

# Photonic Crystal-Based Optical Devices

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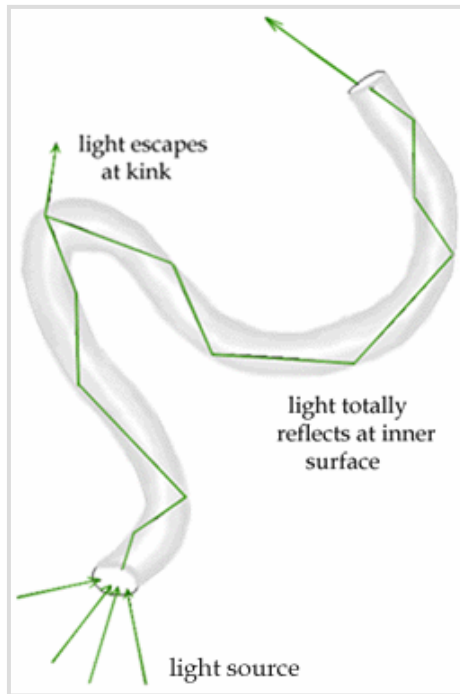
Department of Materials Science and Engineering,  
Frederick Seitz Materials Research Laboratory and  
Beckman Institute for Advanced Science and Engineering

University of Illinois at Urbana-Champaign, Urbana, IL

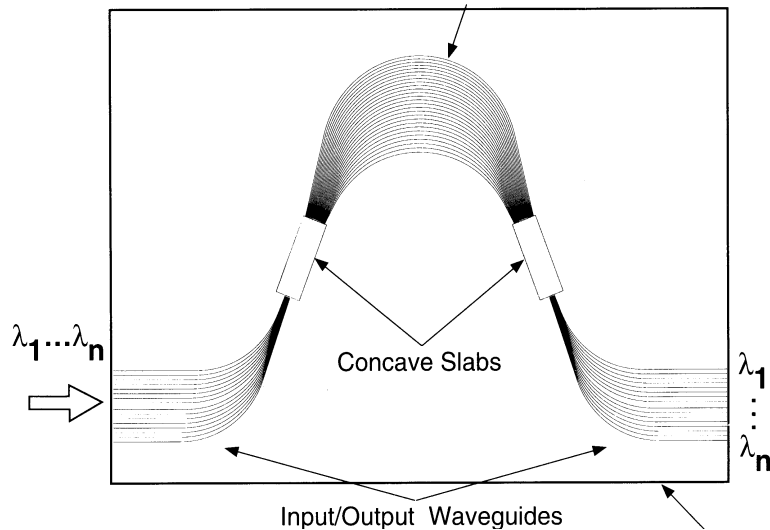
June 2004

Funding: NSF, DOE, ARO – MURI, Beckman Foundation, 3M

# Photonics Today: Interesting, but Exciting?

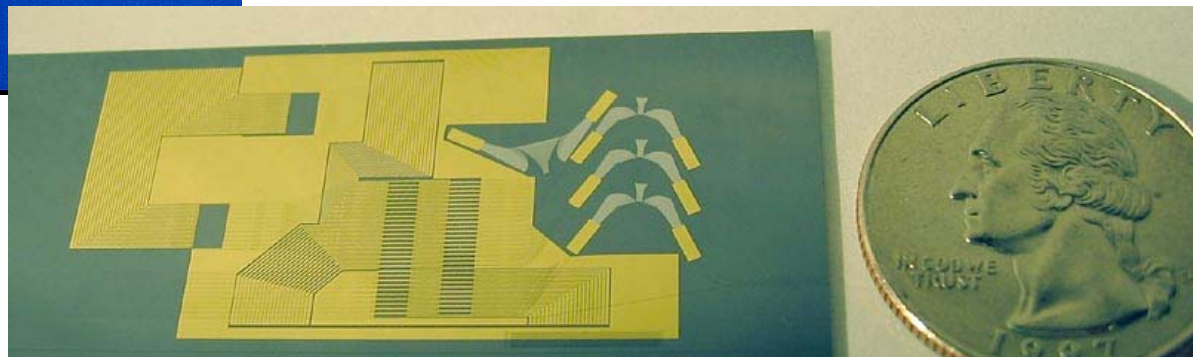
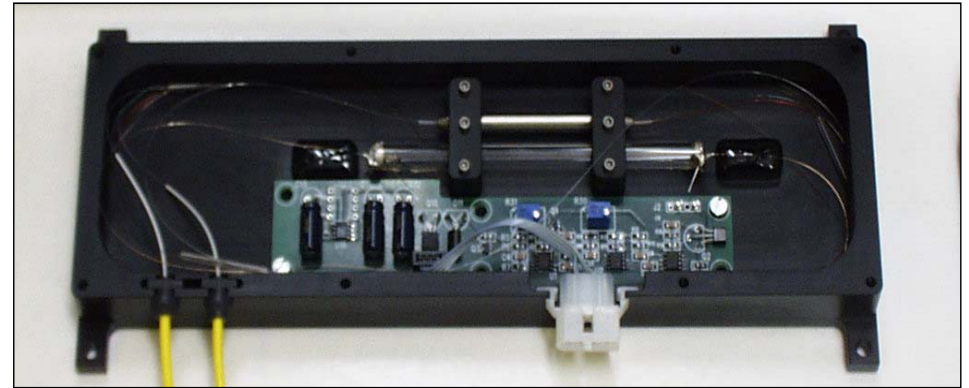
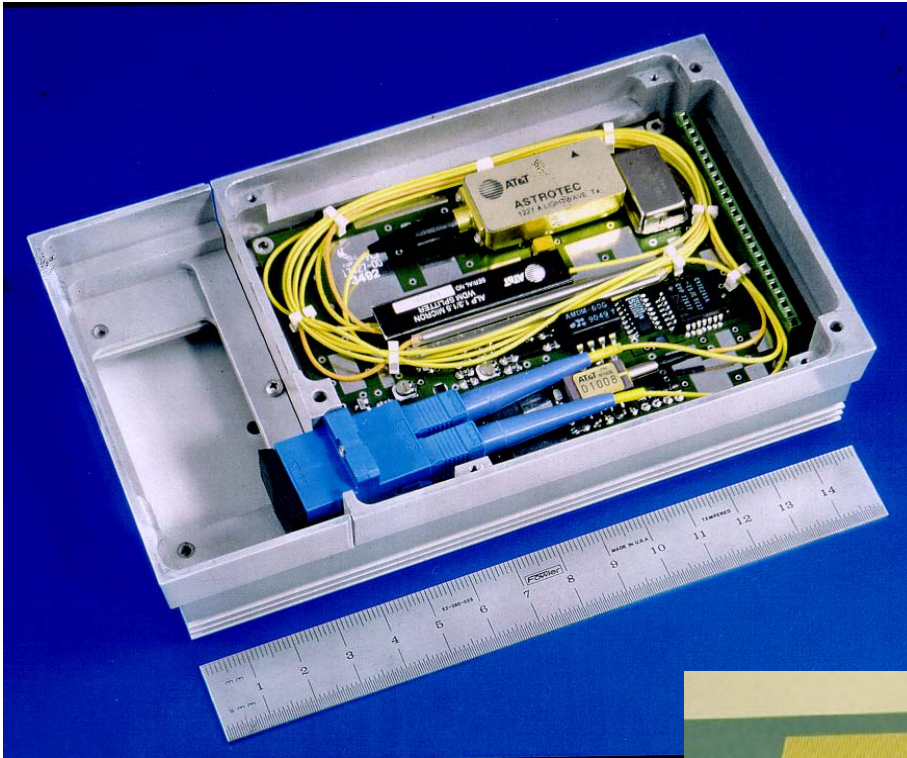


Arrayed Waveguides



It's hard to get excited about 2-D

## Current 2-D Optical Network Devices

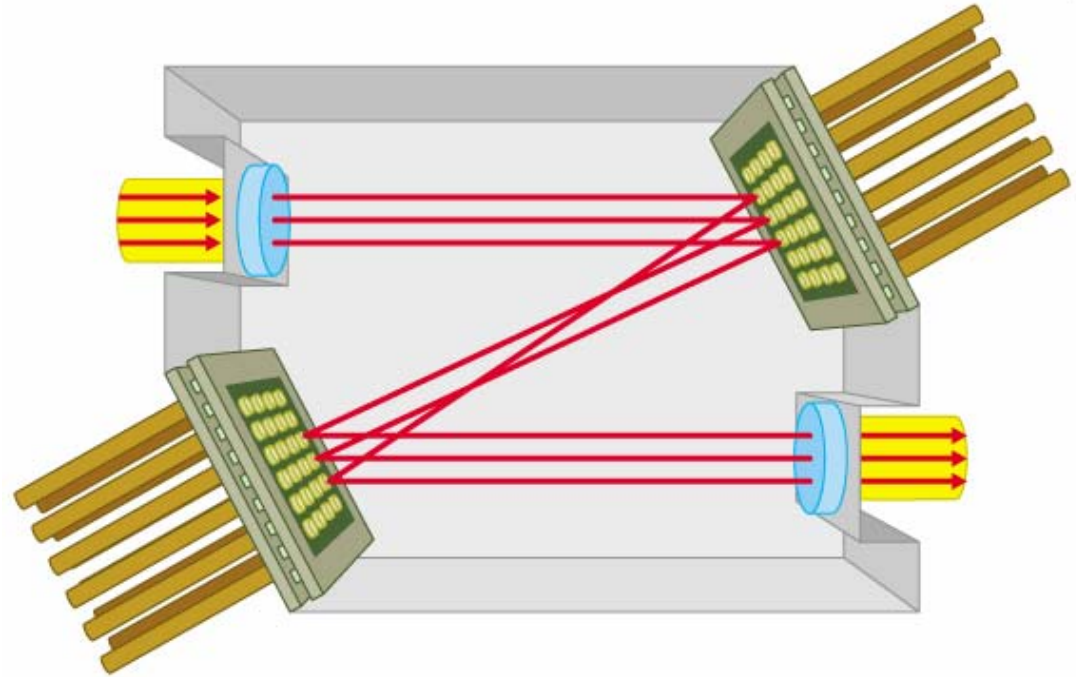
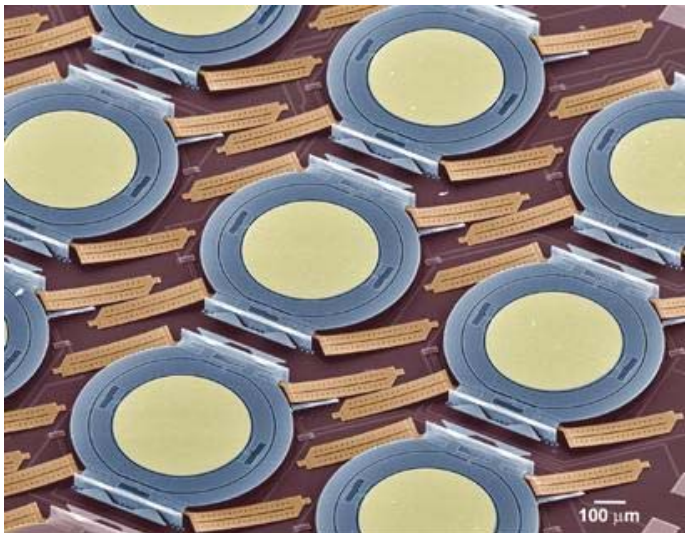
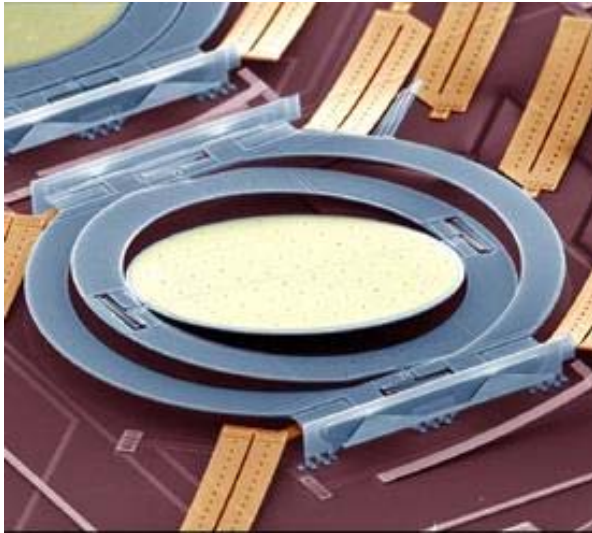


“Innovate to manipulate photons in a flexible, compact way.”

## Lucent's (canceled) WaveStar™ LambdaRouter

2.5 dimensional?

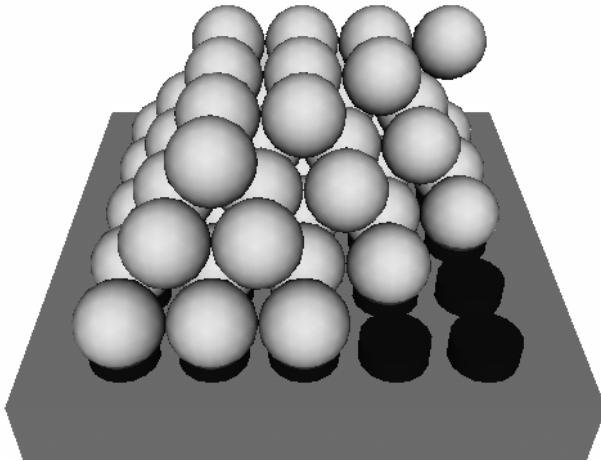
Close-up of single mirror.



**Array of microscopic mirrors, each able to tilt in various directions, to steer light.**

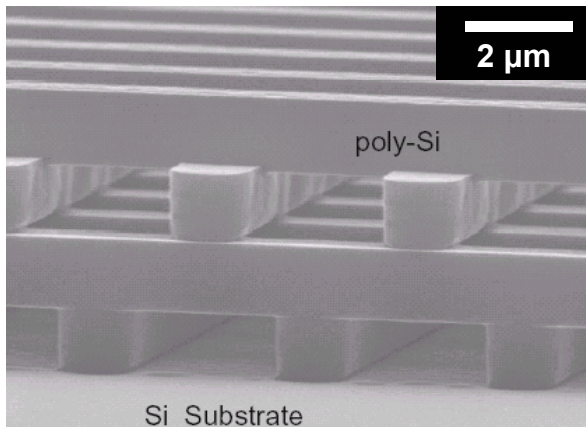
## So, how to get to 3-D?

### Colloidal self-assembly



Ref: many, many groups!

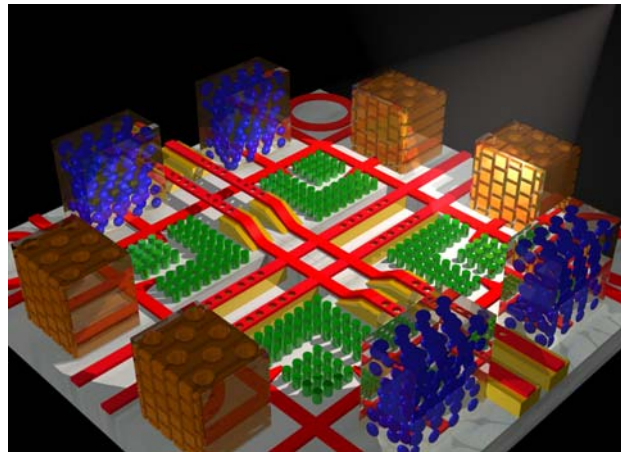
### Lithography



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

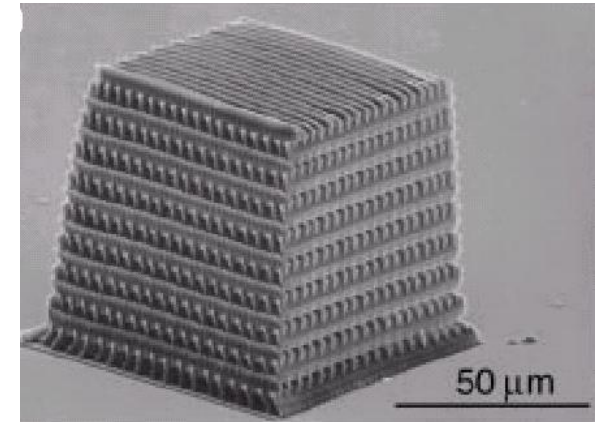
### 3-D Applications

- Low-loss waveguides
- Optical cavities
- Zero-threshold microlasers
- Light-emitting diodes
- All-optical transistors
- Improved photoreactors
- Tunable filters



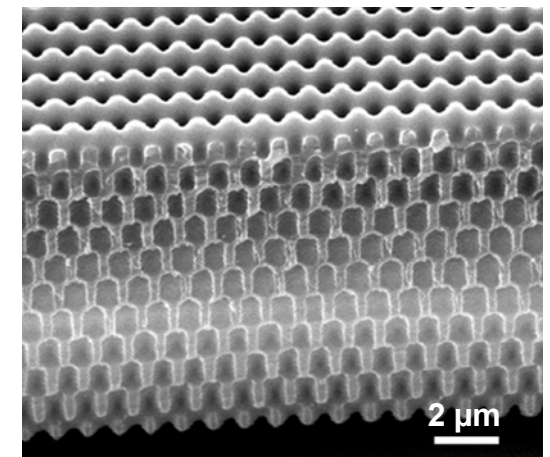
Prof. John Joannopoulos  
<http://ab-initio.mit.edu/photons/index.html>

### Multiphoton polymerization



Cumpston et al. *Nature* **1999**, 398, 51.

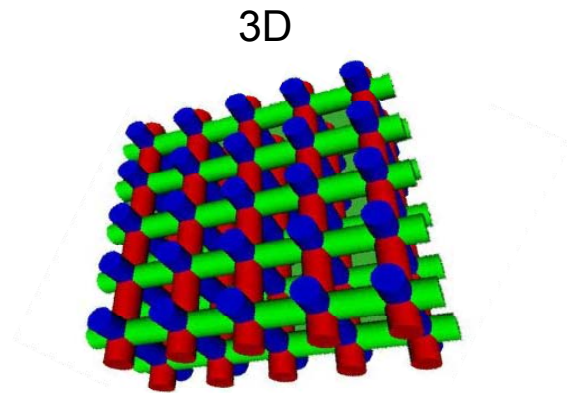
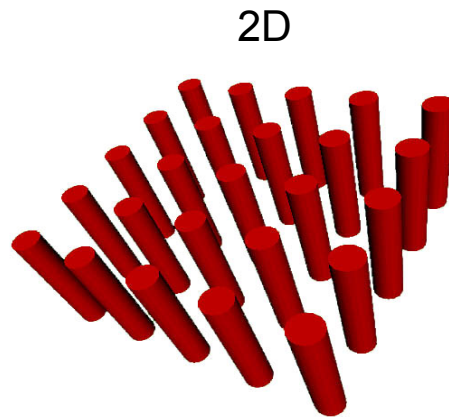
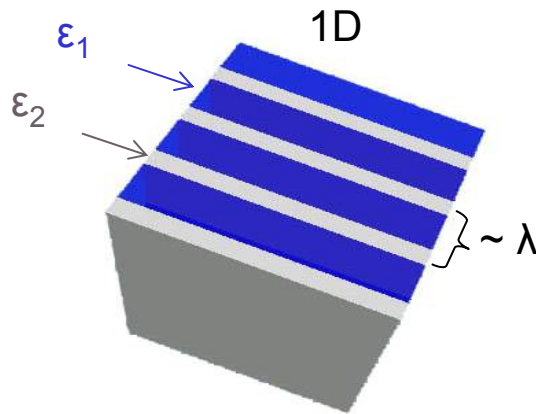
### 4-beam holography



Turberfield A. J., et al., *Nature* 2000  
Wiltzius, P. et al., *Chem. Mater.* **2002**

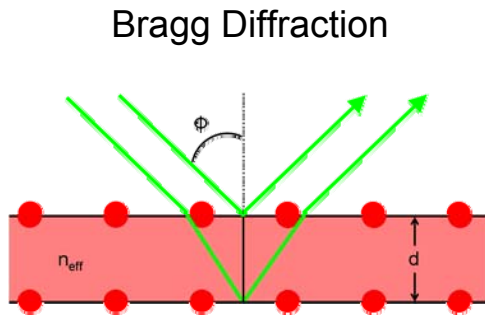
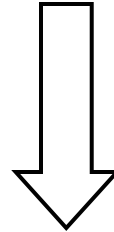
# Photonic Crystal Primer

Requirements for a Photonic Crystal: 1) Periodicity in the dielectric constant; 2) Domain sizes  $\sim \lambda$



Figures modified from: <http://www.elec.gla.ac.uk/groups/opto/photoniccrystal/Welcome.html>

## Properties of a Photonic Crystal:

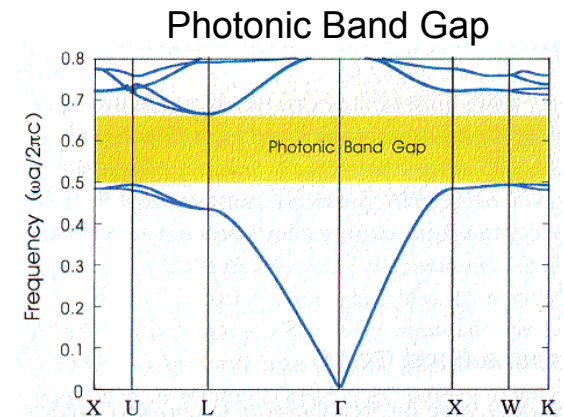


$$m\lambda = 2d (n_{\text{eff}}^2 - \sin^2 \Phi)^{1/2}$$

**Light Modulation**

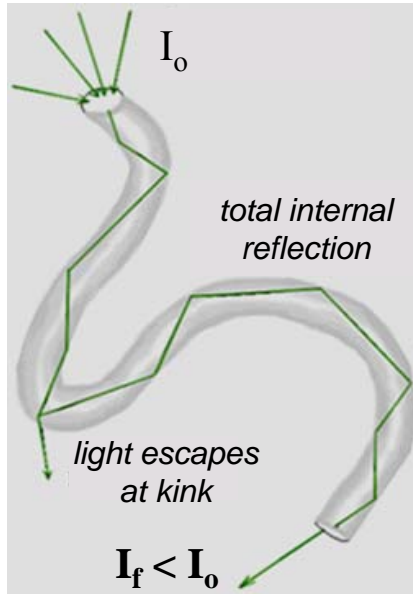
weak strong

↑ index contrast  
→ appropriate geometry



# Example PBG Application: Waveguiding

## Current Principle: Total Internal Reflection



Inherent losses typically  $> \sim 0.2$  db / km



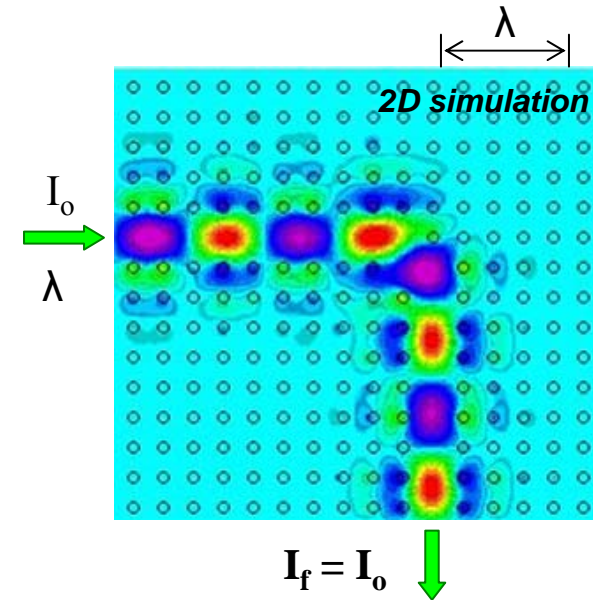
Cannot tolerate bend radii  $< 5$  cm



**Require periodic amplification of signal**

**Not suitable for small bend radii**

## PBG-Based: Frequency Confinement



Defects create states in the bandgap



Forbidden frequencies are confined within defects



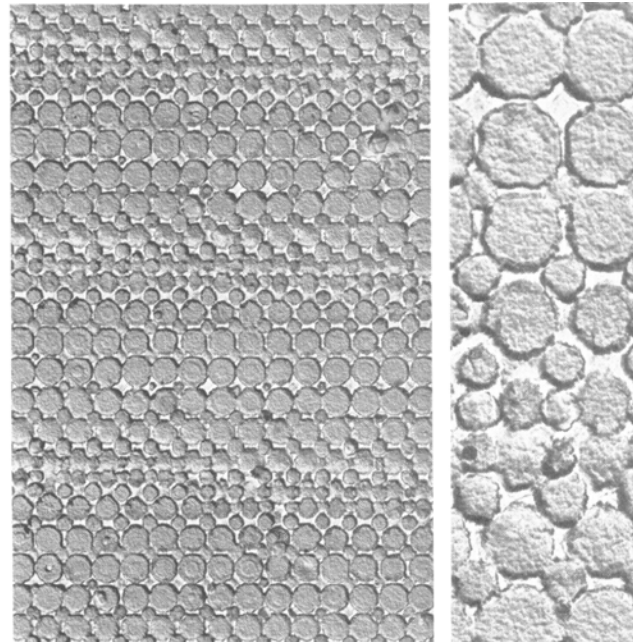
**100% transmission around bend radii  $\sim \lambda$ !**

## 3-D Self-Assembly: Colloidal Crystals (Opals)

Opal

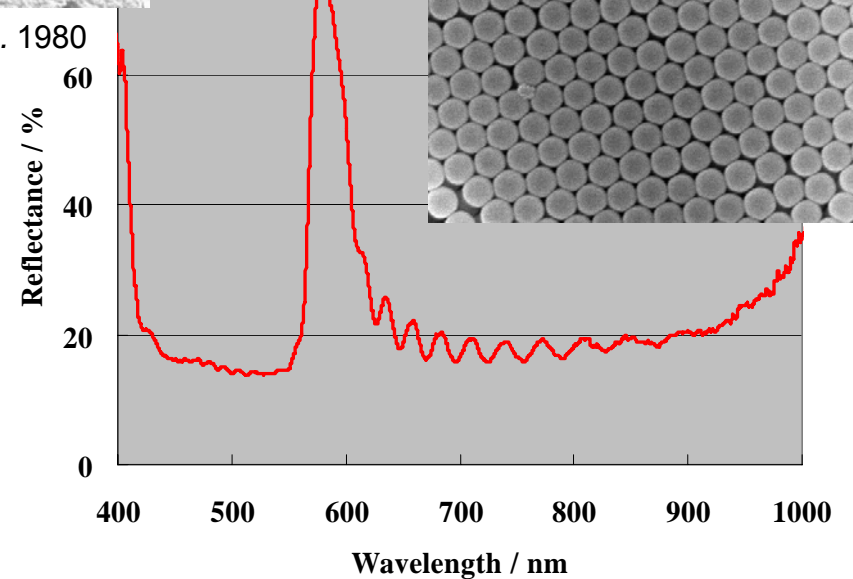
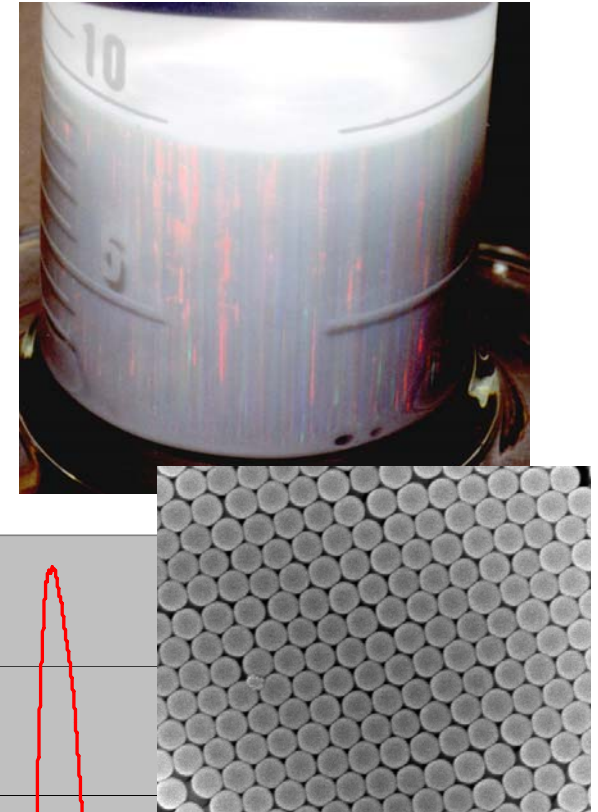


SEM of opal cross-section



J.V. Sanders, *Phil. Mag. A.* 1980

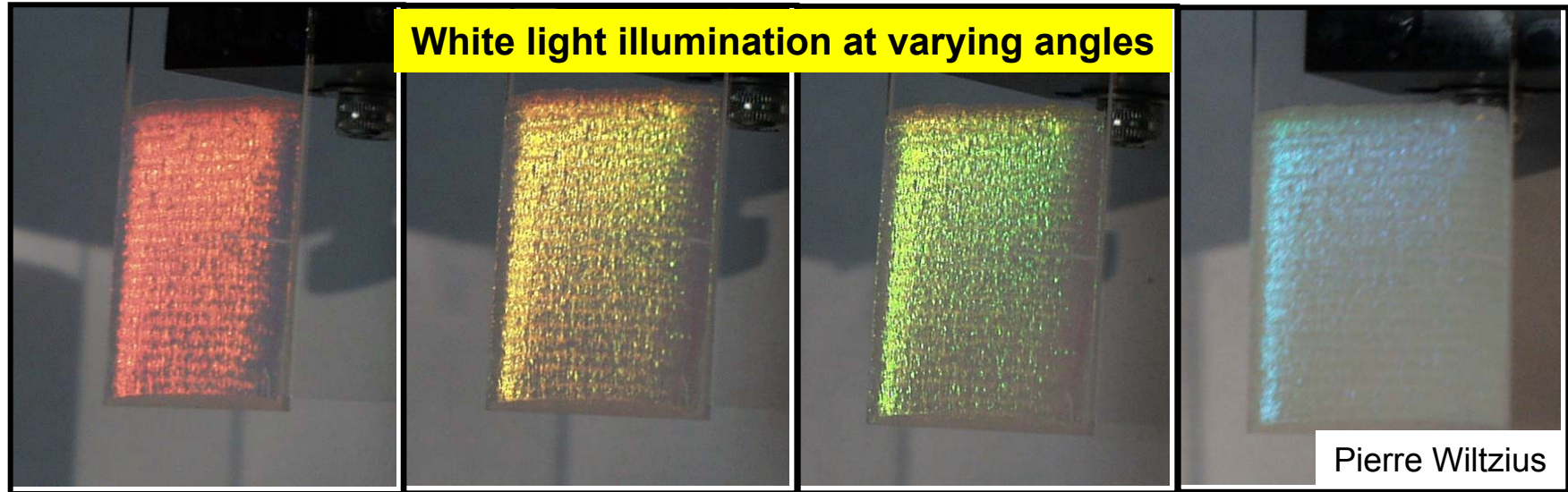
synthetic "opal"  
formed from ~500 nm silica spheres



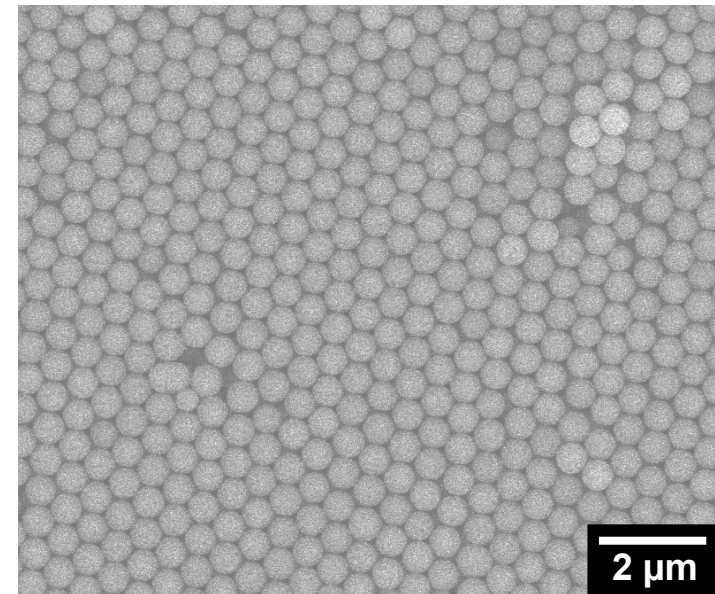
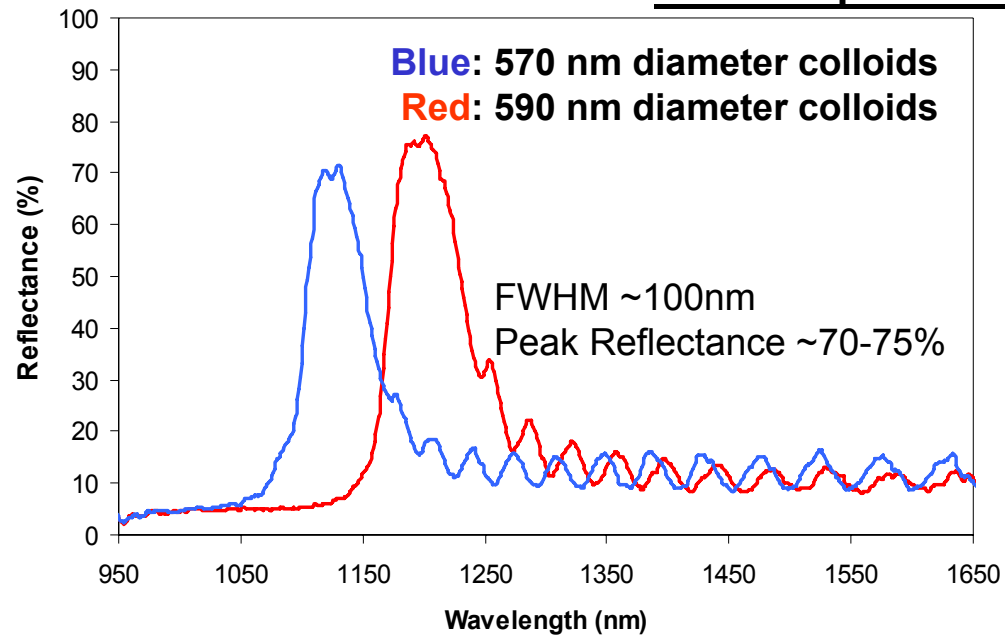
- Natural Opals consist of periodically arranged silica spheres in a matrix
- The colors of an opals are due to Bragg diffraction of light by planes of silica spheres
- Synthetic Opals are formed by careful assembly of silica spheres from solution



# Colloidal Crystals – Diffraction Yields Color



## Effect of particle diameter



## Defects in Colloidal Crystals?

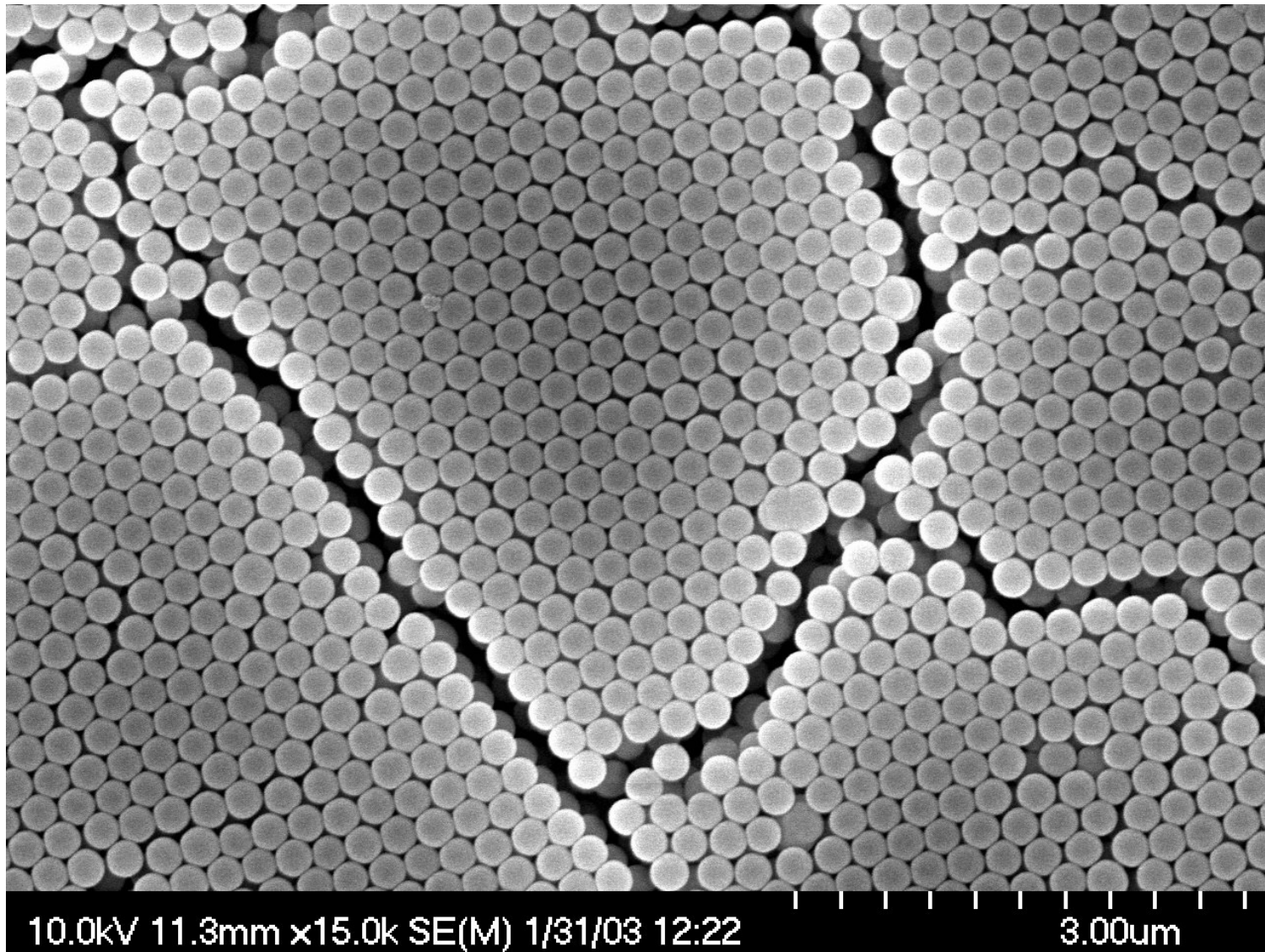
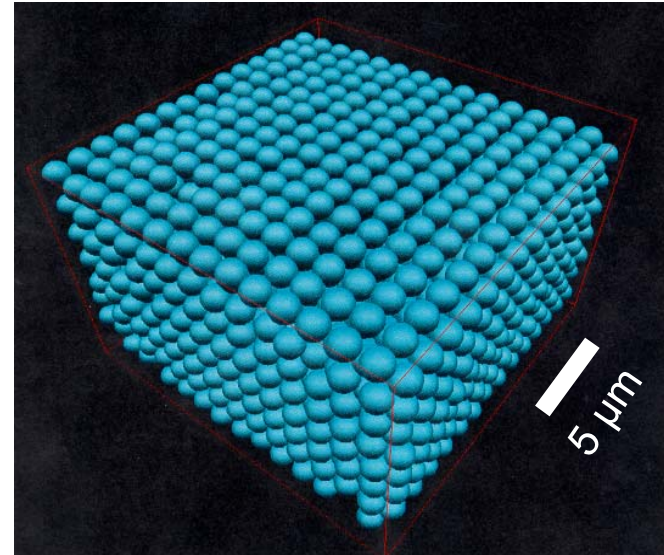
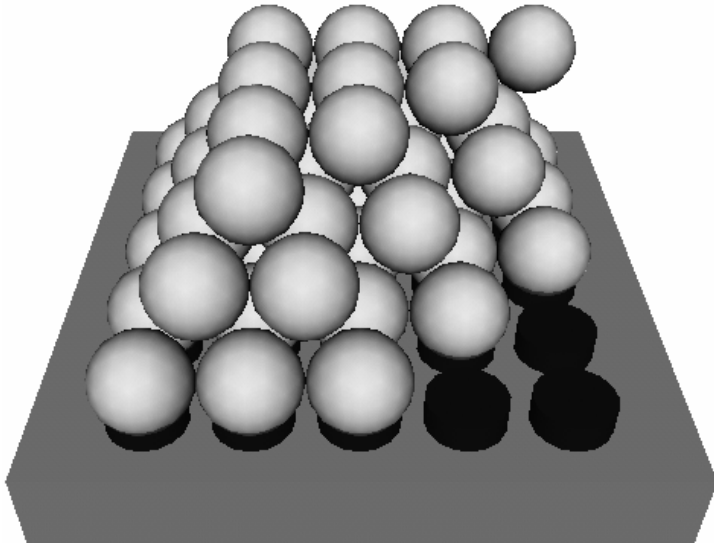
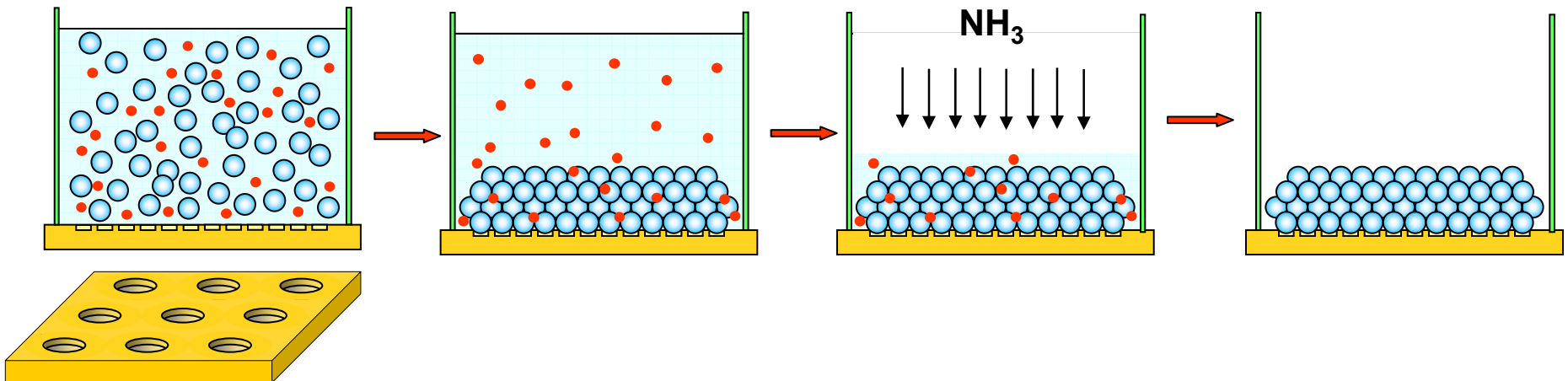


Image courtesy of Satoshi Takeda, Pierre Wiltzius

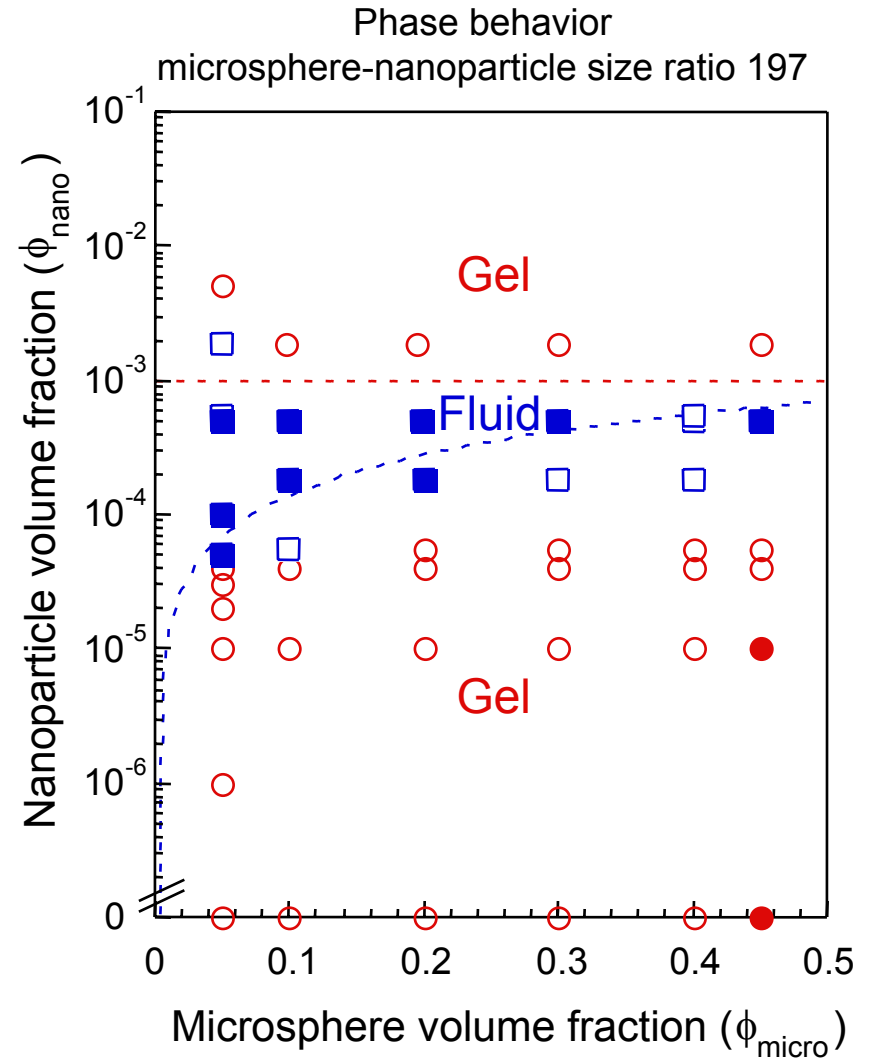
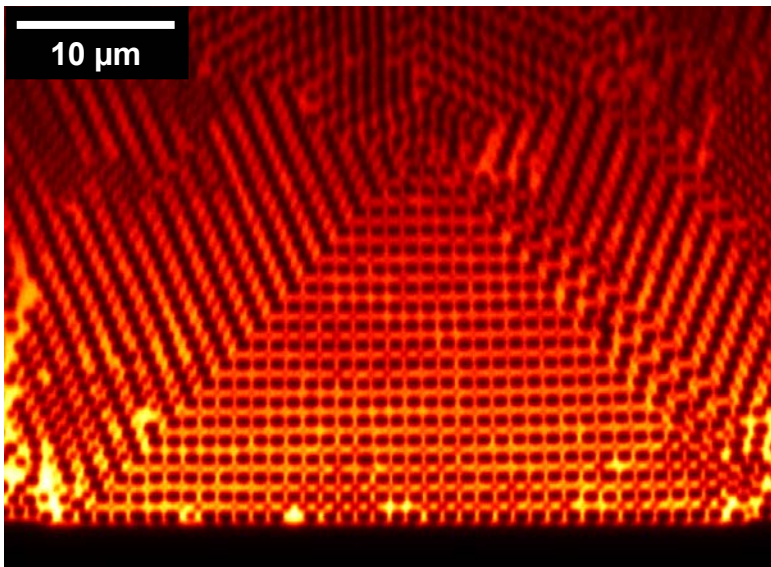
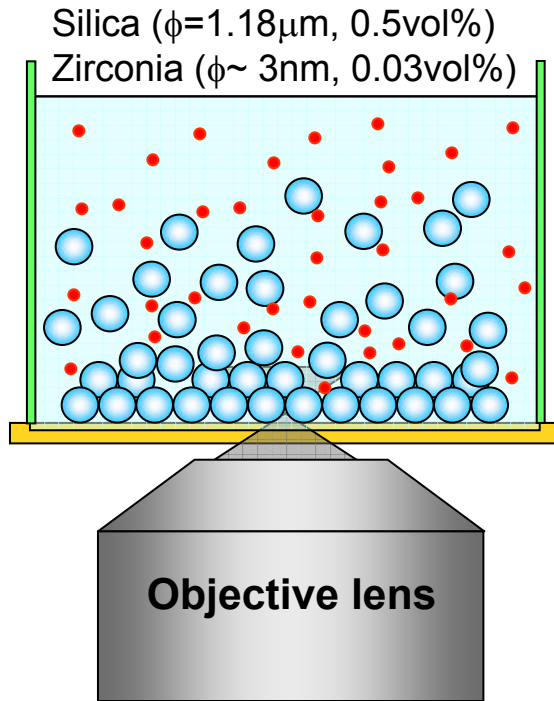


A. van Blaaderen, R. Ruel, P. Wiltzius, *Nature* **1997**, 385, 321.

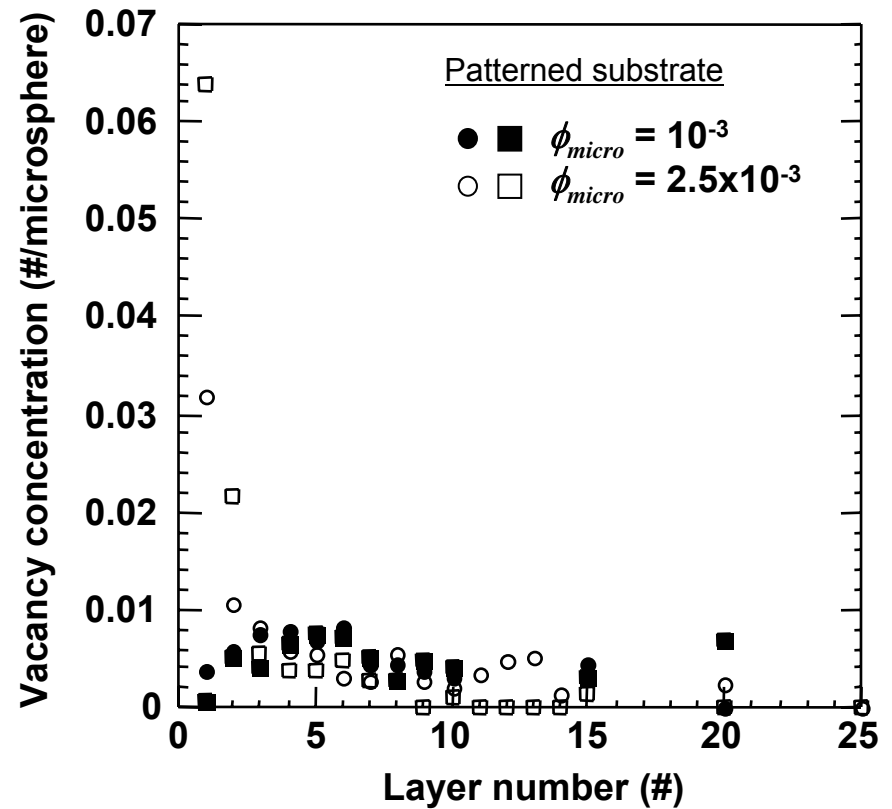
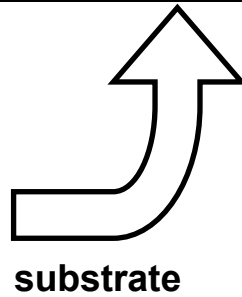
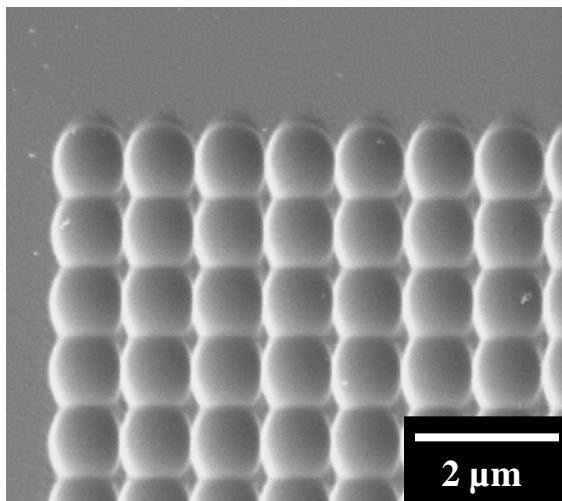
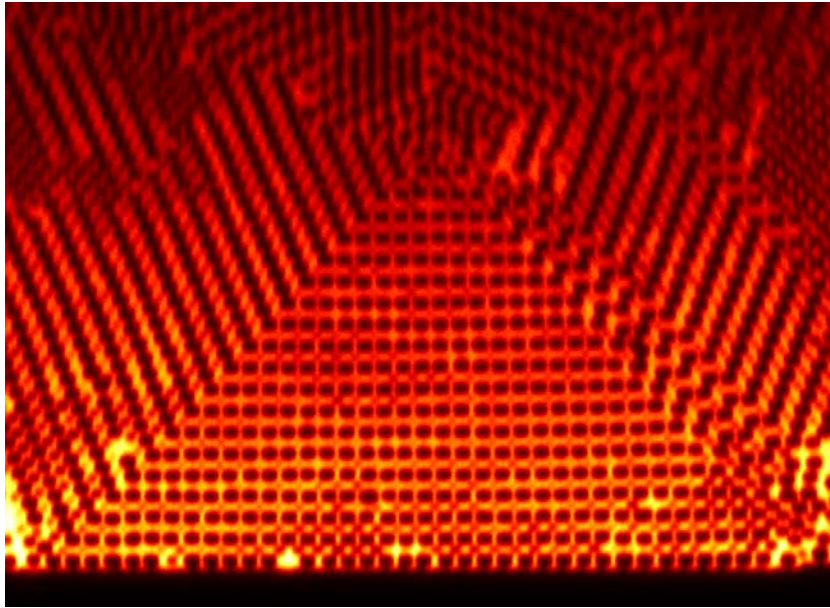
**Colloidal epitaxy → low defect density & defined orientation with respect to the substrate**



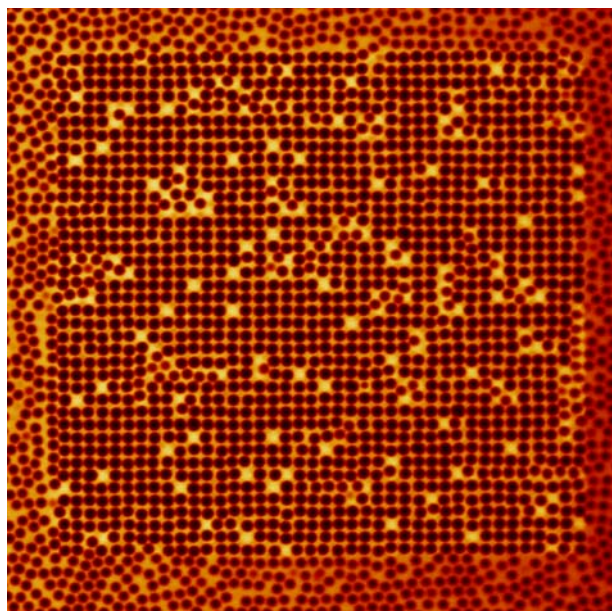
# Gravity Driven Nanoparticle Mediated Colloidal Epitaxy



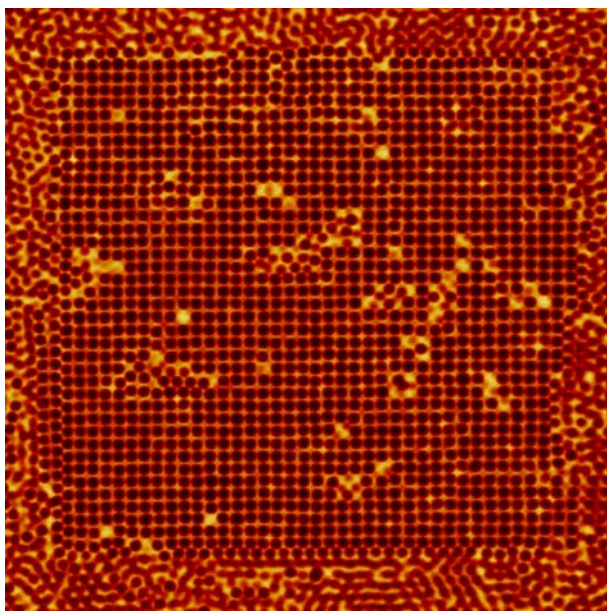
## Vacancy concentration ~1 per 200 particles



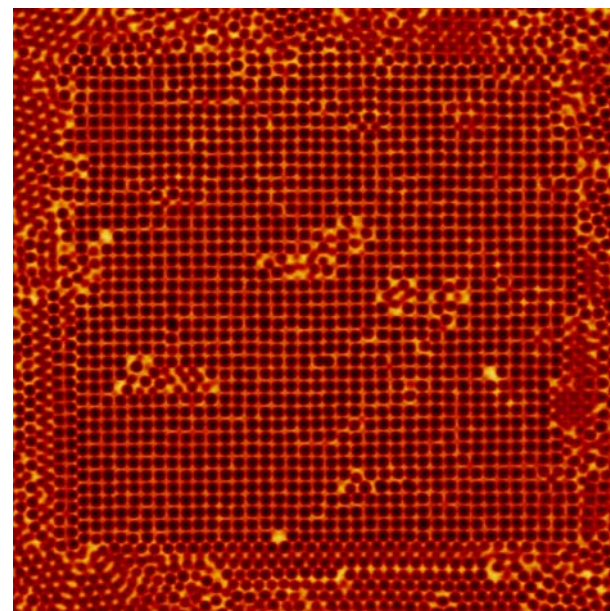
**1<sup>st</sup> layer (40x40)**



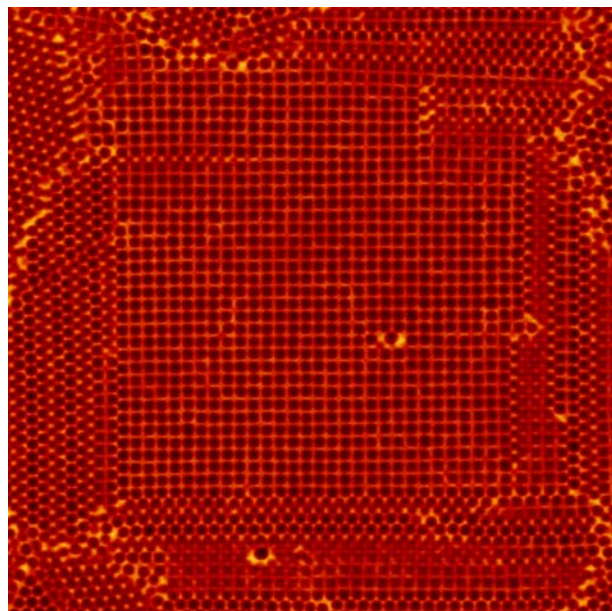
**2<sup>nd</sup> layer (39x39)**



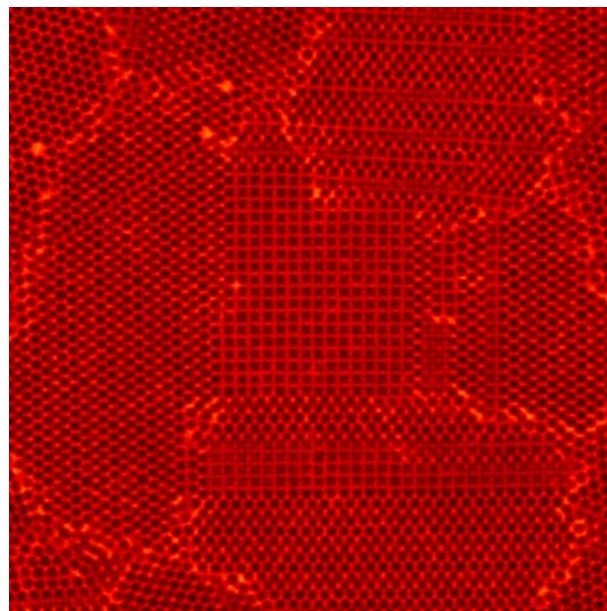
**3<sup>rd</sup> layer**



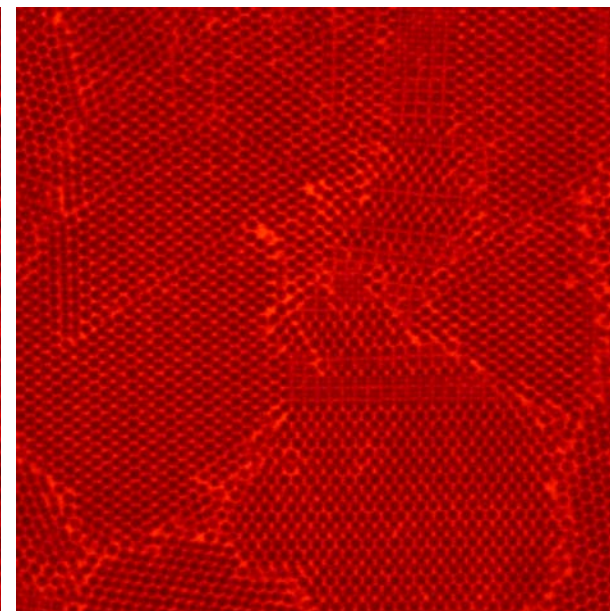
**10<sup>th</sup> layer**

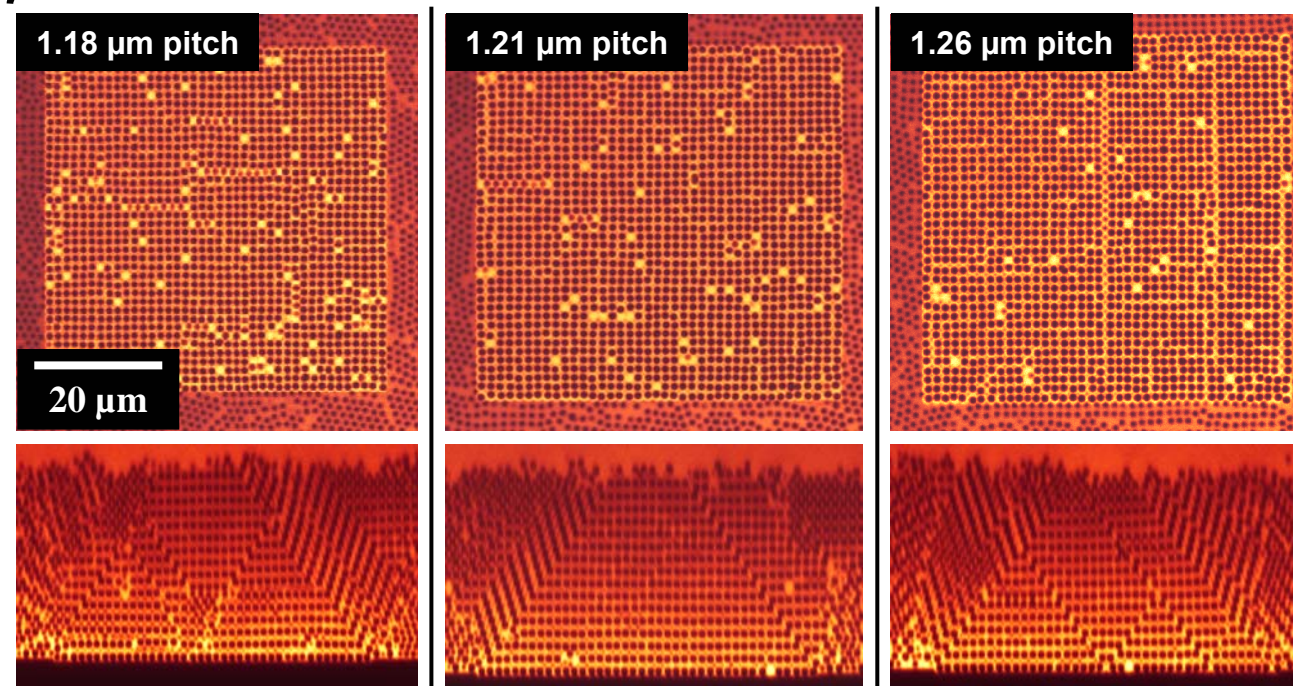
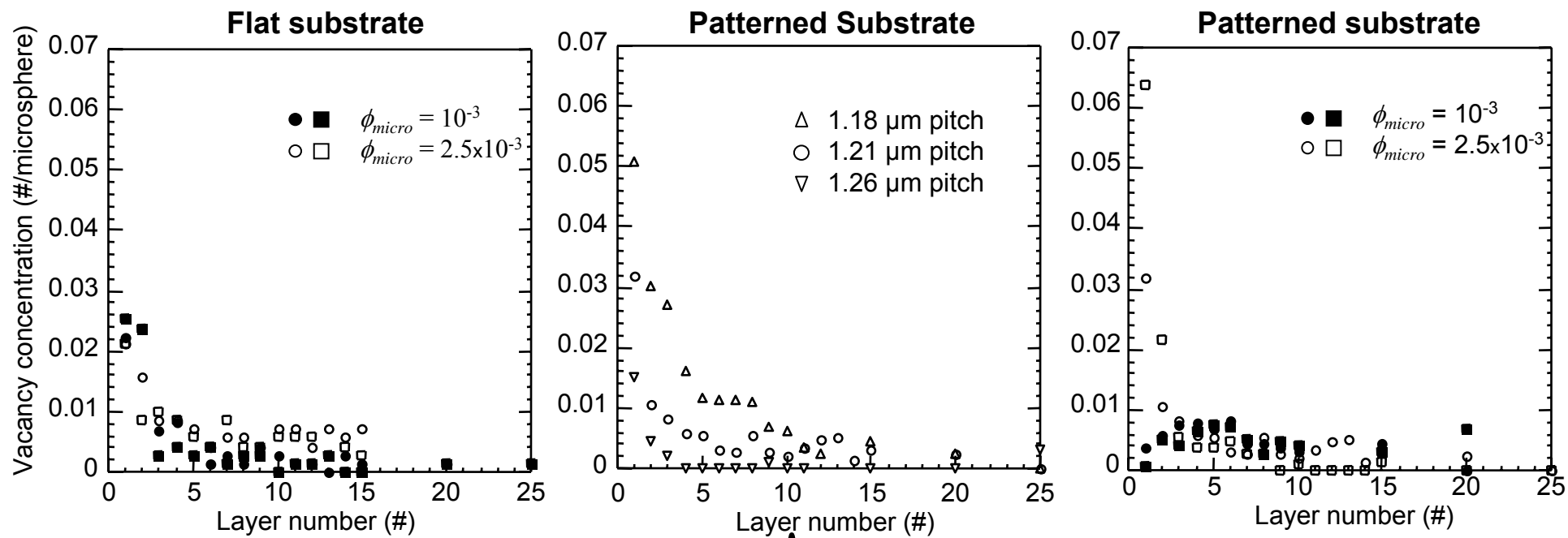


**25<sup>th</sup> layer**



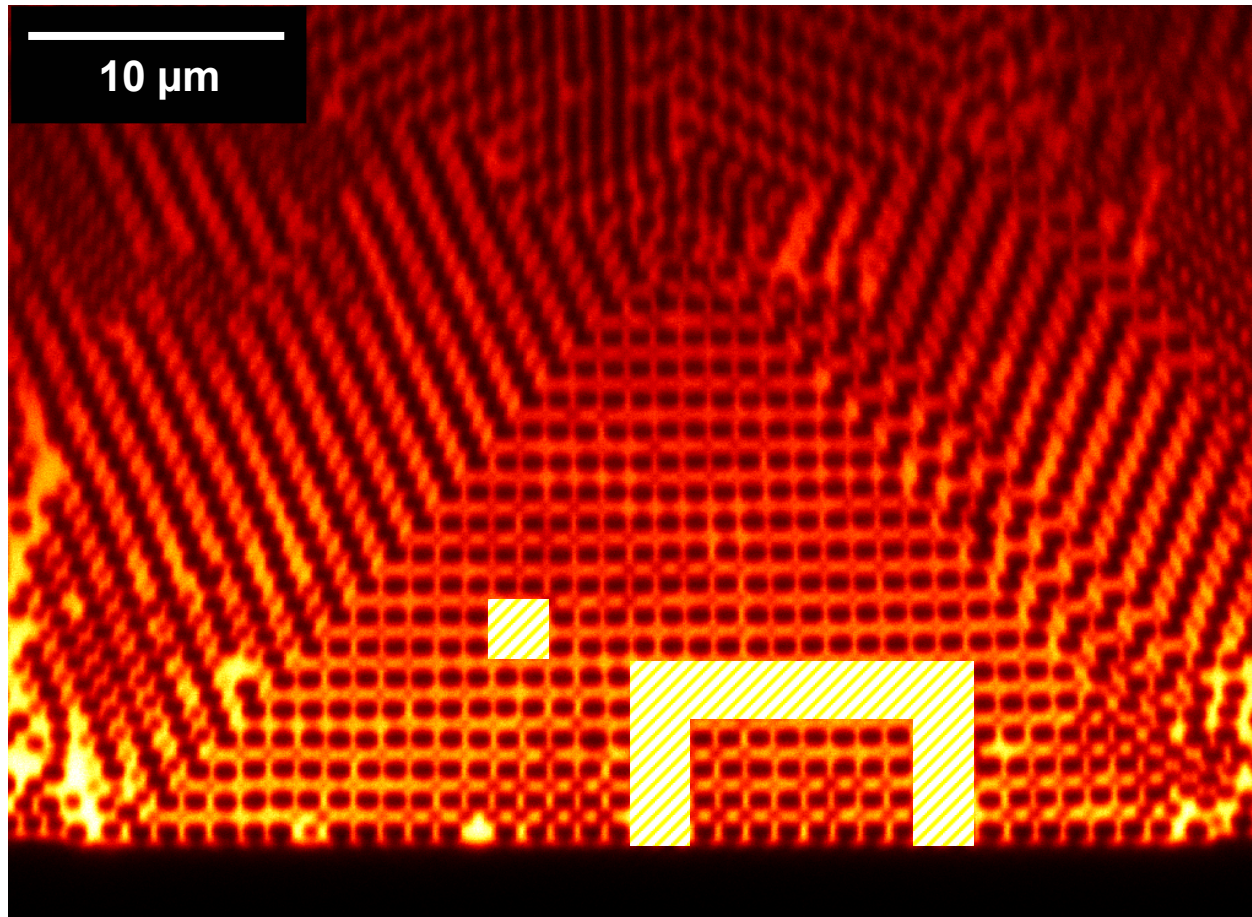
**39<sup>th</sup> layer (2x2)**





## But, defined defects in colloidal crystals?

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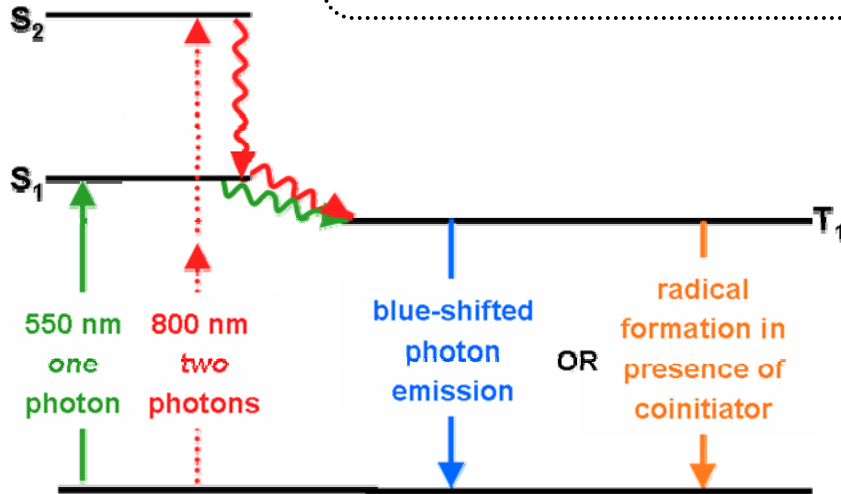


Optical cavities & Waveguides?



# Two-Photon Polymerization (TPP)

**Motivation:** Need method for generation of embedded 3D defect features in self-assembled photonic crystals



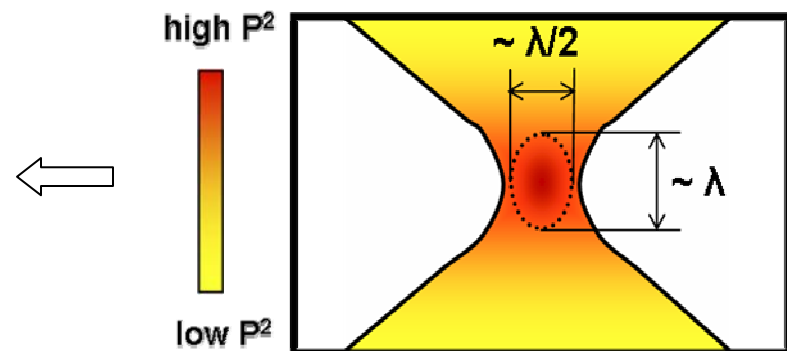
**Absorption Probability**  $\propto P^n$

$P$  = Laser intensity

$n$  = Number of photons involved in the excitation process



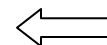
**Multi-Photon Excitation Volume**  $\propto \lambda^3$



**Photopolymerization of high-resolution three-dimensional free-form structures**



S. Kawata, et al, *Nature* 2001, 412, 697.



## System Characteristics

### Beam:

Ti:Sapphire

Pulsed, mode-locked

$\lambda = 780 \text{ nm}$

$\tau \sim 100 \text{ fs}$

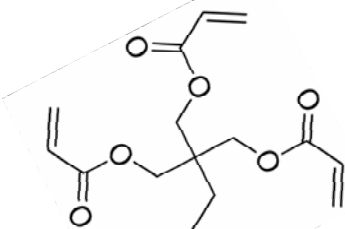
$F = 82 \text{ MHz}$

$P \sim 20\text{-}200 \text{ mW}$

N.A.  $\sim 1.32$

### Monomer:

Trimethylolpropane  
triacrylate (TMPTA)

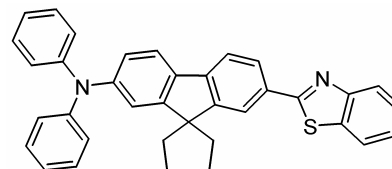


### Intitiator:

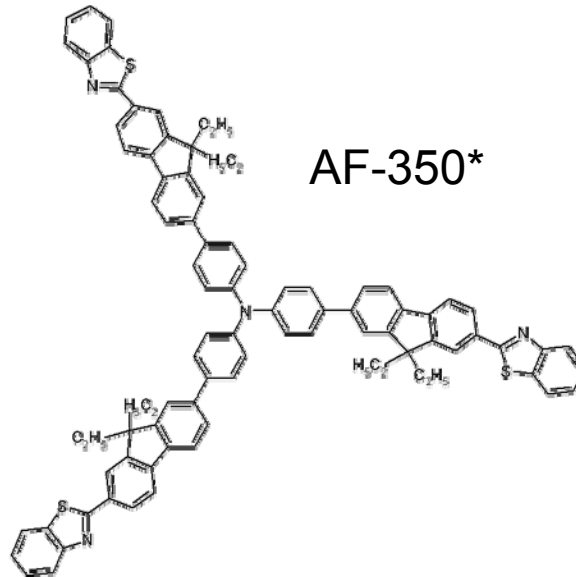
$\sigma \sim 9 \times 10^{-47} \text{ cm}^4 \text{ s} / \text{photon molecule}$

$\lambda_{\text{max}} \sim 780 \text{ nm}$  for two photon excitation

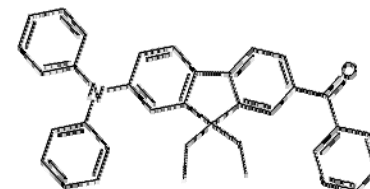
AF-240\*



AF-350\*

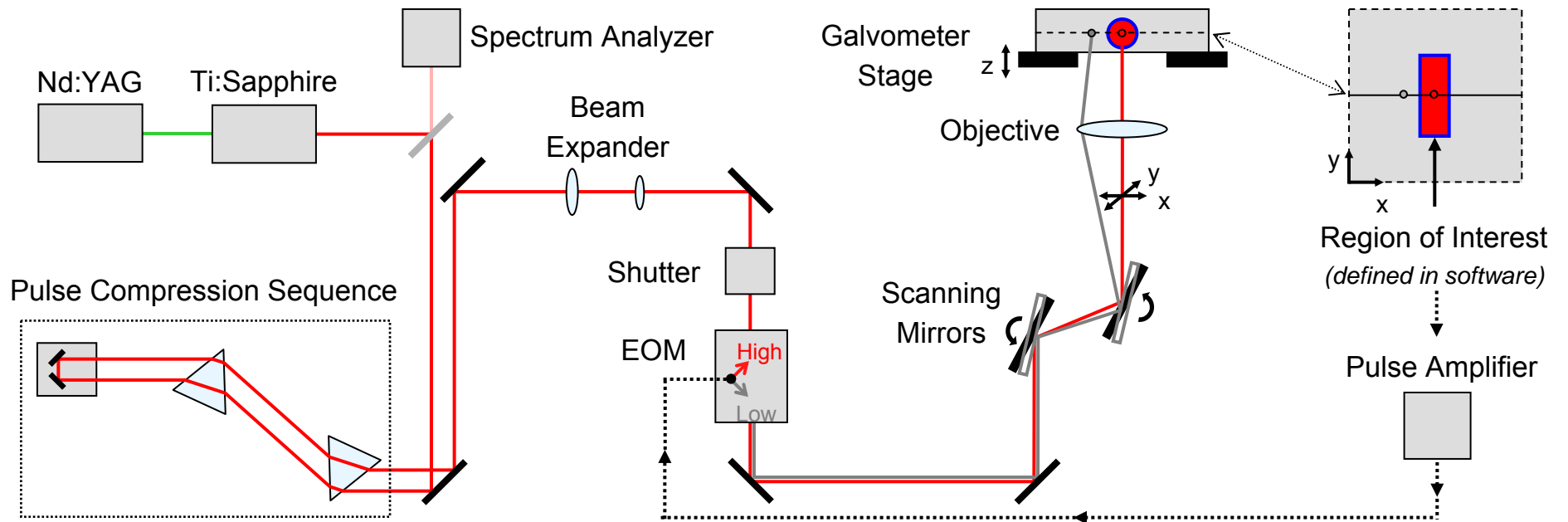


AF-270\*

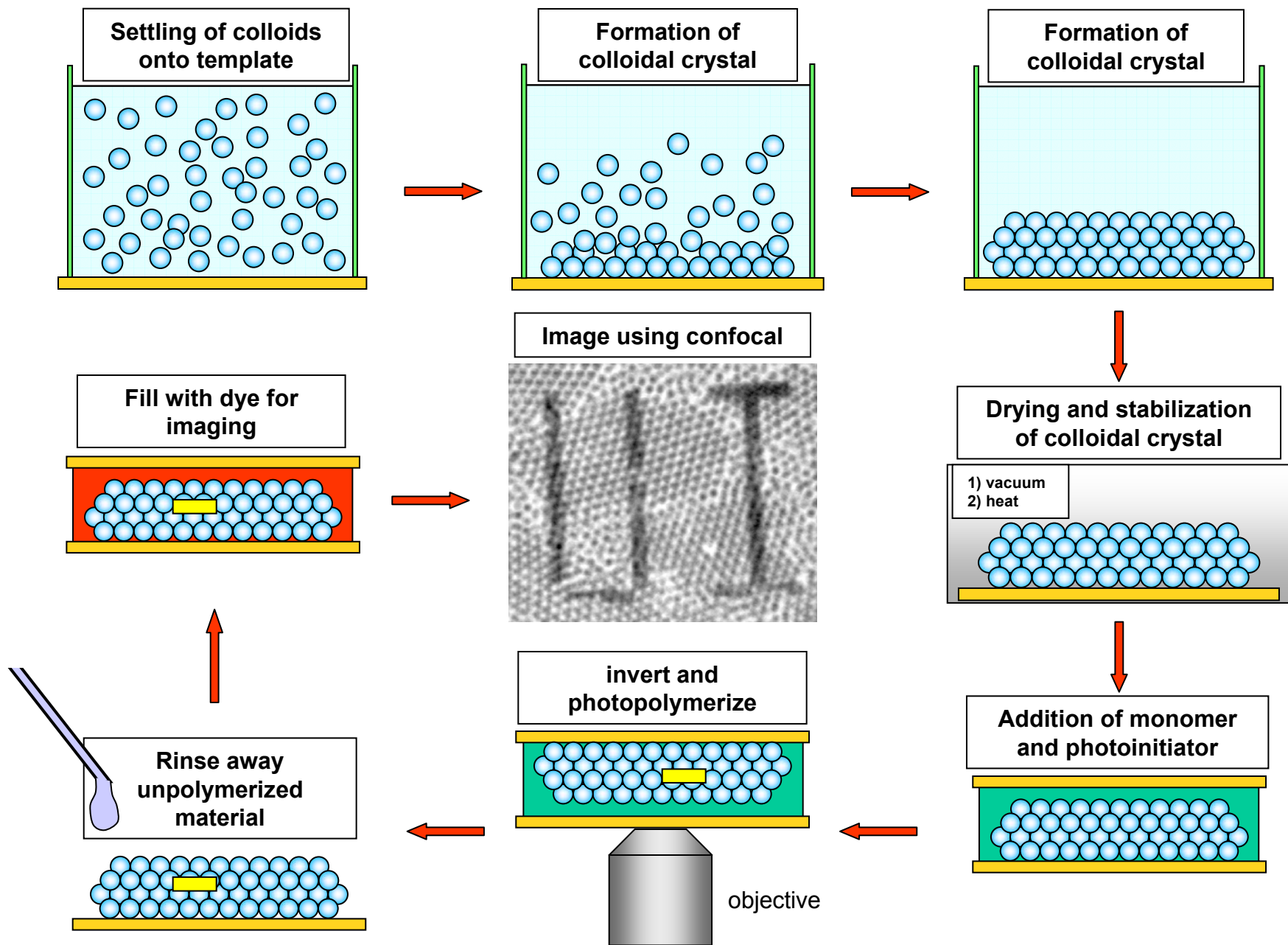


\*Courtesy of Air Force Research Laboratory (e.g. R. Kannan et al. *Chem. Mater.* **2001**, 13, 1896-1904)

# Optics for Multiphoton Polymerization

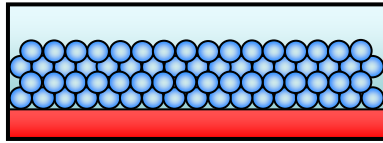


## 3-D Pattern Formation in Colloidal Crystals – Procedure

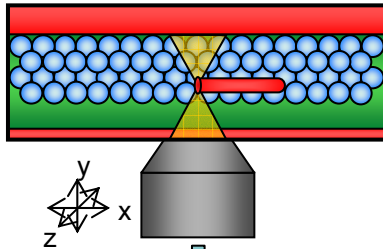


# Imaging of Templated Multiphoton Written Polymers

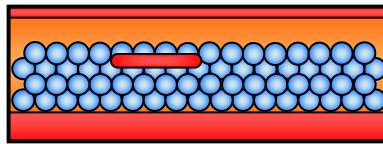
Sedimentation  
of colloidal  
crystal



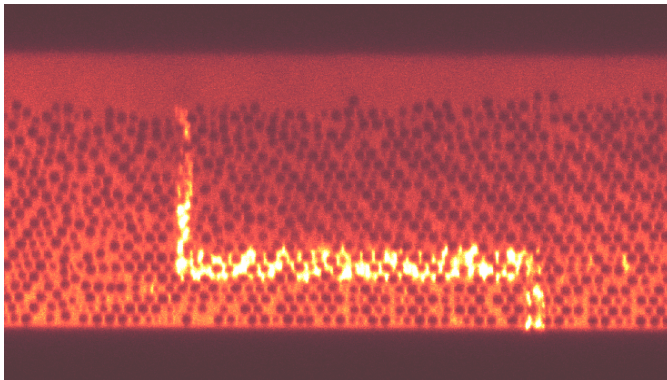
Multi-photon  
polymerization



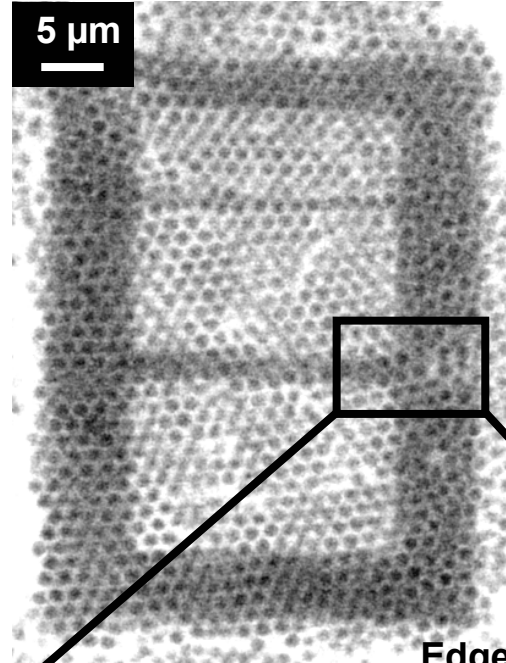
Remove  
unpolymerized  
materials



LSCM,  
side view

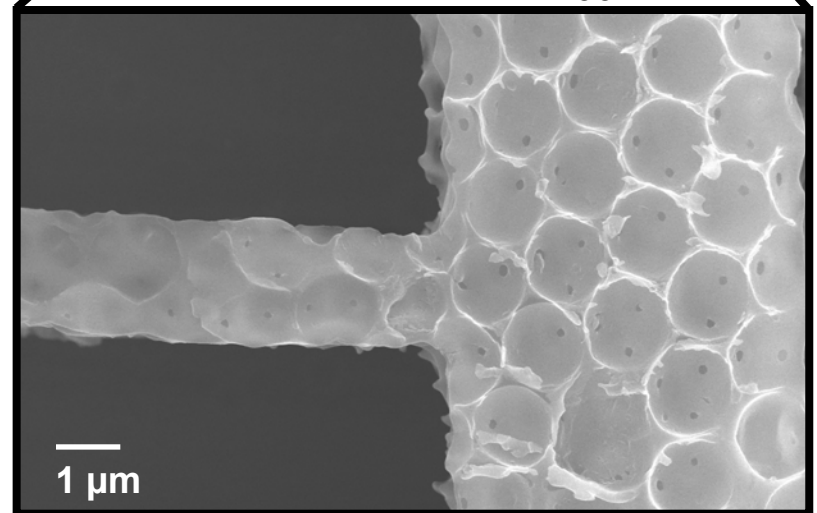


5  $\mu\text{m}$

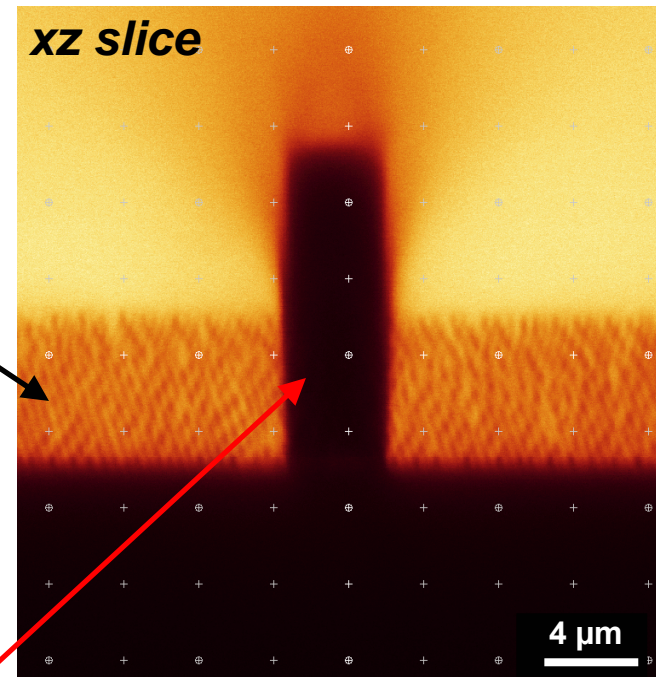
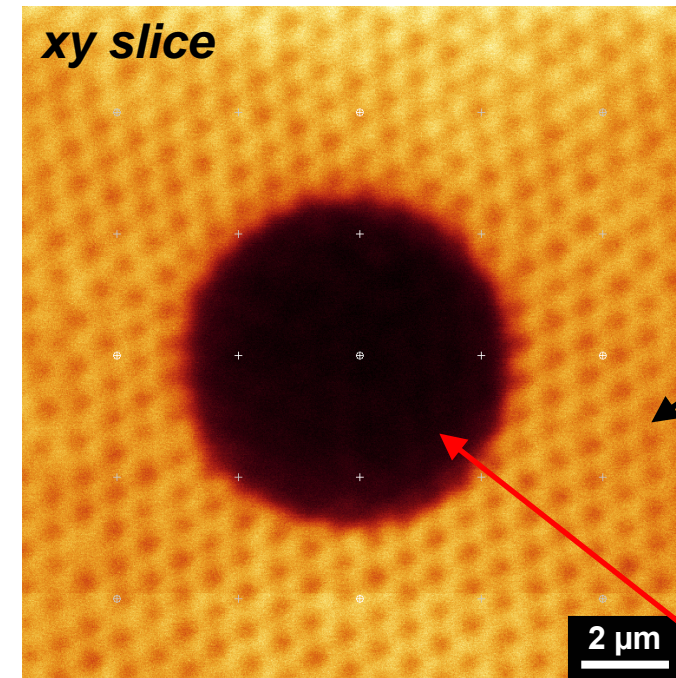


LSCM,  
top view

SEM  
Edge resolution  
 $\leq 100\text{nm}$

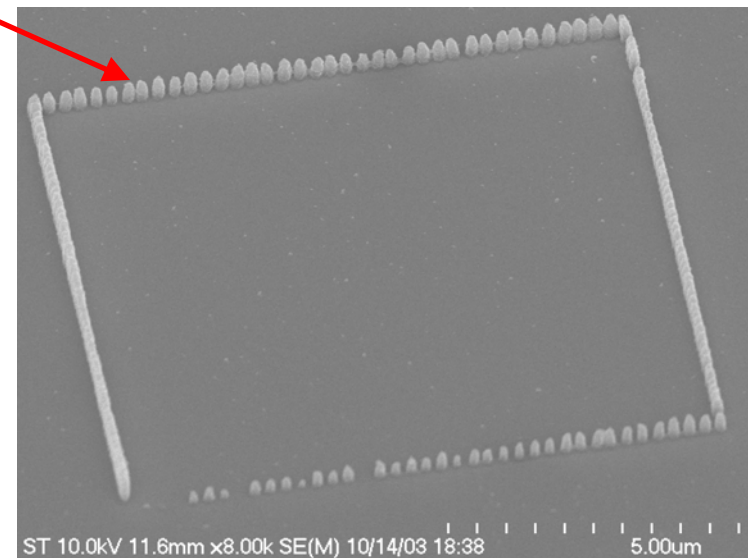
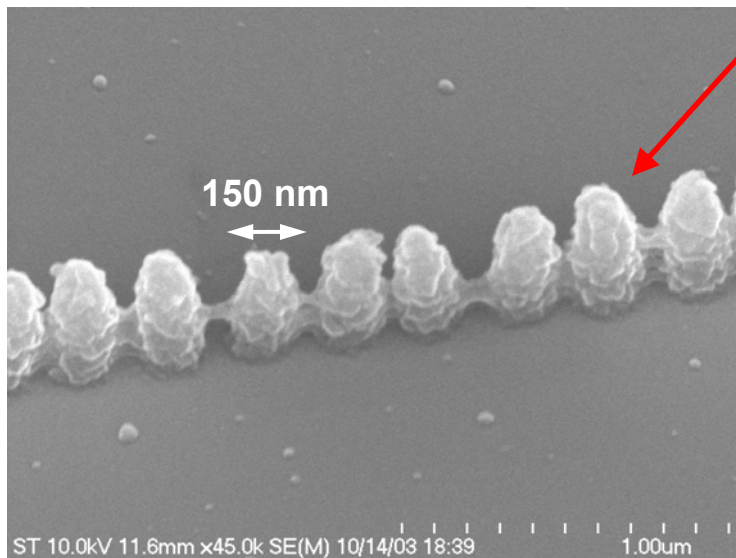


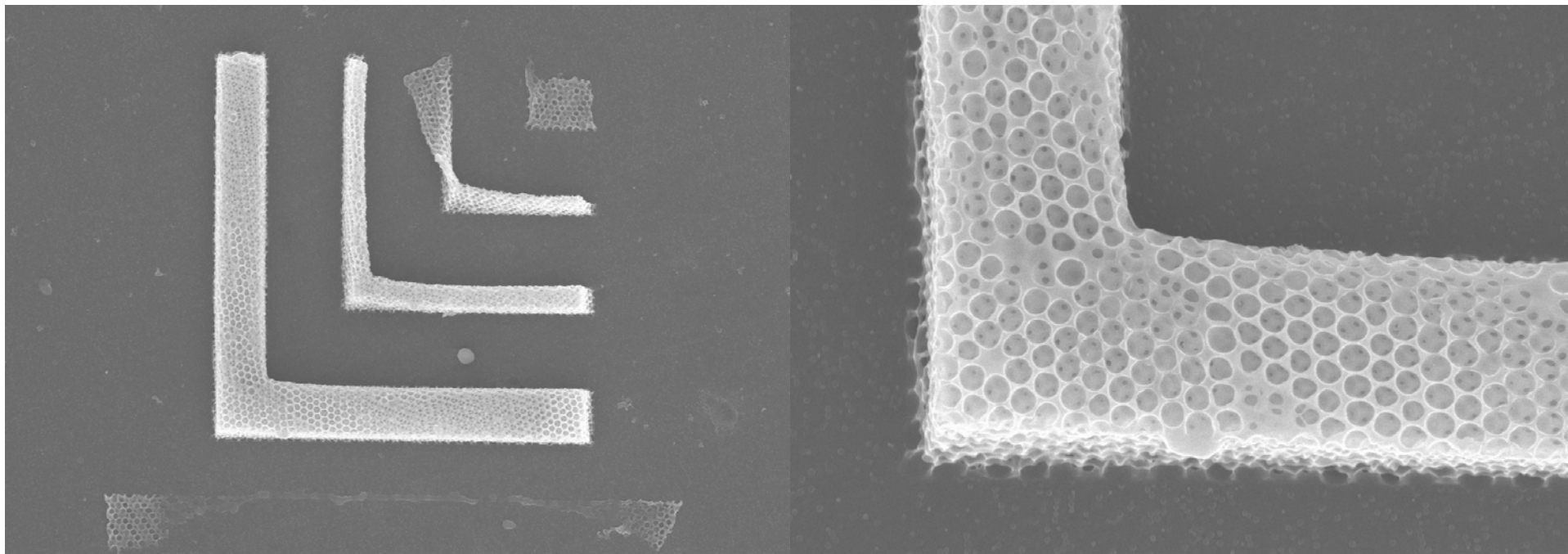
## 2-photon Polymerization in and out of Colloidal Crystals



Colloidal  
Crystal

polymer



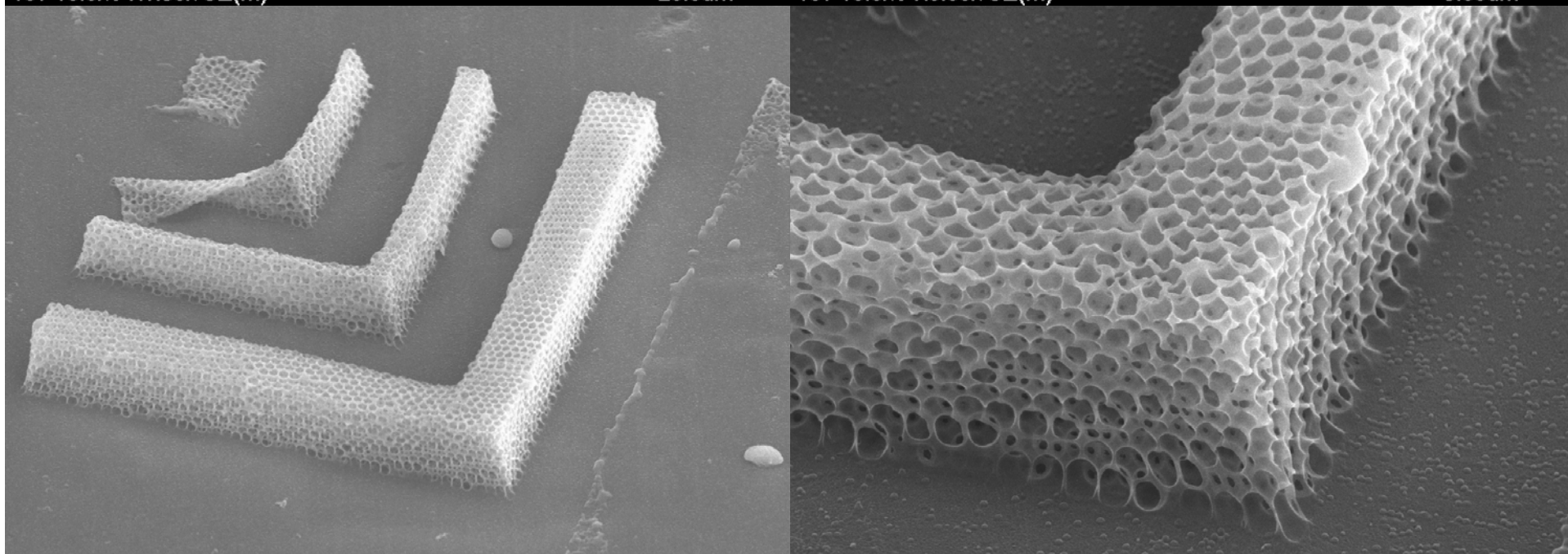


187 10.0kV x1.50k SE(M)

20.0um

187 10.0kV x6.00k SE(M)

5.00um

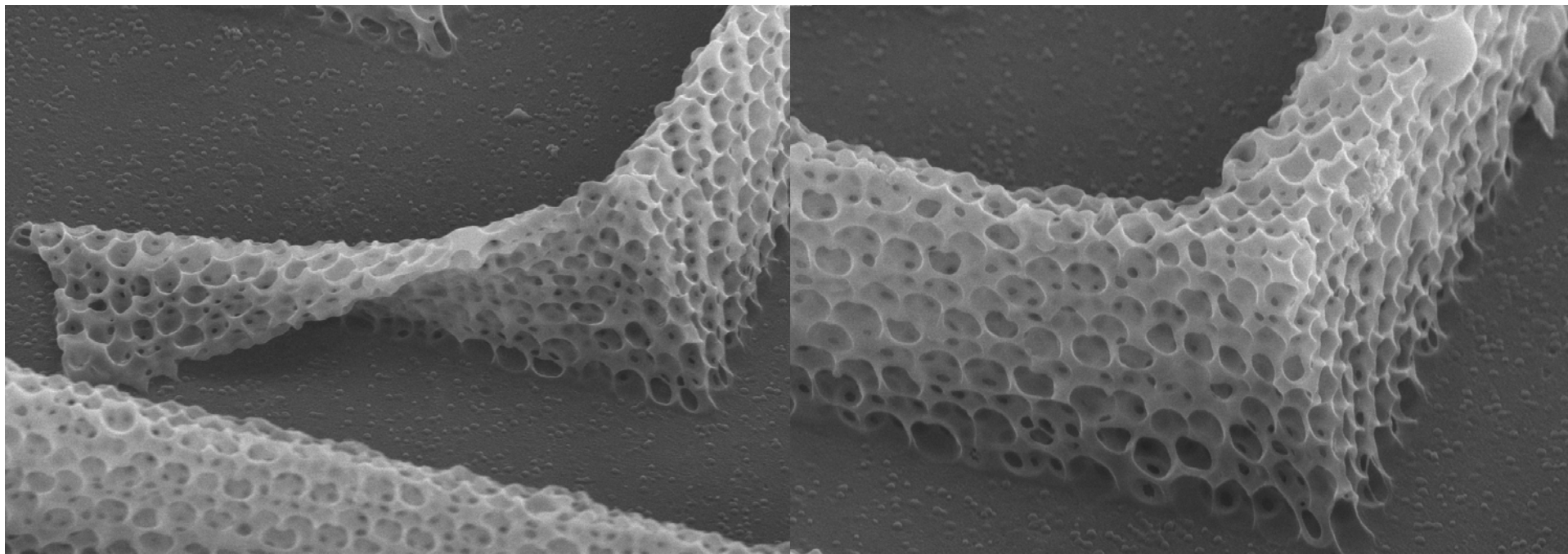


187 10.0kV x2.00k SE(M)

10.0um

187 10.0kV x7.00k SE(M)

5.00um

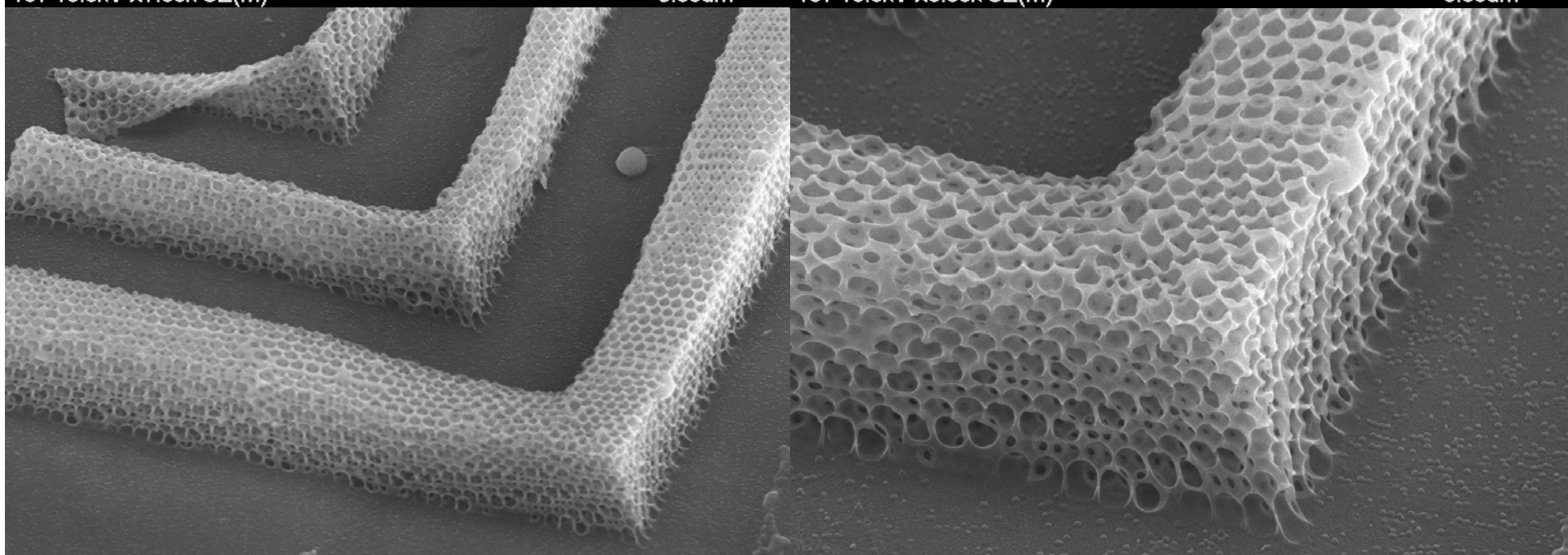


187 10.0kV x7.00k SE(M)

5.00um

187 10.0kV x9.03k SE(M)

3.00um



187 10.0kV x2.99k SE(M)

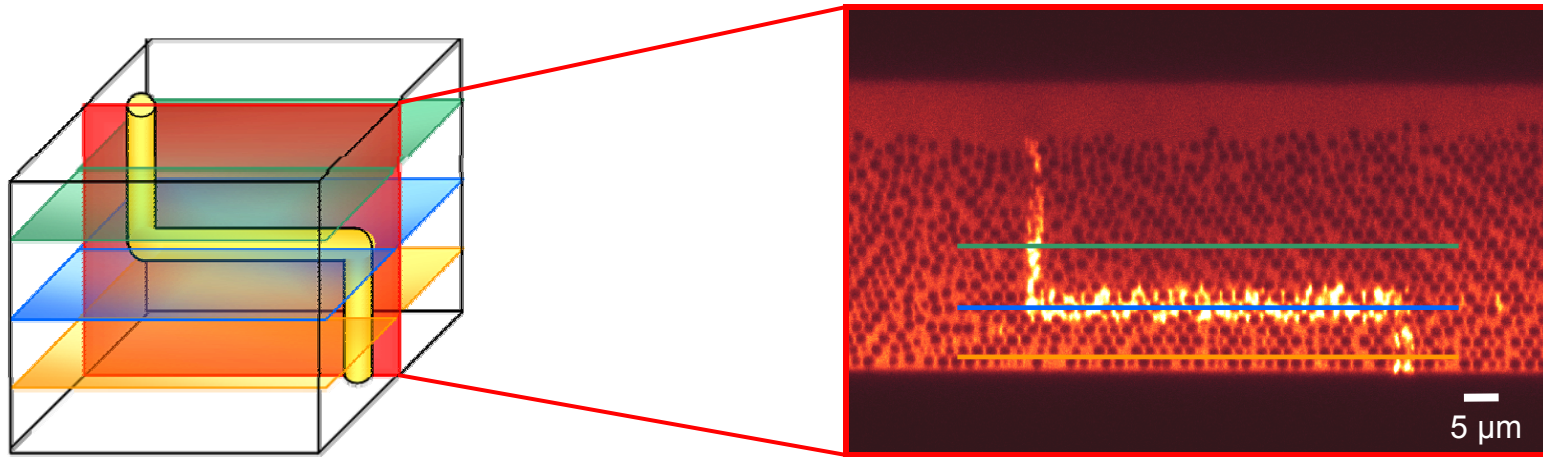
10.0um

187 10.0kV x7.00k SE(M)

5.00um



# Embedded Waveguide Structure Fabrication



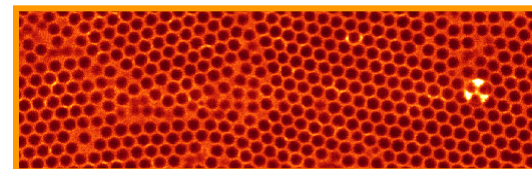
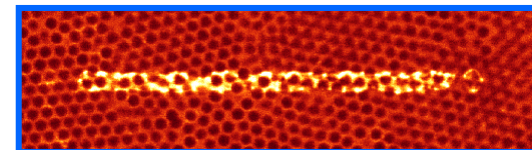
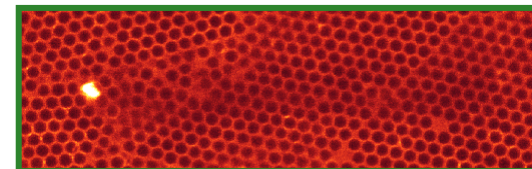
**Successful fabrication of embedded waveguide structures in self-assembled photonic crystals!**

Press Reports:

R.F. Service, *Science*. **2002**, 295, 2399.

T.A. Taton, D.J. Norris, *Nature*. **2002**, 416, 685.

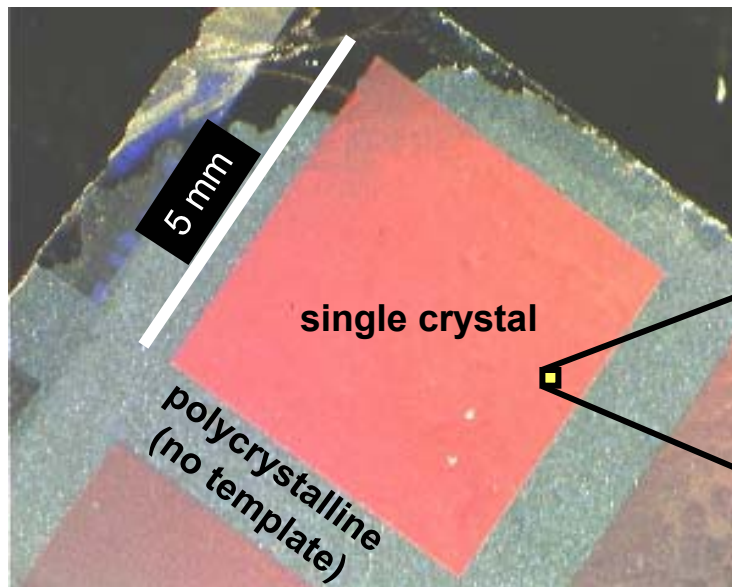
W. Roush, *Technology Review*. **2002**, 105, 22.



## Selenium – a High Refractive Index Filler

Results in high refractive index contrast, highly oriented photonic band gap materials

True fcc colloidal crystal created by settling on a patterned substrate. The colloidal crystal nucleates and grows perpendicular to the 001 face, therefore no stacking faults form.

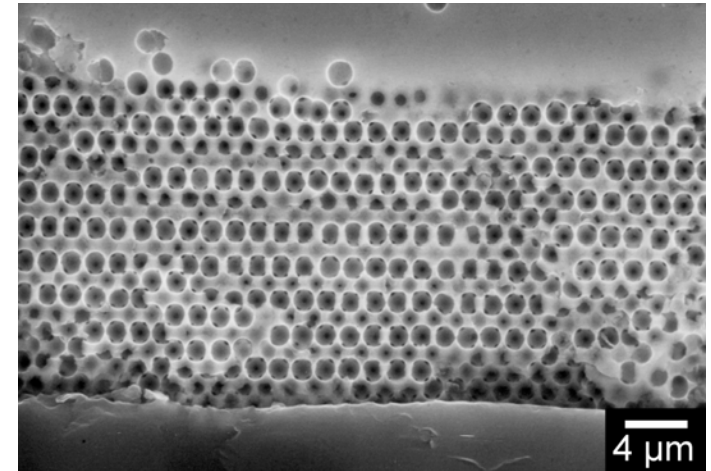


1.6  $\mu\text{m}$  silica colloid settled on a 1.66  $\mu\text{m}$  template. Index matched with DMF ( $n \sim 1.43$ ). White light illumination

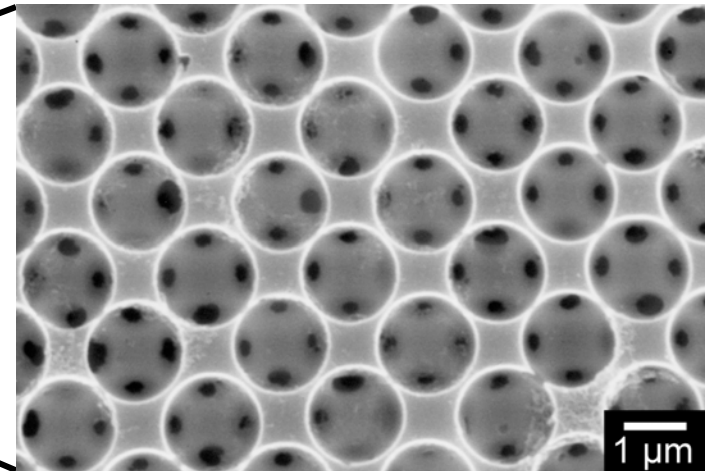
After selenium imbibing and removal of colloidal template



Selenium photonic crystal



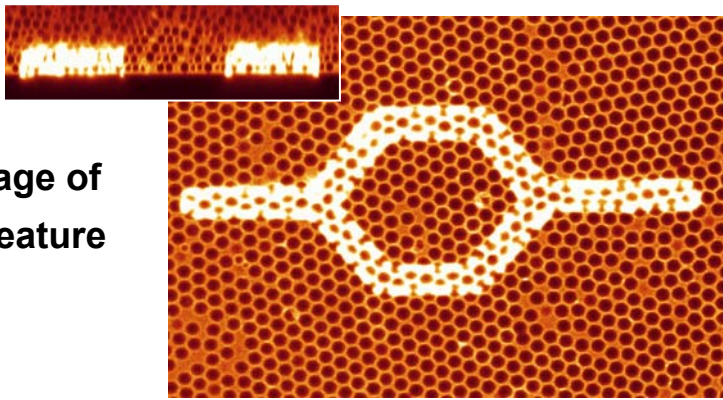
011 face



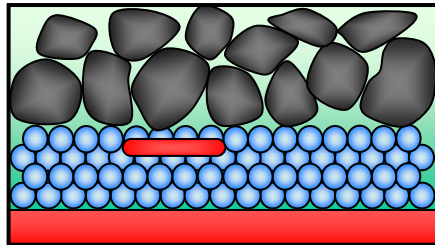
001 face

# Dielectric contrast enhancement: Melt Imbibing of Selenium

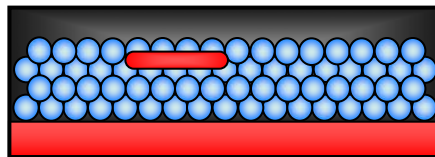
LSCM image of  
polymer feature



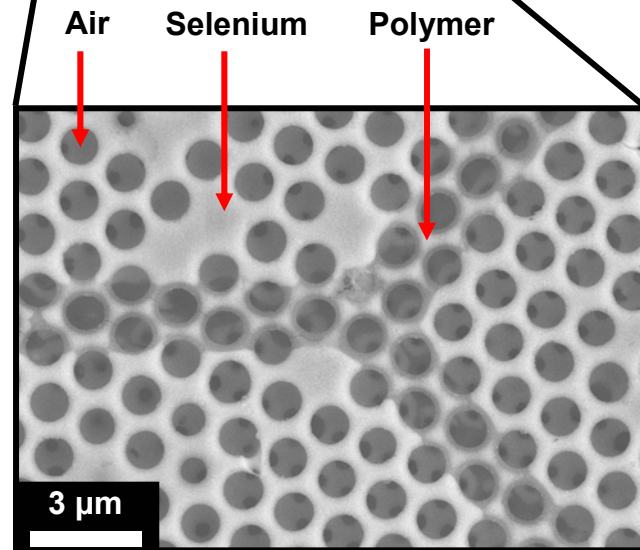
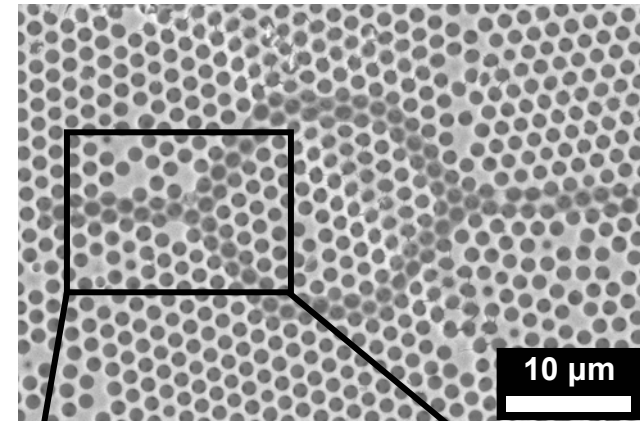
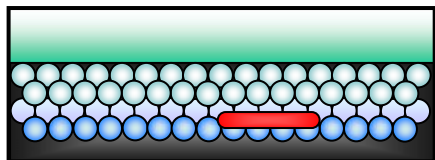
Melt  
selenium  
(~250 C)



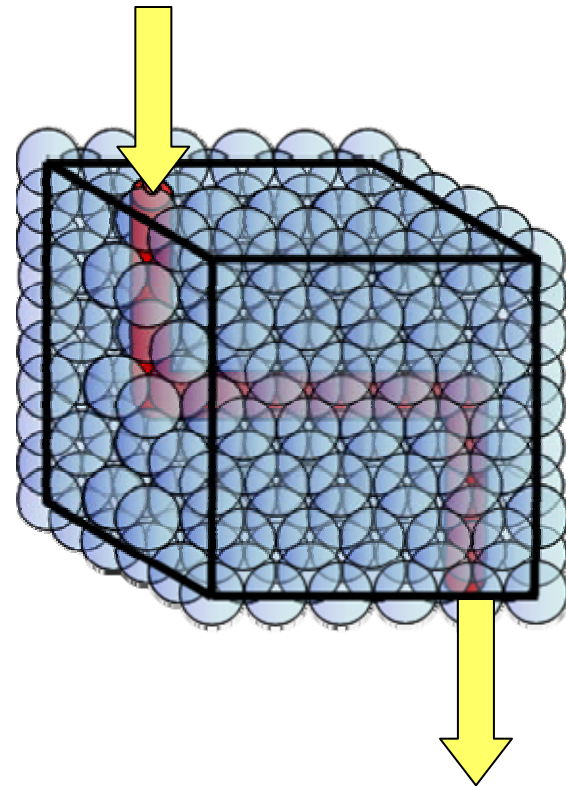
Pressurize



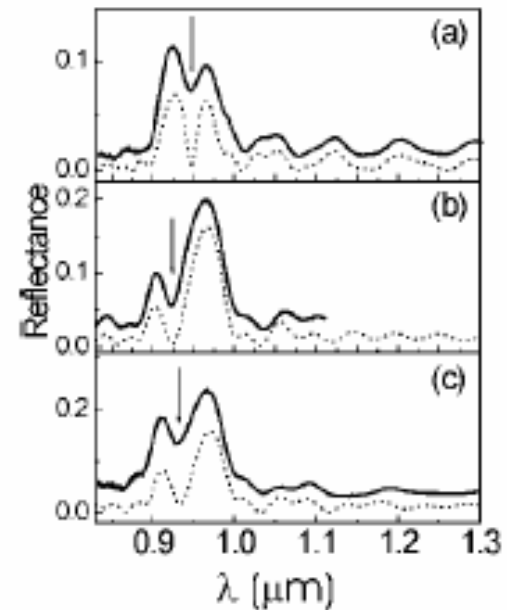
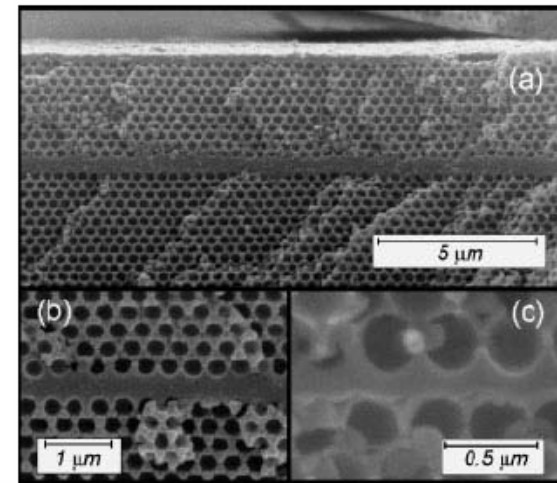
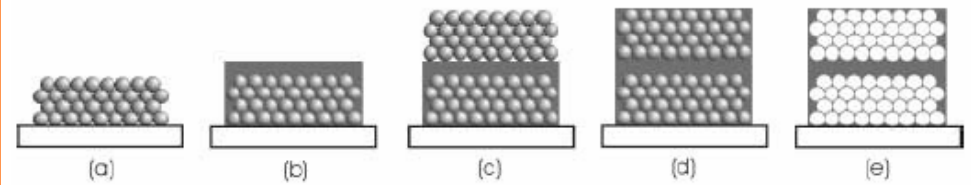
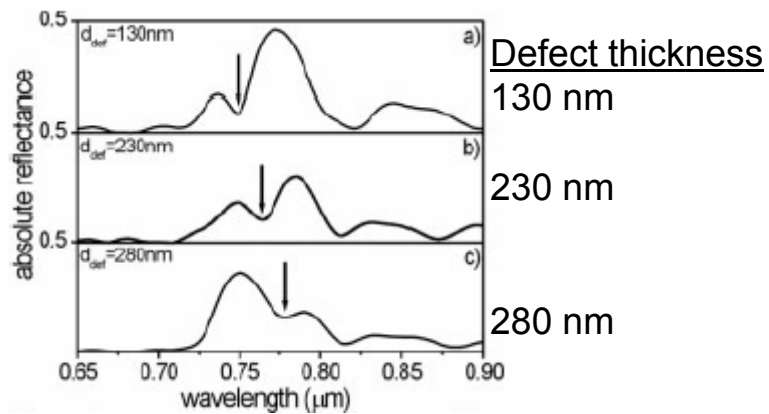
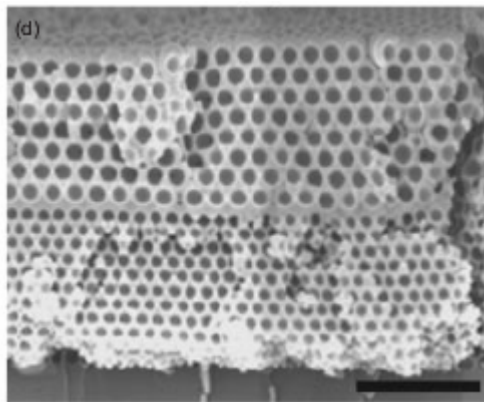
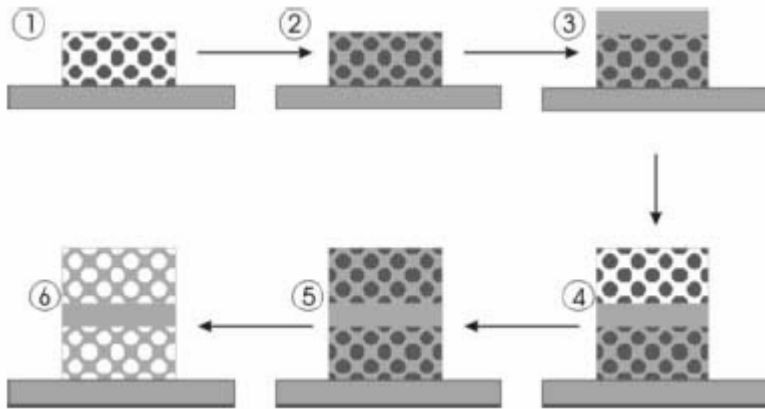
Etch silica  
(HF)



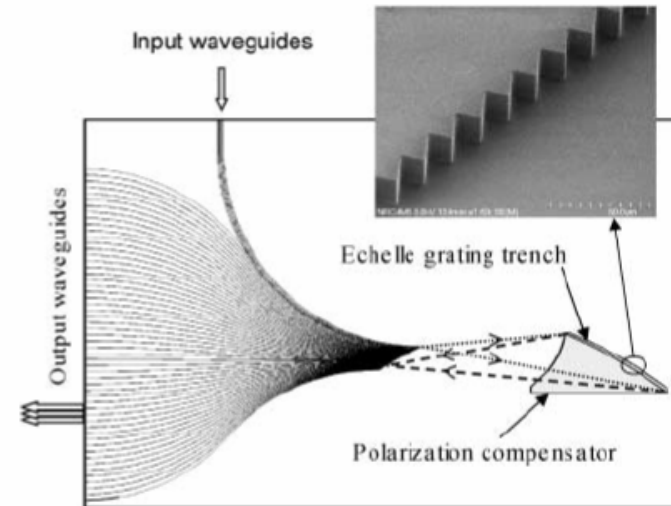
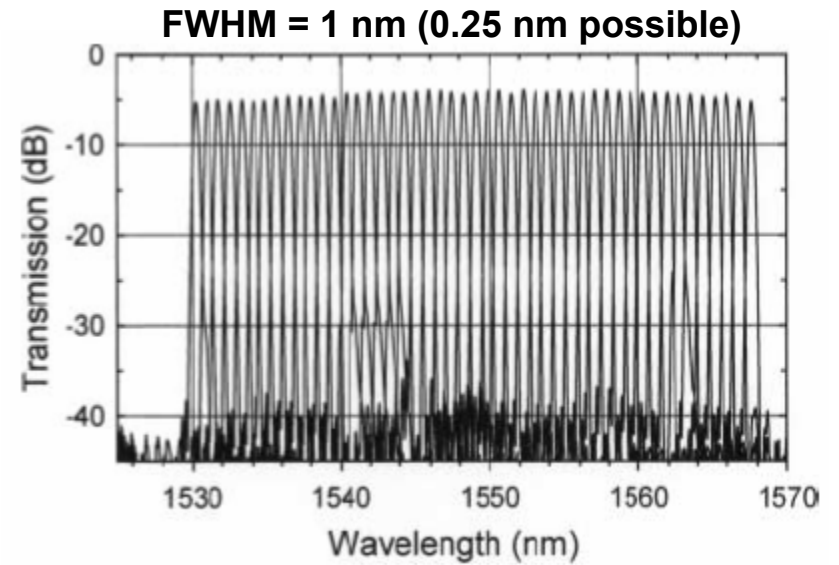
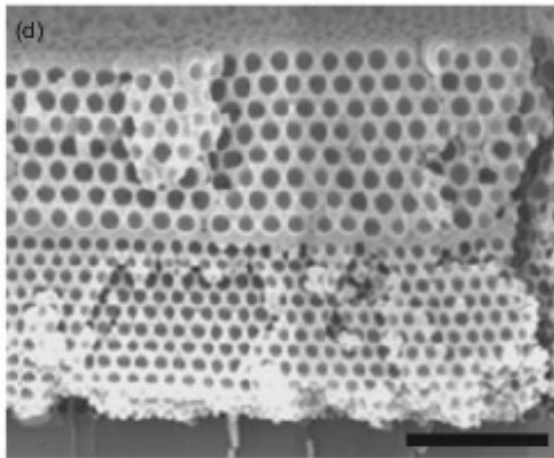
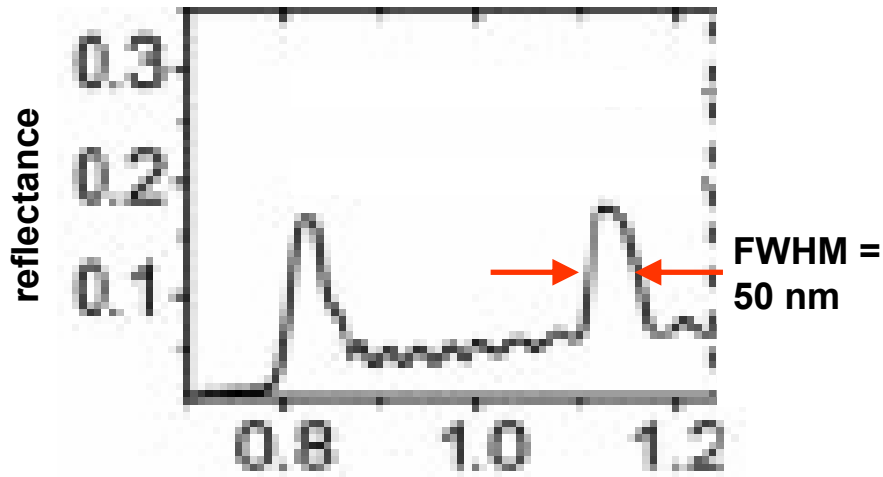
Characterization of transmission  
through embedded waveguides



# Inserted Planar Defects in Colloidal Crystals



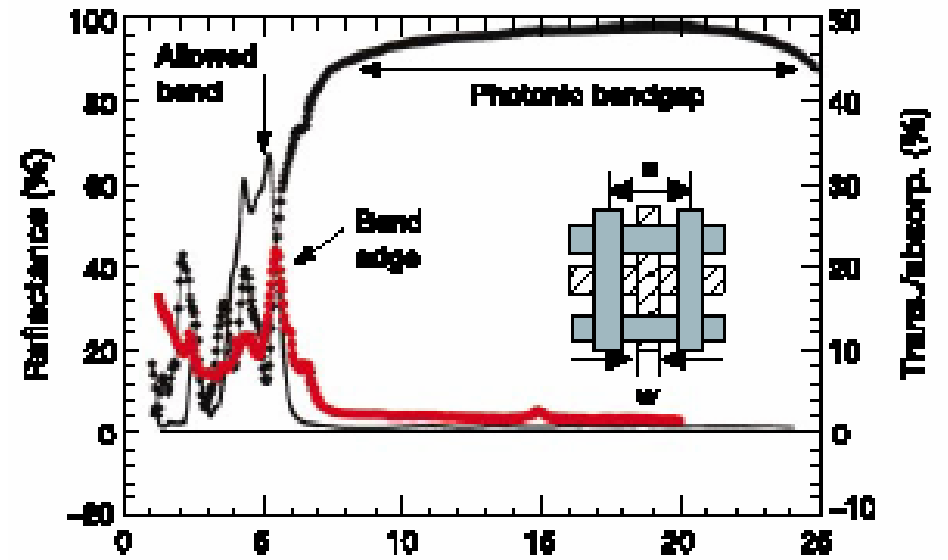
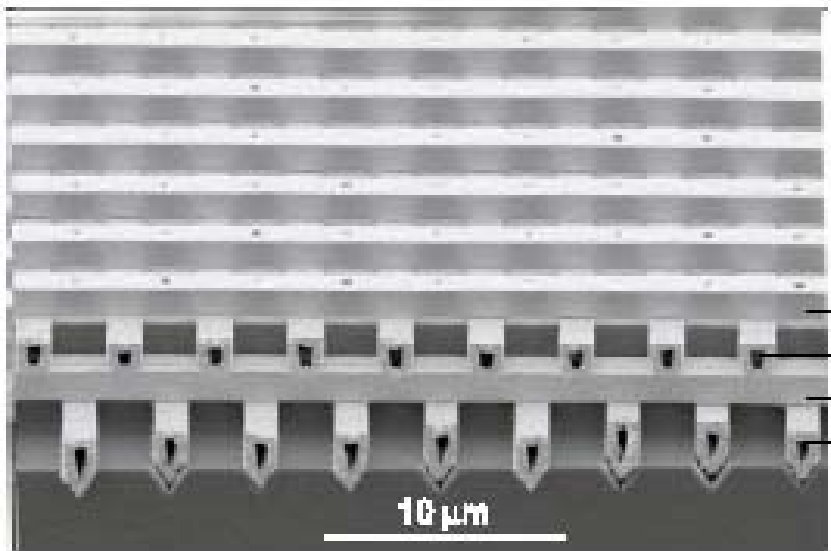
# Integrated Photonics?



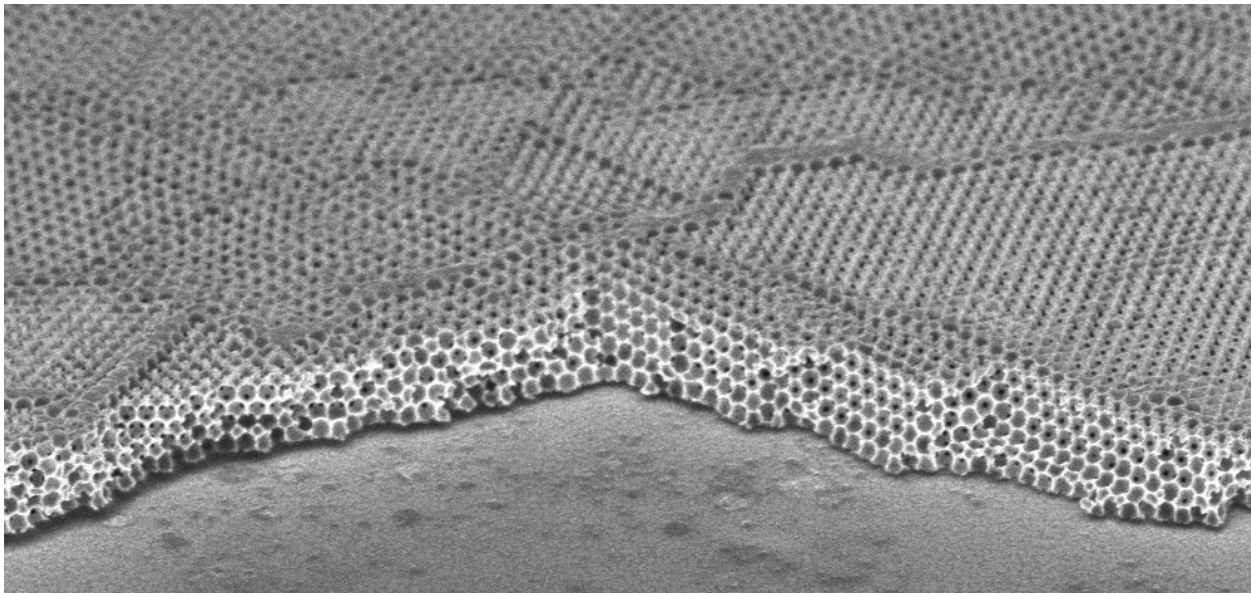
48-channel echelle grating demultiplexer chip.

# Metallic Photonic Crystals

Enhance blackbody emission?

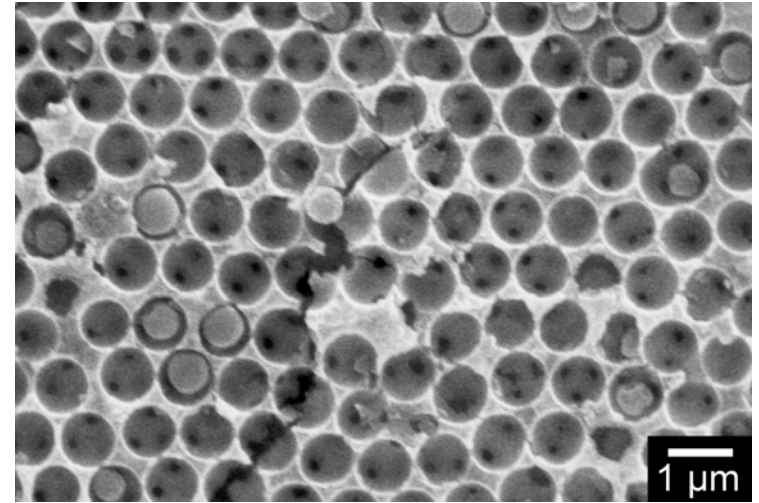
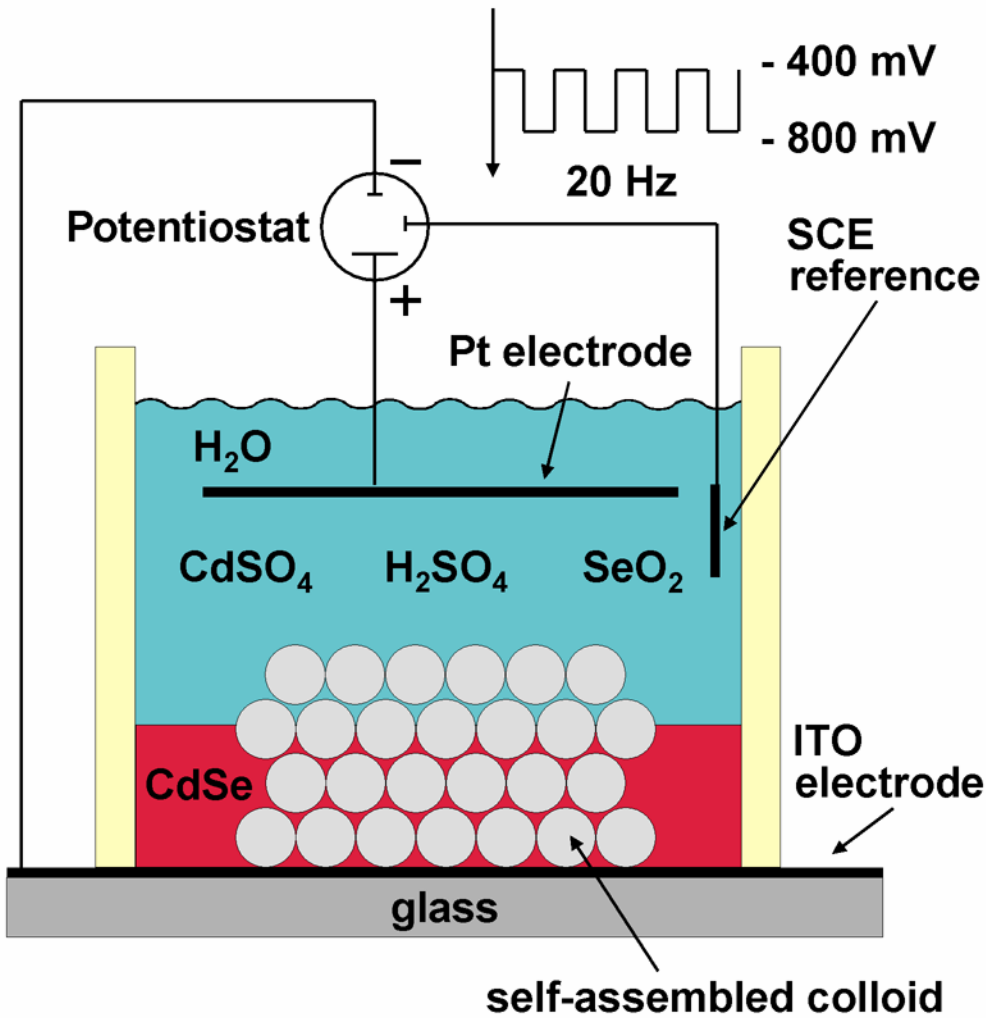


S. Y. Lin, Nature 2002

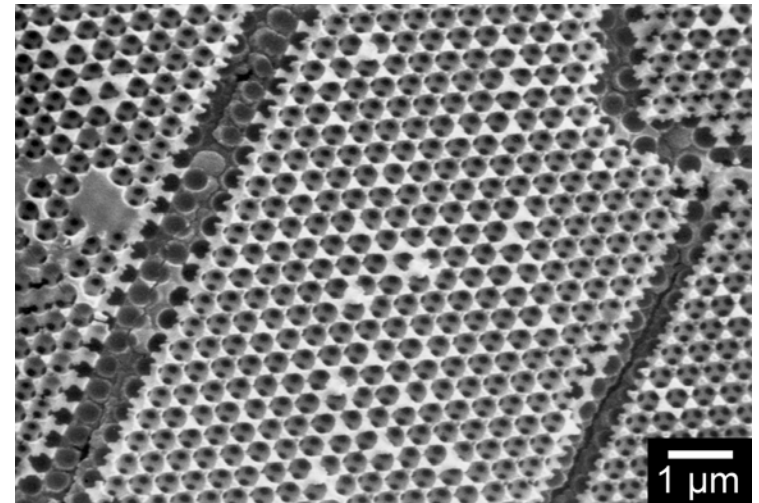


**Electrodeposited Ni inverse Opal**  
Templated by 466 nm PS spheres  
Yun-Ju Lee, P. V. Braun unpublished

# Electrodeposition of Photonic Crystals



CdS

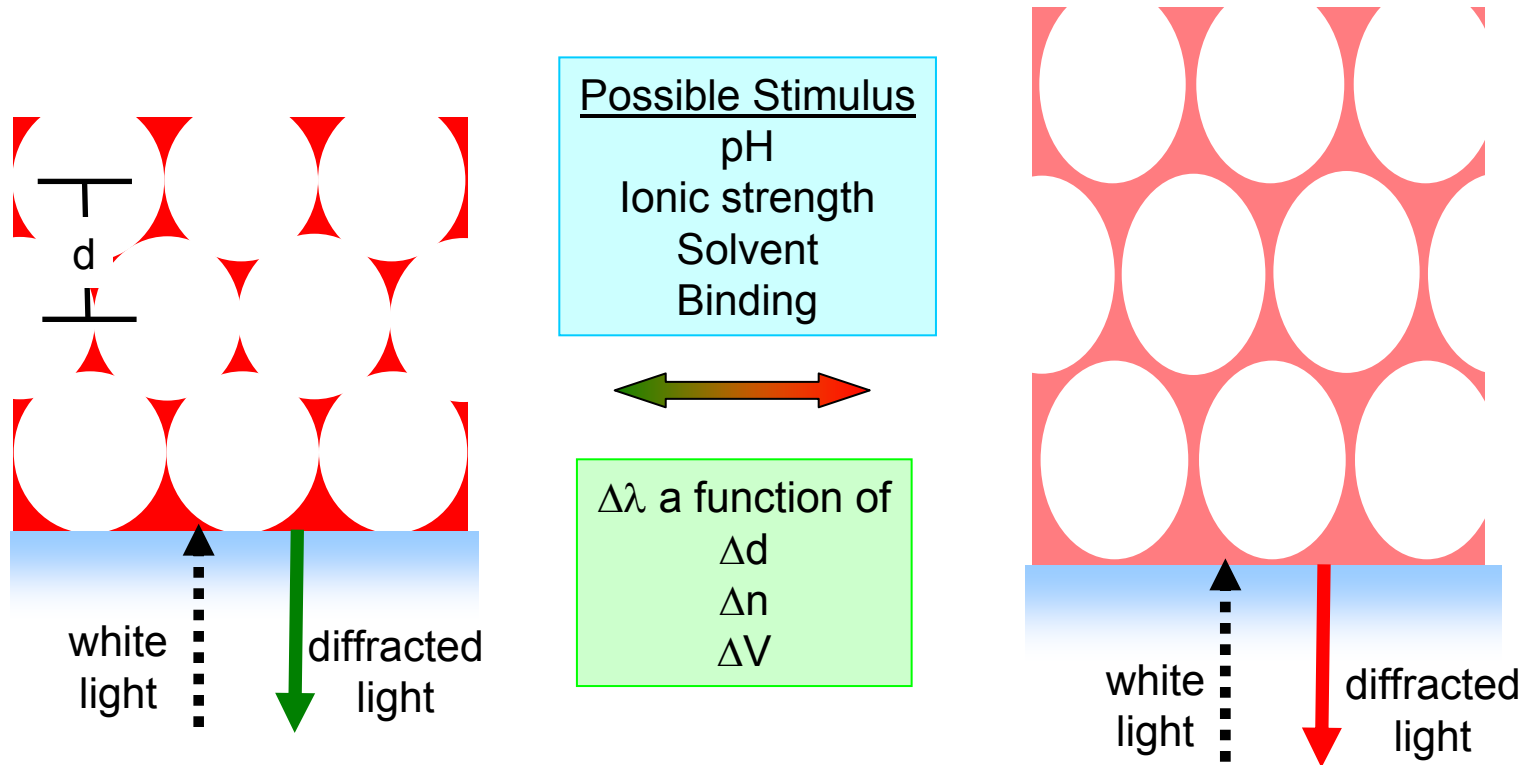


CdSe

After semiconductor electrodeposition, the colloidal particles are removed via solvent



Note: See lectures by Prof. Sandy Asher  
Pioneered the field



Because  $\Delta\lambda \sim \Delta d$ , swelling enables sensing

$$\lambda = 2dn_{eff} \cong 2d \left( \sum_i n_i^2 V_i - \sin^2 \phi \right)^{1/2}$$

$d$  = interlayer distance

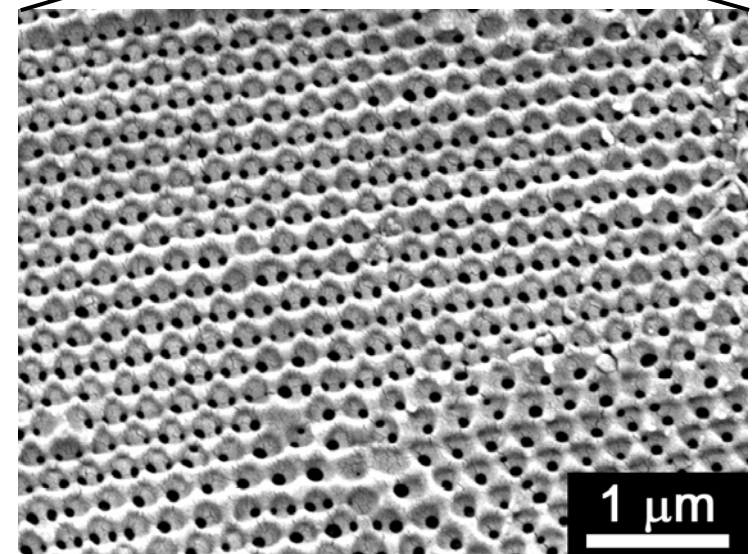
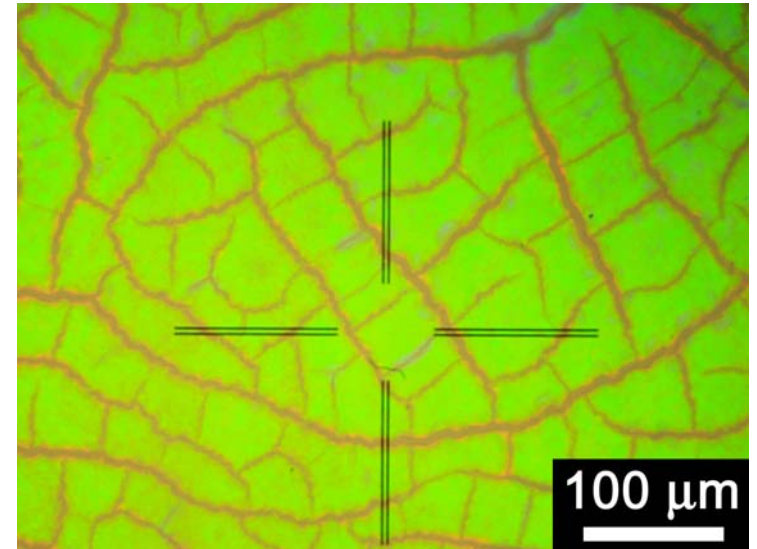
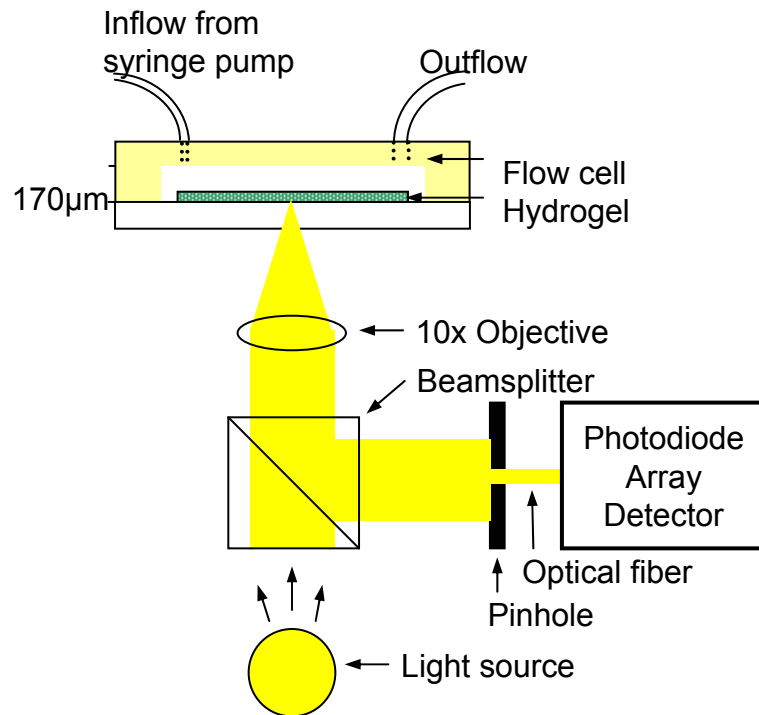
$n_i$  = refractive index of component  $i$

$V_i$  = volume fraction of component  $i$

$\phi$  = angle between incident beam and sample normal

## Polymerization of Templated Hydrogels

1. Assemble colloidal crystal in flow cell
2. Infiltrate with monomer mixture
3. UV irradiate (356 nm, 50 min)
4.  $\text{CHCl}_3$  etch (24 hours)
5. Solvent exchange
6. Structural and optical characterization

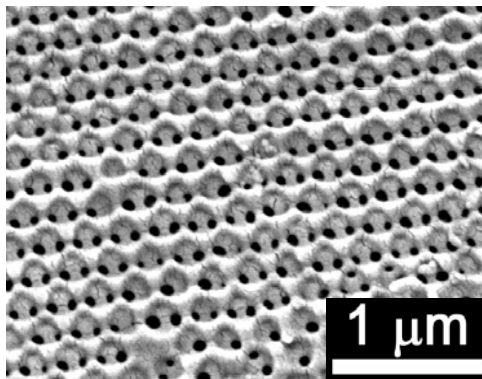
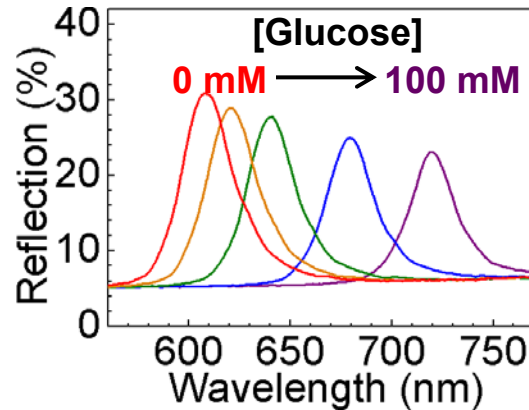
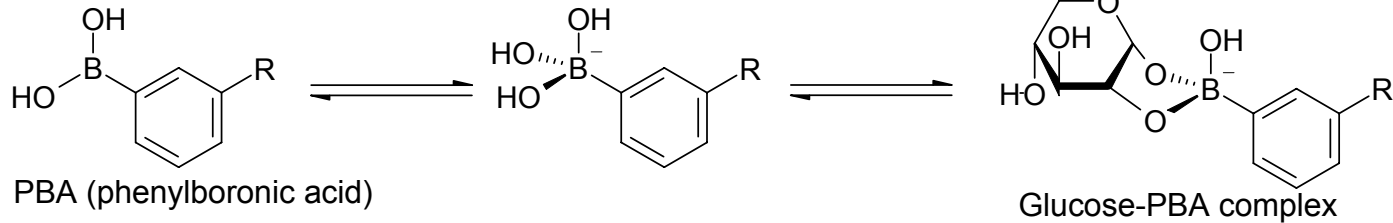


Y.-J. Lee and P.V. Braun, *Adv. Mater.* **2003**, 15, 563

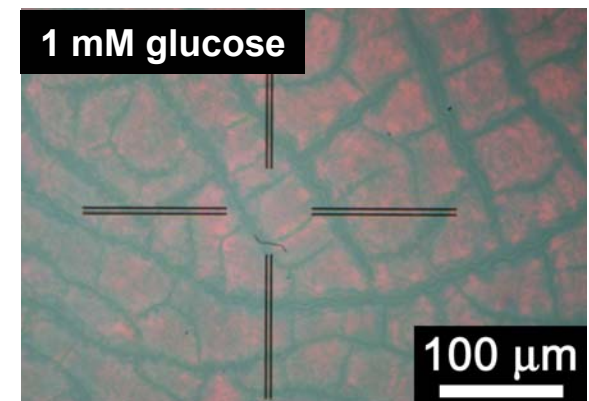
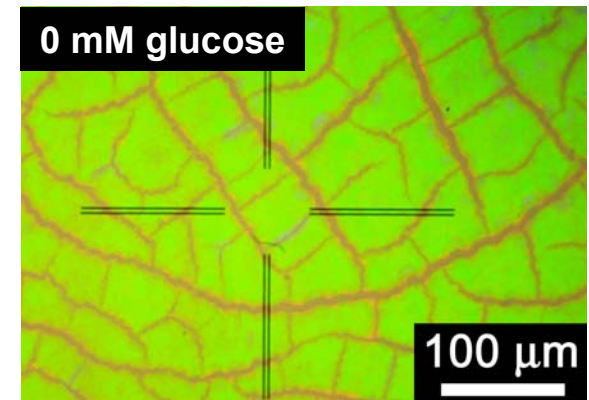
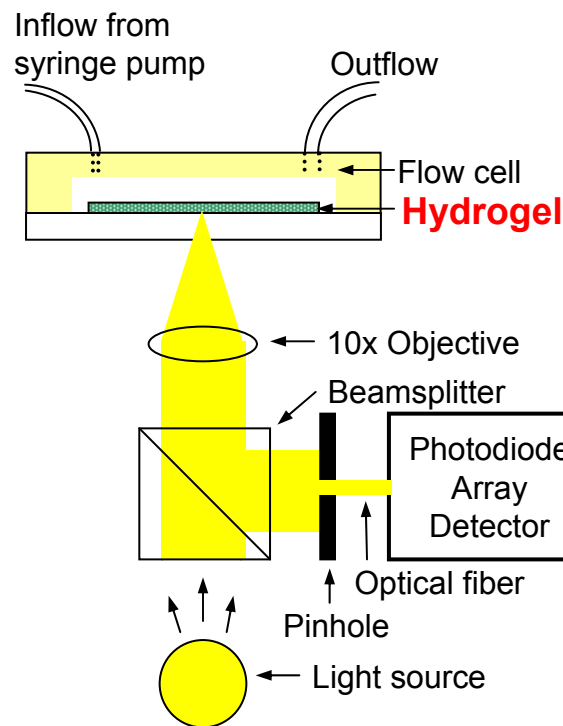
Y.-J. Lee, S. A. Pruzinsky, P.V. Braun, *Langmuir*, in press

# Glucose Sensing with Mesoscale Photonic Crystals

Can also do pH sensing (Adv. Mater. 2003)

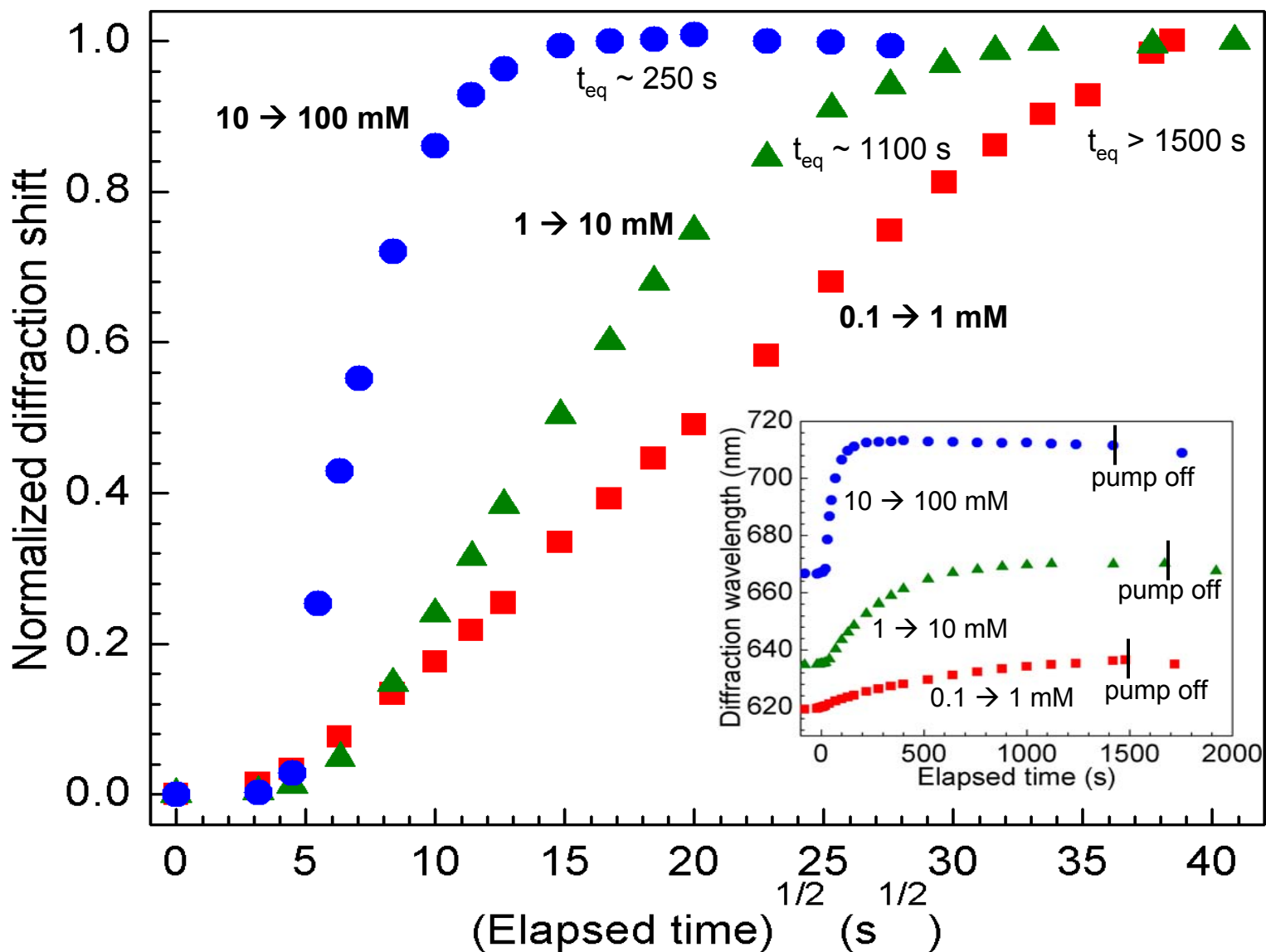


SEM of templated hydrogel



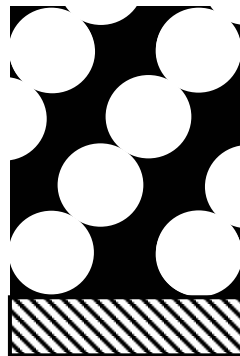
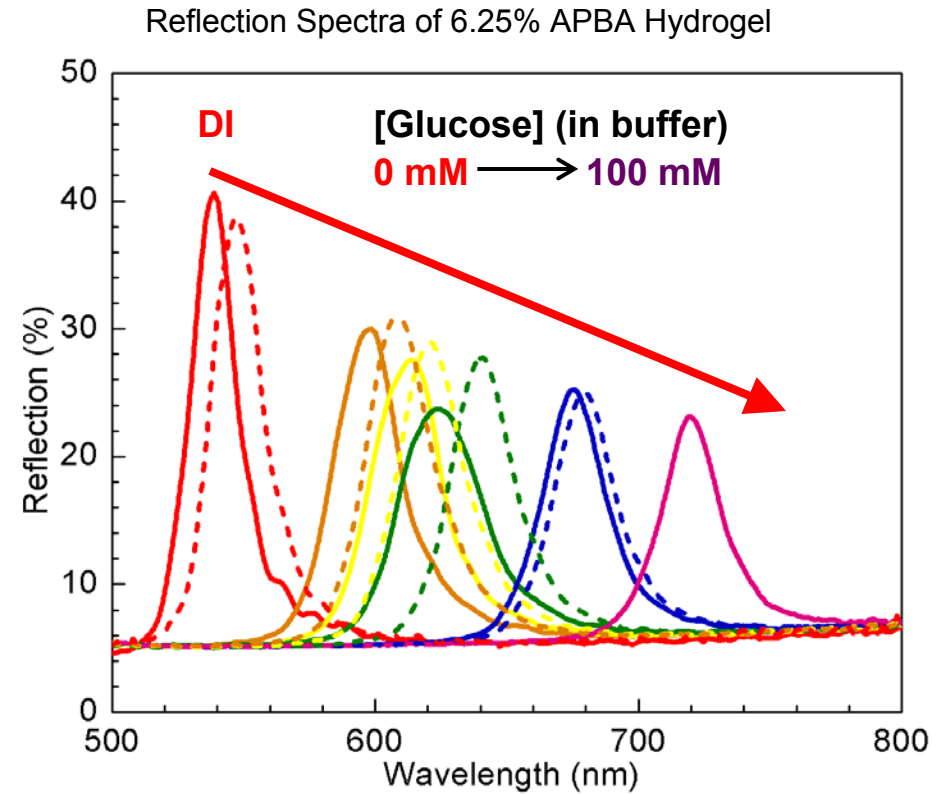
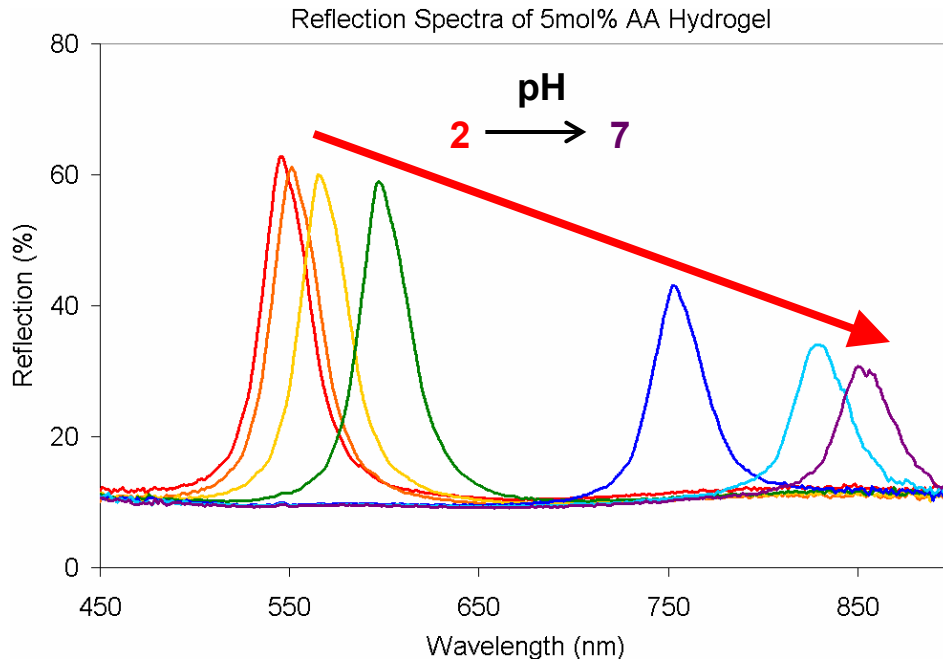
# Kinetics of Glucose Sensing

Increasing [Glu] Diffraction Shift Kinetics



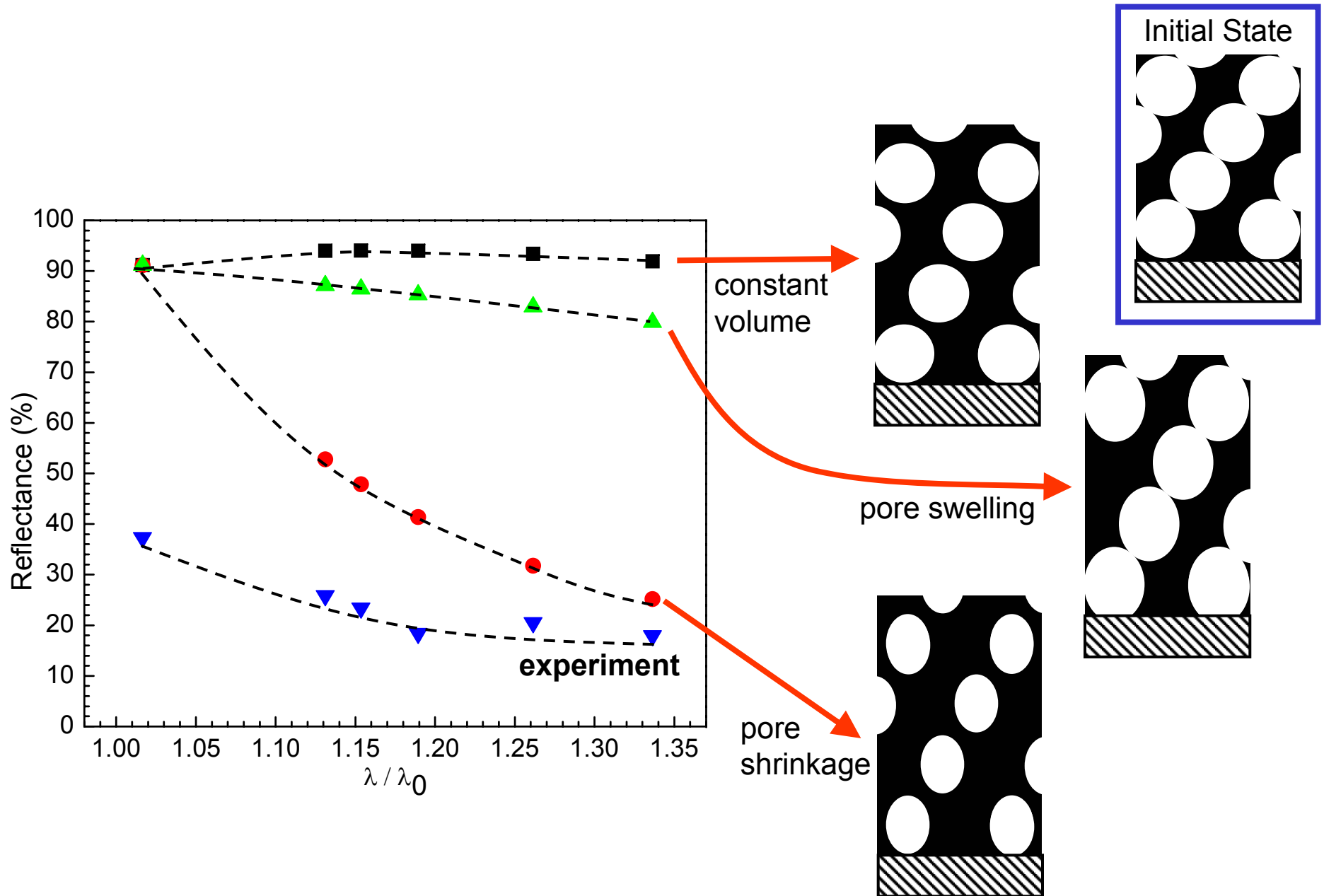
# Dramatic Decrease in Diffraction Efficiency with Swelling

WHY?



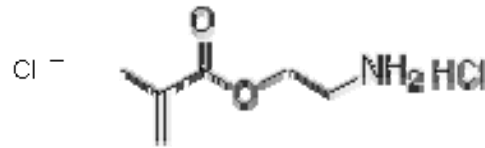
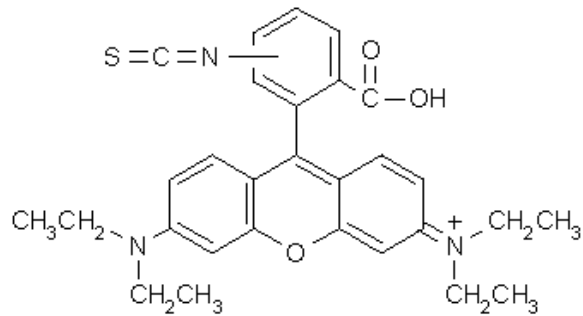
swelling



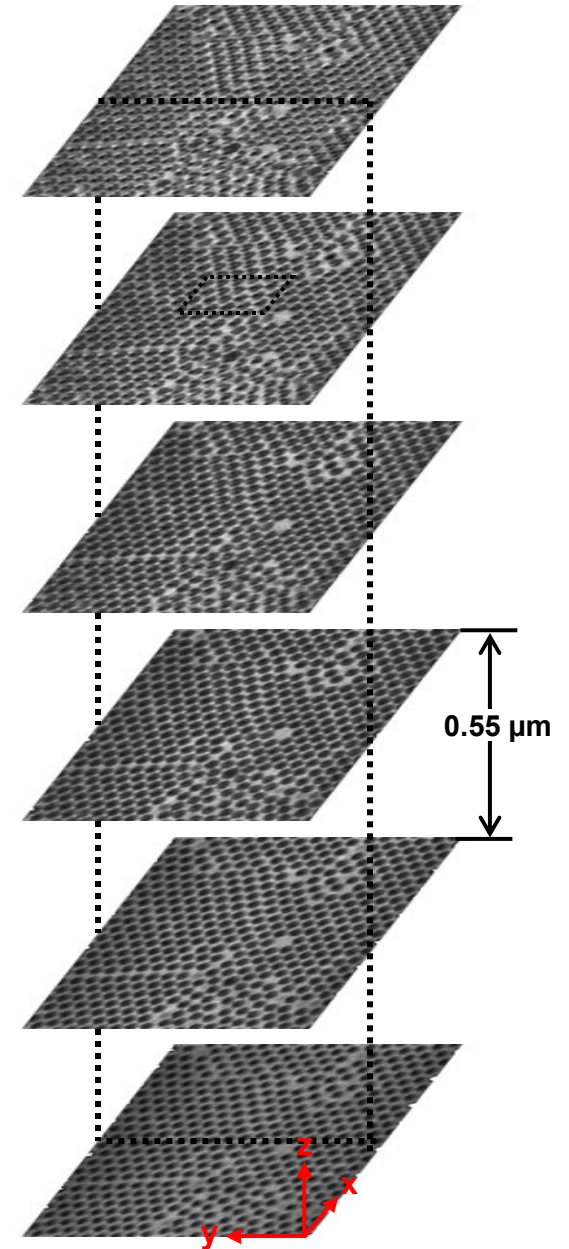


# Confocal Imaging of Inverse Opal Hydrogels

- Synthesize Acrylated Rhodamine B  
Rhodamine B-ITC + 2-Aminoethylmethacrylate·HCl

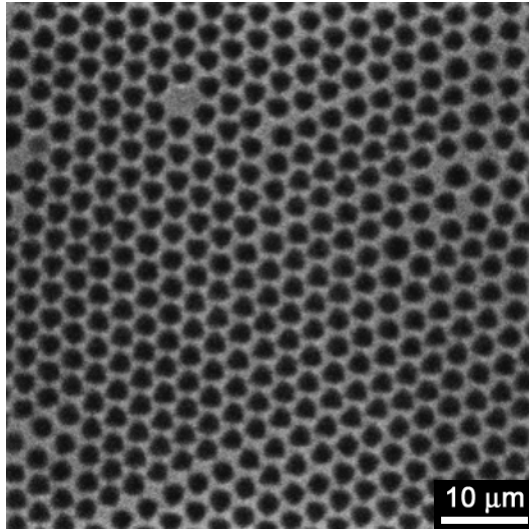


- Polymerize hydrogel in colloidal crystal (PS,  $d = 3 \mu\text{m}$ ,  $t = 25 \mu\text{m}$ ) HEMA + 5% AA + 0.66% EDGM +  $\sim 10 \mu\text{M}$  acrylated Rhodamine B
- Etch colloids
- Image with 2-photon confocal microscopy

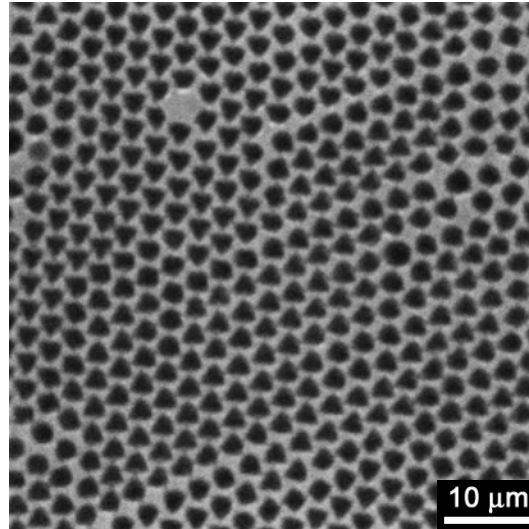


## Two-photon Imaging – Bottom Layer

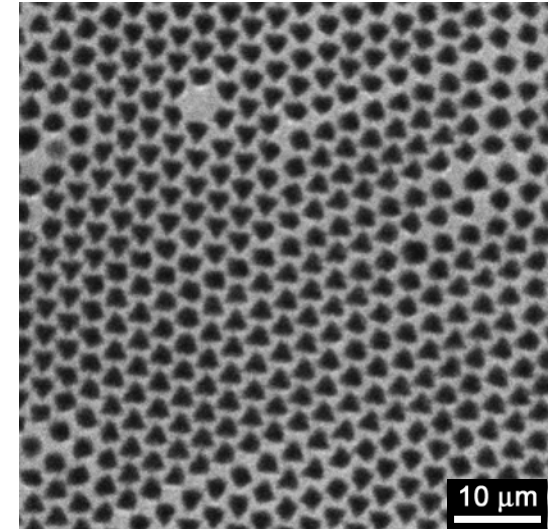
fcc (111), bottom layer



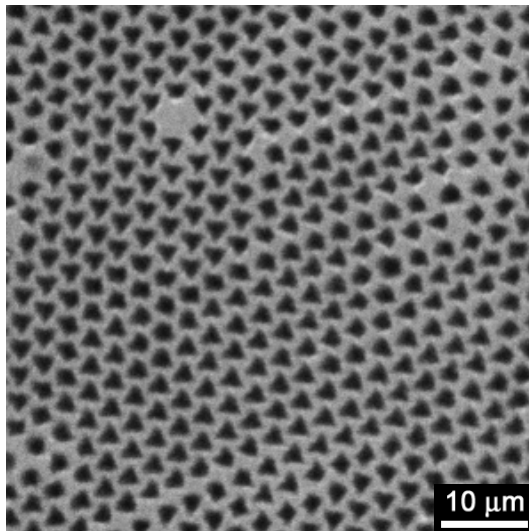
pH 3.4



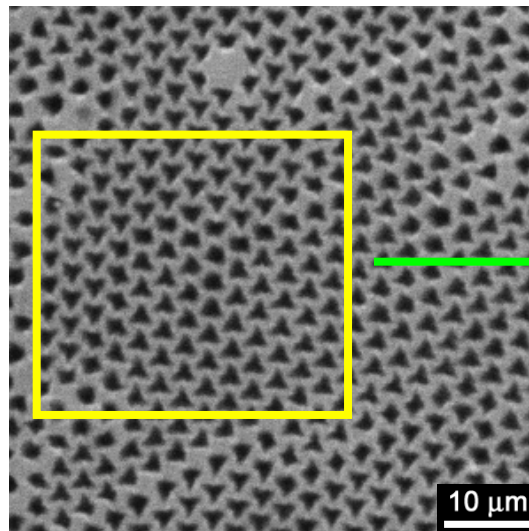
pH 4.5 (~ pK<sub>a</sub>)



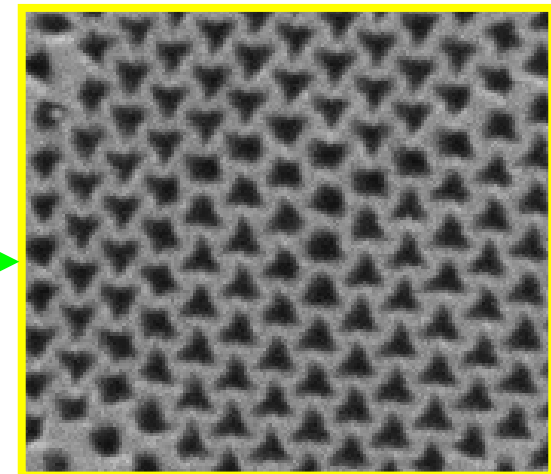
pH 5.0



pH 5.7



pH 6.6

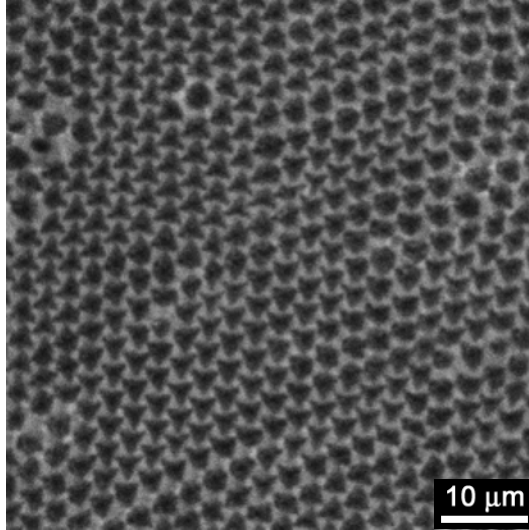


Pore deformation at pH  $\geq$  4.5  
Partial pore closure at high pH  
- Substrate pinning

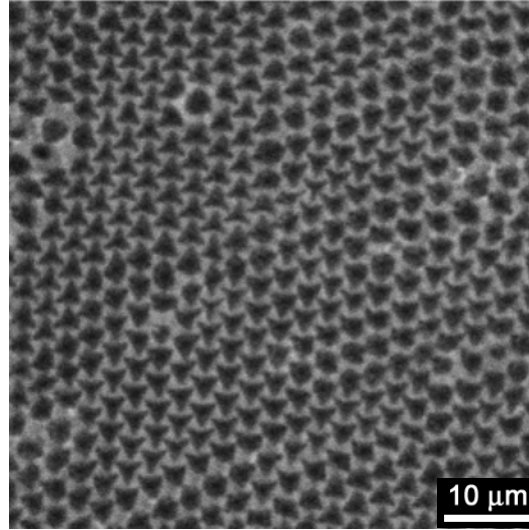


## Two-photon Imaging Results – Layer 2

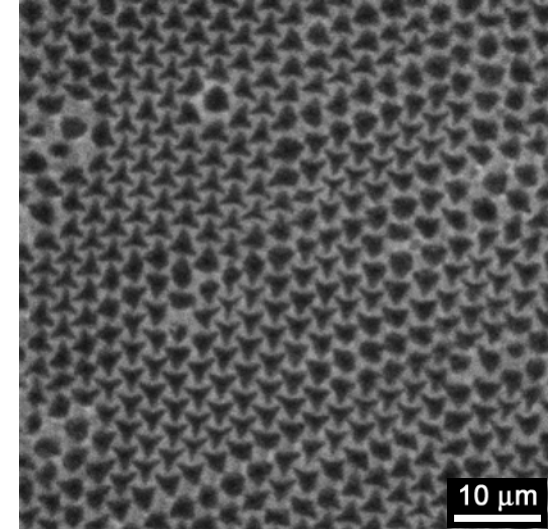
fcc (111), 2<sup>nd</sup> layer



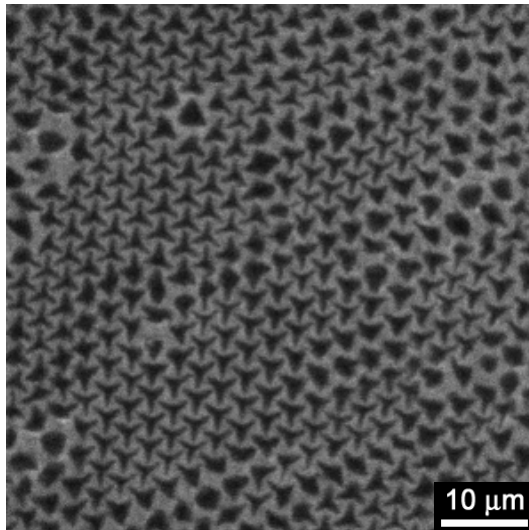
pH 3.4



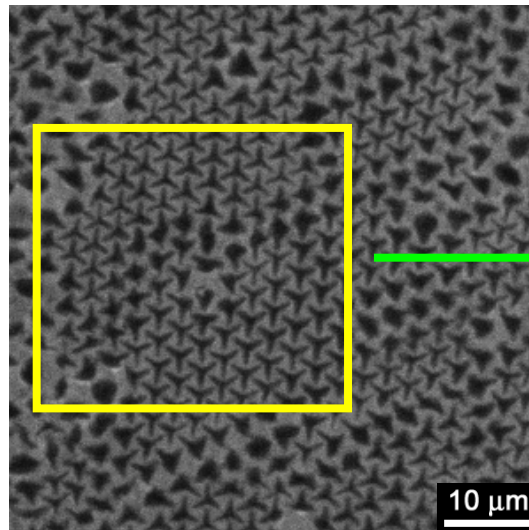
pH 4.5 (~ pK<sub>a</sub>)



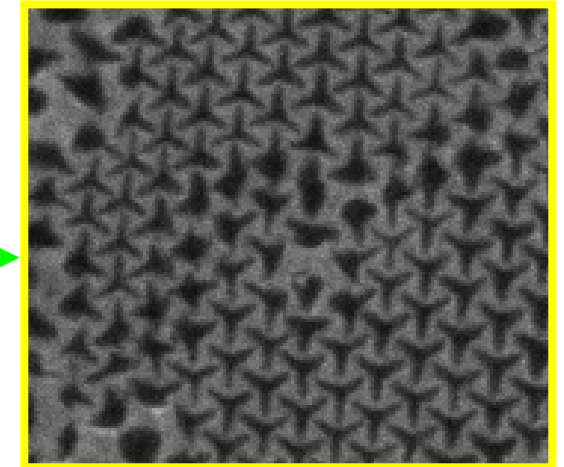
pH 5.0



pH 5.7



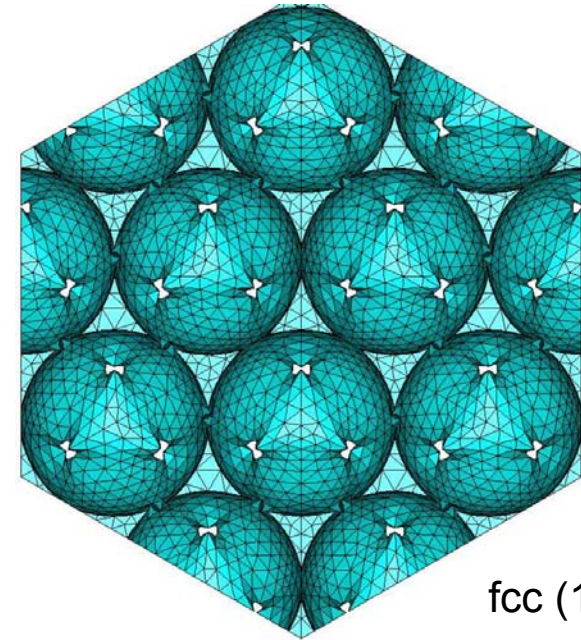
pH 6.6



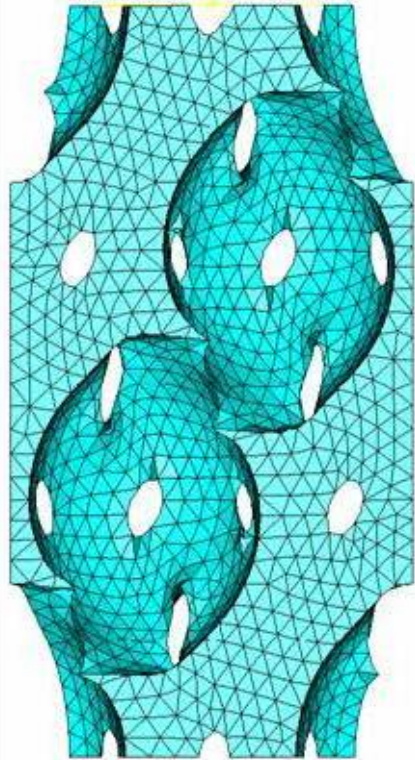
Pore deformation below pH 4.5  
Nearly complete collapse at pH 6.6

## Parameters

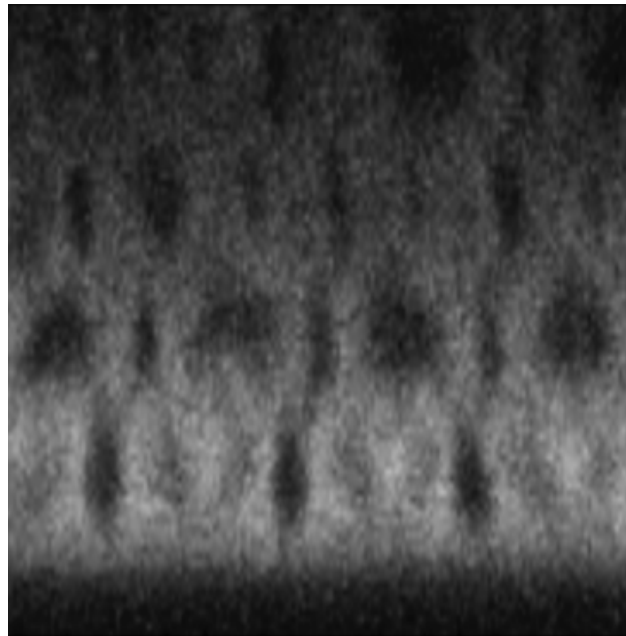
- $\frac{1}{4}$  of an inverse fcc unit cell modeled
- Periodic boundary conditions
- Bottom surface does not move vertically
- Thermal strain applied  $\rightarrow$  59% volume change
- $E = 10^6 \text{ N/m}^2$ ,  $\nu = 0.499$



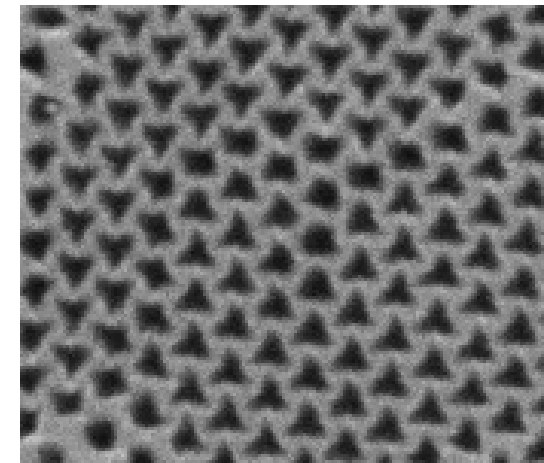
fcc (111)



fcc (110)



~50% volume change



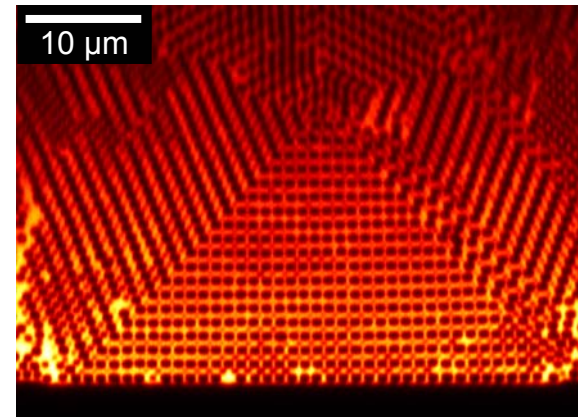
**So, how will this impact the optical response?**

## Conclusions and Acknowledgements

### Colloidal Epitaxy

Binary nanoparticle-colloid suspensions enable the formation of crack-free, low defect density dry colloidal crystals

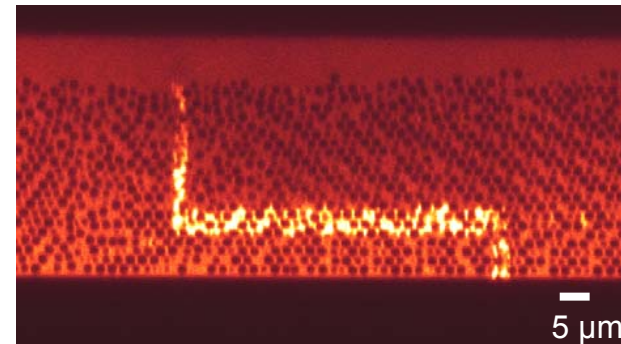
**Dr. Wonmok Lee, Dr. Michael Bevan, Prof. Jennifer Lewis**



### Waveguides

Direct writing of 3-D structures in colloidal crystals through multiphoton polymerization

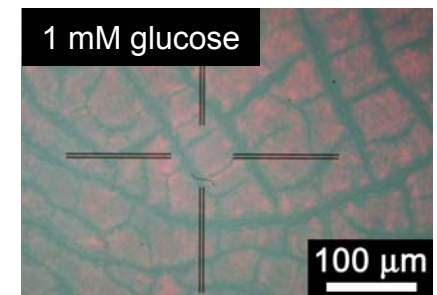
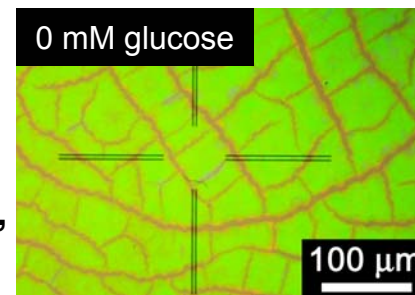
**Stephanie Pruzinsky, Dr. Wonmok Lee**



### Chemical Sensors

Optically active structures formed from chemically responsive inverse opal hydrogels

**Yun-Ju (Alex) Lee, Stephanie Pruzinsky, Carla Heitzman, Walter Frey, Prof. Harley Johnson**



Funding: NSF, DOE, ARO – MURI, Beckman Foundation, 3M

Paul Braun: pbraun@uiuc.edu; www.mse.uiuc.edu