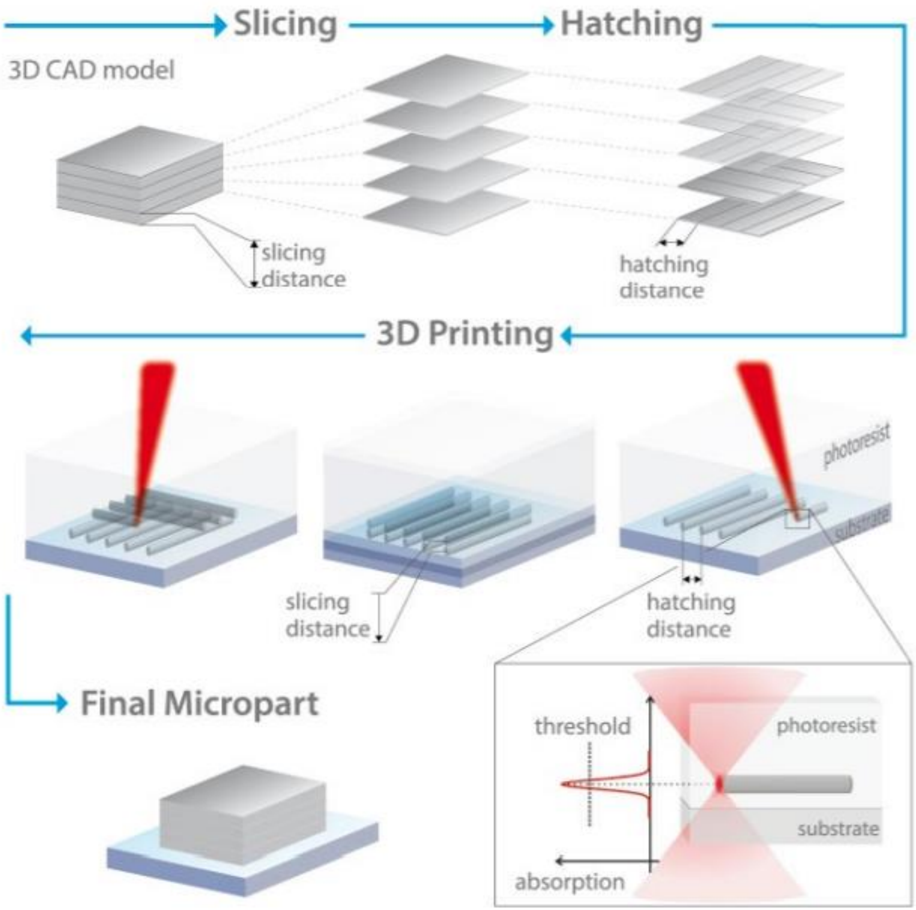
- Slicing: distance between exposures in z
- Hatching: lateral distance between two adjacent lines in the same layer



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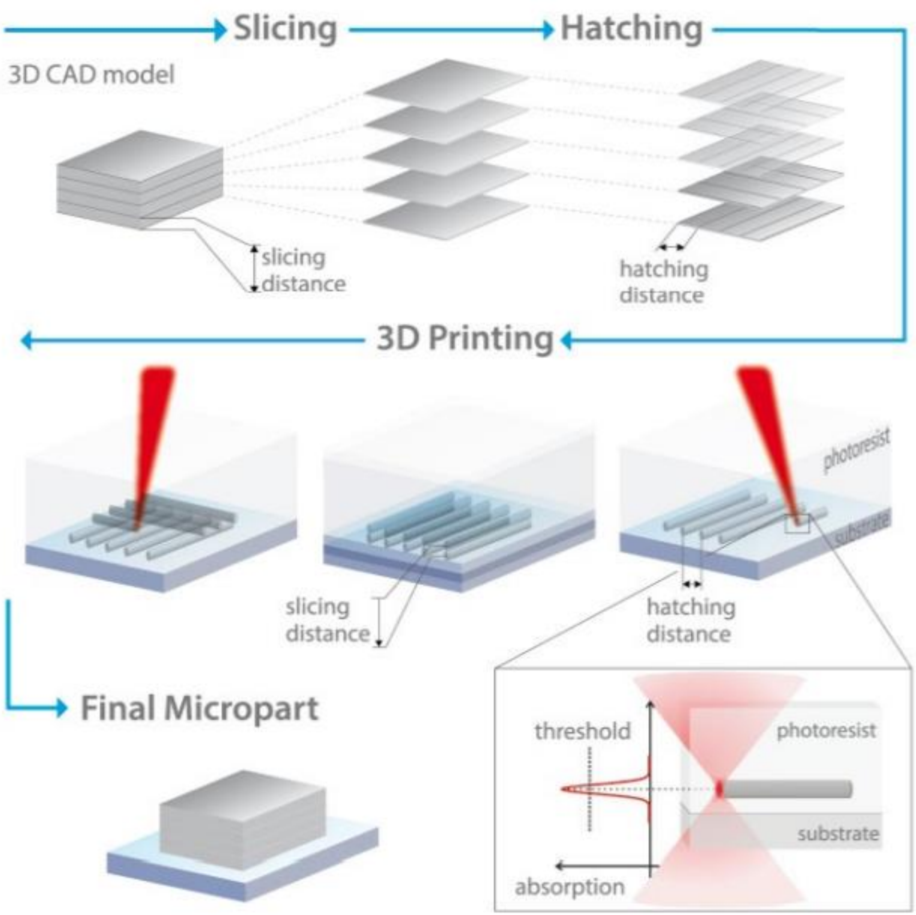
- Slicing/hatching ultimately also affect dosage



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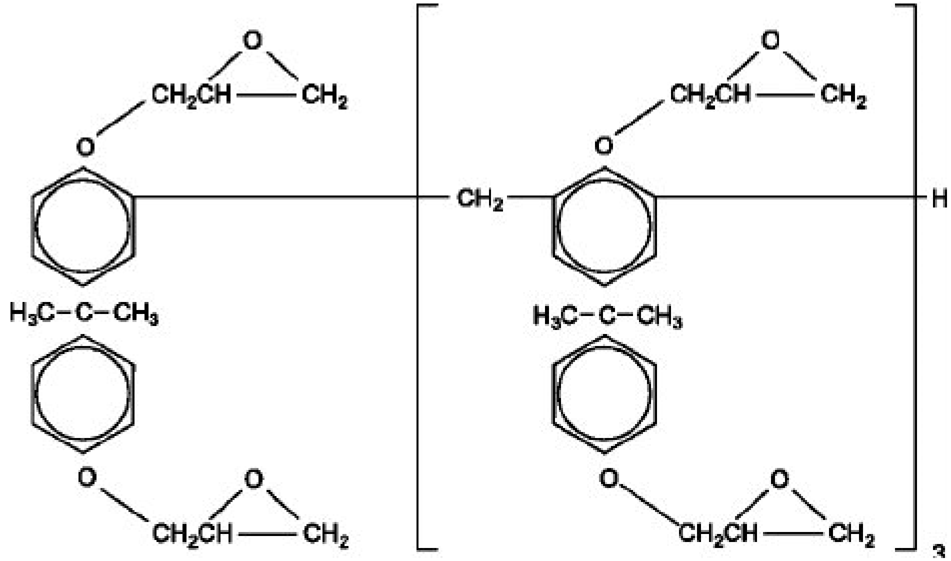
Resist for TPL

- Originally used SU-8 negative resist (cationic polymerization mechanism), prevents bleaching
- Nanoscribe uses proprietary IP-Dip (polyacrylate negative resist)
- Resolution dependent on objective + resist and substrate combination
- Resist can be drop casted or spun

SU-8 Molecule



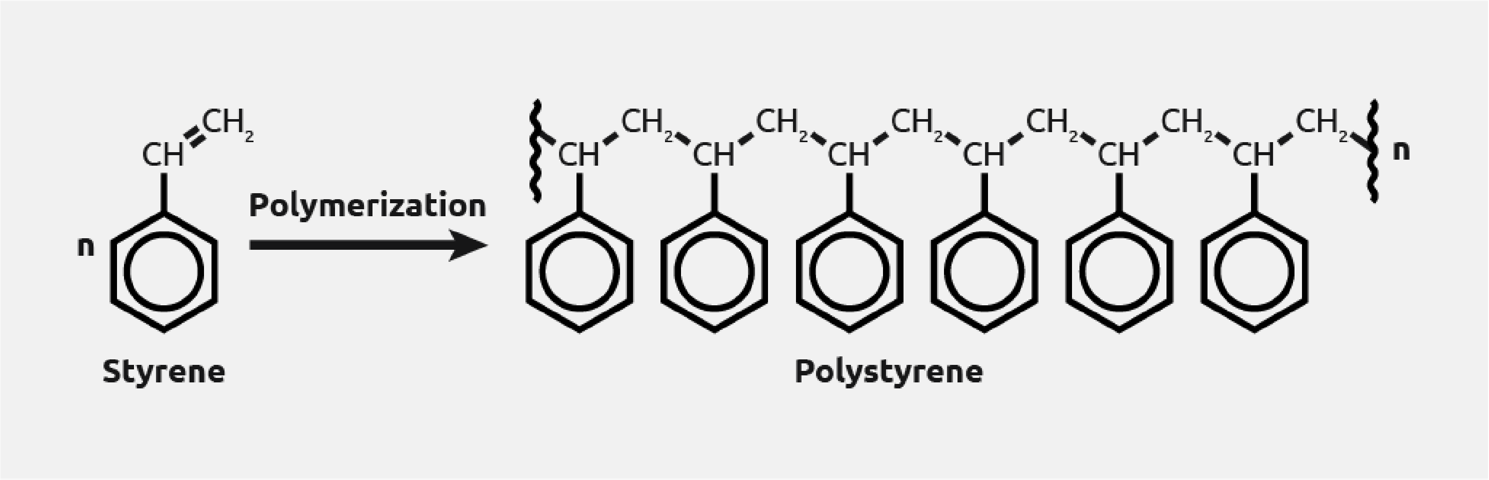
Genolet, G., et al *Review of Scientific Instruments* 70, 2389-2391 (1999)

Polymerization

- Polymerization is the process that describes reactions that result in the combination of single "**monomer**" molecules into longer "**polymer**" chains
- Photoresins which "photopolymerize": Many mechanisms, **chain growth polymerization/radical propagation mechanism is simplest/fastest**

Chain Growth Polymerization

Monomer **Polymer**

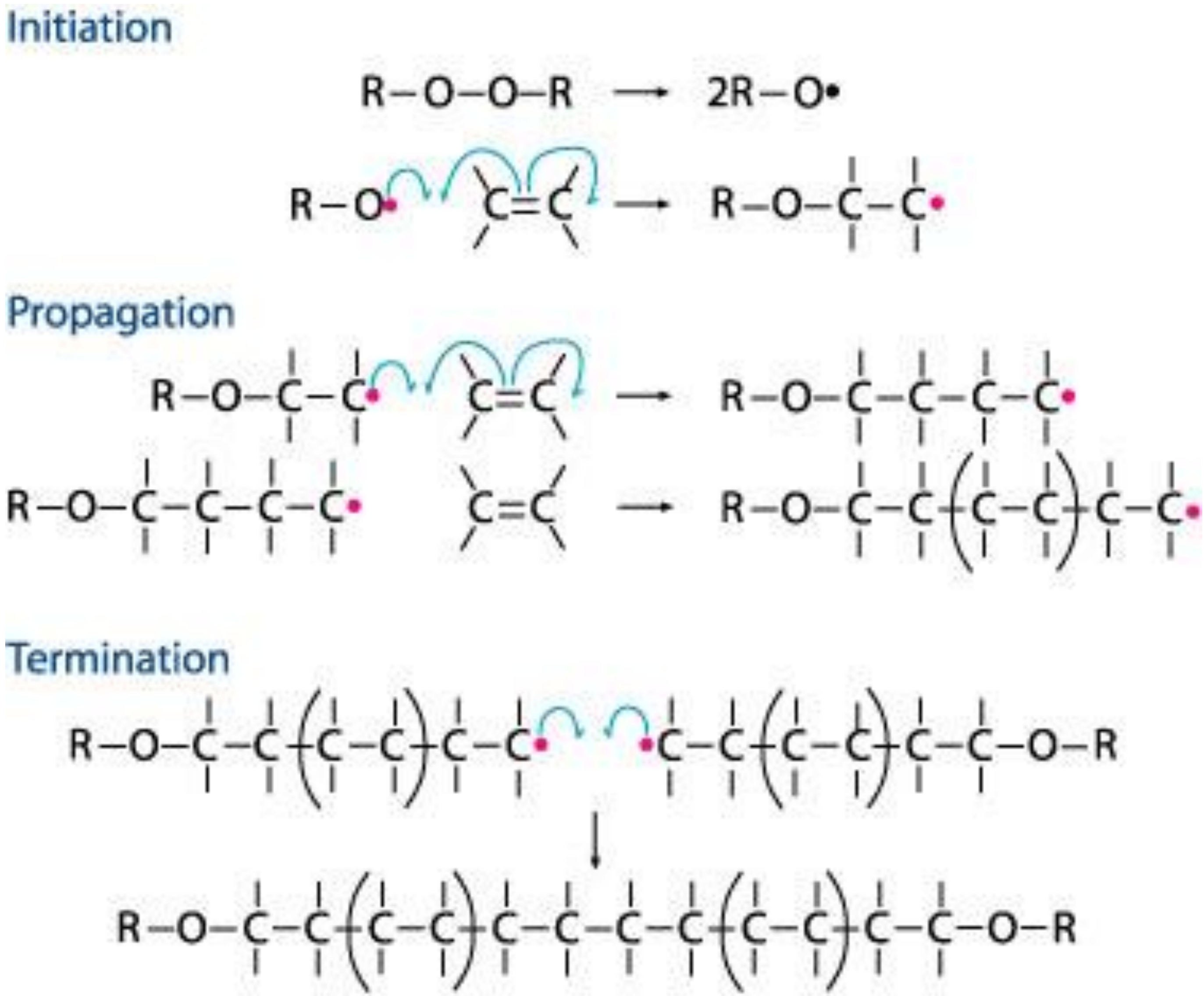


Chain Growth

Initiation	Propagation	Termination
Energy source creates an active site	Addition of monomer to chain which contains new active center	Active site terminates and polymerization no longer occurs

- A growing polymer chain has an “active” site where subsequent “monomers” are added
- These reactions must have an “initiation” and “propagation” step

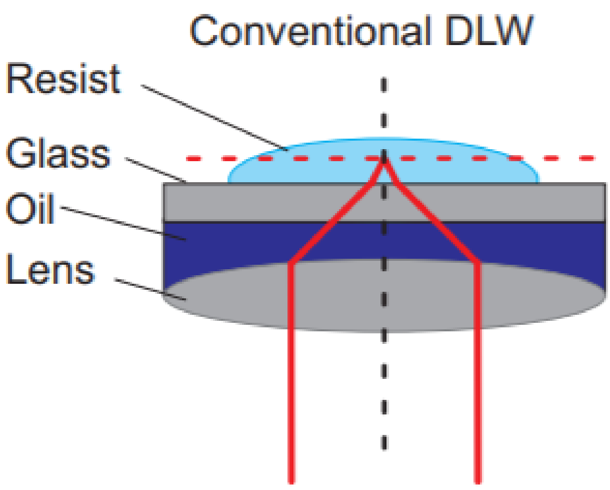
Radical Polymerization



Printing Configurations

1) Oil Immersion (Conventional)
2) Dip-in laser lithography (DiLL)
3) Air

- Transparent substrate
- Focused through bottom
- Index matching immersion oil (prevent refraction of beam)
- Best for short structures (spherical aberrations at greater height)



Objective

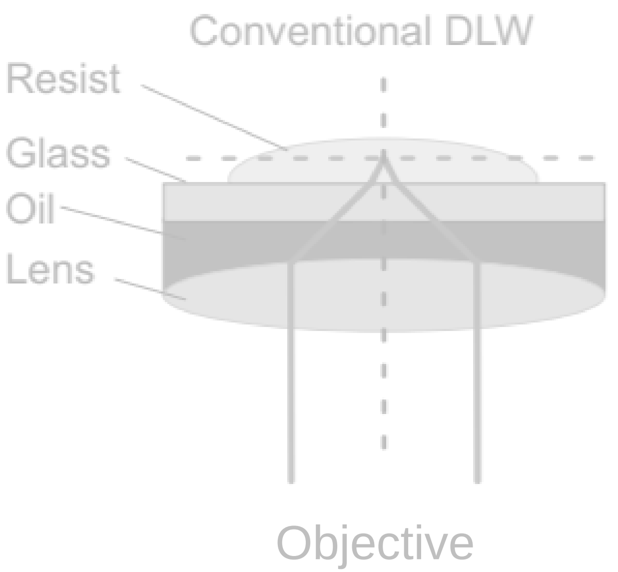
Printing Configurations

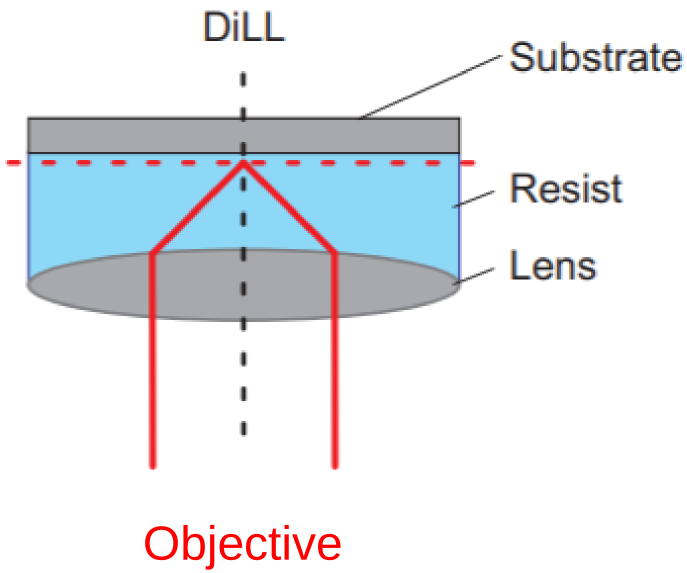
1) Oil Immersion (Conventional)

2) Dip-in laser lithography (DiLL)

3) Air

- Opaque substrate
- Focused from top
- No interface to limit structure height
- Resists must index match
- Resist must not damage objective

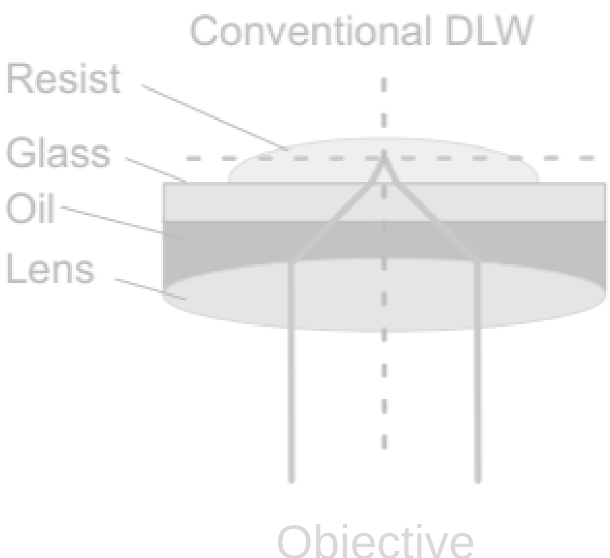


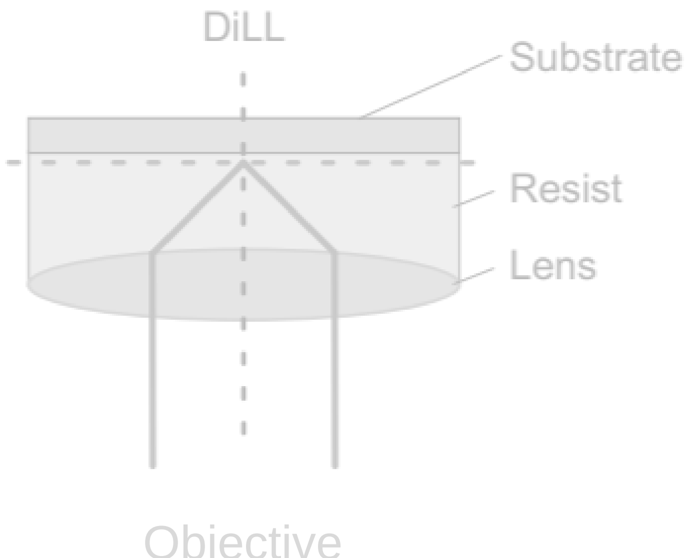


Printing Configurations

1) Oil Immersion (Conventional)
2) Dip-in laser lithography (DiLL)
3) Air

- Transparent or opaque substrate
- Focused from bottom or top
- Weaker interface

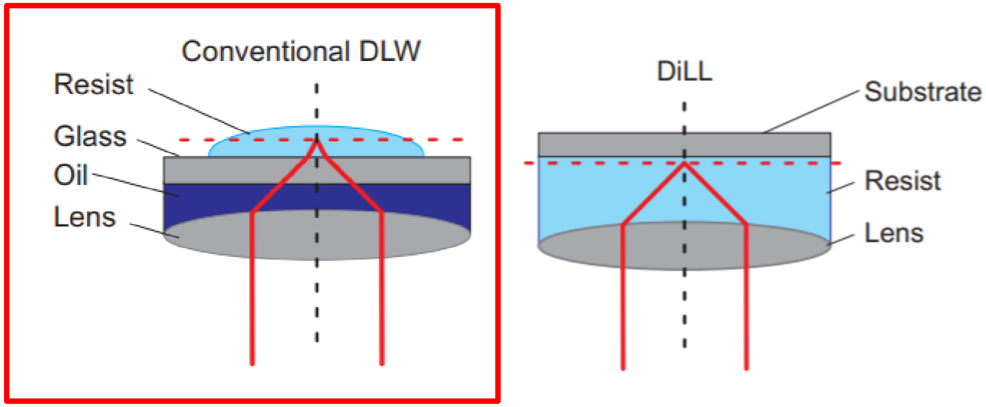




Substrate Preparation for Various Resists

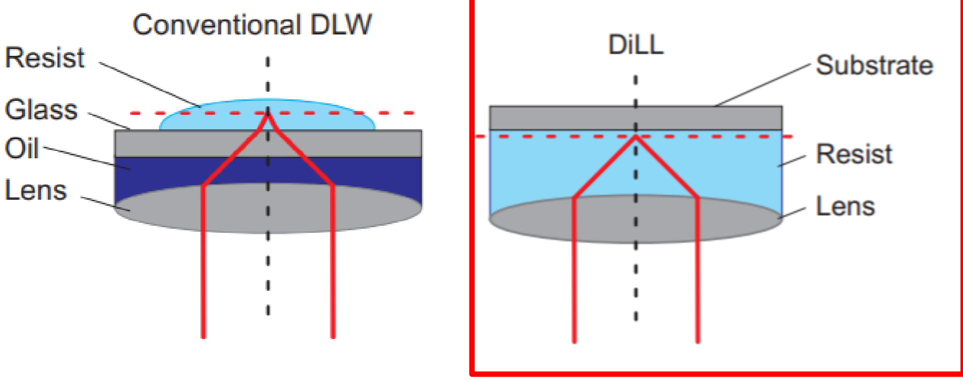
Conventional: Transparent substrates (e.g. glass), any resist

- May prefer other substrate for post-processing



Nanoscribe User Manual. Germany: Nanoscribe GmbH (2015)

DiLL: Opaque substrates, resist must be compatible with microscope objective



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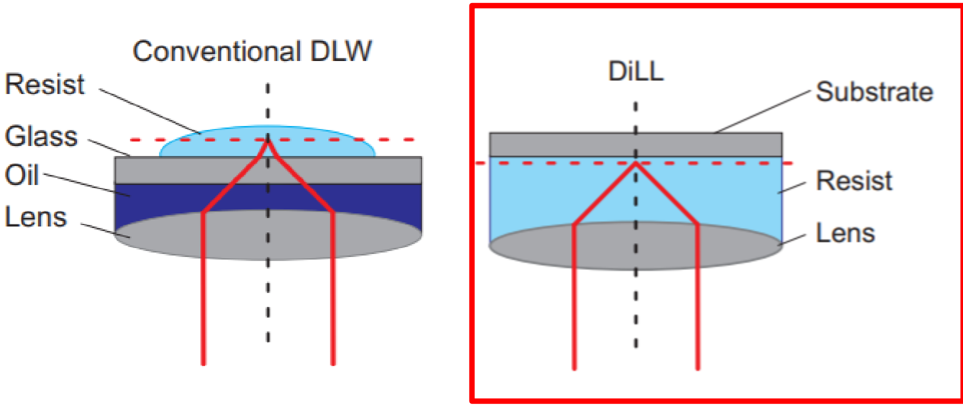

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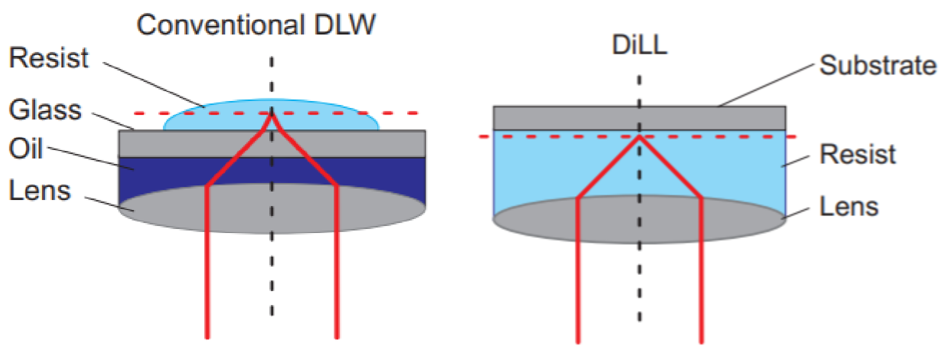
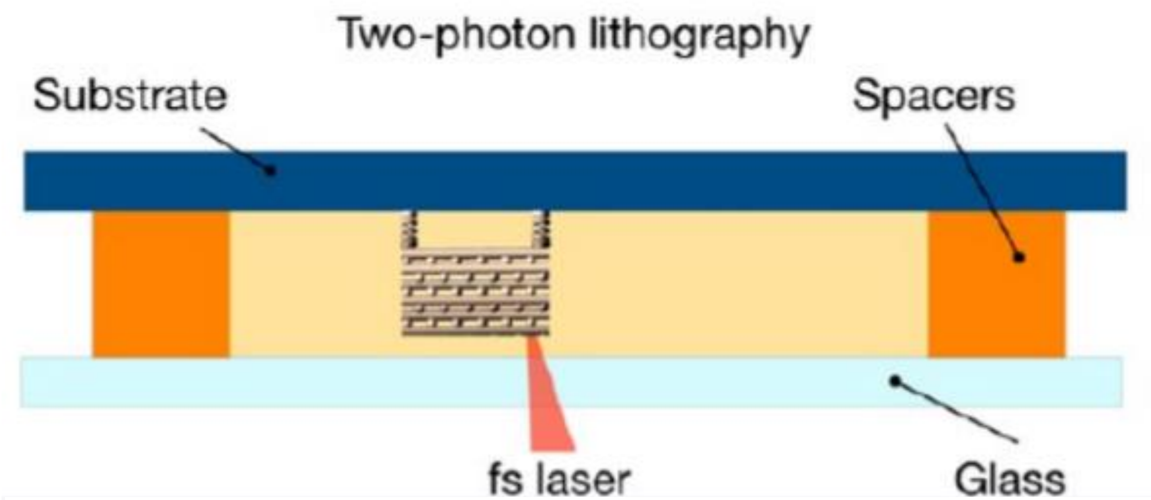
What if we want to use more "exotic" resists that may not be compatible with objective (or keep it clean), AND use an opaque substrate (e.g. Si)?

"Sandwich" method:
Opaque substrates, any resist

- Height limited by spacers
- Can be problematic during removal of glass for development



Nanoscribe User Manual. Germany: Nanoscribe GmbH (2015)



Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

Importance of Index Contrast

- Resist/substrate interface must be located to know where to start write

$$\Delta n = n_{\text{substrate}} - n_{\text{resist}}$$

index contrast between resist/substrate

Δn

Lesser Δn

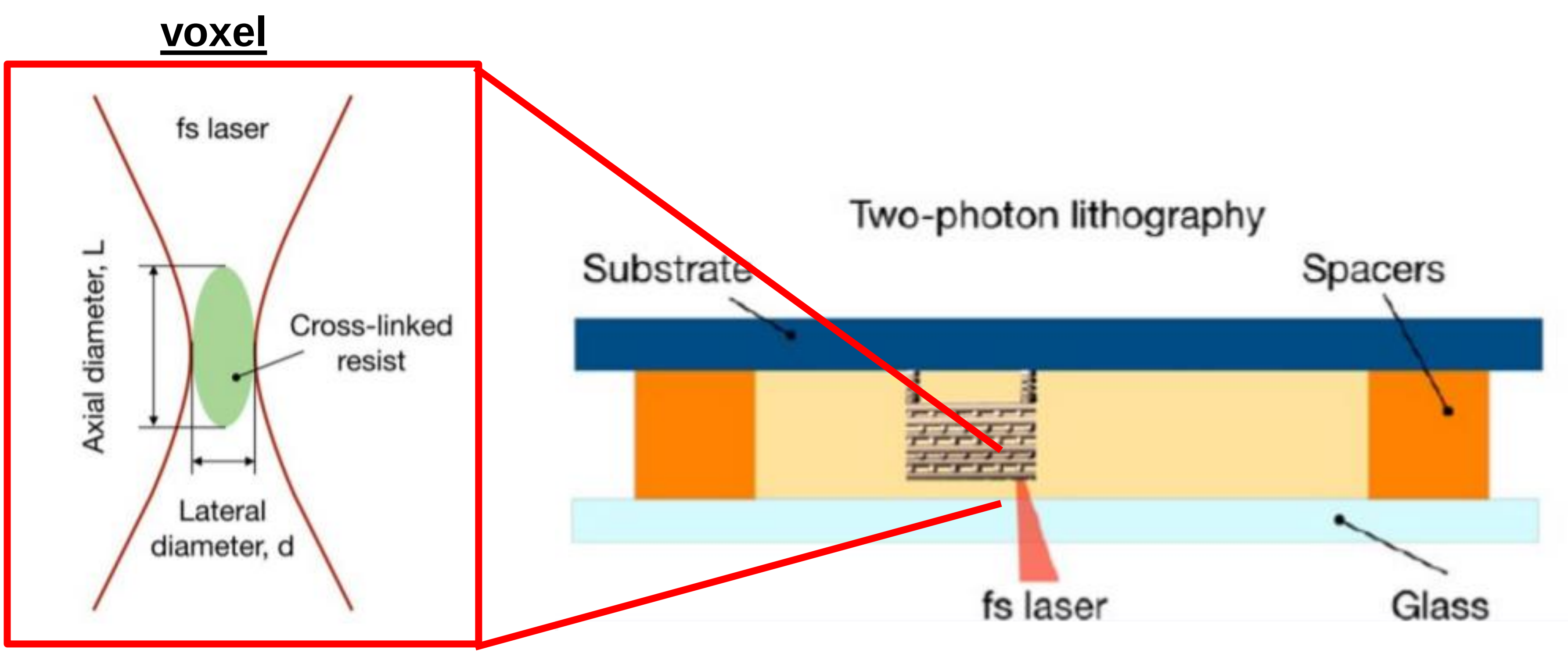
- Need to minimize refraction

Greater Δn

- Δn required to enable back-reflection signal
- Needs to be greater at lower magnifications
- Thin coatings of high reflectivity material can be deposited for contrast in DiLL (e.g. ITO, Al_2O_3, Au), can lead to "explosions"

Resolution and Dosage

Laser spot is focused by a microscope objective down to an elliptical **voxel** within the resist



Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

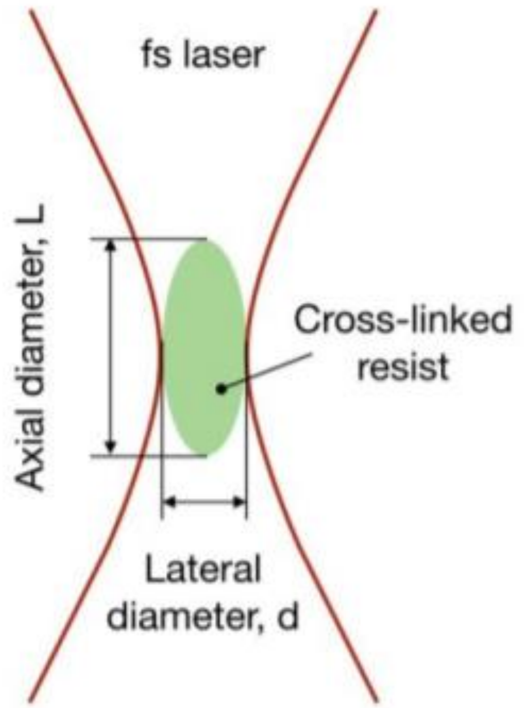
Resolution and Dosage (Voxel)

Voxel is extremely important in TPL

Resolution

- Resolution determined by objective magnification and resist
- Focused spot = voxel, elliptical by nature
- Important to know voxel size for given write parameters
- High magnification = high resolution, but small write field (may require stitching!)

Ex: Proprietary IP-Dip
500 nm lateral res
200 nm linewidths



Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

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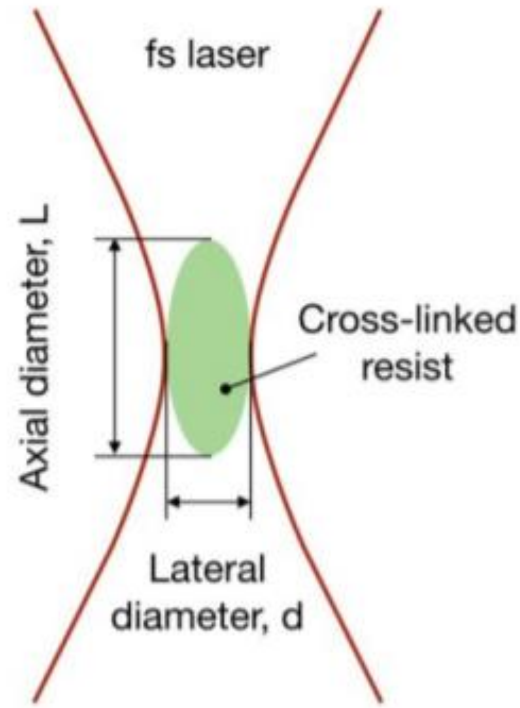
Dosage

- The laser power + time = dose
- Dose increased by increasing the **laser power** or increasing exposure time (**scan speed**)
- Dose is ~(ScanSpeed)$^{1/2}$



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stitching

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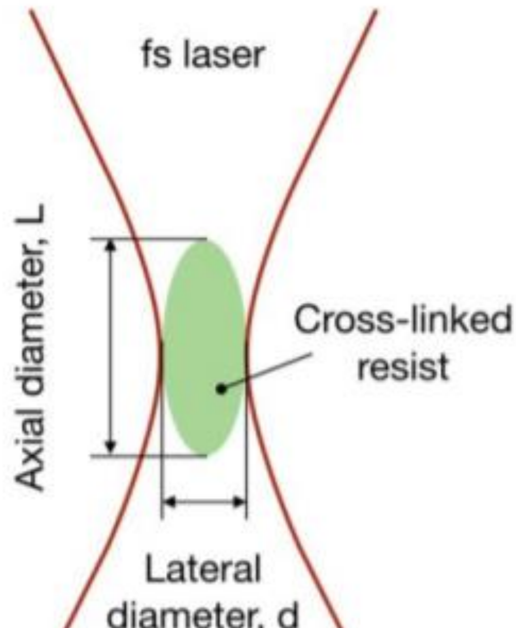


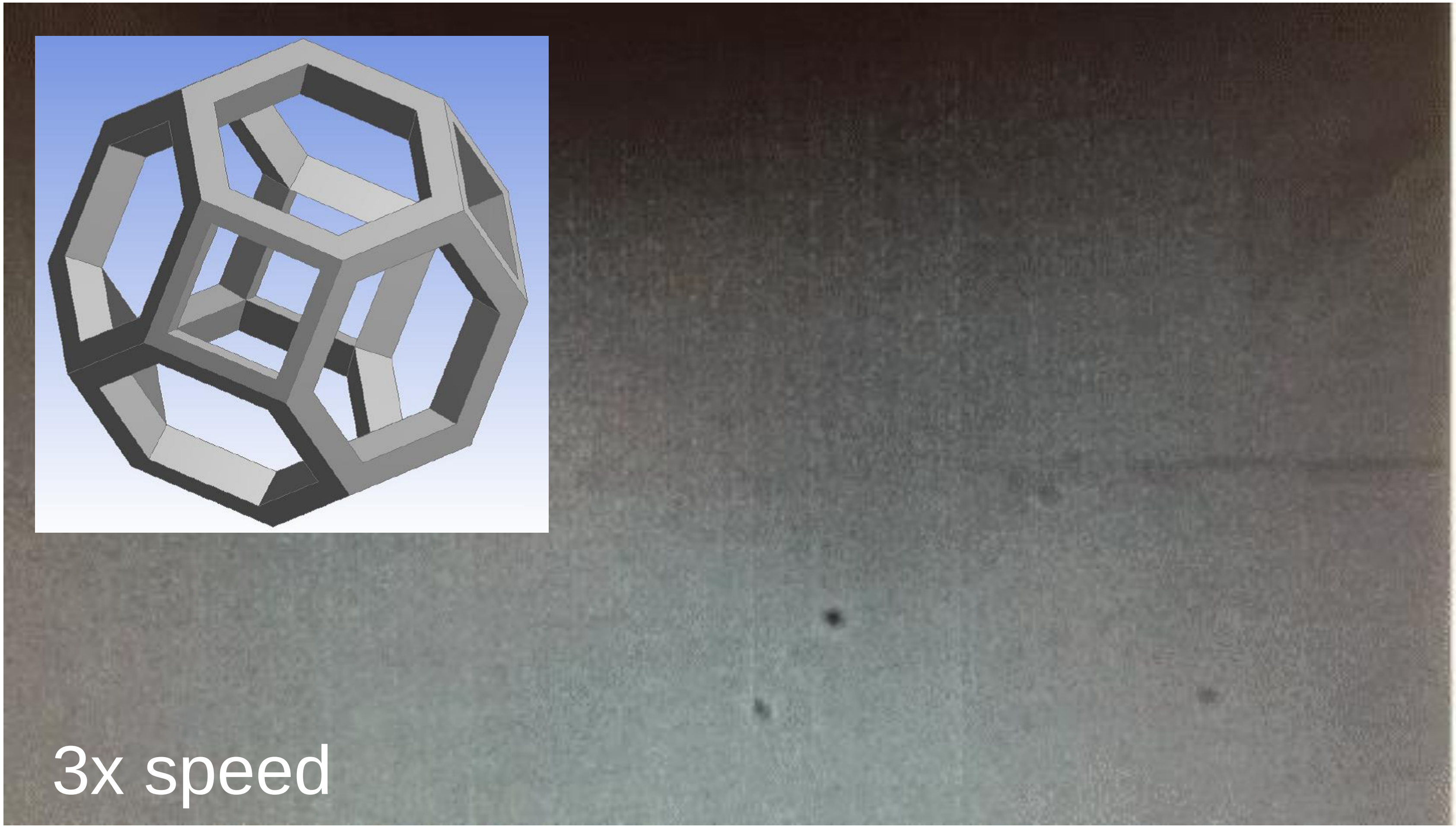
1) Resolution set by elliptical voxel
2) Write parameters: Laser power and scan speed

3520 (2020)

Process Flow

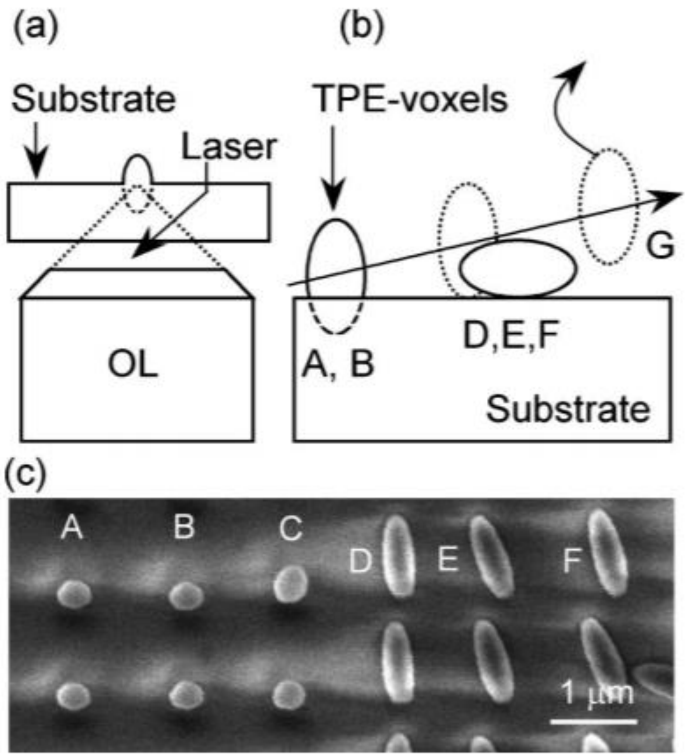
Design STL/GWL file	Design pattern to be written with software (hatching, slicing, etc)
Prepare substrate/resist	What considerations are required with regards to printing configuration? What resist?
Spin/Drop-Cast Resist	Depending on resist and printing configuration, how will the resist be applied?
Find Substrate-Resist Interface	Is the index-contrast of the given resist/substrate stack sufficient? Are there back reflections?
Writing (Dosage, Scan Speed)	Choosing writing parameters similar to any conventional lithography
Development	Removing unexposed regions (negative resist) or exposed regions (positive resist)

TPL Write of Tetrakaidodecahedron



2x2 single layer of tetrakaidodecahedron with 20 um unit cell

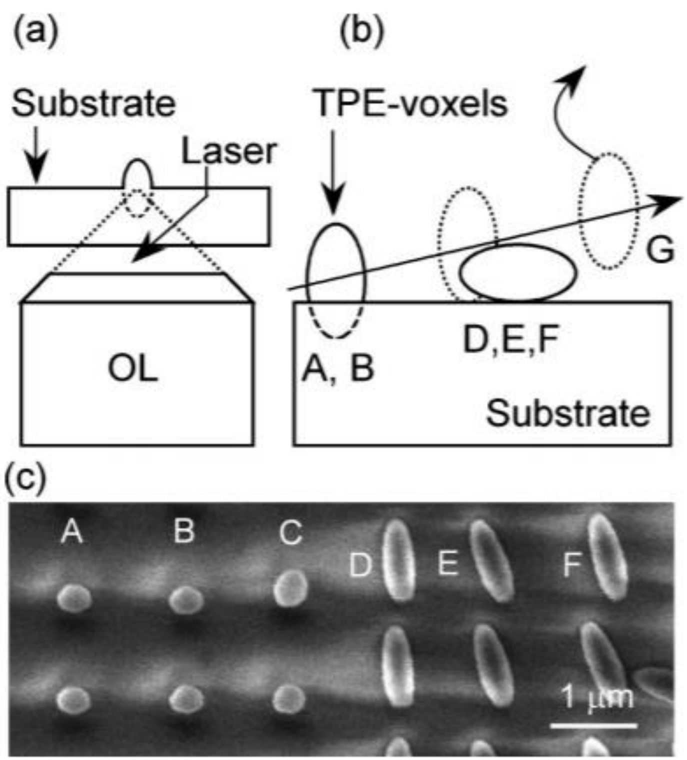
Determination of Voxel Size



Sun, H-B., et al. *Apl. Phys. Lett.* 80 (20), 3673-3675 (2002)

Knowing that voxel size is set by parameters and is important because it determines resolution…

Determination of Voxel Size



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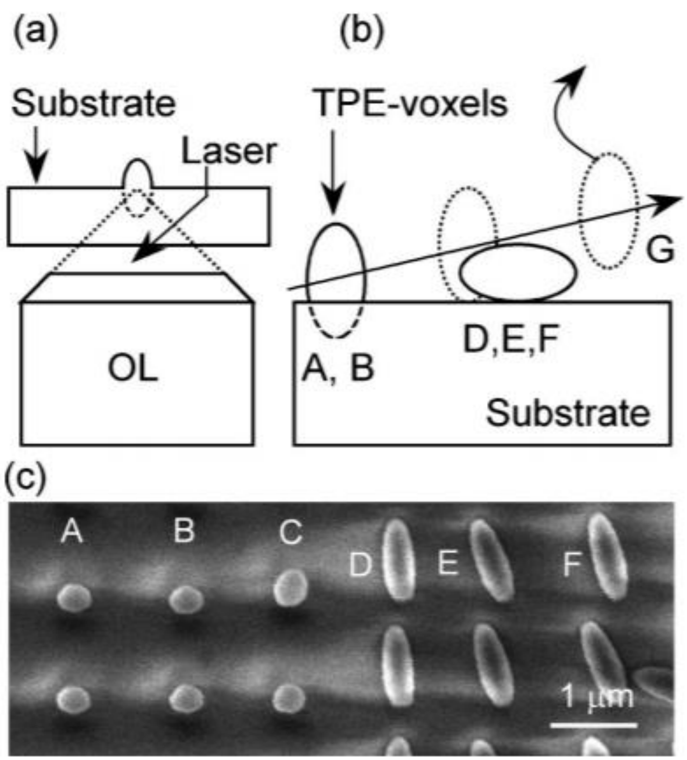
Knowing that voxel size is set by parameters and is important because it determines resolution…

Important to know voxel size!

Determination of Voxel Size



Sun, H-B., et al. *Apl. Phys. Lett.* 80 (20), 3673-3675 (2002)

- Laser focused at substrate/resist interface
- Expose **single voxel** at various *z* heights near interface
- Voxels exposed perfectly at one edge will fall and can be measured in SEM

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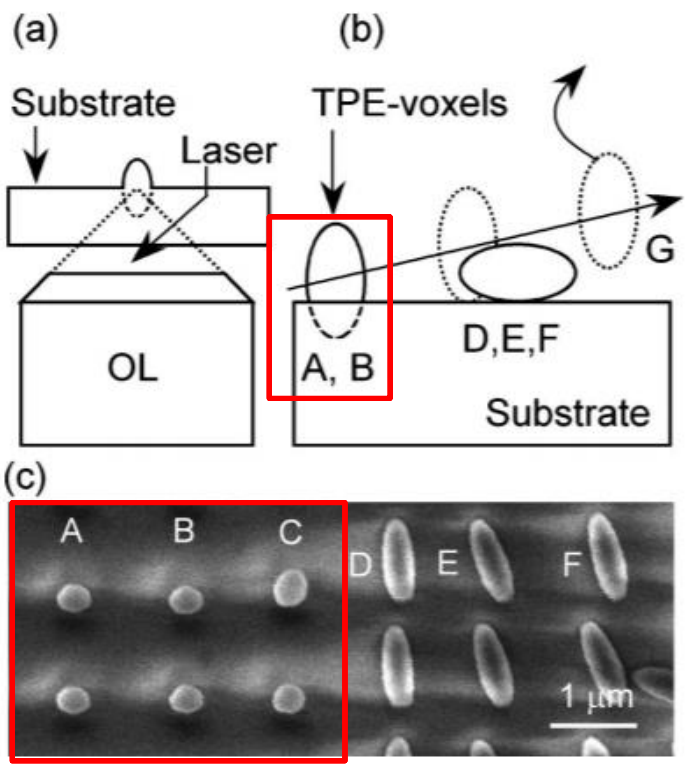
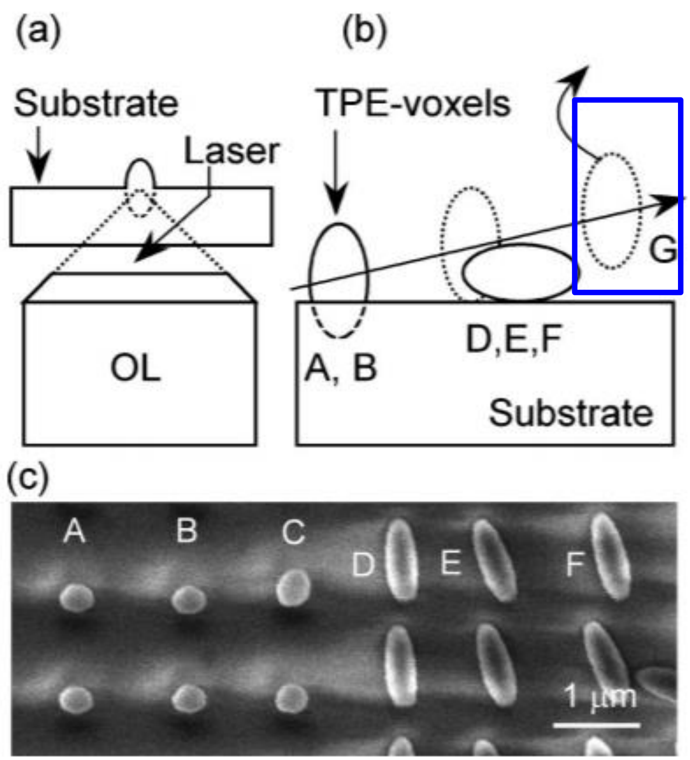


Sun, H-B., et al. *Apl. Phys. Lett.* 80 (20), 3673-3675 (2002)

- Laser focused at substrate/resist interface
- Expose **single voxel** at various *z* heights near interface
- Voxels exposed perfectly at one edge will fall and can be measured in SEM

Voxel is partially written in substrate (attached to substrate)

Determination of Voxel Size

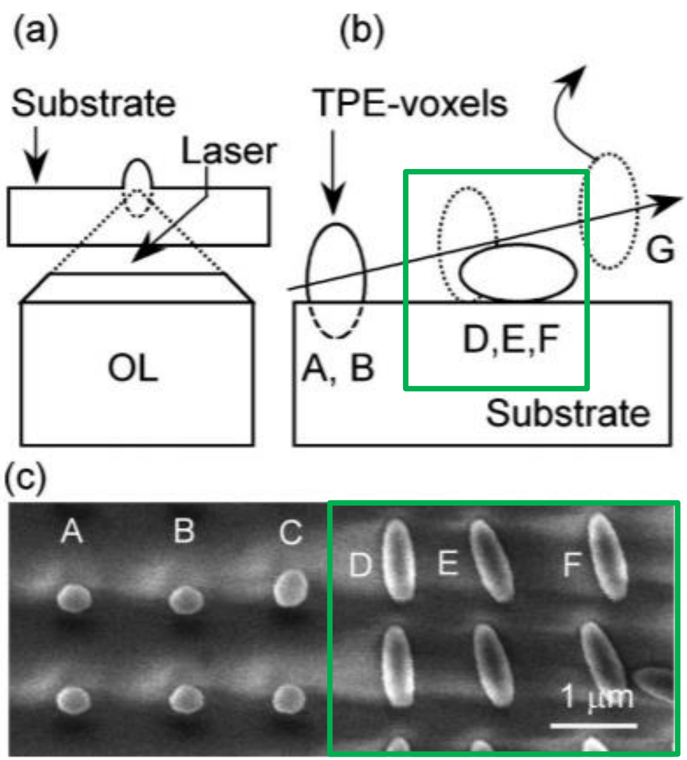


Sun, H-B., et al. *Apl. Phys. Lett.* 80 (20), 3673-3675 (2002)

- Laser focused at substrate/resist interface
- Expose **single voxel** at various *z* heights near interface
- Voxels exposed perfectly at one edge will fall and can be measured in SEM

Voxel is written above substrate and floats away during development

Determination of Voxel Size

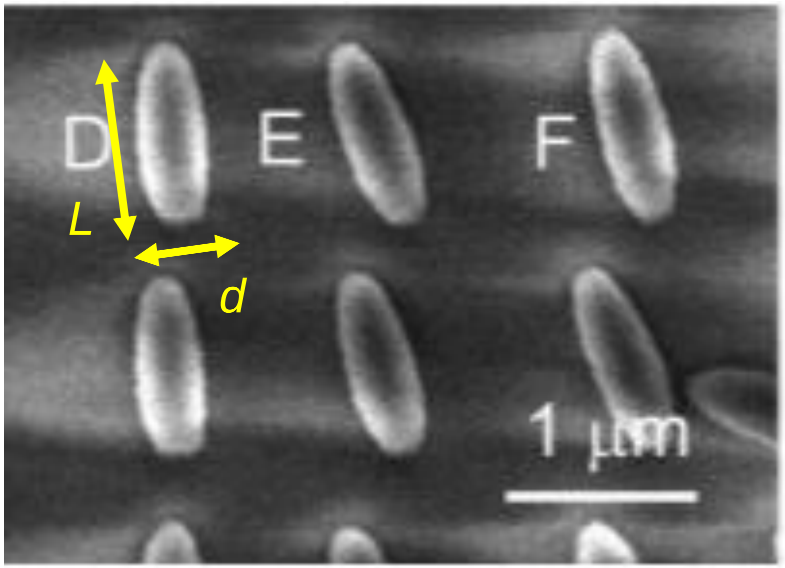


Sun, H-B., et al. *Apl. Phys. Lett.* 80 (20), 3673-3675 (2002)

- Laser focused at substrate/resist interface
- Expose **single voxel** at various *z* heights near interface
- Voxels exposed perfectly at one edge will fall and can be measured in SEM

Voxel is written just above the substrate and falls over but is attached

Determination of Voxel Size



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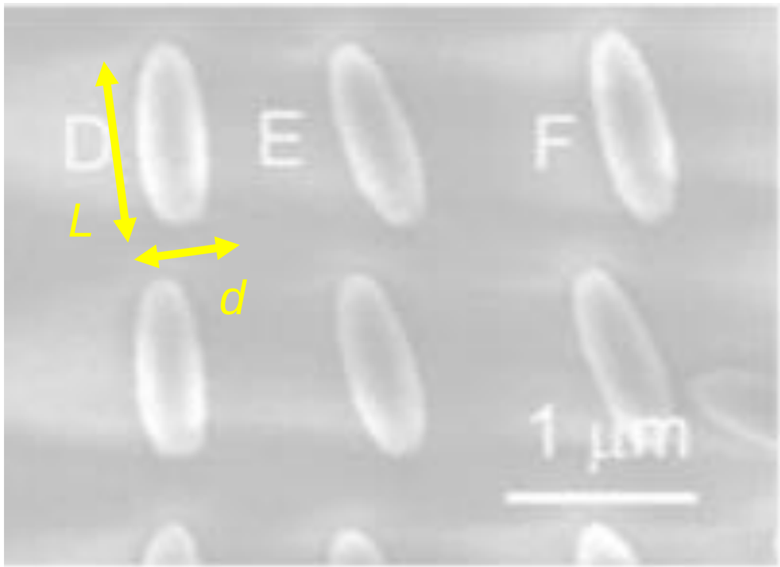
- Laser focused at substrate/resist interface
- Expose **single voxel** at various *z* heights near interface
- Voxels exposed perfectly at one edge will fall and can be measured in SEM

Height and width of voxel can be measured to determine minimum resolution for fixed resist/substrate and write parameters!

Determination of Voxel Size



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Experiments take time and have a non-zero cost. Can we develop an analytical model to predict voxel size?

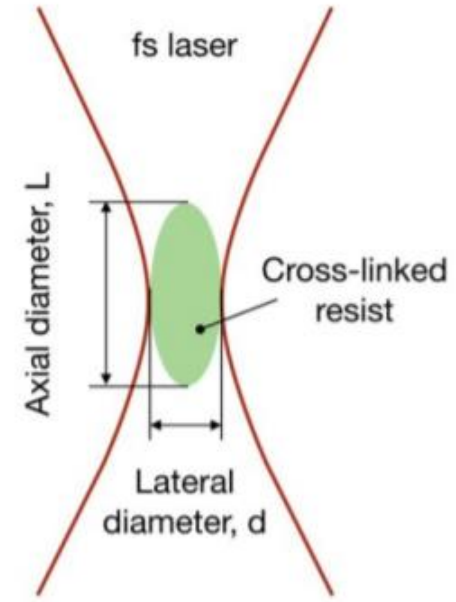
Voxel Shape Model

Voxel Height, $L = 2z_r\sqrt{F^{1/2} - 1}$

Voxel Width, $d = w_0\sqrt{\log F}$

$z_r \equiv$ Rayleigh distance (nm)

$w_0 \equiv$ laser beam waist (nm)



Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

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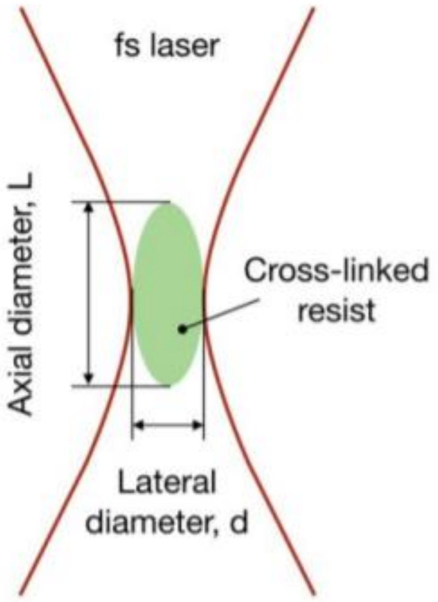

Laser Parameter

$$F = \frac{\nu N_0^2 \sigma_2 t \tau_L}{C}$$

$\nu \equiv$ laser pulse repetition rate (Hz)
$t \equiv$ exposure time (s)
$\tau_L \equiv$ laser pulse duration (s)
$N_0 \equiv$ photon flux during laser pulse

Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

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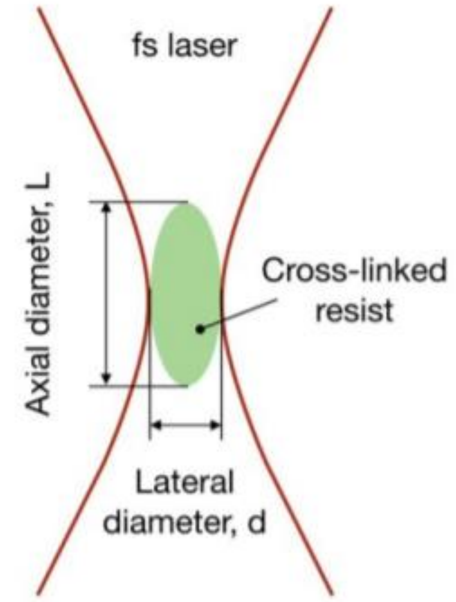

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$t \equiv$ exposure time (s)
$\tau_L \equiv$ laser pulse duration (s)
$N_0 \equiv$ photon flux during laser pulse
$\sigma_2 \equiv$ effective two-photon cross section (cm^4 s)

Resist Parameter

$$C = \log \frac{\rho_0}{\rho_0 - \rho_{th}}$$

$\rho_0 \equiv$ photoinitiator density (wt %)
$\rho_{th} \equiv$ radical polymerization threshold density (wt %)

Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

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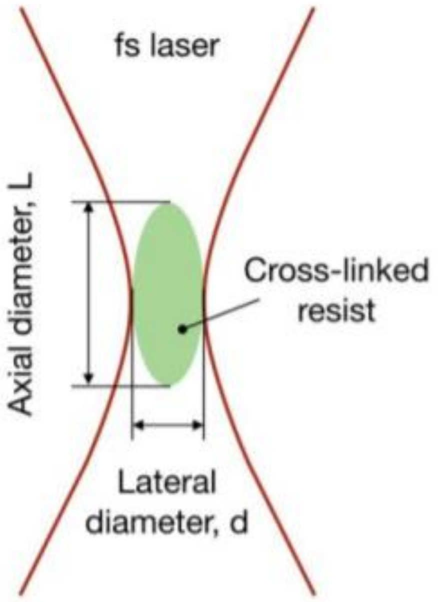

Laser Parameter

$$F = \frac{\nu N_0^2 \sigma_2 t \tau_L}{C}$$

Resist Parameter

$$C = \log \frac{\rho_0}{\rho_0 - \rho_{th}}$$

$N_0 \equiv$ photon flux during laser pulse

$$N_0 = \frac{2(P\Gamma)}{(\pi w_0^2 \tau_L)(\nu \hbar \omega_L)}$$

$P \equiv$ laser power

$\Gamma \equiv$ fraction of light reaching photoresist

$\omega_L \equiv$ laser frequency

Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

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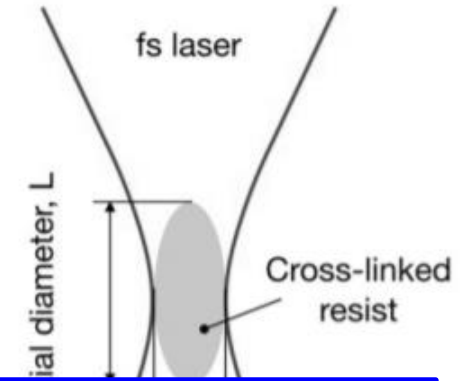


Plug in/rearrange…

Express **voxel height (*L*)** and **voxel width (*d*)** as function of experimental parameters **laser power (*P*)** and **exposure time (*t*)**

Laser Parameter

$$F = \frac{\nu N_0^2 \sigma_2 t \tau_{\mathrm{L}}}{C}$$

$N_0 \equiv$

$$N_0 = \frac{2(P\Gamma)}{(\pi w_0^2 \tau_{\mathrm{L}})(\nu \hbar \omega_{\mathrm{L}})}$$

Resist Parameter

$$C = \log \frac{\rho_0}{\rho_0 - \rho_{\mathrm{th}}}$$

$P \equiv$ laser power

$\Gamma \equiv$ fraction of light reaching photoresist

$\omega_{\mathrm{L}} \equiv$ laser frequency

Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

Voxel Shape Model

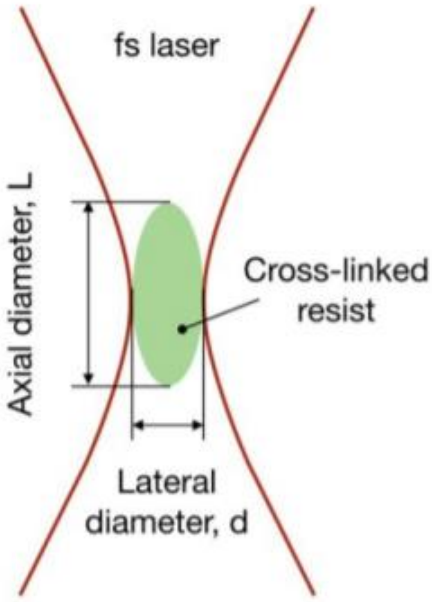
Voxel Height, $L = 2z_r\sqrt{(\alpha t P^2)^{1/2} - 1}$

Voxel Width, $d = w_0\sqrt{\log(\alpha t P^2)}$

$z_r \equiv$ Rayleigh distance (nm)

$w_0 \equiv$ laser beam waist (nm)

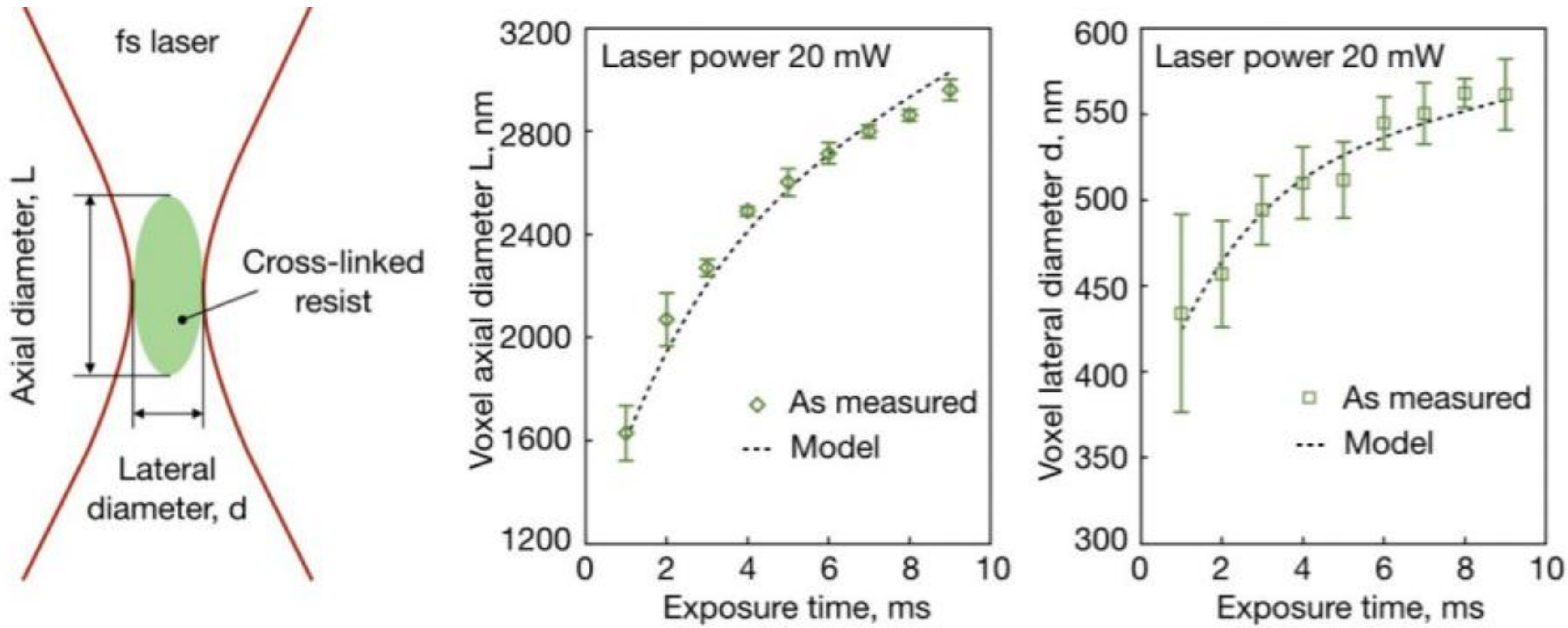
$$\alpha = \frac{\nu\sigma_2}{C\tau_L}\left(\frac{2\Gamma}{(\pi w_0^2)(\nu\hbar\omega_L)}\right)^2$$



- α is a parameter set by the hardware
- Voxel parameters (*L* and *d*) are dependent on **experimental parameters** (laser power and exposure time)
- Two fitting parameters: z_r and w_0

Serbin, J., et al. *Optics Letters* 28 (5), 301-303 (2003)
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

Example of Model Applied to TiO_2 Resist

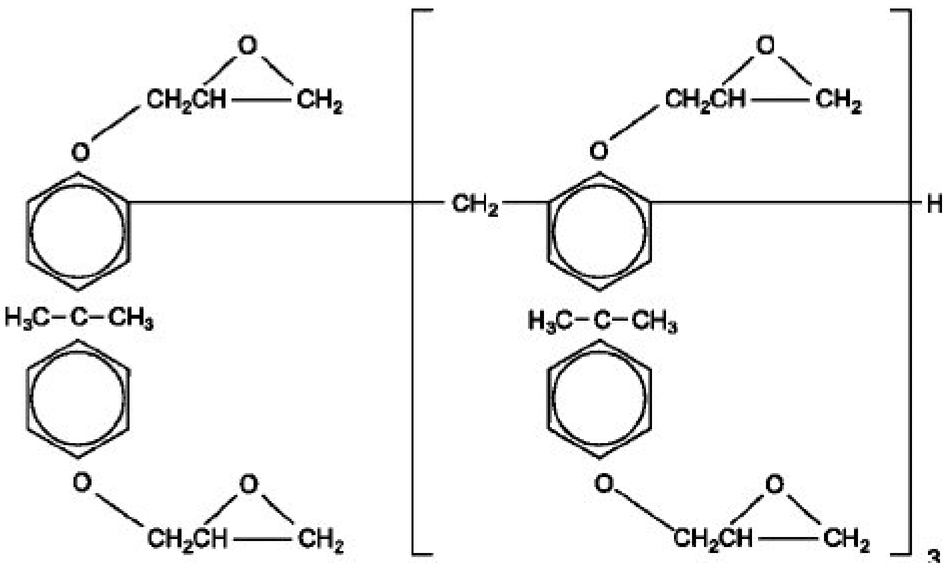


Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

TPL in polymers

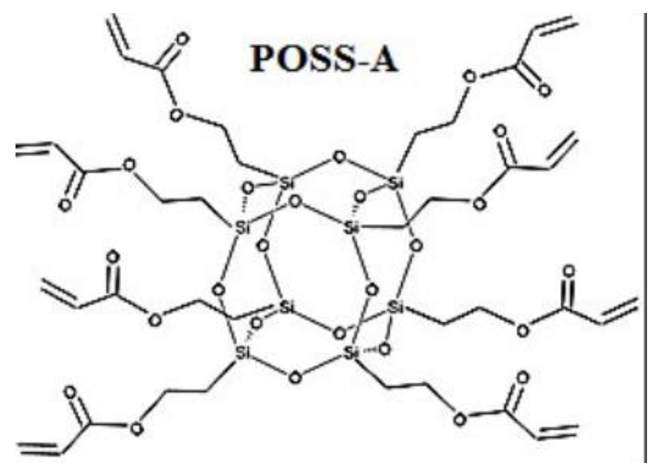
- Traditionally limited to polymers/epoxies (e.g. SU-8, IP-Dip)
- Polyhedral oligomeric silsesquioxane (POSS) for SiO_2 fabrication
- Available materials: Polymer and SiO_2 (silicate networks)

SU-8 Molecule



Genolet, G., et al *Review of Scientific Instruments* 70, 2389-2391 (1999)

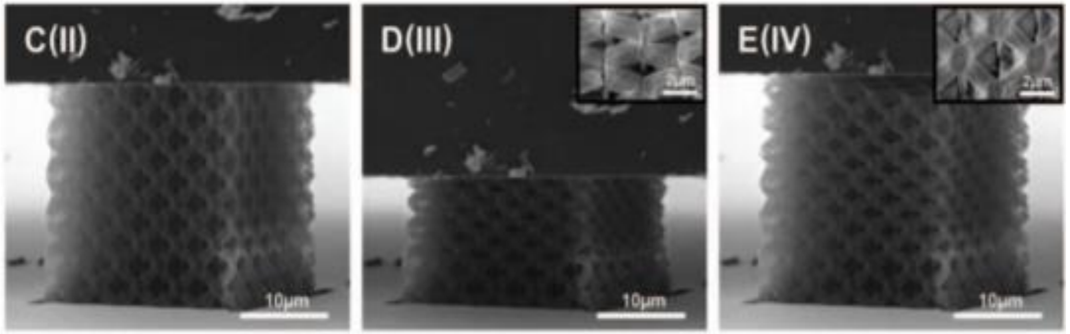
POSS



Tegu, E. et al., *Chem. Mater.* 16 (13), 2567–2577 (2004)
Borah, D. et al., *Nanomaterials* 8 (1), 32 (2018)

Applications of TPL (Mechanics)

Ductile Ceramic Lattices



Meza, L., et al. *Science* 345 (6202), 1322-1326 (2014)

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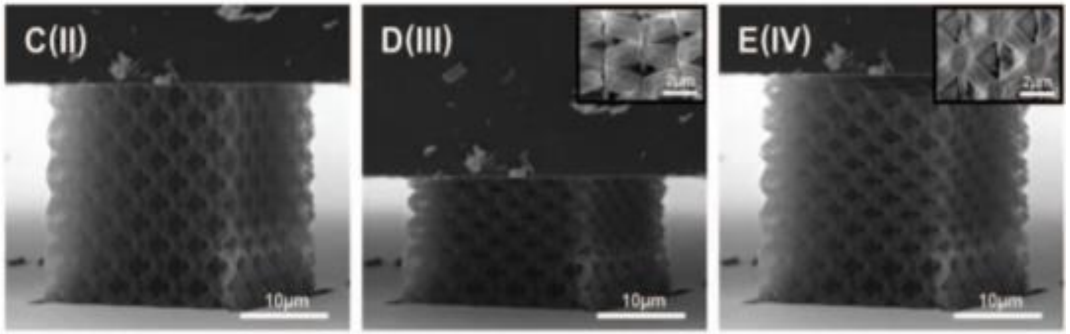
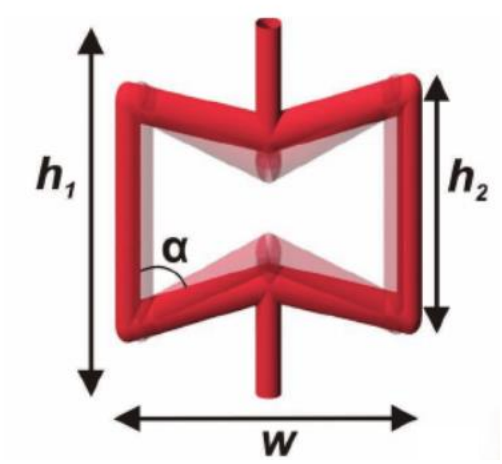
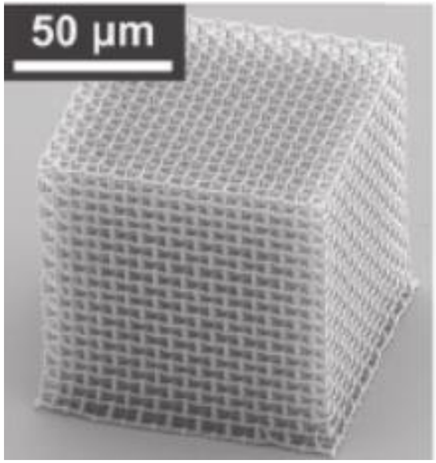
Ductile Ceramic Lattices



Meza, L., et al. *Science* 345 (6202), 1322-1326 (2014)

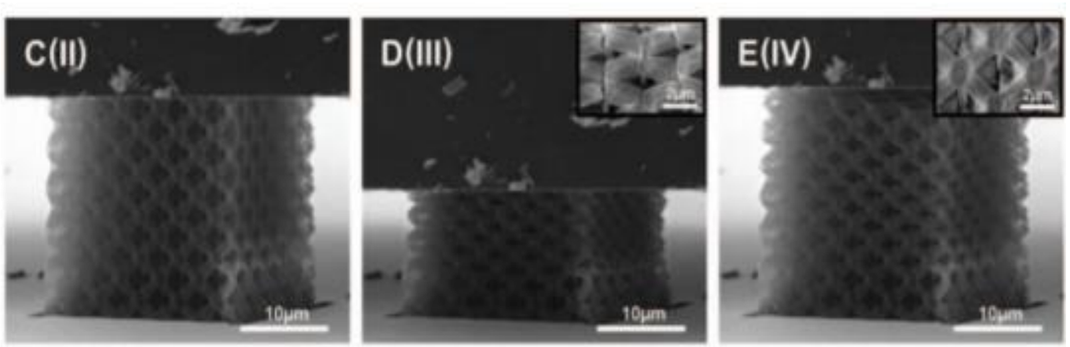
Negative Poisson Ratio Metamaterials





Buckmann, T., et al. *Adv. Mat. 24*, 2710-2714 (2012)

Ductile Ceramic Lattices



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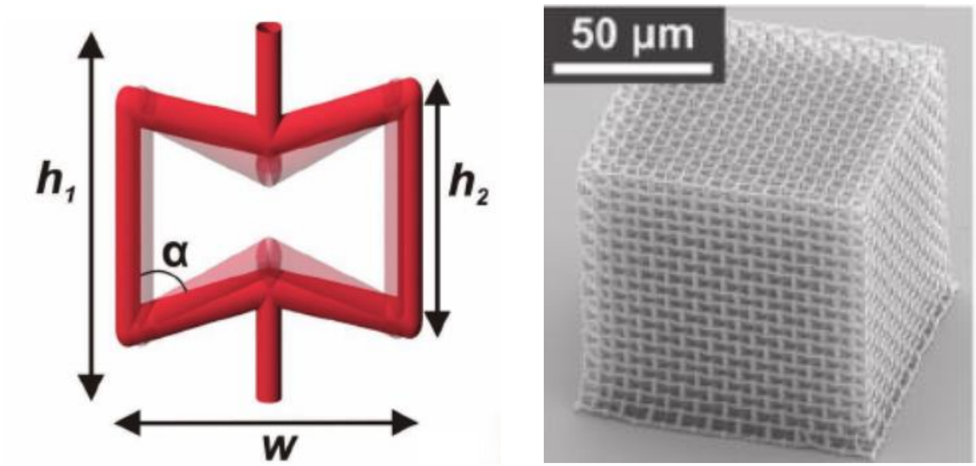
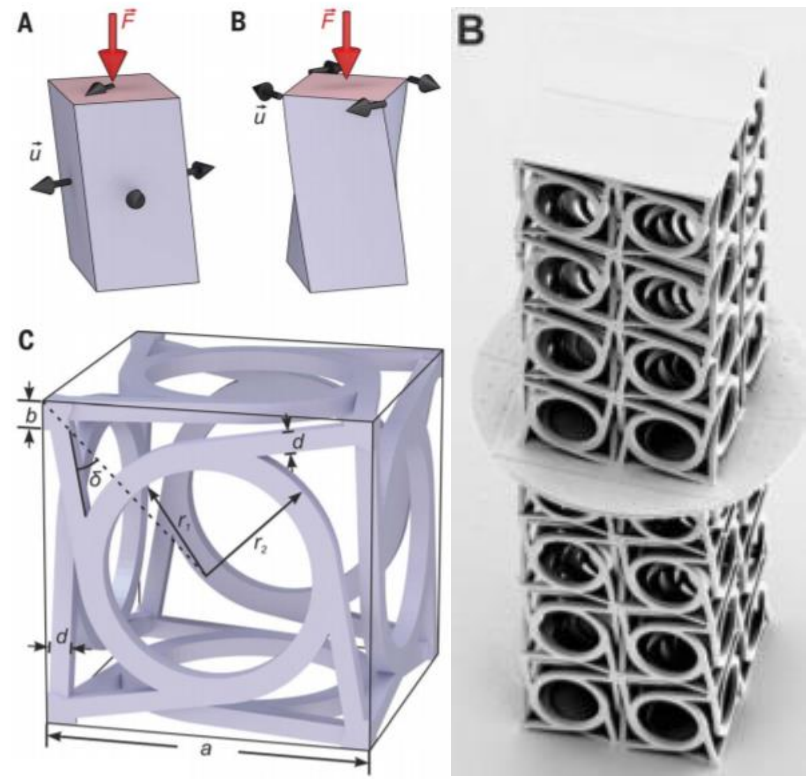
Negative Poisson Ratio Metamaterials



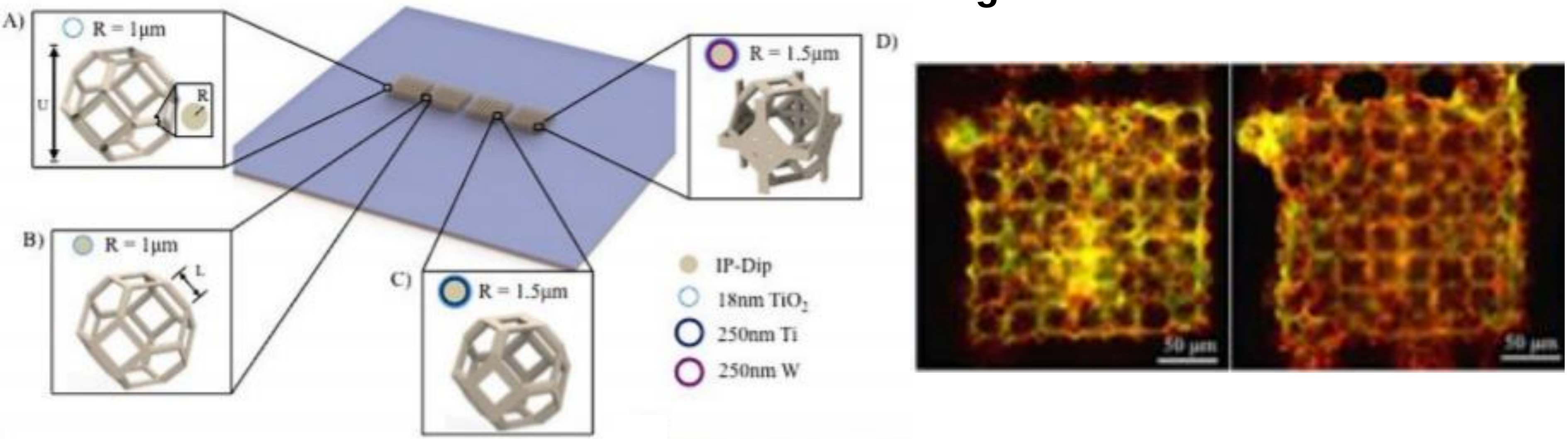
Buckmann, T., et al. *Adv. Mat. 24*, 2710-2714 (2012)

Twisted Mechanical Metamaterials

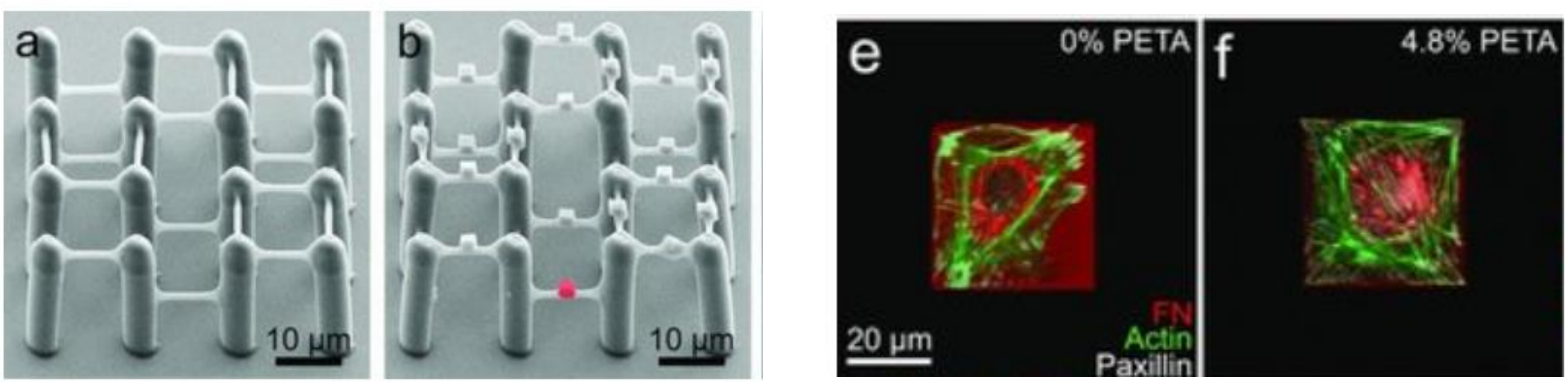


Freznel, T., et al. *Science 358*, 1072-1074 (2017)

Cell Scaffolding

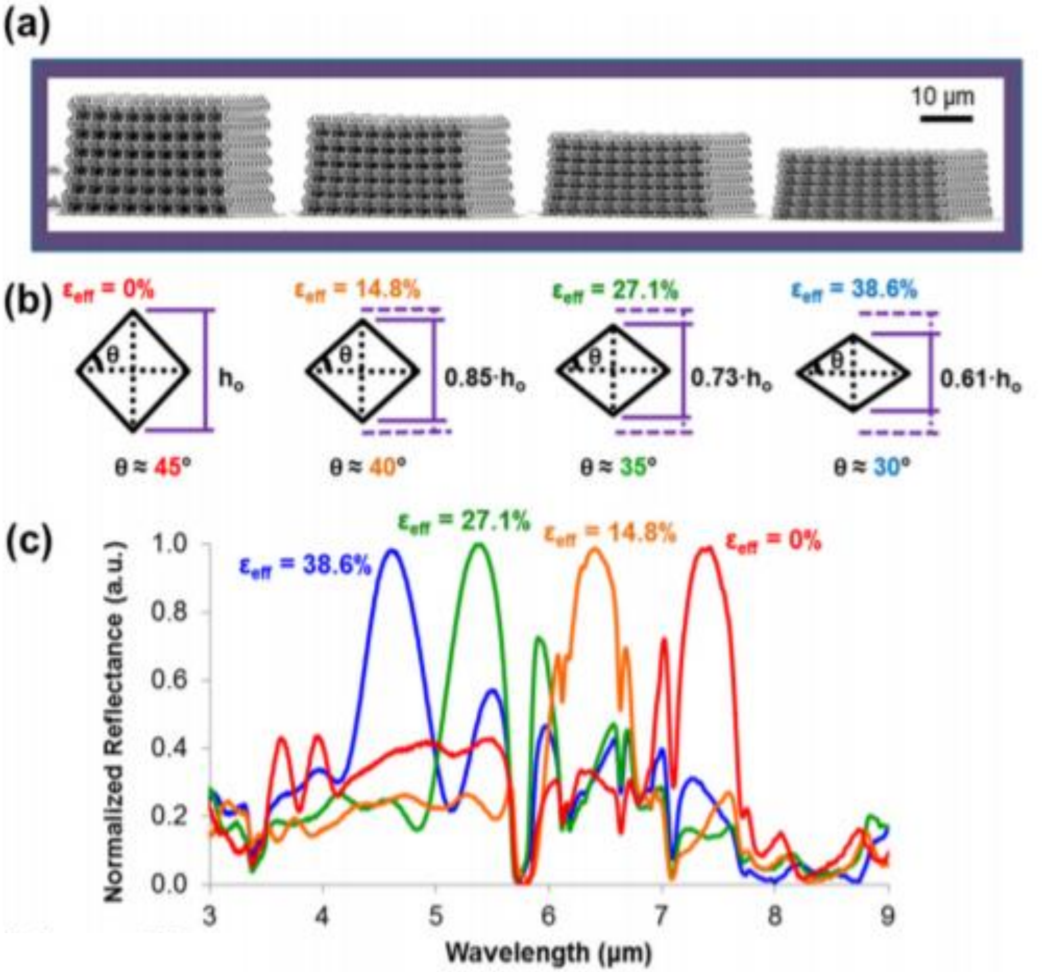


Maggi, A., et al. *Acta Biomater.* 63, 294-305 (2017)



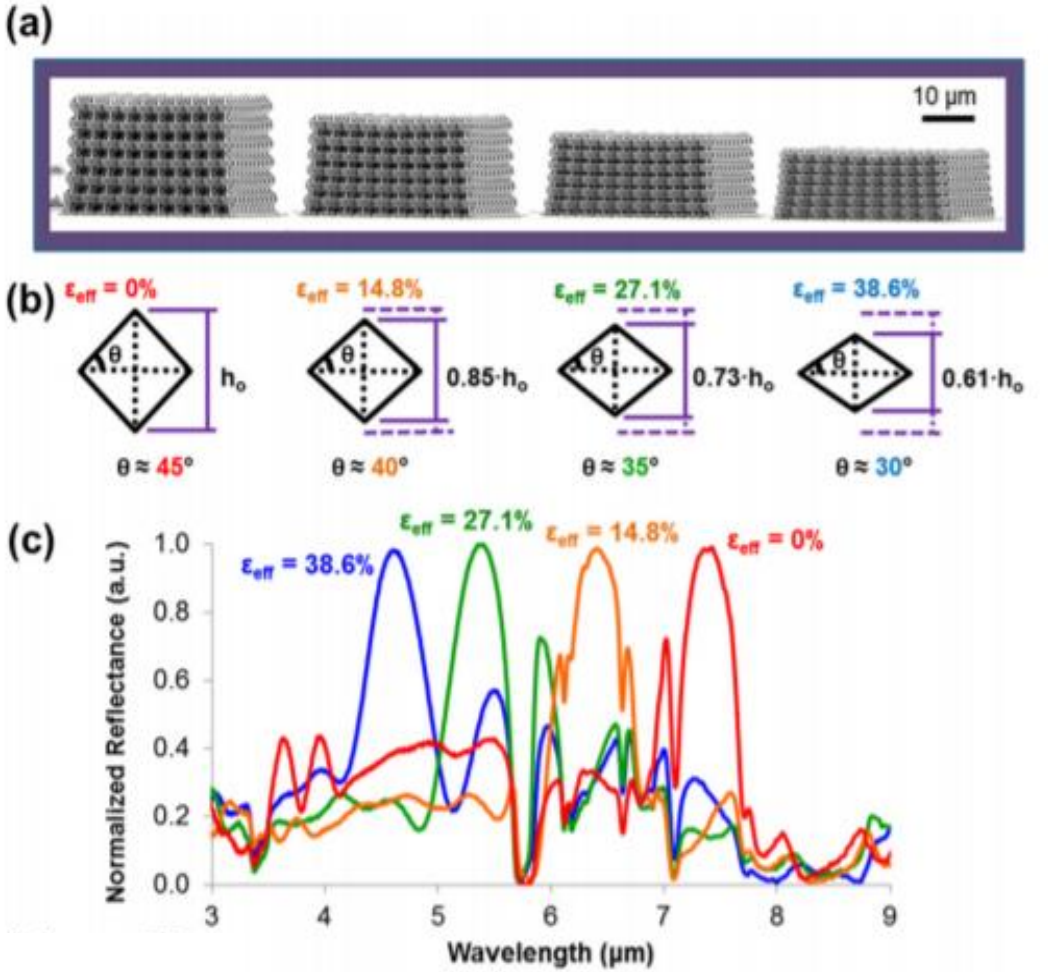
Klein, F., et al. *Adv. Mater.* 23 (11), 1341-1345 (2011)

Mechanically Tunable Photonic Crystals



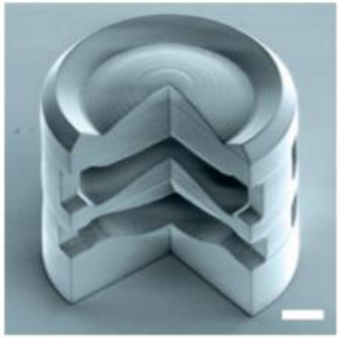
Chernow, V., et al. *Apl. Phys. Lett.* 107, 101905 (2015)

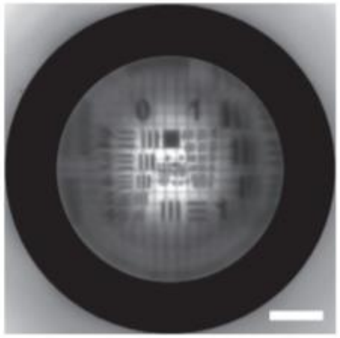
Mechanically Tunable Photonic Crystals



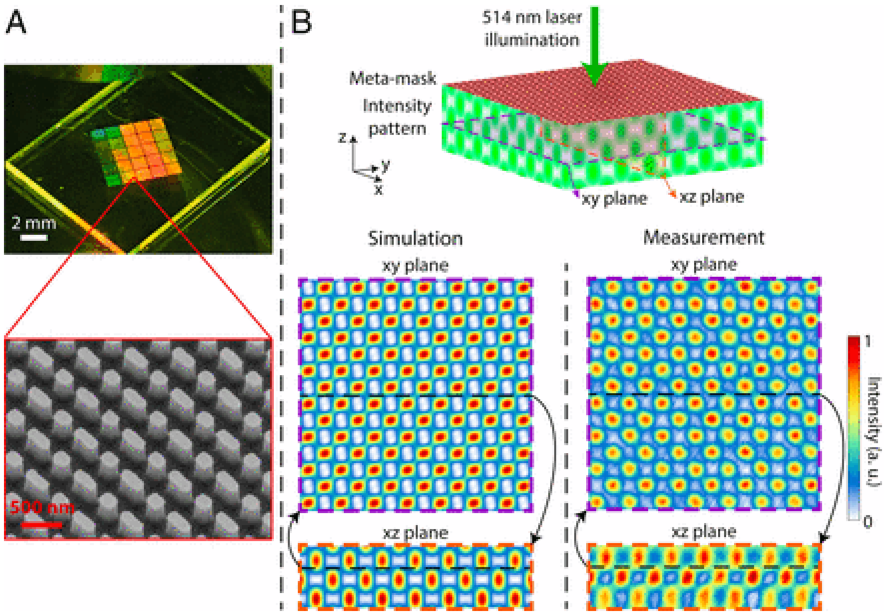
Chernow, V., et al. *Apl. Phys. Lett.* 107, 101905 (2015)

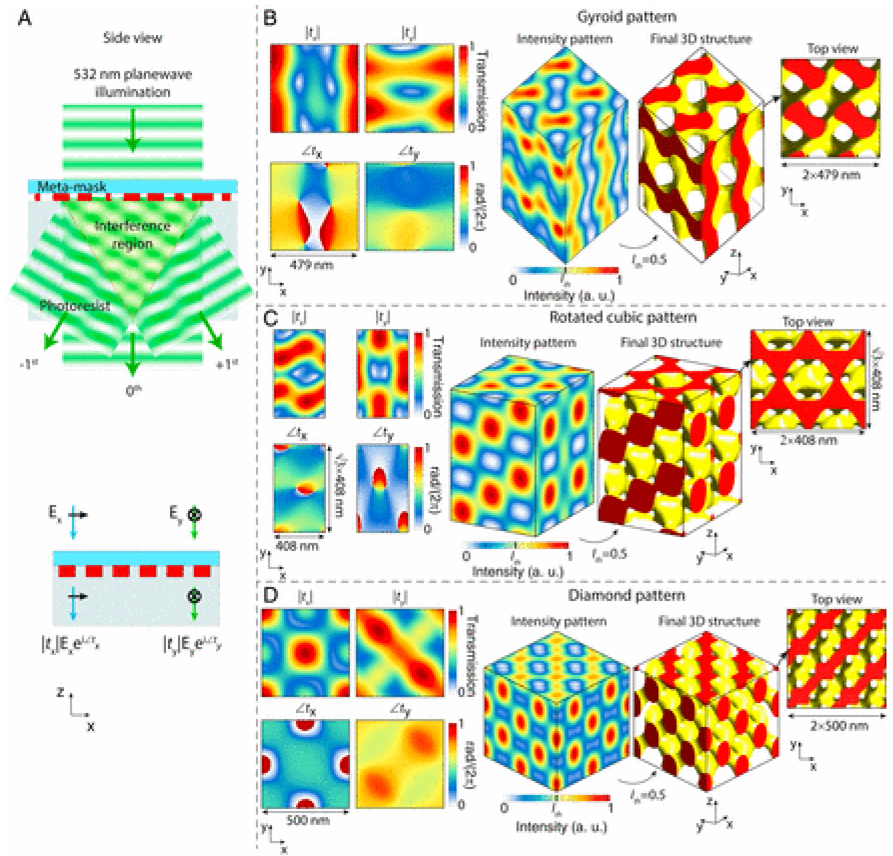
Microscale Multi-Lens Objectives





Gissibl, T., et al. *Nat. Photonics* 10, 554-560 (2016)

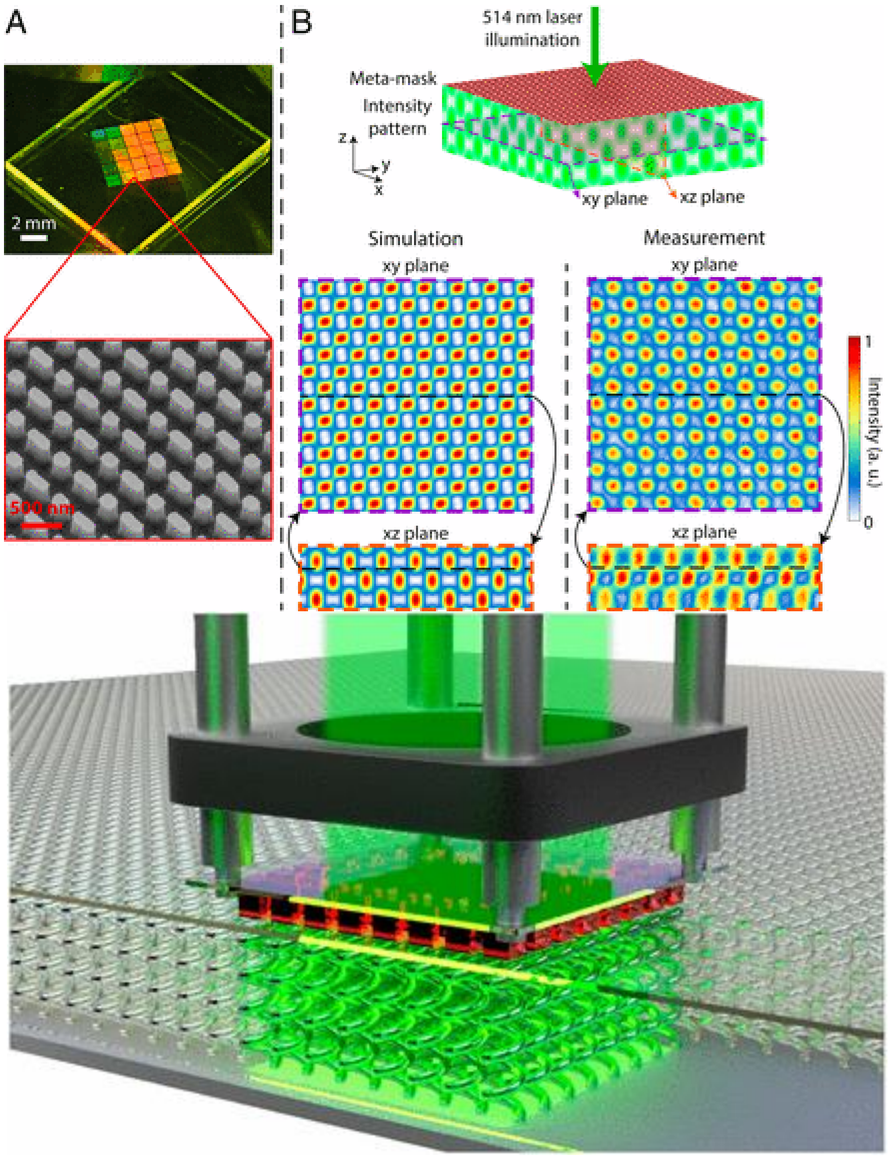


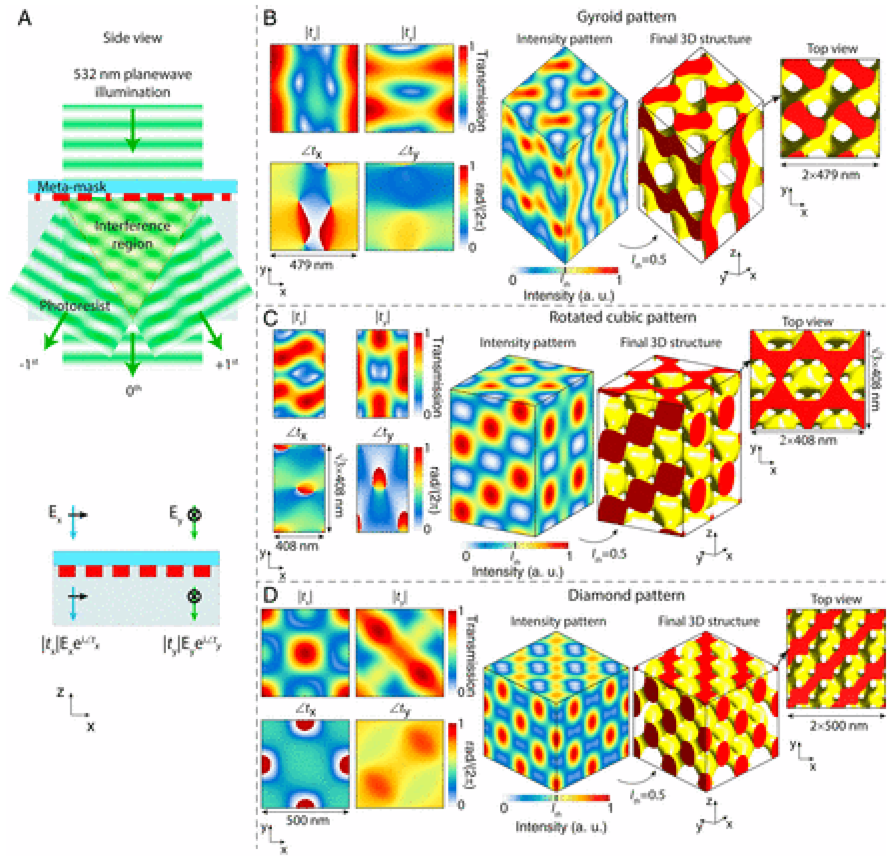


Challenge of small feature size vs throughput!

Kamali, S.M., et al. *PNAS* 116 (43), 21379-21384 (2019)

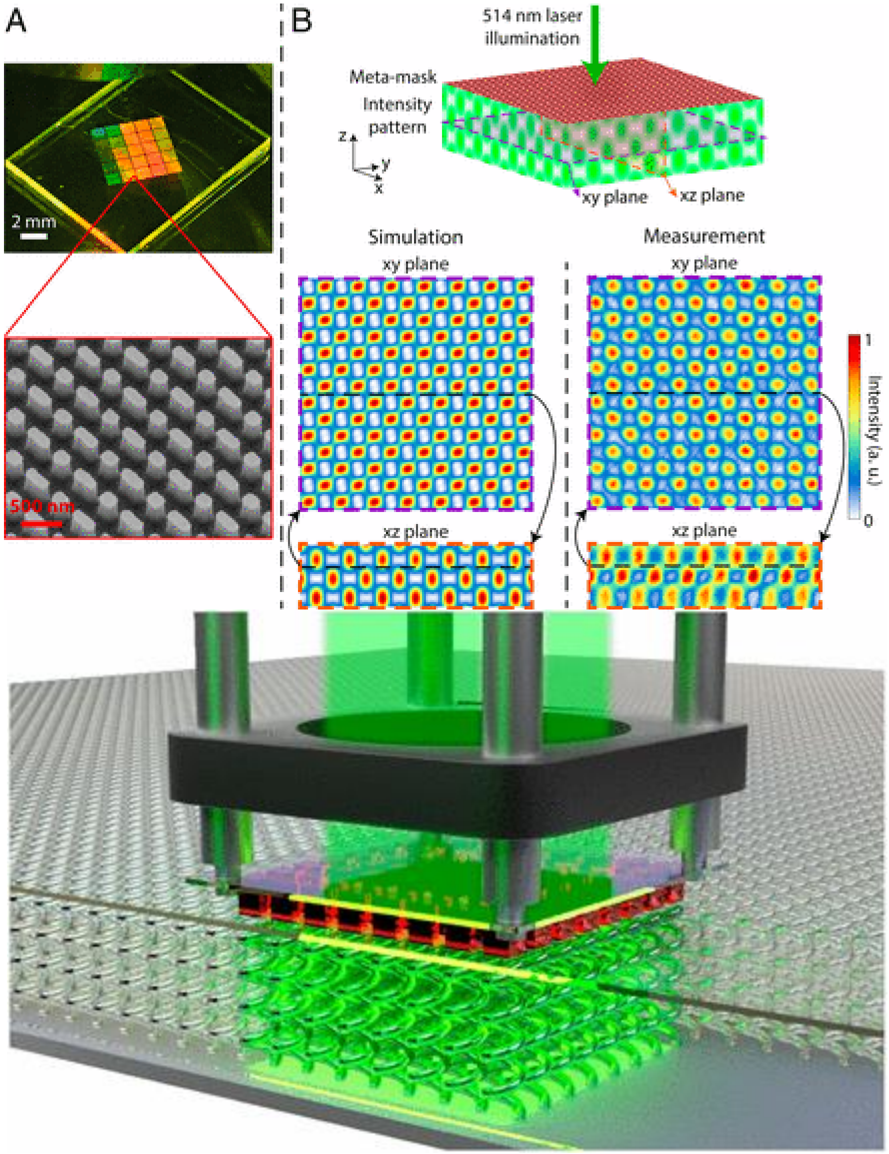
Scalability

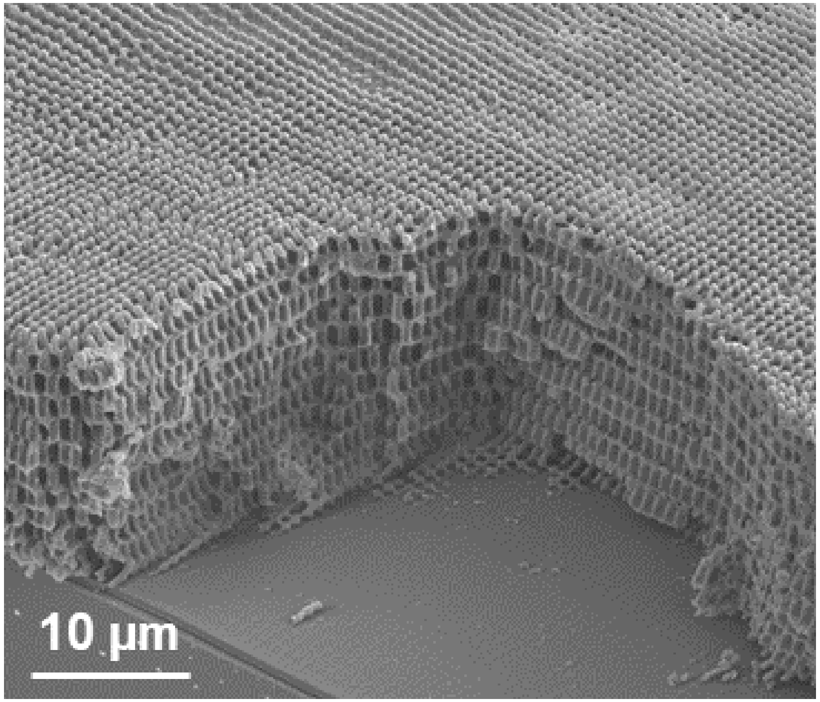




Metasurface mask to control intensity profile, scanned in position

Scalability





Kamali, S.M., et al. *PNAS* 116 (43), 21379-21384 (2019)
Courtesy of Phillippe Pearson

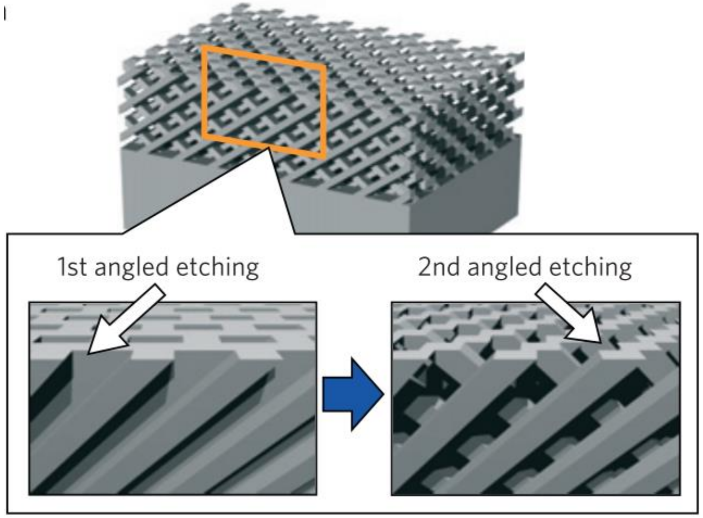
Complex Fabrication processes to fabricate 3D structures in various materials:

- **Multi-angled etching**
- Micromanipulation and Stacking
- Double Inversion

- Limited geometries
- Active area of development

Multi-angled etching

Silicon, n~3.48 at 1.5 μm



Takahashi, S. et al., *Nat. Mater.* **8(9)**, 721–725 (2009)

Complex Fabrication Methods for Other Materials

Complex Fabrication processes to fabricate 3D structures in various materials:

- Multi-angled etching
- **Micromanipulation and Stacking**
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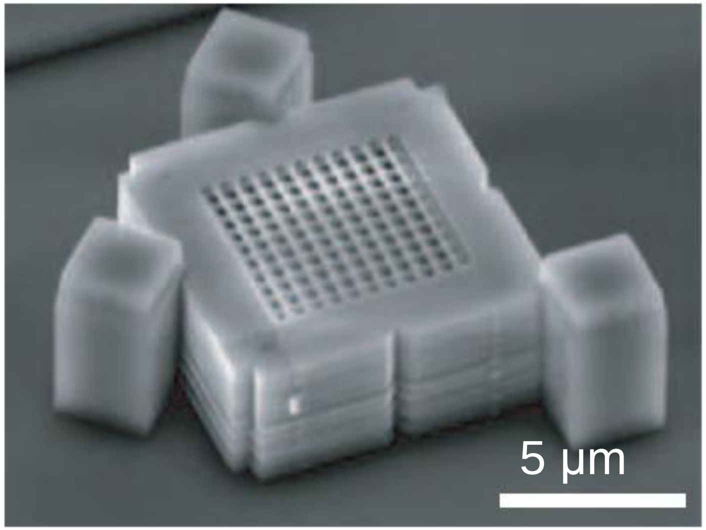
Micromanipulation and stacking

GaAs, n~3.36 at 1.5 μm



Aoki, K. et al., *Nat. Photonics* **2(11)**, 688–692 (2008)

- Extremely time consuming, very manual process
- Not scalable

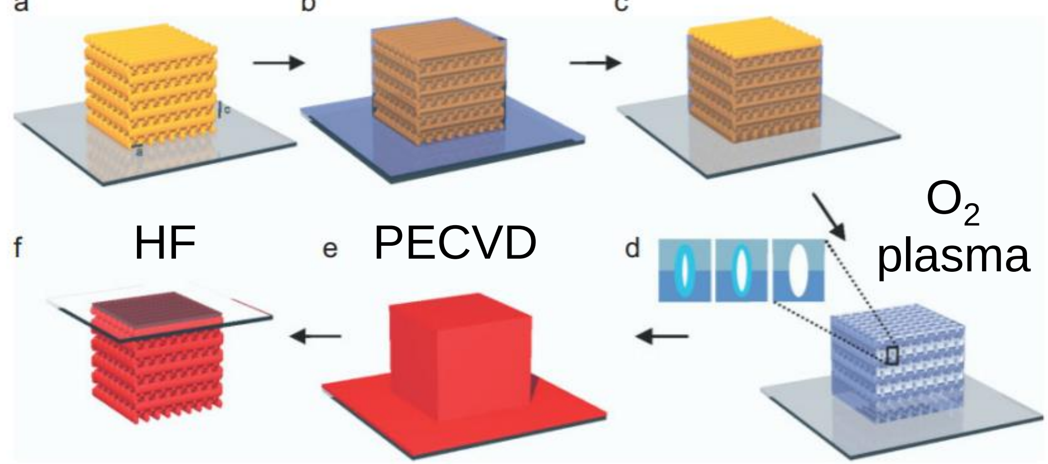
Complex Fabrication Methods for Other Materials

Complex Fabrication processes to fabricate 3D structures in various materials:
- Multi-angled etching
- Micromanipulation and Stacking
- **Double Inversion**

- Many fabrication steps
- HF-resistant materials/substrates only

Double Inversion

Si, TiO_2, Cu, etc.



Extremely Limited Choice of Pre-Ceramic Materials for AM

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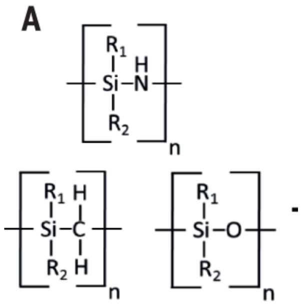
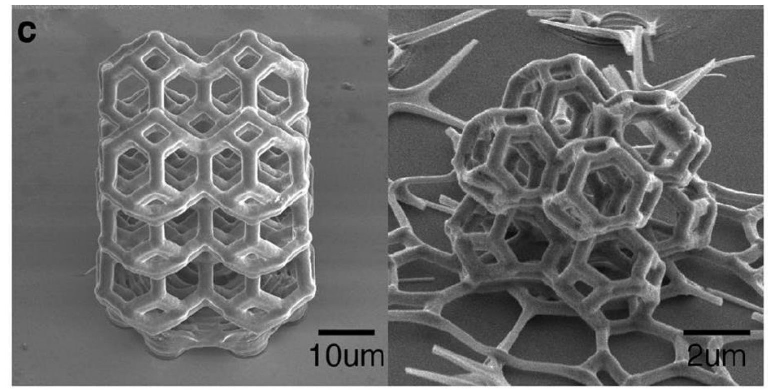
Silicon oxycarbide



UV curable monomers
& UV photo initiator

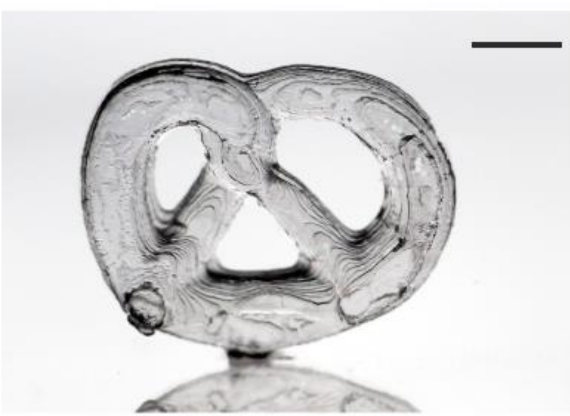
Eckel, Z. C. et al., *Science* **351** (6268), 58–62 (2016)

Zinc oxide



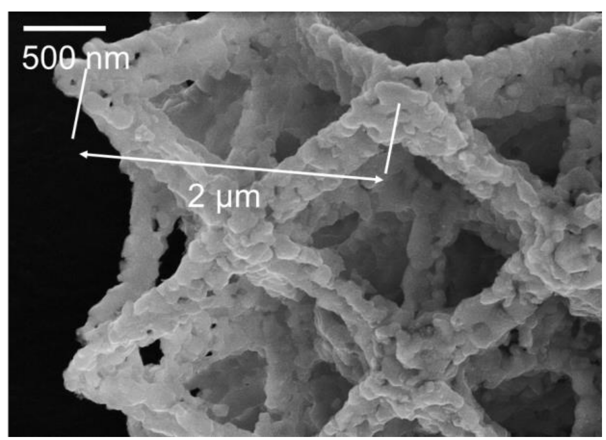
D. W. Yee et al. *Adv. Mater.* **1901345** (2019)

Silica



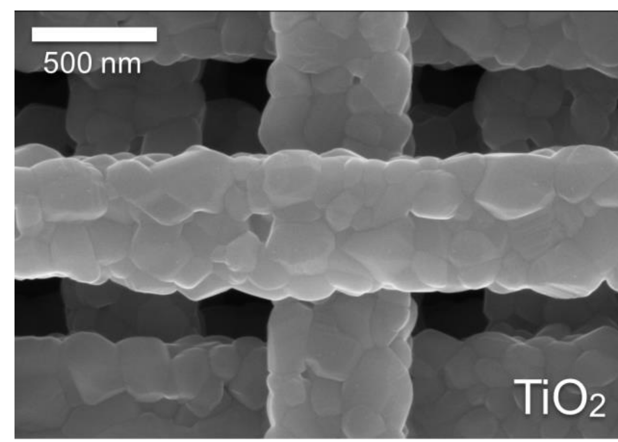
Kotz, F. et al., *Nature* **544** (7650), 337–339 (2017)

Nickel



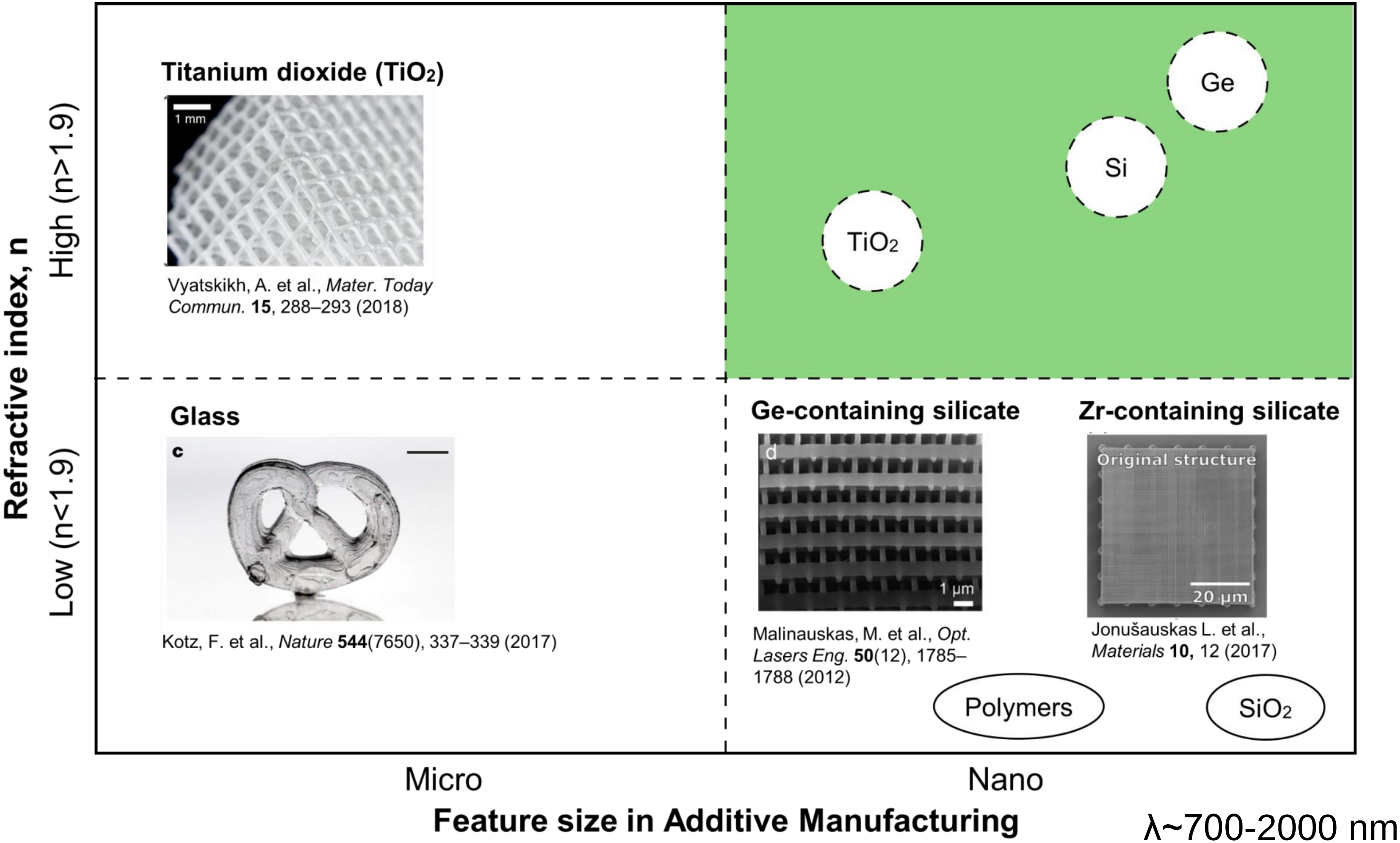
Vyatskikh, A. et al., *Nat. Commun.* **9**, 593 (2018)

Titanium dioxide



Vyatskikh, A. et al., *Proc. SPIE* **10930-16** (2019)

Limited Choice of High Refractive Index Materials for AM of 3D Dielectrics



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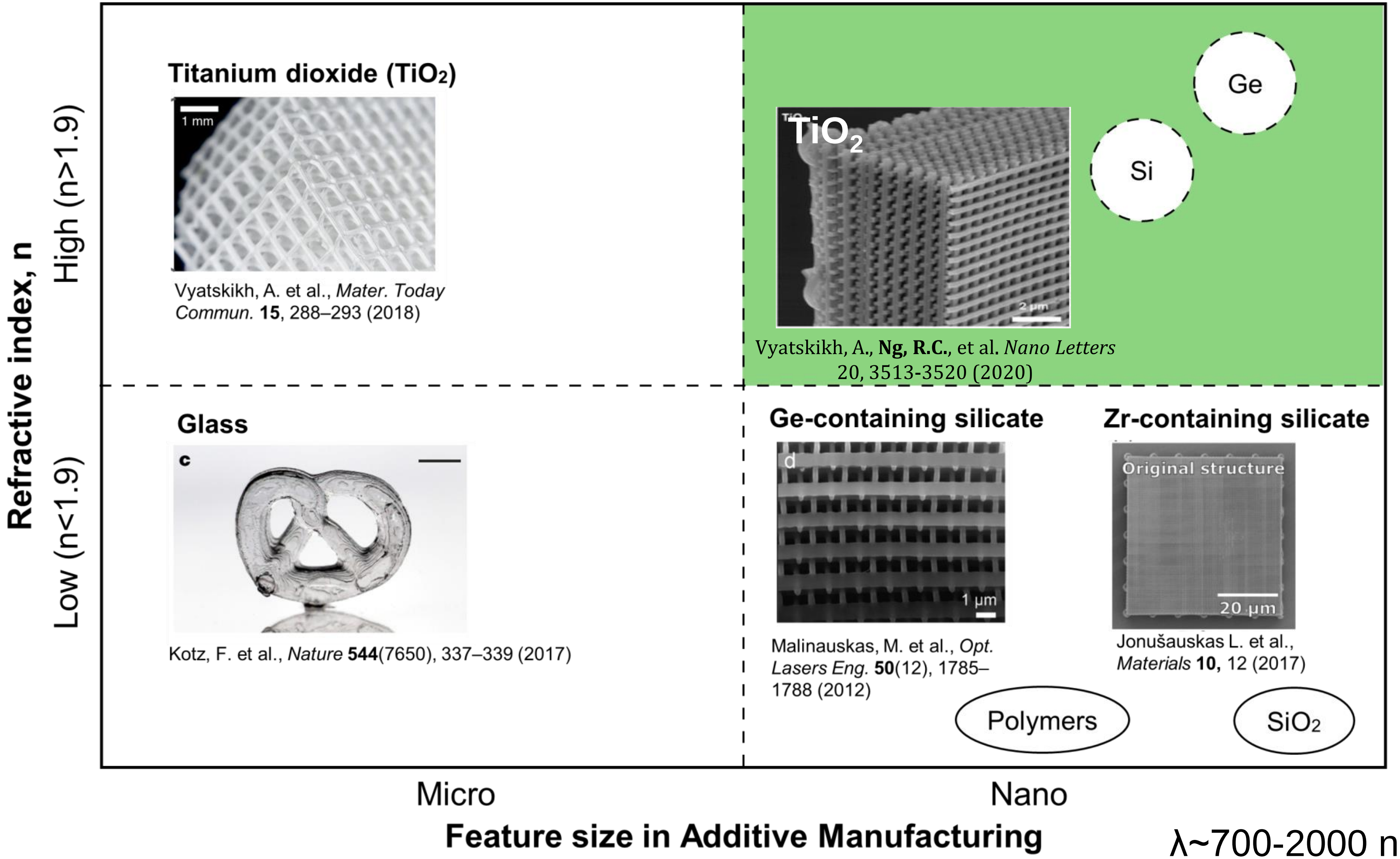
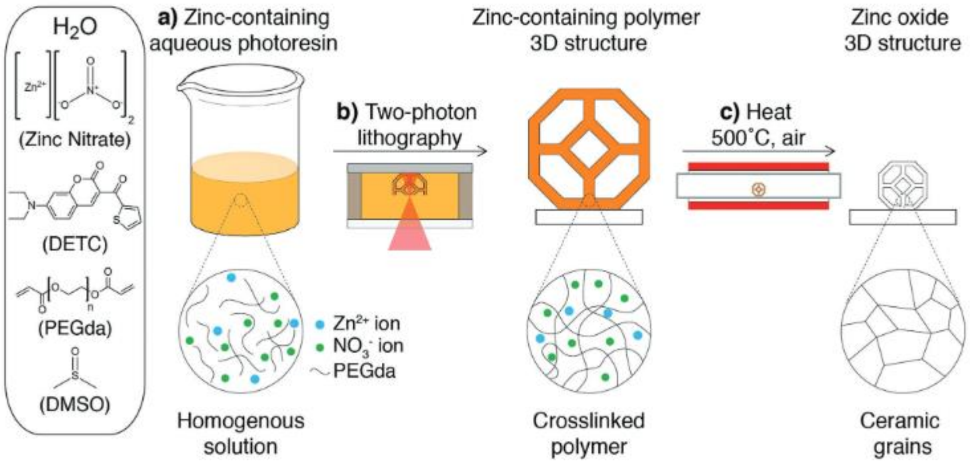


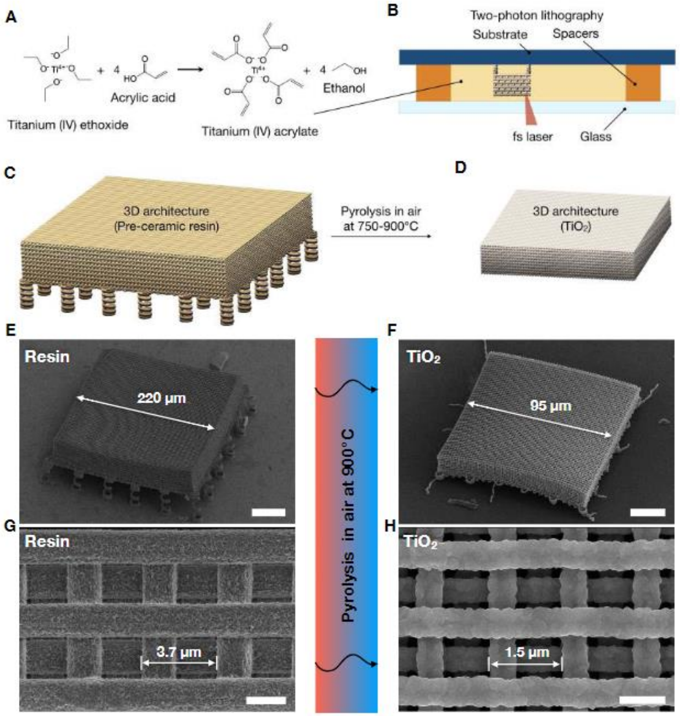
λ~700-2000 nm

Additive Manufacturing via Resin Development

Material choice previously very limited in 3D….



Yee, D., et al. *Advanced Materials* **31**, 1901345 (2019)



Vyatskikh, A., et al. *Nature Communications* **9**, 593 (2018)

- Any metal oxides (reduced, nitridized, etc to other materials)
- Lower porosity than existing literature (effective refractive index)
- One step fabrication (two with pyrolysis)

Enables facile fabrication of 3D structures in many different materials

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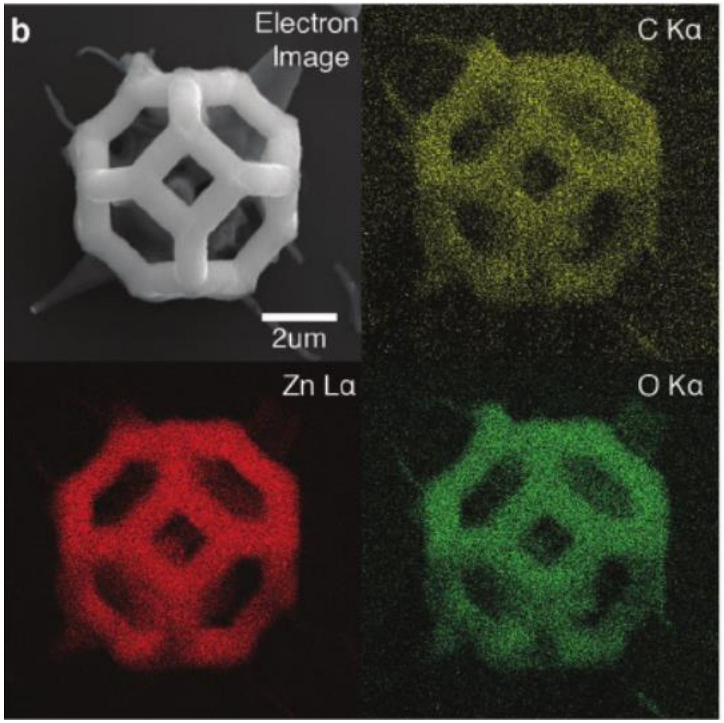

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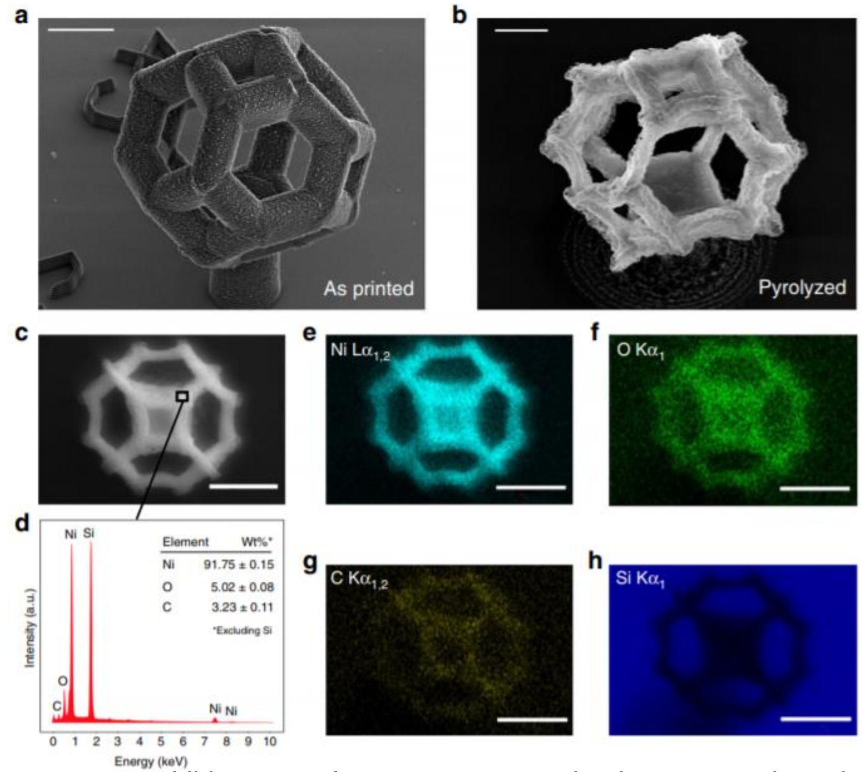

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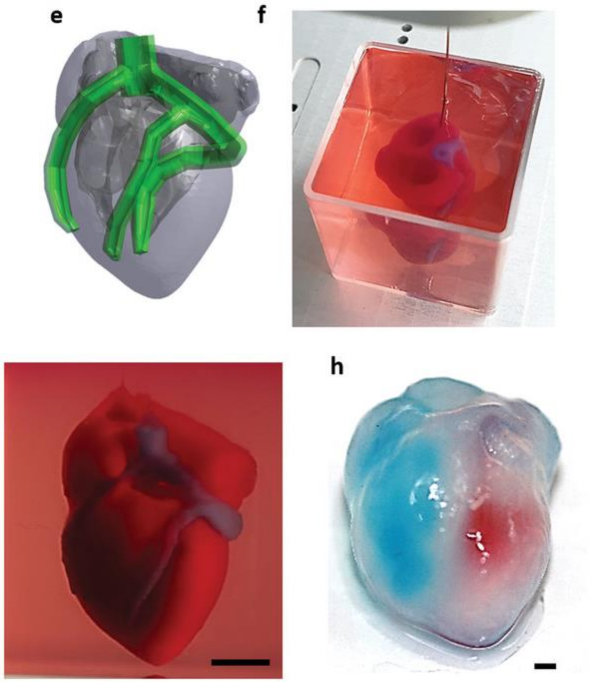
Biomedical

Cells

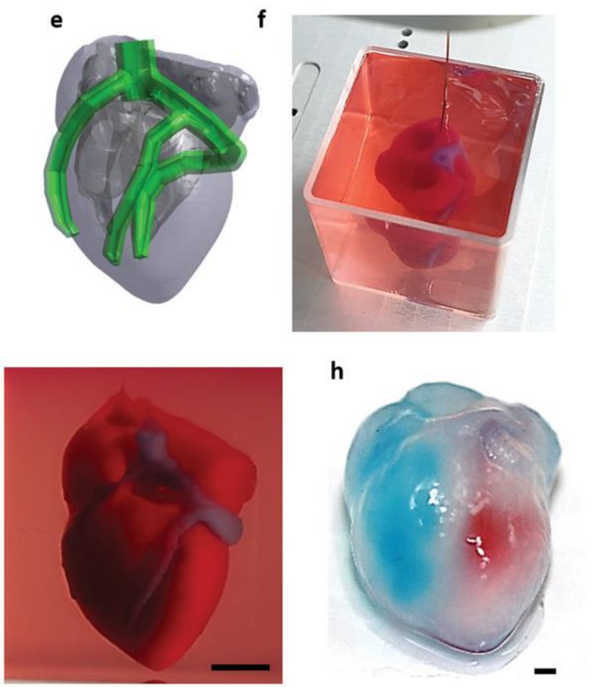


Noor, Nadav, et al. *Adv. Sci.* 6 (2019): 1900344.

Applications of TPL in Other Materials

Biomedical

Cells



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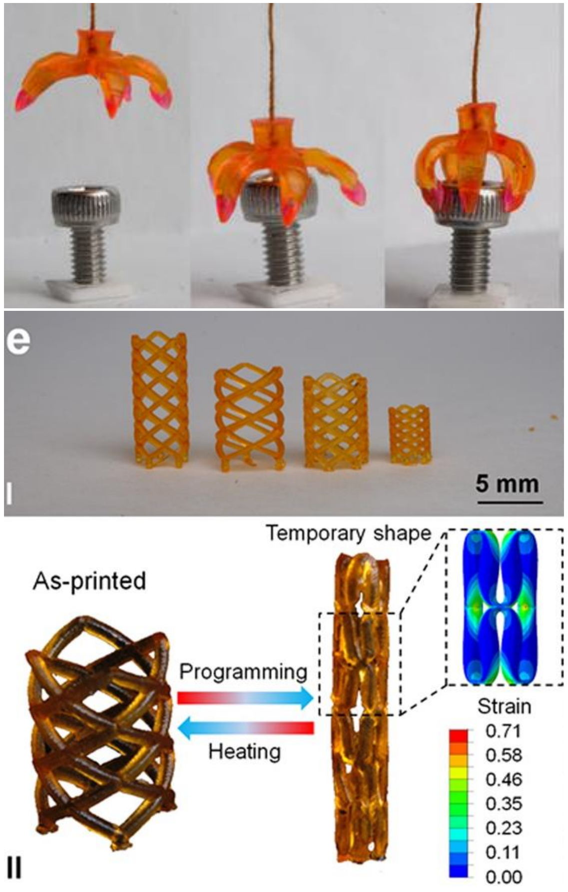
Devices

Stimuli responsive materials



Ge, Qi, et al. *Sci. Rep.* 6 (2016): 31110.

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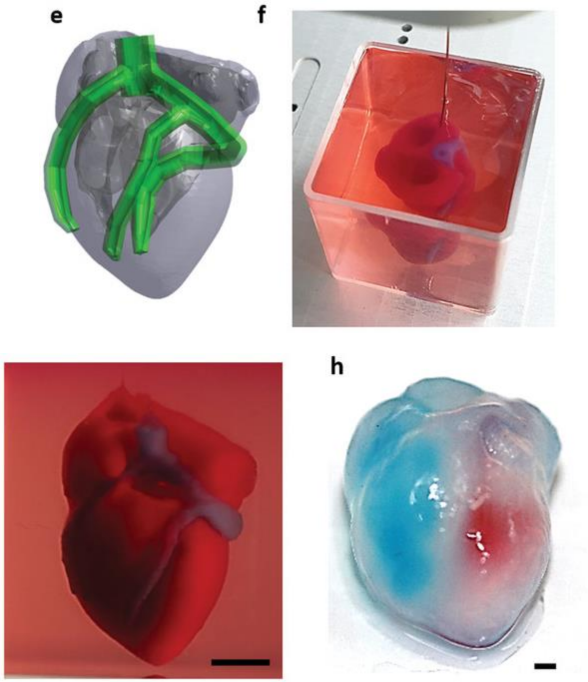

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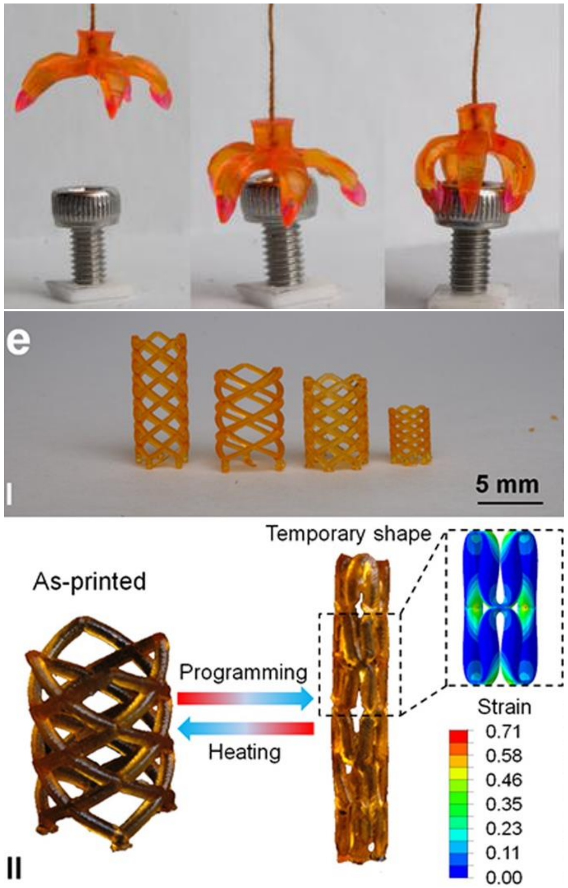

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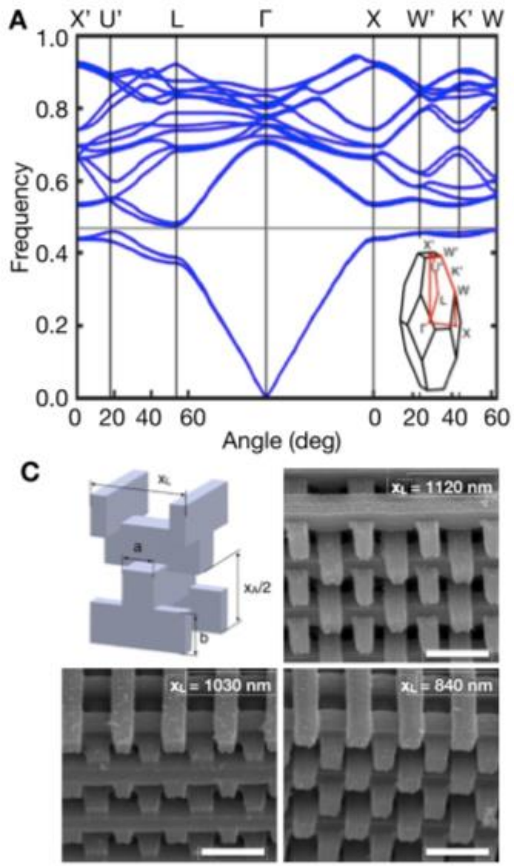
Optical

High refractive index materials



Vyatskikh, Andrey et al. *Nano Lett.* (2020).

Courtesy of Dr. Daryl Yee

Applications of TPL in Other Materials

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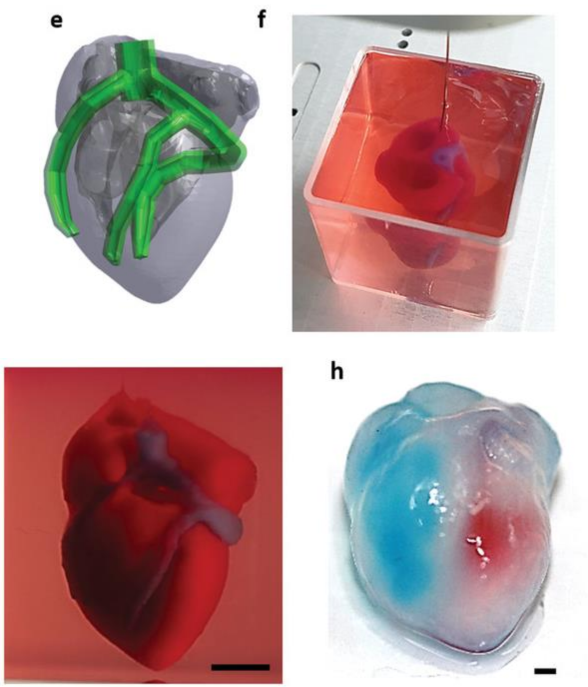

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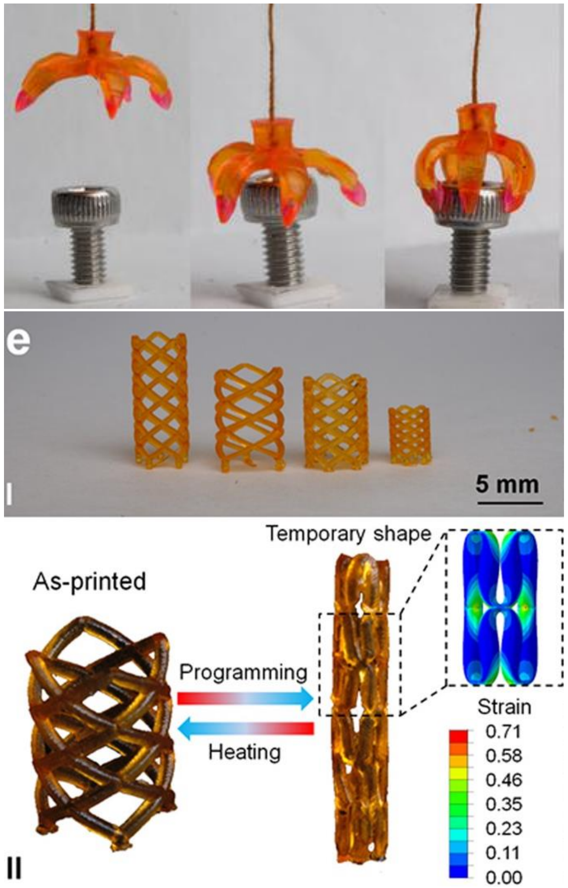

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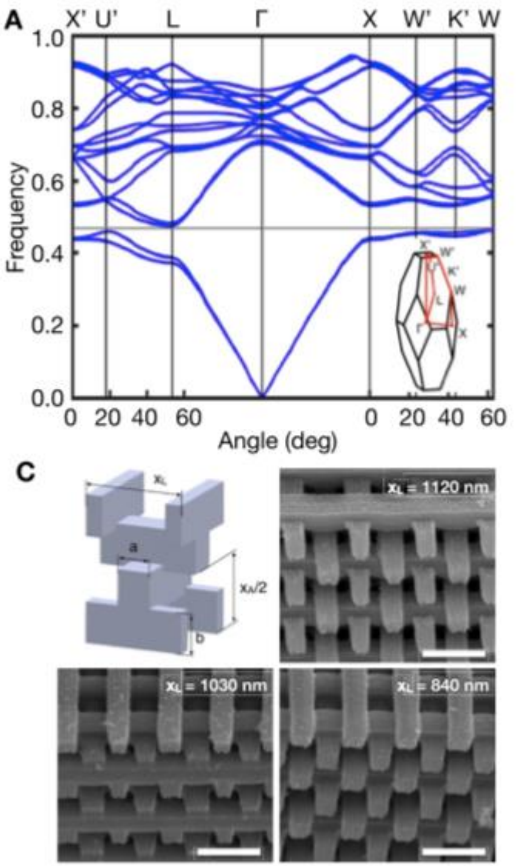

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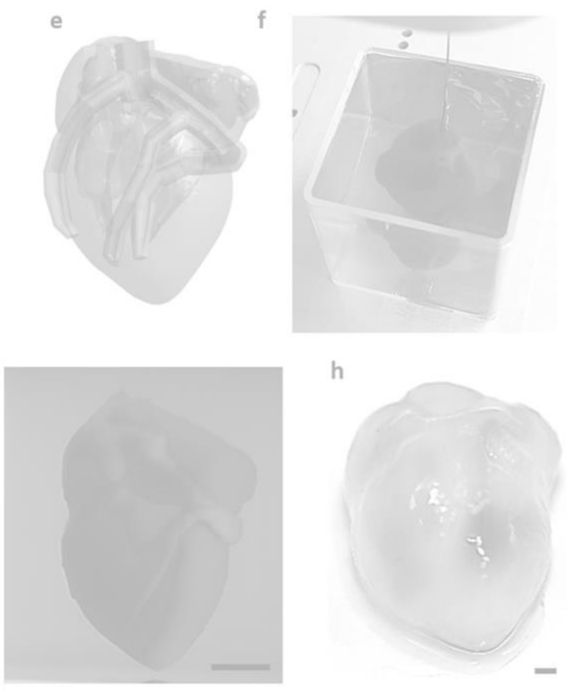

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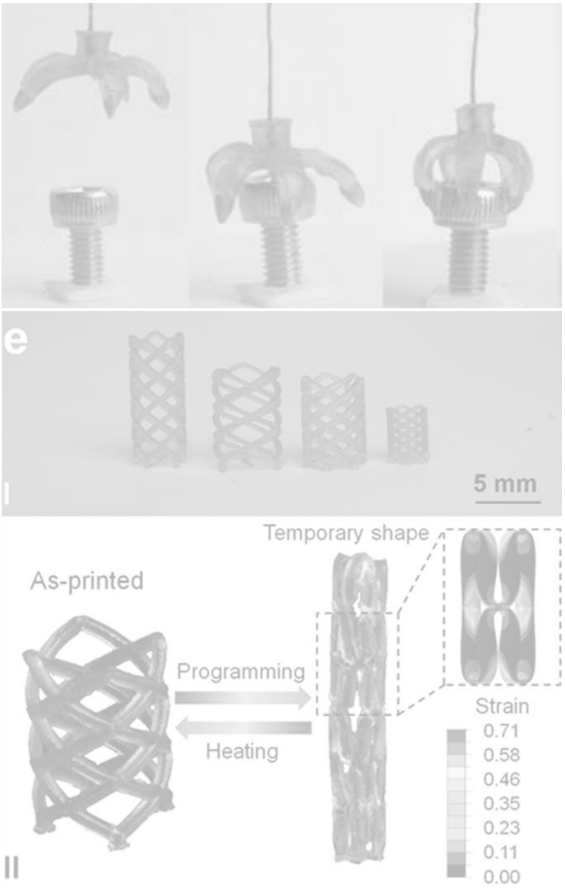

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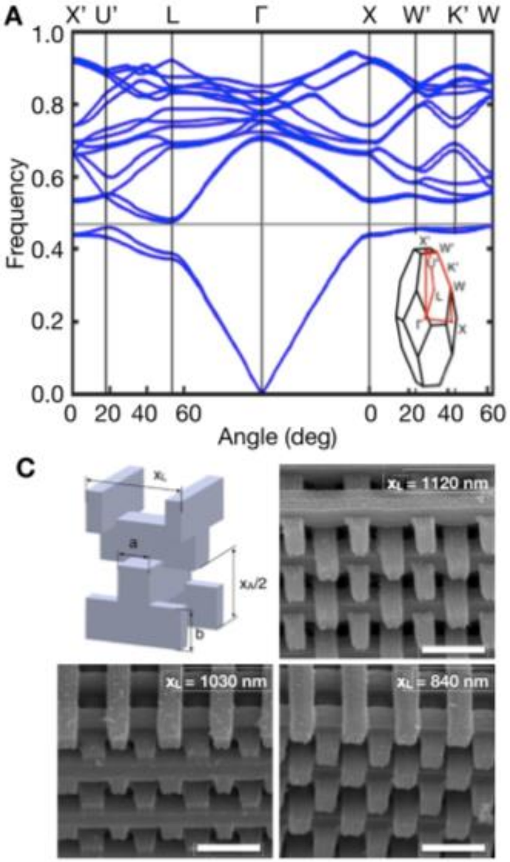

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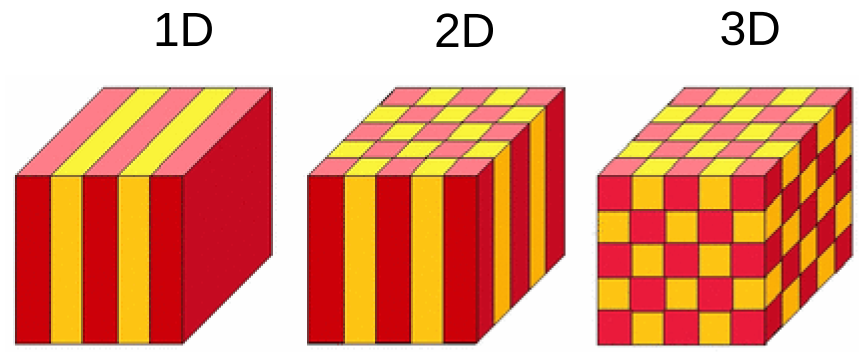
Photonic Crystals

- Traditional planar photonics cannot confine light in 3D
- Enables: 3D photonic circuits, emission control (band gap effects), other phenomena (dispersion effects)



Joannopoulos, et al. *Molding the Flow of Light*. 2nd ed. Princeton, NJ: Princeton UP, 2008

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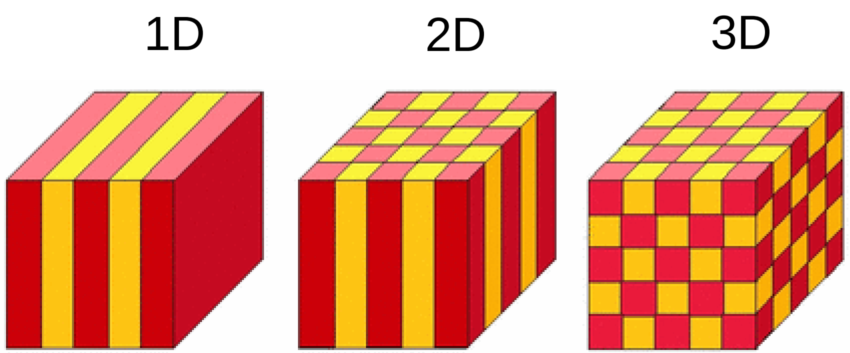

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Full photonic bandgap in woodpile structures: $n > 1.9$
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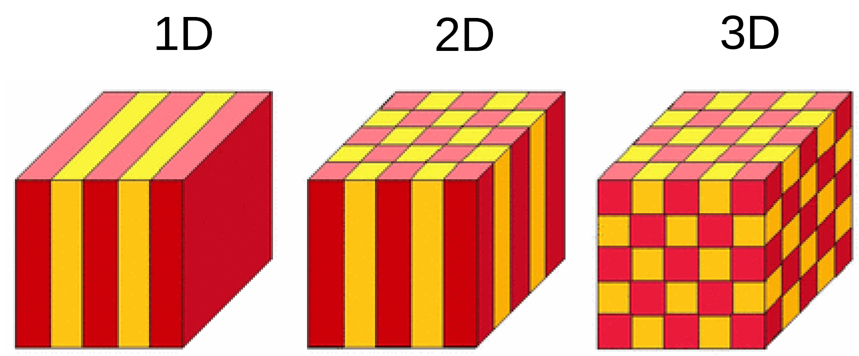

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Von Freymann, G., et al. *Chem Soc Rev* **42**, 2528 (2013)

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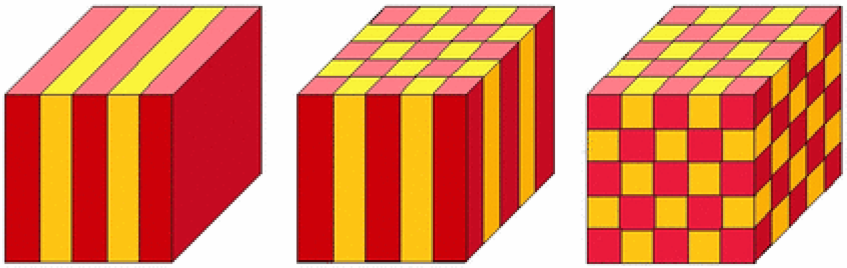

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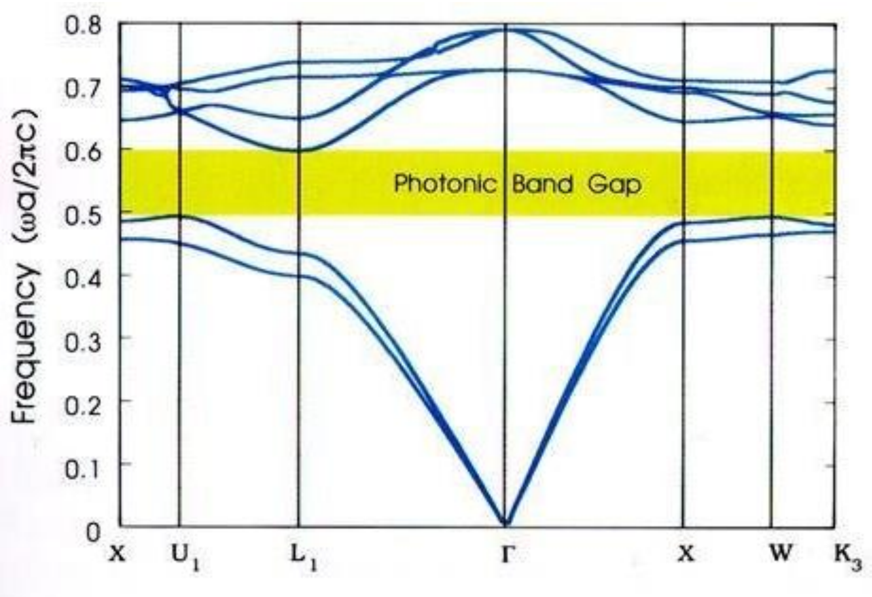
Additive Manufacturing?

Von Freymann, G., et al. *Chem Soc Rev* **42**, 2528 (2013)

Structural Color in Pyrolyzed 3D Photonic Crystals

Photonic Band Gap



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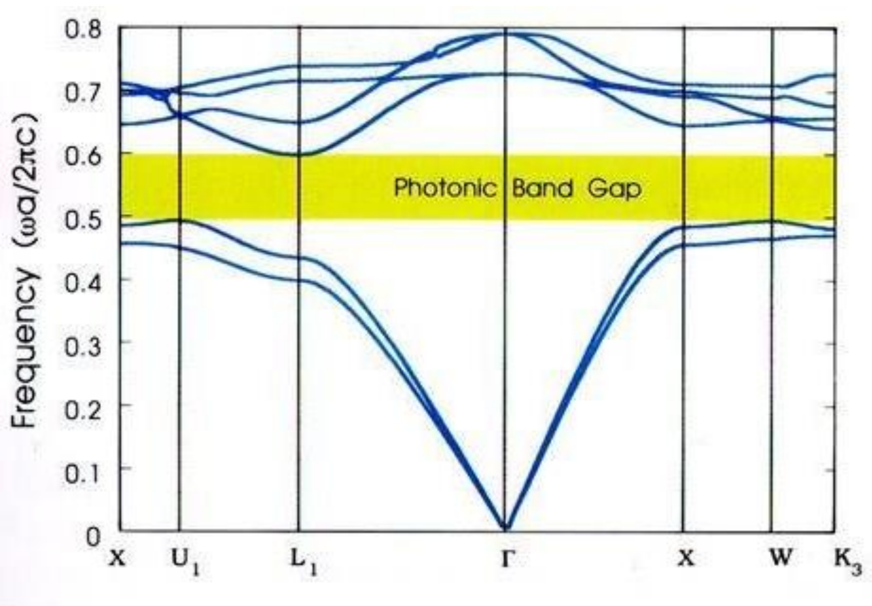
- PhCs possess band gap on order of periodicity, range of frequencies over which light cannot propagate
- Frequencies within band gap are reflected

Photonic Band Gap



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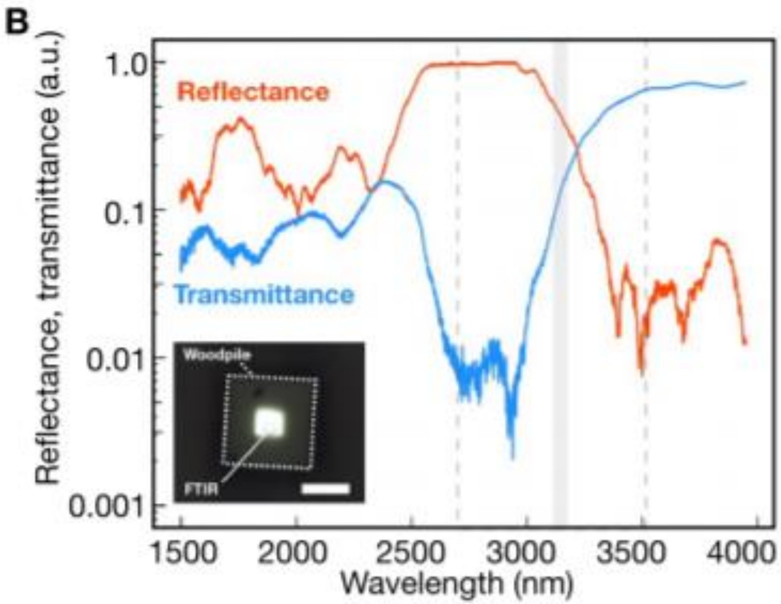

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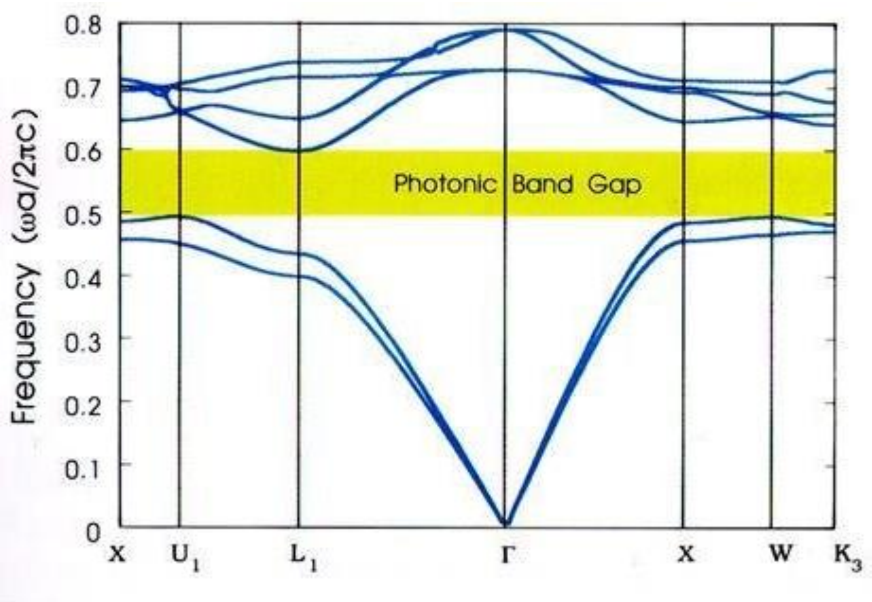

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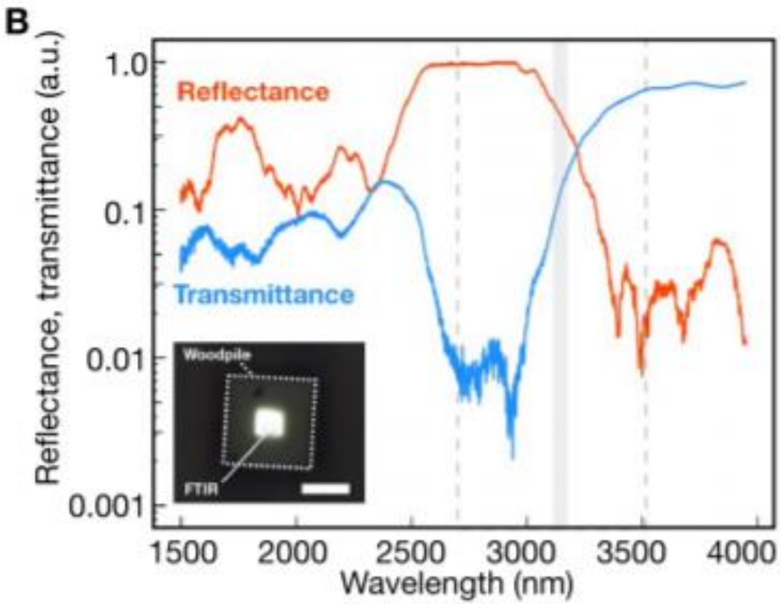

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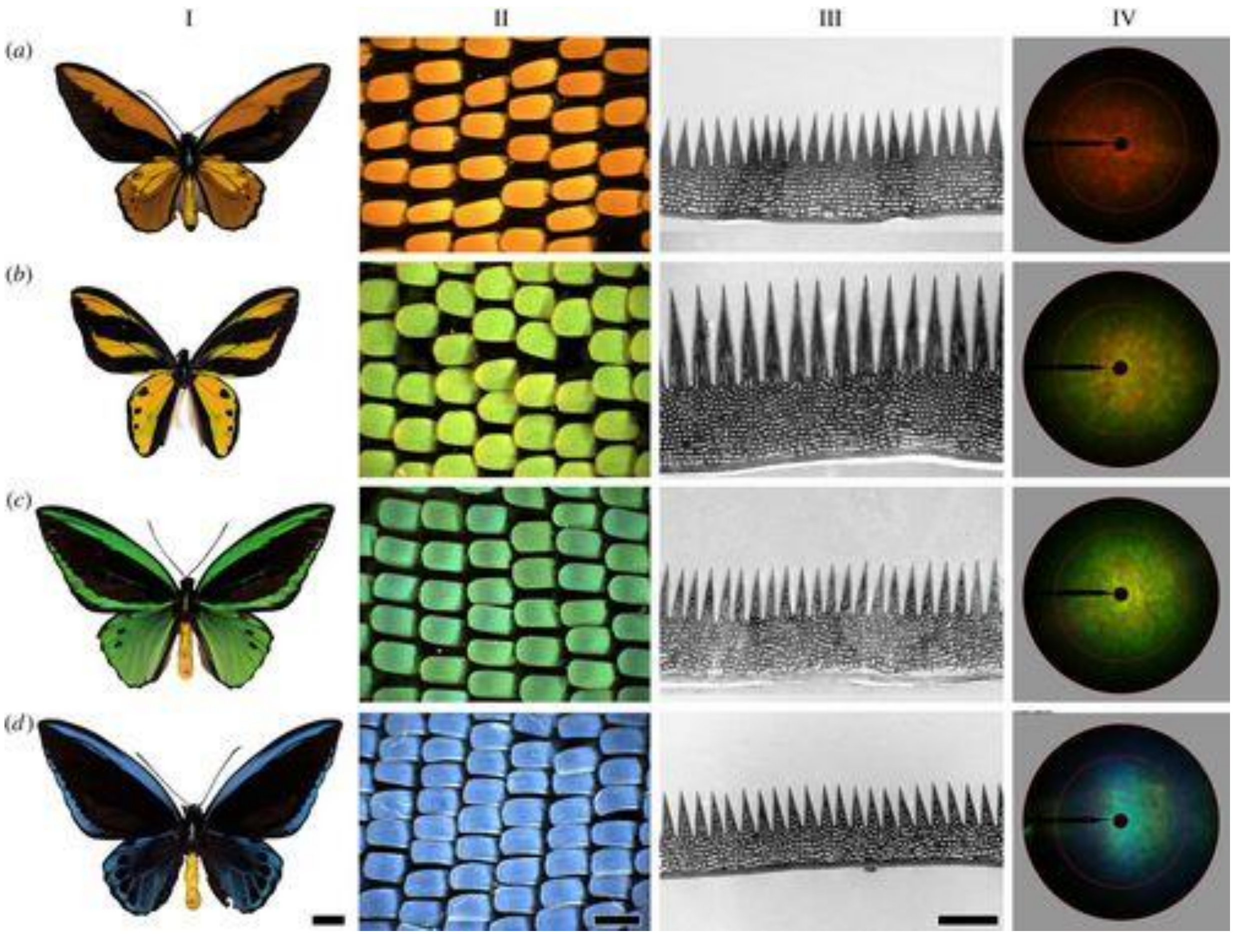
This band gap effect can lead to structural color (color result of geometry)

Structural Color



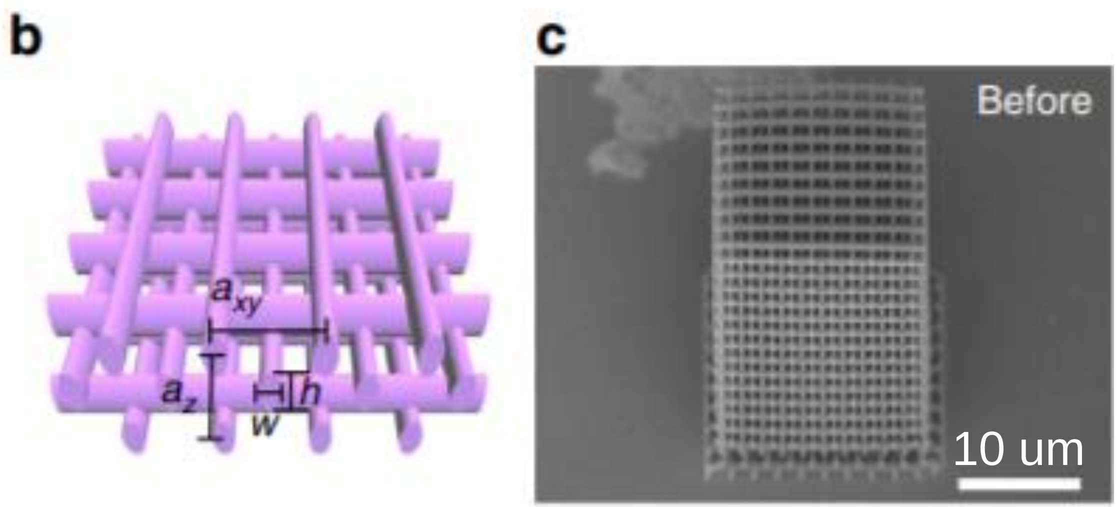
Wilts, B.D., et al. *J. R. Soc. Interface* 12, 20150717 (2015)

Ingram, A., et al. *Phil. Trans. of the R. Soc. B Bio. Sci*. 363 (1502), 2465-2480 (2008)

- Butterfly wing color comes from pigments, and **structural color**
- Color results from periodicity on the nanoscale

Heat Treatment to Obtain Structural Color

- TPL writes on um scale (IR optical response), can we reach visible?



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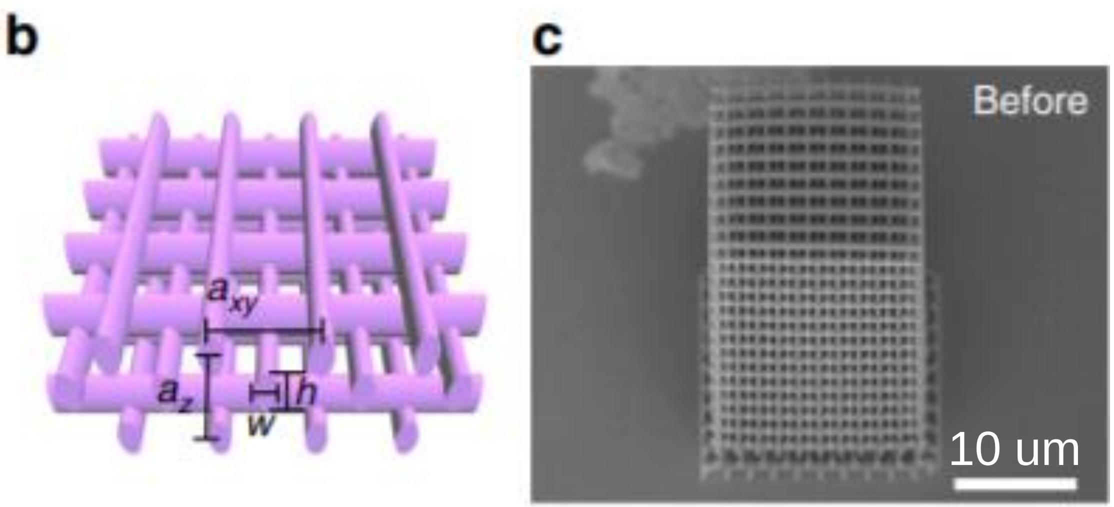
  Shrink the lattice?



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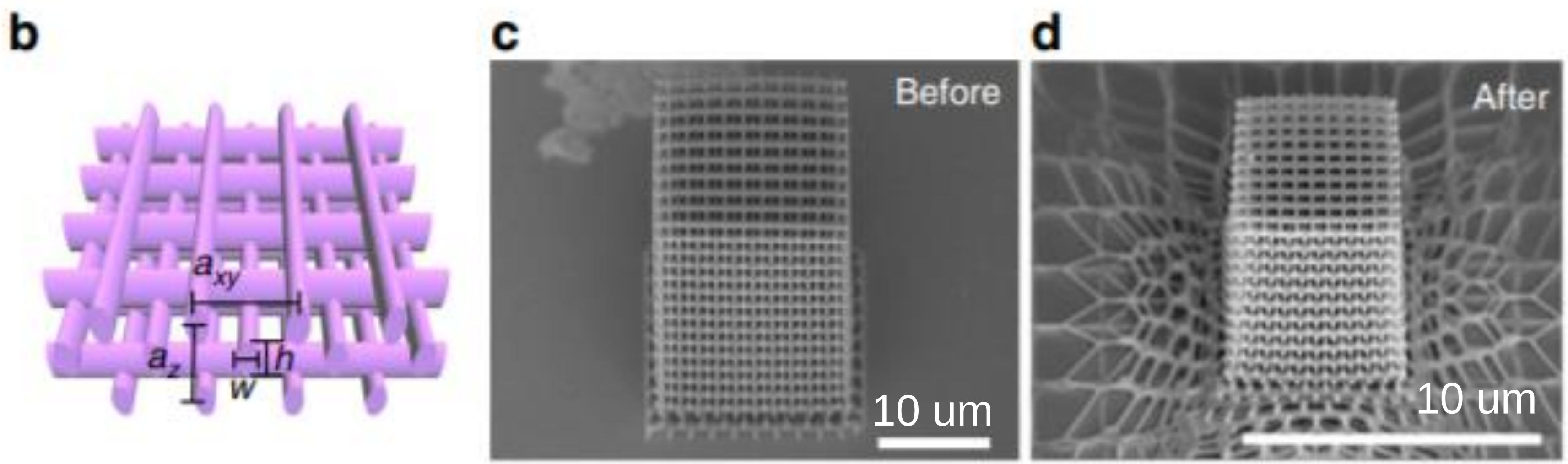
Shrink the lattice?

Process:

- TPL followed by heat-shrinking pyrolysis (450 C)
- Heating at “low” T prevents conversion to lossy glassy carbon
- Lattices down to ~280 nm lateral period, up to 80% lateral shrinkage
- Different lattice constants can freely be printed within a given structure



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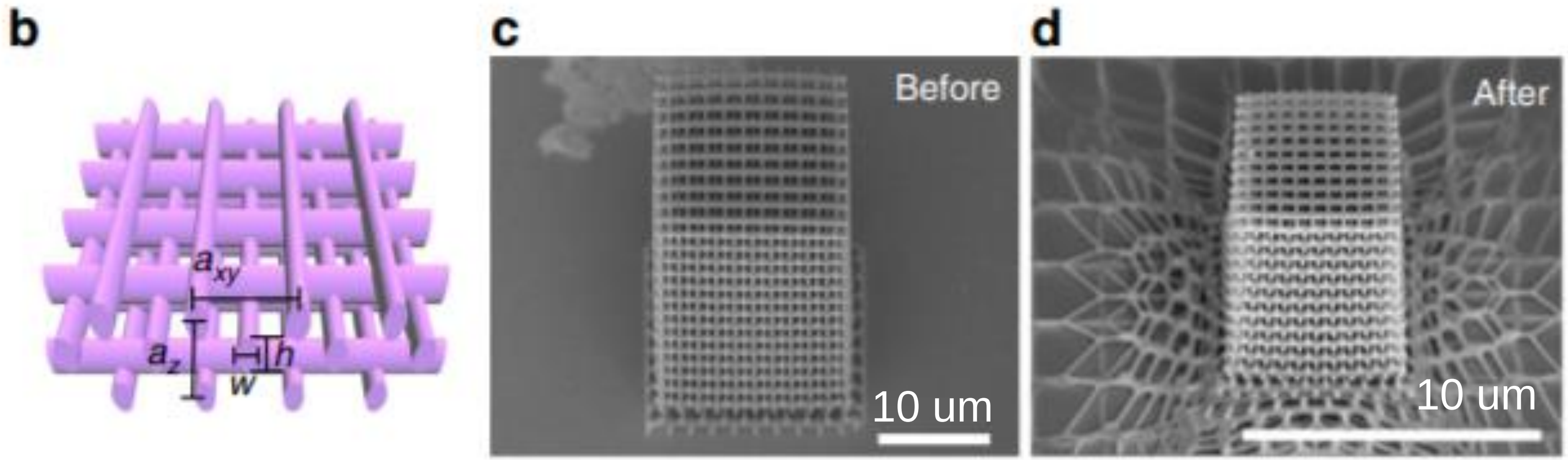
- Structural colors can be printed that do not degrade like pigments/dyes!
- Applications for photonic circuits or free-form optical filters



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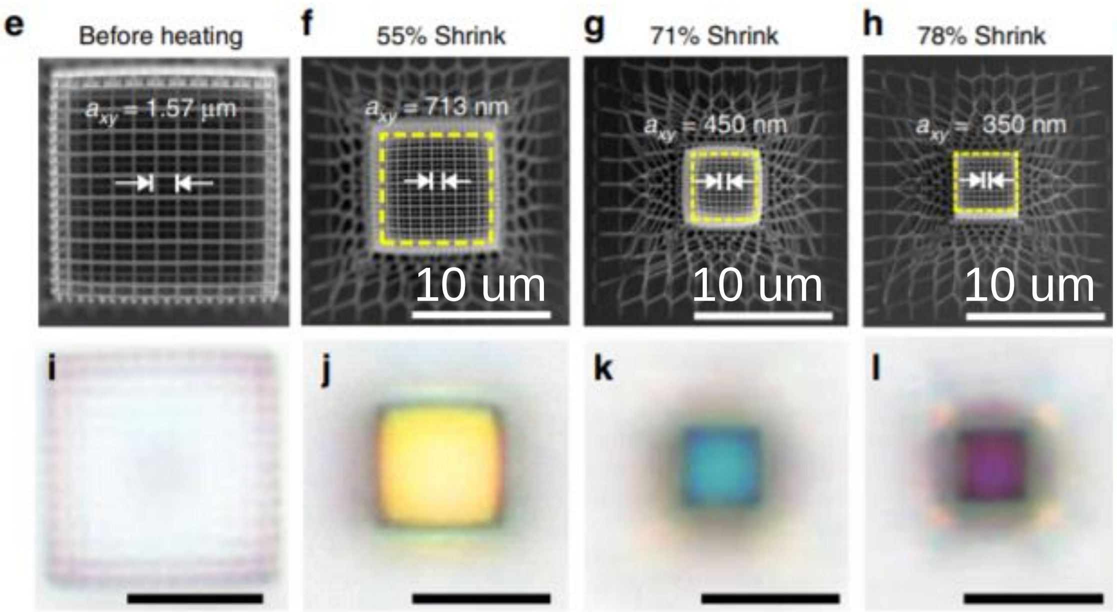
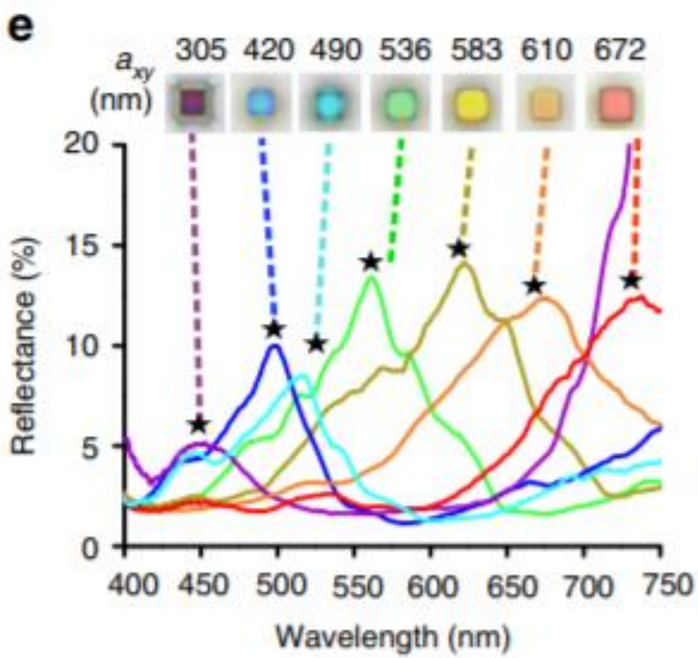
Shrinking crystal changes lattice constant, and thus band gap frequency





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Structural Color in 3D PhCs

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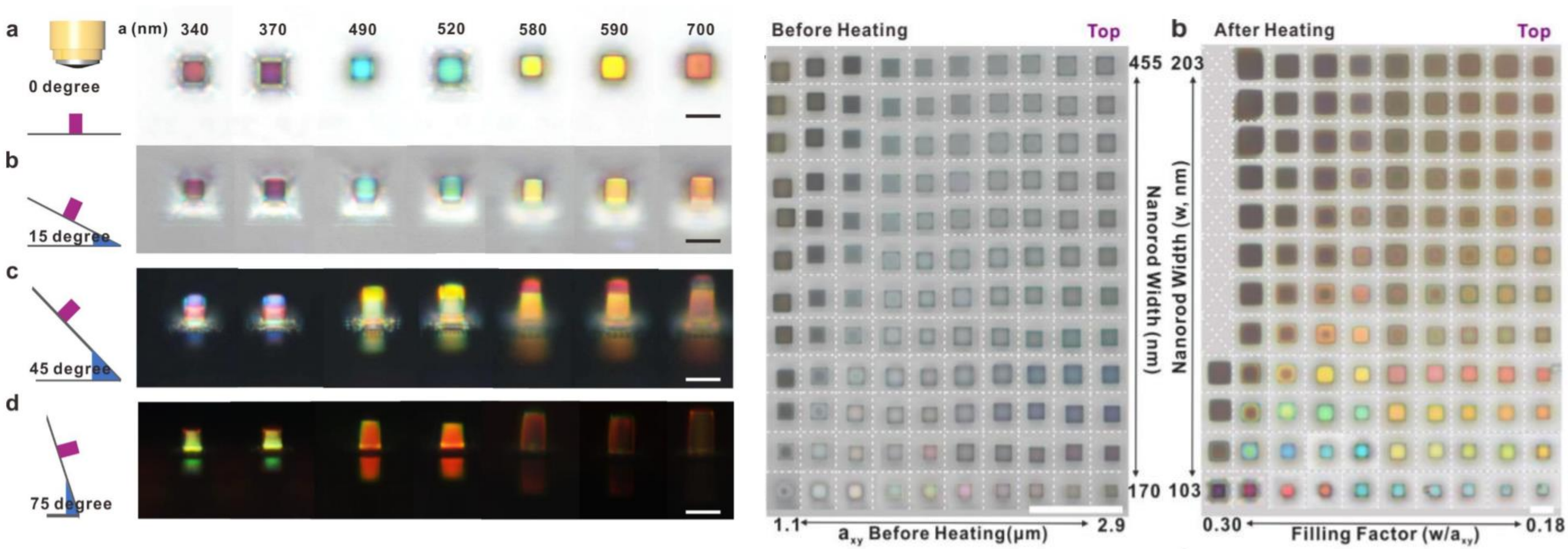

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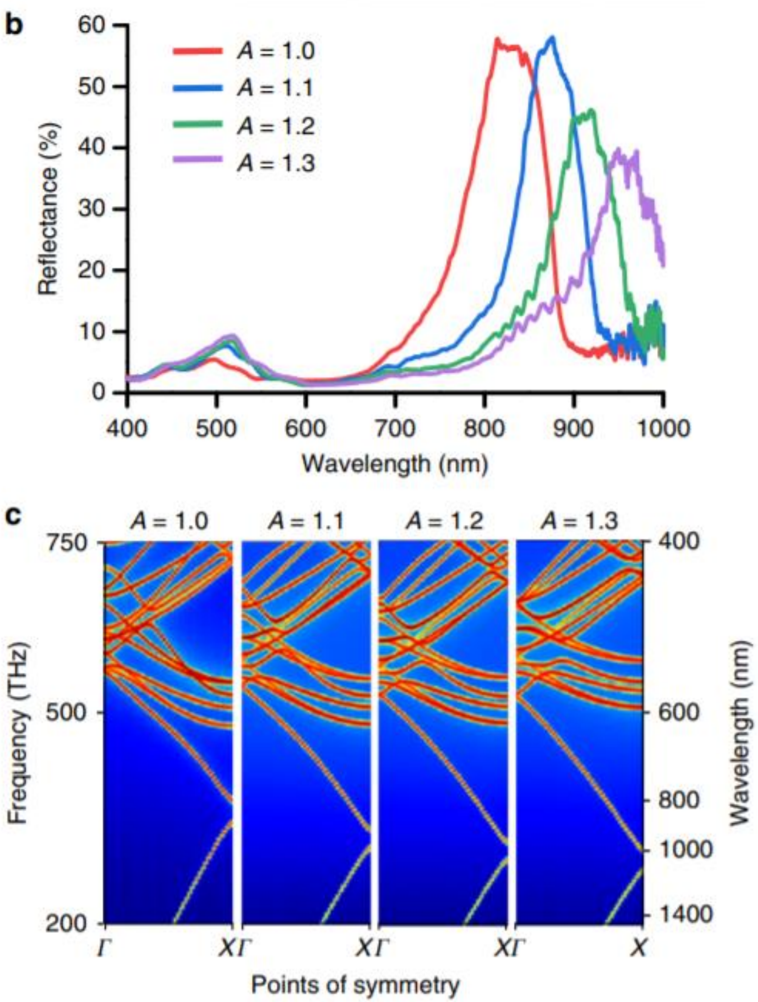

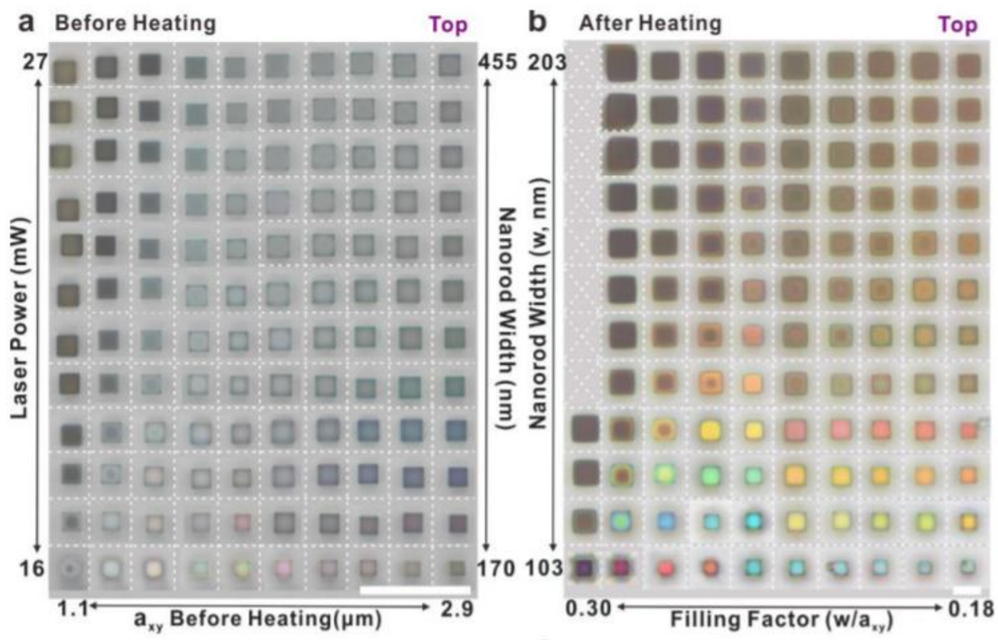

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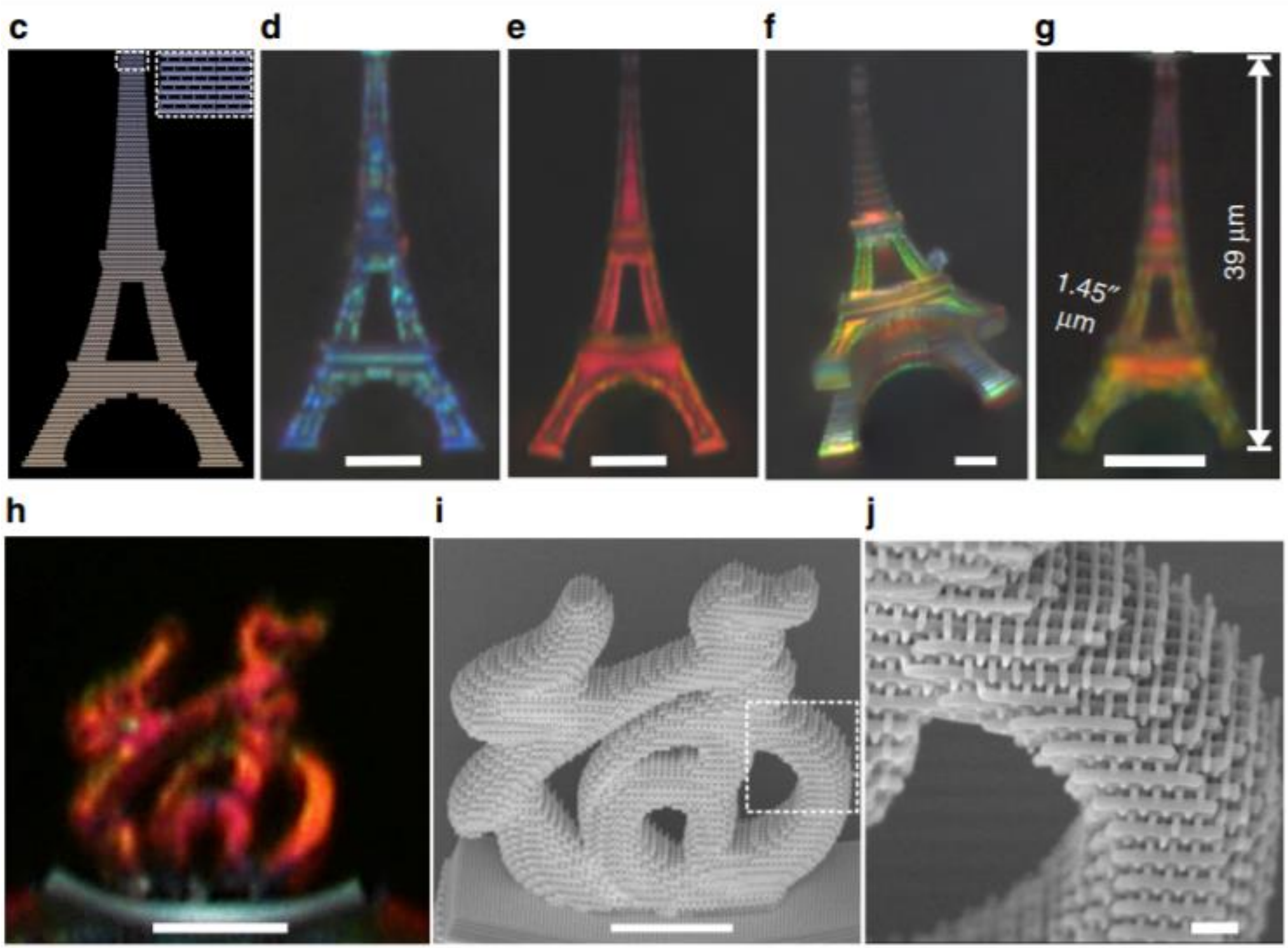

Scale bars = 10 um (1 um in j)

First demonstration of all color 3D dielectric structural color

Liu, Y., Wang, H., Ho, J., **Ng, R.**, et al. *Nature Comm.* 10, 4340 (2019)

Structural Color Summary

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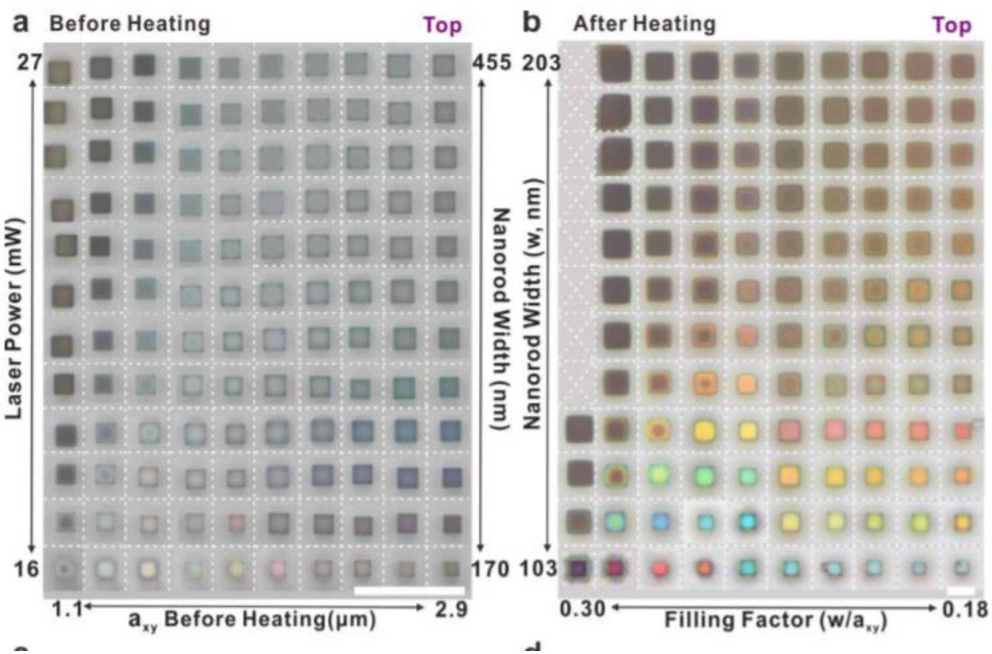
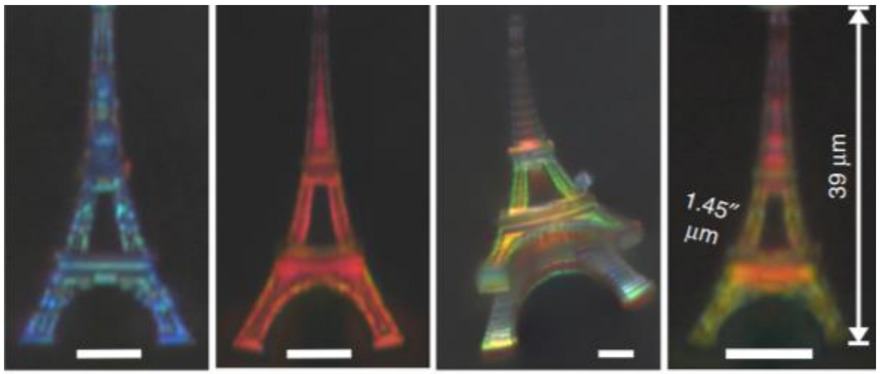
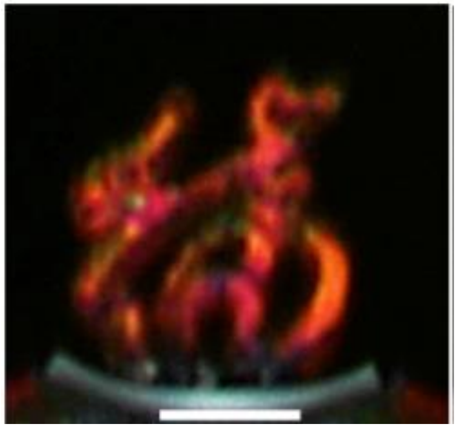
EXCELENCIA SEVERO OCHOA

- Free-form optical elements can be printed with structural color based on lattice period (optical band gap effect)
- Structures (and color) are resistant to degradation relative to existing dyes/pigments



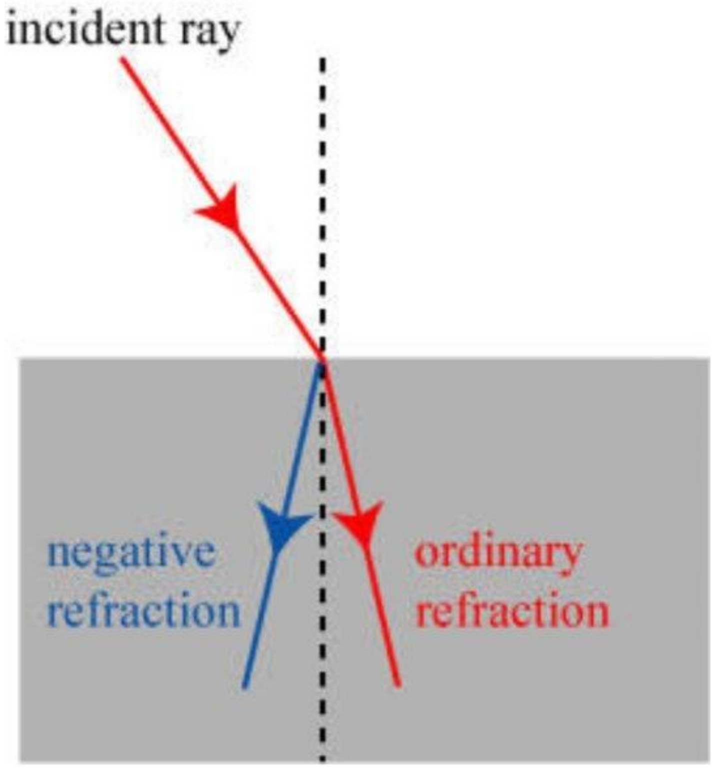




Liu, Y., Wang, H., Ho, J., **Ng, R.**, et al. *Nature Comm.* 10, 4340 (2019)

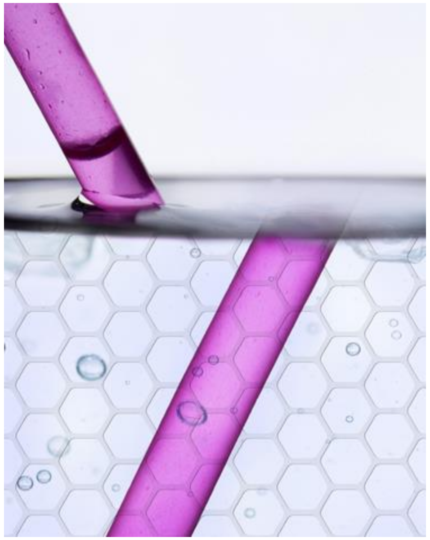
All-Angle Negative Refraction in 3D Core-Shell Polymer-Ge Photonic Crystals

Refraction and Negative Refraction



Refraction

Negative Refraction



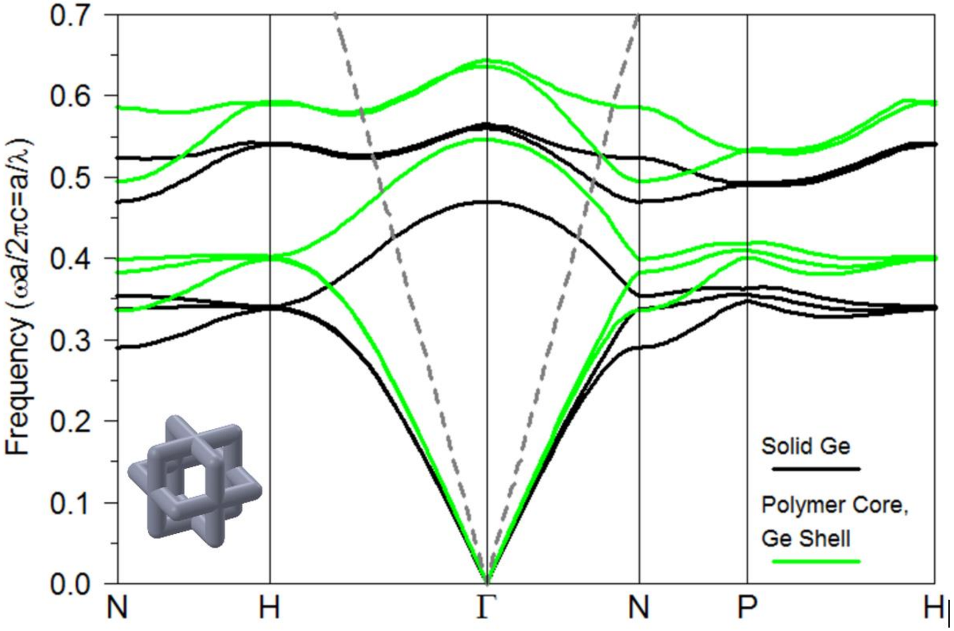
http:://www.spieosauemk.team

http:://www.quantamagazine.org

- Refraction describes light passing an interface of two materials
- Though not found in natural materials, negative refraction first proposed by Veselago in 1968
- All angle negative refraction requires 3D structures

Dispersion Engineering in PhCs

Negative refraction in 3D core-shell photonic crystals



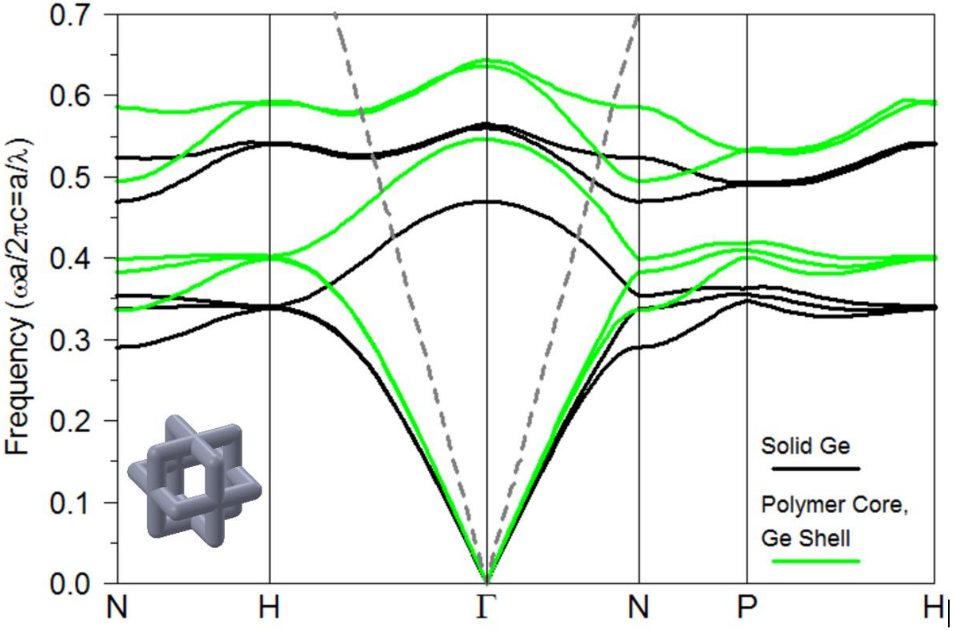
Previously, experimental demonstrations in microwave, and theoretical demonstrations of AANR in 3D

Wealth of information given by a "bandstructure"

Chernow, V., **Ng, R.** et al. (Under Review)

Dispersion Engineering in PhCs

Negative refraction in 3D core-shell photonic crystals



Wealth of information given by a "bandstructure"

$$n_g = \frac{c}{v_g}$$

$$v_g = \frac{\partial \omega}{\partial k}$$

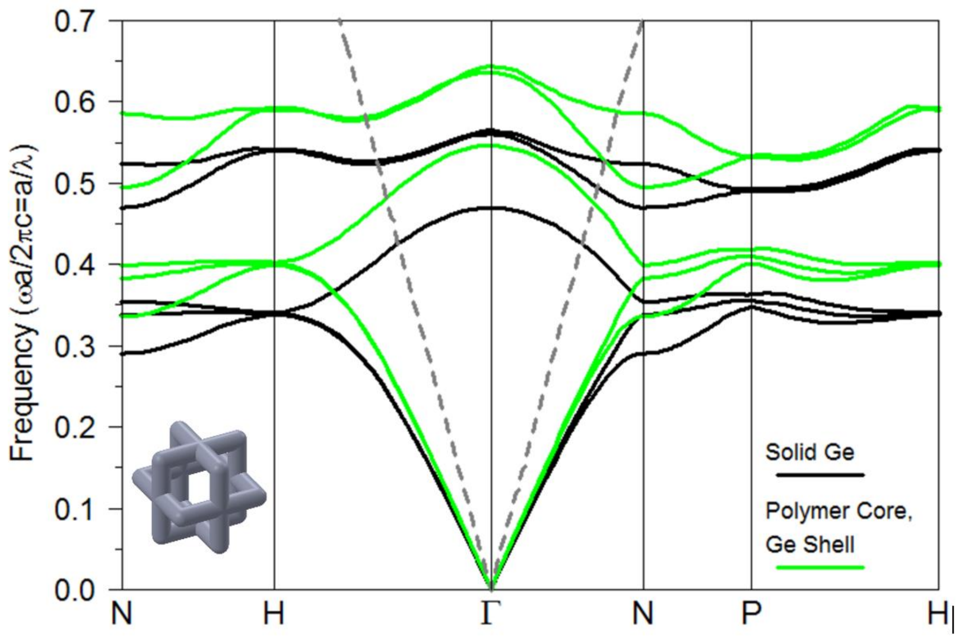
$n_g \equiv$ group index
$c \equiv$ speed of light
$v_g \equiv$ group velocity
$\omega \equiv$ frequency
$k \equiv$ wavevector

More generally, notion of dispersion engineering based on band structure (rather than band gap effects):

- Negative refraction/Subwavelength-Imaging
- Superprism effects
- Self-collimation effects

Dispersion Engineering in PhCs

Negative refraction in 3D core-shell photonic crystals



$$n_g = \frac{c}{v_g}$$

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n_g ≡ group index
c ≡ speed of light
v_g ≡ group velocity
ω ≡ frequency
k ≡ wavevector

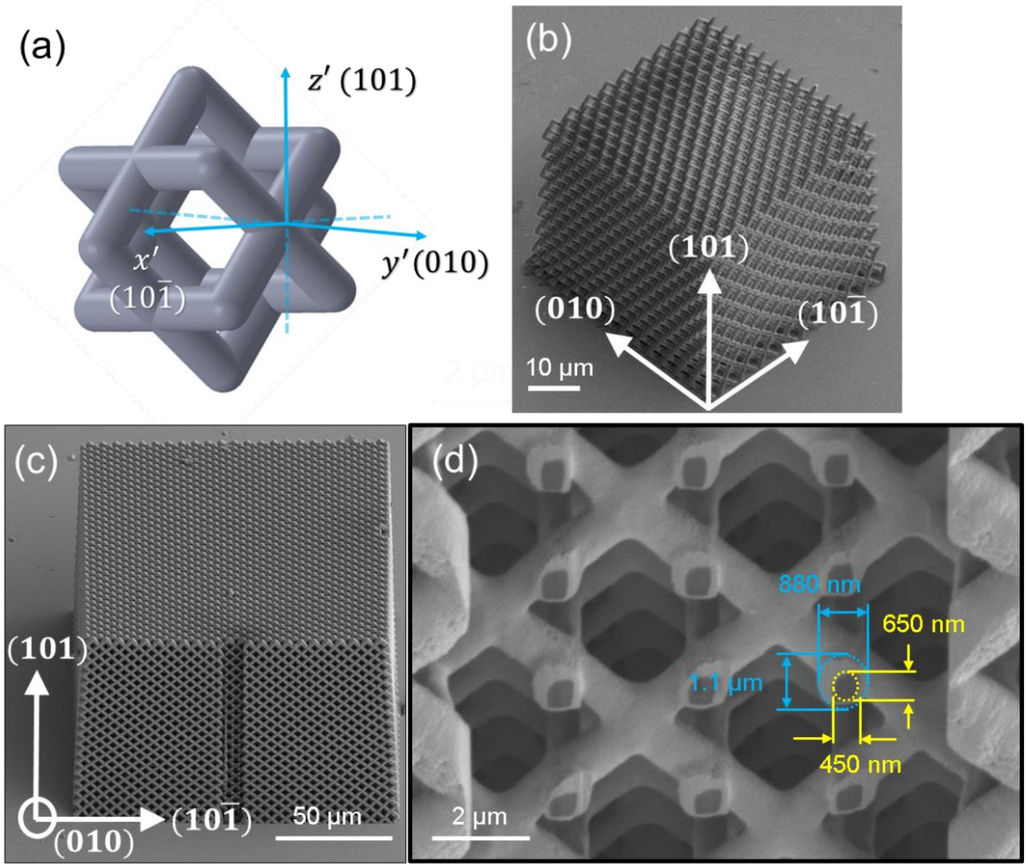
More generally, notion of dispersion engineering based on band structure (rather than band gap effects):

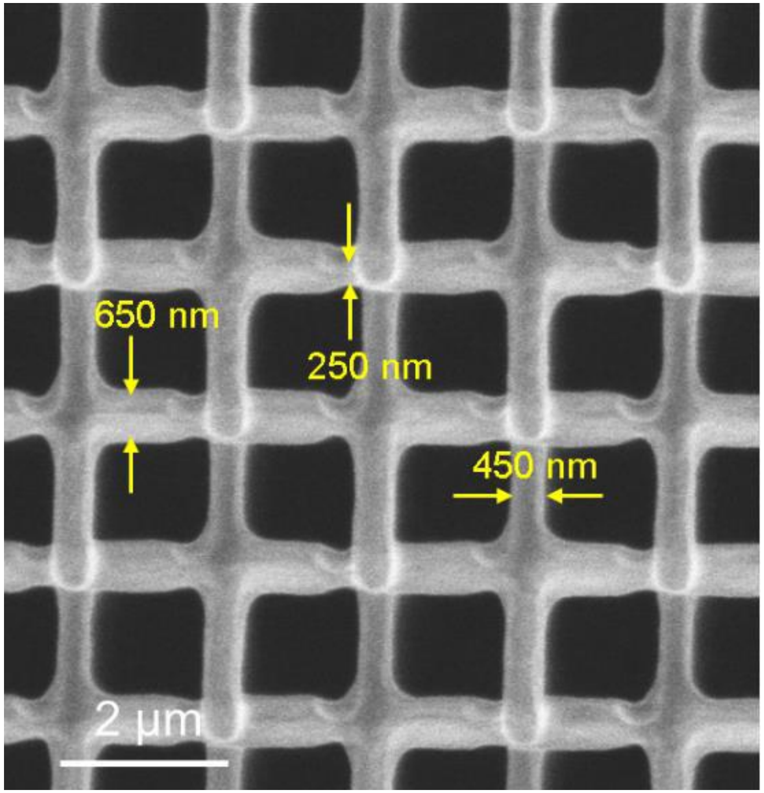
- Negative refraction/Subwavelength-Imaging
- Superprism effects

Wealth of information given by a

There exists no easy way to make monolithic Ge structures

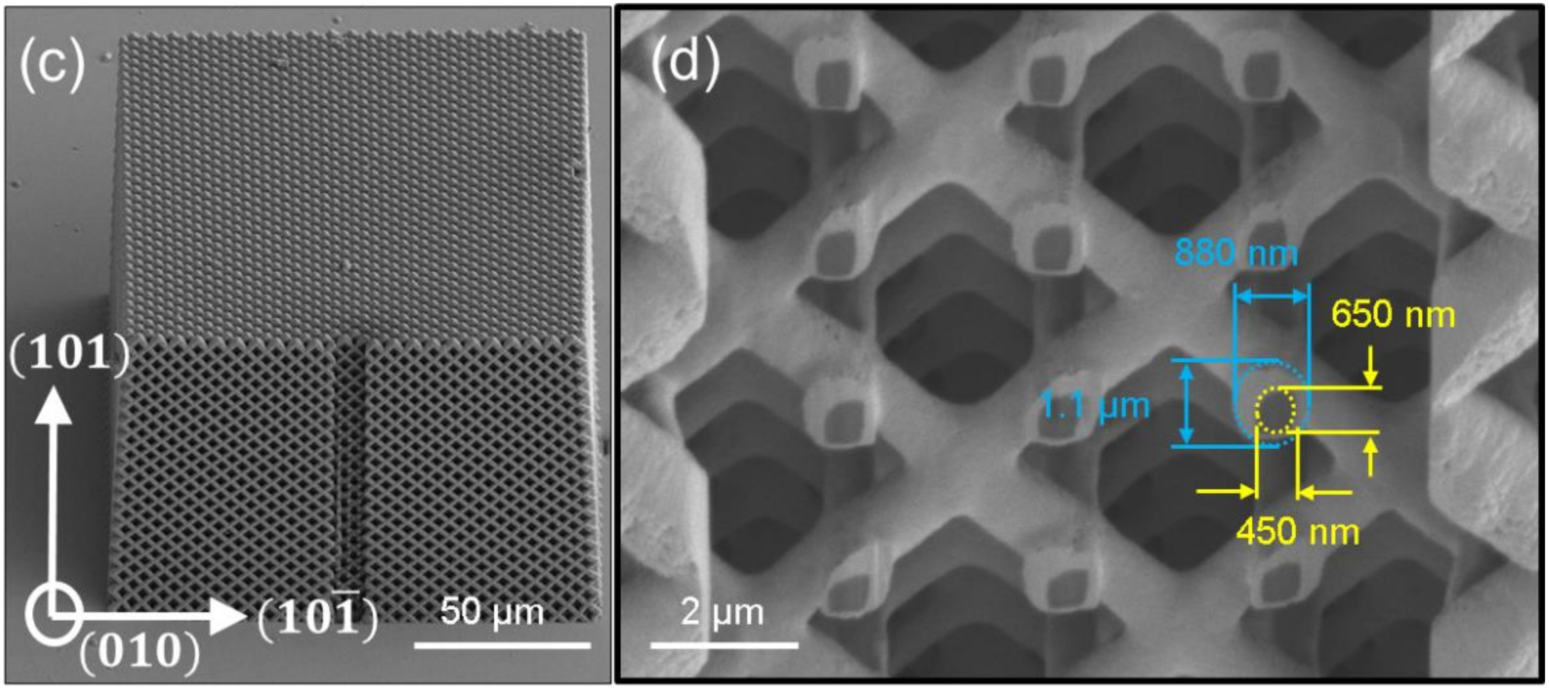
Negative refraction (NR) in 3D requires high index materials: Core-shell polymer-Ge lattice = Complex fabrication!!!





Chernow, V., **Ng, R.** et al. (Under Review)

Negative refraction (NR) in 3D requires high index materials: Core-shell polymer-Ge lattice = Complex fabrication!!!



Fabrication

TPL → O_2 plasma etching → Ge sputtering each side

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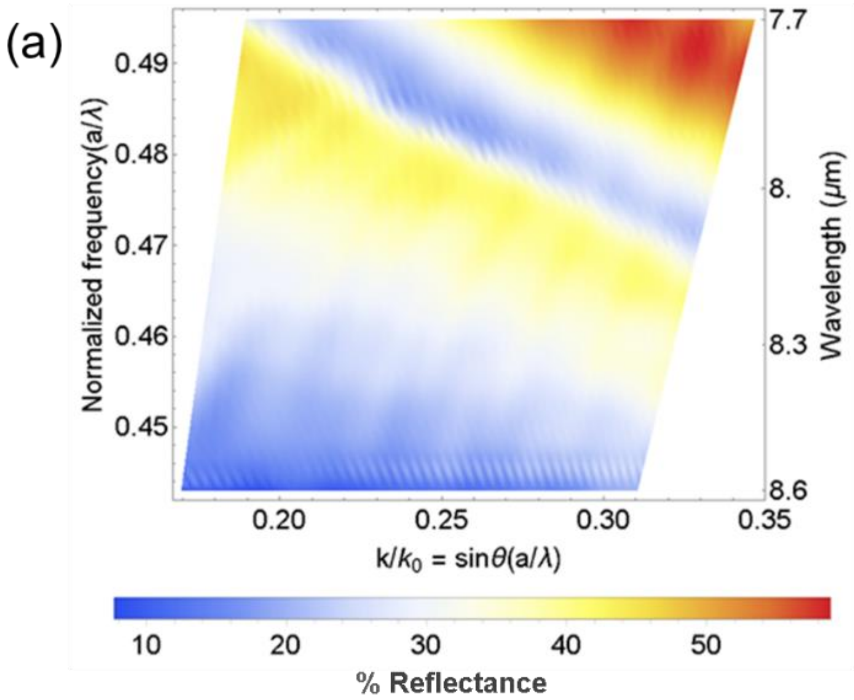
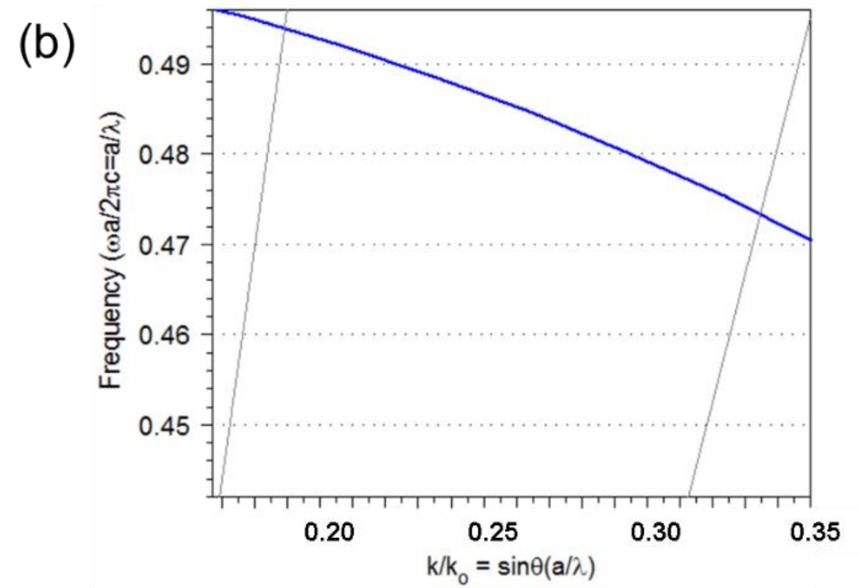
Angle-Resolved Spectroscopic Reflectance

Experiment



Simulation



NR band above the light line can be measured, matches simulation!

Negative average index of -0.67

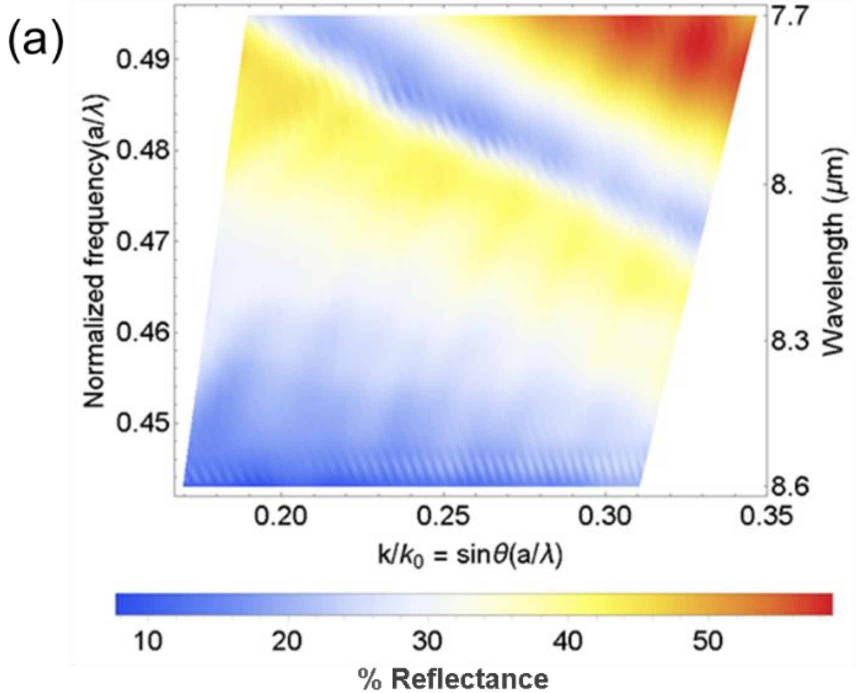
Chernow, V., **Ng, R.** et al. (Under Review)

Institut Català de Nanociència i Nanotecnologia

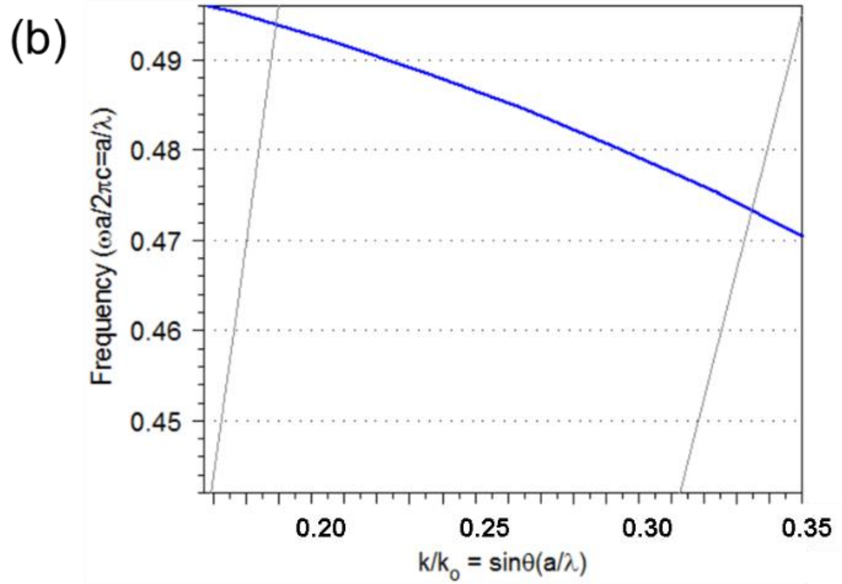
EXCELENCIA SEVERO OCHOA

Angle-Resolved Spectroscopic Reflectance

Experiment



Simulation



NR band above the light line can be measured, matches simulation!
Negative average index of -0.67

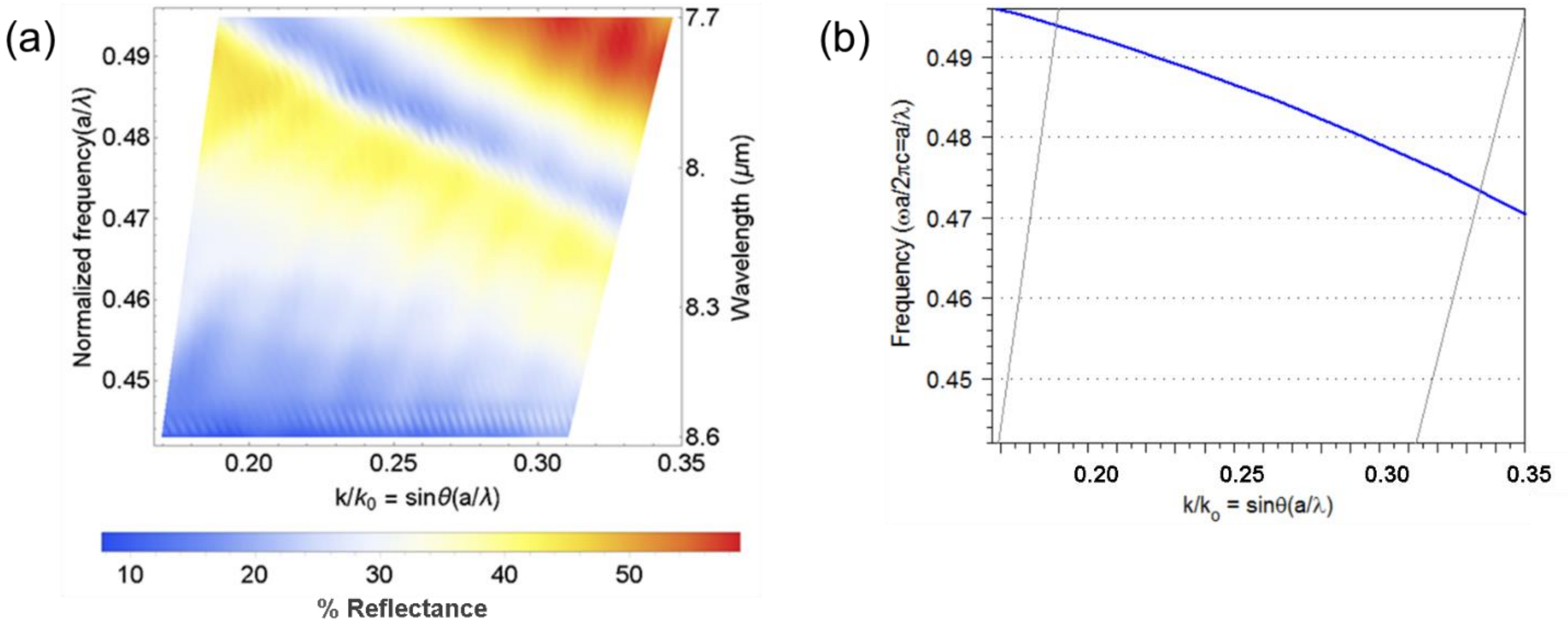
First experimental observation of all angle NR in infrared!

Chernow, V., **Ng, R.** et al. (Under Review)

Institut Català de Nanociència i Nanotecnologia

Angle-Resolved Spectroscopic Reflectance

Experiment **Simulation**



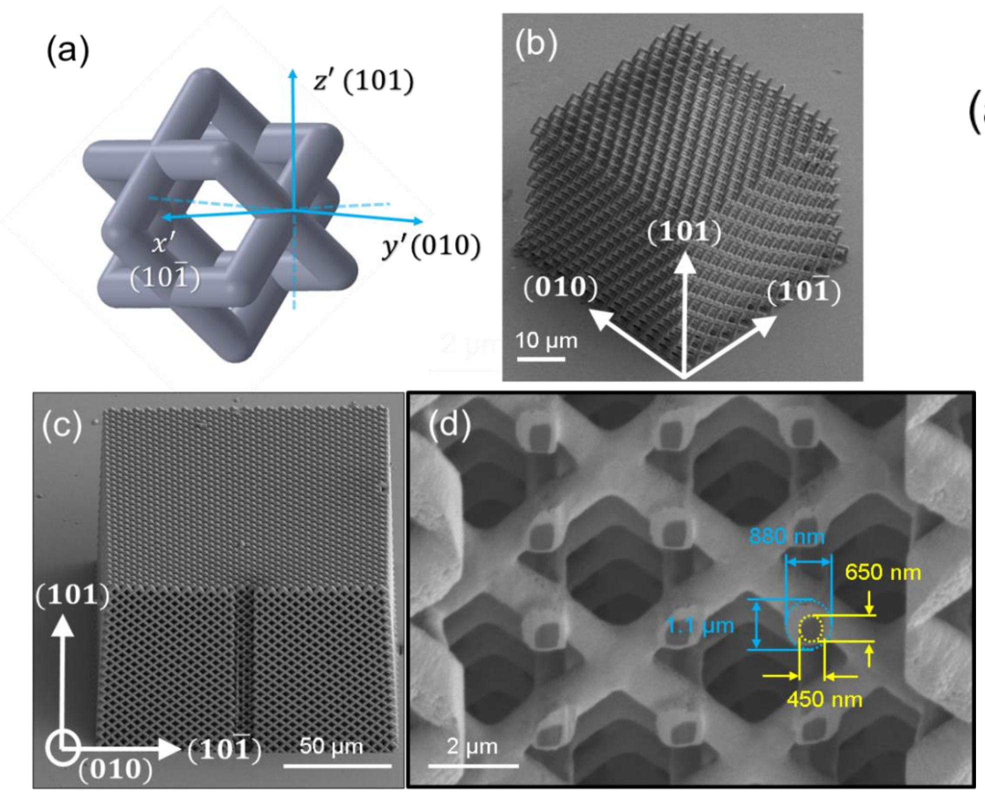
3D NR requires high index materials, AM can facilitate fabrication

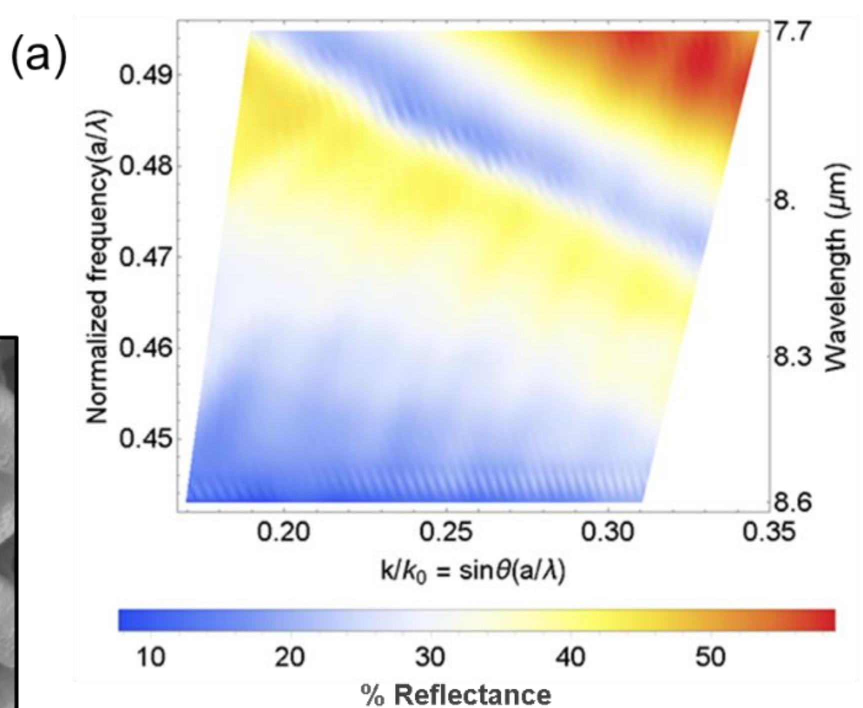
New suite of materials drastically increases the parameter space for dispersion engineering

Chernow, V., **Ng, R.** et al. (Under Review)

Negative Refraction in 3D PhCs Summary

- While negative refraction has previously been demonstrated in the visible/IR, fully 3D all-angle NR requires 3D structures
- We experimentally demonstrated 3D AANR for first time in the IR in core-shell polymer-Ge lattices, with n = -0.67

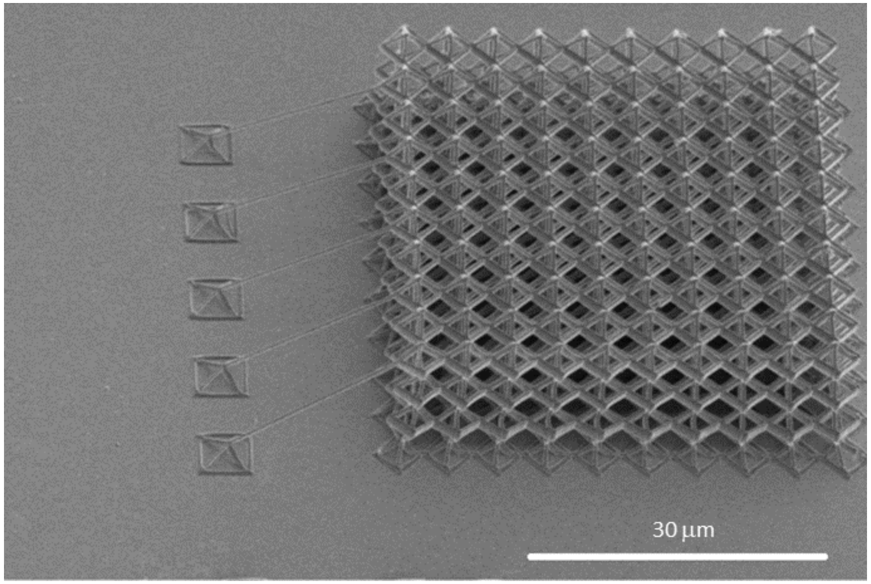


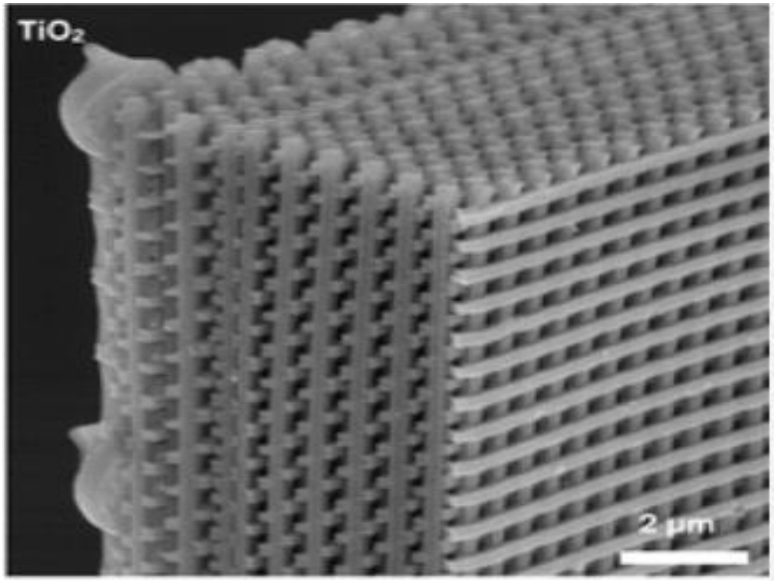


Chernow, V., **Ng, R.** et al. (Under Review)

Summary

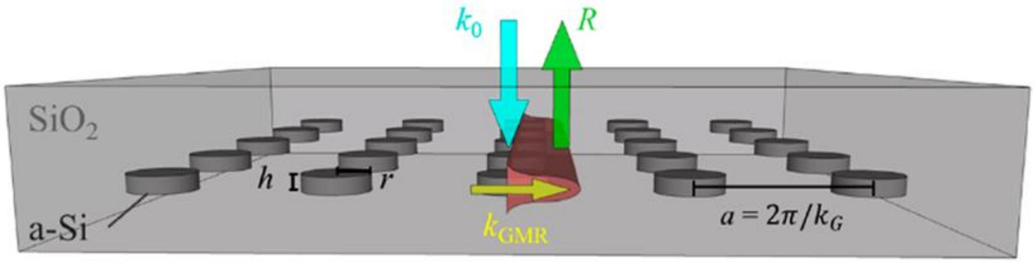
- TPL is a powerful tool to fabricate complex 3D architectures
- Fabrication of 3D non-polymeric structures is complicated (micromanipulation, double inversion, layer by layer fab)
- Additive manufacturing offers a quick, facile route to fabrication in many different materials

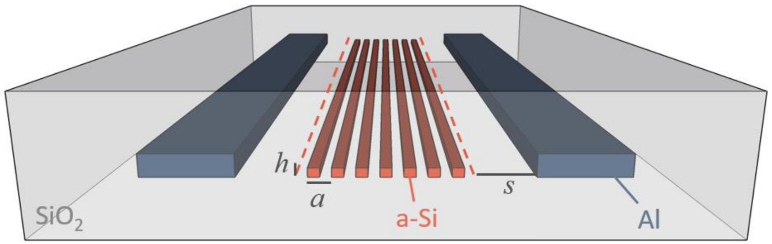


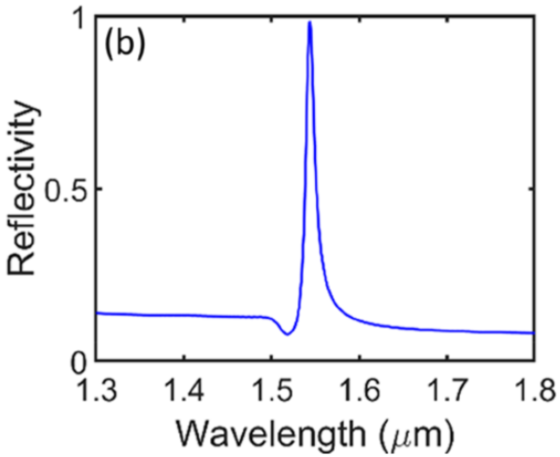


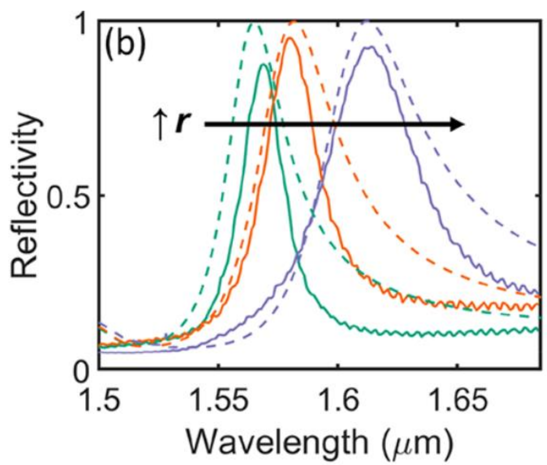
Vyatskikh, A., et al. *Nano Letters* 20, 3513-3520 (2020)

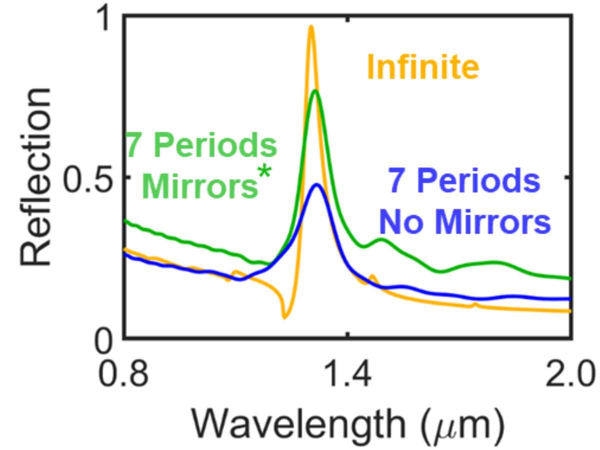
Guided Mode Resonances for Hyperspectral Filtering

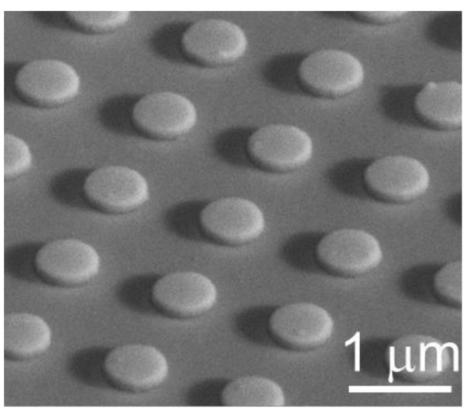












Ng, et al. *ACS Photonics* **6**, 265-271 (2019)

Ng, R., et al. *Applied Physics Letters* **117**, 111106 (2020)

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- Sotomayor-Torres Group
- Prof. Mario Amado Motero
- Prof. Enrique Diez
- Prof Jose María de Teresa Nogueras

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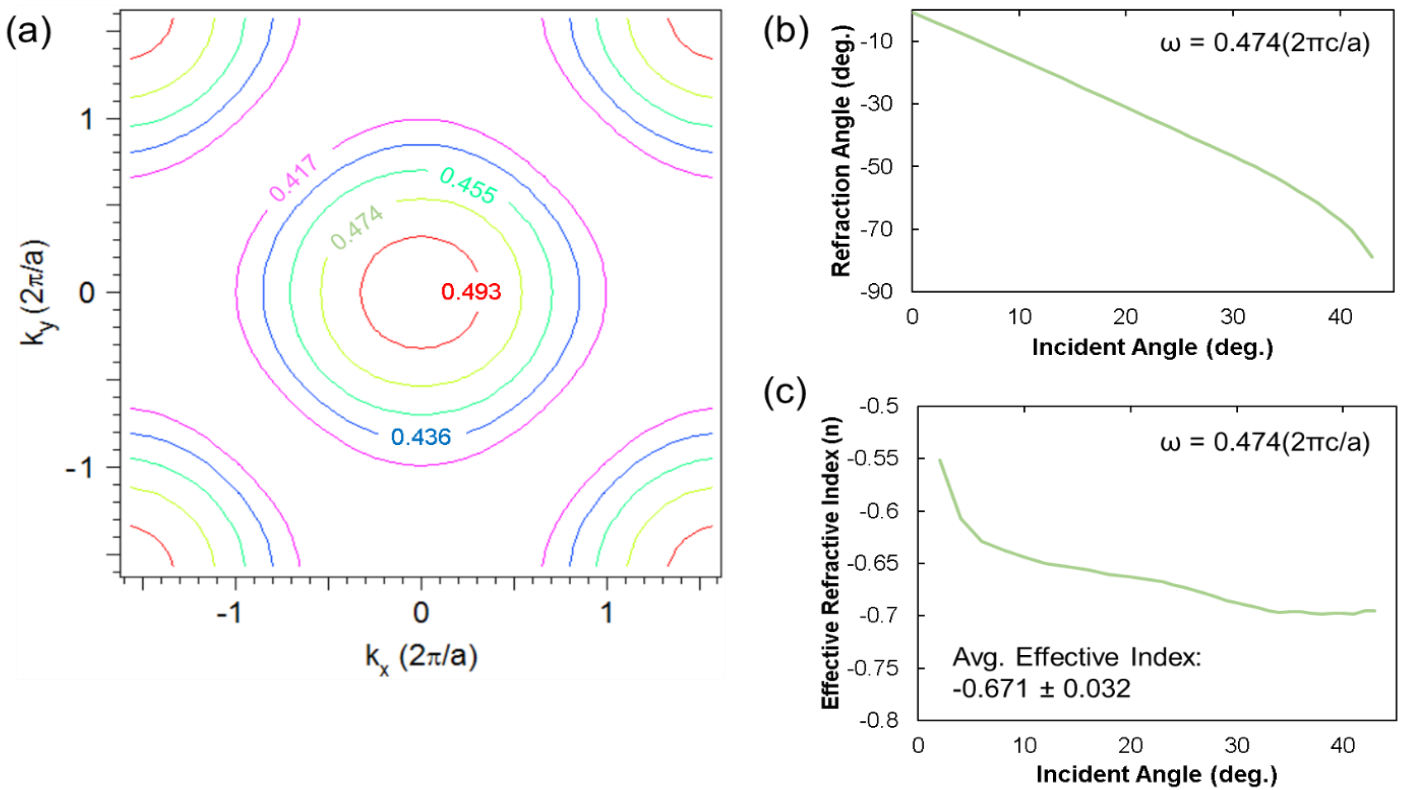
Sotomayor-Torres Group

Negative Refraction in PhCs



Chernow, V., **Ng, R.** et al. (Under Review)

- Extra resource for polymerization in 3D printing with polymers

Ligon, S.C., et al. *Chem Rev* **117** (15), 10212-10290 (2017)

- Lots of resources with mathematical/physics modeling of TPL, or higher order polymerizations