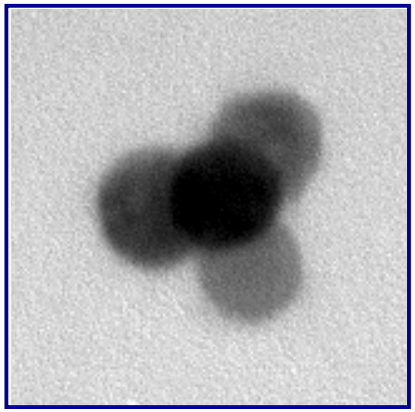
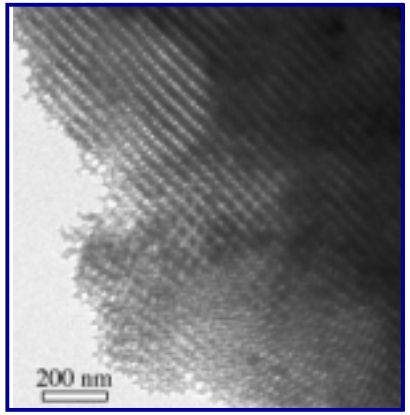
Nanomaterials:

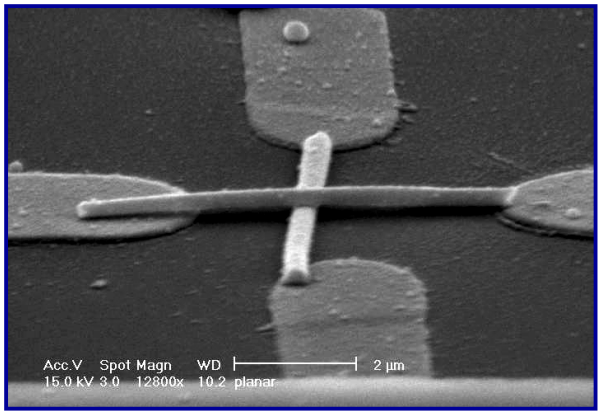
Synthesis and Assembly

Thomas E. Mallouk
Department of Chemistry, The Pennsylvania State University

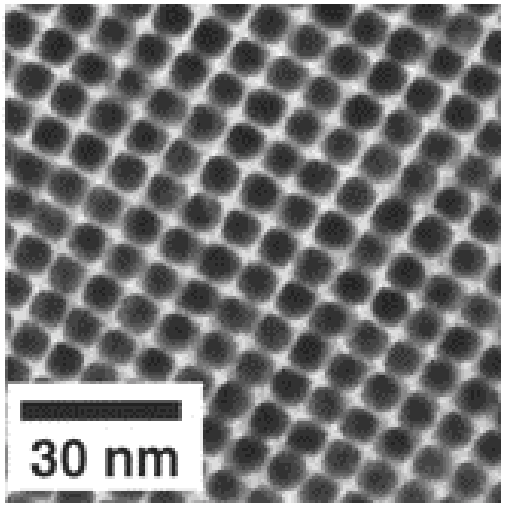
Foresight Conference Tutorial, November 2, 2000





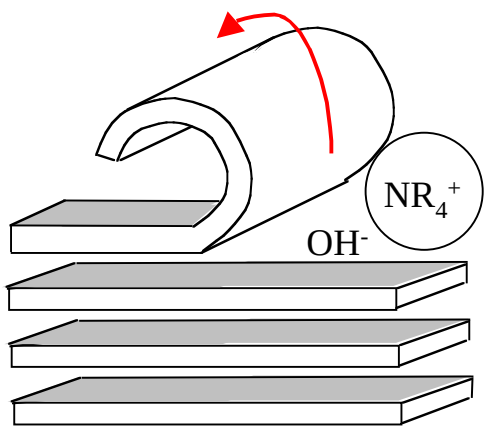


Inorganic nanomaterials have interesting physical properties

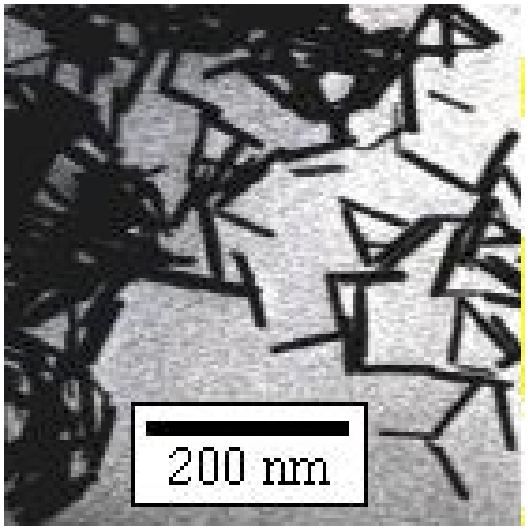


Superparamagnetic
6 nm FePt cubes

S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* 2000, *287*, 1989.



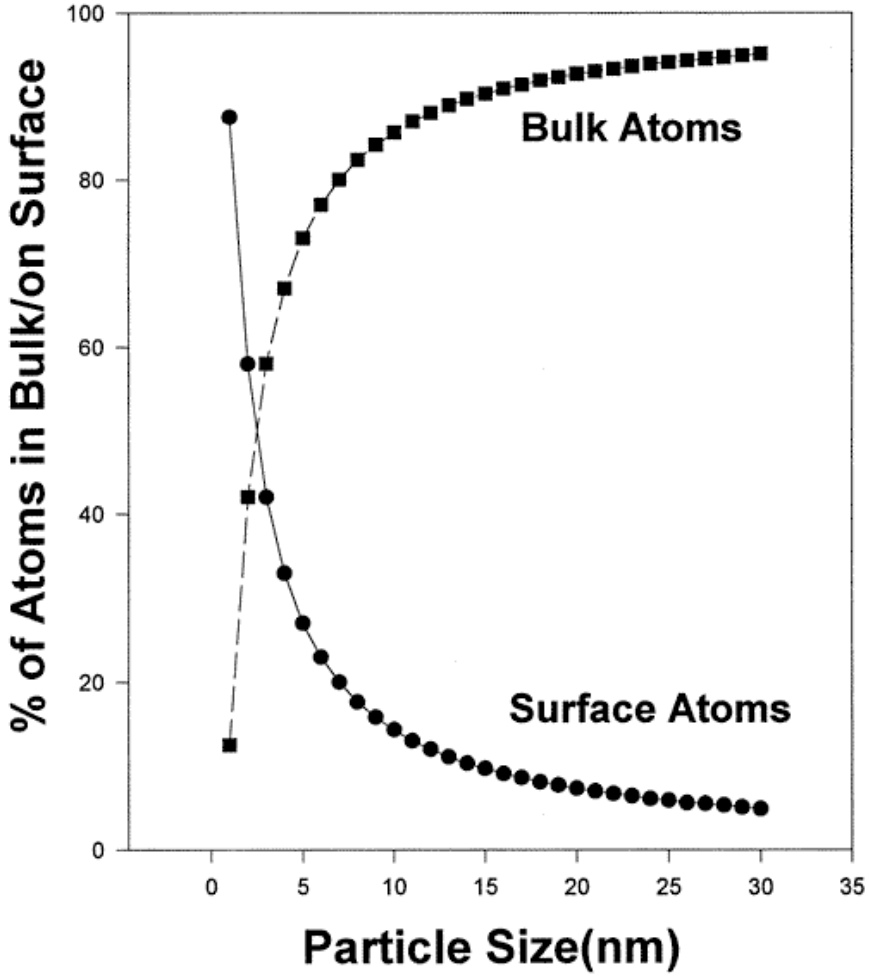
$H_2La_2Ti_3O_{10}$



High dielectric metal oxide "scrolls"

R. E. Schaak, et al. *Chem. Mater.* 2000

Special Properties of Nanomaterials



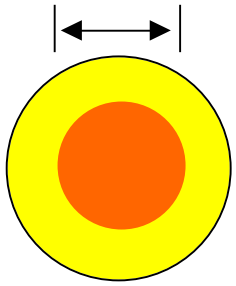
High surface/bulk ratio

- Catalysis
- Nanoparticle reagents
- Heat dissipation
- Laminar flow

Finite size effects

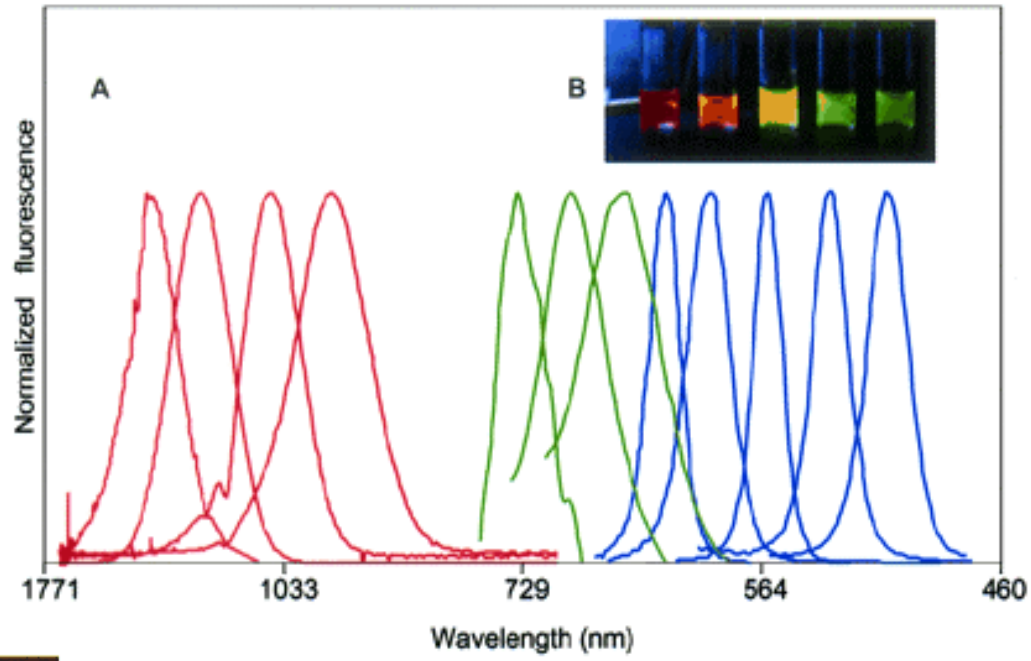
- Quantum confinement
- Interparticle tunneling
- Proximity effects
- High probability of defect-free crystals

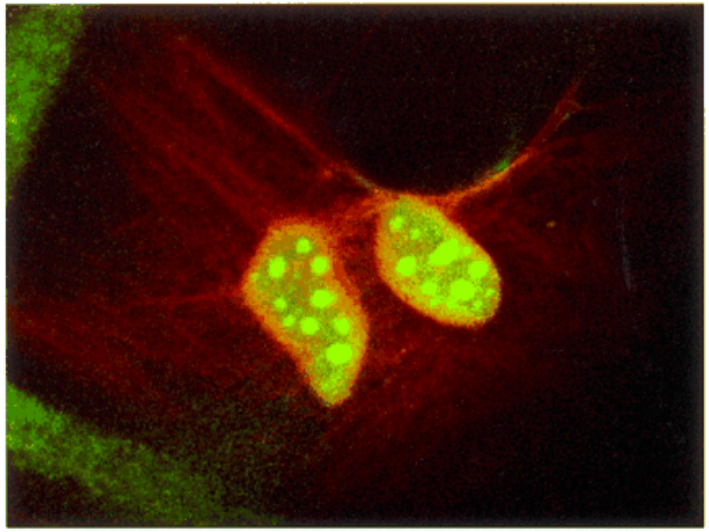
2.1 - 4.6 nm



CdSe/CdS core-shell particles

Excitons confined to core





Defect-free nanocrystals

→ high fluorescence quantum yield

Dual fluorescence
labeling of actin
filaments and fibroblasts

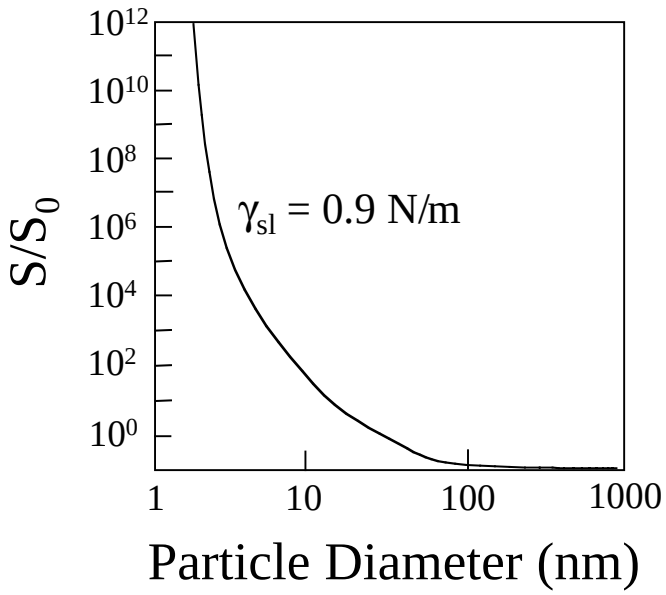
A. P. Alivisatos et al., *Science* 1998, 281, 2013.

Dissolution and Melting of Nanoparticles

Solubility increases and melting point decreases for nanoparticles

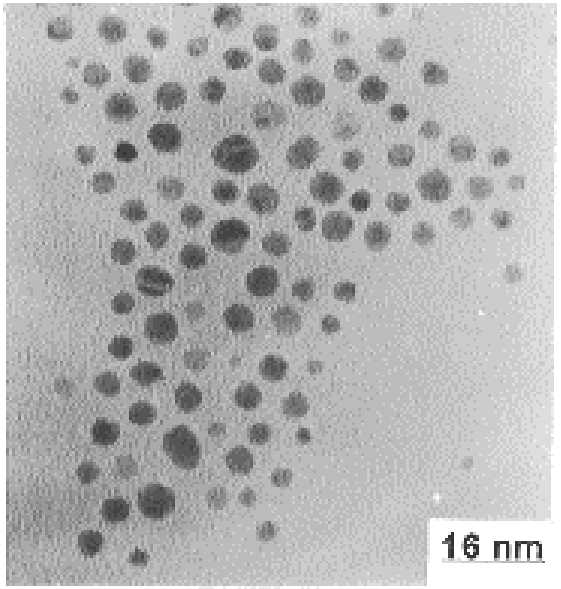
Ostwald-Freundlich relationship

$$S = S_0 \exp\left[\frac{\gamma_{sl} V}{RTd_P}\right]$$



Au nanocrystal opals

Large particles grow at the expense of small ones



J. R. Heath, *Lamgmuir* 1996

Motivation for studying inorganic nanomaterials:

Functional nanoscale assemblies

- Electronics
- Robotics
- Solar Energy Conversion
- Nano-Batteries and Fuel Cells
- Separations and Analysis
- Photonics

Intricate, non-periodic structures

Sub-lithographic length scale

Inorganic materials properties

Lessons from biology

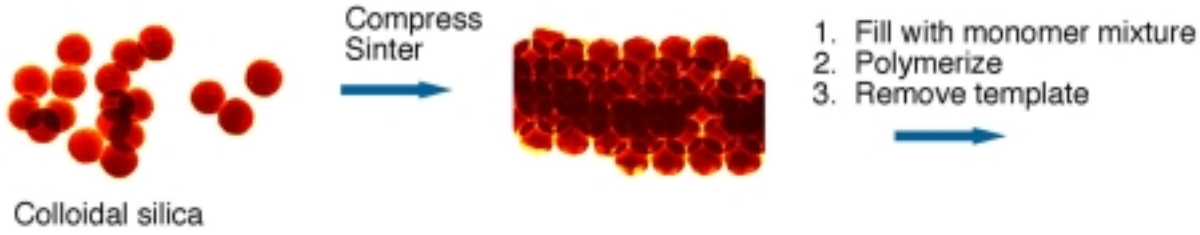
- Molecularly precise building units with asymmetric shapes:
  α-helices, beta sheets, nucleic acid duplexes and loops
- Recognition is non-covalent, highly shape-dependent:
  4-helix bundles, DNA-protein, ribosome-RNA complexes
- Hierarchical assembly to imprecise functional units:
  membranes, chromosomes, cells, organs, people

Colloidal crystals

Interesting for applications in optics, sensors, separations

So far, building blocks are spheres and high symmetry polyhedra

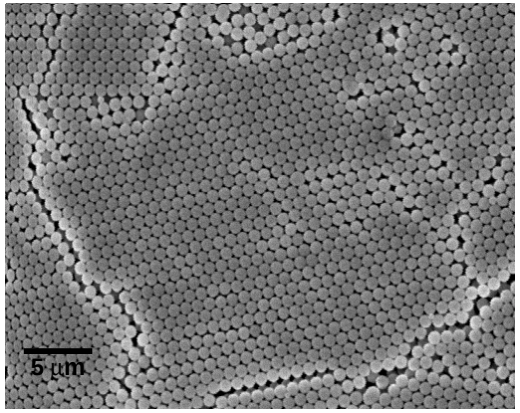
→ limited structural variety

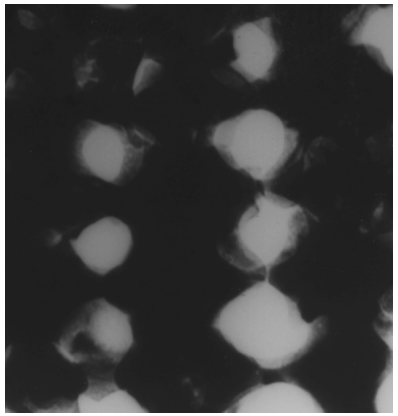


polymer
"inverse opal"

Johnson, et al., *Science* 1999, *283*, 963.

860 nm
silica opal
thin film



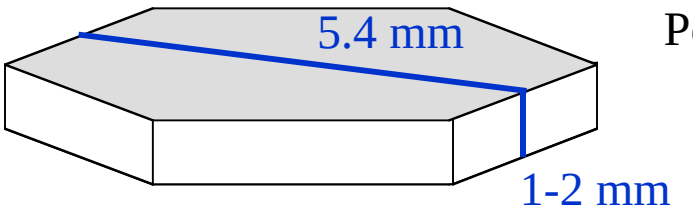


Pt inverse opal with
12 nm "necks"

Particle Assembly - Proof of Concept
Non-covalent assembly of asymmetric polygons

Bowden, N.; Terfort, A.; Carbeck, J.; Whitesides, G. M. *Science* **1997**, *276*, 233.

"Cookie cutter" fabrication of mm scale shapes

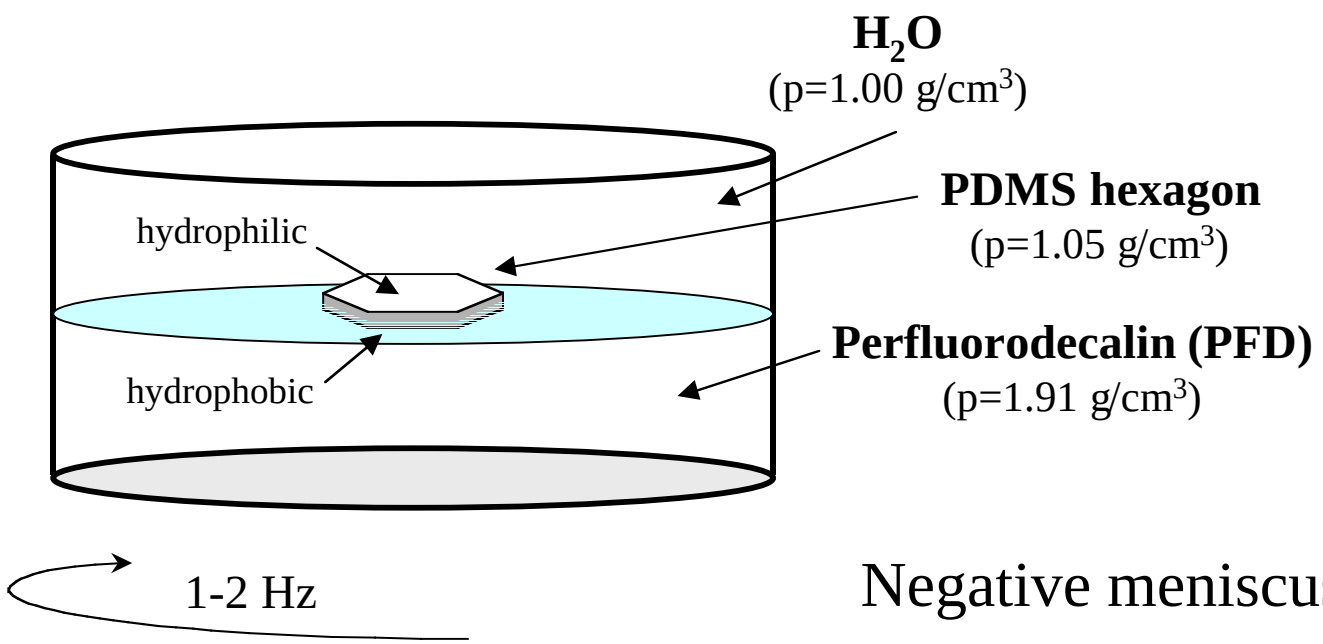


Poly(dimethylsiloxane) (PDMS)

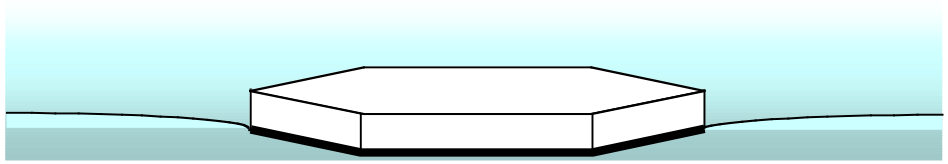
- hydrophobic ($OSiMe_2$)
- hydrophilic in O_2 plasma

Assembly at a planar interface

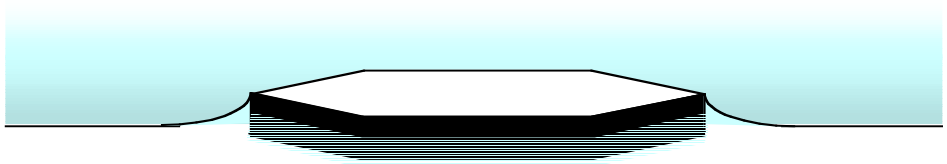
- Hexagons confined to a plane for 2D assembly
- Agitated in interfacial plane to bring hexagons into contact



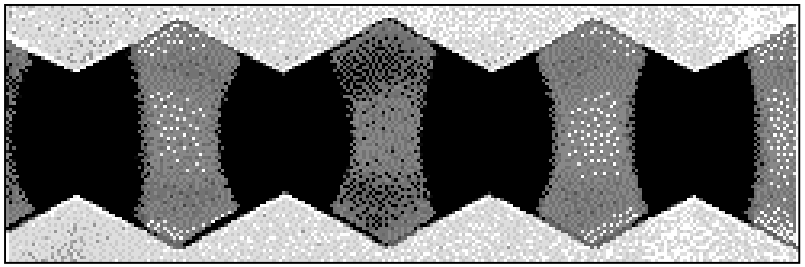
Negative meniscus (hydrophilic edges)



Positive meniscus (hydrophobic edges)

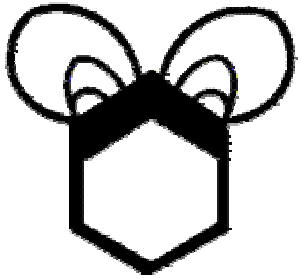


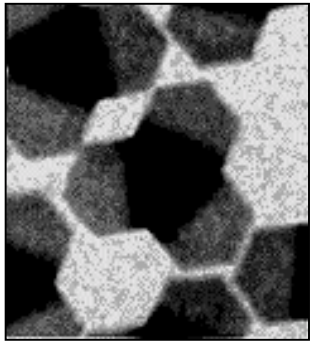
Linear chain formation - [1,4] hexagons



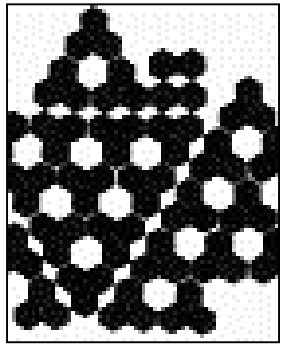
Trimer formation - [1,2] hexagons

tilted [1,2] hexagon





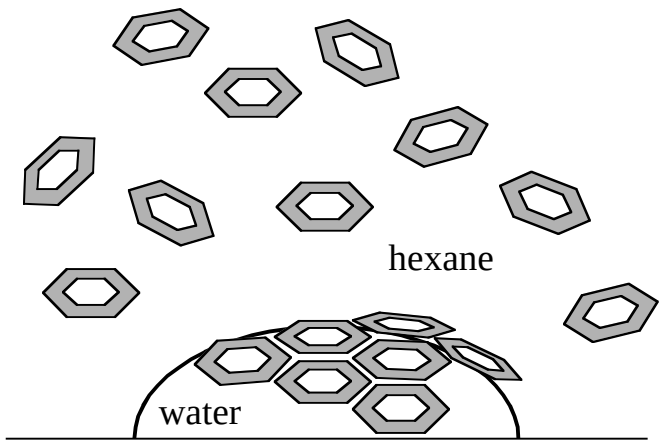
Trimers
(thermodynamic assembly)

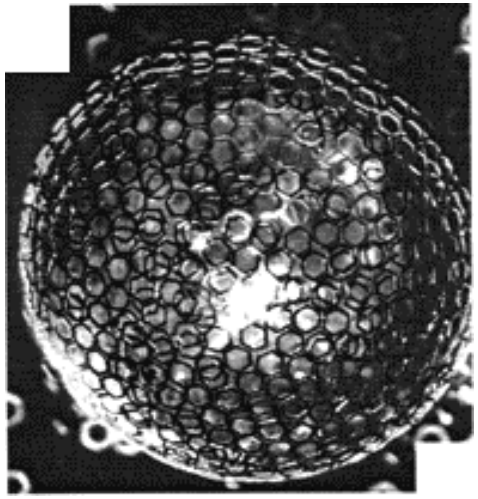


Trimer superlattice
(slower rotation speed, less stable interactions)

Bowden, N.; Choi, I. S.; Grzybowski, B. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 5373.

Self assembly of millimeter-scale 3-D objects

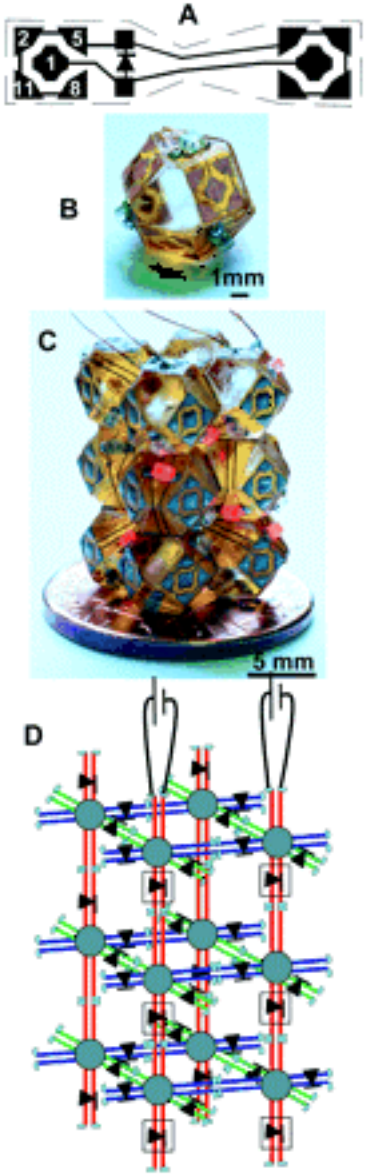


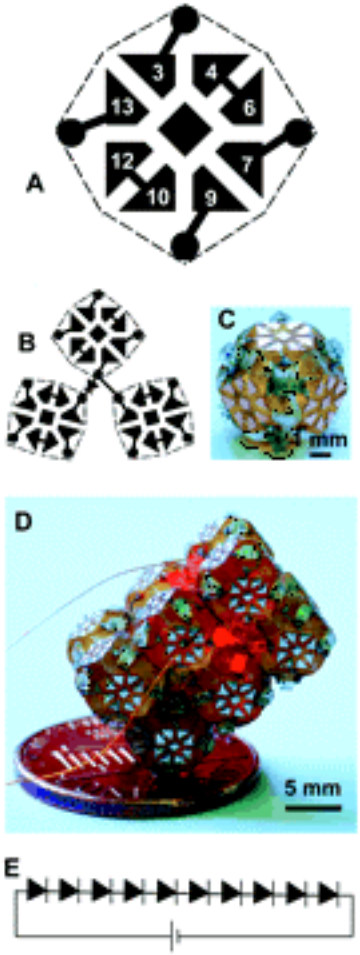


Terfort, A.; Bowden, N.; Whitesides, G. M. *Nature* **1997**, *386*, 162.
Huck, W. T. S.; Tien, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, *120*, 8267.

Self-assembly of 3-D circuits from millimeter-scale components

- Series or parallel wiring
- Circuit connectivity is programmed by asymmetry of building blocks





D. H. Gracias, J. Tien, T. L. Breen, C. Hsu, G. M. Whitesides, *Science* 2000, *289*, 1170.

Key questions for **nanoscale** assembly

- Synthetic techniques for asymmetric objects

  Bottom up (molecule precise) or cookie cutter (top down)?

  What is the minimal tool kit (balls, polygons, rods, helices…)?

- Assembly issues

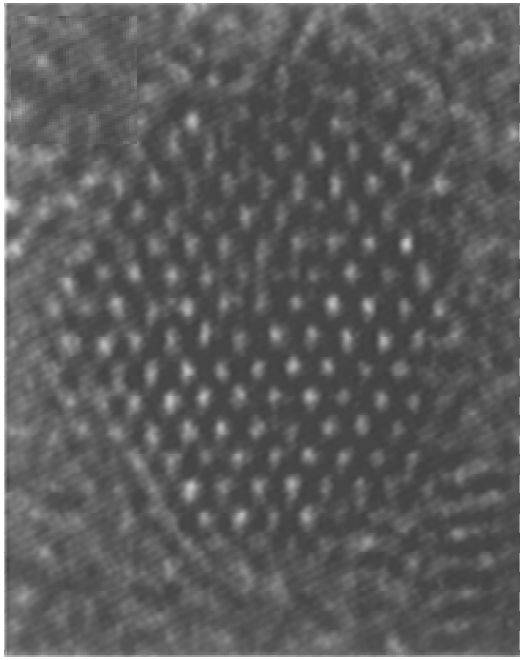
  Proof of concept with small systems (dimers, host guest complexes, linear arrays)

  Combine small scale assembly with lithographic patterning

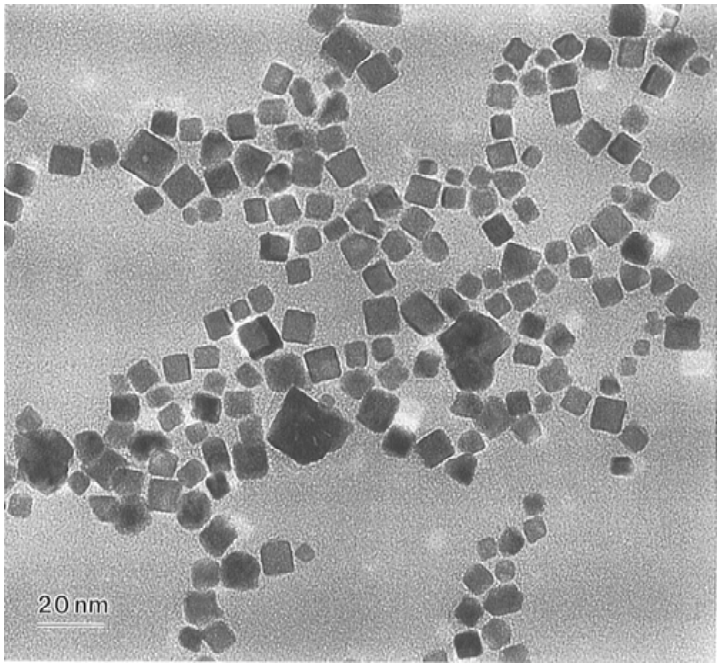
What does the nanoparticle toolbox look like now?

Synthesis of non-spherical nanoparticles

- Uniformity is hard to achieve (but improving!)
- Symmetry is still too high for shape-directed assembly

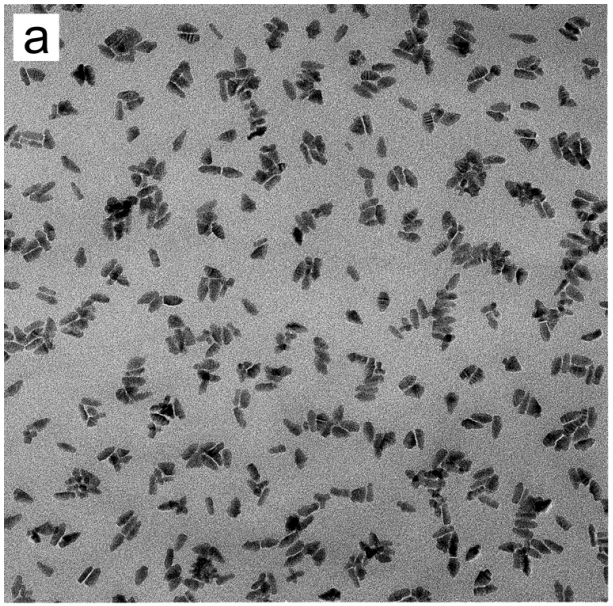


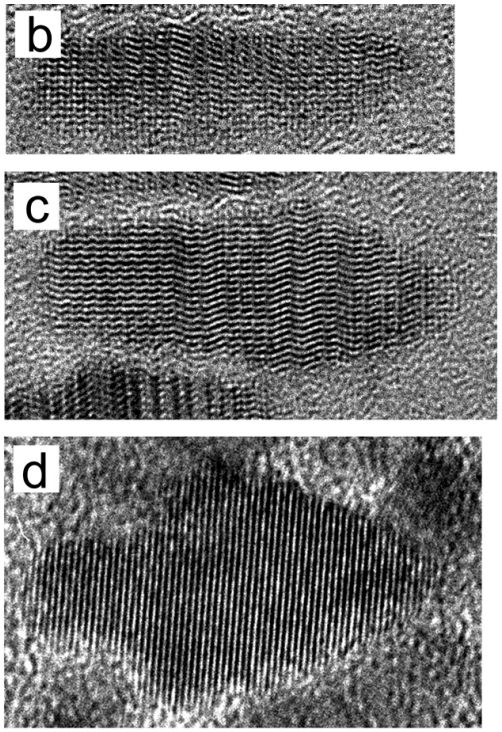
Faceted CdSe (wurzite) nanocrystal (A. P. Alivisatos)

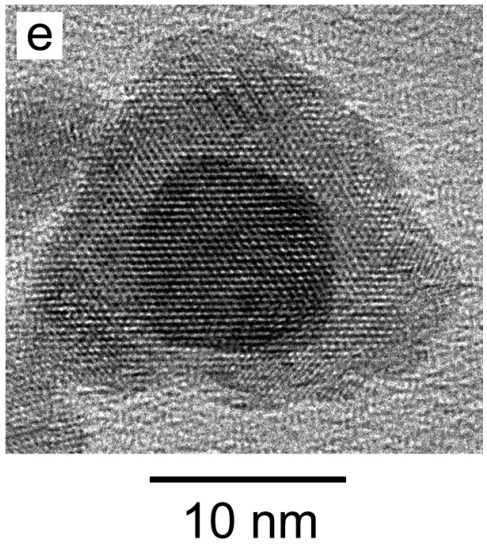


Pt nano-cubes (M. A. El-Sayed)

CdSe Nanorods and “Arrowheads”

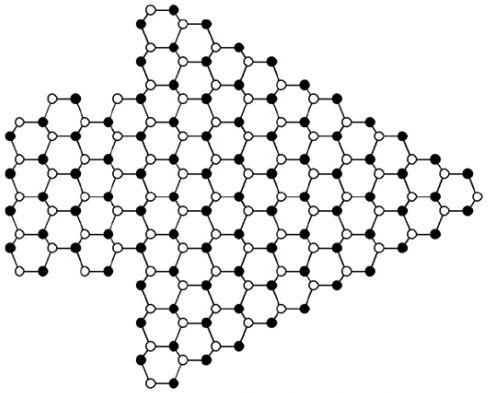






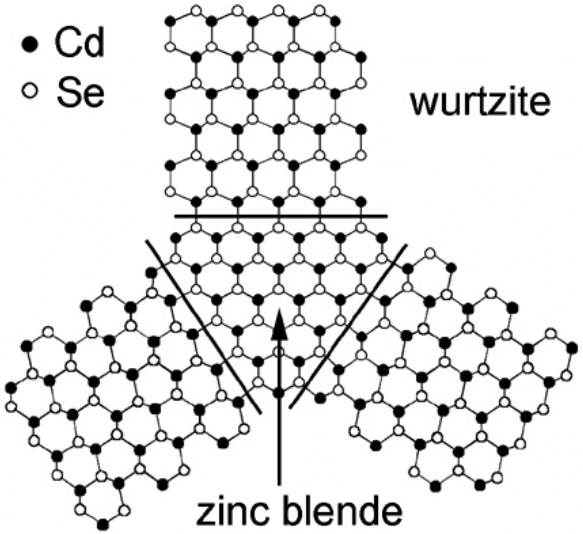
- Nanocrystal habit controlled by surfactant composition

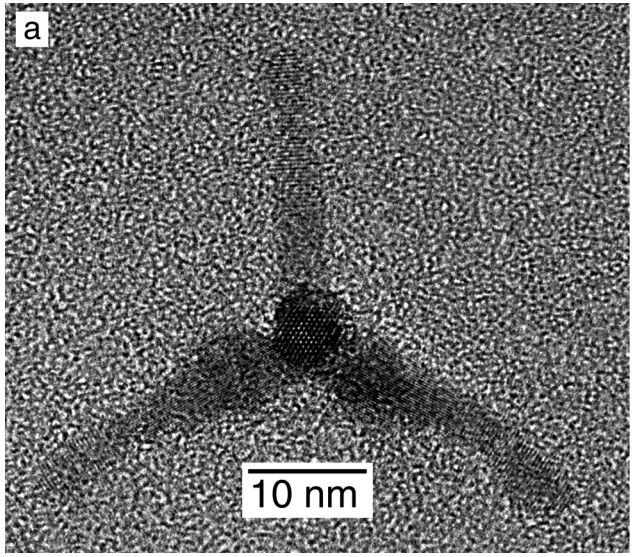
- Multiple injection/growth cycles develop specific crystal faces

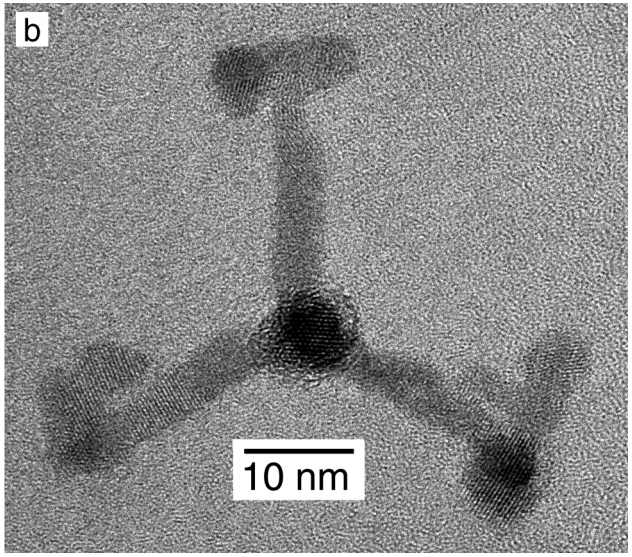


L. Manna, E. C. Scher, A. P. Alivisatos, *JACS* 2000 (in press).

CdSe Tetrapods

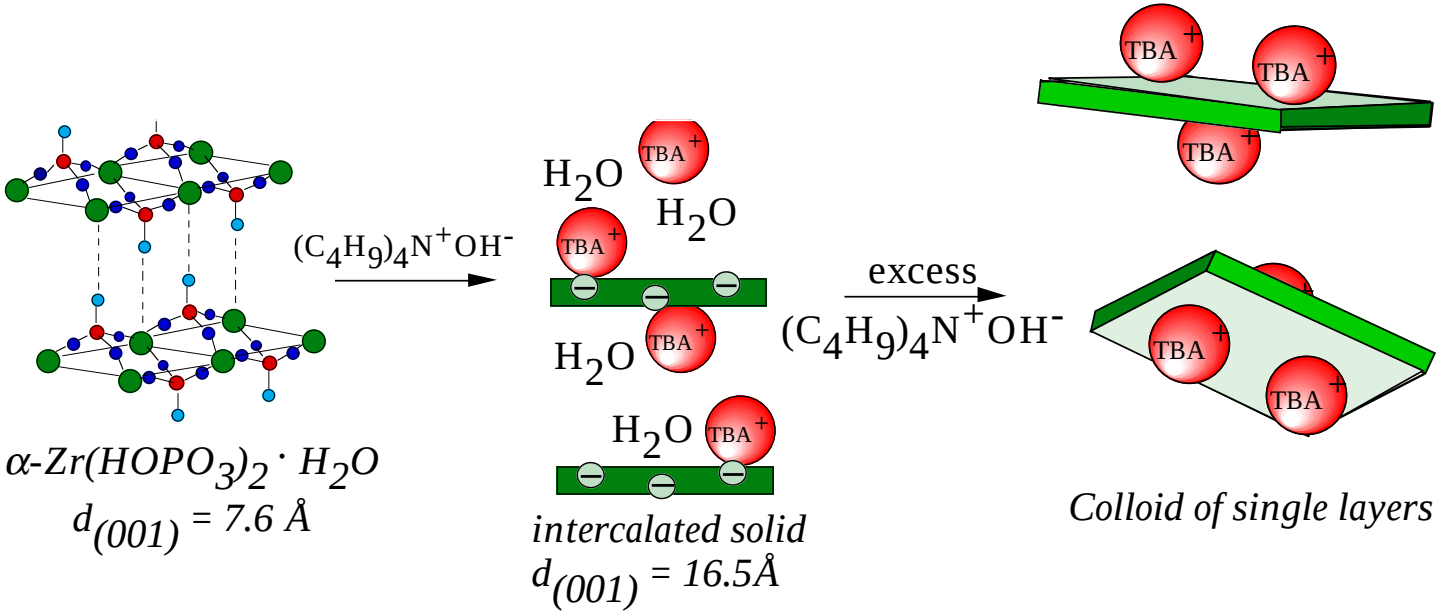


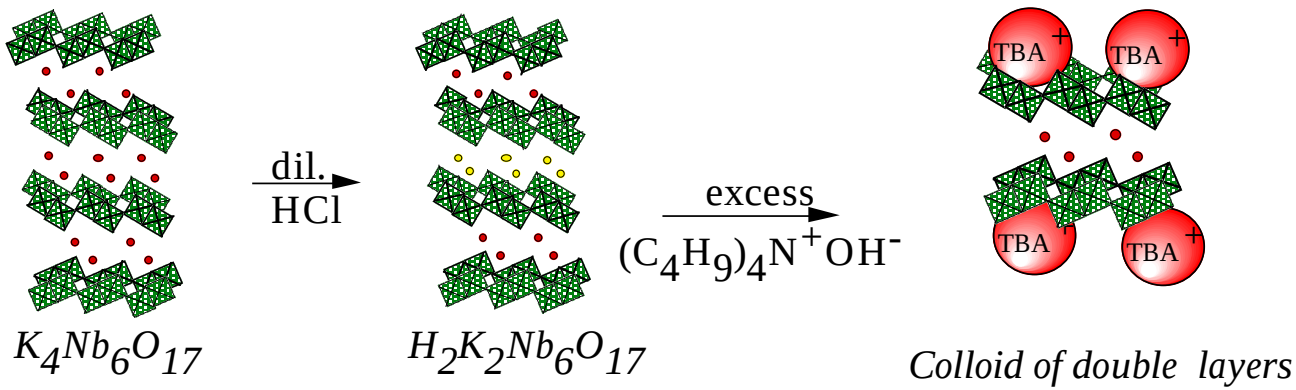




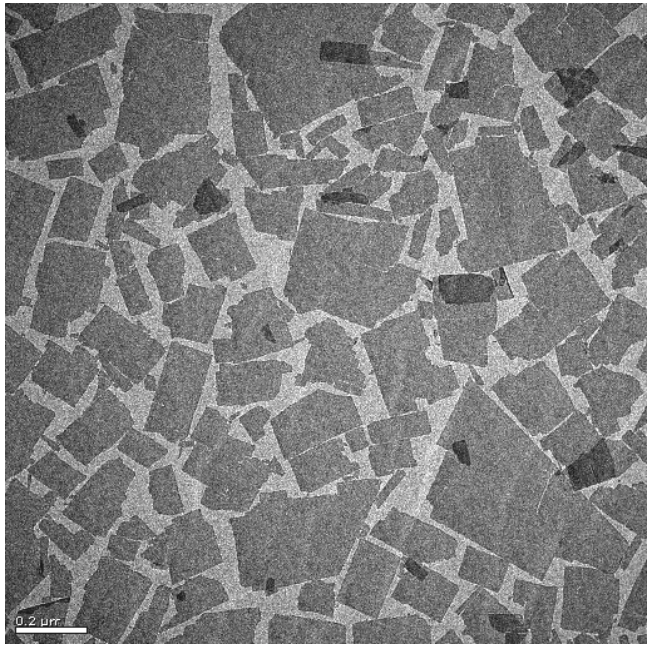
L. Manna, E. C. Scher, A. P. Alivisatos, *JACS* 2000 (in press).

Nanoscale sheets from lamellar precursor solids



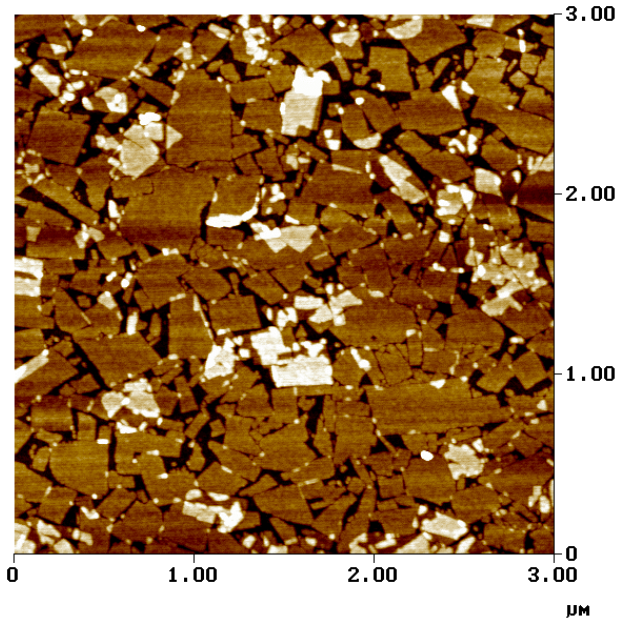


Exfoliated sheets are crystalline and exactly 1 molecule thick, but are irregularly shaped



TEM of 1.5 nm thick $TBA_{0.17}H_{0.83}Ca_2Nb_3O_{10}$ sheets

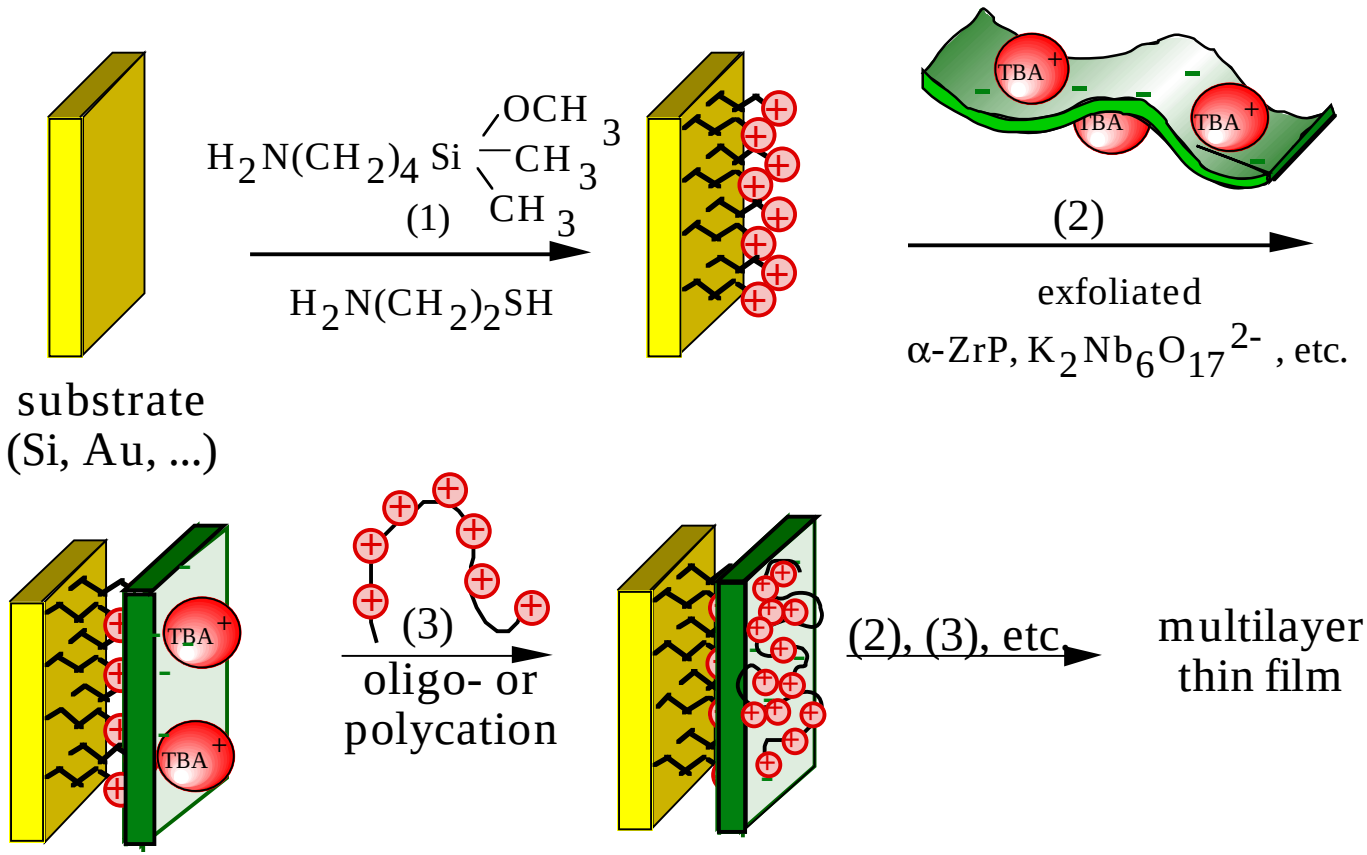
AFM Image



$TBA_{0.17}H_{0.83}Ca_2Nb_3O_{10}$ sheets tile densely on a Si/polycation (PDDA) surface

Sequential Anion-Cation Adsorption

Molecular 'Beaker' Epitaxy



S. W. Keller et al., *J. Am. Chem. Soc.* 1994, *116*, 8817.
E. R. Kleinfeld, G. L. Ferguson *Science* 1994, *265*, 370.

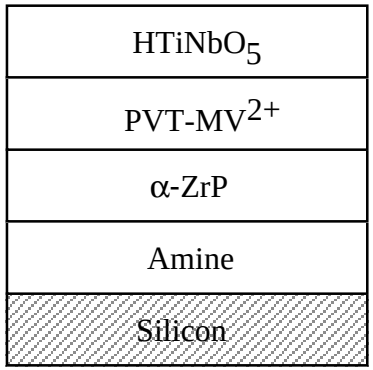
Layer-by-layer assembly of irregular sheets

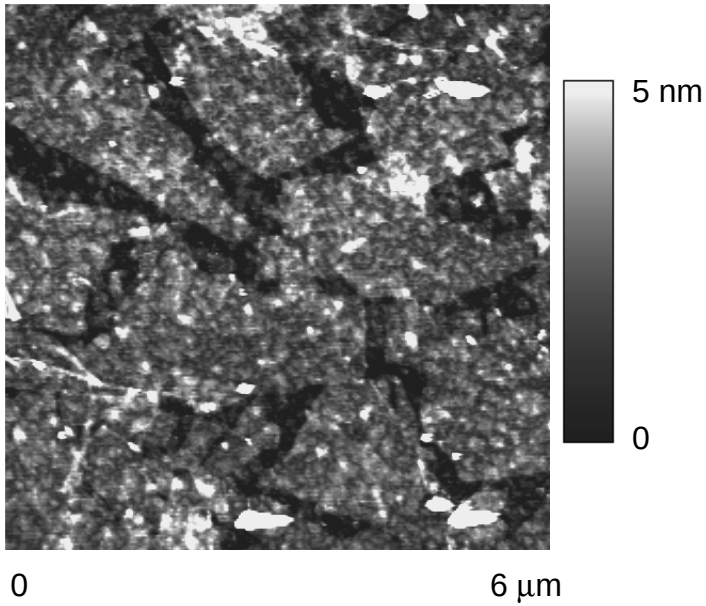
Structure is well controlled in stacking directions

No control in the horizontal directions

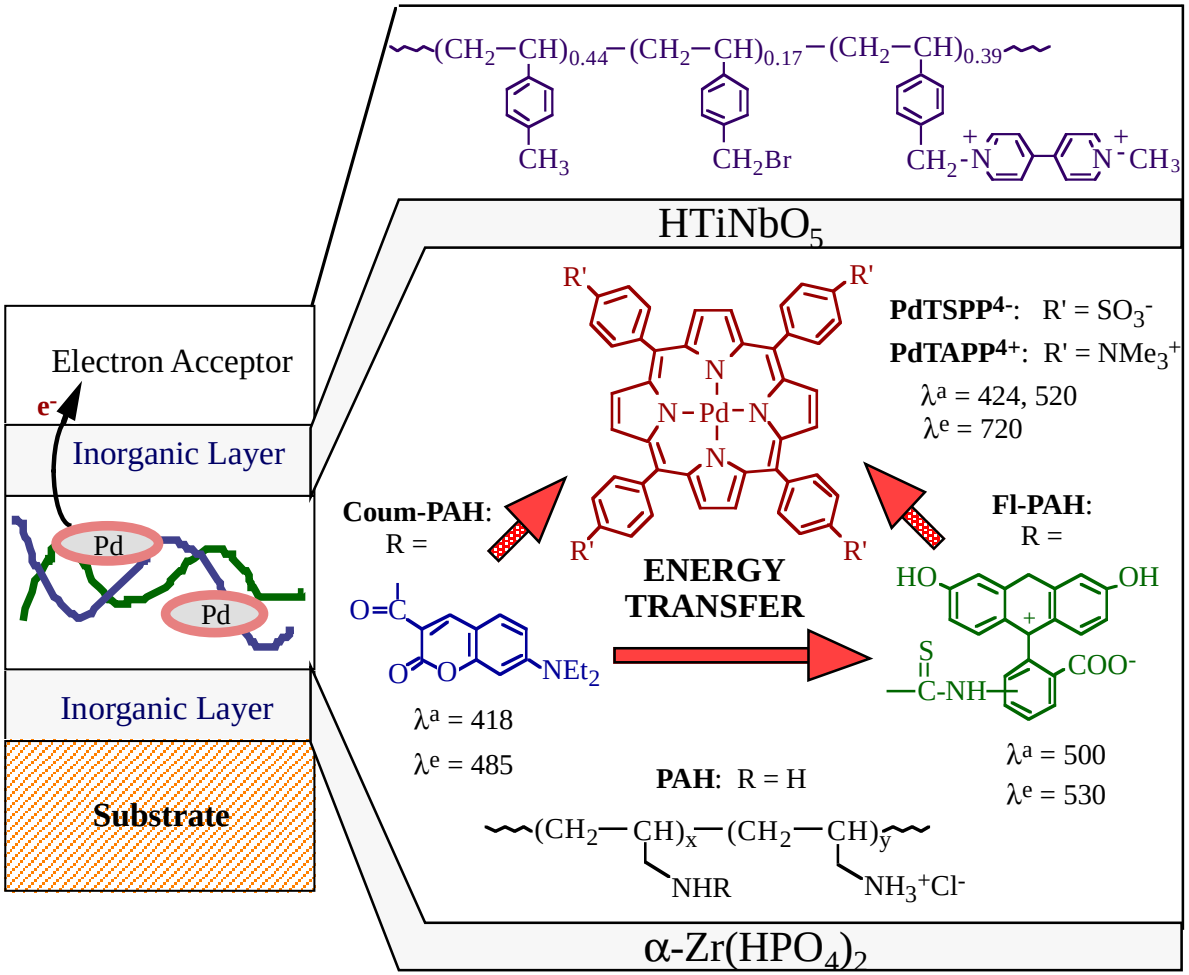
Complex stacking sequences are accessible

Large variety of inorganic and organic building blocks





Multi-step energy/electron transfer cascades

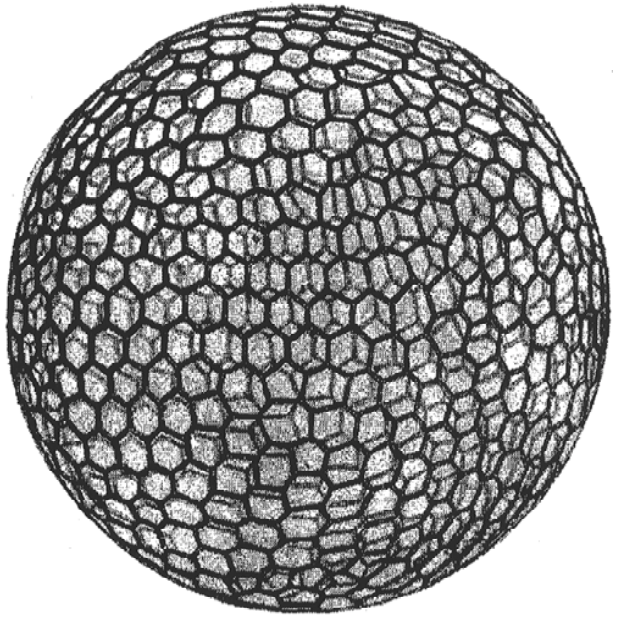


- Densely tiled sheets separate redox polymer layers by 1 nm
- Light-driven 4-step energy/electron transfer sequence with >60% quantum yield

D. M. Kaschak et al., *J. Am. Chem. Soc.* 1999, *121*, 3435.

Biomimetic materials synthesis

Macromolecular templating
Morphogenesis



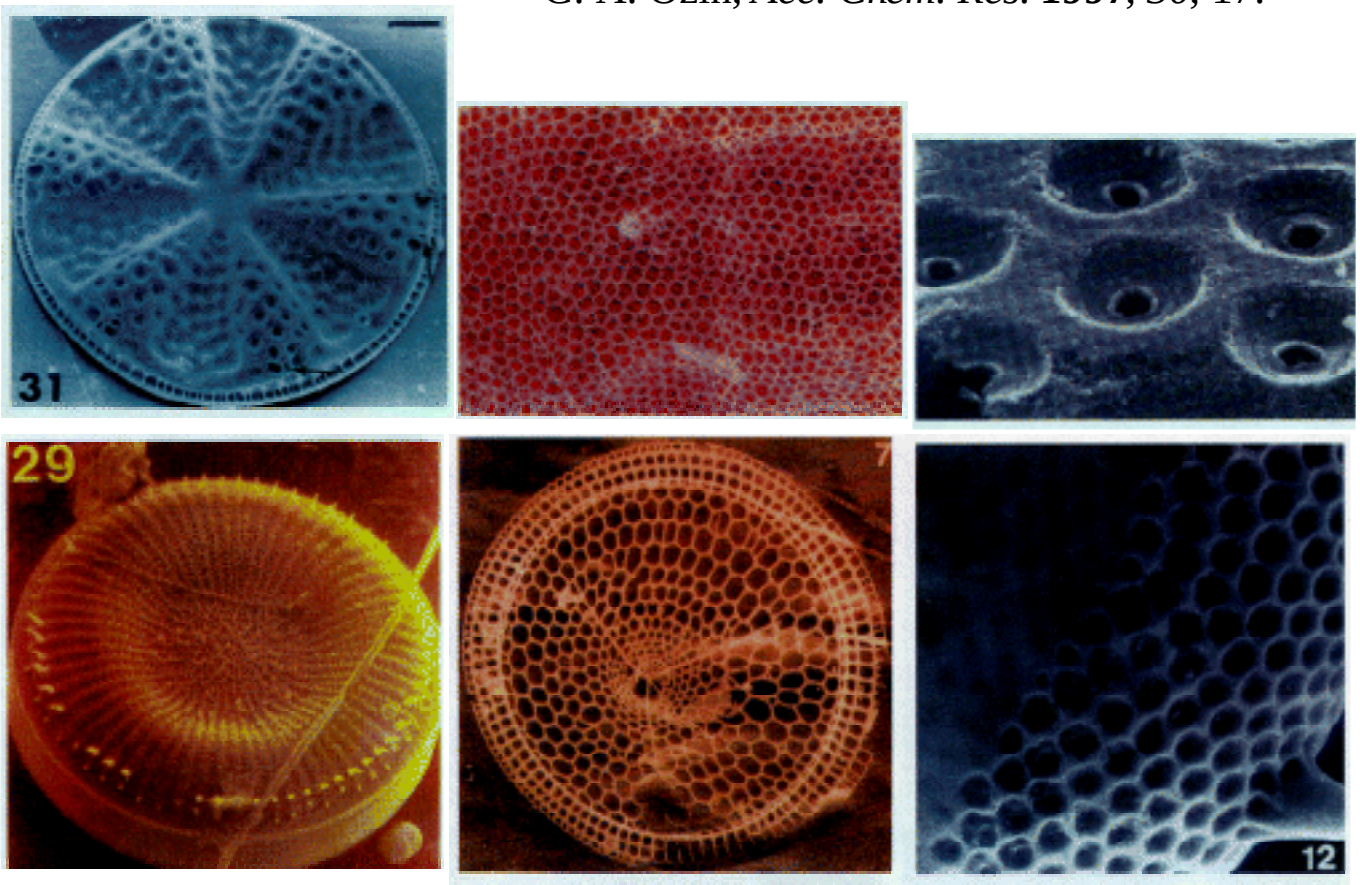
Aulonia hexagona

spheroidal hexagonal
network skeleton

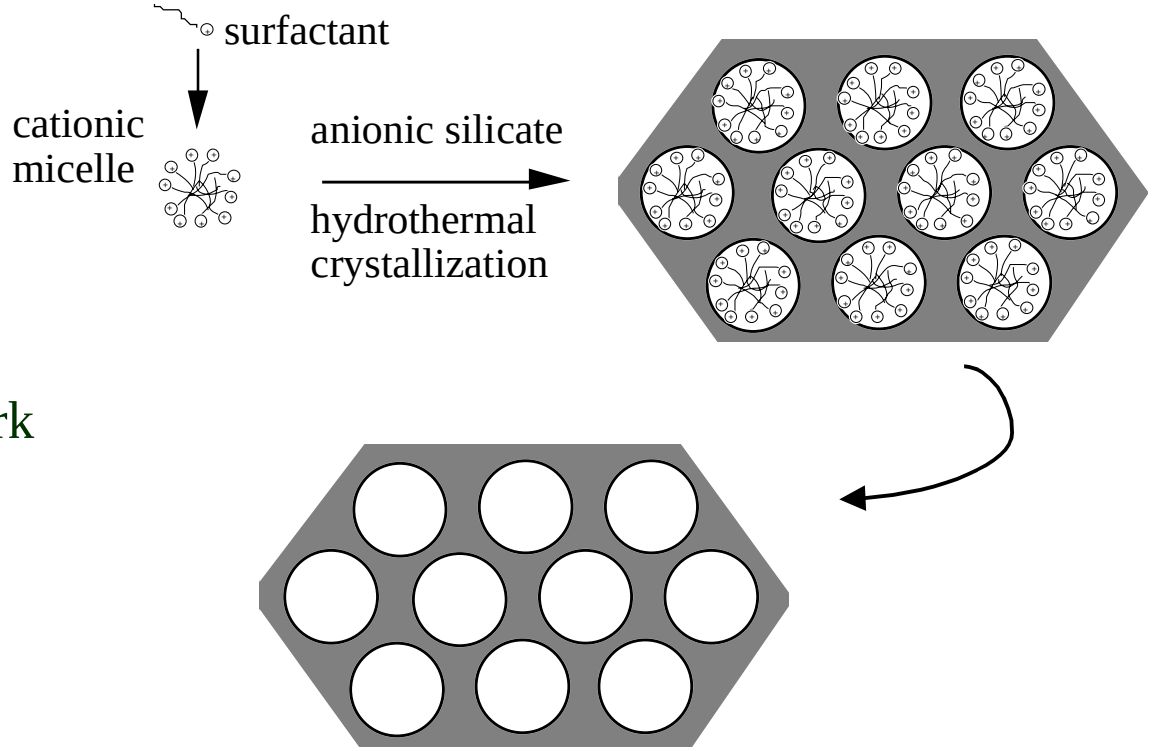
This is **not** made by assembling polygons around a droplet!

Natural discoid silicates

G. A. Ozin, *Acc. Chem. Res.* **1997**, *30*, 17.

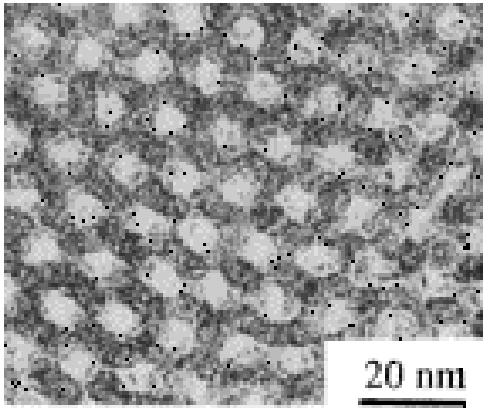


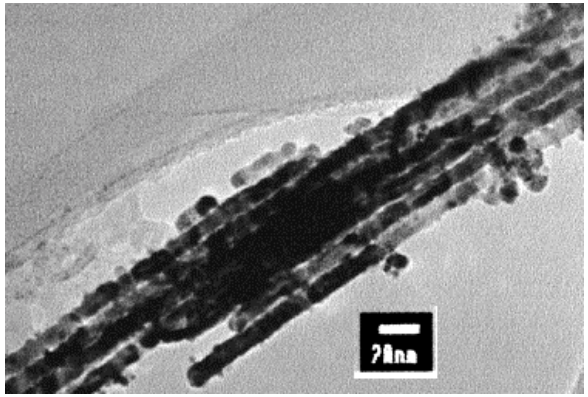
Mesoporous Molecular Sieves



- 1-D or 3-D pore network
- Template (surfactant or block copolymer) directs structure

SBA-15



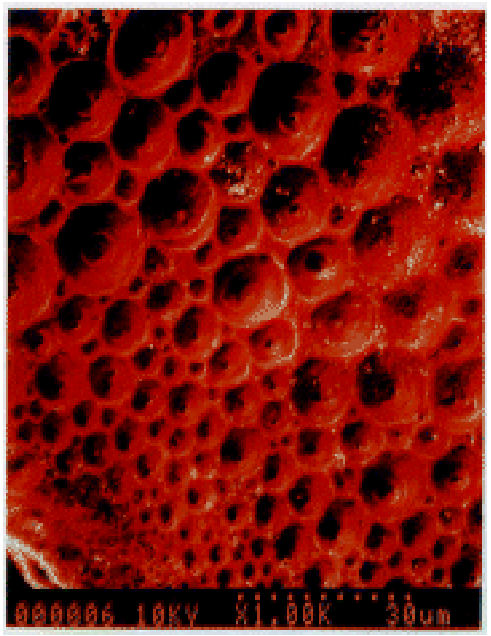


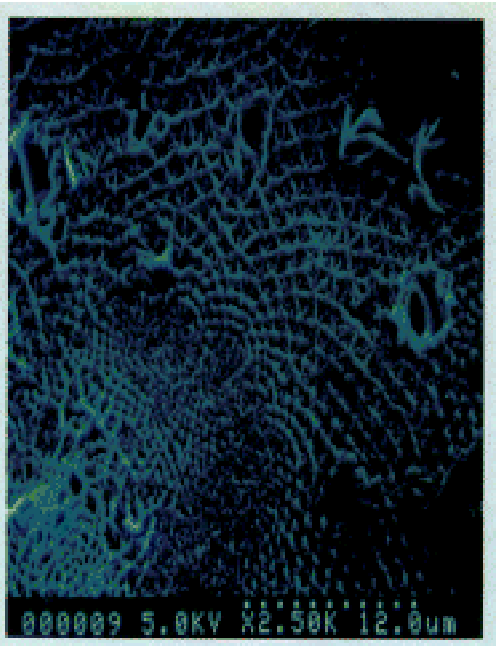
7 nm dia Pt replica wires

G. Stucky, et al., *Chem. Mater*. 2000, *12*, 2069

Biomimetic porous silicates

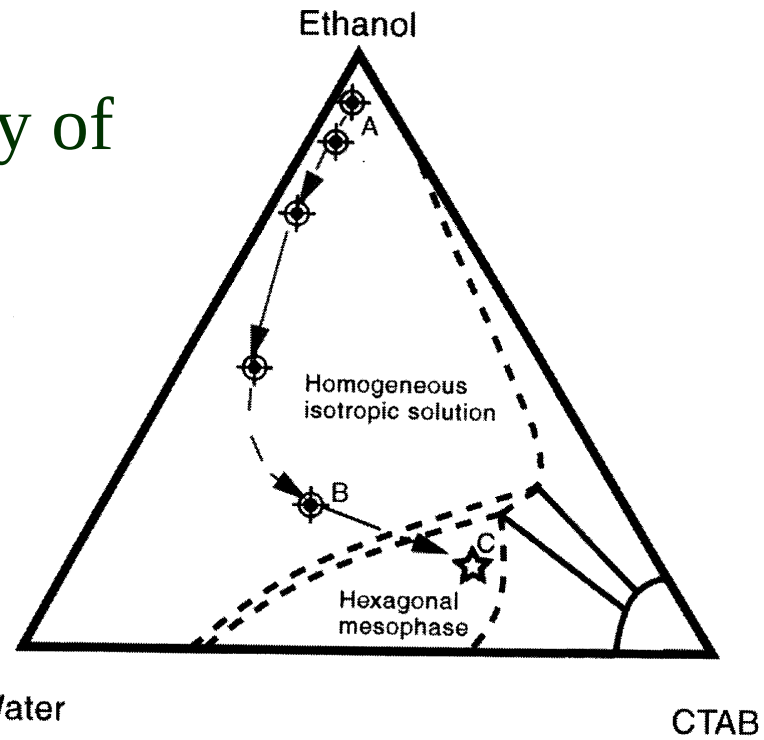
G. A. Ozin, *Acc. Chem. Res.* **1997**, *30*, 17.

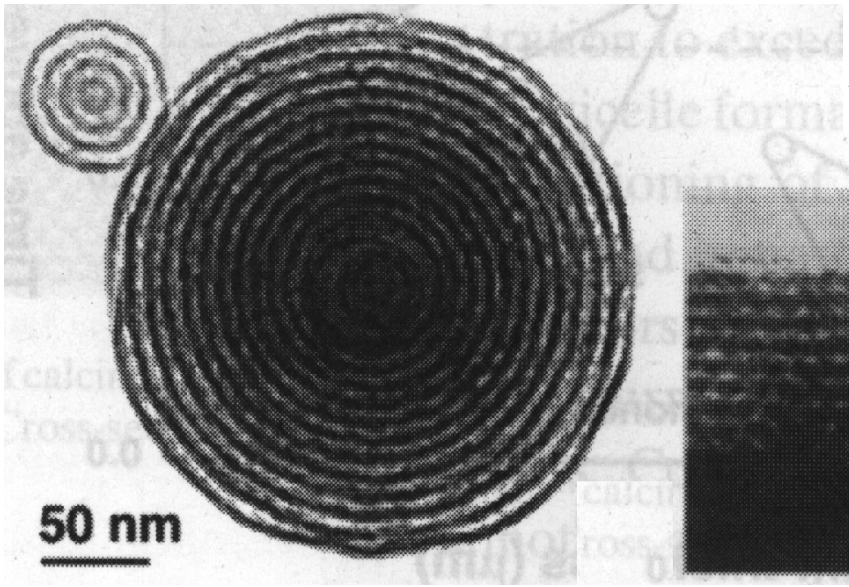


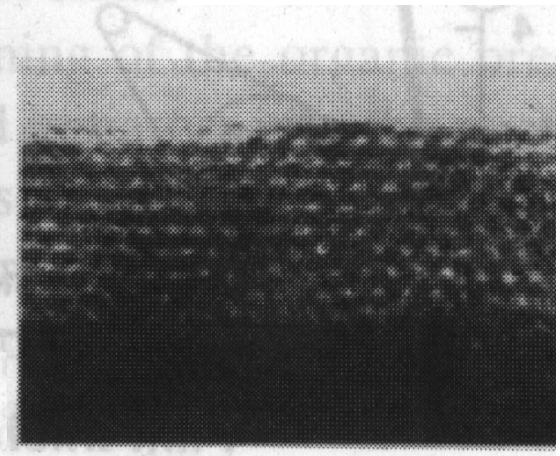


Controlling the Morphology of Mesoporous Materials

Thin Films and “Onions”





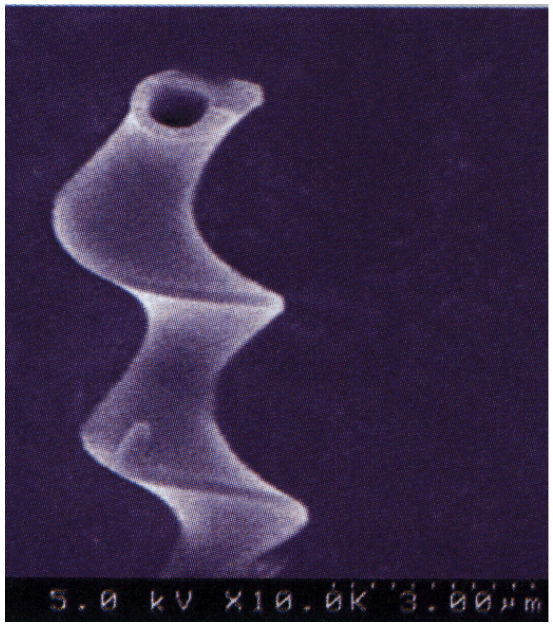


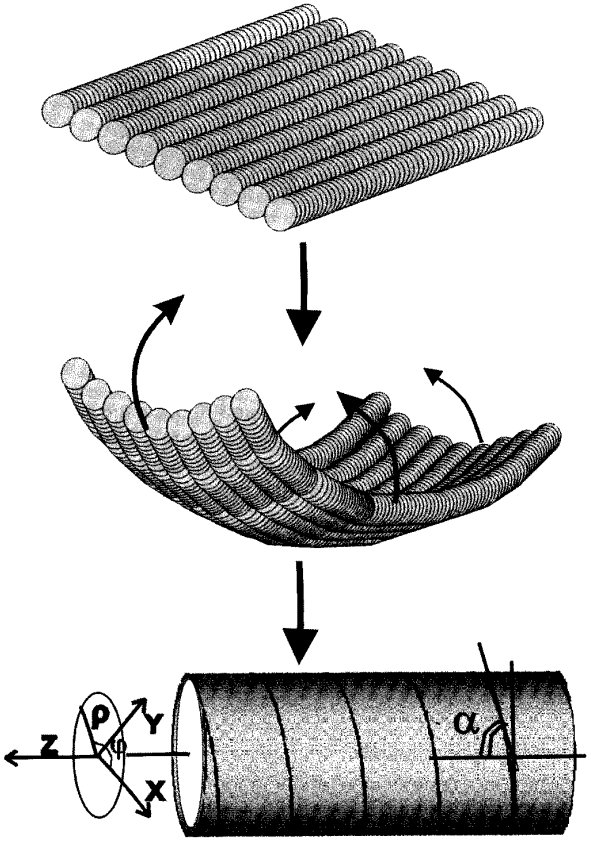
C. J. Brinker, et al. *Adv. Mater.* 1999, *11*, 579.

Discoids, fibers, spheres, open spirals

- Silicate crystallization around lyotropic templates
- Nucleation, polymerization, differential contraction control shape evolution

G. A. Ozin, *Can. J. Chem.* 1999

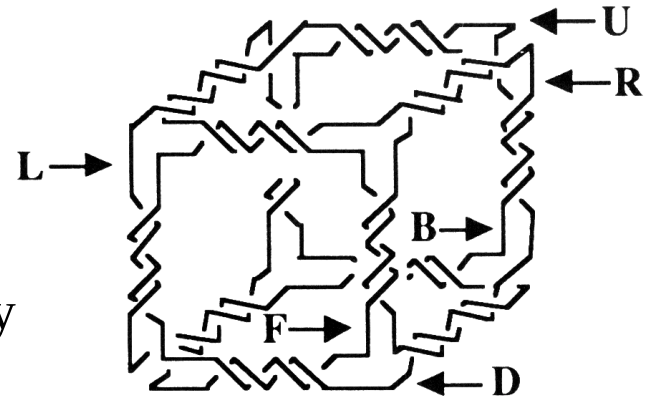




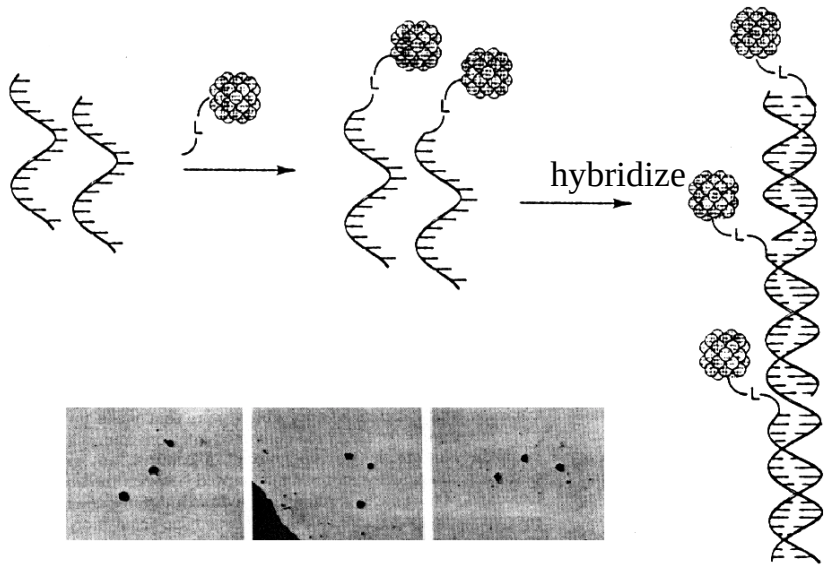
Asymmetric glue for symmetric nanoparticles

DNA Base Pairing

Highly specific binding
Temperature, sequence → reversibility

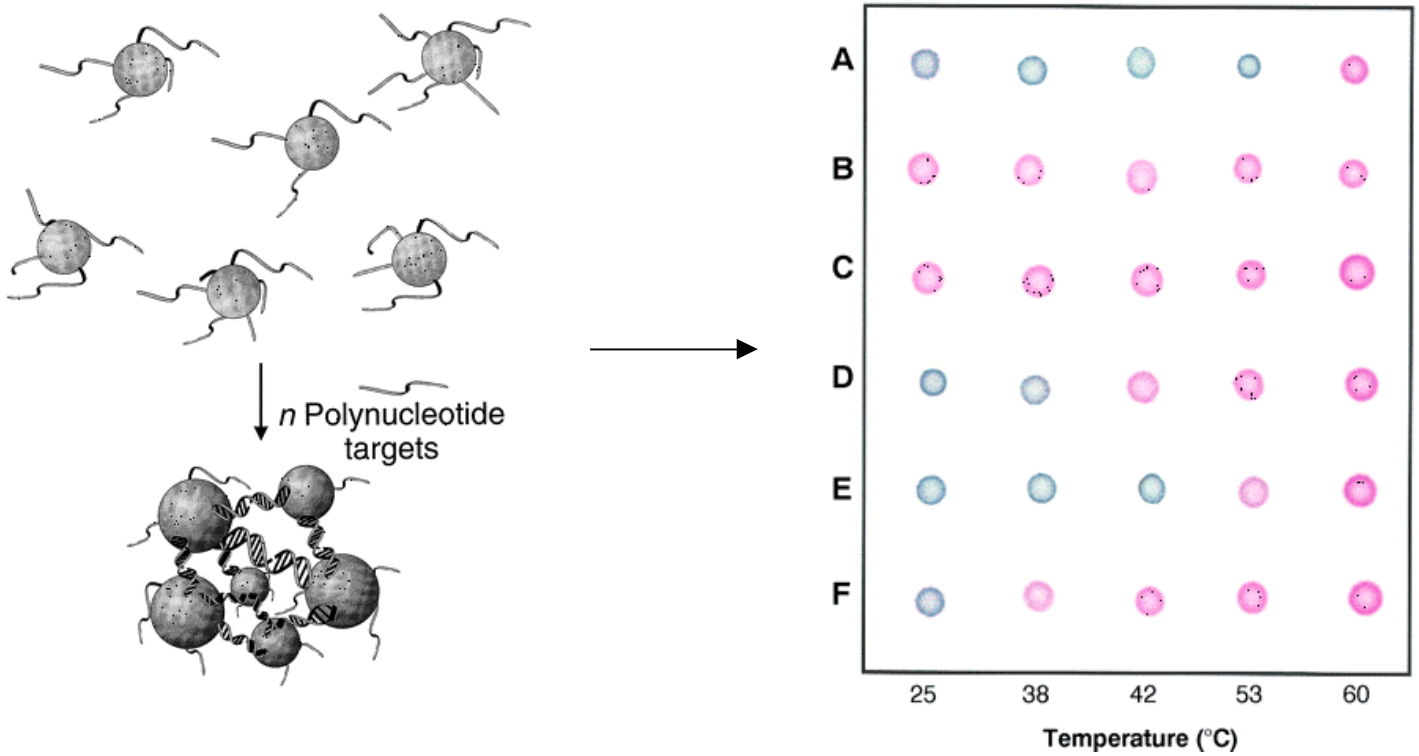


N. Seeman, Acc. Chem. Res. 30, 357 (1997).



A.P. Alivisatos et al., Nature 382, 609 (1996)
C.A. Mirkin et al., Nature 382, 607 (1996)

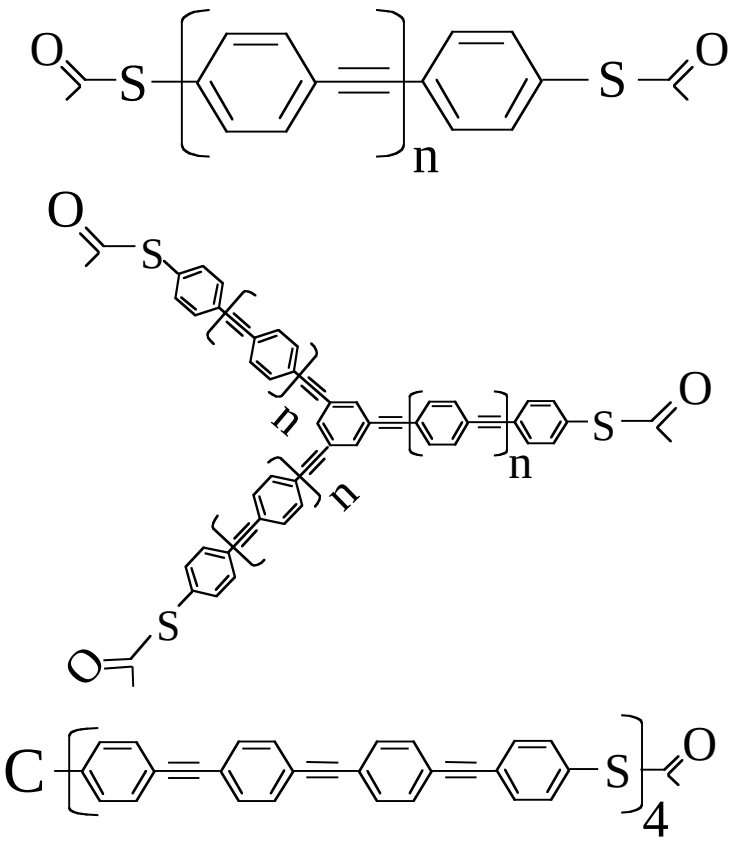
Oligonucleotide linking of nanoparticles

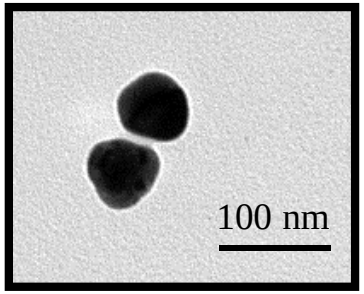


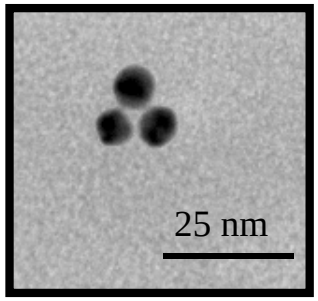
Change in plasmon absorbance band is a litmus test for a specific polynucleotide target

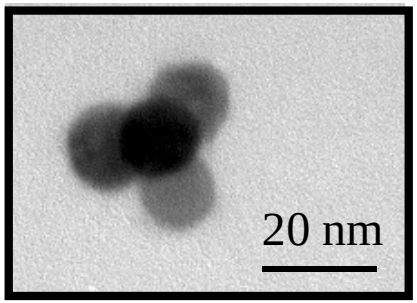
C. A. Mirkin, et al., *Science* 1997, *277*, 1078.

Linker-controlled formation of nanoparticle dimers, trimers, and tetramers







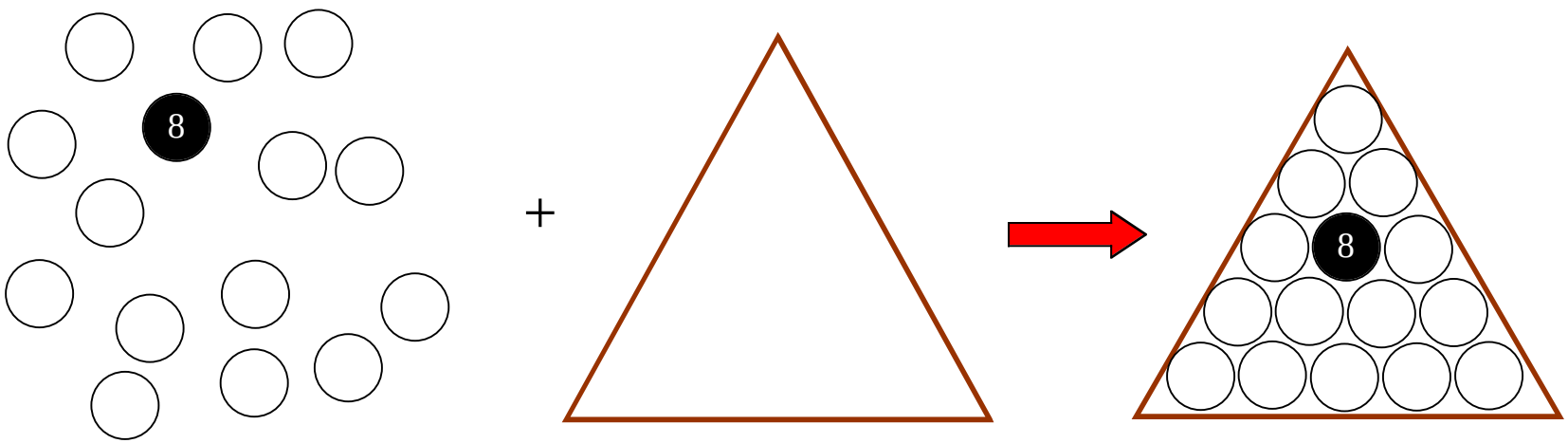


L. C. Brousseau III, J. P. Novak, D.L. Feldheim
(North Carolina State University)

Building complex structures from symmetric objects

- Function block approach

Substrate patterns impose order on self-assembled nanostructures



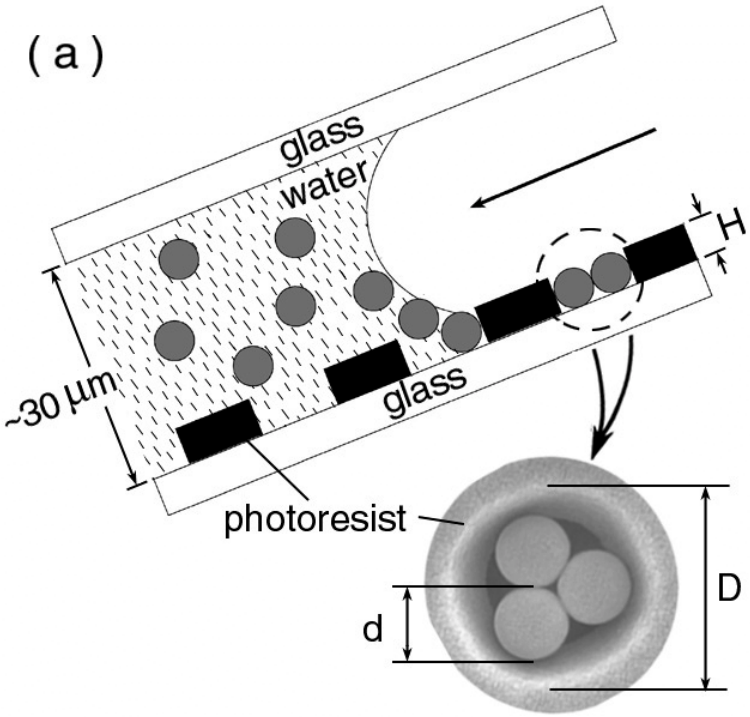
Self-assembling nanoscale objects

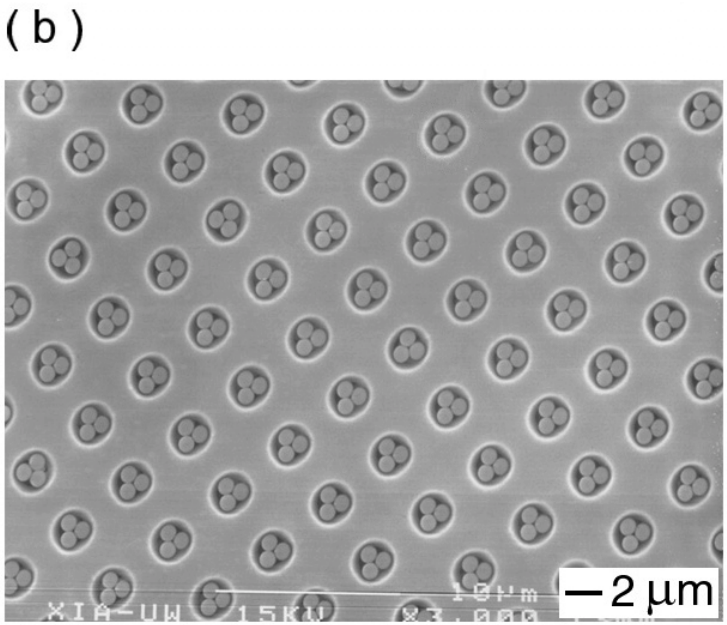
"Nano-frame"

Regular function block

Control of ***nanoscale*** arrangment by ***lithographic scale*** patterning

Sphere assembly driven by capillary forces





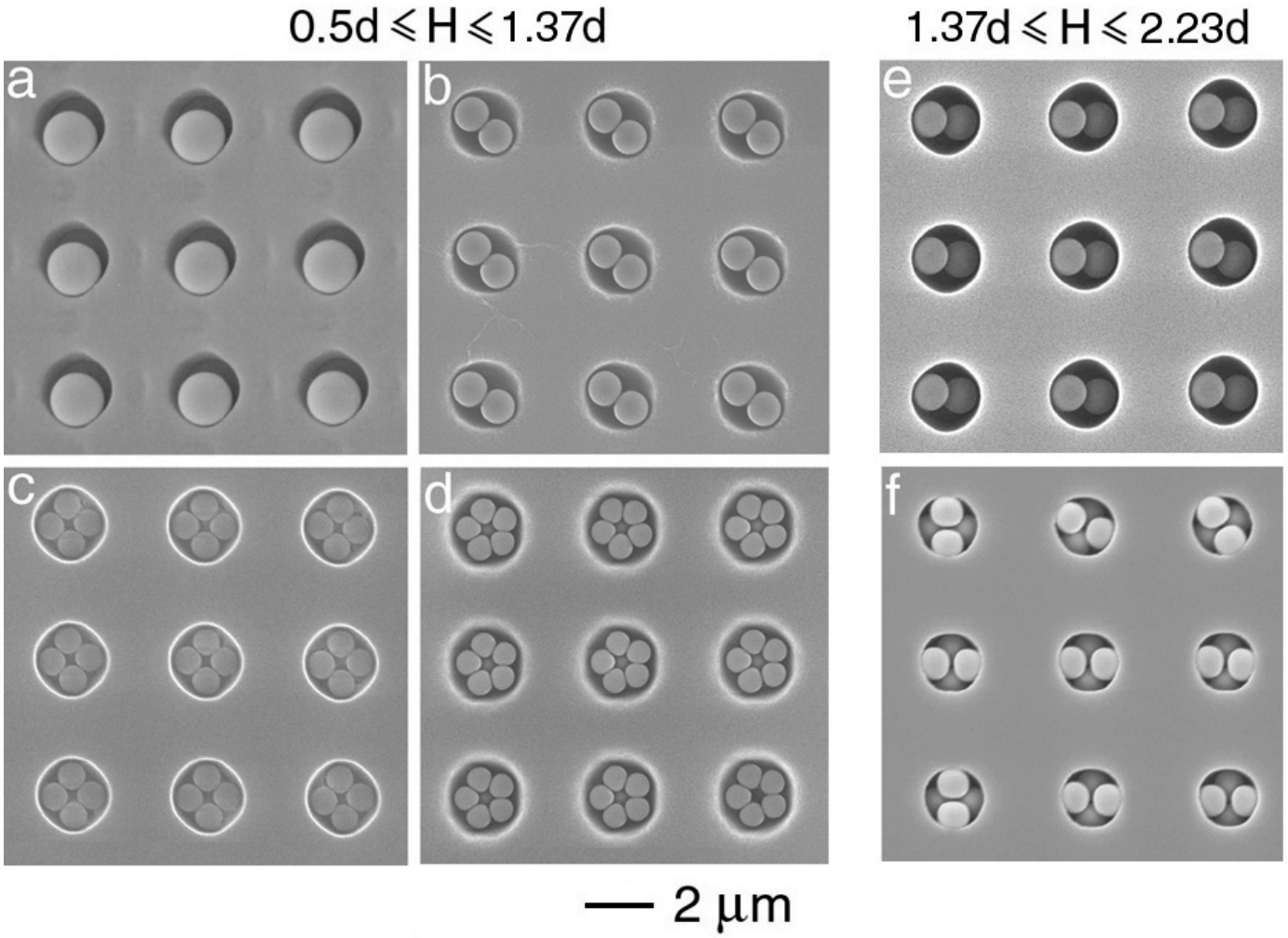
- Dimensions of holes and spheres determine packing arrangement
- Flow controls orientation of spheres

Younan Xia, U. of Washington

Control over the structure of the cluster by changing the ratio between the dimensions (D, H) of the holes and the diameter (d) of the polymer beads.

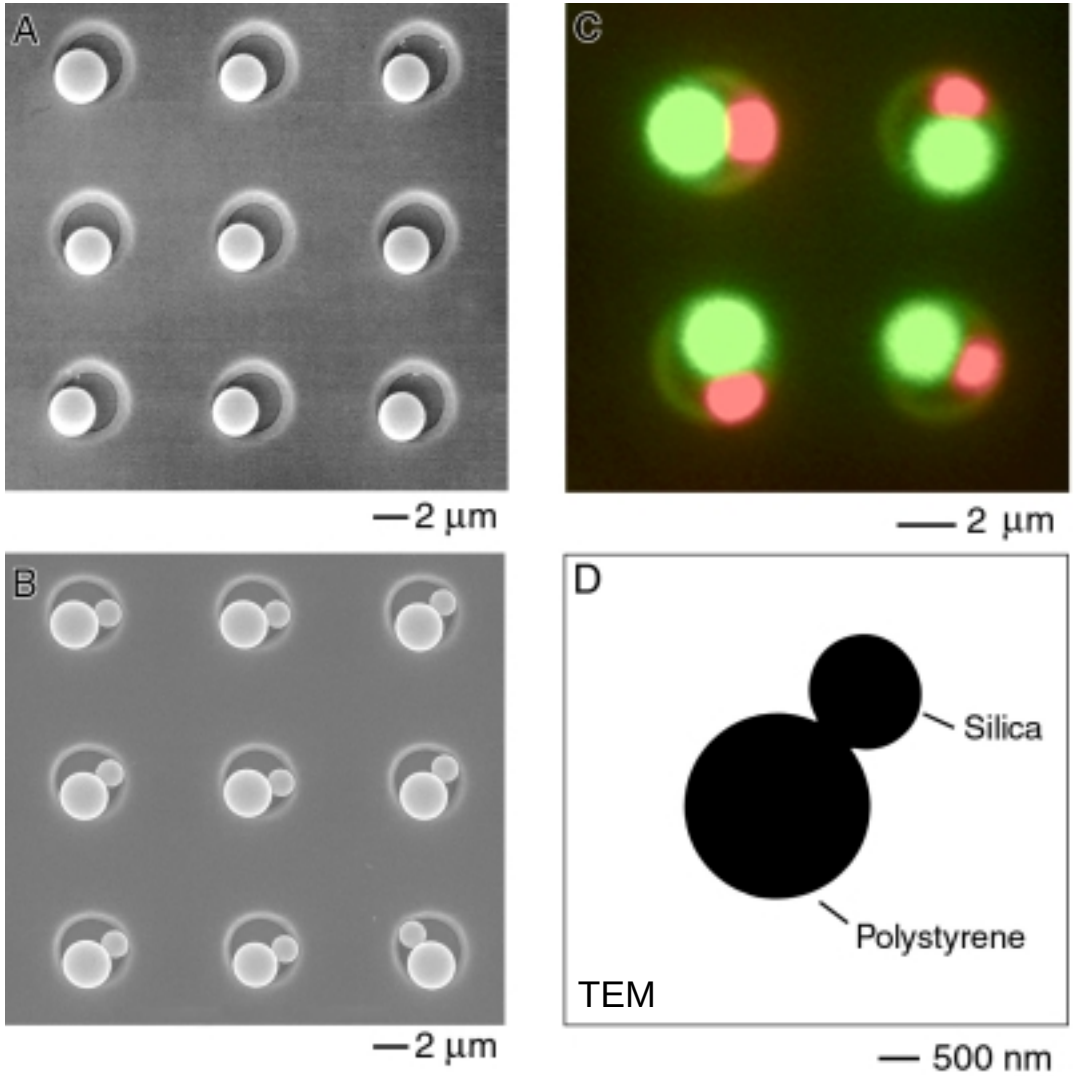
D/d	Single-layered (0.5d ≤ H ≤ 1.37d)		Double-layered (1.37d ≤ H ≤ 2.23d)	
1.00 - 2.00	monomer		dimer	
2.00 - 2.15	dimer		tetrahedron	
2.15 - 2.41	triangle		octahedron	
2.41 - 2.70	square		bi-square-pyramid	
2.70 - 3.00	pentagon		* Blue is the top layer	
3.00 - 3.30	hexagon		* Red is the bottom layer	

Younan Xia, U. of Washington



Younan Xia, U. of Washington

Synthesis of asymmetric bead dimers



Younan Xia, U. of Washington