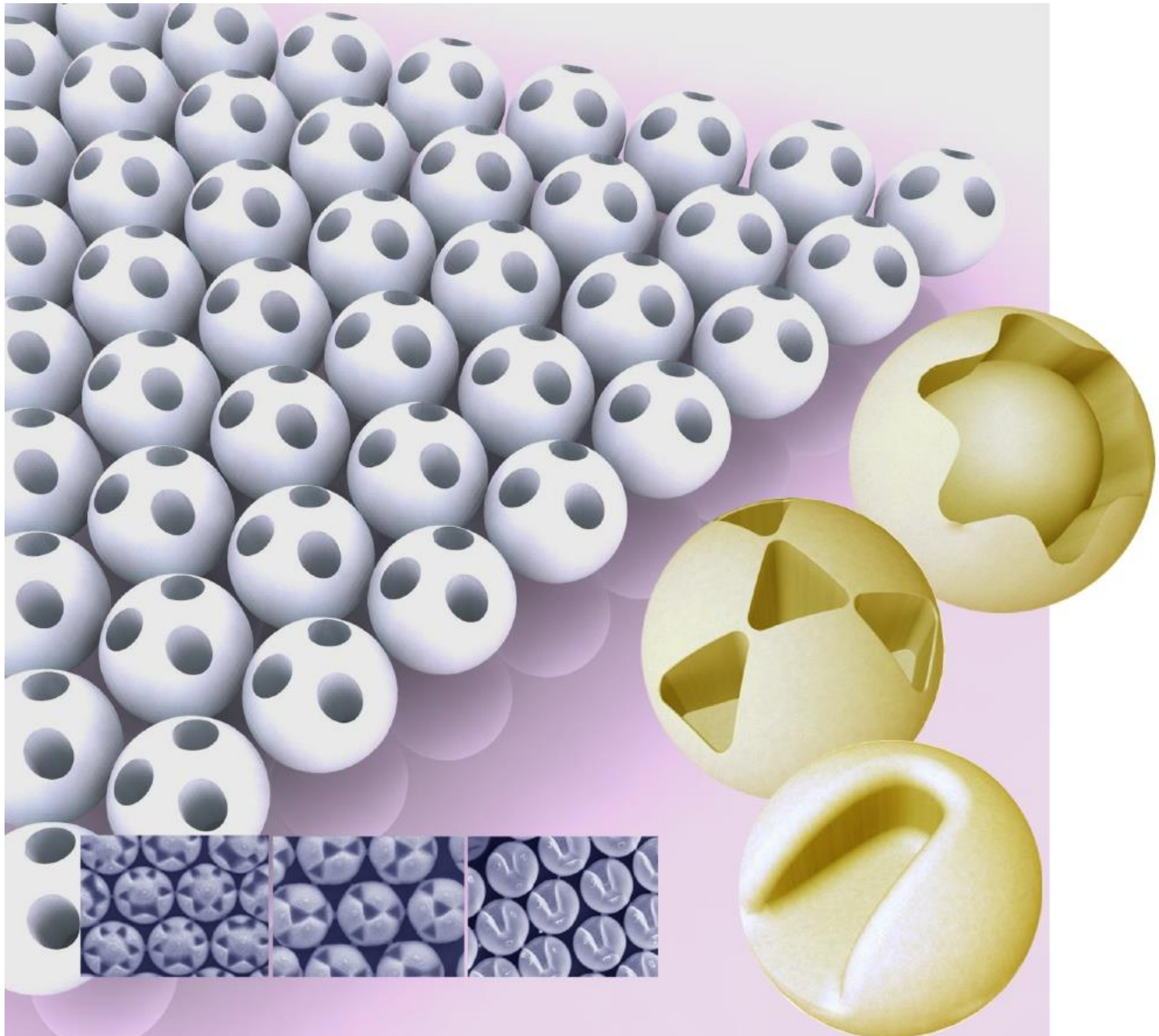
Self-Assembly of Colloidal Particles



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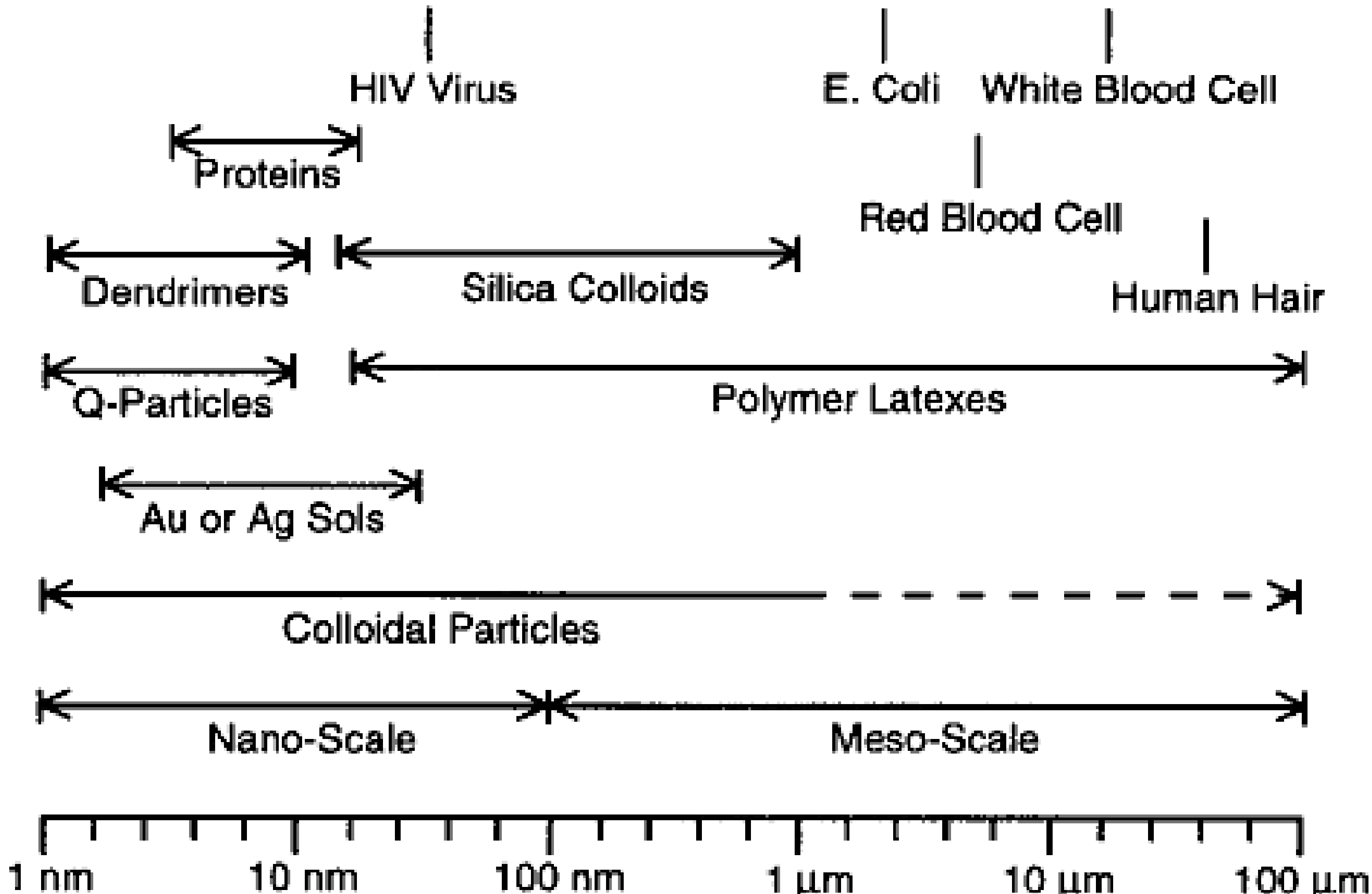
Representative Colloidal Systems

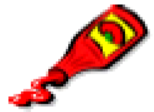


(*Adv. Mater.* **12**, 693, 2000)

Examples of Colloidal Dispersions

Food industry

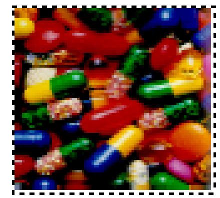
- Dairy products
- Dressings
- Chocolate
- …



Côte d'Or

Pharmaceutics and cosmetic

- Water-insoluble pharmaceutics
- All kind of gels, emulsions and cosmetics



Photographic industry

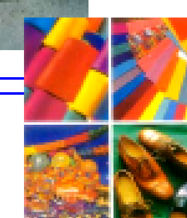
- Photographic emulsions (films)
- X-ray plates and films
- Photocopy materials (paper, ink…)

Electrical an Electronic industry

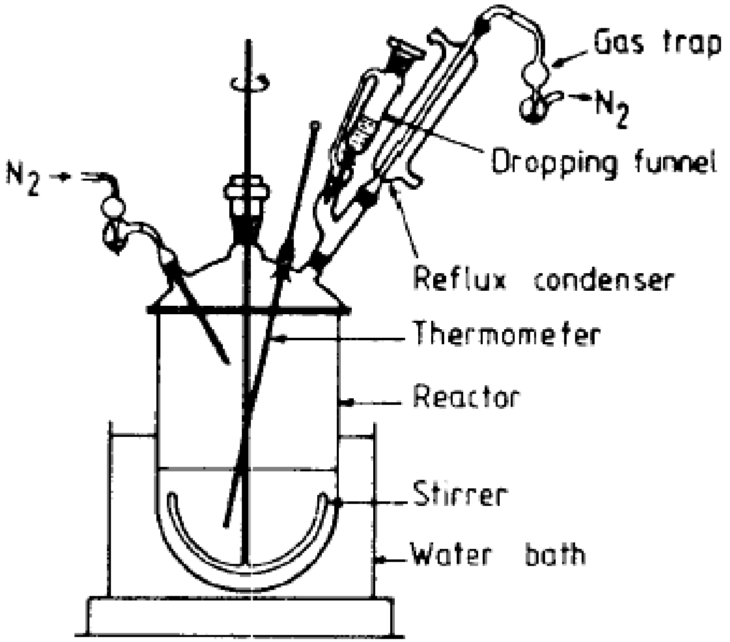
- Materials for displays:
  - phosphors
  - liquid crystals
  - Isolating materials

Other

- Agrochemicals, paints, dyestuffs, cement, bitumen….

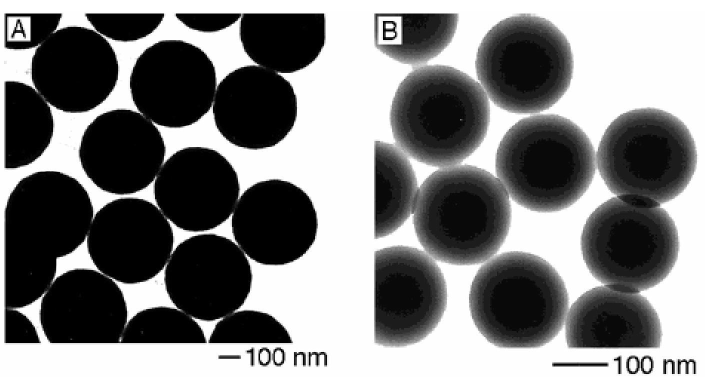


Emulsion Polymerization Preparation of Monodisperse Polymer Latex Colloids



$T = 60^\circ C$

$X-X \rightarrow 2X^{\cdot}$	free radical formation
$M + X^{\cdot} \rightarrow XM^{\cdot}$	initiation
$XM_n^{\cdot} + M \rightarrow XM_{n+1}^{\cdot}$	propagation
$XM_n^{\cdot} + {}^{\cdot}M_mX \rightarrow XM_{m+n}X$	termination

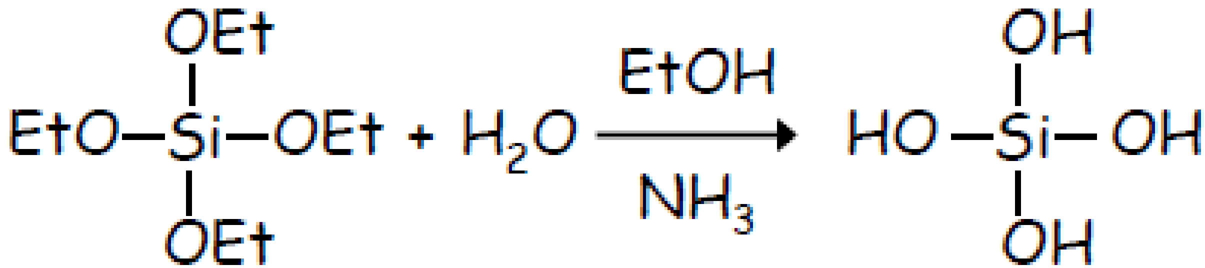


Polystyrene

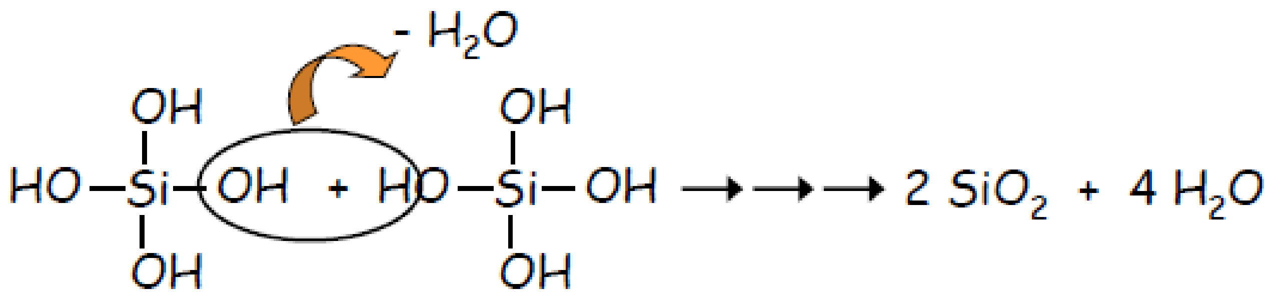
Emulsion Polymerization Process

Synthesis of Monodisperse Silica Microspheres - Stober Process

Hydrolysis:



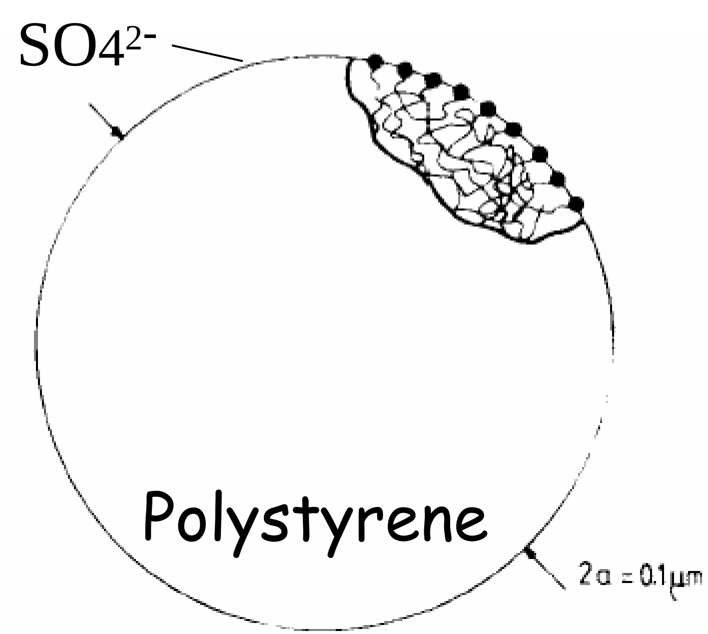
Condensation

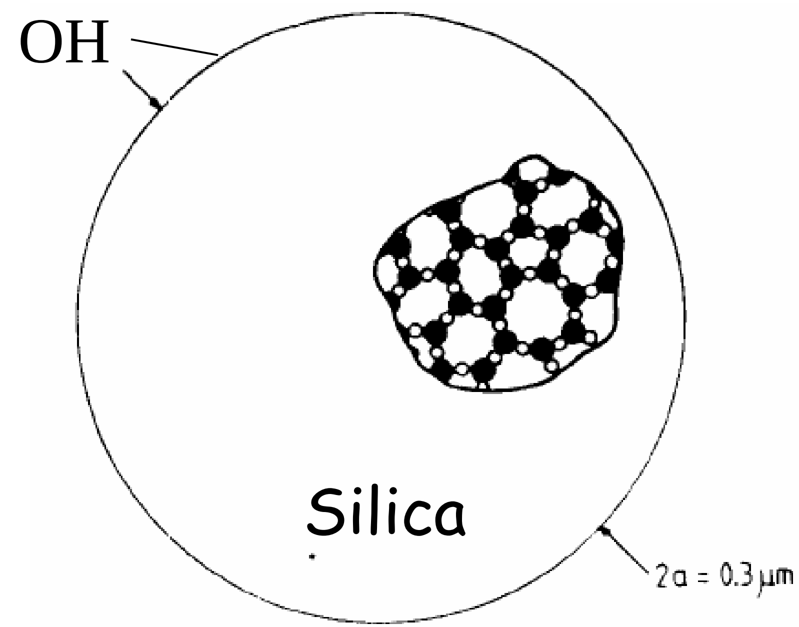


Diameter Control

Size (nm)	TEOS (M)	H_2O (M)	NH_3 (M)
275	0.3	5.0	0.5
750	0.3	10.0	2.0

Origin of Surface Charge - ζ Potential

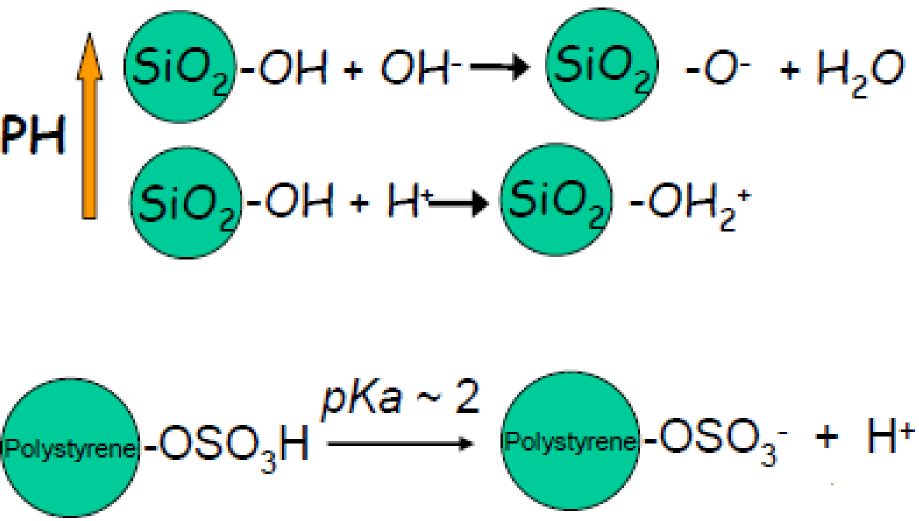


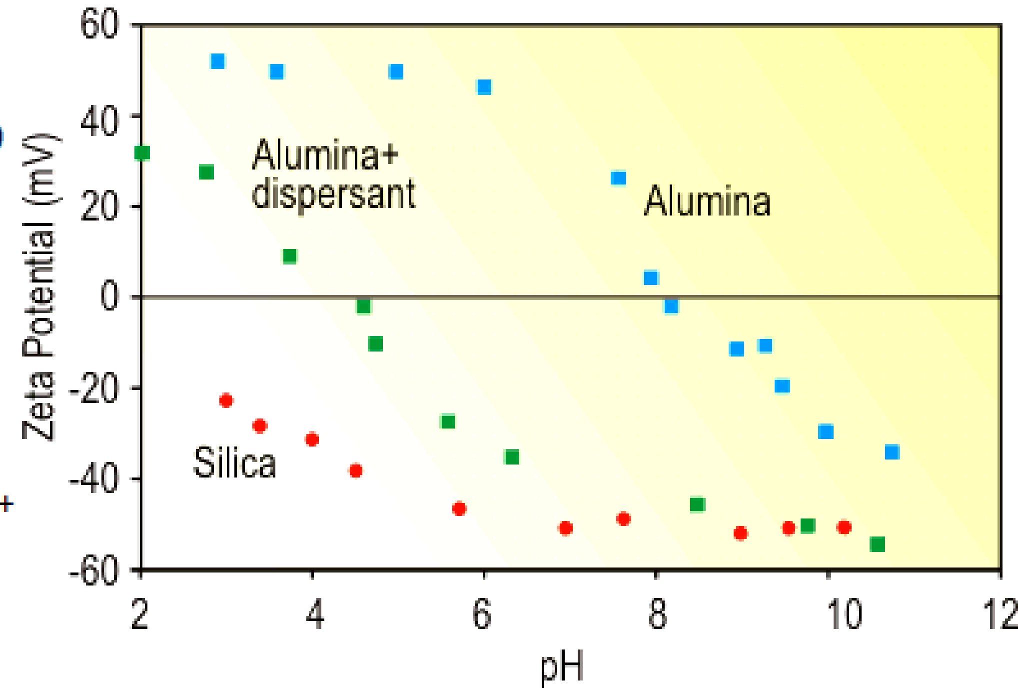


Polymer chains are entangled and each chain starts and ends with a charged group, which can dissociate in water to provide an electrostatic charge Z*e

Three-dimensional $(SiO_2)_n$ network of Stober silica

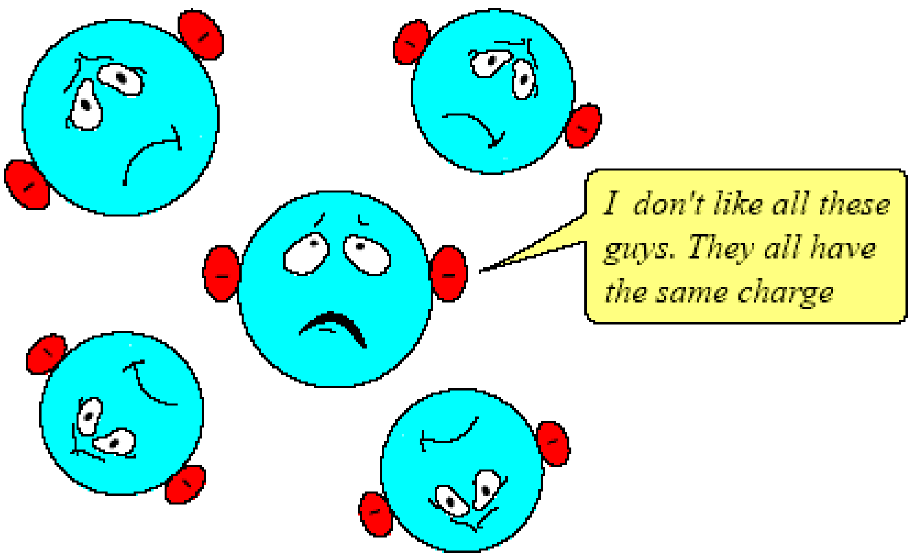
Solution pH Determines Particle ζ-Potential

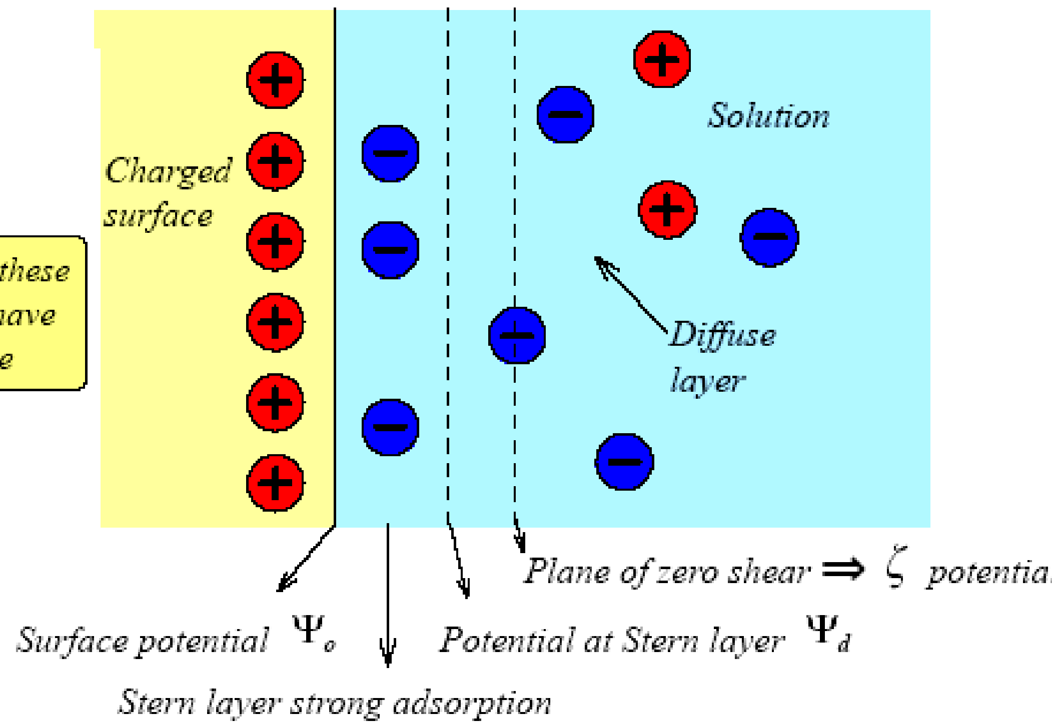




ζ-potential of polystyrene and other latex particles are pH independent, while that of silica is highly pH dependent.

Electrostatic (Repulsive) Force & Electric Double-Layer





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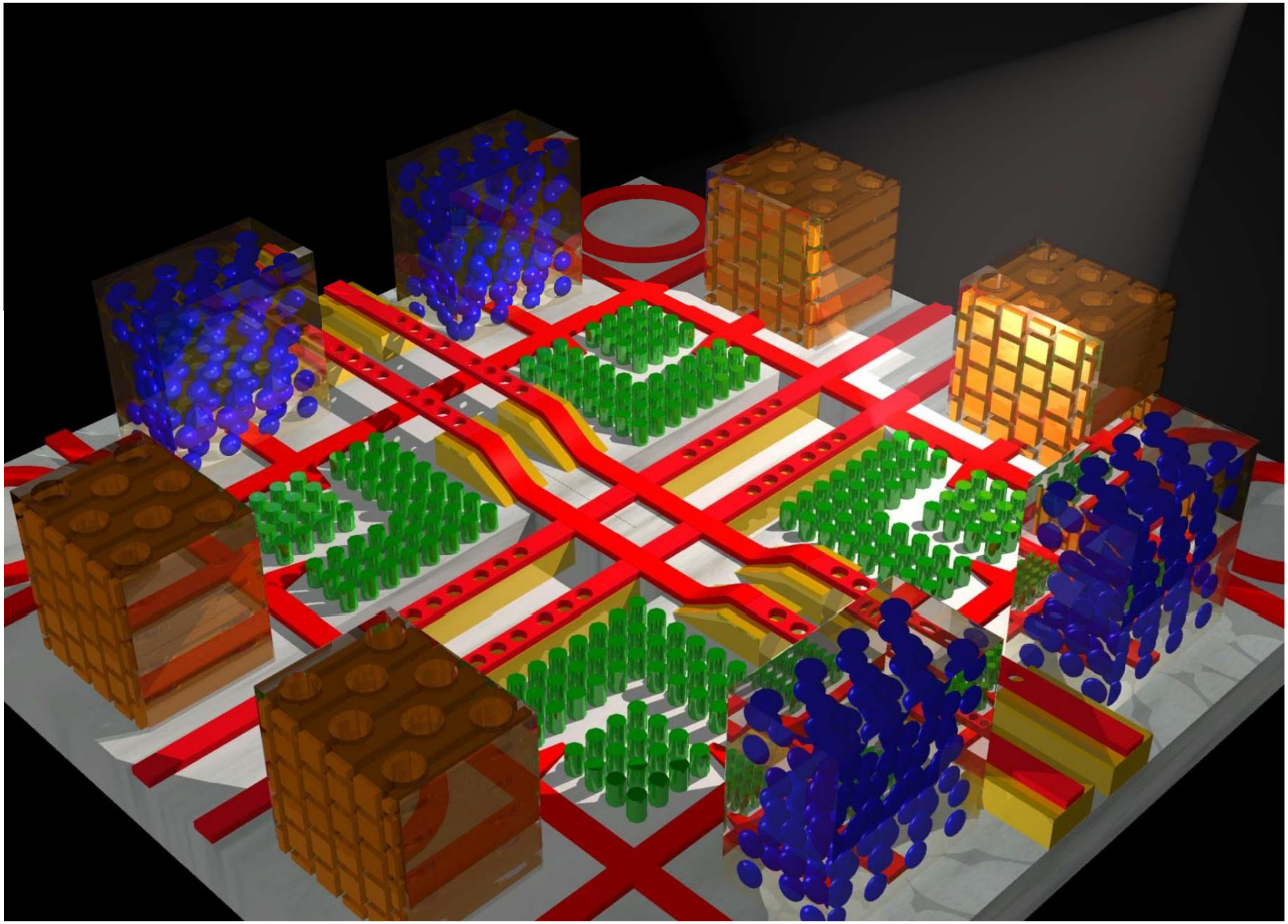
Commercial Monodisperse Colloidal Particle

Company	Contact Information	Size Range	General Comments
Bangs Laboratories [b]	(+1) 317 570 7020 (Tel) (+1) 317 570 7034 (Fax) info@bangslabs.com www.bangslabs.com	0.020–5.0 μm (Polystyrene) 0.3–5.0 μm (Silica)	Polystyrene (dyed, fluorescent, magnetic) and silica spheres Surface groups: carboxylic acid, aliphatic amine, chloromethyl amide, epoxy, hydrazide, aldehyde, aromatic amine, hydroxyl. Also streptavidin, secondary antibodies, Protein A, and biotin.
Duke Scientific [b]	(+1) 650 424 1177 (Tel) (+1) 650 424 1158 (Fax) info@dukesci.com www.dukesci.com	0.020–1.0 μm (Polystyrene) 0.5–1.6 μm (Silica)	Polystyrene (dyed, fluorescent) and silica spheres. Surface groups: carboxylic acid, sulfate, and a variety of others.
Dyno Particles AS	(+47) 63 89 71 00 (Tel) (+47) 63 89 74 72 (Fax) mike.griffiths@pss.aus.net www.pss.aus.net	0.5–20 μm	Polystyrene spheres (0–80% crosslinker DVB for 2–20 μm). Surface groups: carboxylic acid, amine, hydroxyl, and sulfate.
Interfacial Dynamics [b]	(+1) 503 684 8008 (Tel) (+1) 503 684 9559 (Fax) idclatex@teleport.com www.idclatex.com	0.020–10.0 μm	Polystyrene spheres (dyed, fluorescent). Surface groups: carboxylic acid, sulfate and a variety of others.
Nissan Chemicals	(+1) 713 532 4745 (Tel) (+1) 713 532 0363 (Fax) snowtex.com	0.003–0.100 μm	Colloidal silica (various dispersing media), antimony pentoxide.
Polyscience [b]	(+1) 215 343 6484 (Tel) (+1) 215 343 0214 (Fax) polysci@tigger.jvnc.net www.polysciences.com	0.05–90 μm (Polystyrene) 0.05–0.45 μm (Silica)	Polystyrene (dyed, fluorescent), silica, and glass spheres. Surface groups: carboxylic acid and sulfate.
Seradyn	(+1) 317 266 2956 (Tel) (+1) 317 266 2991 (Fax) seradyn_particles@seradyn.com ww.seradyn.com	0.05–5.0 μm	Polystyrene spheres (dyed, fluorescent, magnetic). Surface groups: carboxylic acid, streptavidin, and sulfate.

Photonic Crystals: Periodic Surprises in Electromagnetism



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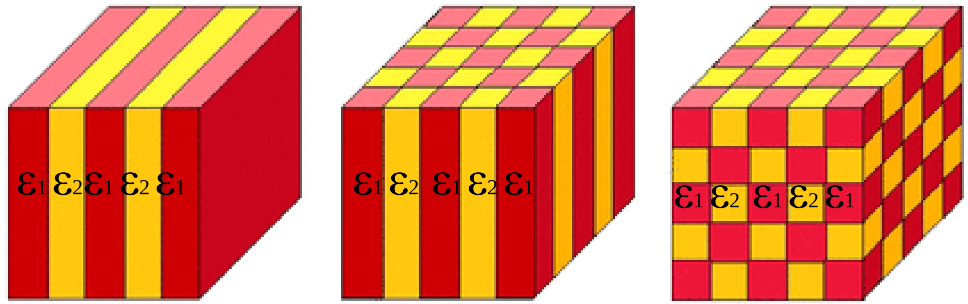
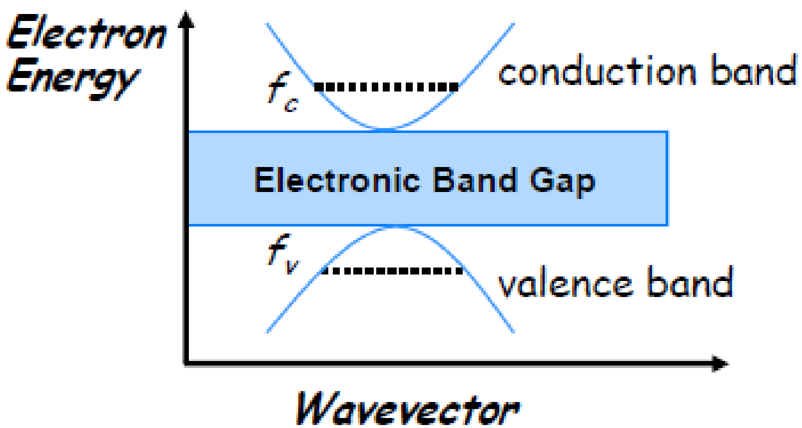
Photonic Crystals

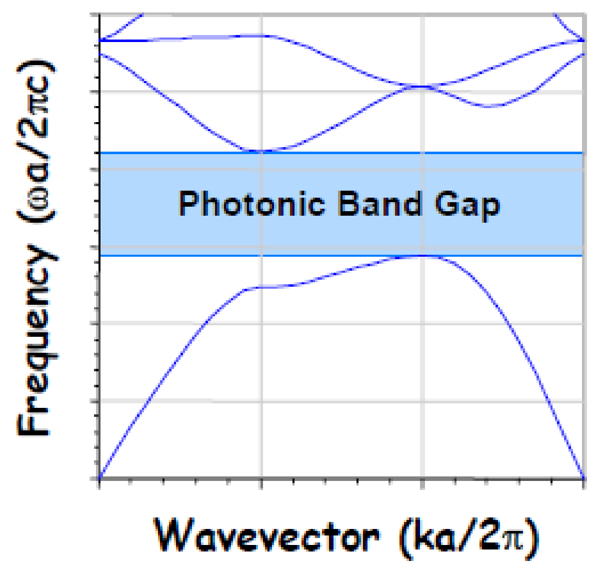
Photonic crystals are periodic dielectric materials.



1-D 2-D 3-D

(J.D. Joannopoulos et al., *Photonic Crystals: Modeling the Flow of Light*, 1995)





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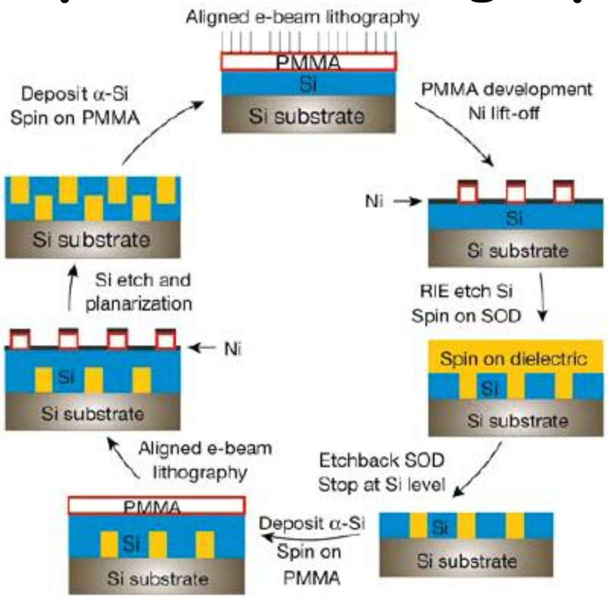
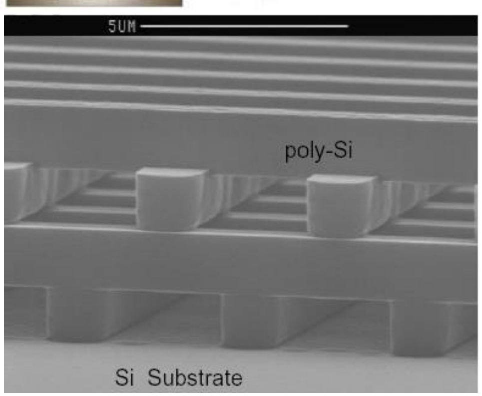
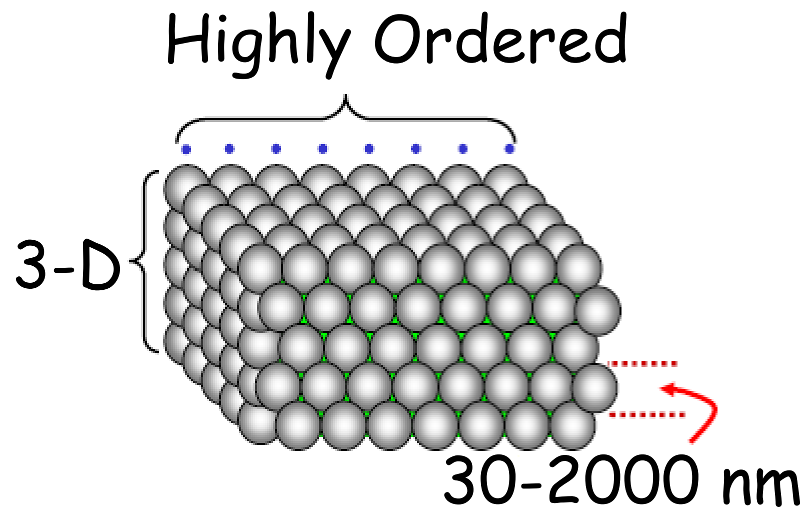
Fabrication of 3D Photonic Crystals

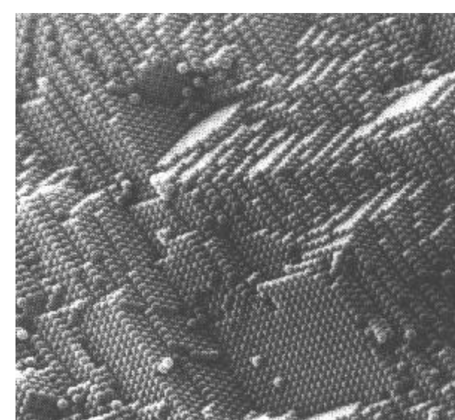
Top-Down Lithography





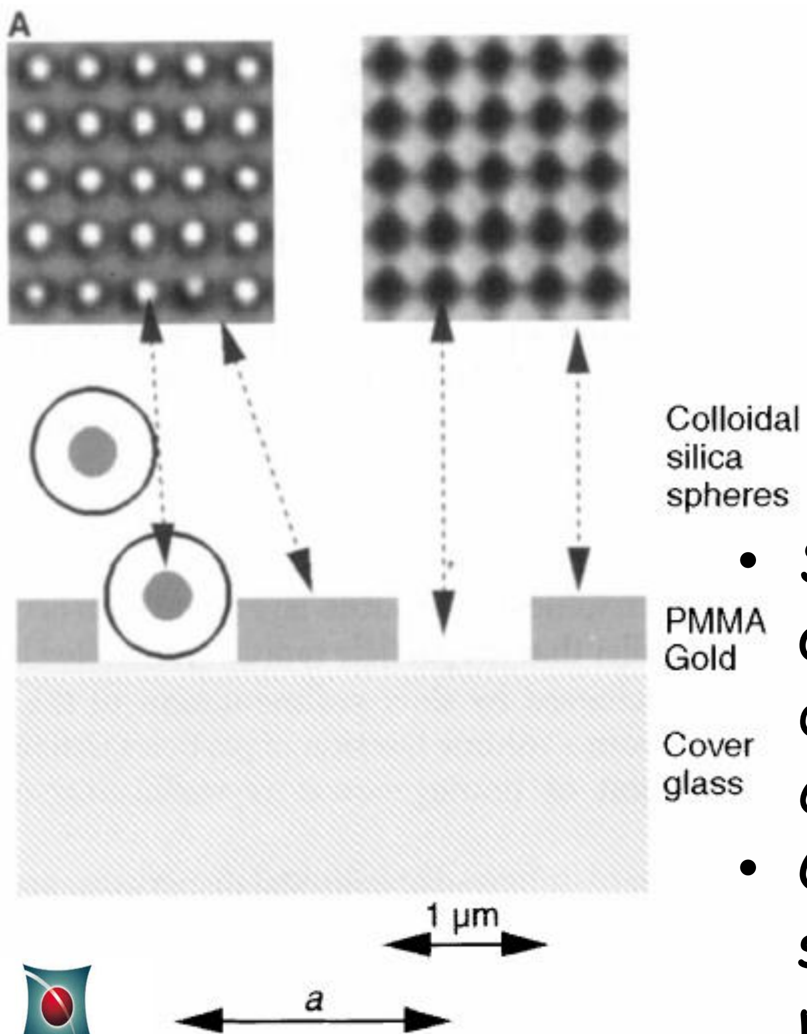
Bottom-Up Assembly

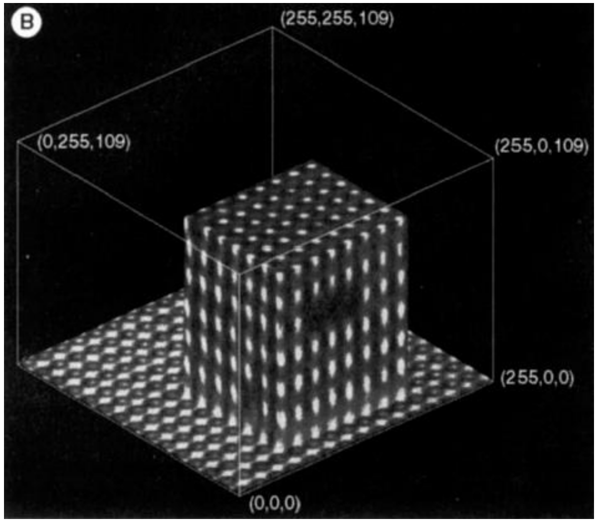




(M. Qi et al., *Nature* **429**, 538, 2004) (http://aussie-opal.com/lr2mulbl.jpg)

Colloidal Epitaxy for Colloidal Single Crystals





- Slow deposition of colloidal particles onto a patterned substrate can direct the crystallization of bulk colloidal single crystals.
- Confocal microscopy reveals real-space structure of fluorescent particles.

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

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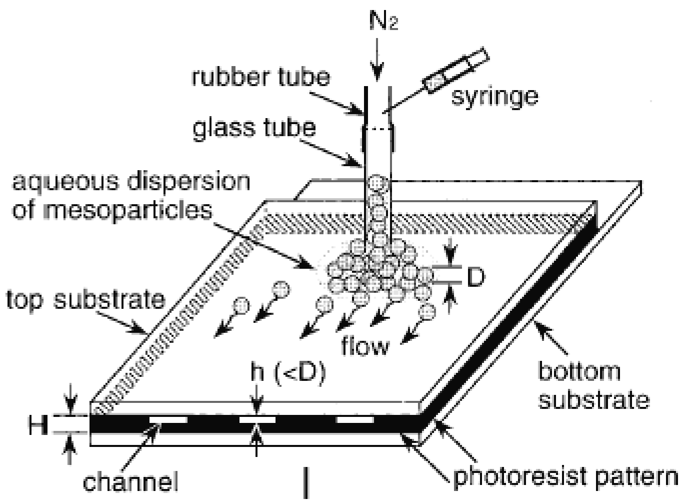
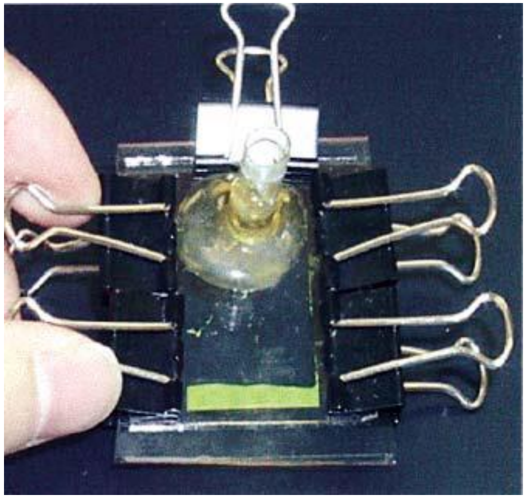
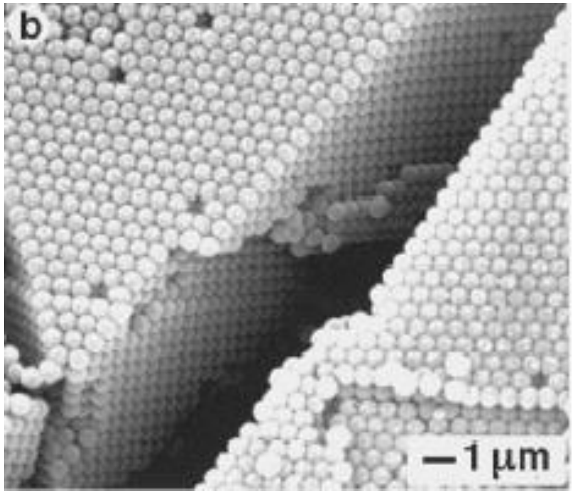
Physical Confinement Induced Crystallization







- A large variety of colloidal particles, including silica, polymer latex, titania, AgSe, Se have been assembled using the physical confinement method.
- Patterned relief structures on substrate lead to assemblies of colloidal particles with different surface topologies.

(*Adv. Mater.* **10**, 1028, 1998)

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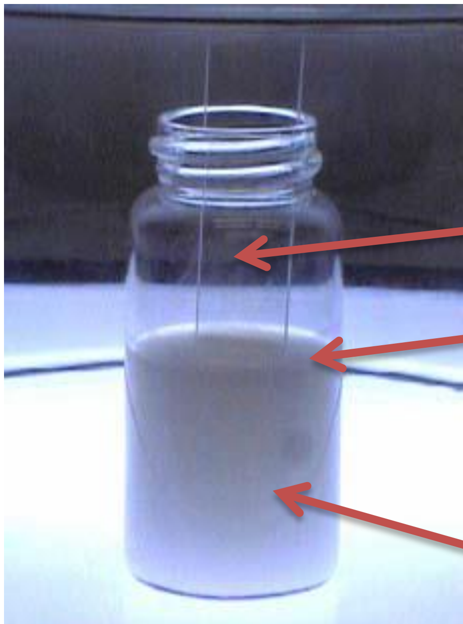
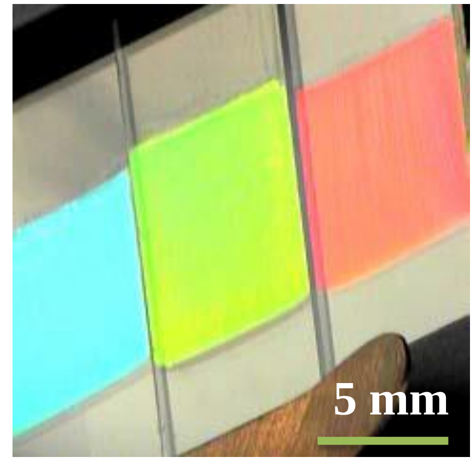
Vertical Convective Self-Assembly



Glass slide

Glass vial

Silica/ethanol dispersion

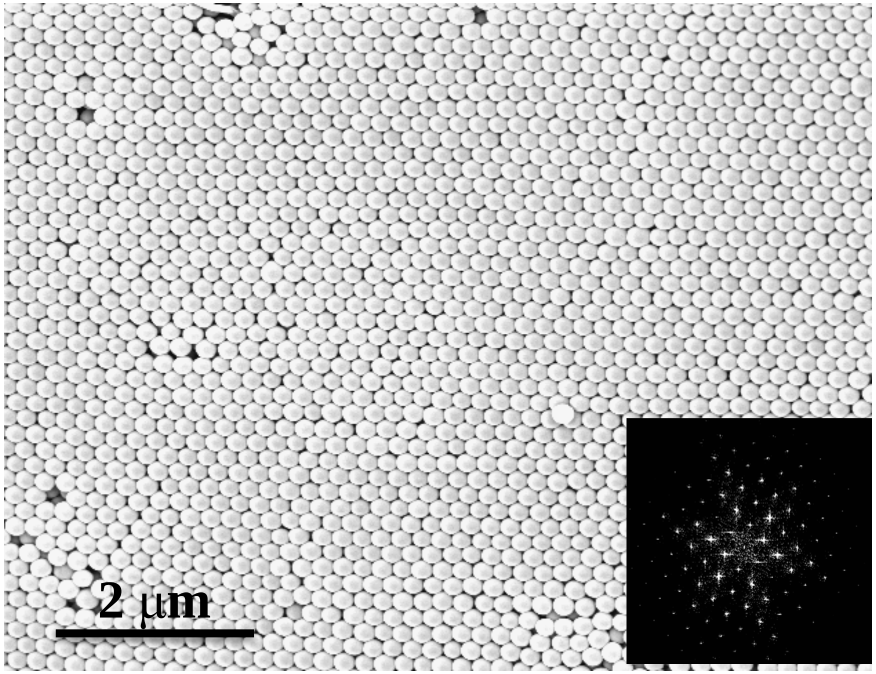


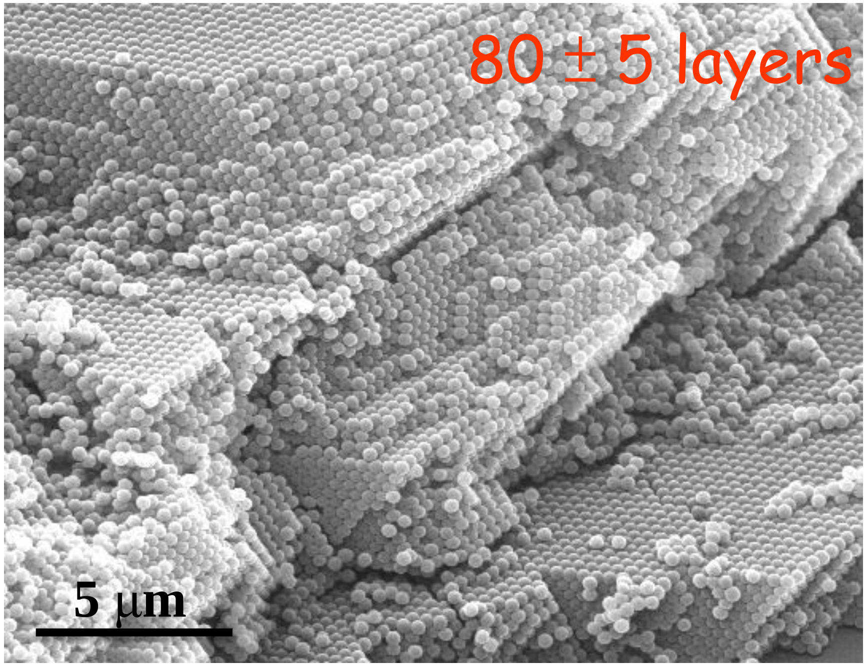
From left to right: 310 nm, 350 nm, 380 nm silica spheres.

- Substrate: glass, Si.
- Substrate shapes: planar, curved.
- Colloids: silica, latex.
- Crystal size: centimeters.
- Crystallization time: days.

(*Chem. Mater.* **12**, 1431, 1999)

Planar Colloidal Single Crystals





- Single-crystalline ordering over centimeter scale.
- Method provides thick (~ 100 μm) films.

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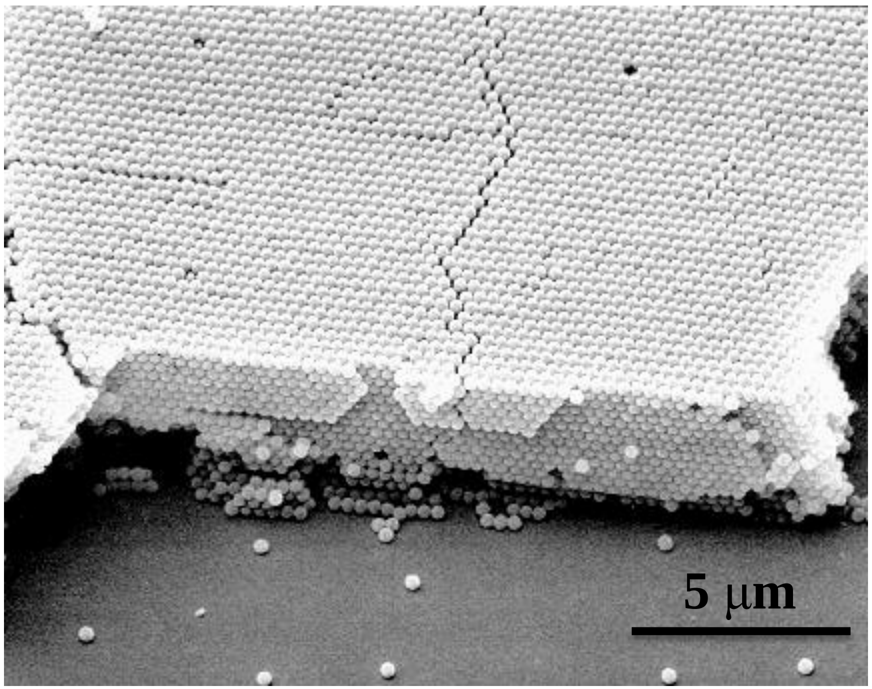
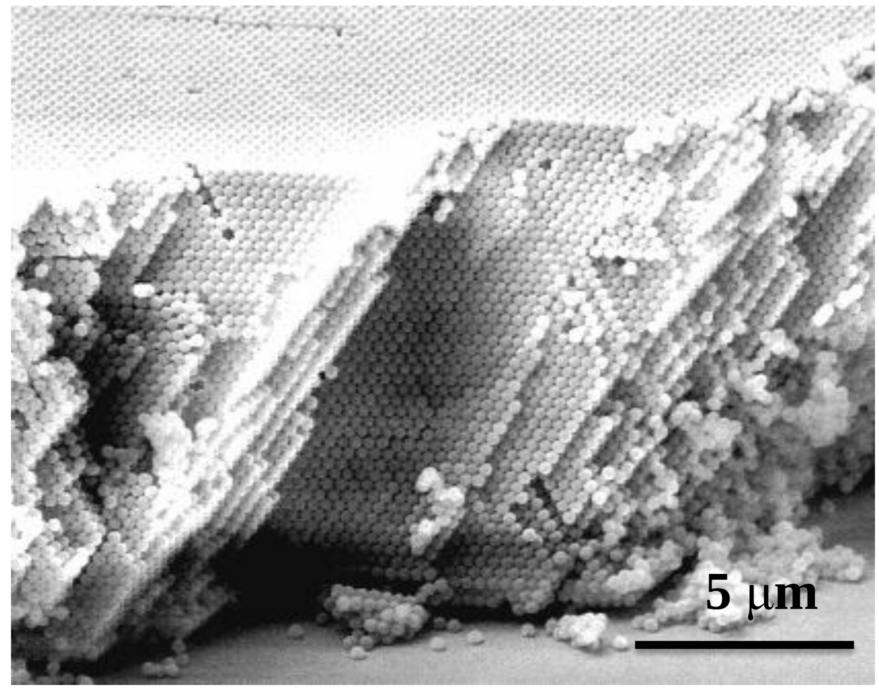
Crystal Thickness & Particle Conc.



Lower Particle volume fraction
--- 10 layers



Higher Particle volume fraction
--- 50 layers

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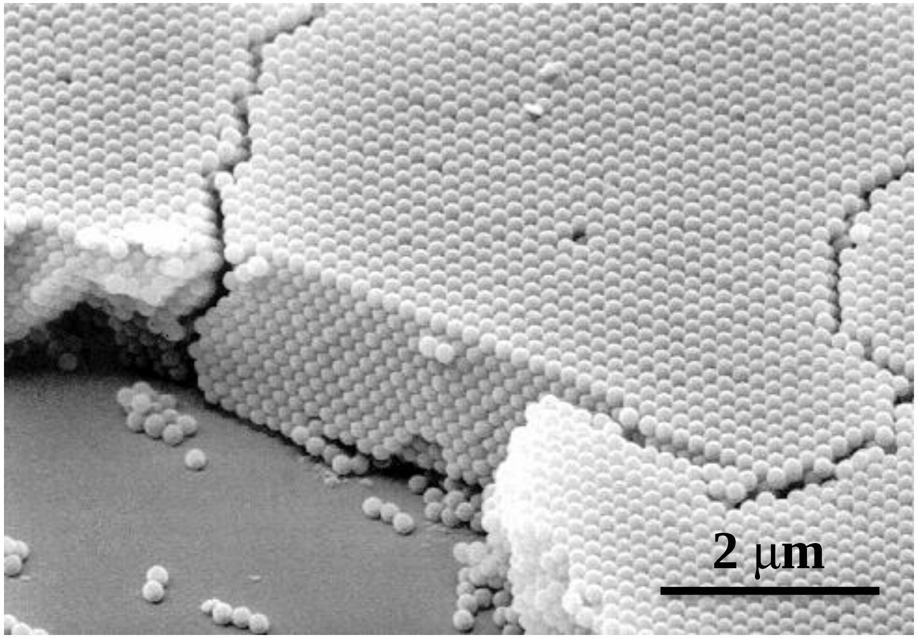
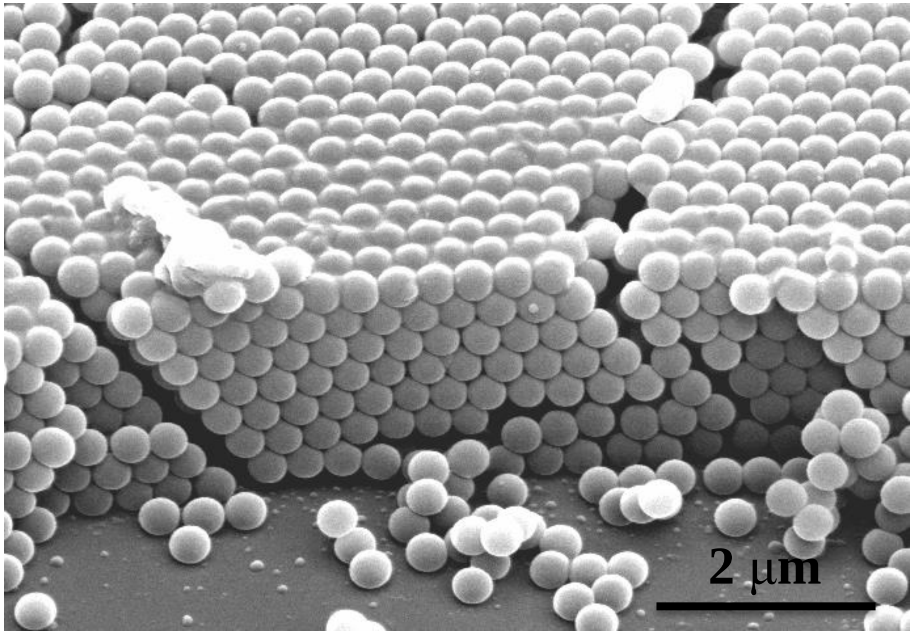
Crystal Thickness & Particle Size



Particle size = 200 nm
--- 14 layers



Particle size = 400 nm
--- 7 layers

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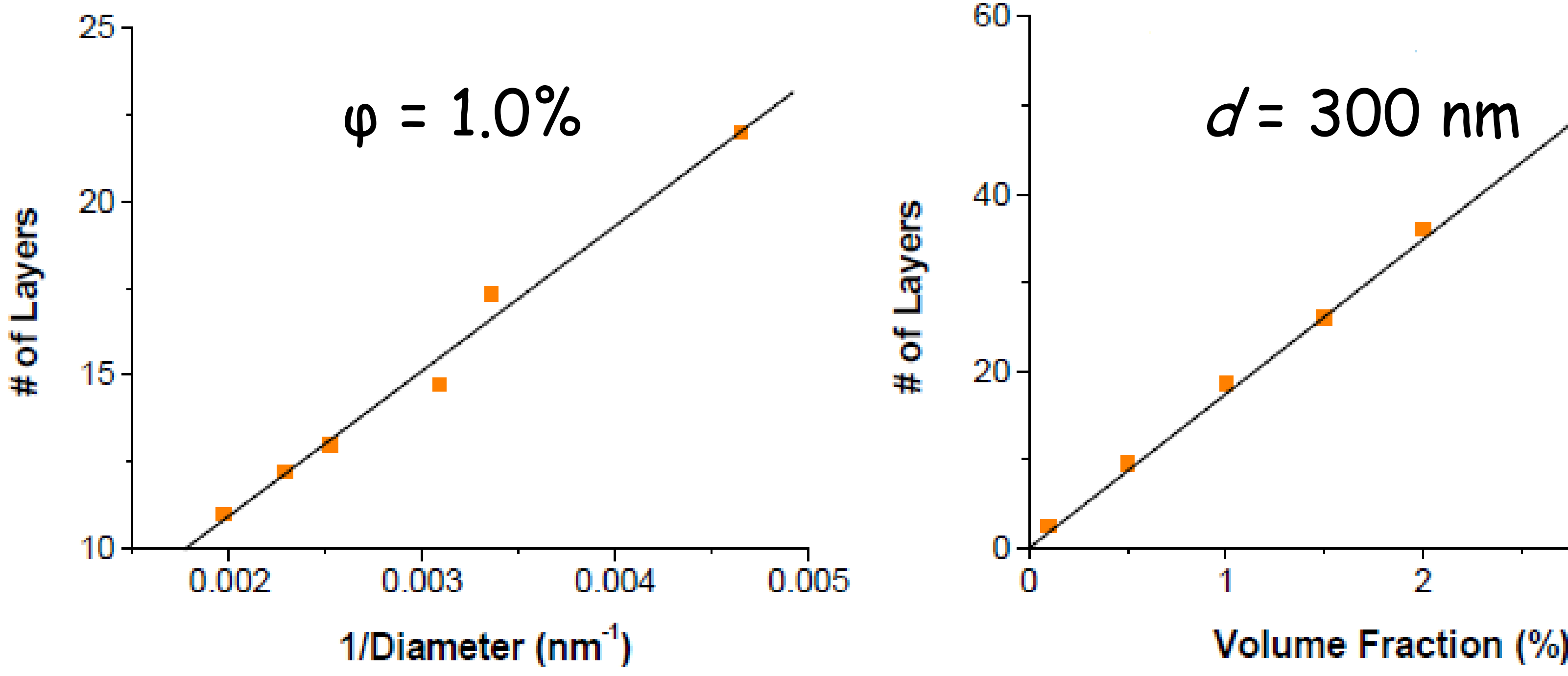
Good Agreement of Data and Theory Using Film Formation Model



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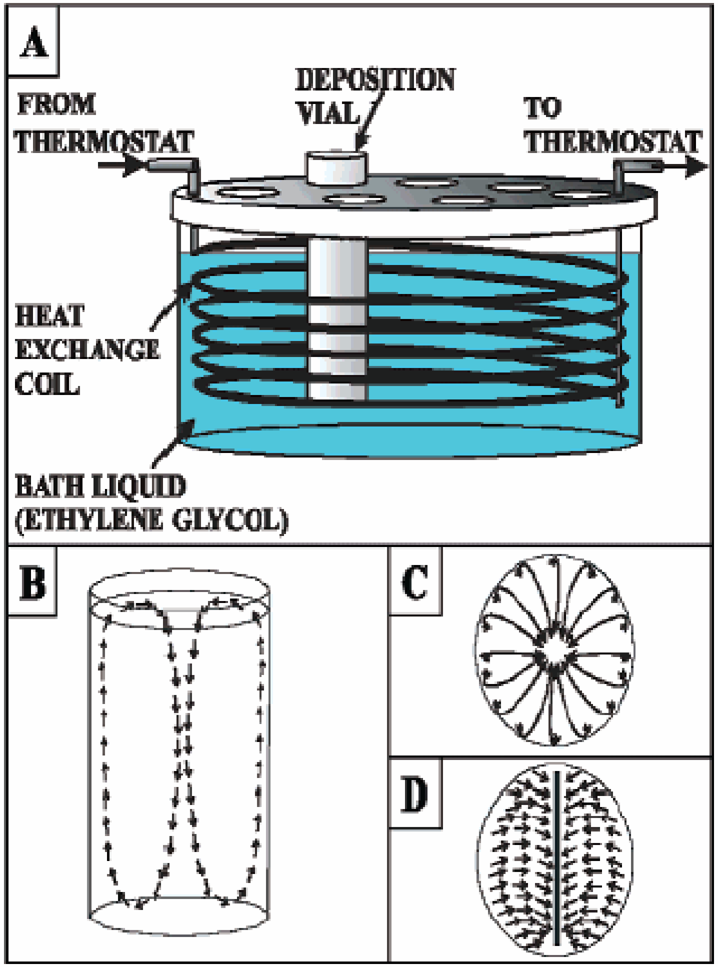
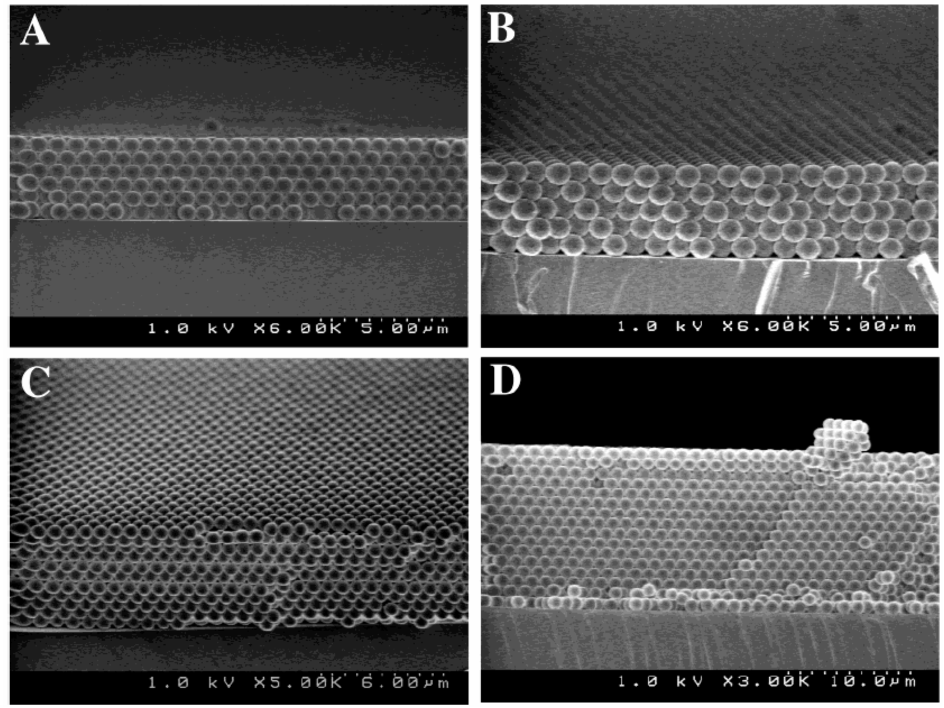
Extending the Size Range of Particles Using Convective Self-Assembly





Convection induced by a temperature gradient keeps sedimenting large particles suspended in the dispersion during the convective self-assembly process.

(*J. Am. Chem. Soc.* **125**, 15589, 2003)

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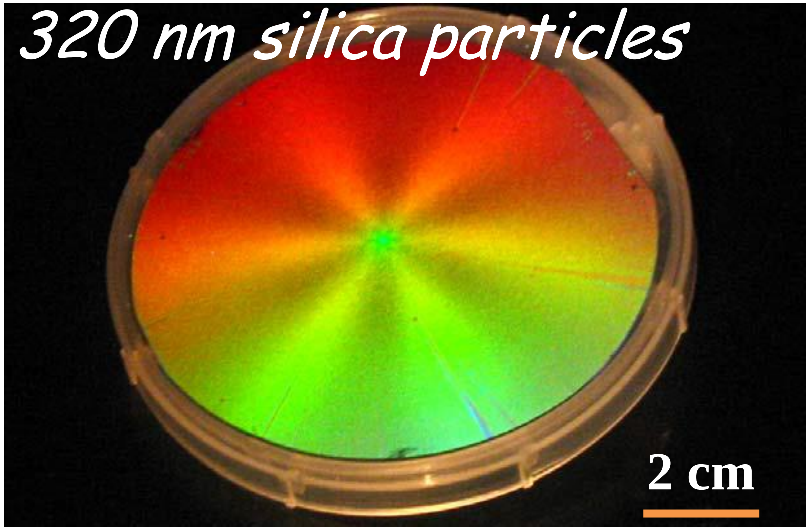
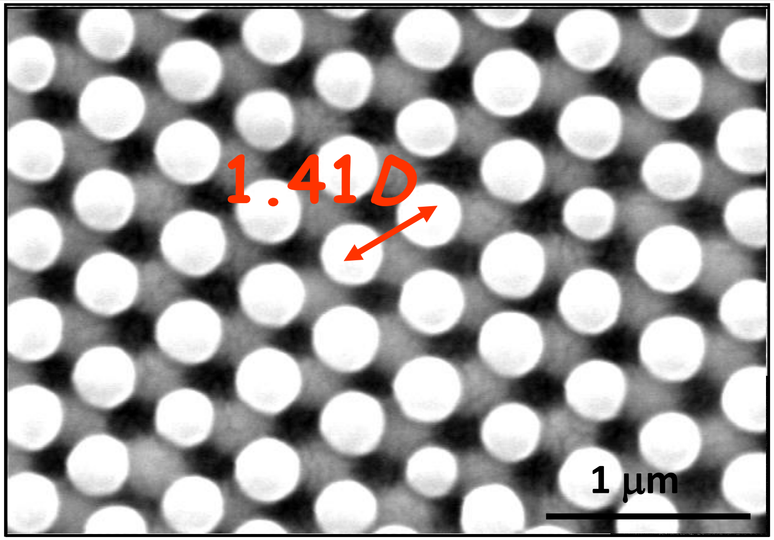
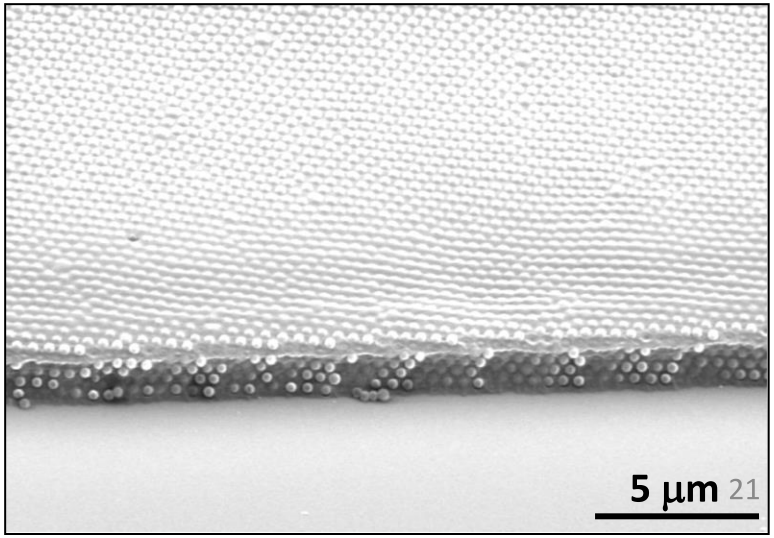
Colloidal Crystals by Spin-Coating



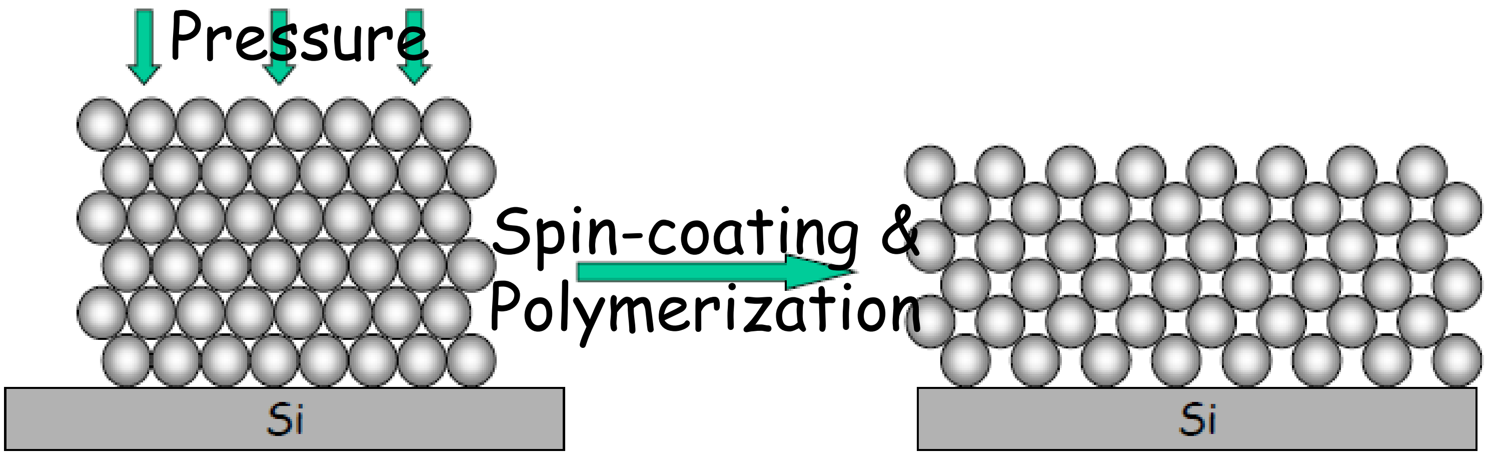




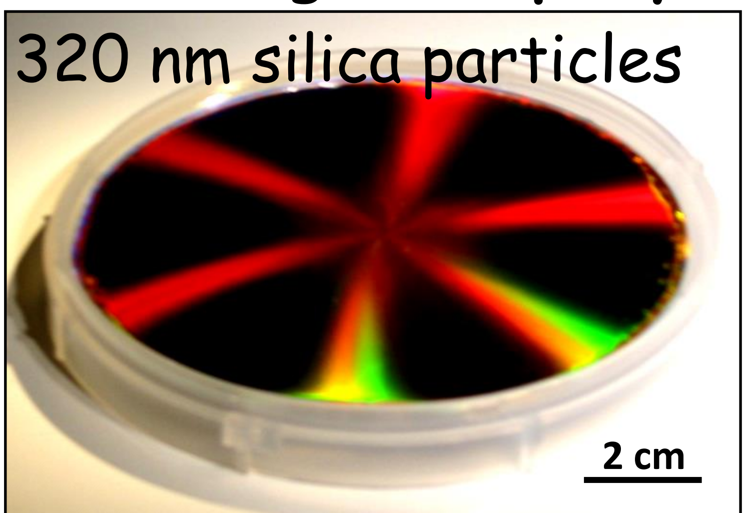
- The six-arm star is caused by Bragg's diffraction of visible light.
- The particle spacing and crystal thickness are controllable.

Jiang, P. et al, *J. Amer. Chem. Soc.* (2004)

Spin-Coating Mechansim



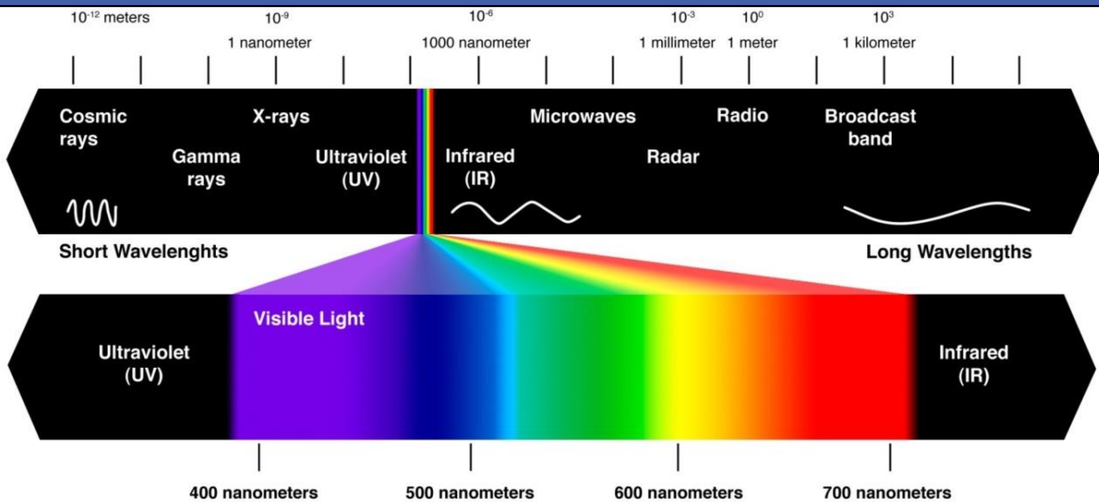
Shear aligned hcp layers **Non-close-packed crystal**



- Shear force causes the formation of hexagonal close-packed layers.
- Normal pressure created by material spin-off and polymerization squeeze hcp layers into each other to form ncp structures.

Jiang, P., *Chemical Communications* (2005)

Colloidal Crystals on Polymer

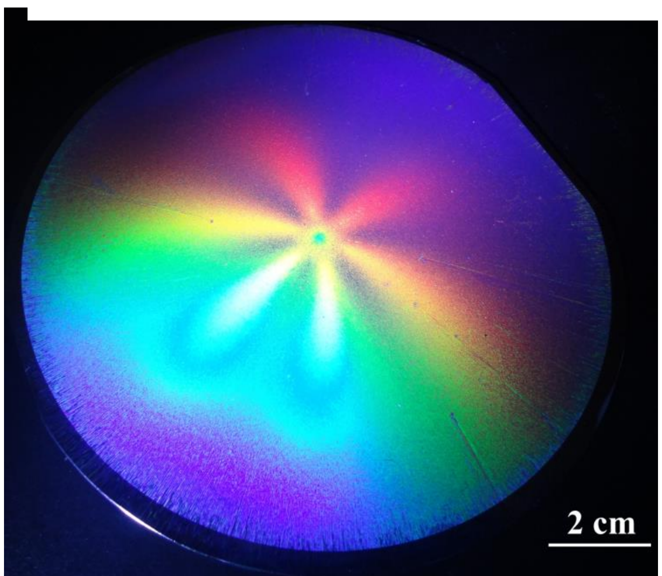


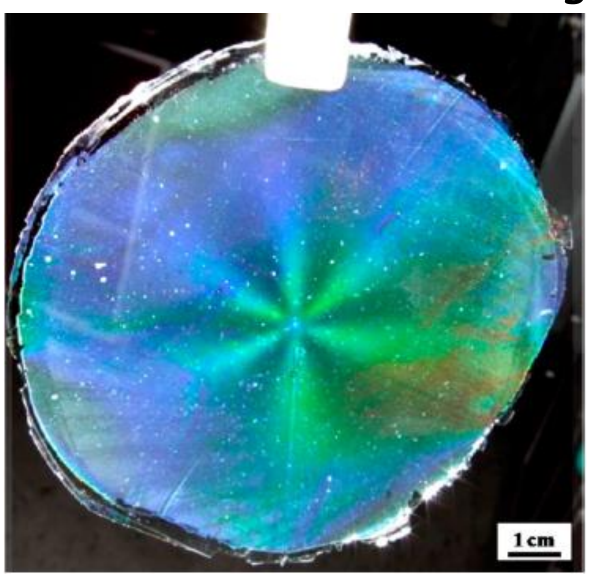
Bragg's Law

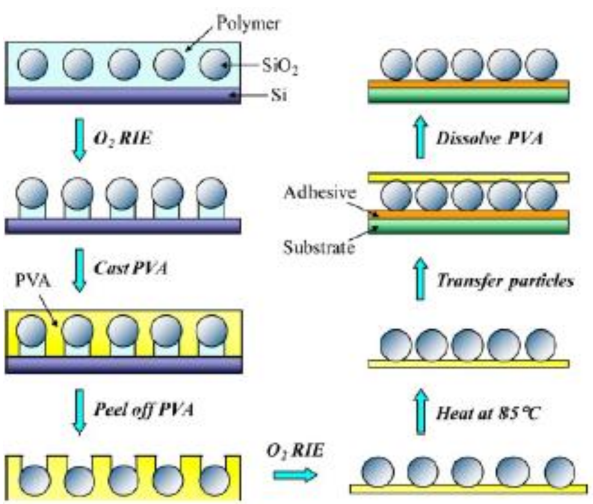
$$\lambda_{\max} = 2 n_{avg} d$$

n - Refractive Index
d - Inter-Plane Distance

Jiang, P. et al, *Chem Mater* (1999)







Yang, H. et al, *Langmuir* (2013)

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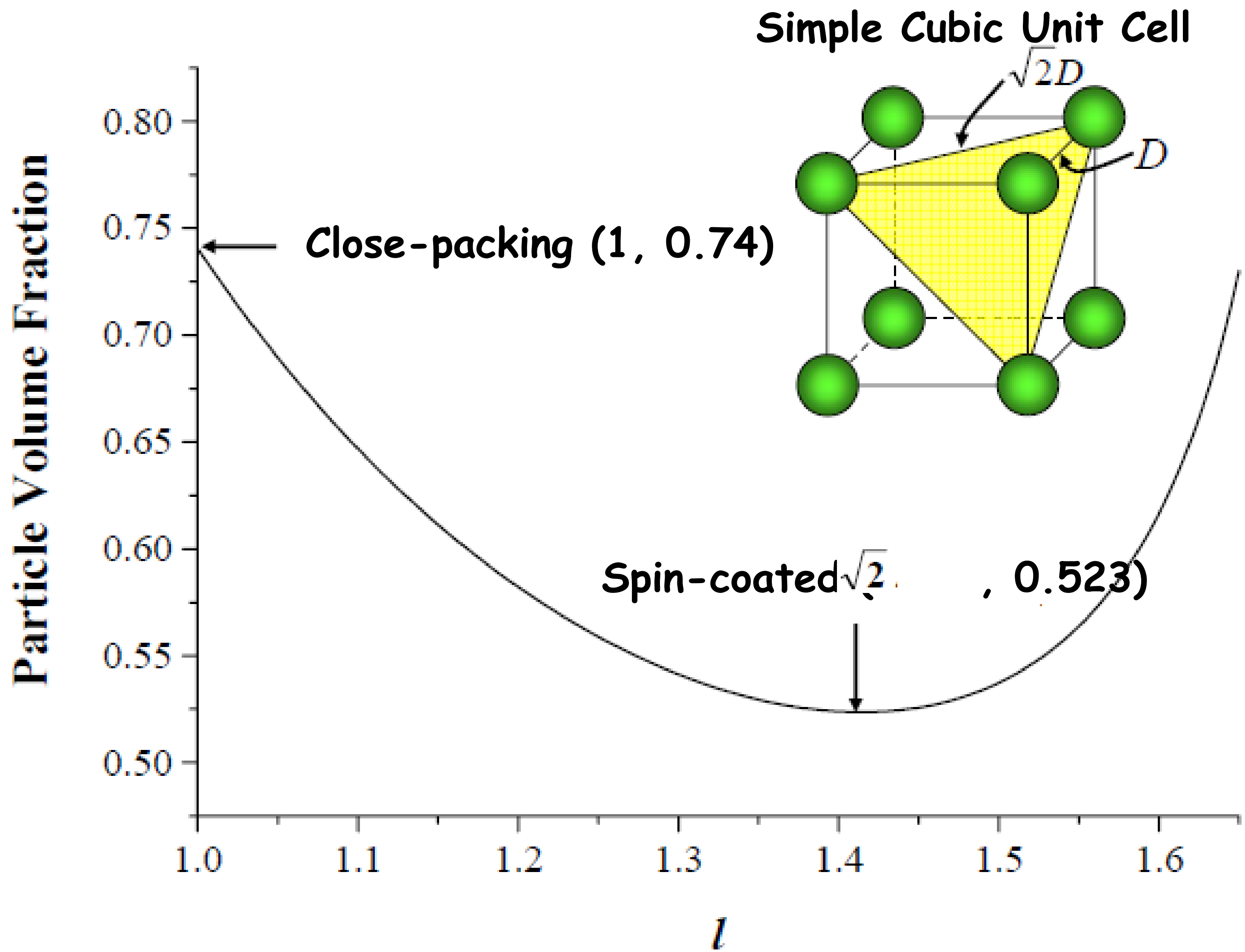
Minimal Volume Fraction Achieved by Spin Coating



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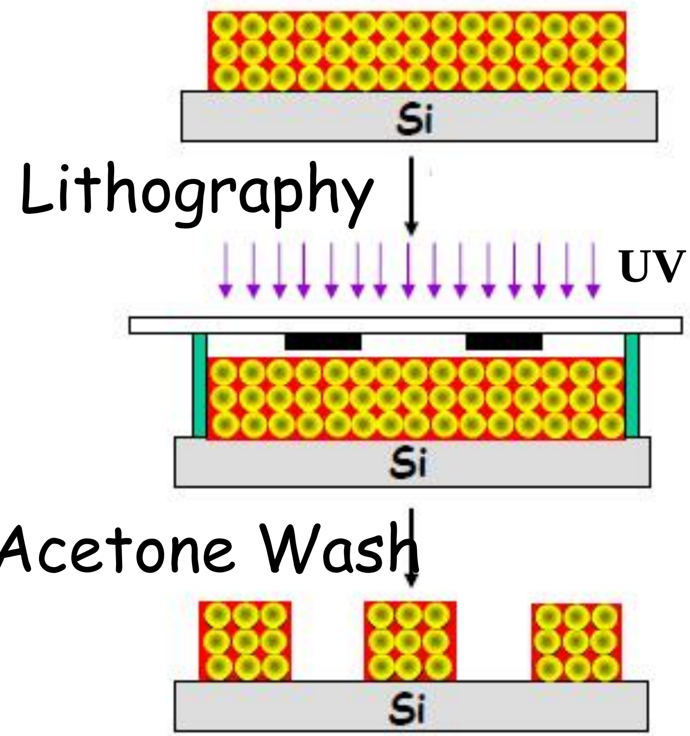
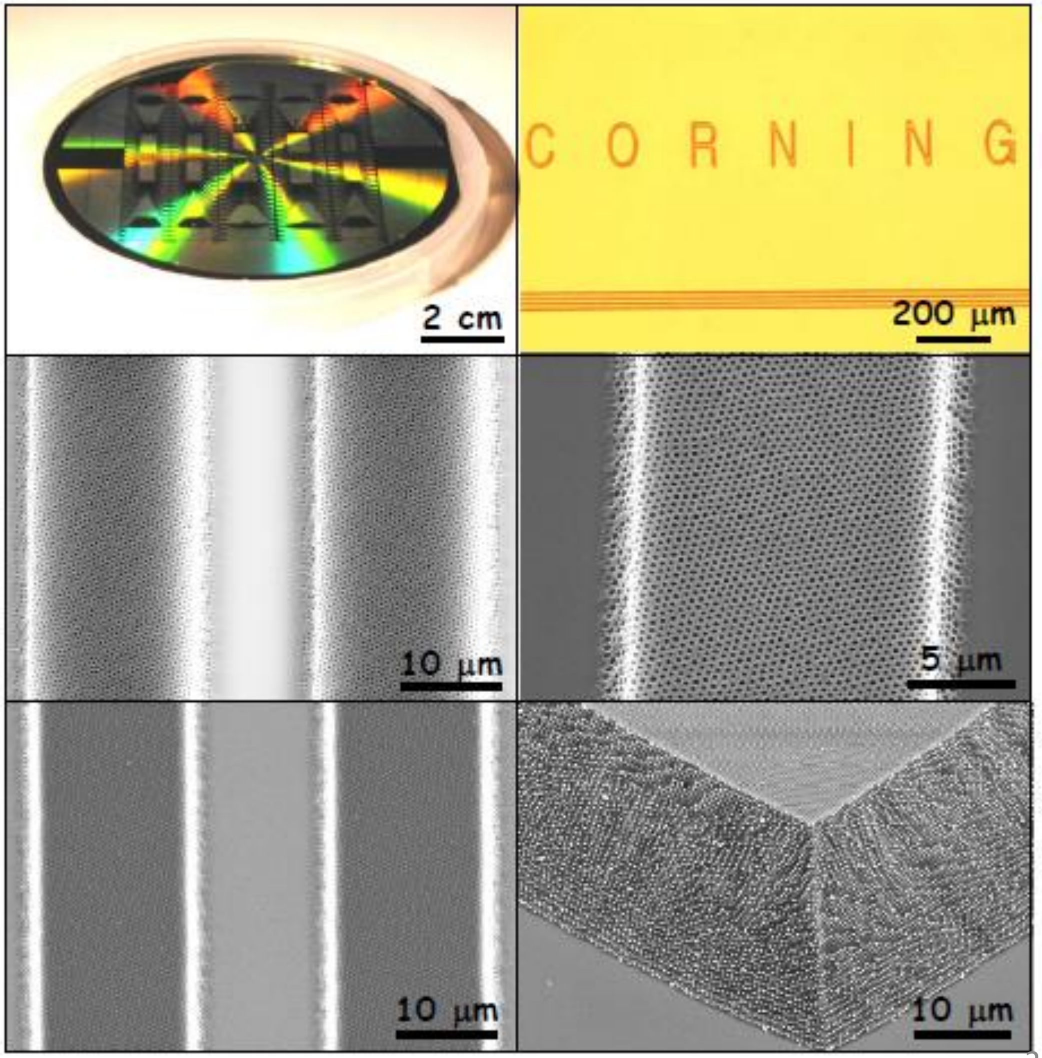
Compatible With Standard Microfabrication





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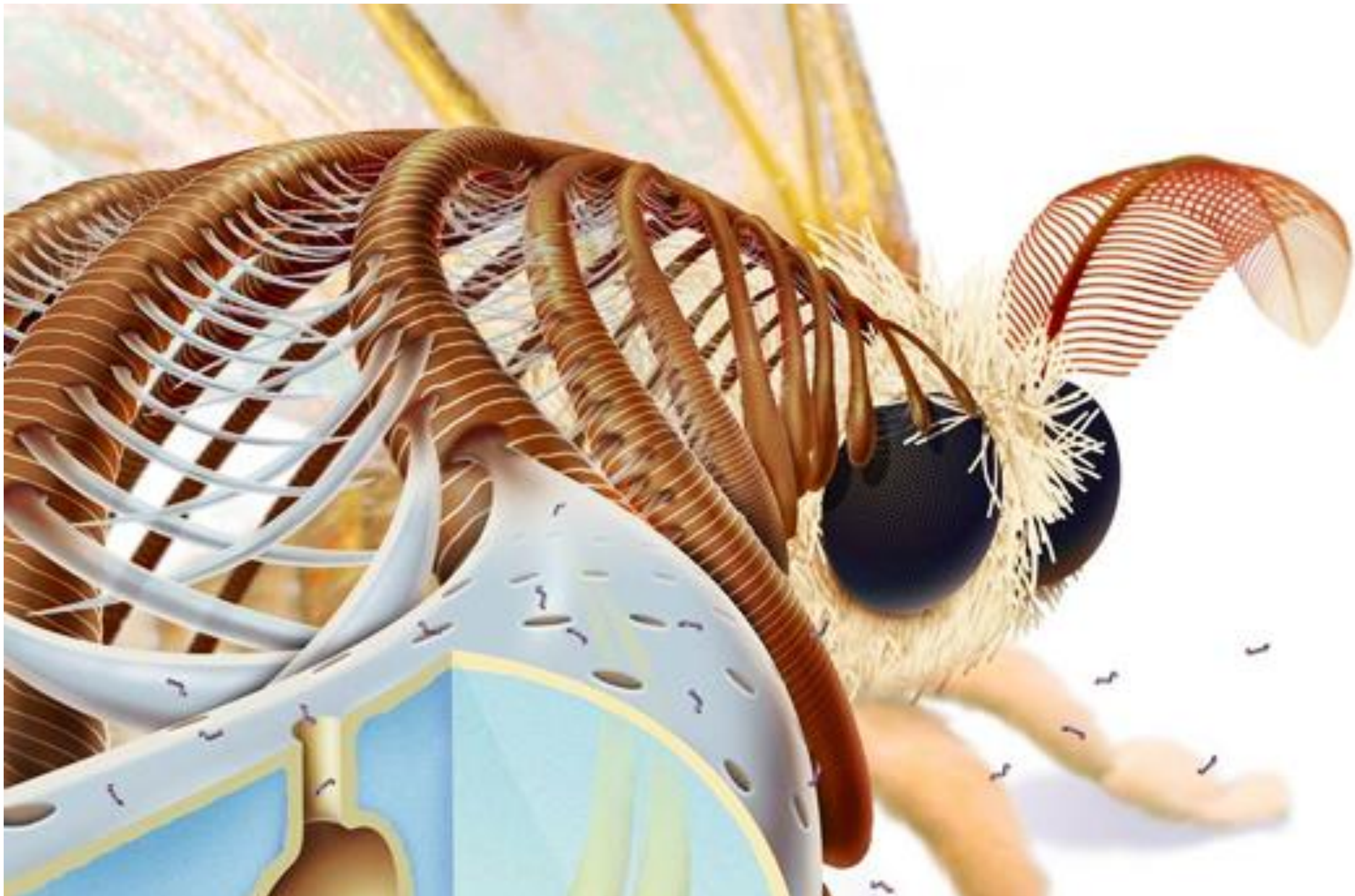
Nature is the Ultimate Nanotechnologist
Antireflection Coatings



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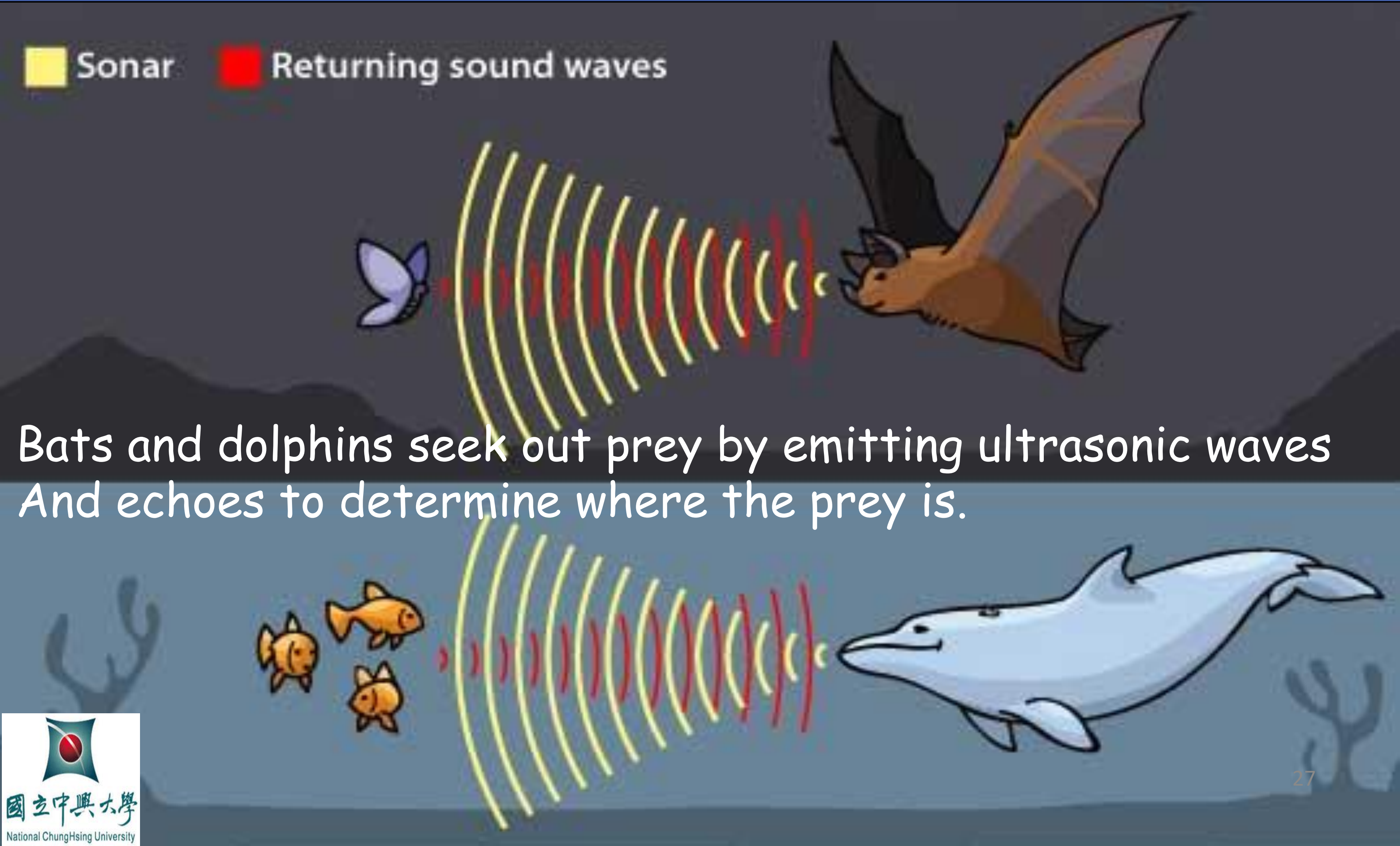
Bat / Dolphine Biosonar



Bats and dolphins seek out prey by emitting ultrasonic waves
And echoes to determine where the prey is.

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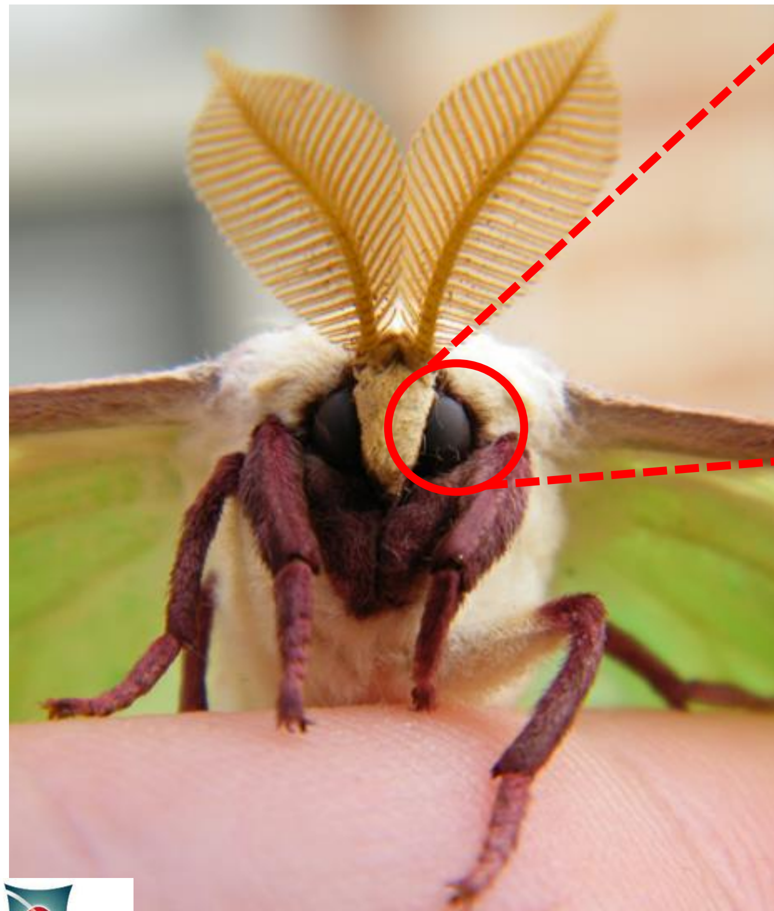
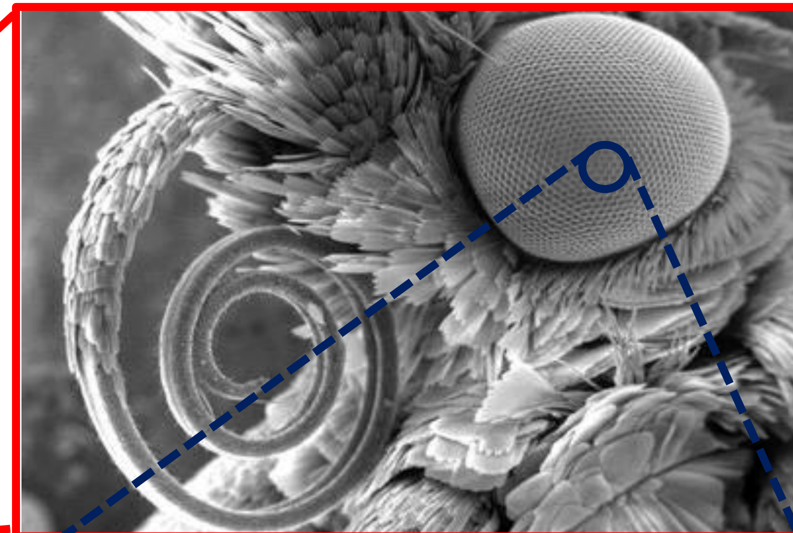
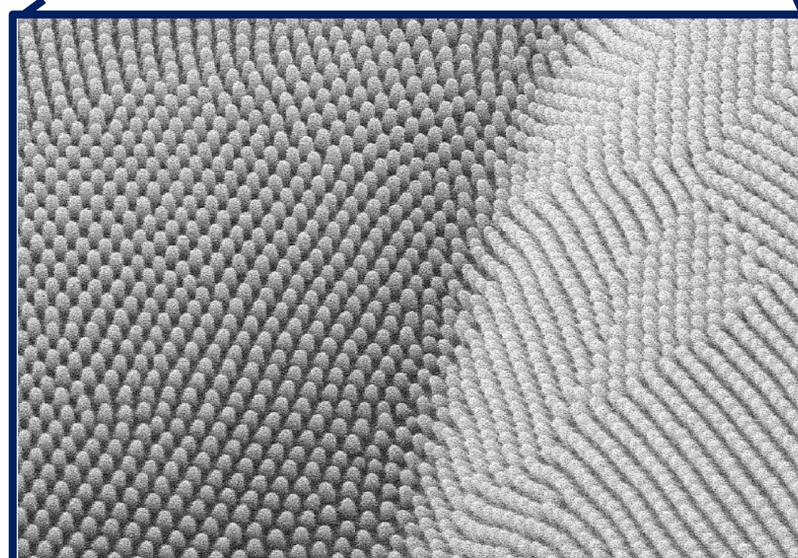
Moth-Eye Structures







Moth

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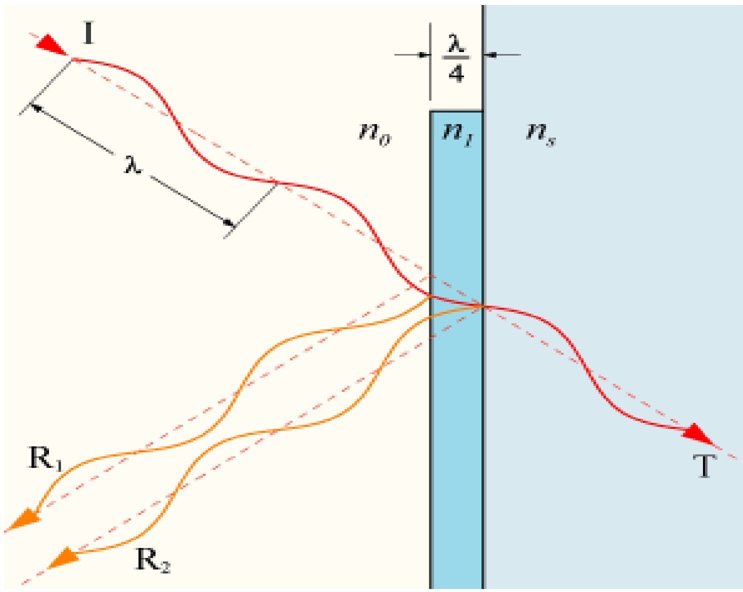
Antireflection Coating Applications



Optimum Refractive Index Value

$$n_1 = \sqrt{n_0 n_S}$$

Reflection Coefficient

$$R = \left(\frac{n_0 - n_S}{n_0 + n_S}\right)^2$$

Antiglare Coatings

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Artifactual Antireflection Coatings