Mimicking Nature through Directed Materials Assembly

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2006 Boulder Summer School

Physics of Soft Matter: Complex Fluids and Biological Materials

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MRL
THE FREDERICK SEITZ MATERIALS RESEARCH LABORATORY

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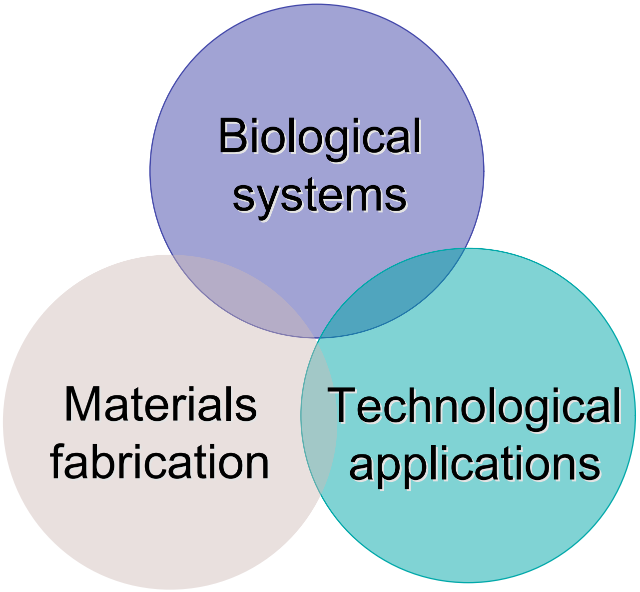
Bio-inspired Materials - Learn from nature, impact technology



Biological systems

Materials fabrication

Technological applications

Identify *biological systems* with unique micro- and nano-designs that lead to superior optical and mechanical properties

Develop new bio-inspired *materials fabrication* strategies for mimicking such structures

Impact *technological applications* ranging from novel photonics, electronics, structural materials, sensors, tissue engineering… and MORE!

Adapted from J. Aizenberg (Lucent/Bell Labs)

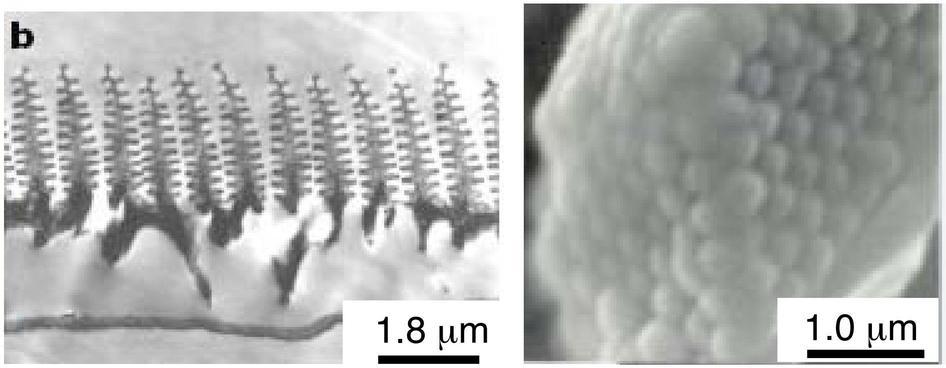
Nature Uses Complex Designs to Enhance Properties

Butterfly *Morpho rhetenor*

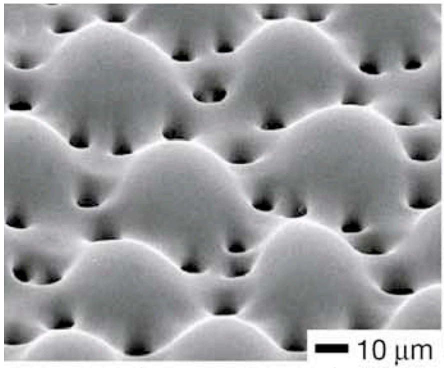
Weevil beetle

Ophiocomid brittlestars

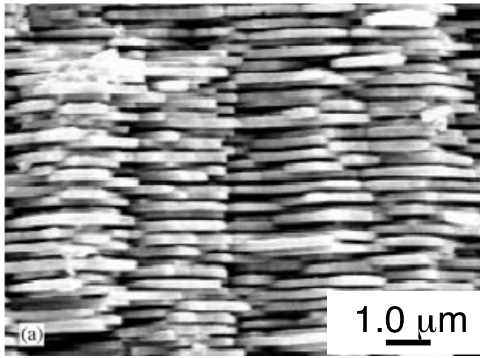
Abalone seashell



photonic structures



microlens arrays



nanocomposites

- Nature uses nanometer-to-micrometer scale architectures to produce striking optical effects and superior mechanical properties

- These natural designs provide inspiration for creating synthetic structures suitable for applications ranging from integrated optical circuits to composites

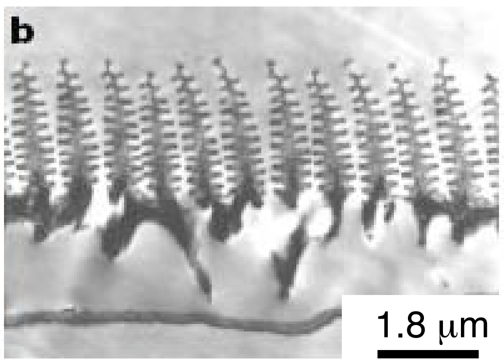
Natural Designs that Guide and Focus Light

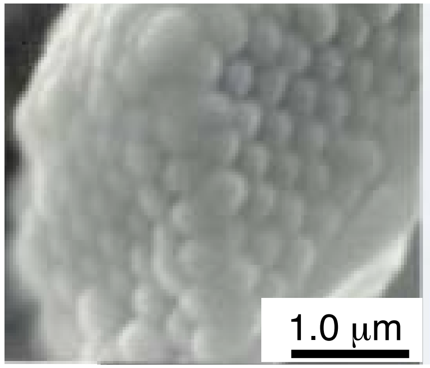
Butterfly *Morpho rhetenor*

Weevil beetle

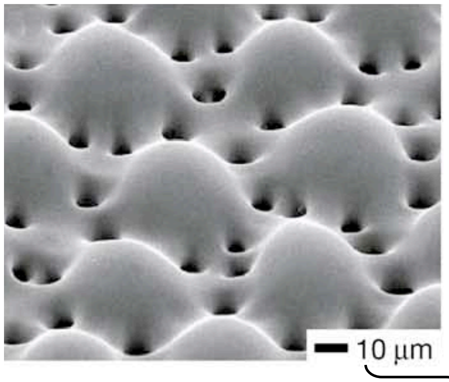
Ophiocomid brittlestars

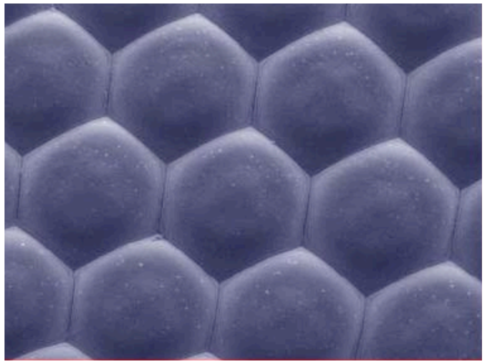
Housefly



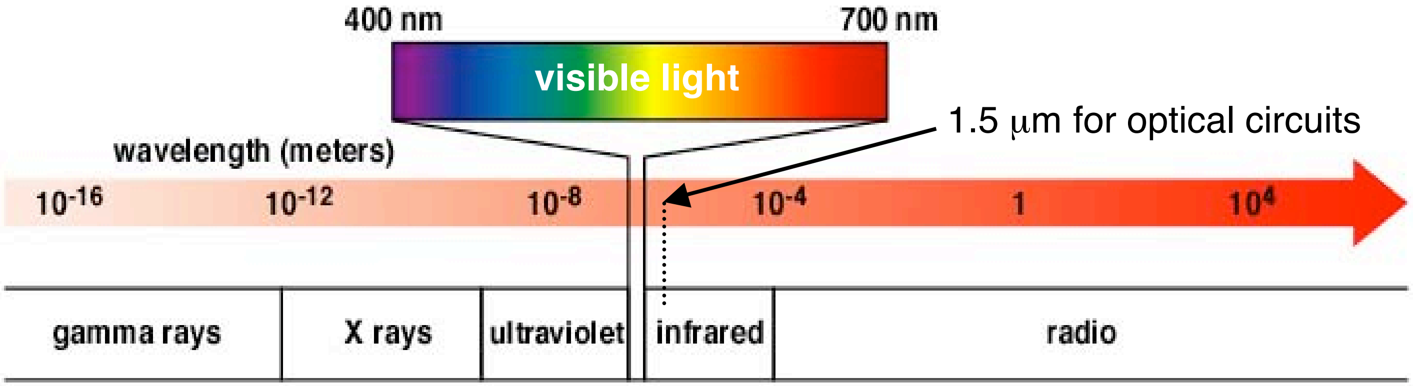


photonic structures

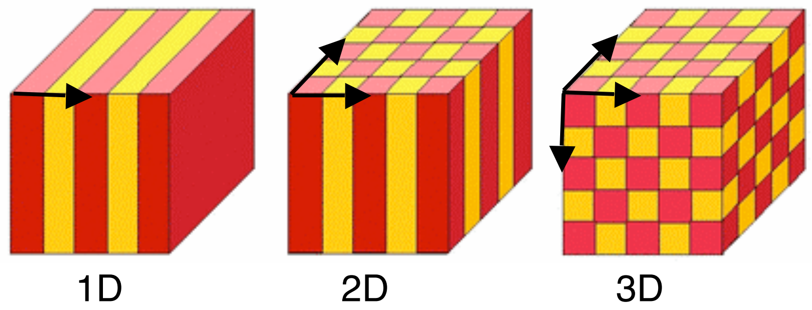




microlens arrays



Photonic Structures: Controlling the flow of light



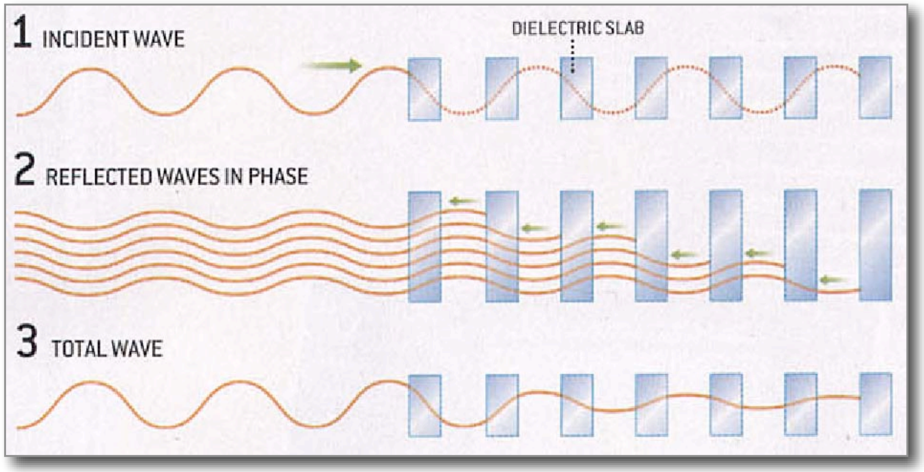
🟥 High refractive index material

🟨 Low refractive index material

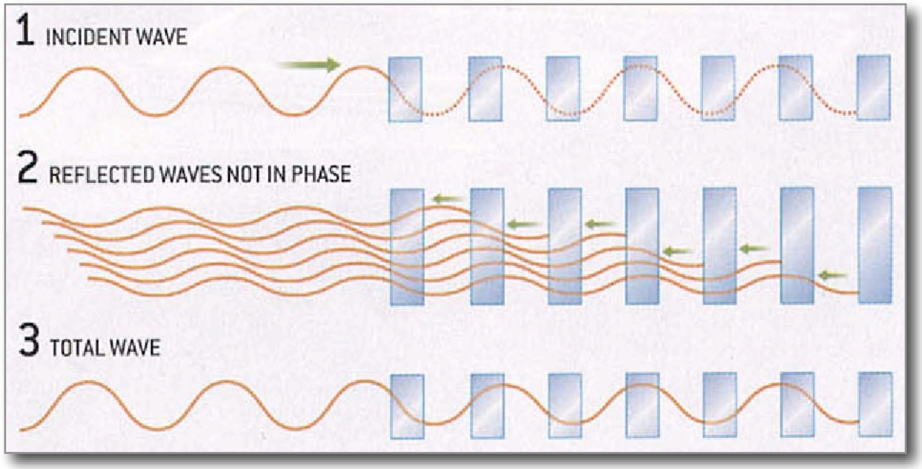
Photonic crystals = semiconductors of light

Periodic structures with a varying refractive index that prevents light in a certain wavelength range from propagating in 1D, 2D, or 3D

One dimensional (1D) Periodic Structure



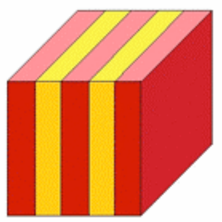
λ in bandgap does not propagate



λ not in bandgap propagates

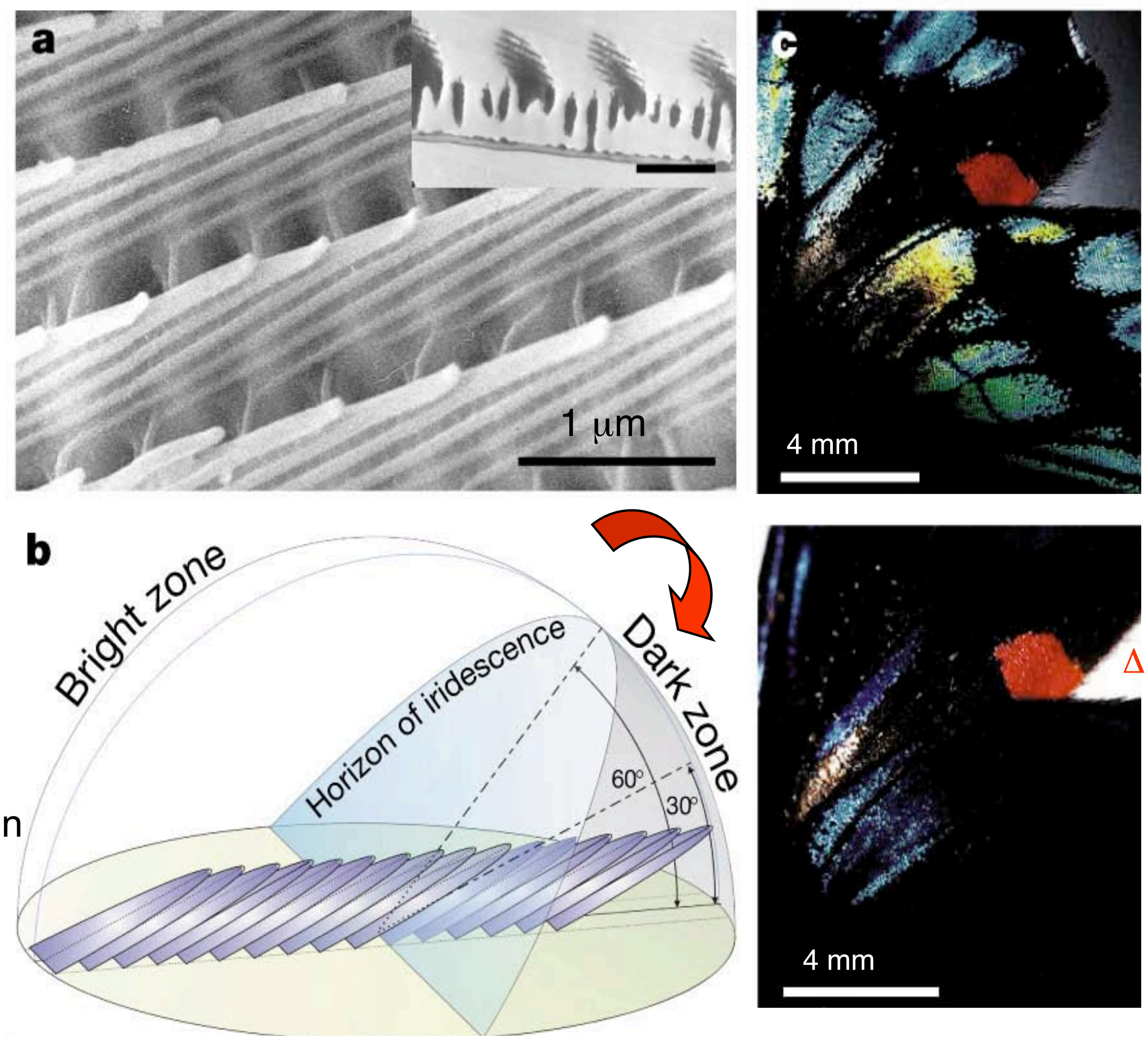
E. Yablonovitch, *PRL*, 58, 2059-62, (1987).
E. Yablonovitch, *Scientific American*, December, 2001.

Butterfly A. *meliboeus*: Iridescent Scales



1D Photonic Structure

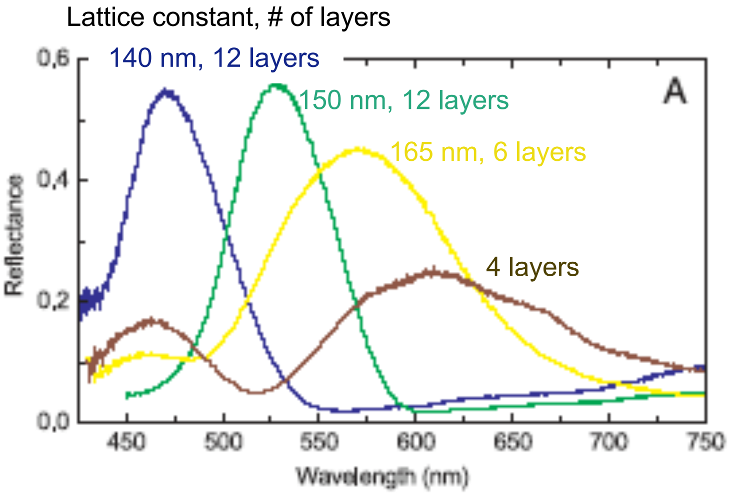
- Highly tilted multilayer scales of cuticle and air (30° to normal)
- Iridescence is either “on” or “off” depending on the viewing angle
- Strong flicker contrast from minimal wing motion (a few degrees)

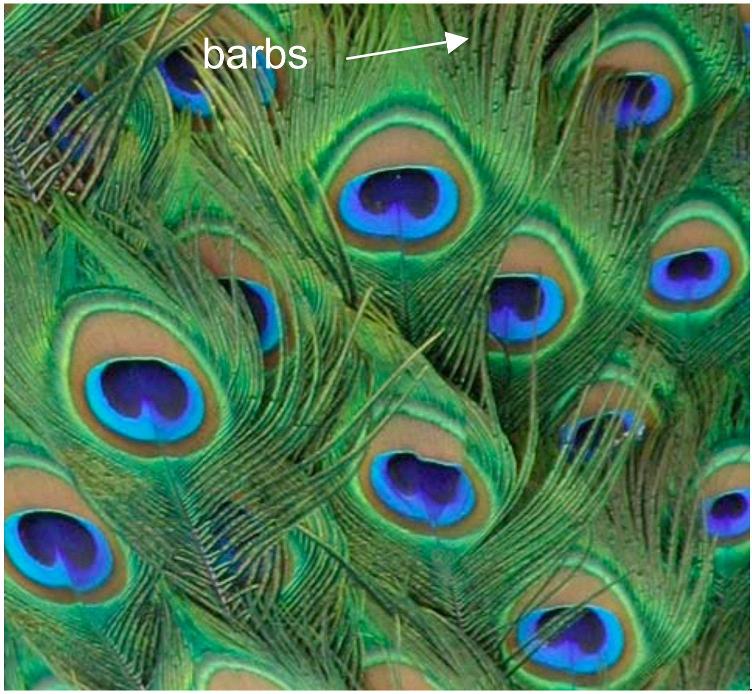


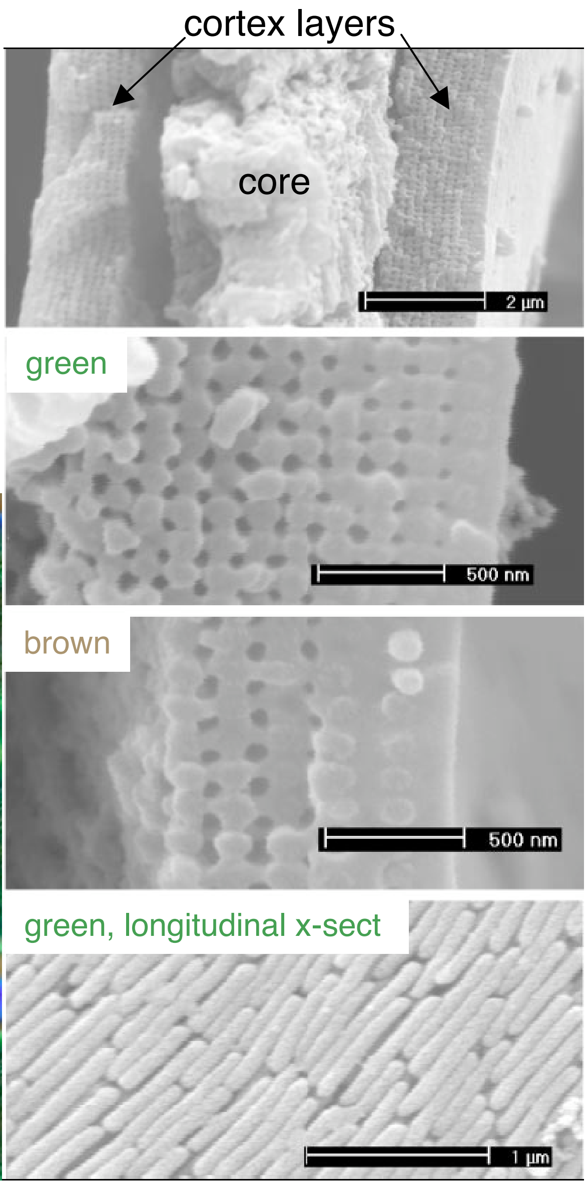
Δ viewing angle by 15°

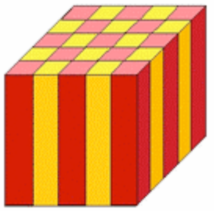
P. Vukusic, et al., *Nature*, 2001 **410** 36

Male Green Peacock (*Pavo muticus*): Colored Feathers







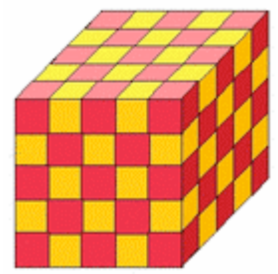


2D Photonic Structure

- barbules consist of medullar core and cortex layer
- Cortex layer composed of melanin rods + air holes
- Coloration due to periodic structure in cortex layer
  - variations in lattice constant or # of layers

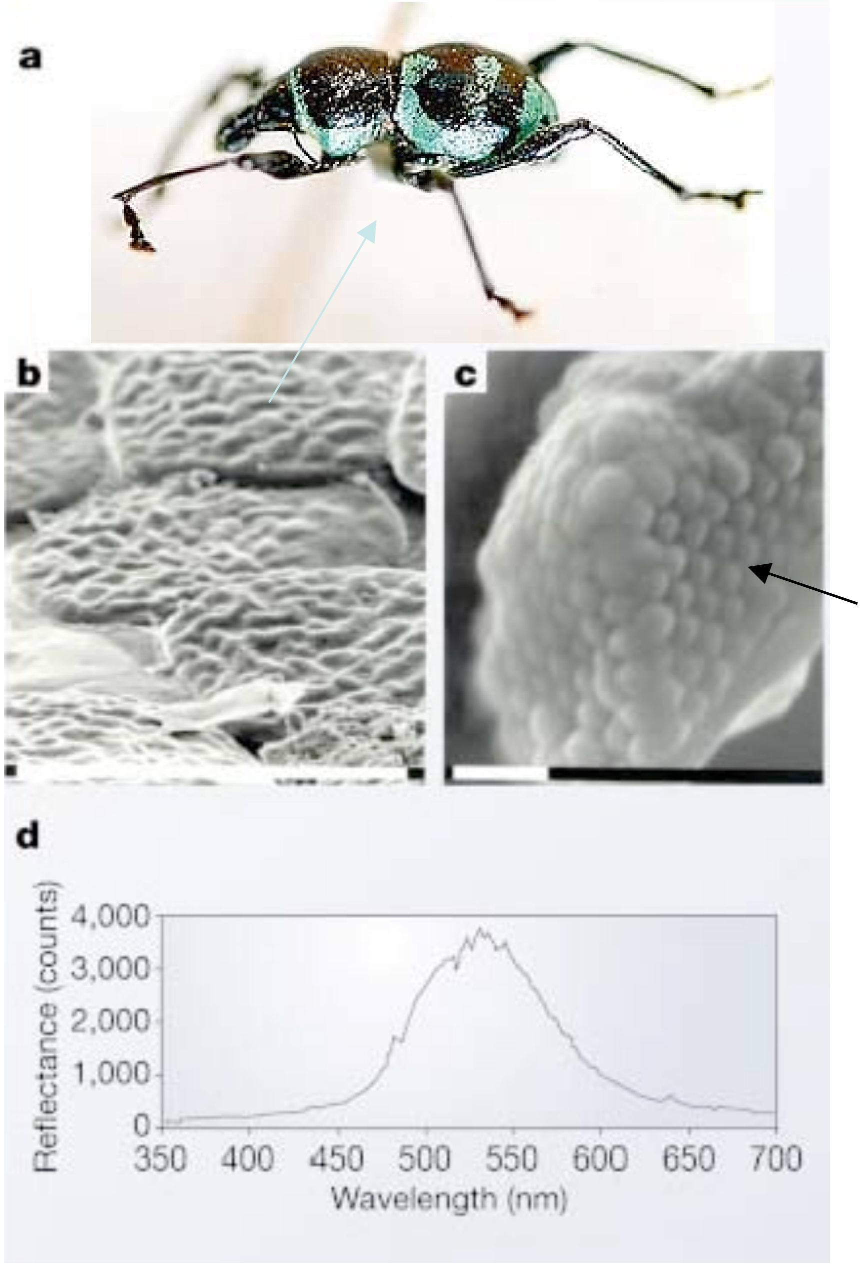
J. Zi, et al., *PNAS*, **100** 12576-12578 (2003).

Weevil Beetle: Opalescent Structure



<u>3D Photonic Structure</u>

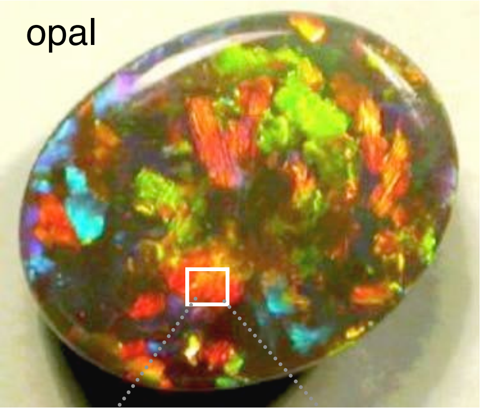
- beetle's exoskeleton consists of surface scales ~ 0.1 mm in size
- scales contain a periodic array of ~ 250 nm spheres
- Reflectance peak at λ = 530 nm gives rise to color



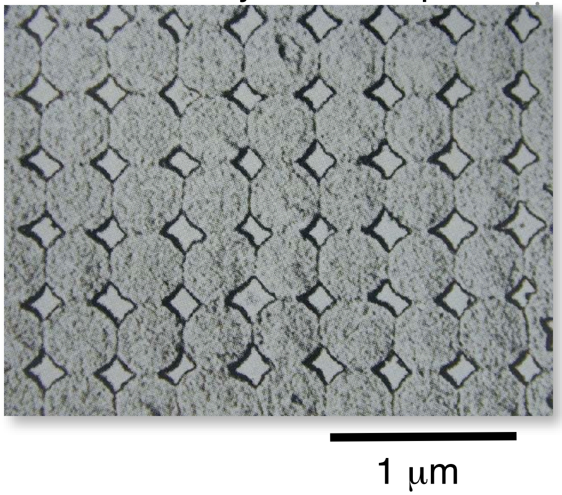
250 nm spheres

A. Parker et al. Nature **426** 18 786-7 (2003).

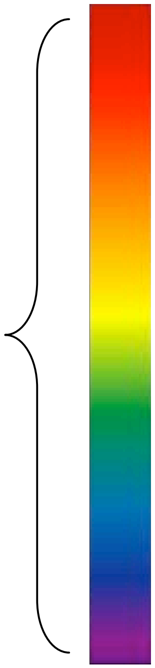
Photonic Structures: Nature’s Crayons



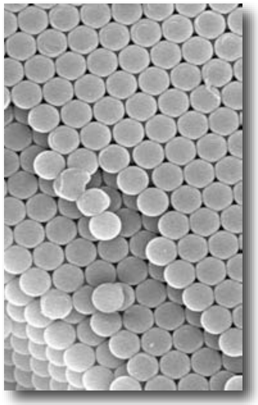
Periodic array of silica spheres



λ = 700 nm

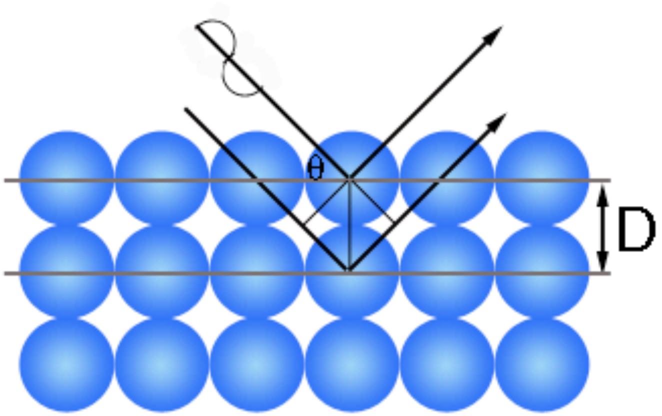


λ = 400 nm

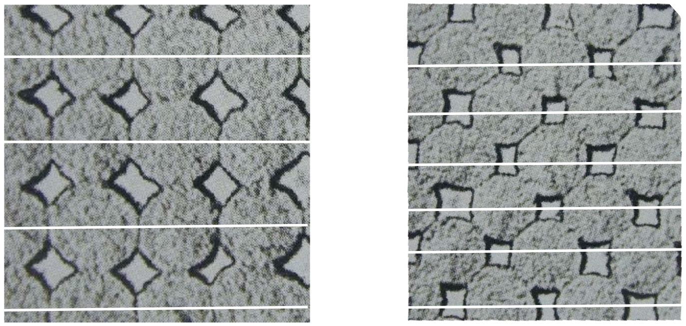


3D structure

Bragg diffraction



$$n\lambda = 2D\sin\theta$$

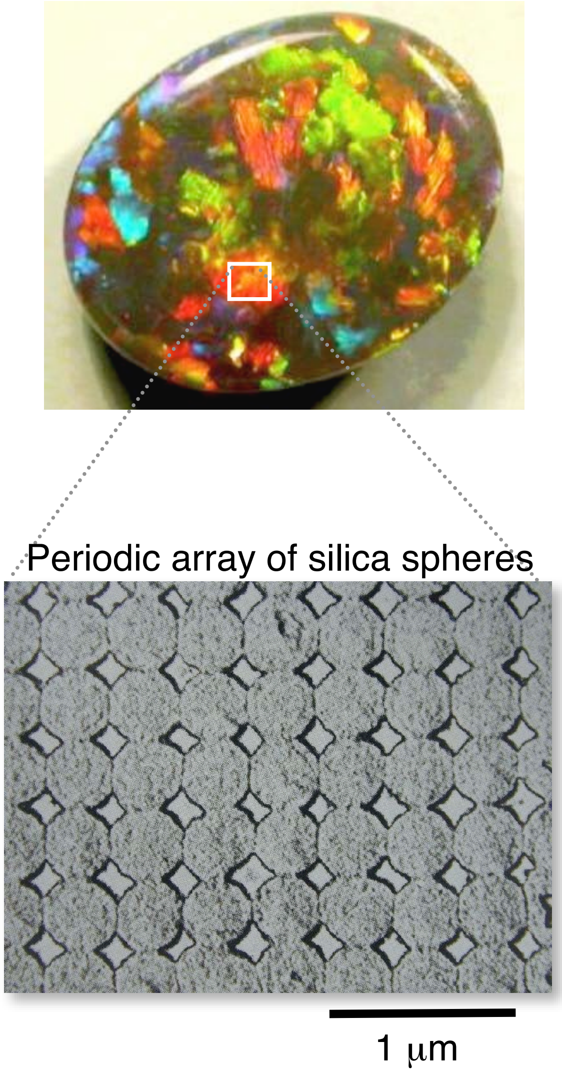


- lattice spacing, D, varies with sphere size and crystal orientation

P.J. Darragh, et al., *Nature*, 209, 5018, 13-16 (1966).

Periodicity Matters…

Precious opal



Periodic array of silica spheres

1 μm

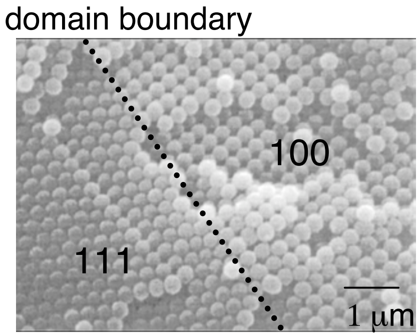
Common opal

Random packing of silica spheres

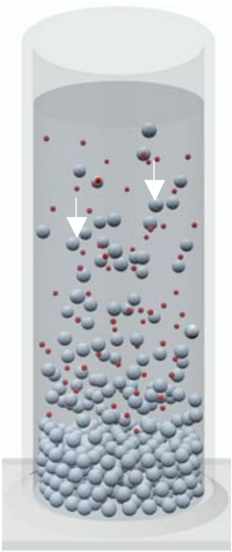
1 μm

P.J. Darragh, et al., *Nature*, 209, 5018, 13-16 (1966).

Colloidal Assembly of Synthetic Opals



Prog Quant Electron **23** 51 (1999)

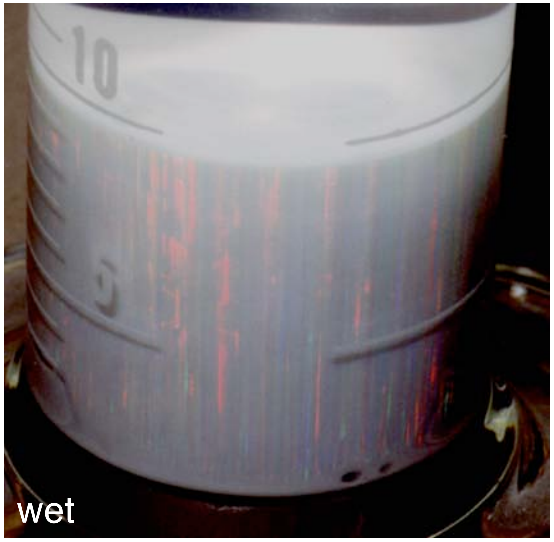


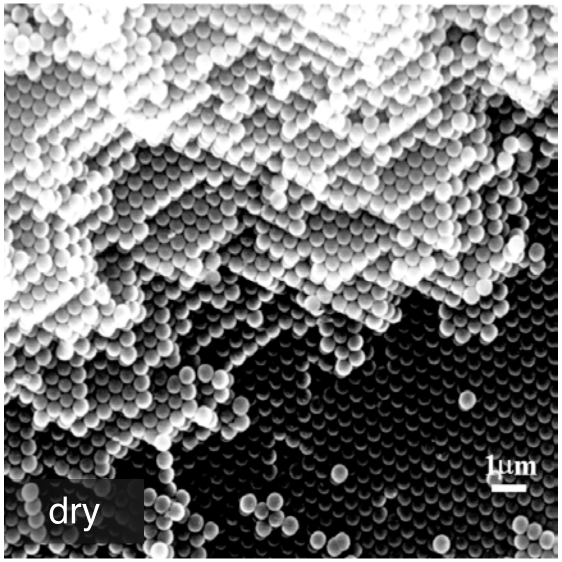
silica microspheres suspended in water experience gravitational settling

$$V = \frac{d^2(\rho_{silica} - \rho_{water})g}{18\eta}$$

where:
d = colloid diameter
ρ = density
g = gravitational constant
η = viscosity of liquid

1 μm silica particle settles ~ 1 cm in 5 h

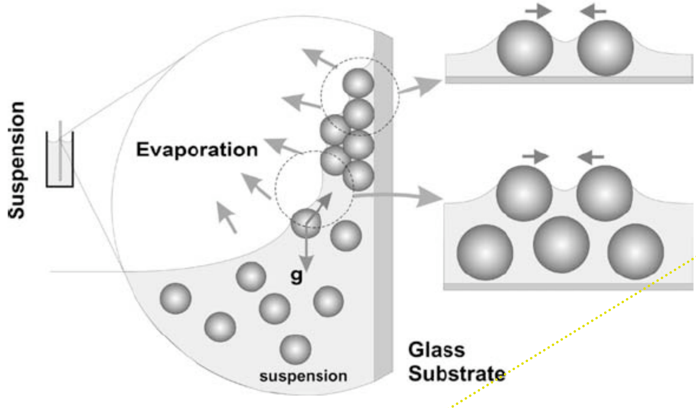


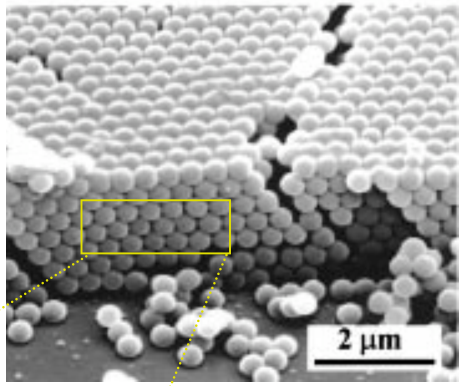


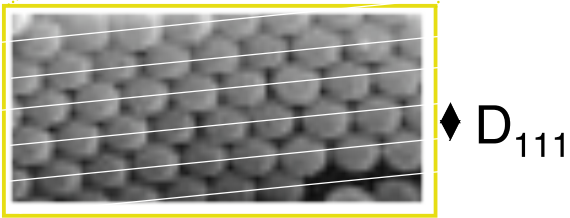
V. Tohver et al., *PNAS*, (2001).

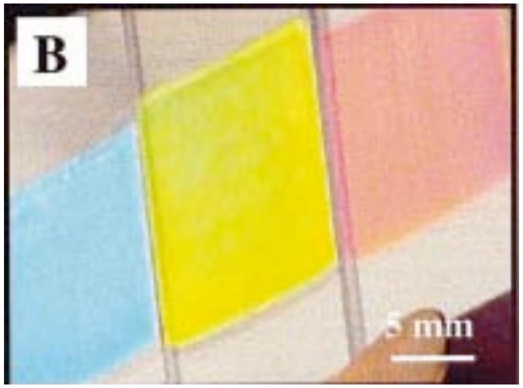
Evaporative Assembly of Colloidal Crystals

dip coating









307 nm 353 nm 384 nm

increasing colloid diameter, $d_{colloid}$

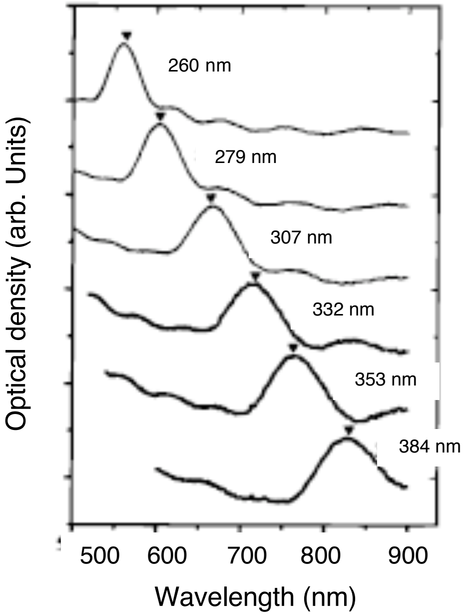
$$\lambda_{max} = 2n_{eff}D_{111}$$

where D_{111} = interlayer spacing

$= (2/3)^{1/2} d_{colloid}$

$n_{eff} = [\phi n_{colloid}^2 + (1-\phi) n_{air}^2]^{1/2}$

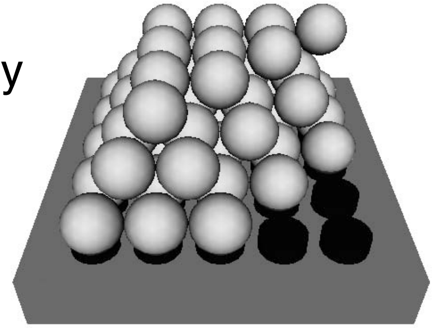
ϕ = colloid volume fraction (0.74)



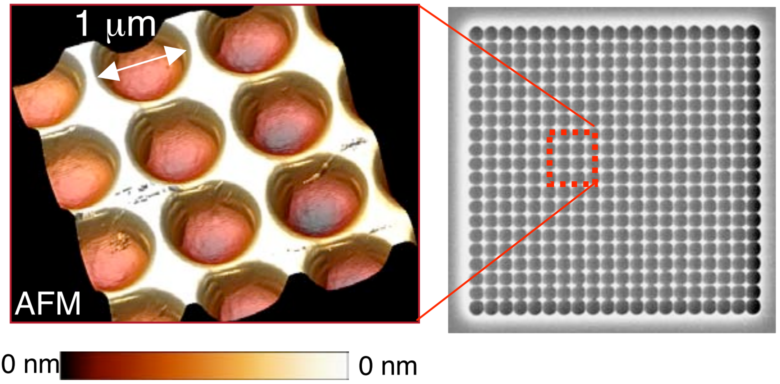
P. Jiang, *et al. Chem. Mater.* **11** 2132-2140 (1999)

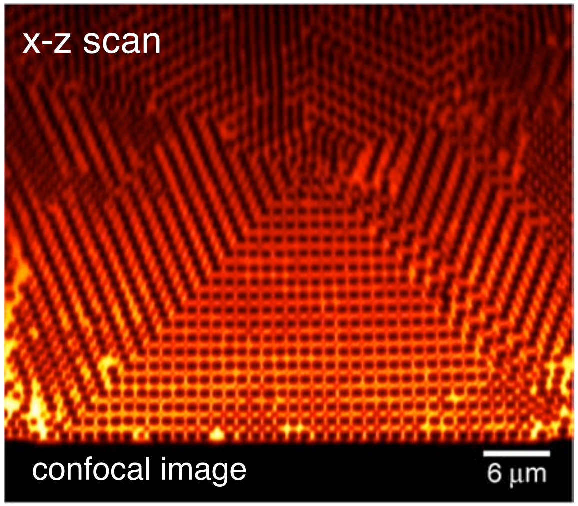
Directed Assembly of Single Domain Colloidal Crystals

colloidal epitaxy



A. van Blaaderen et al.
Nature 385 (321), 1997.

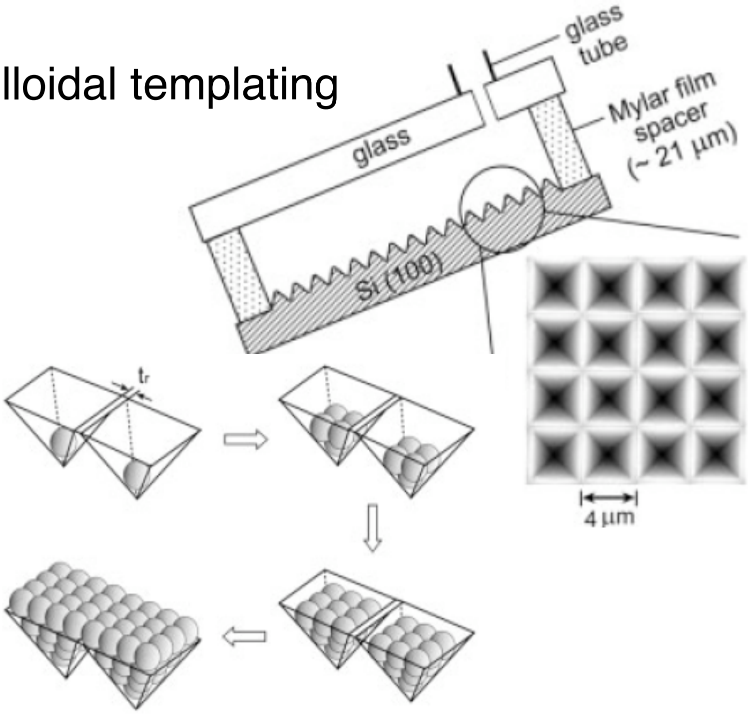


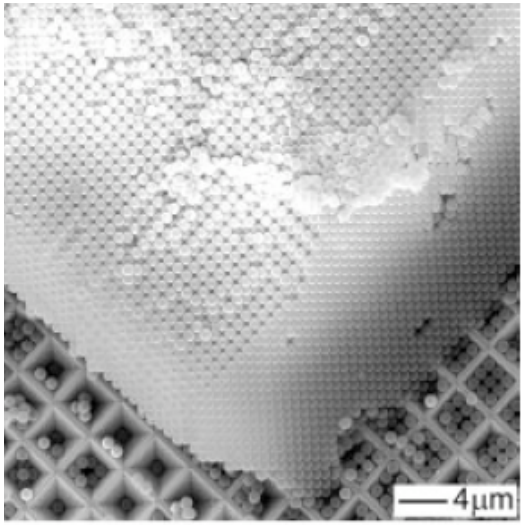


W. Lee et al., *Langmuir* (2004).

single crystals of
controlled orientation
(100) fcc

colloidal templating



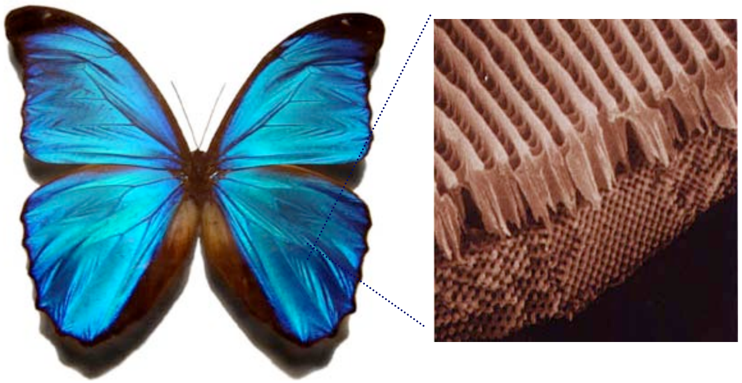


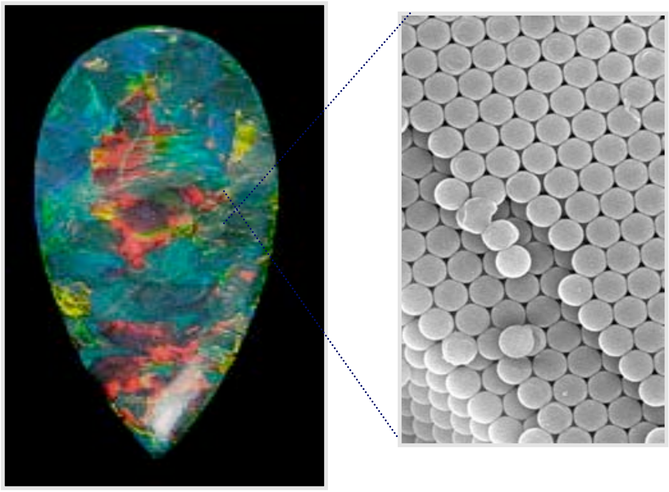
Y. Xia et al., *Advanced Materials* 14, 8 605 (2002).

Natural and Synthetic Photonic Structures

A periodic structure with a varying refractive index that prevents electromagnetic radiation in a certain wavelength range from propagating

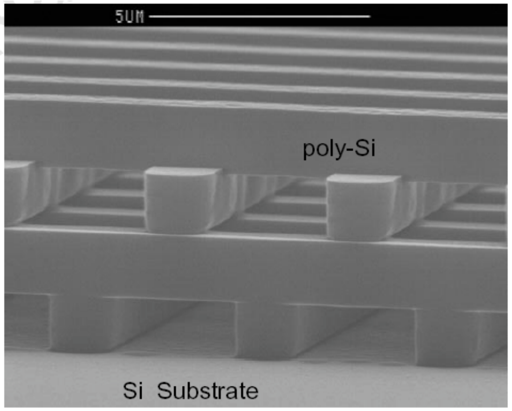
Nature: Partial photonic band gap

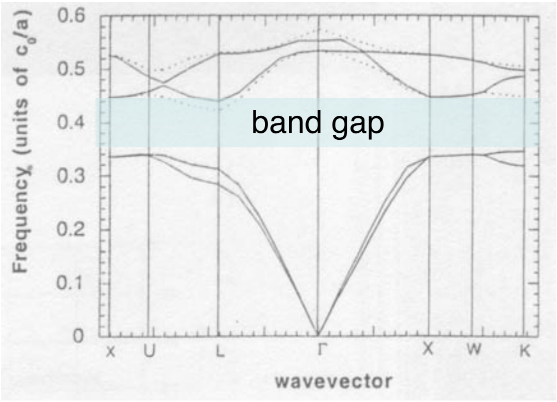


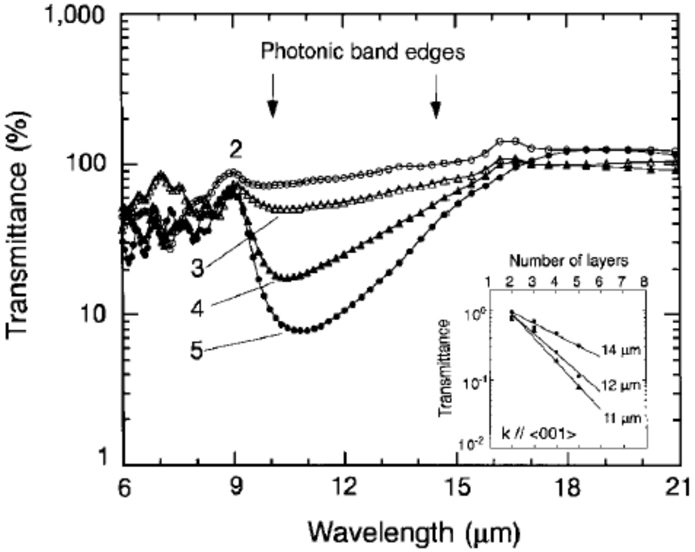


refractive index ~ 1.4-1.5

Synthetic materials: Complete photonic band gap







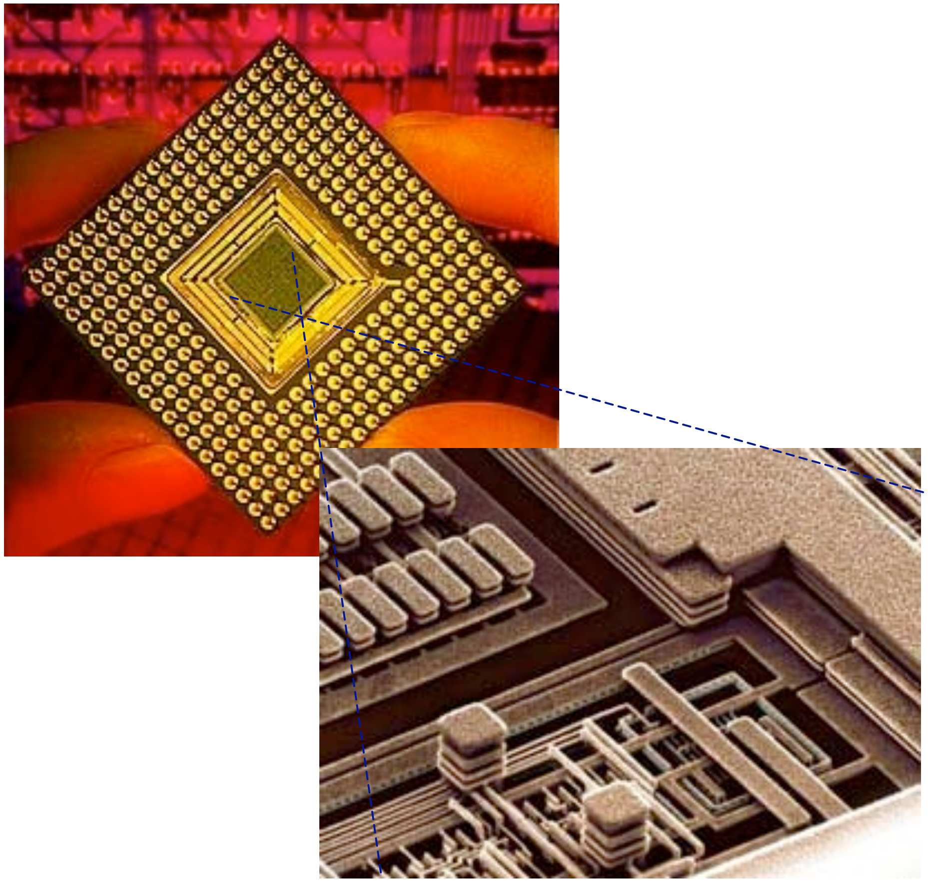
Silicon rods have refractive index of 3.6

- band gap λ ~ 2x lattice constant
- gap position & size increase with Δn, # of layers

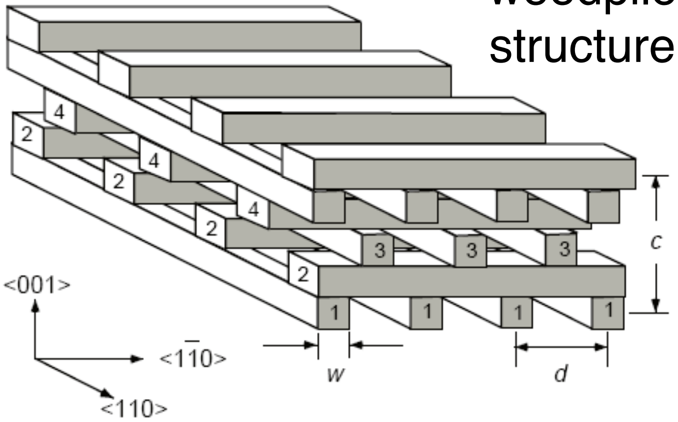
S. Lin *et al.*, *Nature* **394**, 251 (1998).

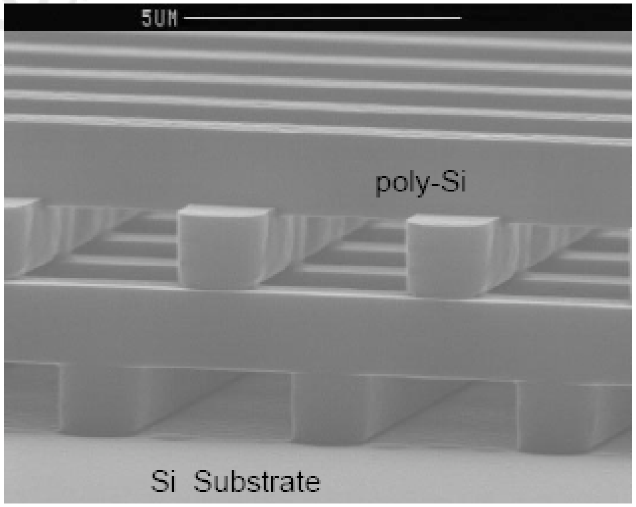
Conventional Silicon Lithography for 3D Photonic Structures

Same technology used to create microchips



woodpile structure

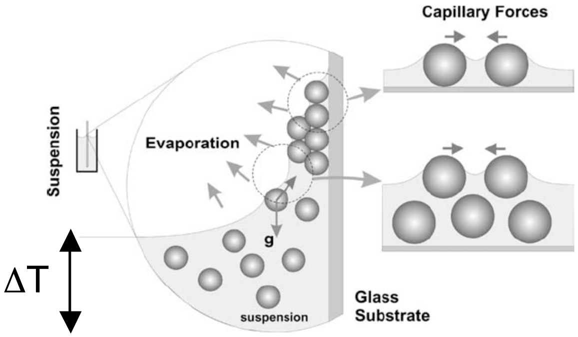


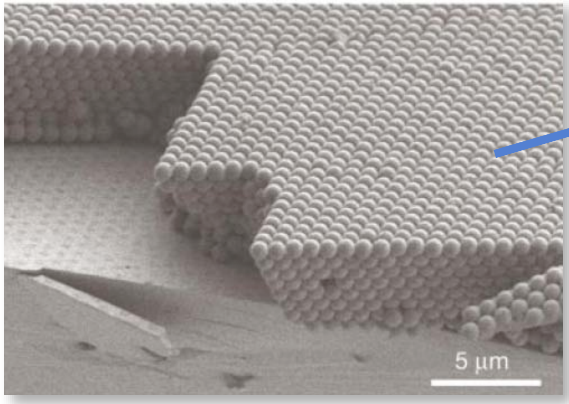


S. Y. Lin, et al., *Nature*, 1998 **394** 251-253

- costly and time consuming process
- multiple lithographic and planarization steps
- high degree of structural control

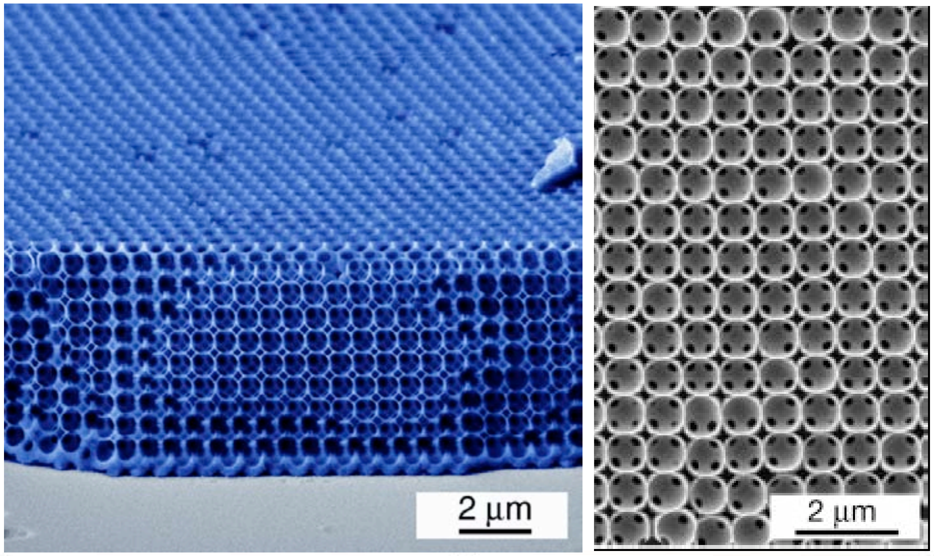
Colloidal Crystal Templates for 3D PBG Materials

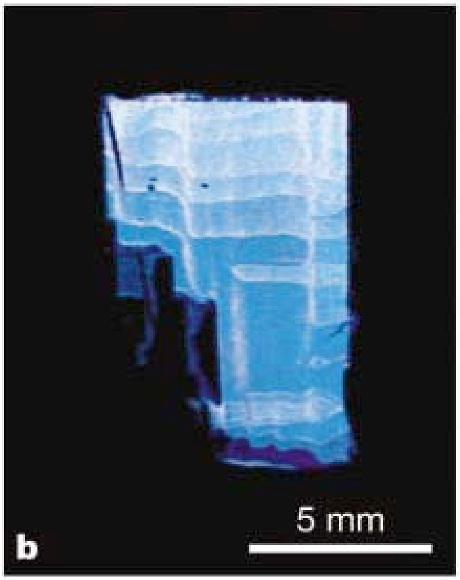




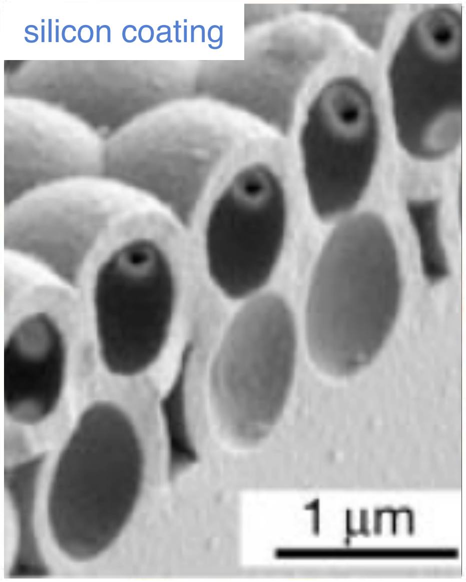
conversion to silicon followed by etching to remove silica spheres

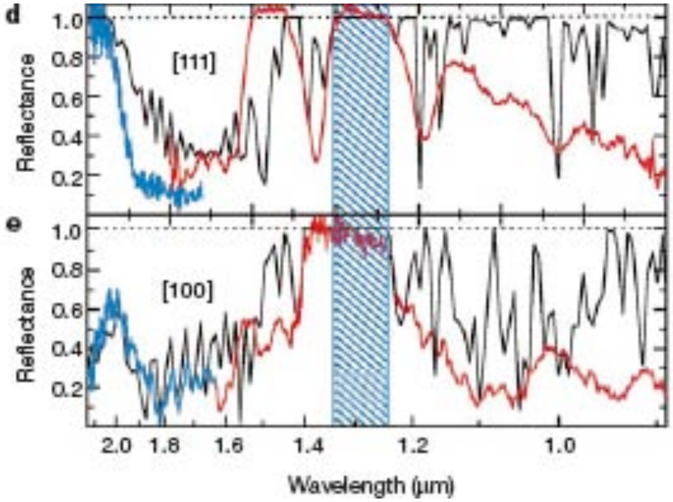
Silicon inverse fcc structure





silicon coating

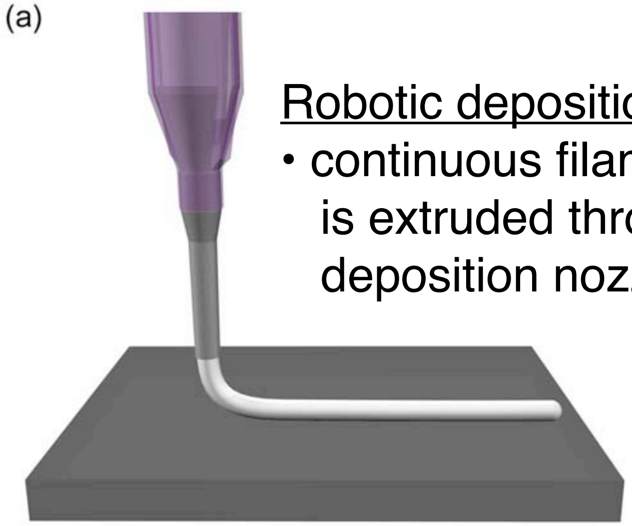




Y. A. Vlasov, et al., *Nature*, 2001 **414** 289-293

Directed Assembly of 3D Periodic Structures

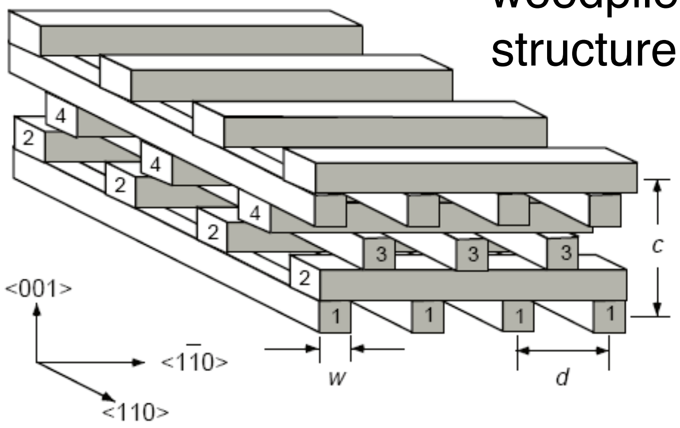
Ink Writing Techniques



Robotic deposition

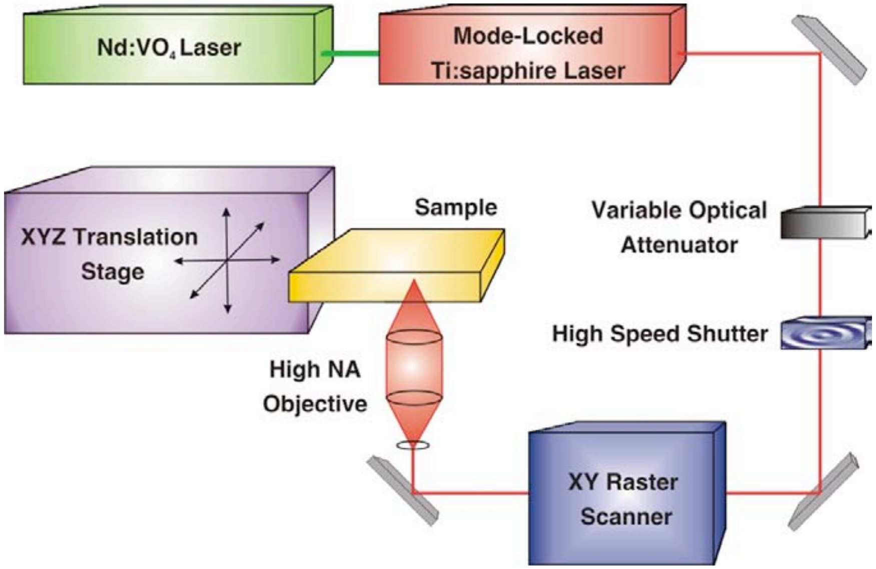
- continuous filament is extruded through deposition nozzle

woodpile structure



J. Lewis and G. Gratson, *Materials Today* (2004).

Laser Writing Techniques



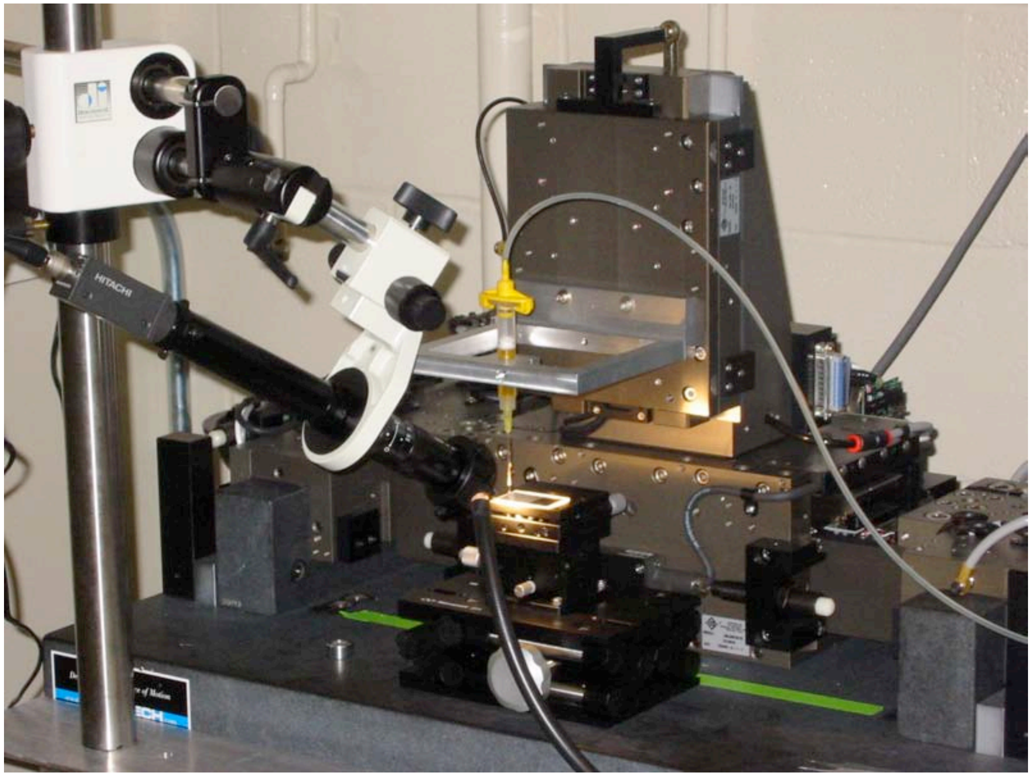
2-photon polymerization (TPP)

- laser beam is translated within a photopolymerizable matrix to induce local cross-linking via a 2-photon initiator

- Computer-controlled translation stage moves a pattern-generating device to create 3D structures with defined architecture

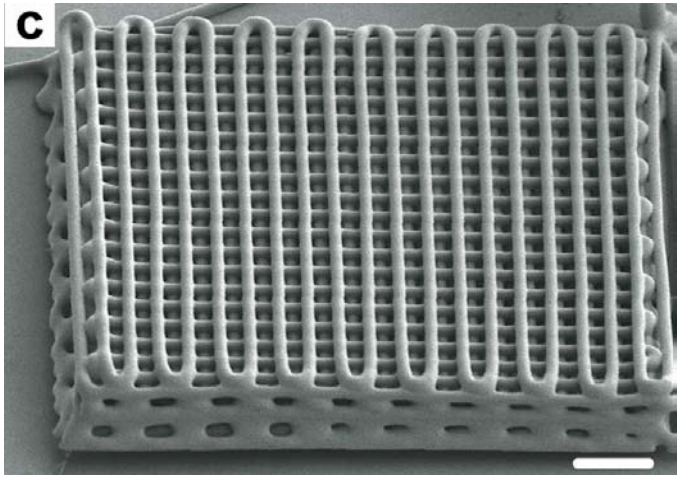
Direct Ink Writing of 3D Polymer Woodpiles

- Robotic deposition of fluid inks (e.g., polyelectrolyte complexes)
- 3D structures are built up layer-by-layer
- Build rates ~ 0.2 - 1 mm/sec
- Nozzle diameter = 0.5 μm - 5 μm

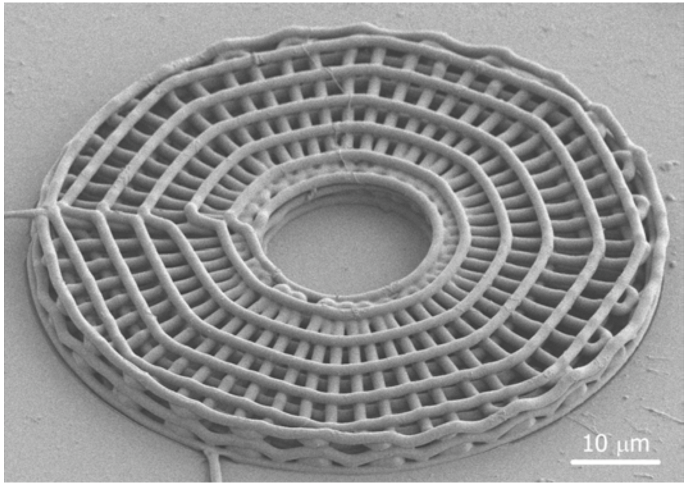


Software: J. Smay (now at Okla. St.)

3-D Lattice



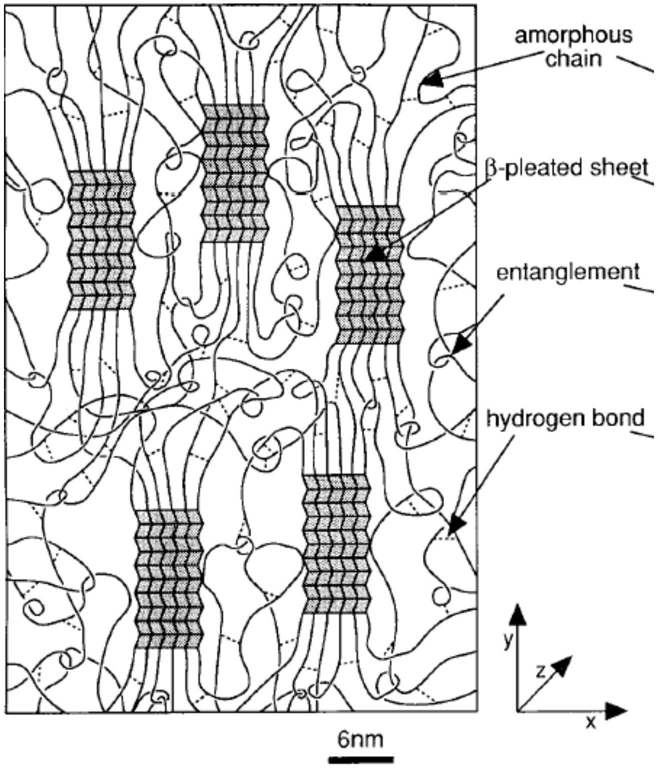
Radial Array



G. M. Gratson, M. Xu, and J. A. Lewis *Nature* (2004).
G.M. Gratson and J.A. Lewis, *Langmuir* (2005).

Nature's Approach for Fine Scale Writing

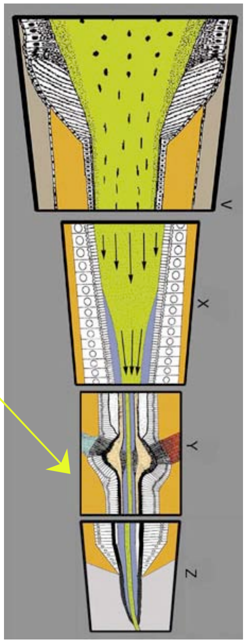
Spinning Dope



J.P. O'Brien, et.al., ***Adv. Mat.***, *10*, 1185 (1998).

Ink - Concentrated protein solution
(~ 40 wt%)

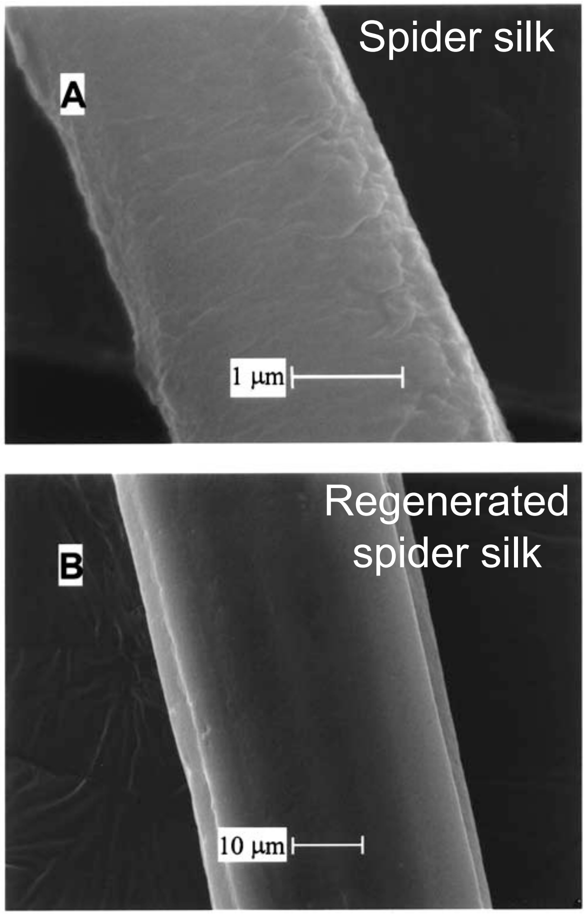
Nozzle - Complex spinneret
w/ *in situ* chemical
triggering



Filament size - **10 nm to**
10 μm

Filament chemistry- varies locally
within web to create proper
elastic "trapping" landscape

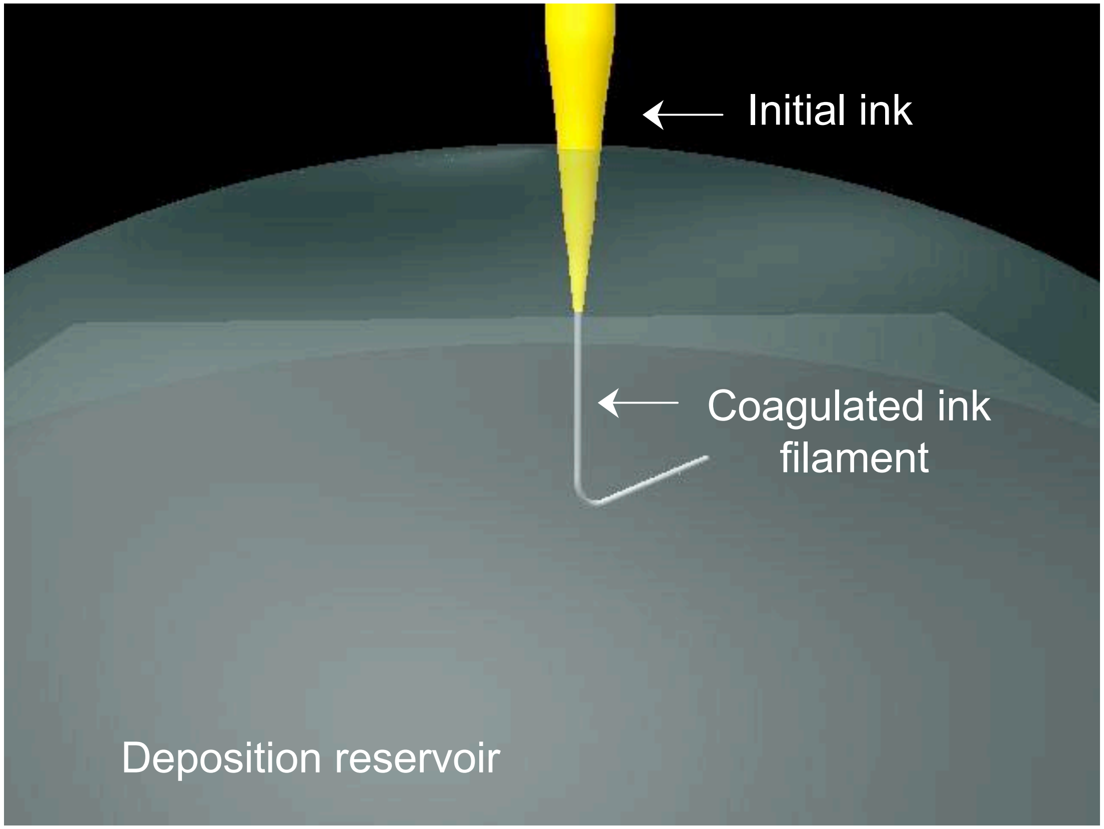
Triggered Changes in Ink Rheology During Direct Writing



Filaments formed by depositing dope (3-20 wt%) into coagulation bath

A. Seidel et.al., ***Macromolecules***, *31*, 6733 (1998).
A. Lazaris et.al., ***Science***, *295*, 472 (2002).

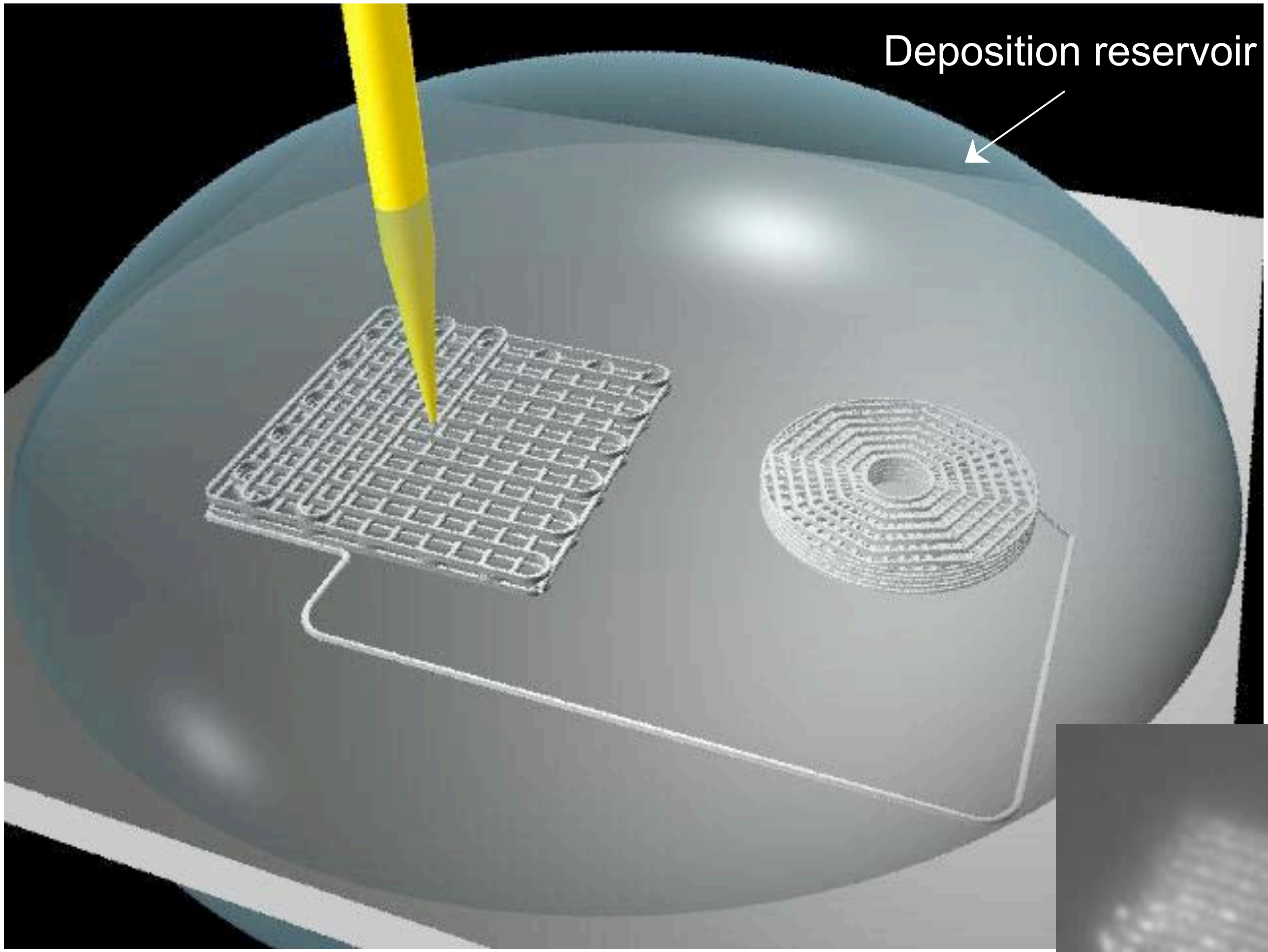
Synthetic "Spinning Dope"



Polymeric ink was created by mixing oppositely charged polyelectrolytes in an aqueous solution (40 wt%)

Deposition reservoir - alcohol + water

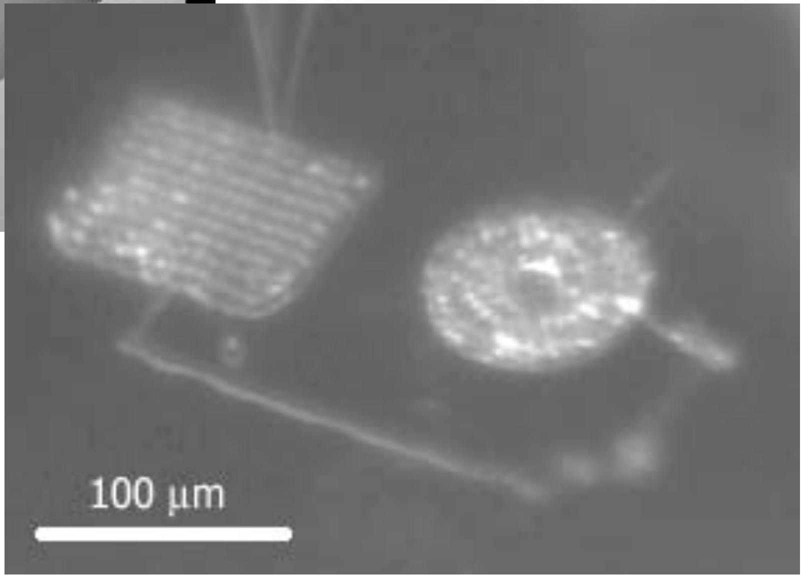
Direct-Write Assembly of Polyelectrolyte Inks



e.g., synthetic PE
(PAA, PEI, PAH...)

biopolymers
(DNA, peptides…)

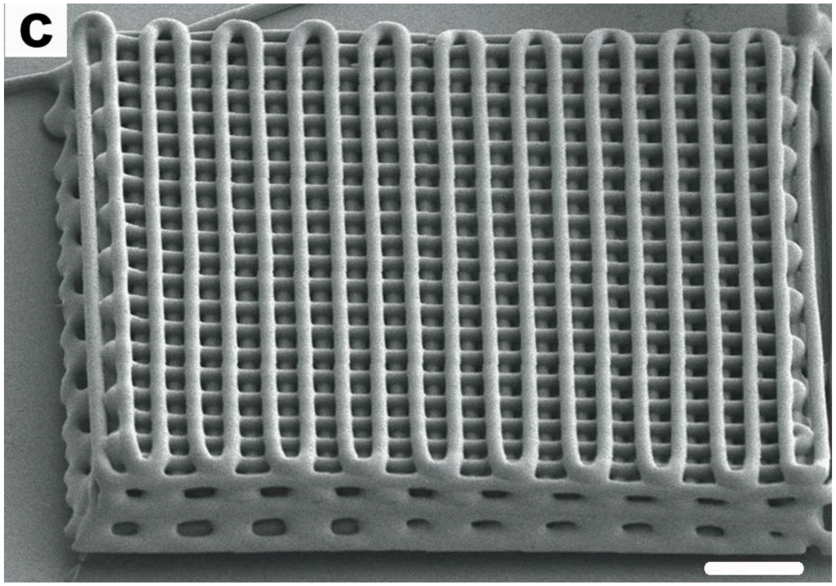
Typical build
time ~ 1-5 min

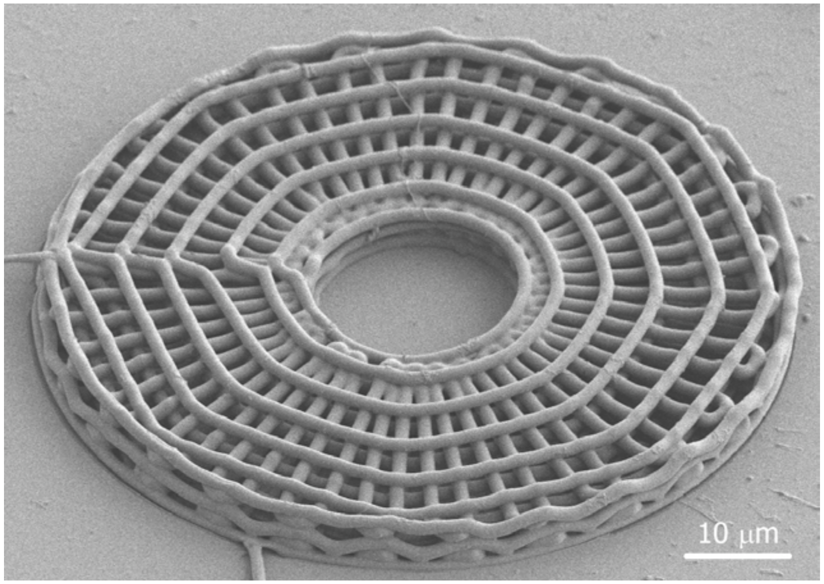


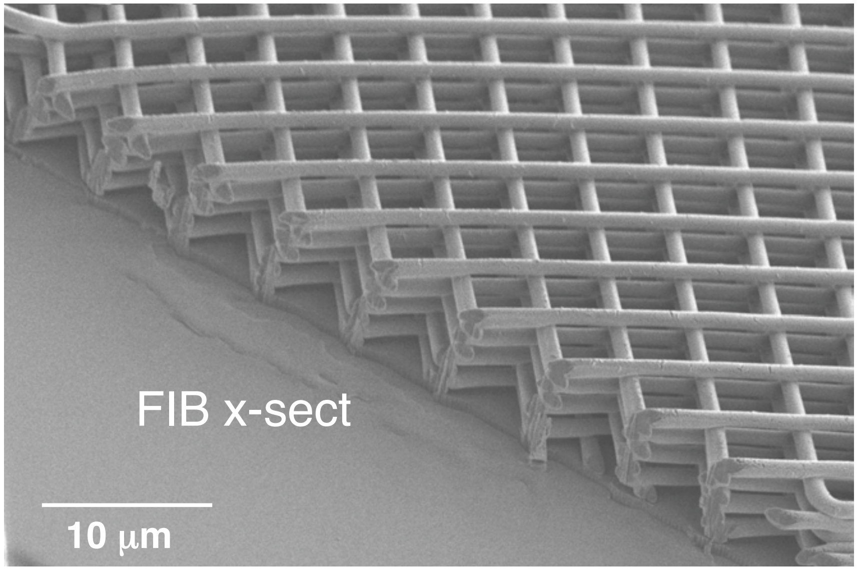
<u>Concentrated polymer inks</u> - mixture of oppositely charged polyelectrolytes (40 wt%) in an aqueous solution

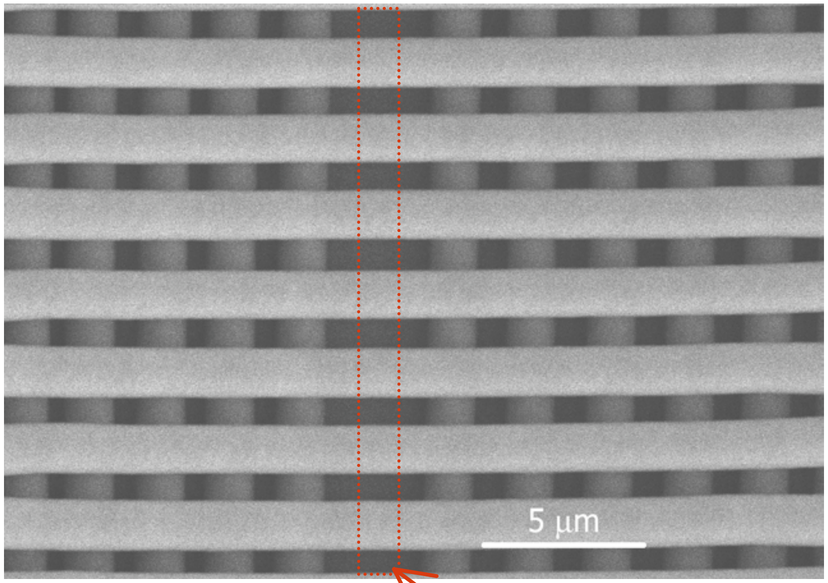
<u>Deposition reservoir</u> - alcohol/water

Direct Writing of Polymer Woodpiles and Radial Arrays





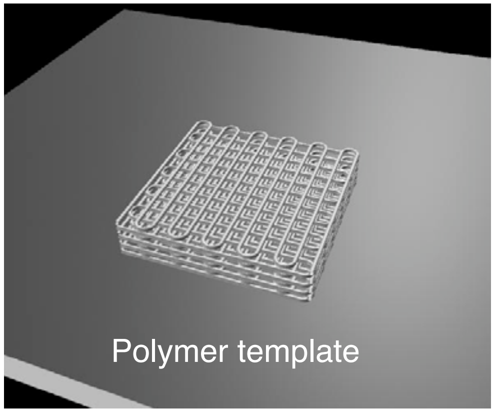


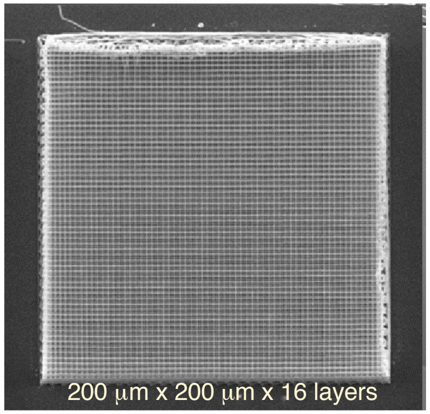


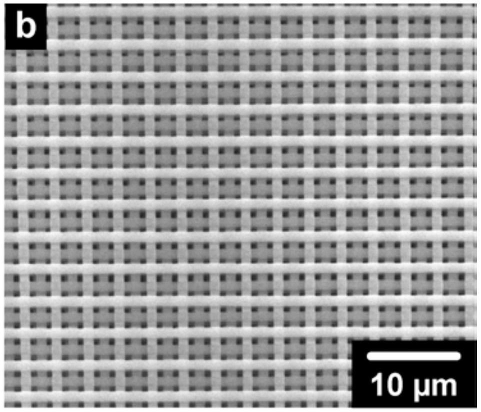
missing rod

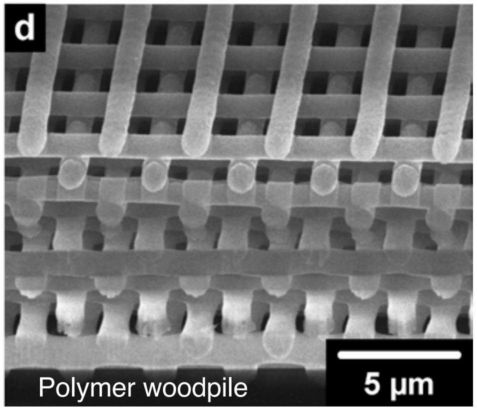
G. Gratson, M. Xu, and J.A. Lewis, *Nature* (2004)

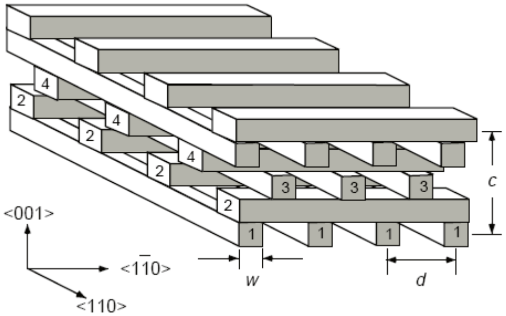
Templating Silicon PBGs from Polymer Woodpiles

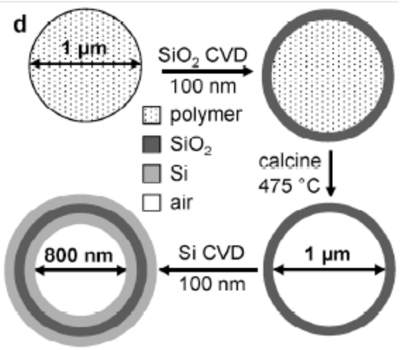


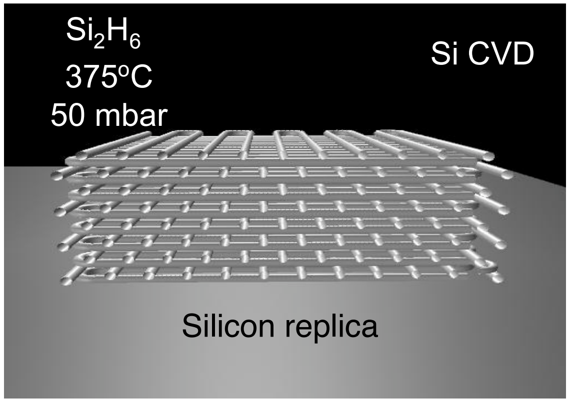


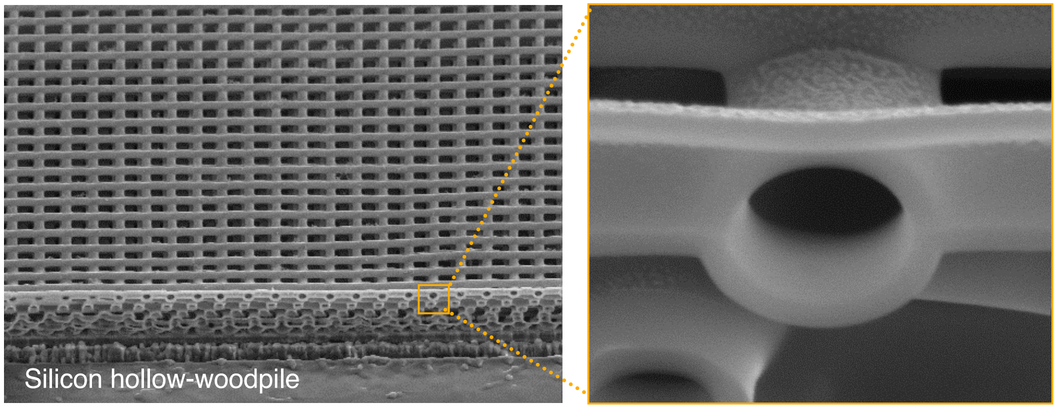






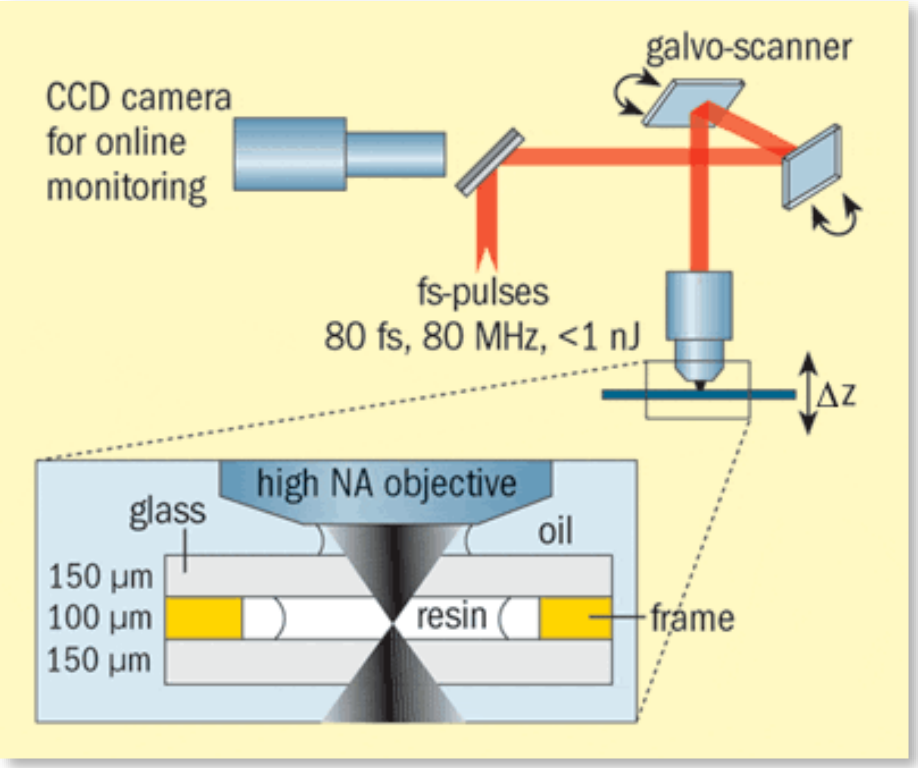




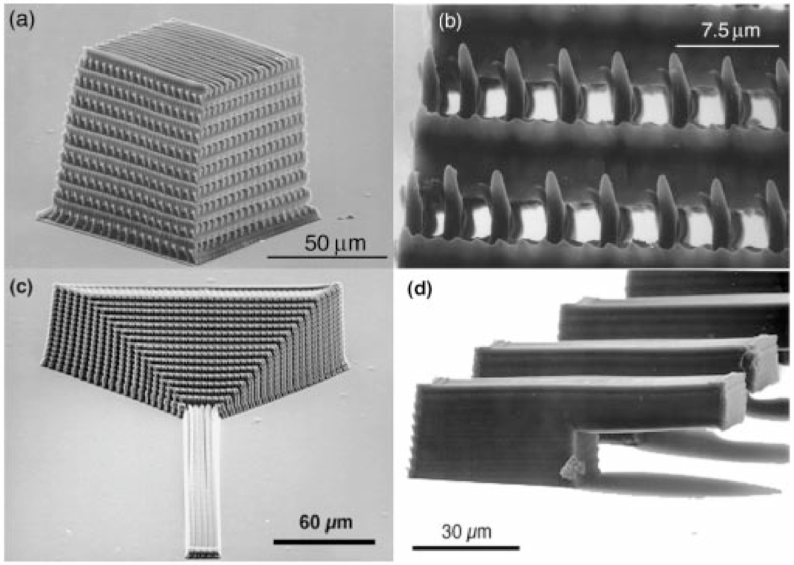


G. Gratson, F. Garcia-Santamaria, V. Lousse, S. Fan, J. Lewis, P. Braun, *Advanced Materials* (2006).

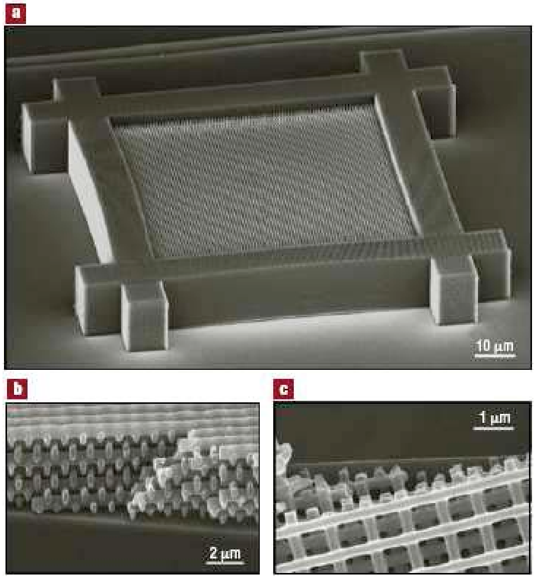
Direct Laser Writing of 3D Polymer Structures



The intensity within the focusing volume is strong enough to induce polymerization of the organic resin



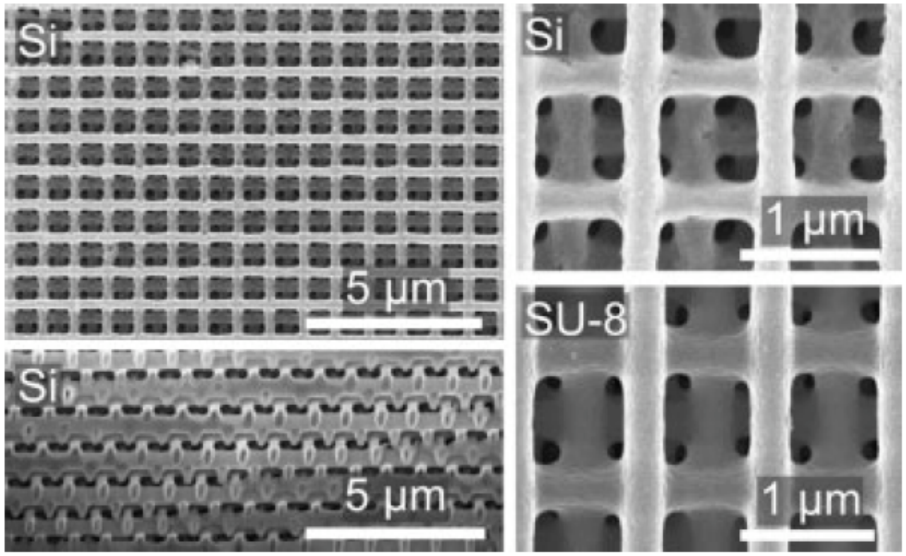
B. H. Cumpston, et al., *Nature*, 1999 **398** 51-54



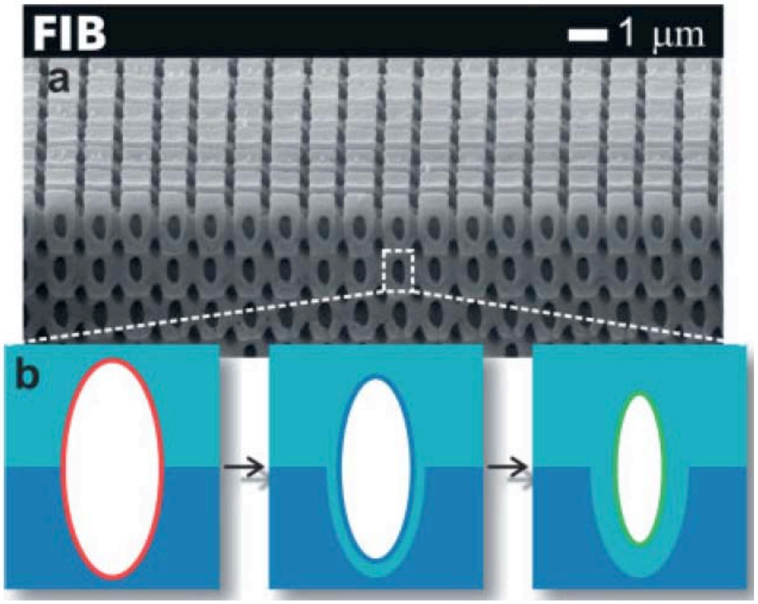
M. Deubel, et al., *Nature Materials*, 2004 **3** 444-447

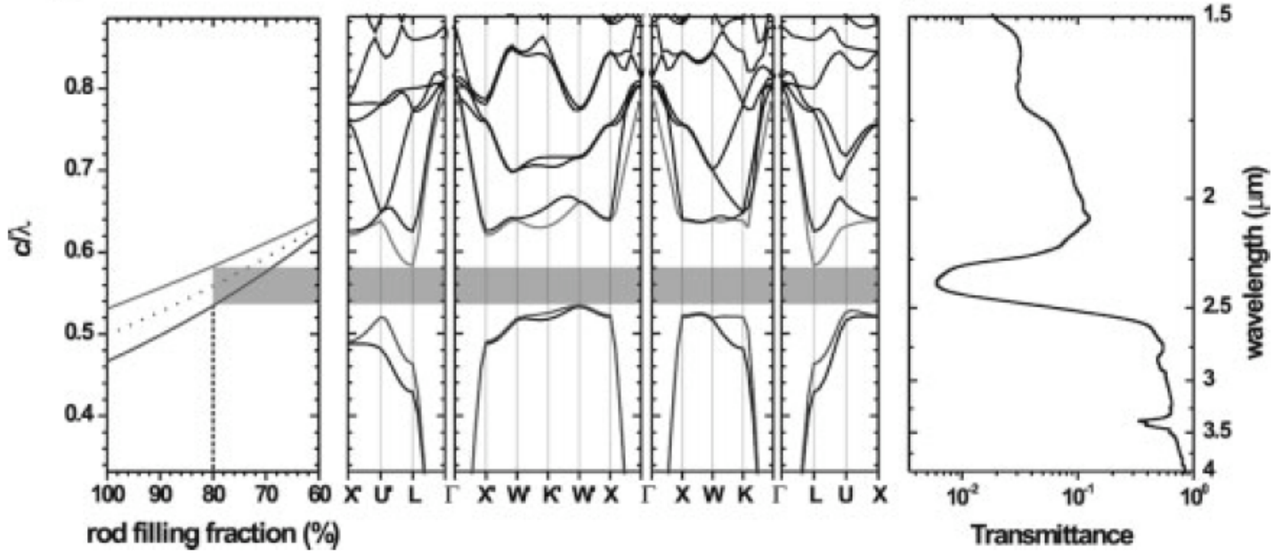
Double Conversion to Silicon Woodpile Structures

Silicon woodpile



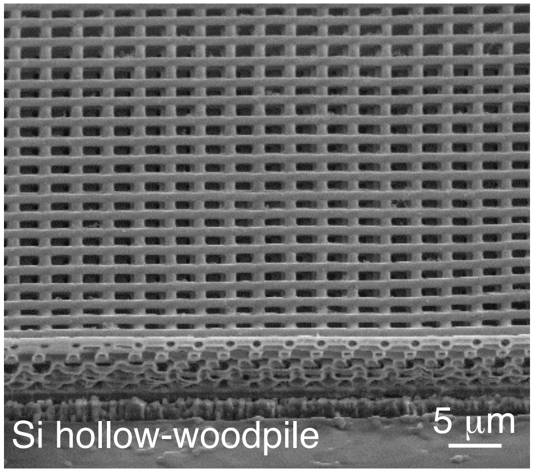
Polymer woodpile





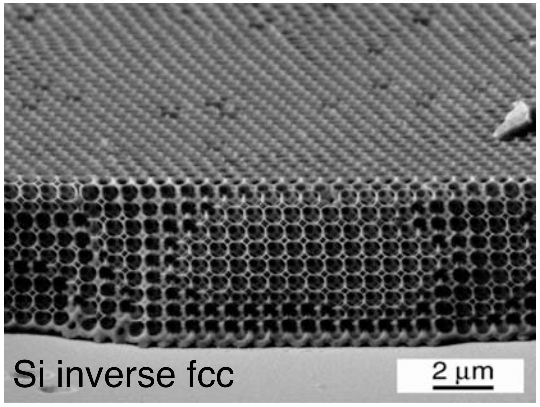
Ozin and co-workers, ***Advanced Materials*** (2006).

Comparison of 3D Fabrication Techniques



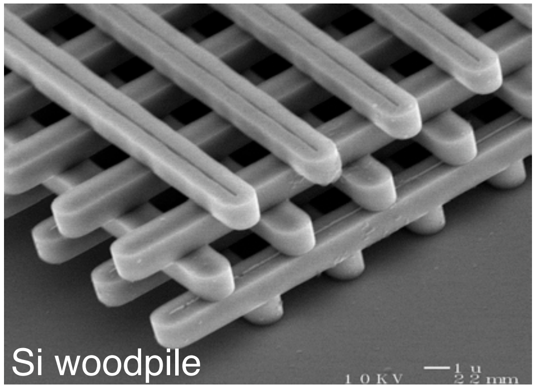
Direct Writing

- 3D structures constructed in minutes
- inexpensive
- wide range of ink designs
- features can be incorporated into CAD design



Colloidal Self Assembly

- 3D structures constructed in several hours
- inexpensive
- limited microsphere chemistry
- controlled feature incorporation difficult



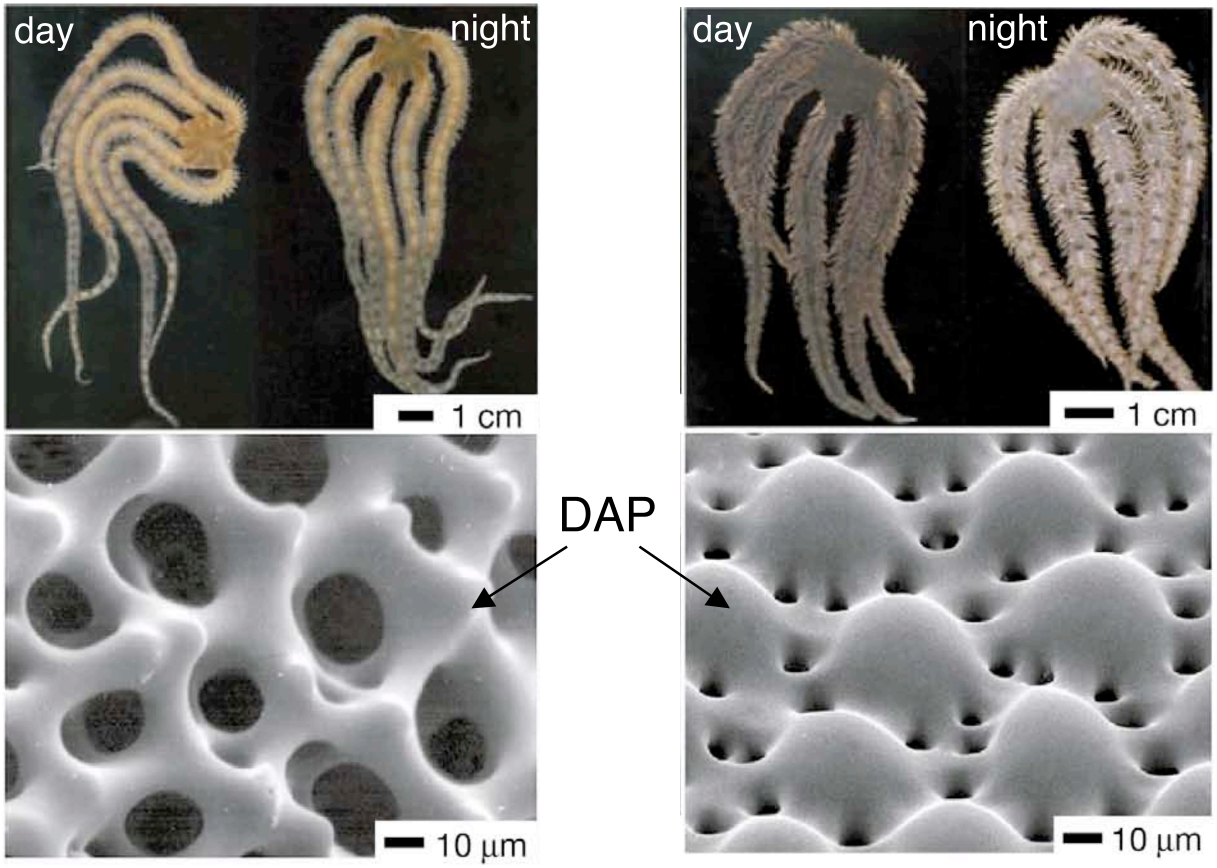
Layer-by-Layer Microfabrication

- 3D structures constructed in several days (multiple lithographic and planarization steps)
- costly $$
- features can be incorporated into design

Brittlestars - Armed for Light Sensing

Light-indifferent
species

*Ophiocoma
pumila*



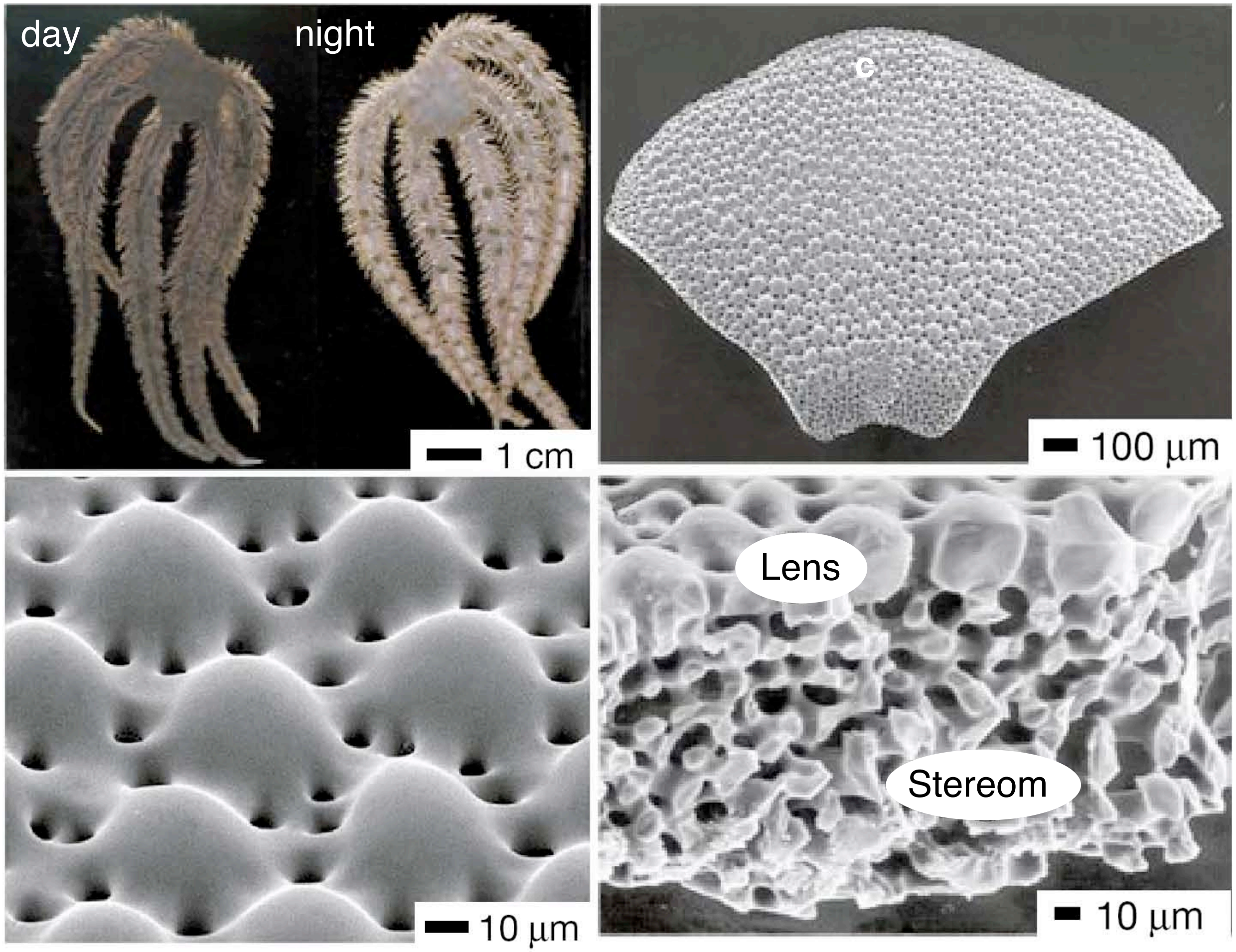
Light-sensitive
species

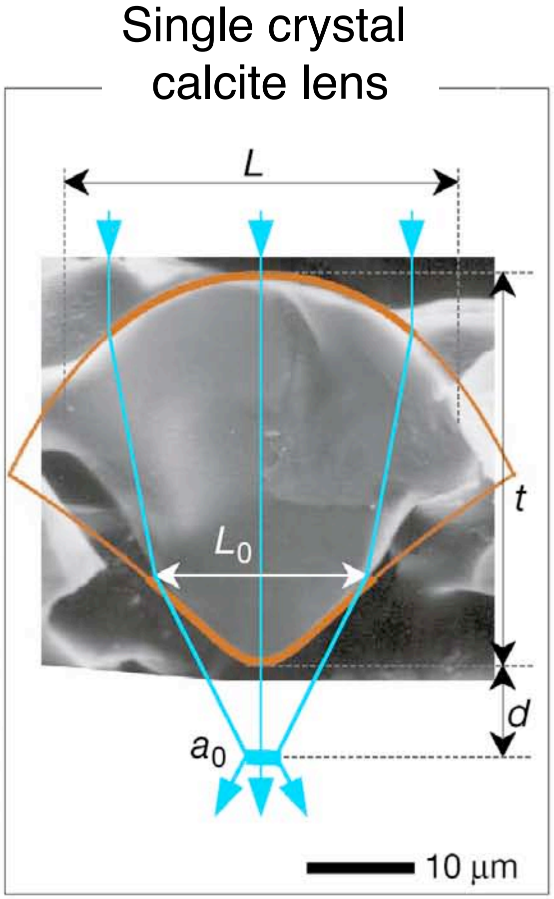
*Ophiocoma
wendtii*

Light-sensitive brittlestar species have developed intricate photoreceptor systems on their dorsal arm plates (DAPs)

J. Aizenberg, et al., *Nature* **412**, 819-822 (2001)

Brittlestars - Novel Microlens Arrays





Calcite ($CaCO_3$) lens are proposed to direct and focus light onto photosensitive tissues

J. Aizenberg, et al., *Nature* **412**, 819-822 (2001)

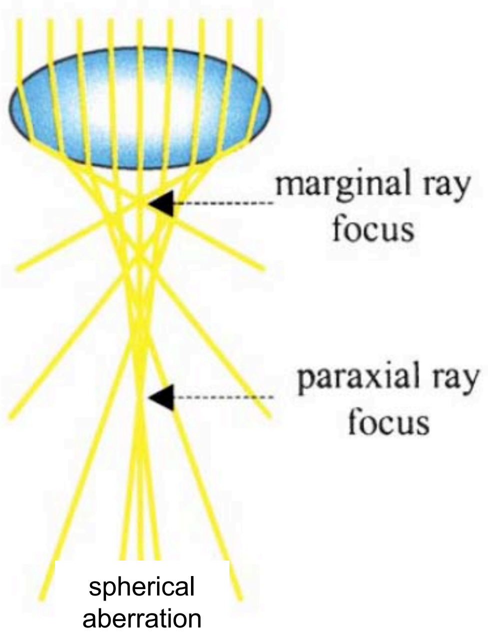
Brittlestars - Novel Microlens Arrays

Ideal thin lens

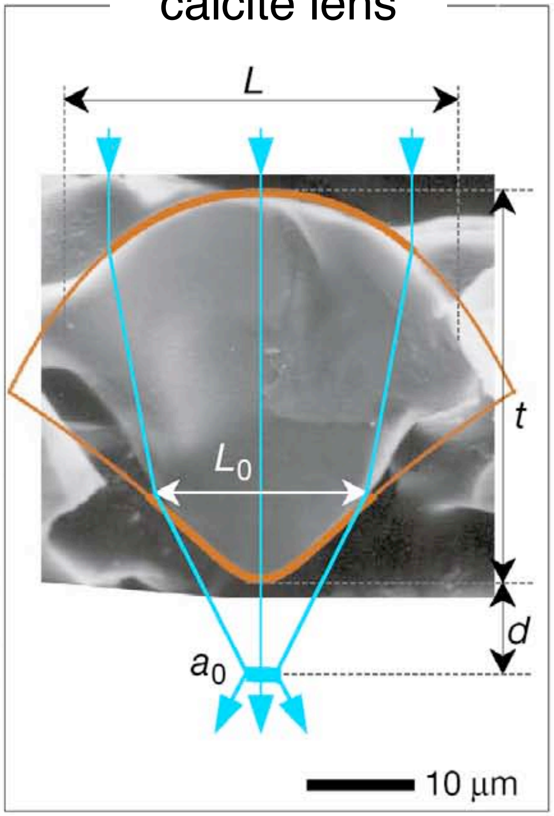
light rays converge
at same point

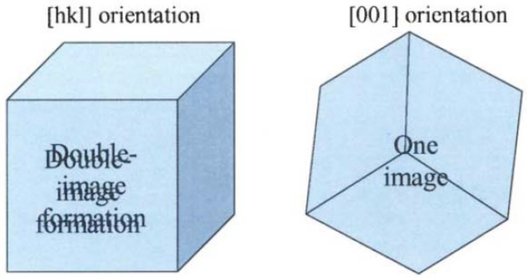
Spherical thick lens

light rays converge
at different points



Single crystal calcite lens





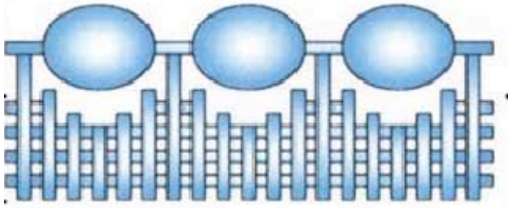
Calcite ($CaCO_3$) lens has a peculiar shape that fully compensates for spherical aberration - 15x brighter intensity than its spherical counterpart

Perfectly oriented in direction of optical axis - making it birefringent-free

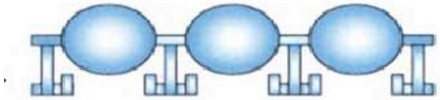
J. Aizenberg, et al., *Nature* **412**, 819-822 (2001).
J. Aizenberg, G. Hendler, J. Mater. Chem. 14 2066 (2004).

Brittlestars - Novel Microlens Arrays

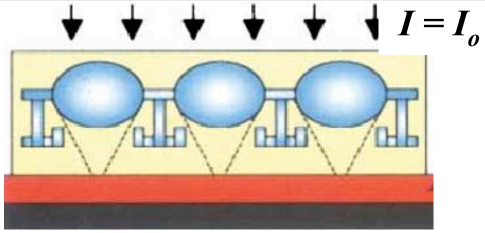
Isolate dorsal arm plate
(remove organic tissue)



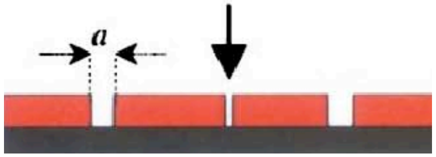
Polish dorsal arm plate
(remove stereom layer)



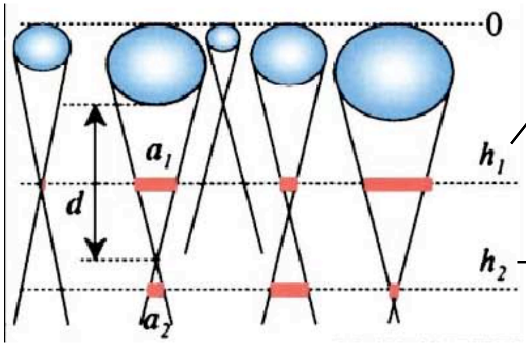
Embed dorsal arm plate
in polymer (PDMS) +
expose positive photoresist

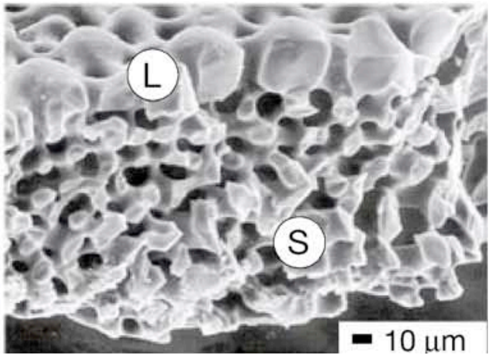


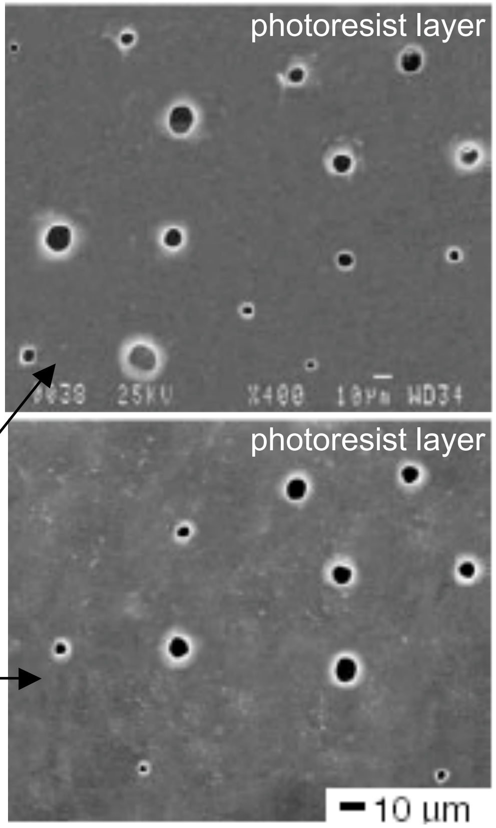
Develop photoresist
and examine



Patterned holes in photoresist
occur where $I > I_o$

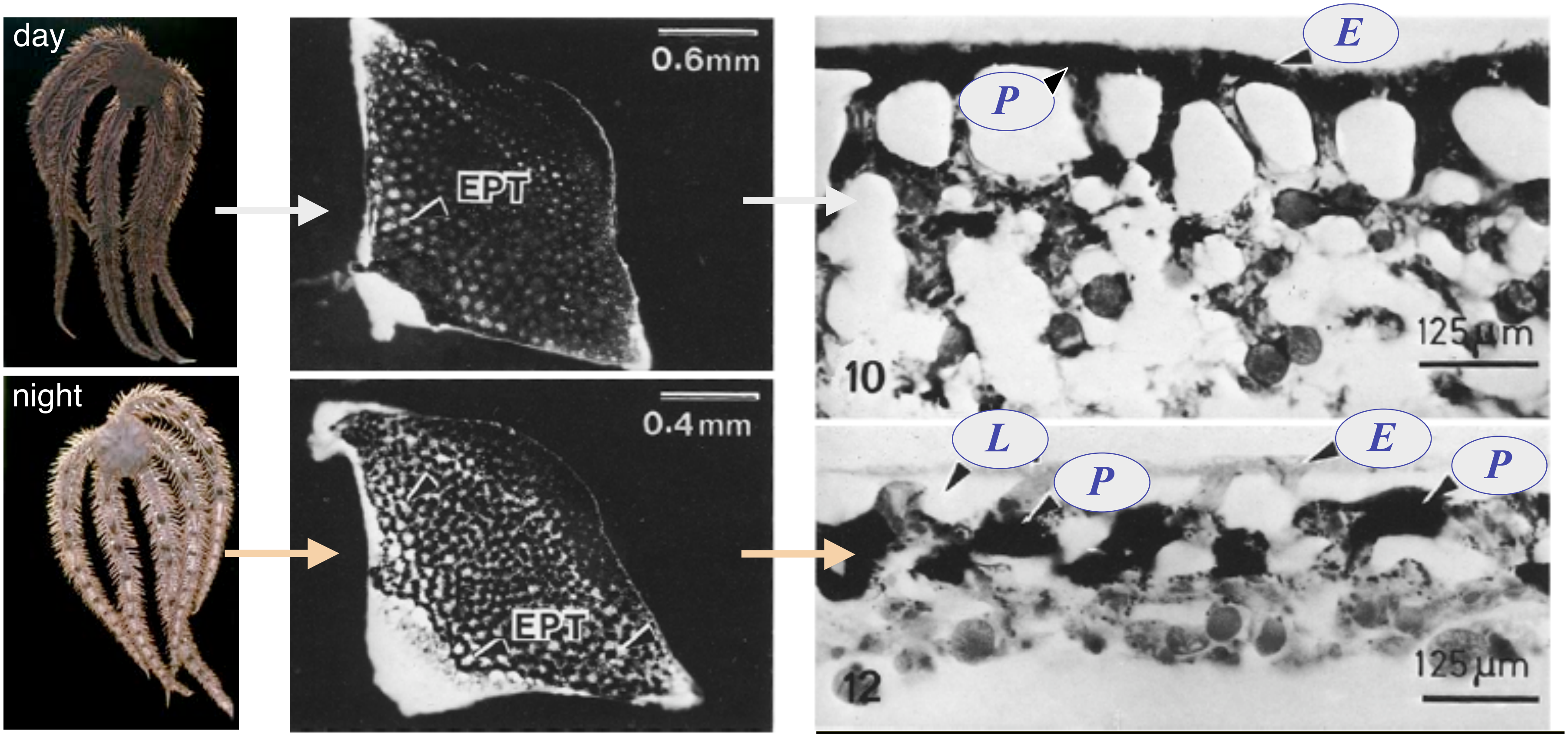






J. Aizenberg, et al., *Nature* **412**, 819-822 (2001)

Brittlestars - Tunable Microlens Arrays



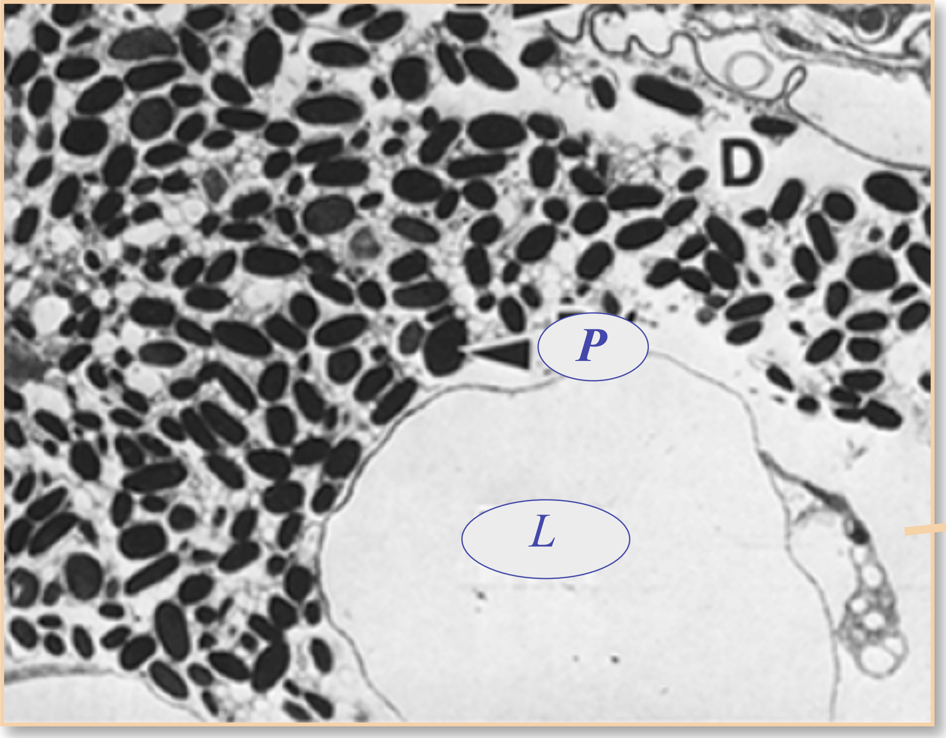
L – lens; P – pigment; E – epidermis

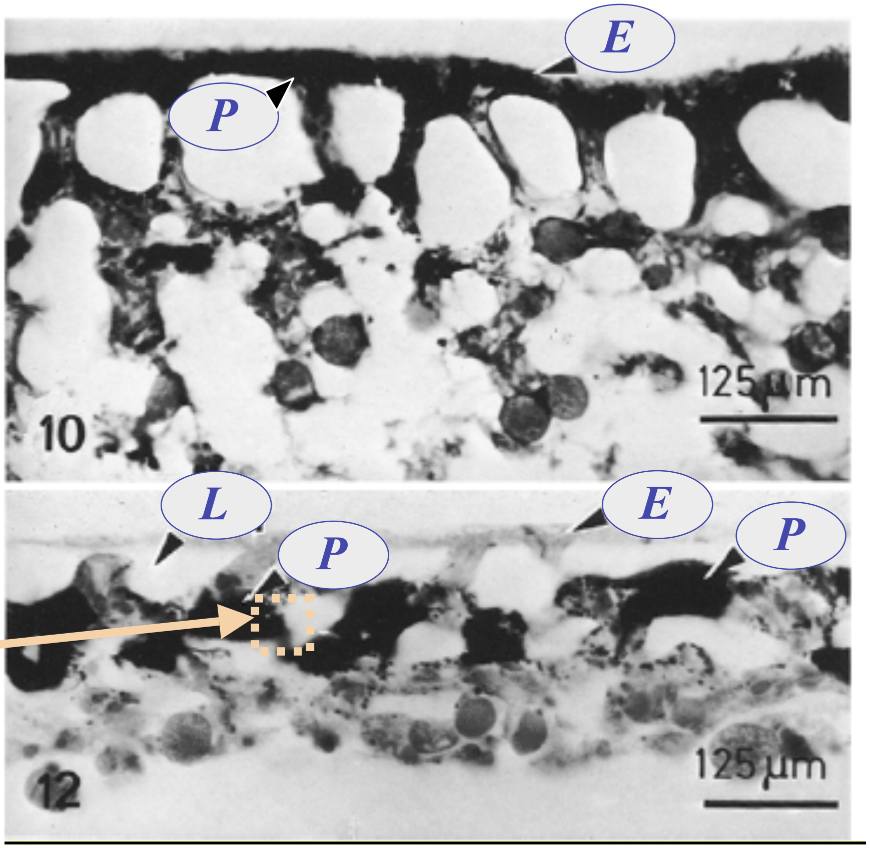
- Color change arises due to (dark) pigment-filled chromatophore cells, which cover the lenses during the day and migrate deeper into the DAP at night

G. Hendler and M. Byrne, Zoomorphology, 107, 261-72 (1987)

Brittlestars - Tunable Microlens Arrays

Pigment = ellipsoidal colloids (~ 1 μm in size)





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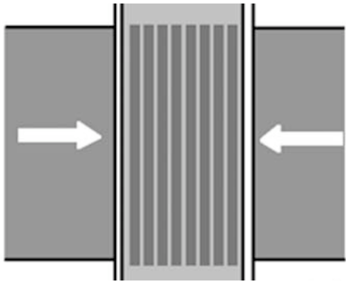
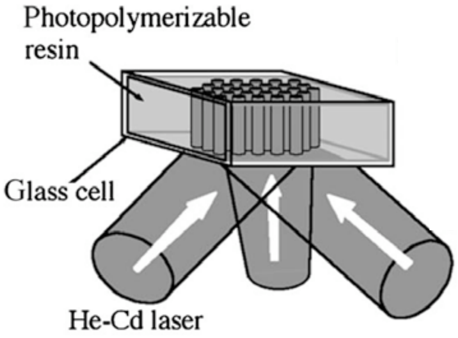
G. Hendler and M. Byrne, Zoomorphology, 107, 261-72 (1987)

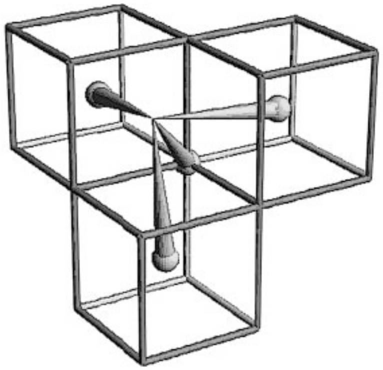
Multibeam Interference Lithography



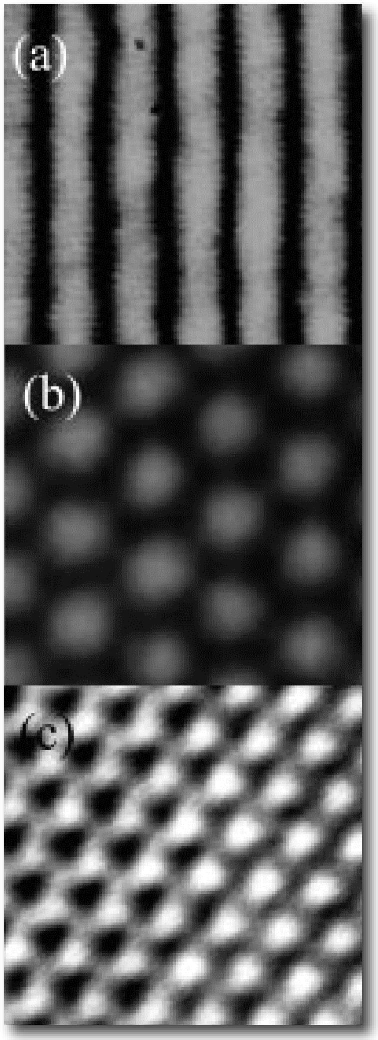
2-Beam (1D pattern)



3-Beam (2D pattern)



4-Beam (3D pattern)



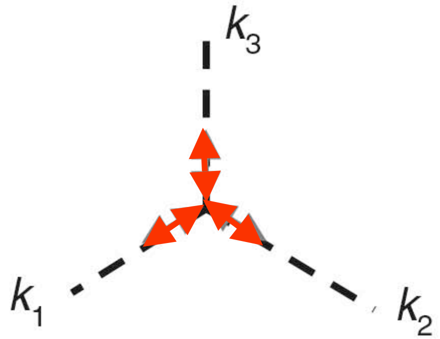
side view

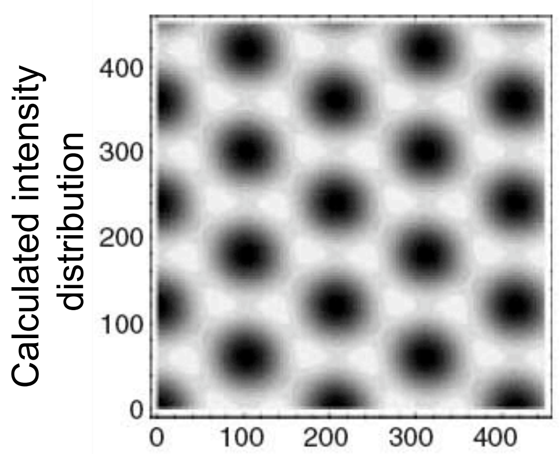
top view

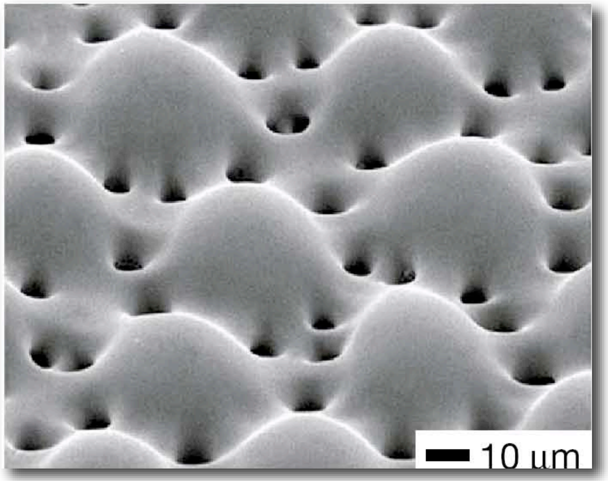
Complex, well defined patterns can be written into photosensitive materials via holographic lithography

Creating Microlens Arrays via Multibeam Interference Lithography

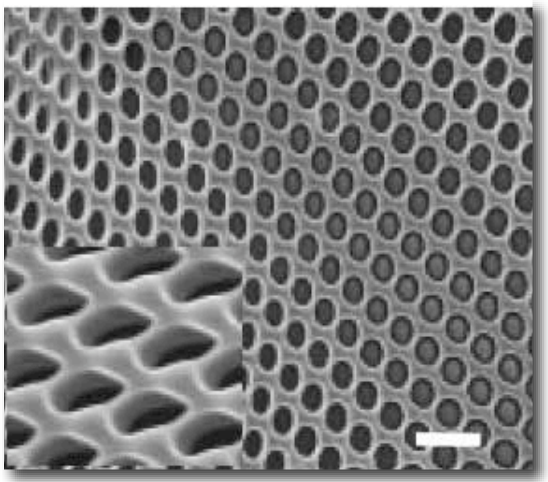
3-beam polarization







Brittlestar



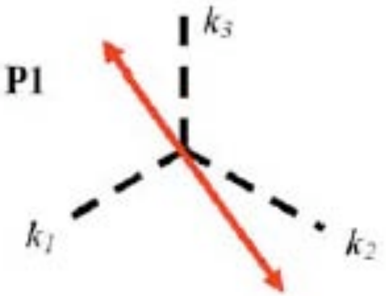
Patterned (neg) photoresist

Complex, well defined patterns can be written into photosensitive materials via holographic lithography

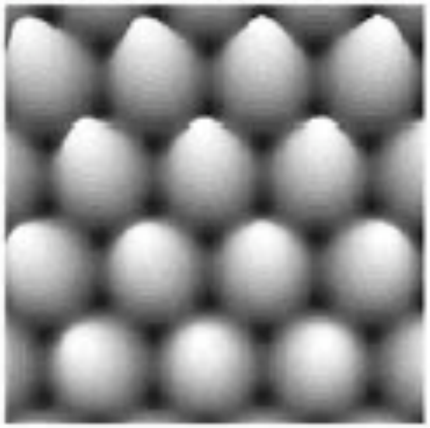
S. Yang et al., Advanced Materials, 17 [4] 435 (2005).

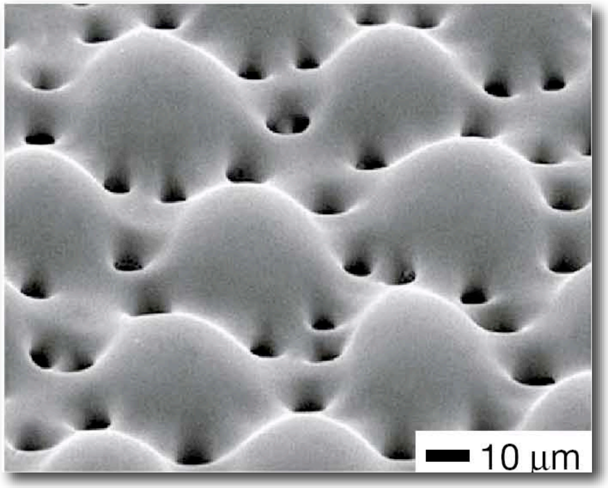
Creating Microlens Arrays via Multibeam Interference Lithography

3-beam parallel polarization

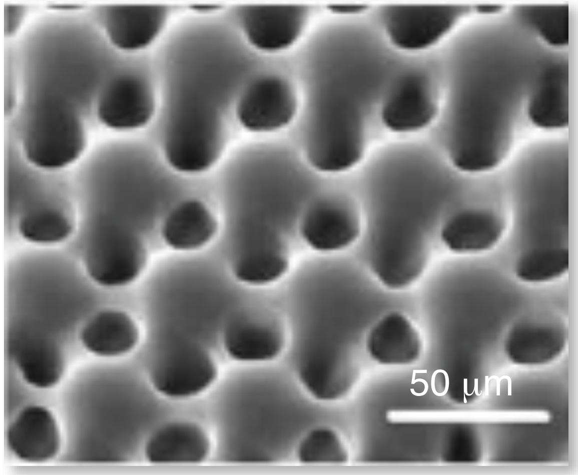


Calculated intensity distribution





Brittlestar



Patterned (neg) photoresist

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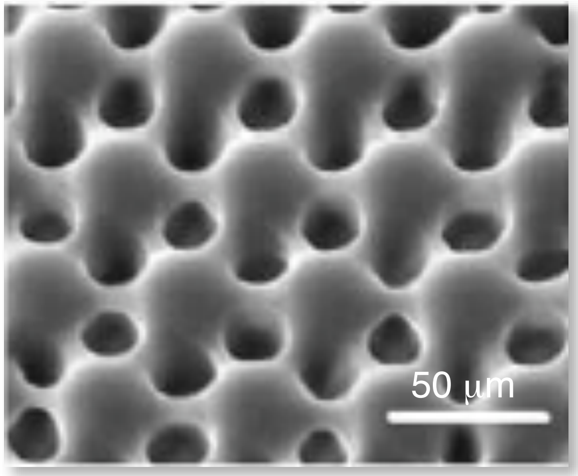
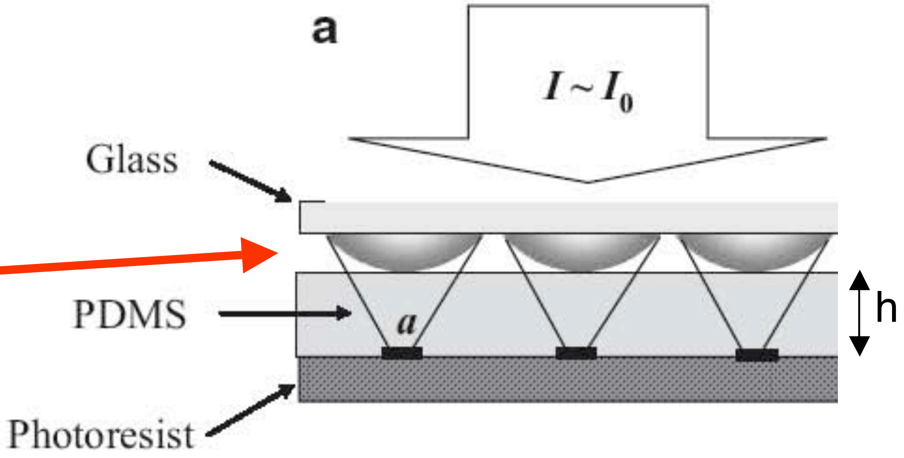
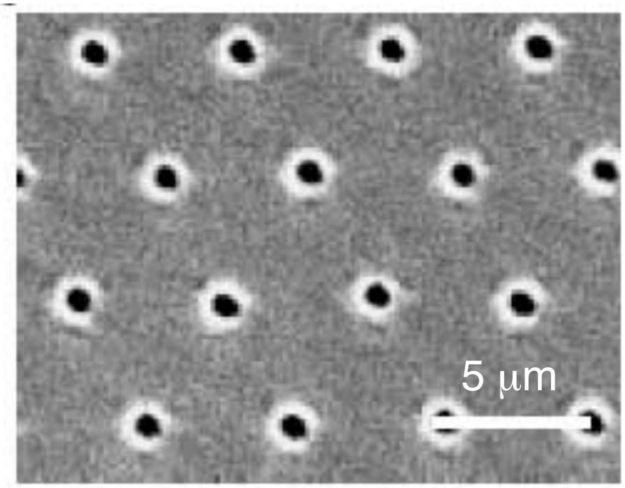
Creating Microlens Arrays via Multibeam Interference Lithography



Patterned features emulate brittlestar

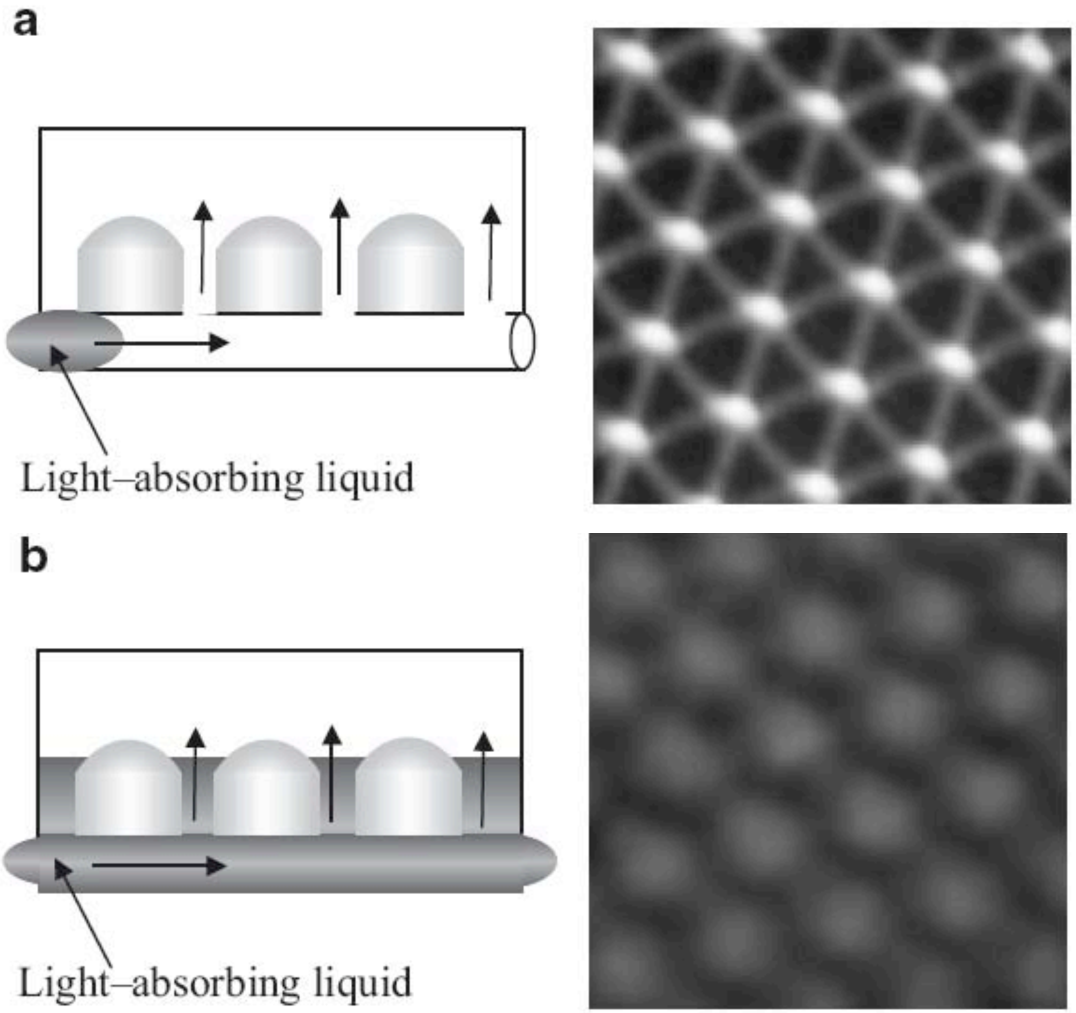




Features patterned into positive photoresist

S. Yang et al., Advanced Materials, 17 [4] 435 (2005).

Creating Microlens Arrays via Multibeam Interference Lithography



Light transmission can be tuned via controlled liquid transport through porous regions of the microlens array

S. Yang et al., Advanced Materials, 17 [4] 435 (2005).

Nacre - A Model for Tough Nanocomposites

Bricks = platelets of calcium carbonate (aragonite phase)

Mortar = 10-50 nm organic layers of proteins, chitin

- 1-5 v/o of composite

Properties

- Strength and toughness
  - 3000x tougher than constituents
- Opalescence due to periodicity
  - Mother-of-pearl nacre

G Mayer. *Science 310*, **2005**, 1144.
Song *et al*. *Biomaterials 24*, **2003**, 3623.
Rubner *et al*. *Nature 423*, **2003**, 925.

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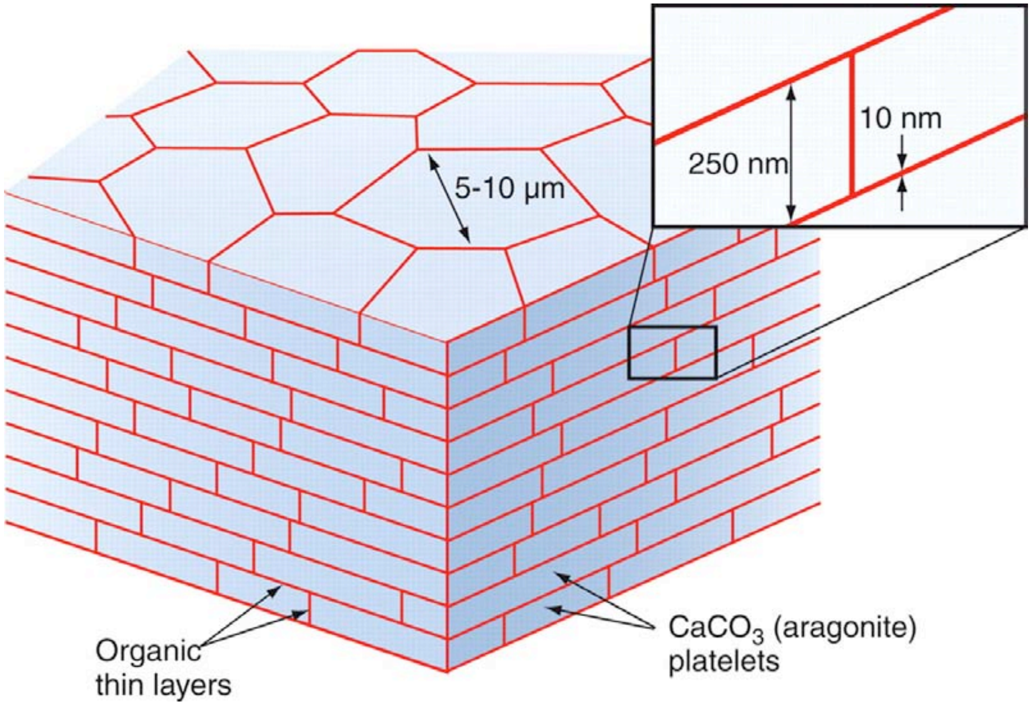

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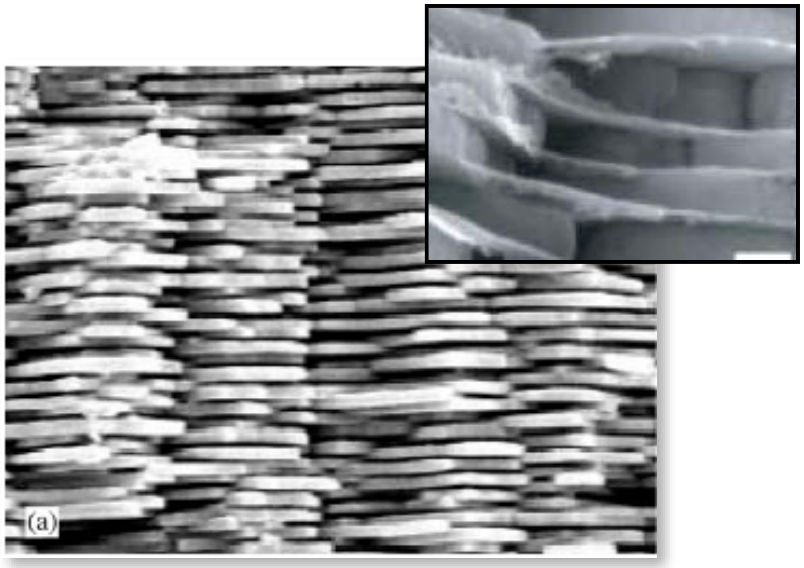
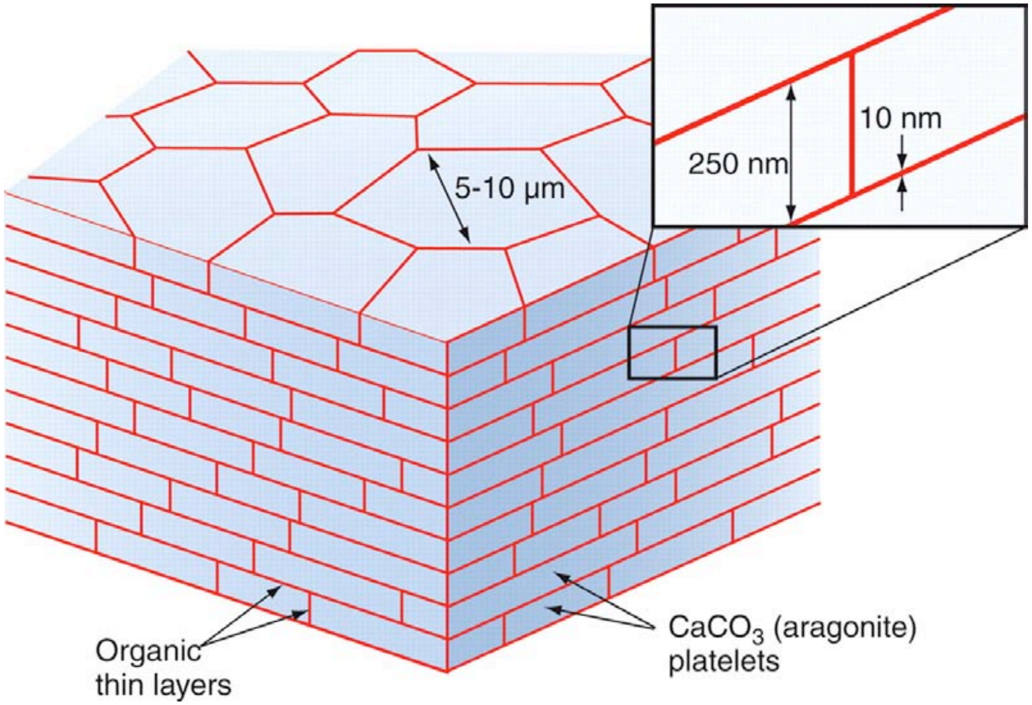
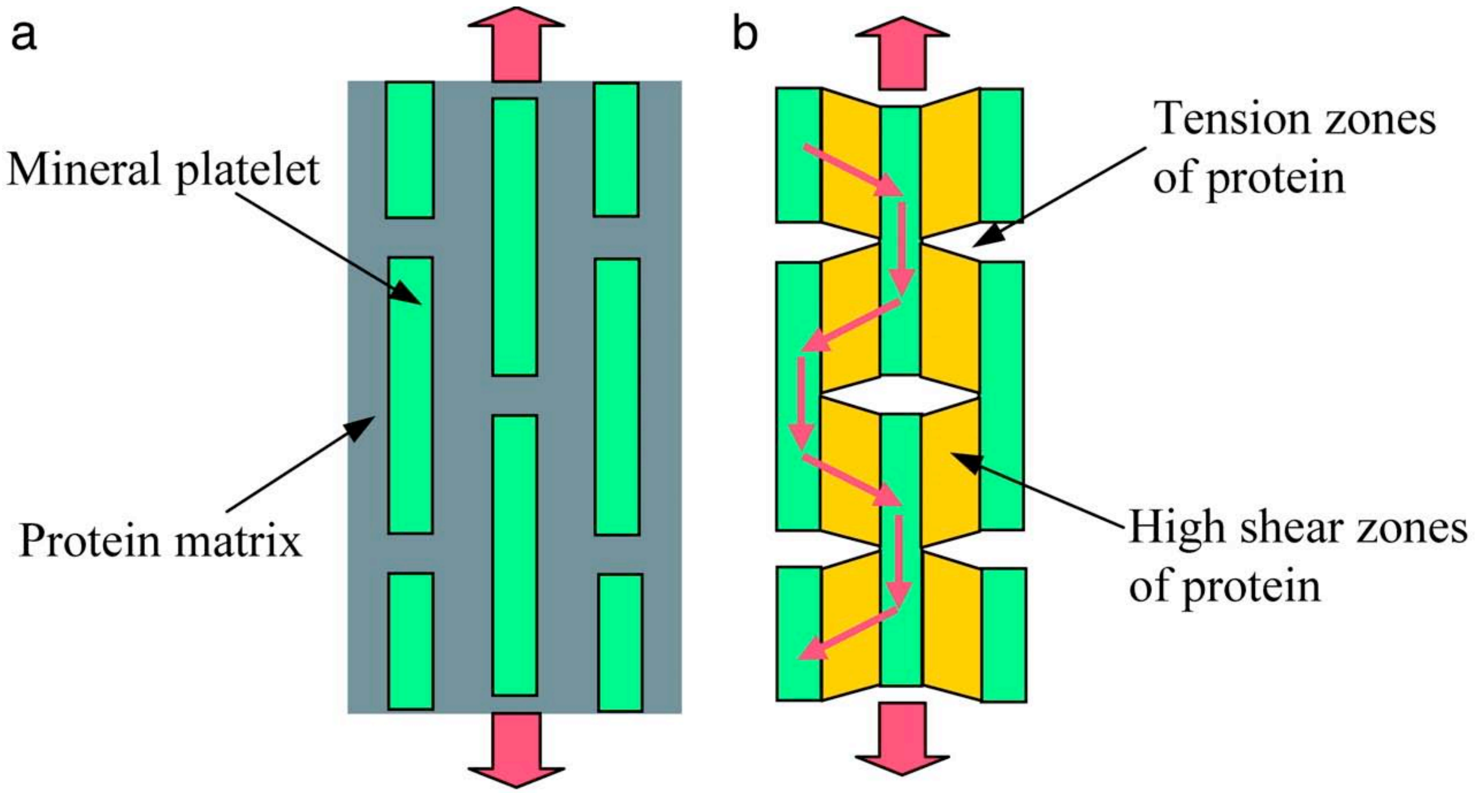




G Mayer. *Science 310*, **2005**, 1144.
Song *et al*. *Biomaterials 24*, **2003**, 3623.

Why is nacre so tough?



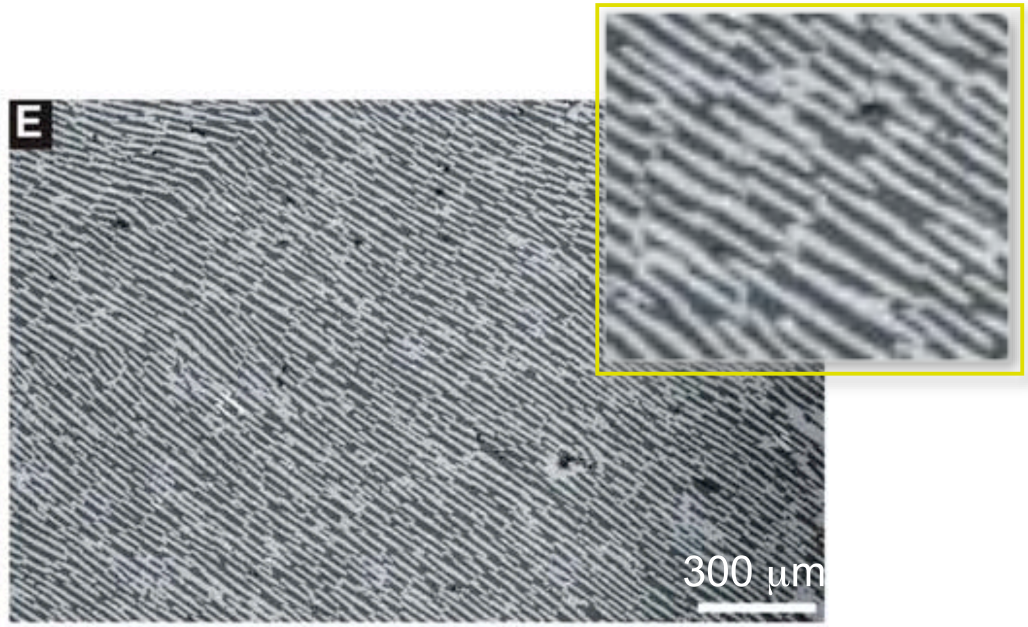
Nacre is a natural laminated nanocomposite

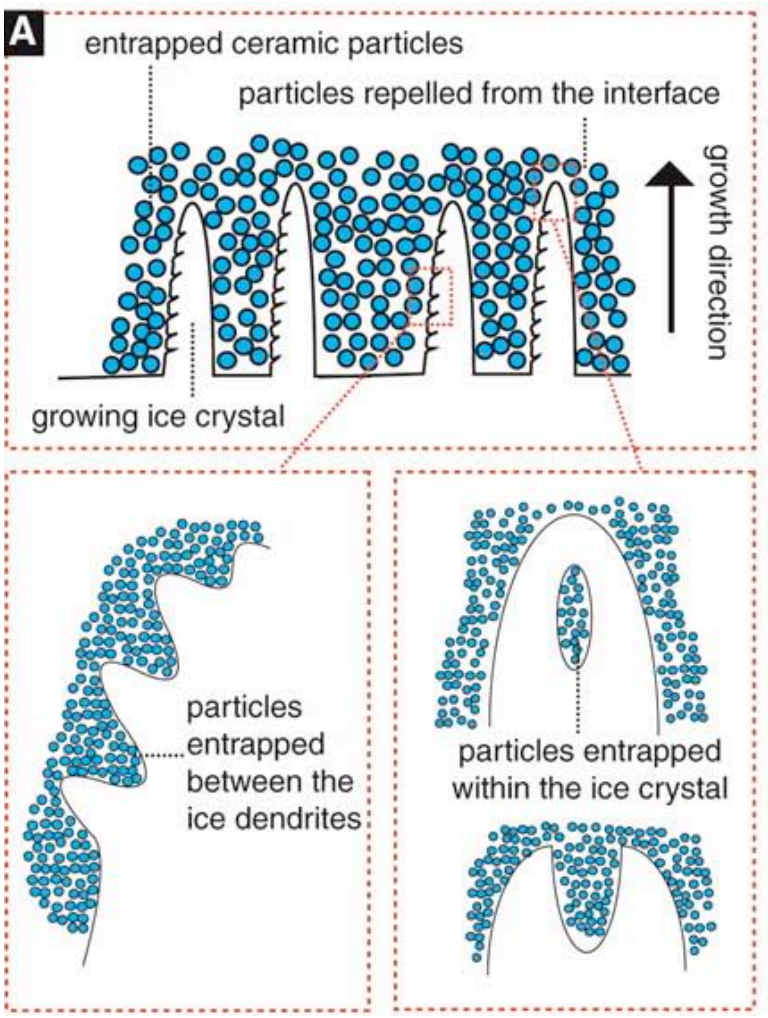
Organic phase aids in crack stabilization and distribution of load

Gao *et al*. *PNAS 100*, **2003**, 5597.

Mimicking Nacre via Directed Colloidal Assembly

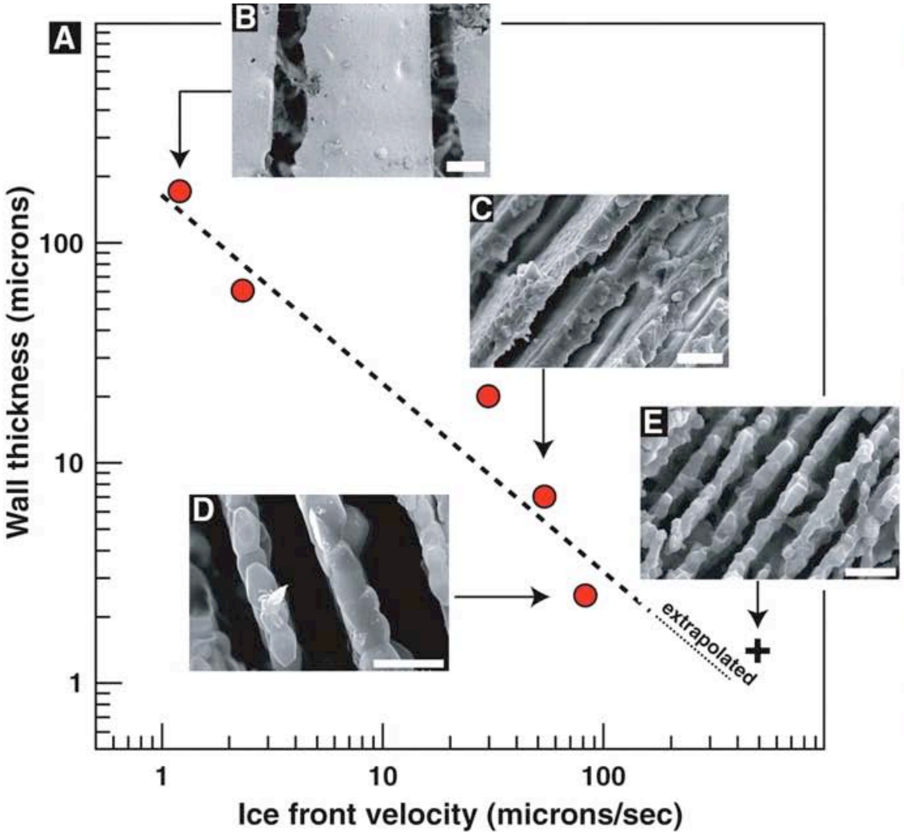
- Directional freezing of colloidal suspension with controlled solidification rates
- Particles concentrate between growing ice crystals
- Sublimation of ice by freeze drying

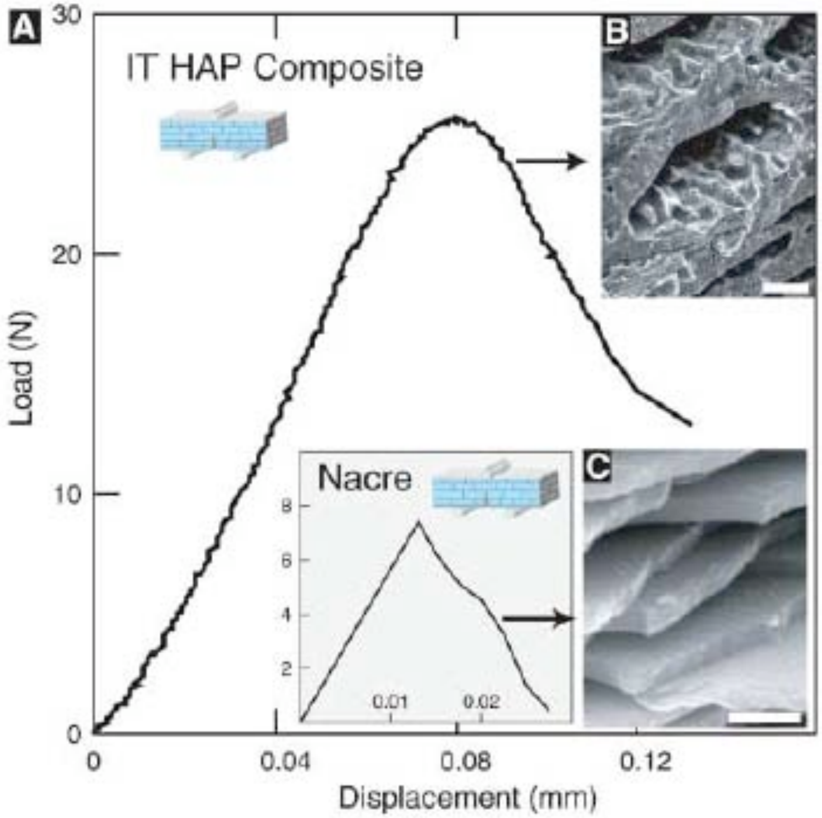




Deville *et al*. *Science 311*, **2006**, 515.

Mimicking Nacre via Directed Colloidal Assembly

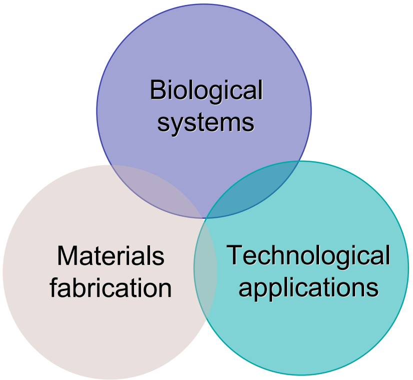




- Platelet thickness controlled by freezing rate
- Load-displacement characteristics similar to that of nacre

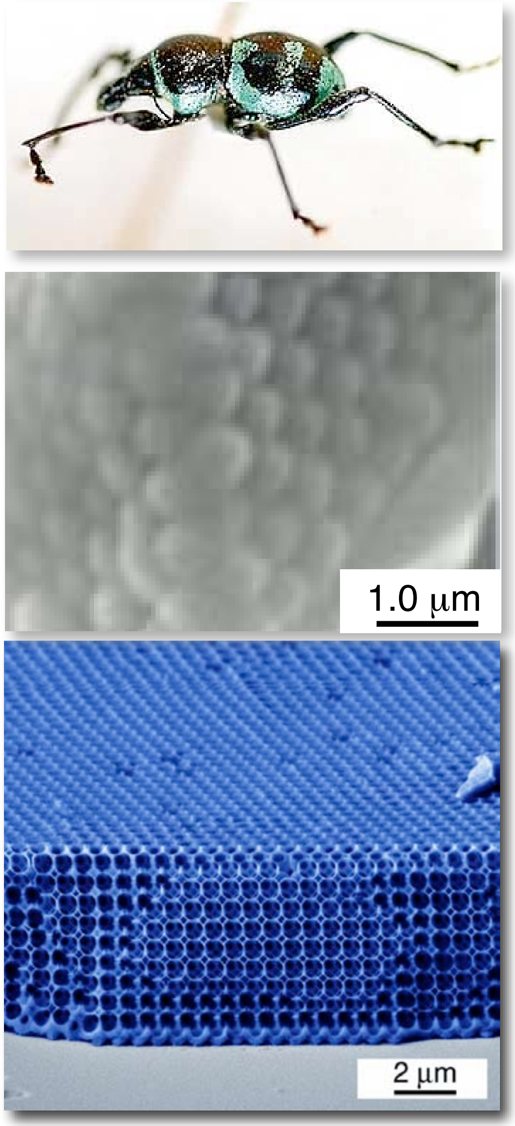
Deville *et al*. *Science 311*, **2006**, 515.

Bio-inspired Materials - Learning from nature, impacting technology

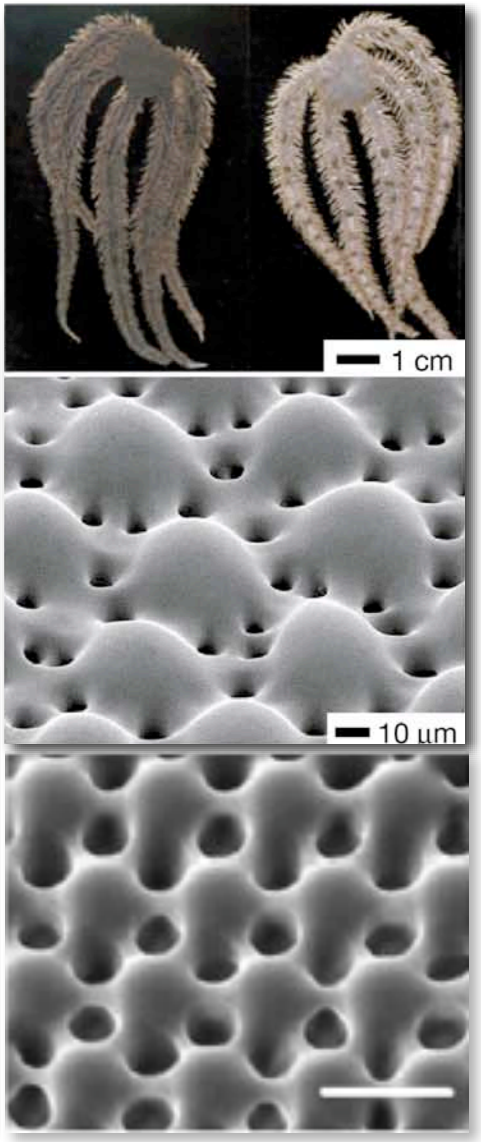

Biological systems

Materials fabrication

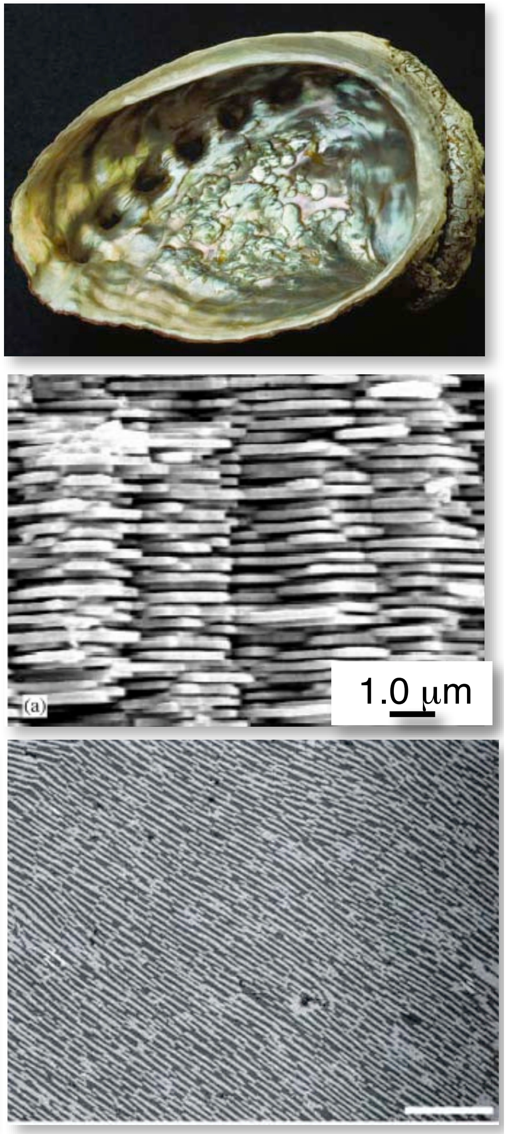
Technological applications



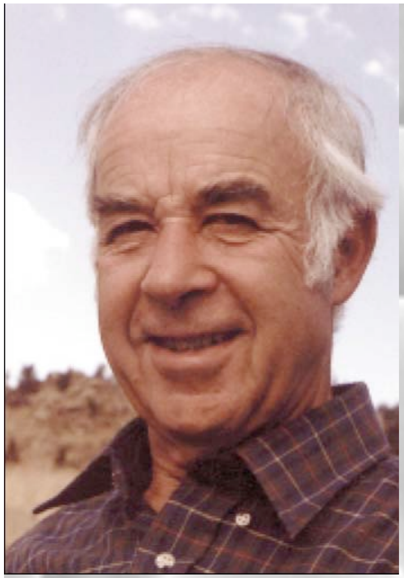
Photonic crystals



Tunable microlens arrays



Nanocomposites



Dedicated to

Hans Thurnauer and his family

for their generous support of my research

MRL
THE FREDERICK SEITZ MATERIALS RESEARCH LABORATORY

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