Templating Nanoparticles with Self-Assembled Matrices

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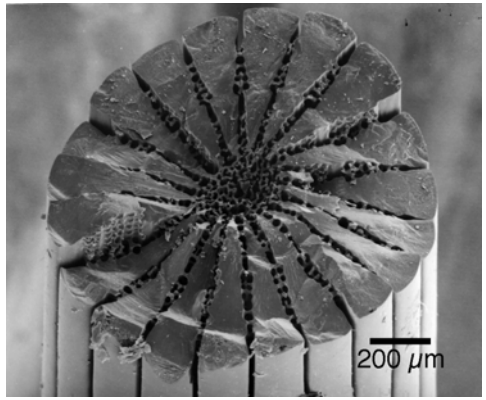
June 2004

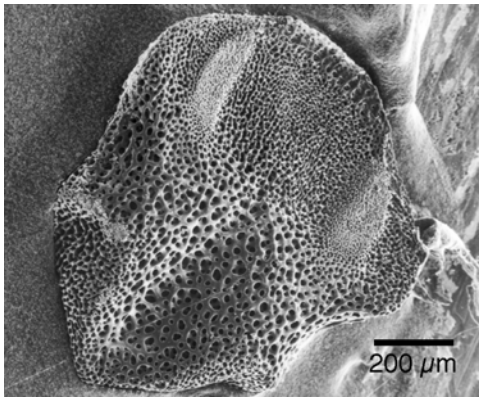
Support: DOE, NSF, ARO-MURI

MSE at Illinois

invertebrates

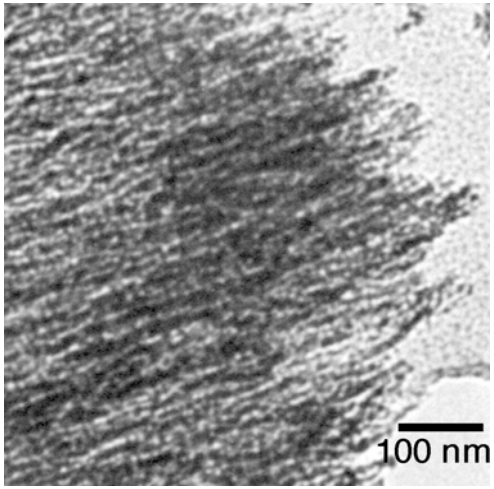


single crystal spine



spongy single crystal

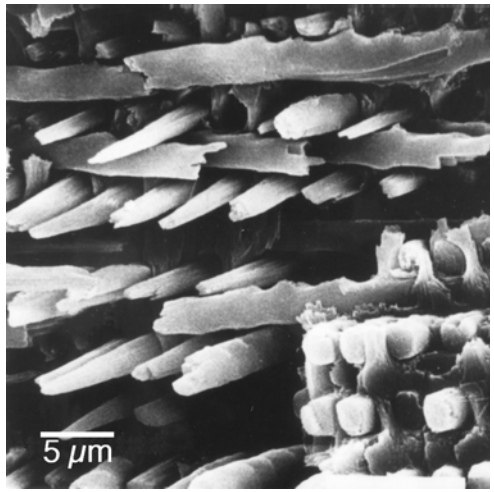
plants



composite fibrils

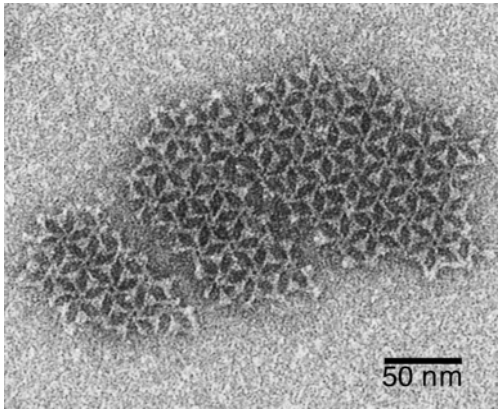
Biological Self-Assembly

mammals



mineral cross-ply

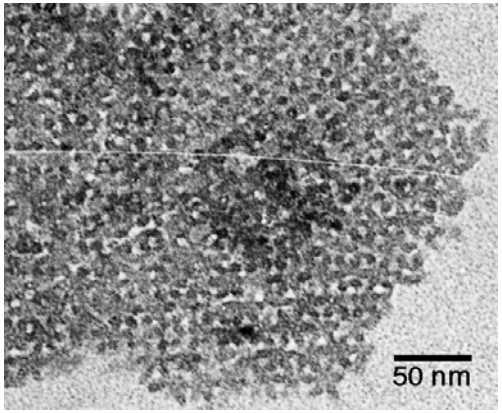
bacteria



protein template

Ca^{2+}

SO_4^{2-}

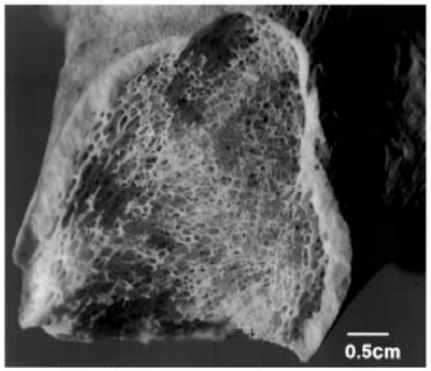


mineralized membrane

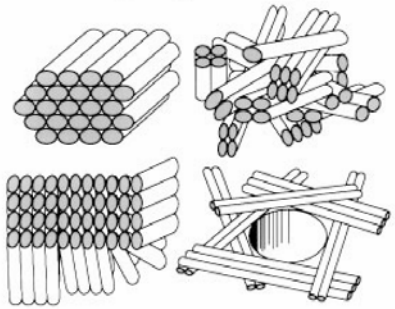
Figures courtesy of:
L. Addadi
C. C. Harrison
S. Schultze-Lam

Bone – Mineral Grown in (with?) a Biomolecular Template

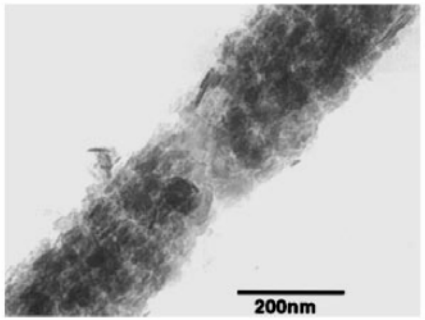
Weiner S., *Annual Rev. Mater. Sci.* 1998, **28**:271



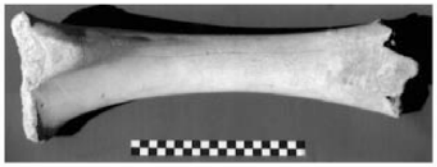
Level 6: Spongy vs Compact Bone



Level 4: Fibril Array Patterns

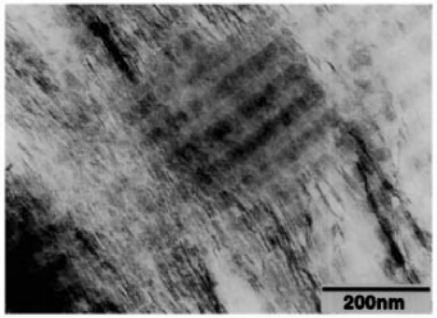


Level 2: Mineralized Collagen Fibril

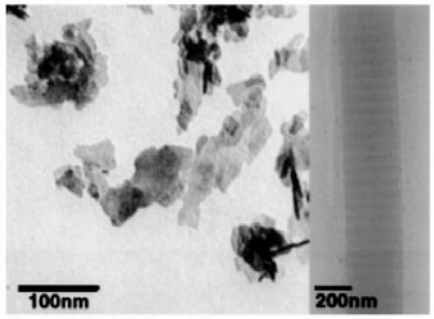


Level 7: Whole Bone

Level 5: Cylindrical Motifs: Osteons

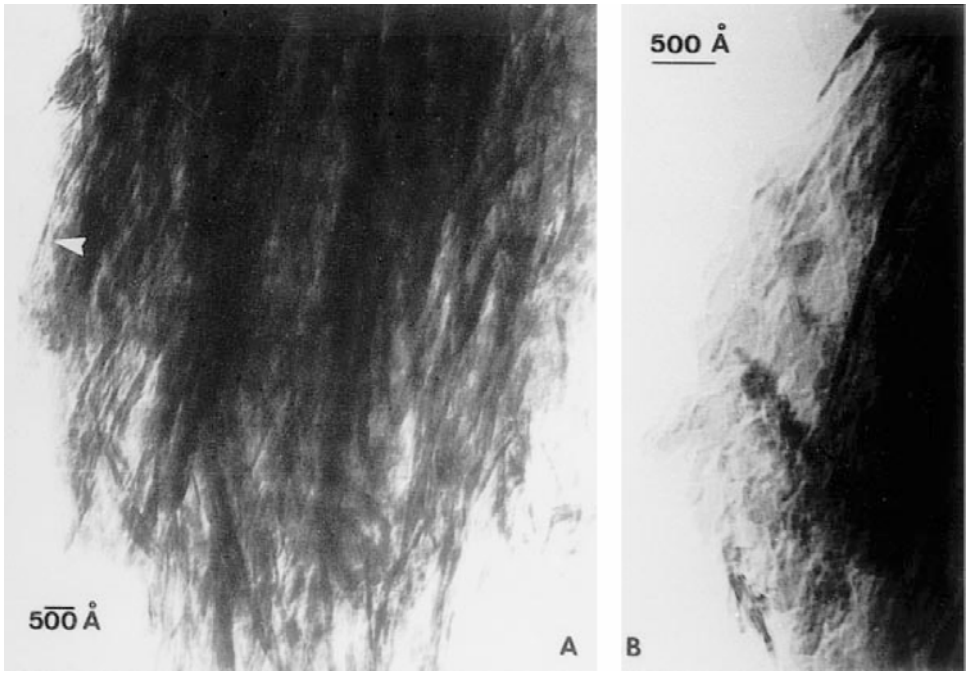


Level 3: Fibril Array



Level 1: Major Components

mineralized bone from a 50-year-old human male femur

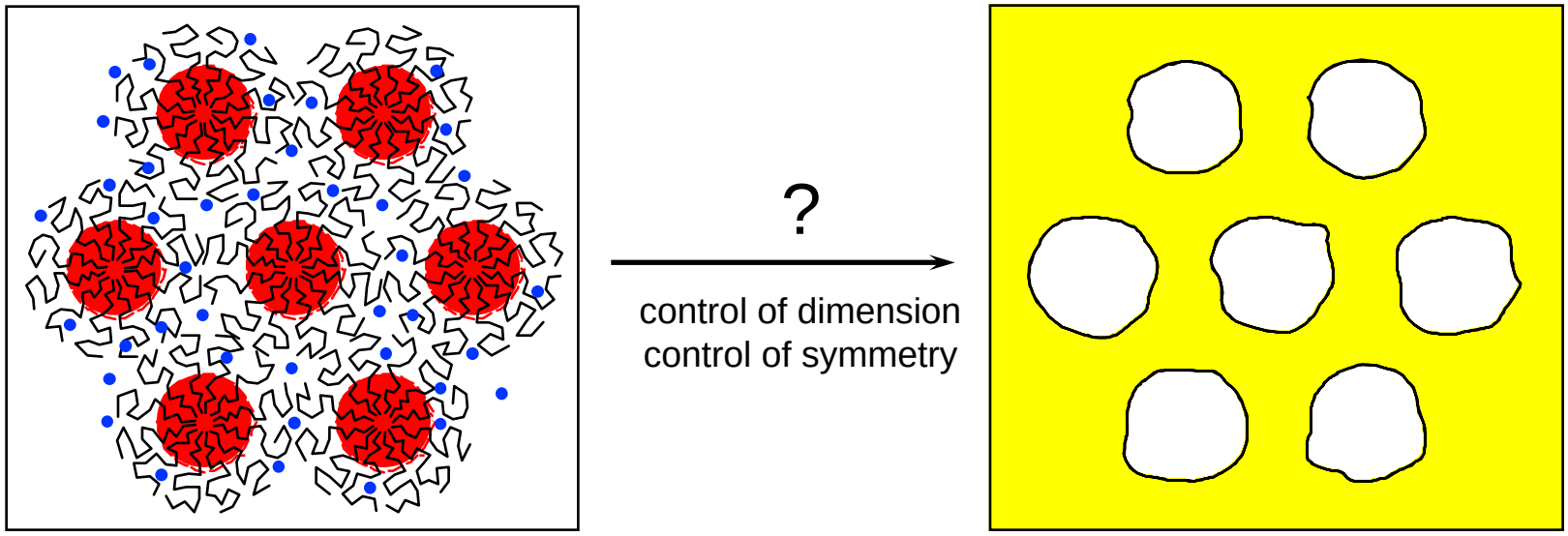


mineral - collagen nanocomposite.

Ziv V., *et al.*, *Microscopy Res. and Technique* 1996, **33**:203

Direct Templating of Semiconductor Nanostructures

"liquid crystal lithography"



lyotropic liquid crystal

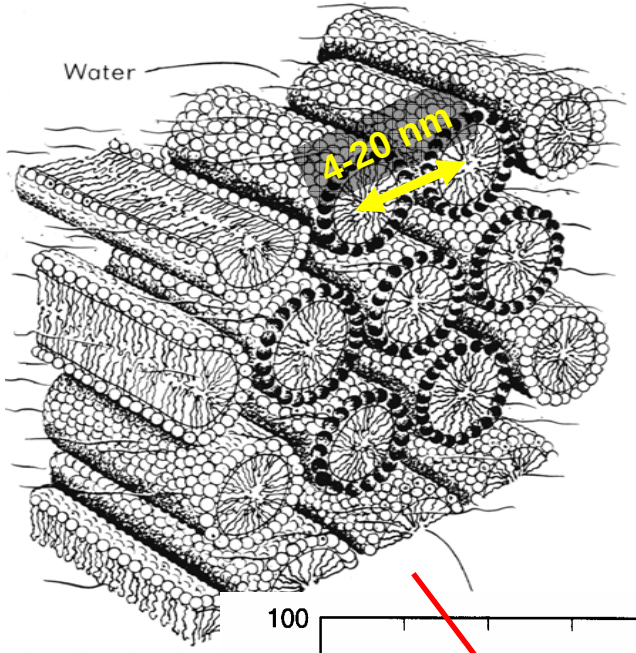
semiconductor nanostructure

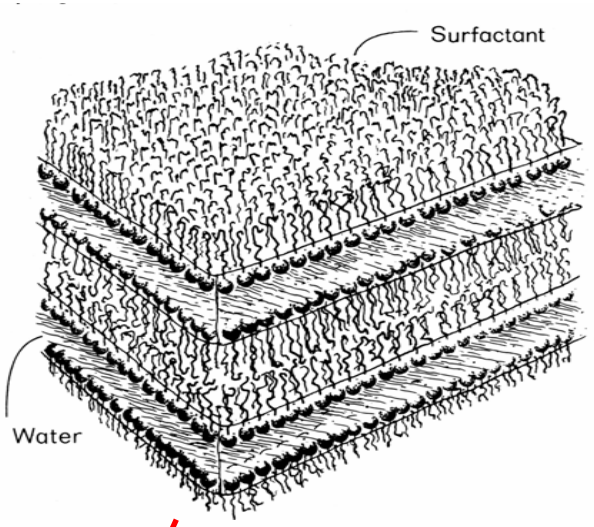
Motivation

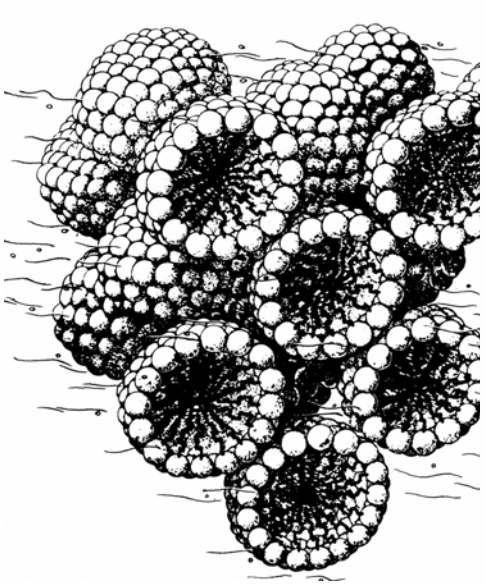
quantum dots
antidots
photoactive zeolites
filter membranes
LEDs
nanocomposites

Braun, various publications 1995-2000

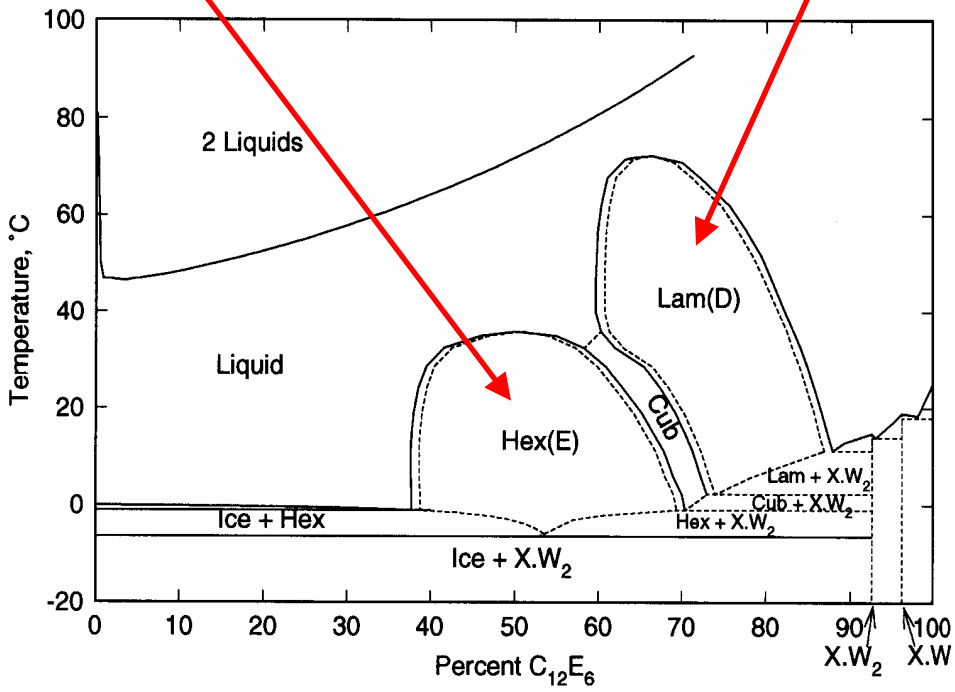
Lyotropic Liquid Crystals

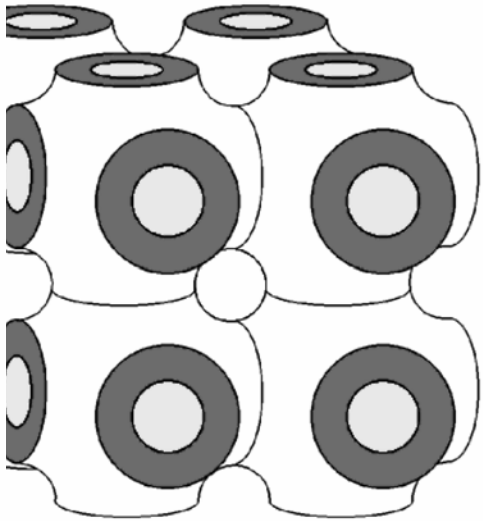




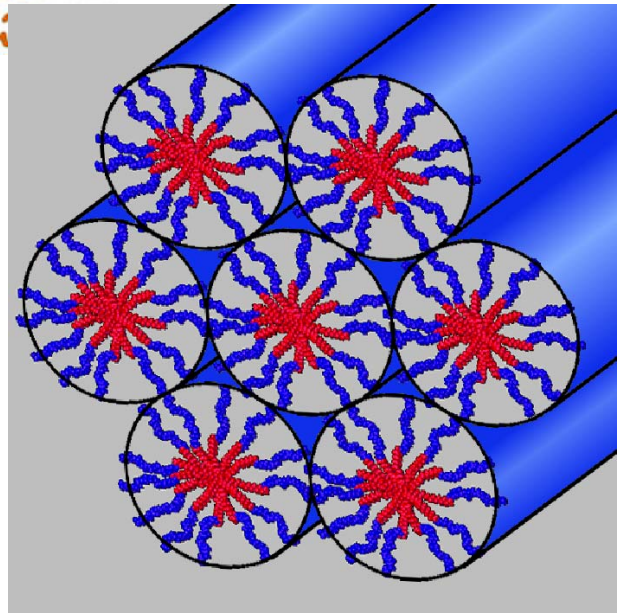


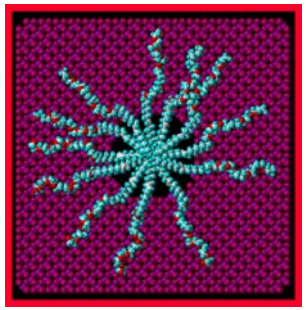
Cubic packing of micelles



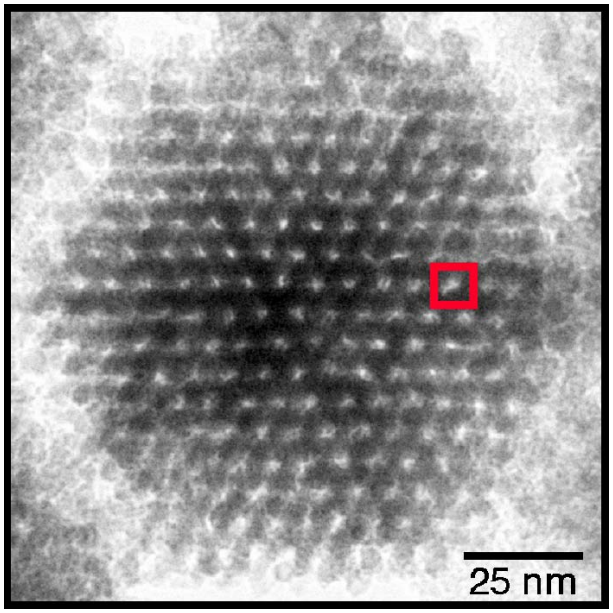


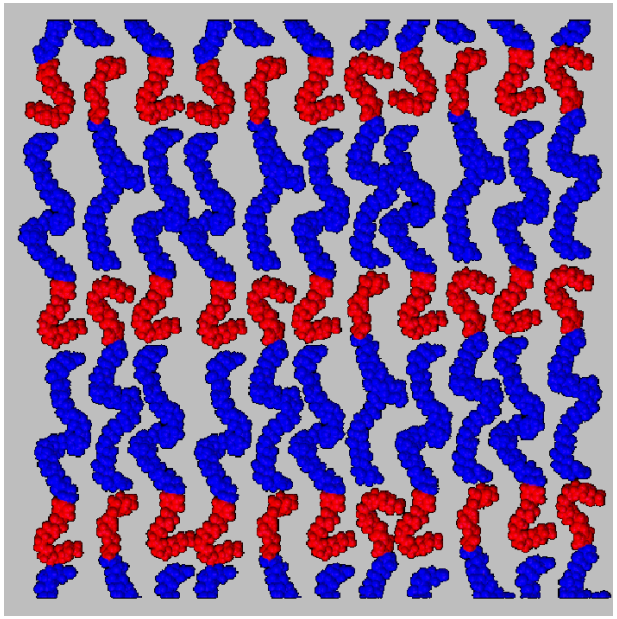
Bicontinuous



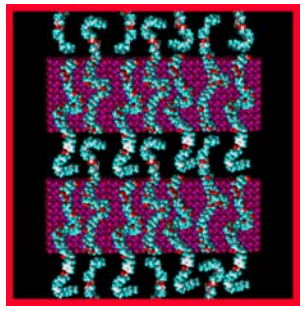


Nature 1996
Chem. Mater. 1997
Science 1997
JACS 1999

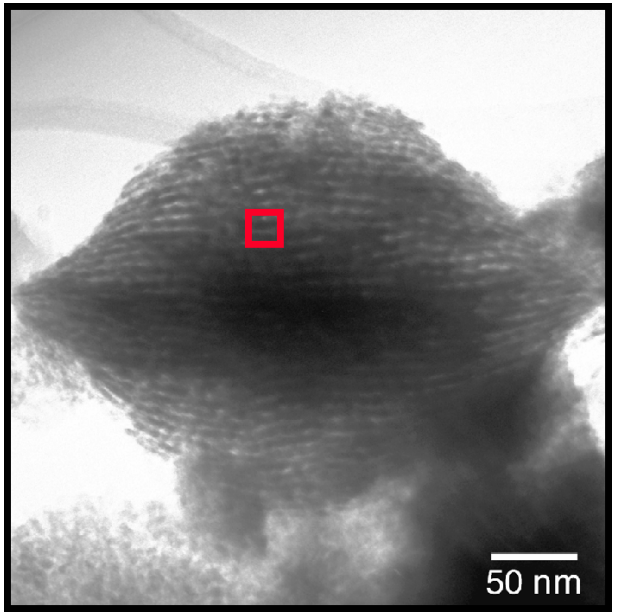




lyotropic liquid crystal



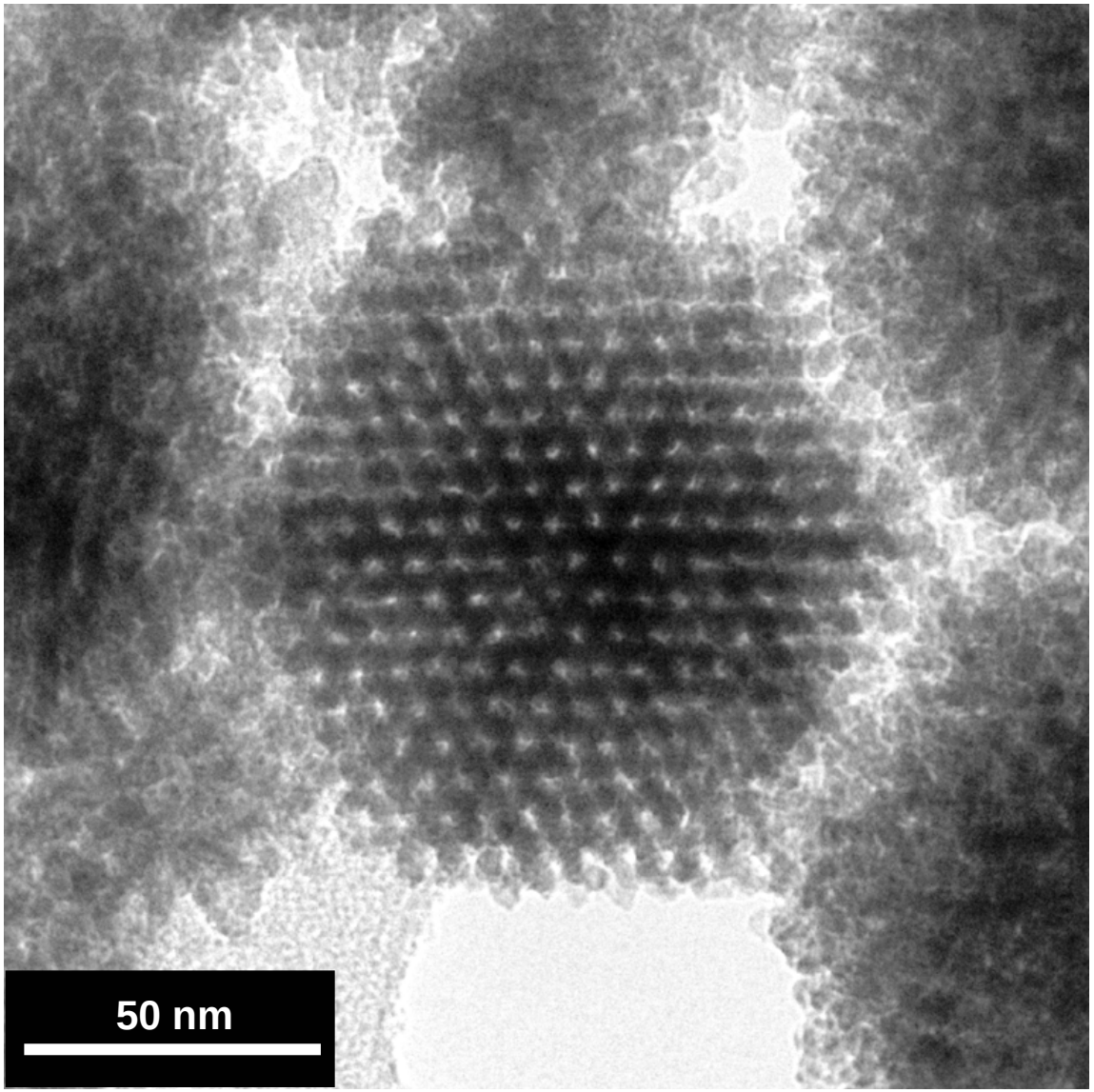
Adv. Mater. 1996



semiconductor nanostructures

P. V. Braun *et al.*

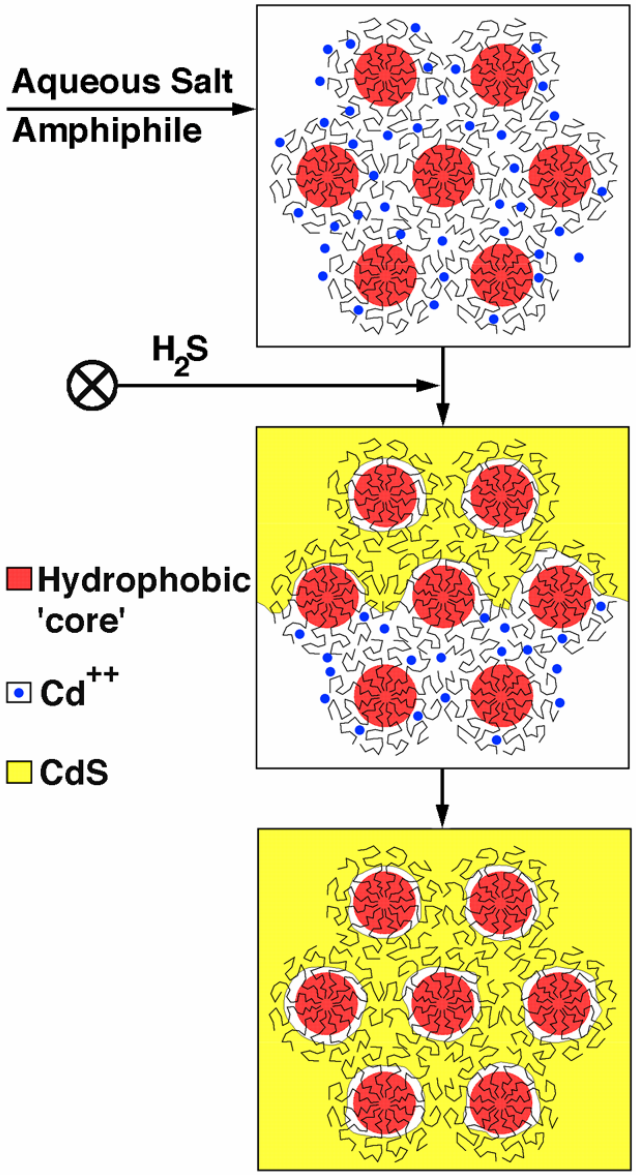
“Best Case”

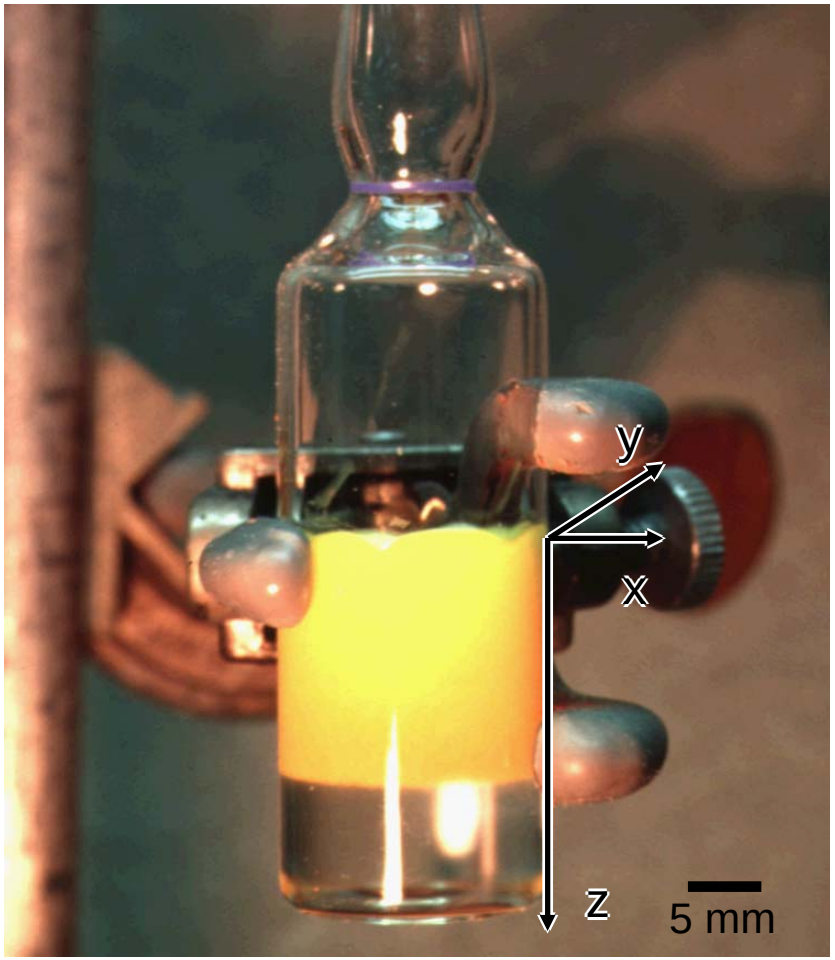


$Cd_{0.5}Zn_{0.5}S$

Bulk Mineralization of Lyotropic Liquid Crystals

synthesis of semiconductor-organic composites



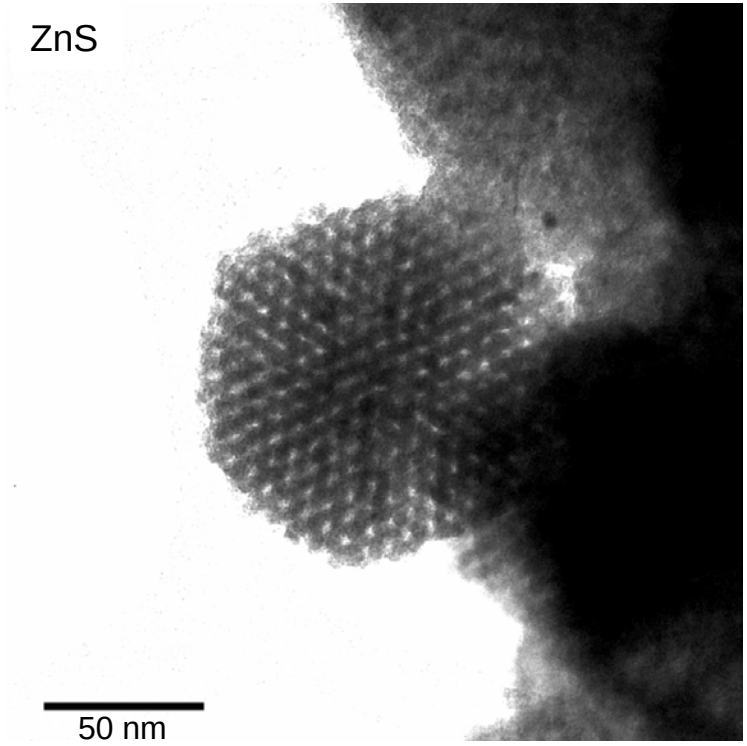


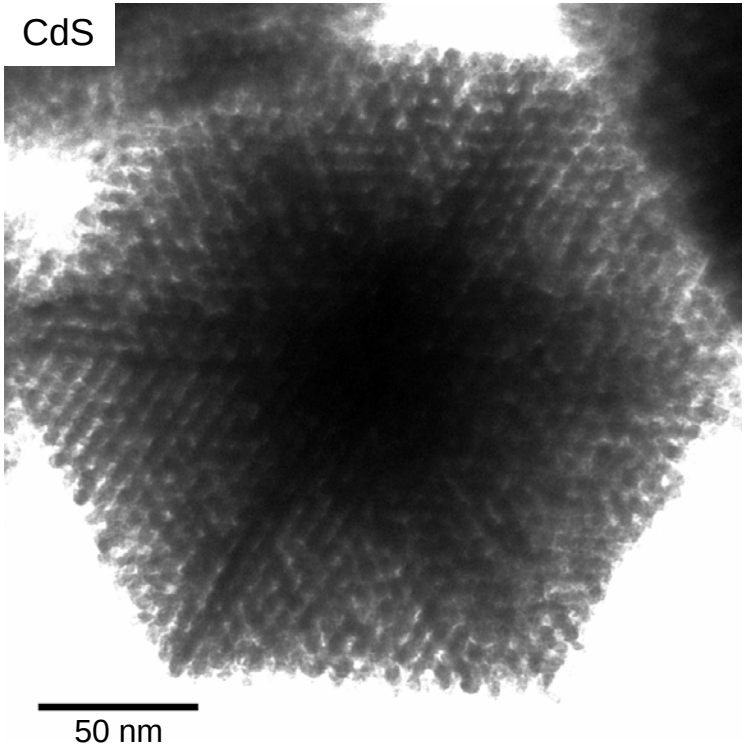
H_2S is introduced at the top of the vial, once it reaches the cadmium ion doped liquid crystal, the precipitation of CdS (yellow) begins immediately.

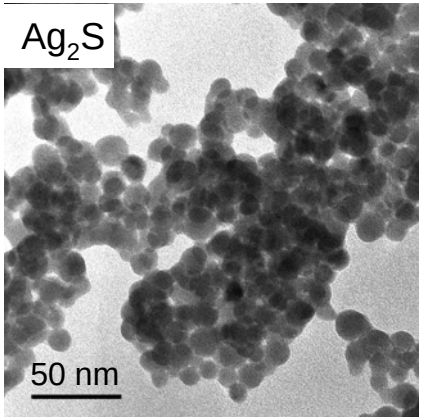
Braun, *JACS* 1999

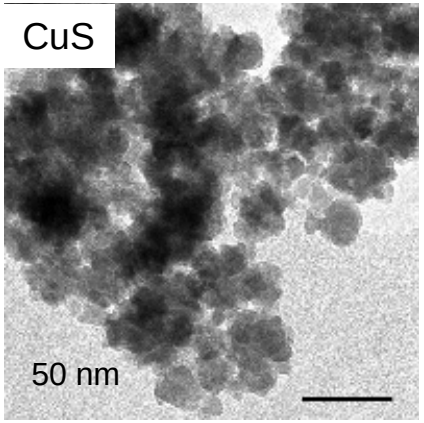
Templating and Nontemplating of II-VI Semiconductors

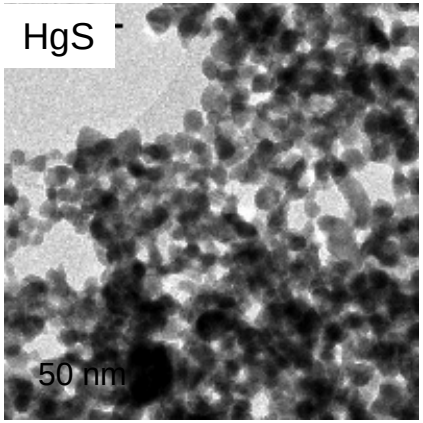
All grown in identical lyotropic liquid crystals

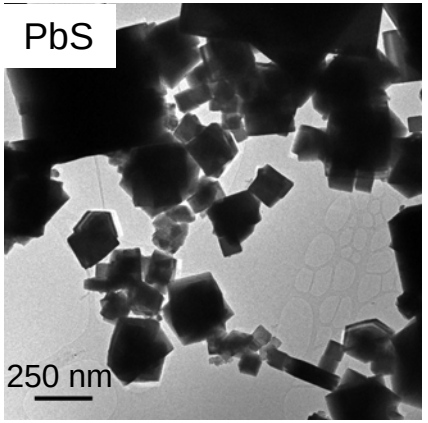








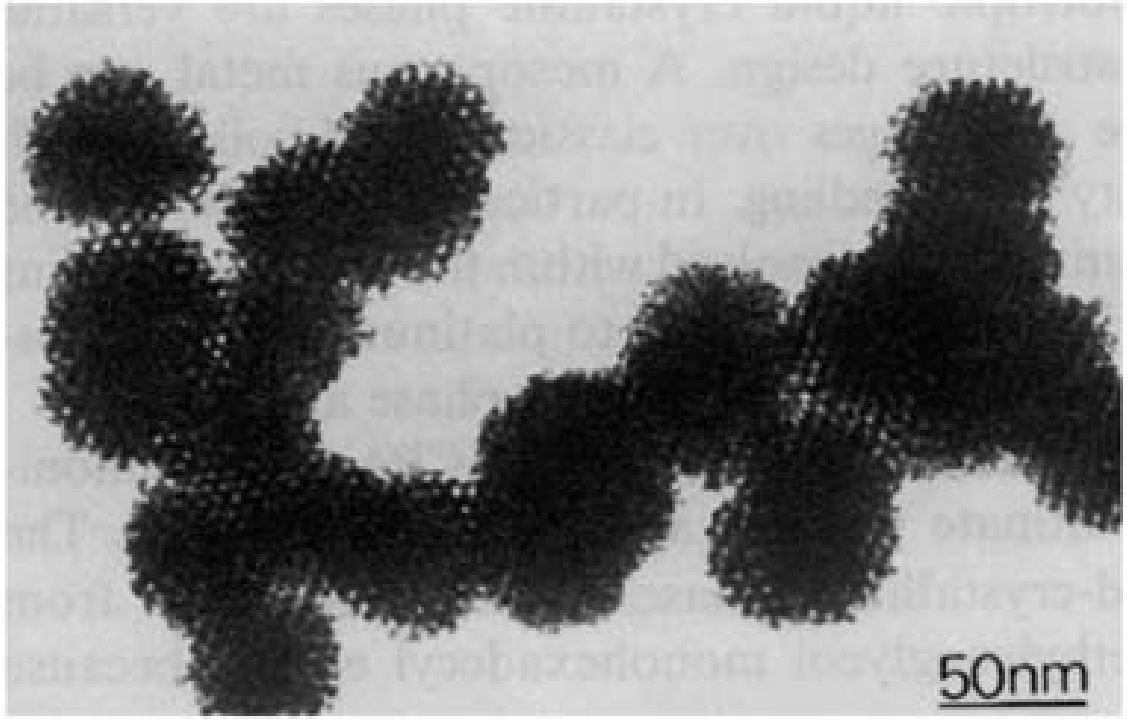




Braun, *JACS* 1999

Liquid Crystal Templating of Metal Nanoparticles

TEM of hexagonally structured mesoporous platinum



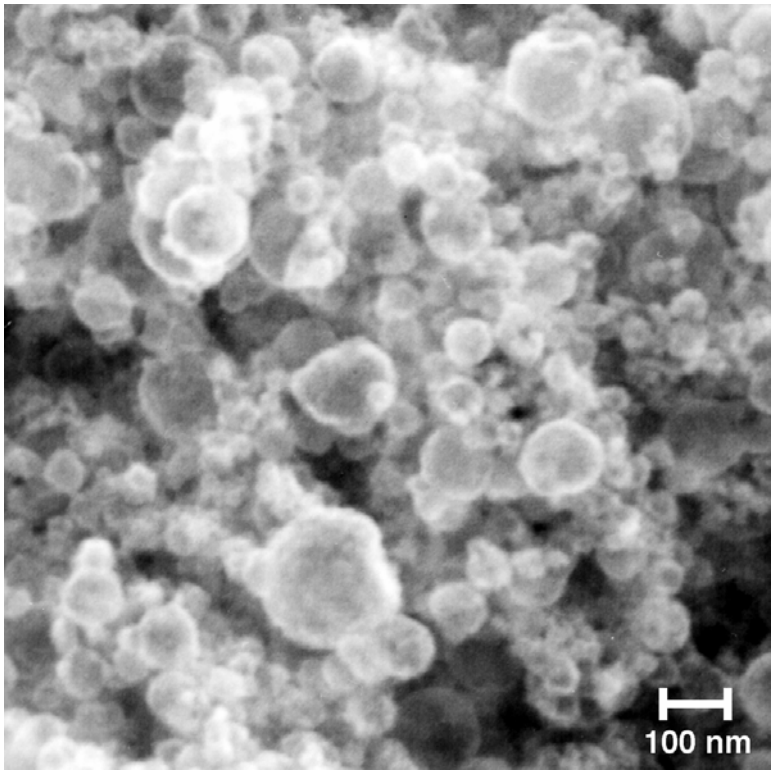
Grown in hexagonal lyotropic liquid crystal

G. S. Attard *et al.,* Angew Chem Int Ed Engl 36:1315 (1997)

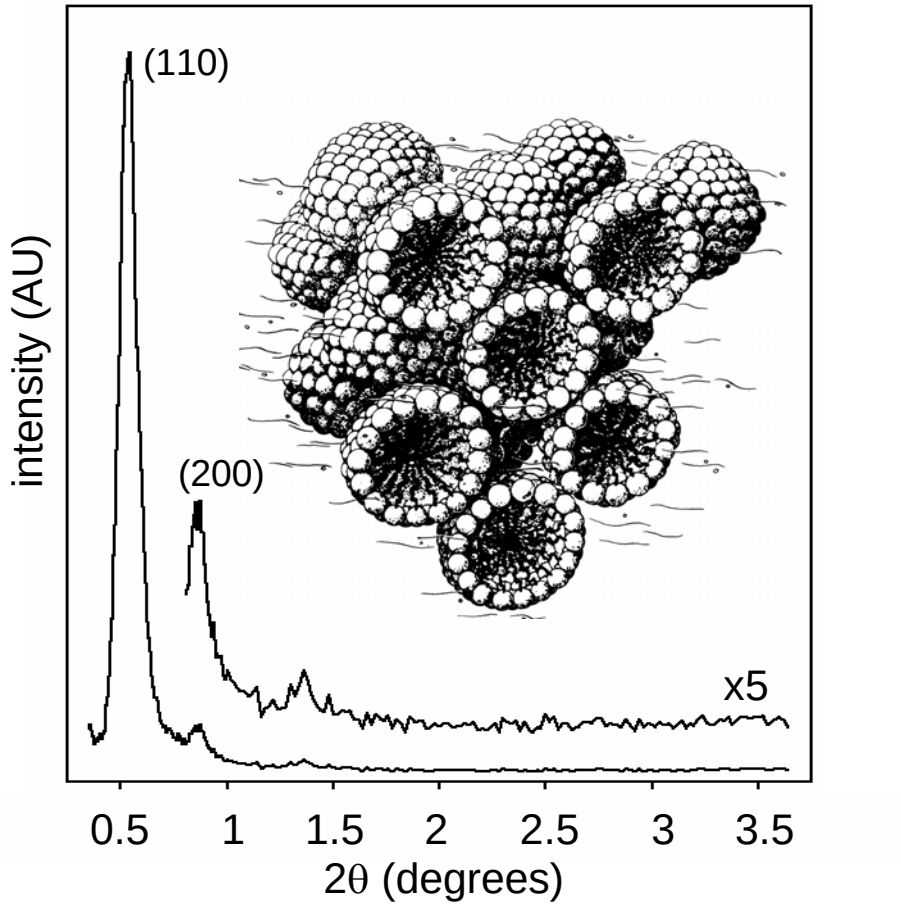
Mineralization of a Cubic Liquid Crystal

Cubic phase formed from:
60% $(EO)_{106}(PO)_{70}(EO)_{106}$
40% 0.1 M $Cd(CH_3CO_2)_2$

SEM of hollow CdS spheres



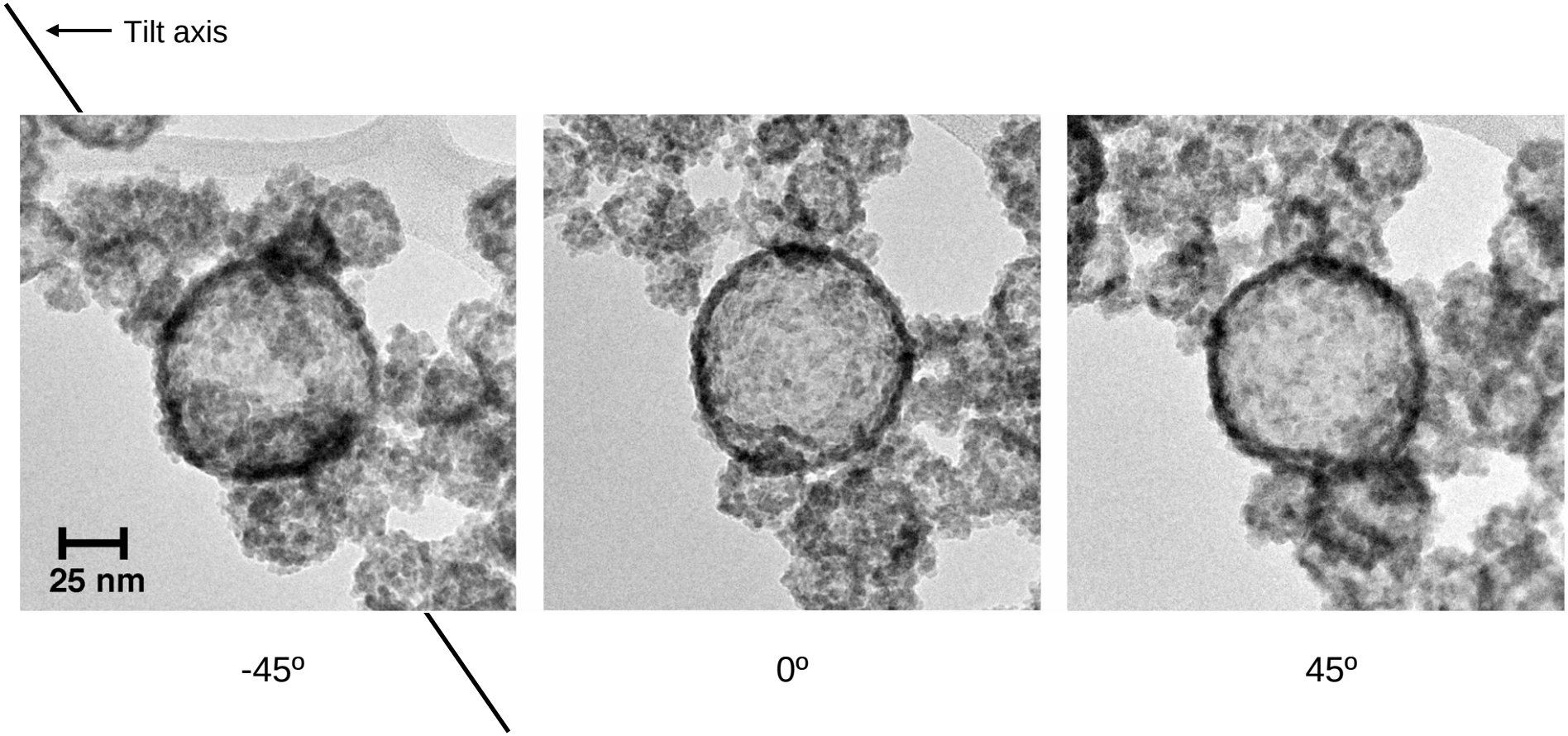
SAXS



Hollow sphere morphology is the result of mineralization around one or more micelles (micelle diameter = 23 nm)

Braun, *Mater. Res. Bull* 1999

Mineralization of a Cubic Liquid Crystal



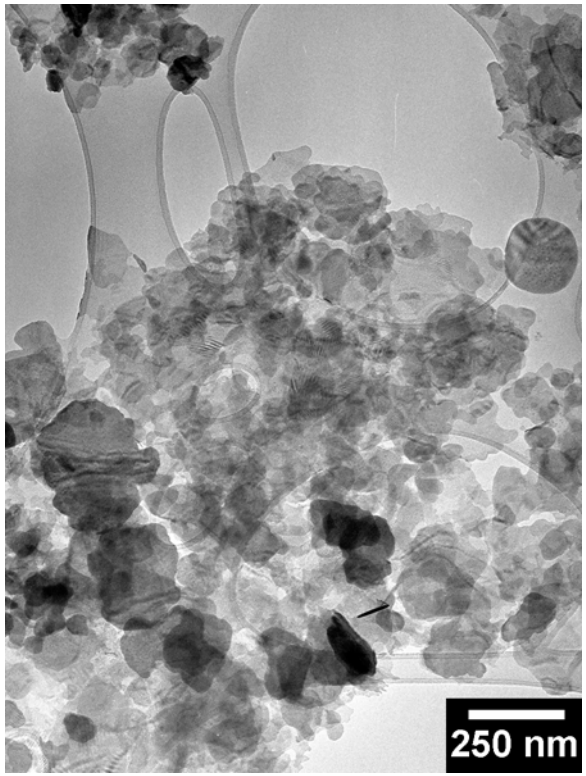
Tilt series confirms hollow sphere morphology

Braun, *Mater. Res. Bull* 1999

BiOCl Synthesized in Lyotropic Liquid Crystals

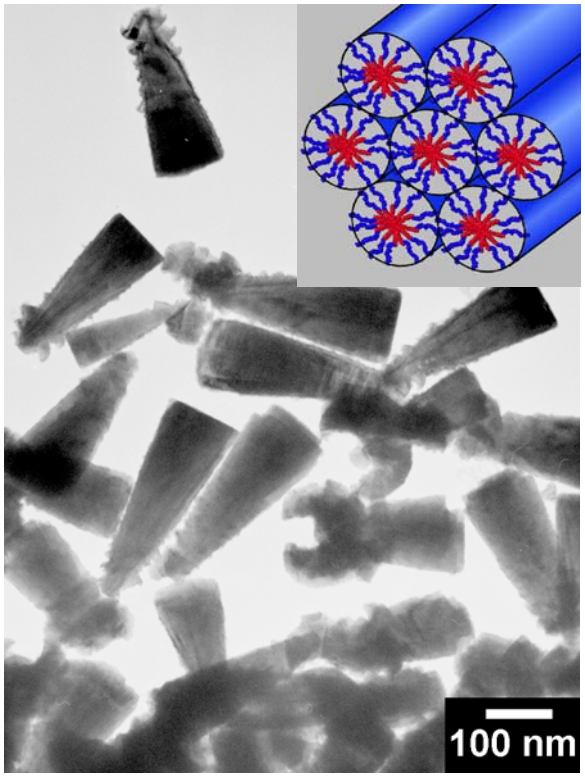
potential precursor for nanostructured thermoelectric materials

water



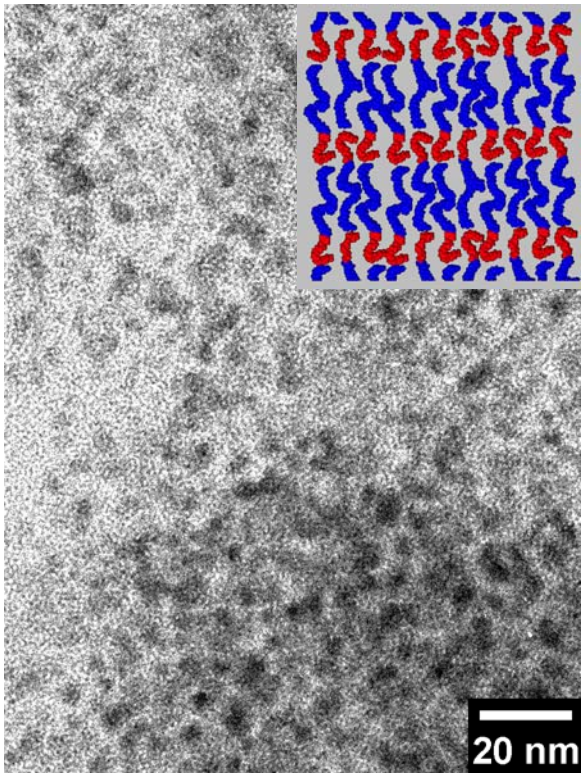
250 nm disks

hexagonal phase
(50% amphiphile, 50% water)



250 by 100 nm arrowheads

lamellar phase
(78% amphiphile, 22% water)



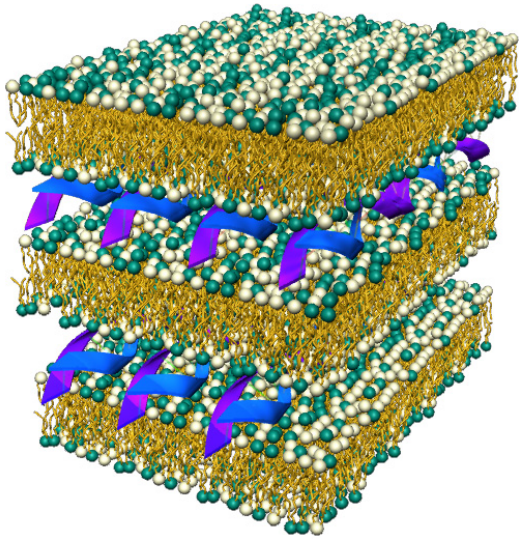
5 nm nanoparticles

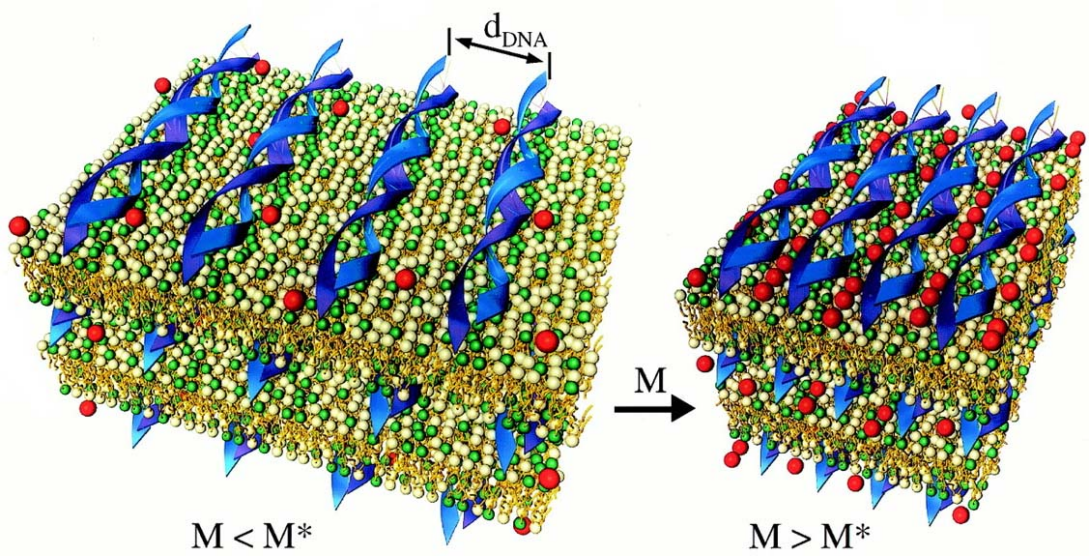
$BiCl_3$ stabilized in $HCl_{(aq)}$, diffuse in NH_4OH gas $\longrightarrow$ BiOCl

Dellinger, Braun, *Scripta Materialia*, 2001

Biological Templating of CdS in DNA-membrane complexes

Organization of ion precursors using DNA-membrane complexes

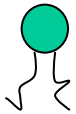




Biopolymer

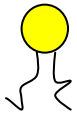
DNA

Cationic Lipid

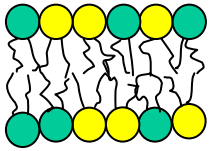


DOTAP

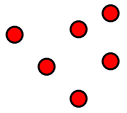
Neutral Lipid



DOPC

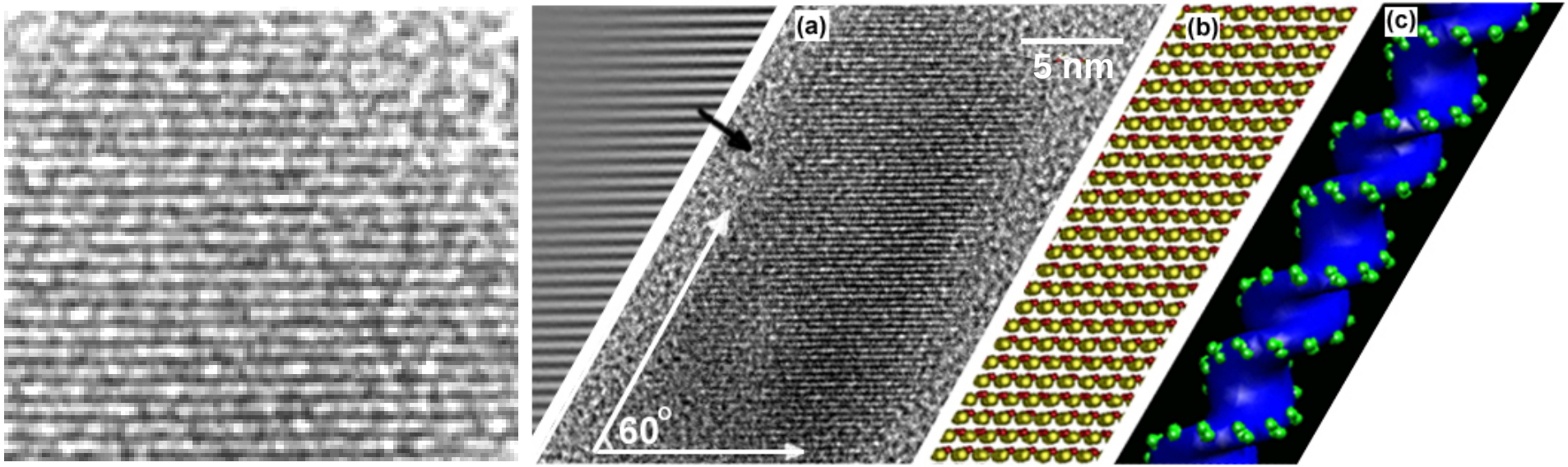


Cadmium ion Cd^{2+}
(precursor to CdS)



Pictures adapted from Rädler J.O. et al, Science (1997) and Koltover I. et al, PNAS (2000).

CdS nanorods –Crystallographic Control

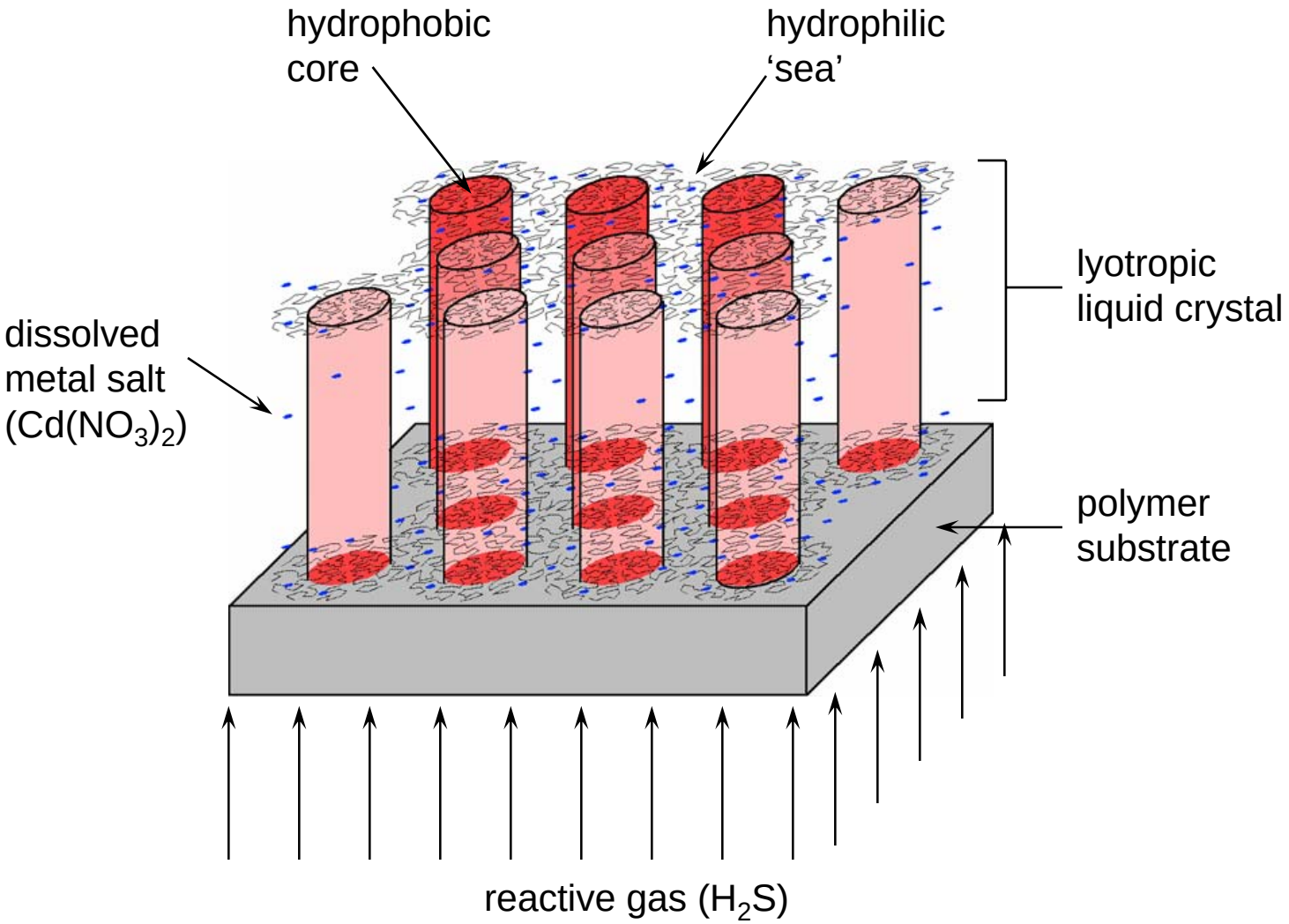


HRTEM CdS lattice DNA

Crystallographic control via biomolecular architecture: Templated nanorods have (002) directions tilted by 60° with respect to the rod axis, in contradistinction to all known templated CdS nanorods

Liang et al., JACS, **125**, 11786-11787 (2003)

Direct Templating of Semiconductor Thin Films



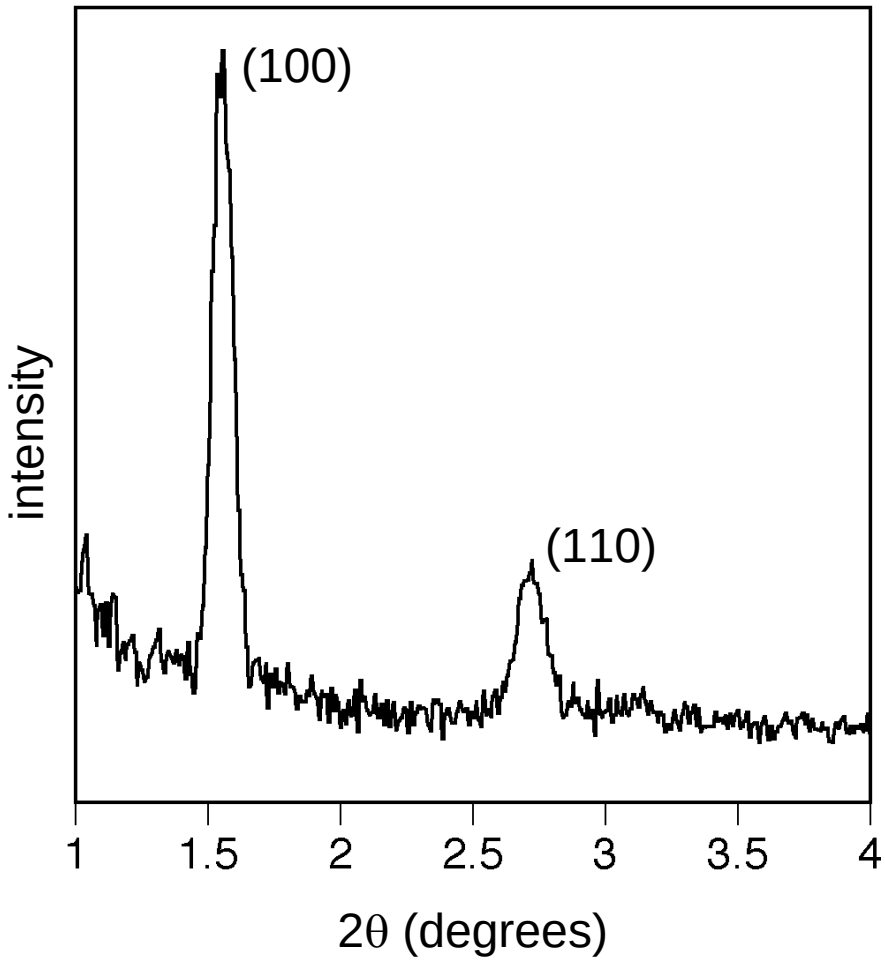
"liquid crystal lithography"

Braun, unpublished

Robust Hexagonal Lyotropic Liquid Crystal

polyol amphiphile

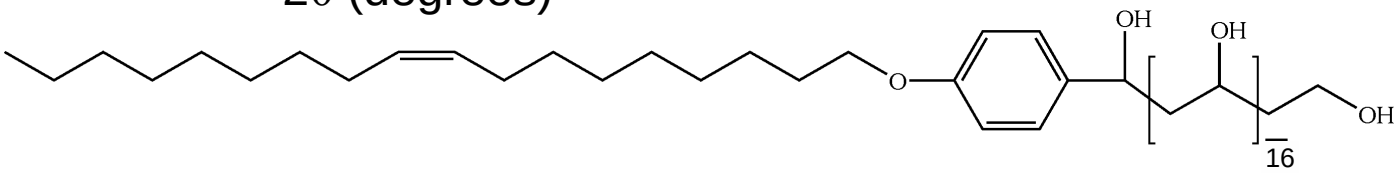
SAXS of polyol amphiphile saturated with water



Thin film templating was attempted with **many** oligo(ethylene oxide) based amphiphiles with **no** success, motivating the synthesis of the polyol amphiphile below

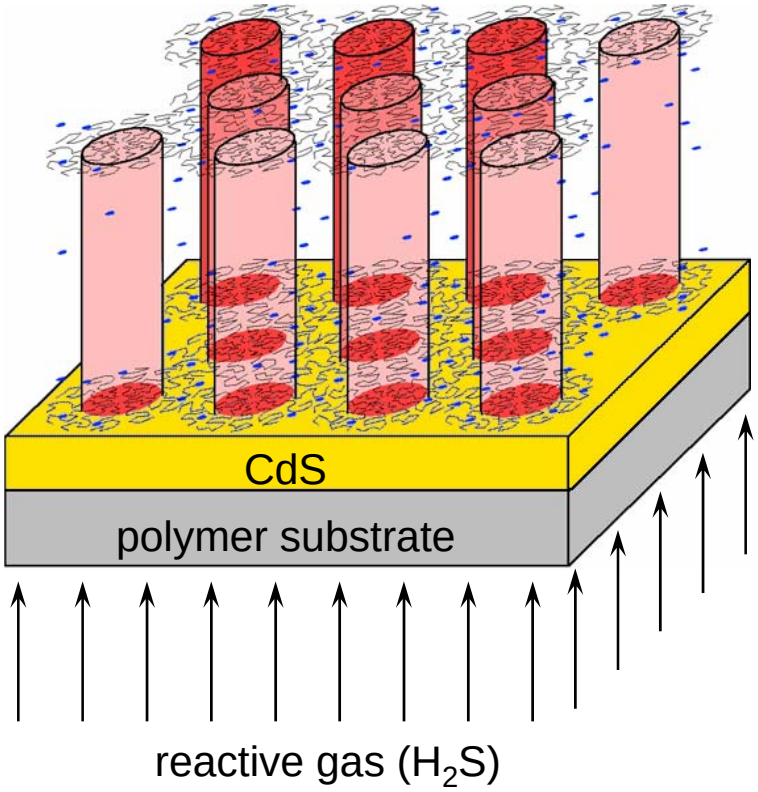
<u>Polyol Amphiphiles-properties</u>

- insoluble in water
- swell forming a hexagonal lyotropic liquid crystal
- synthesized via living cationic polymerization of t-butyl vinyl ether followed by deprotection

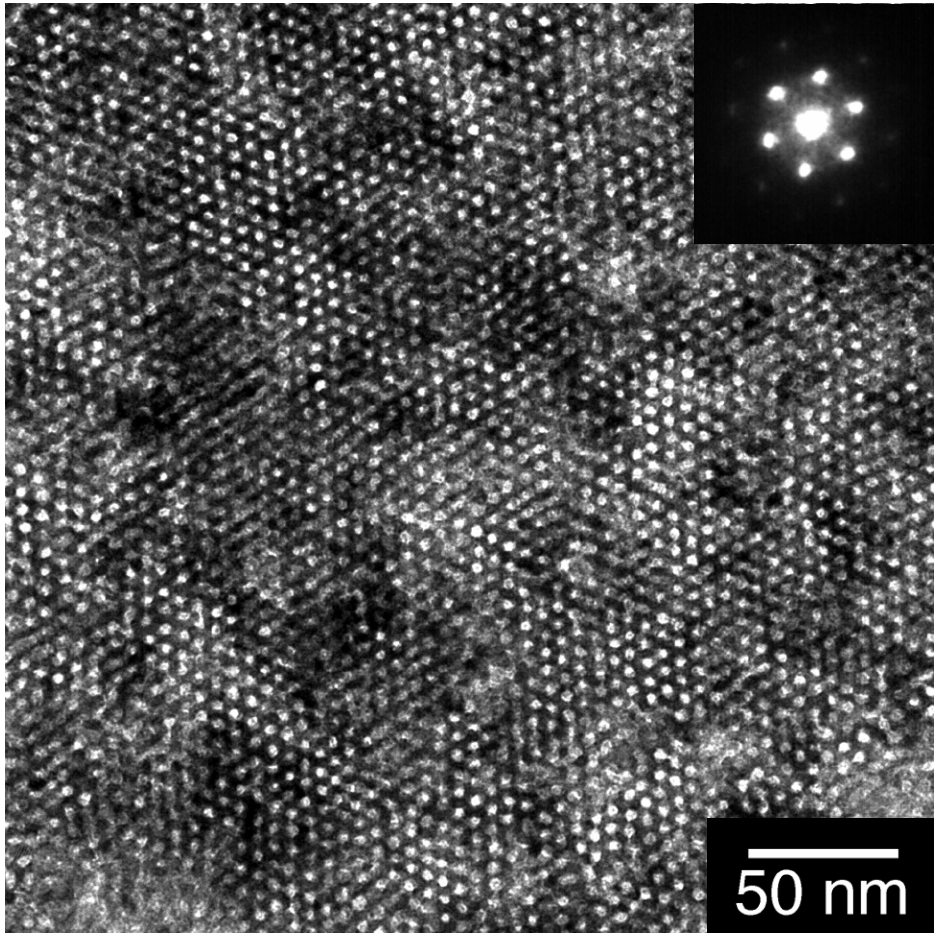


Braun, unpublished

Direct Templating of CdS Films



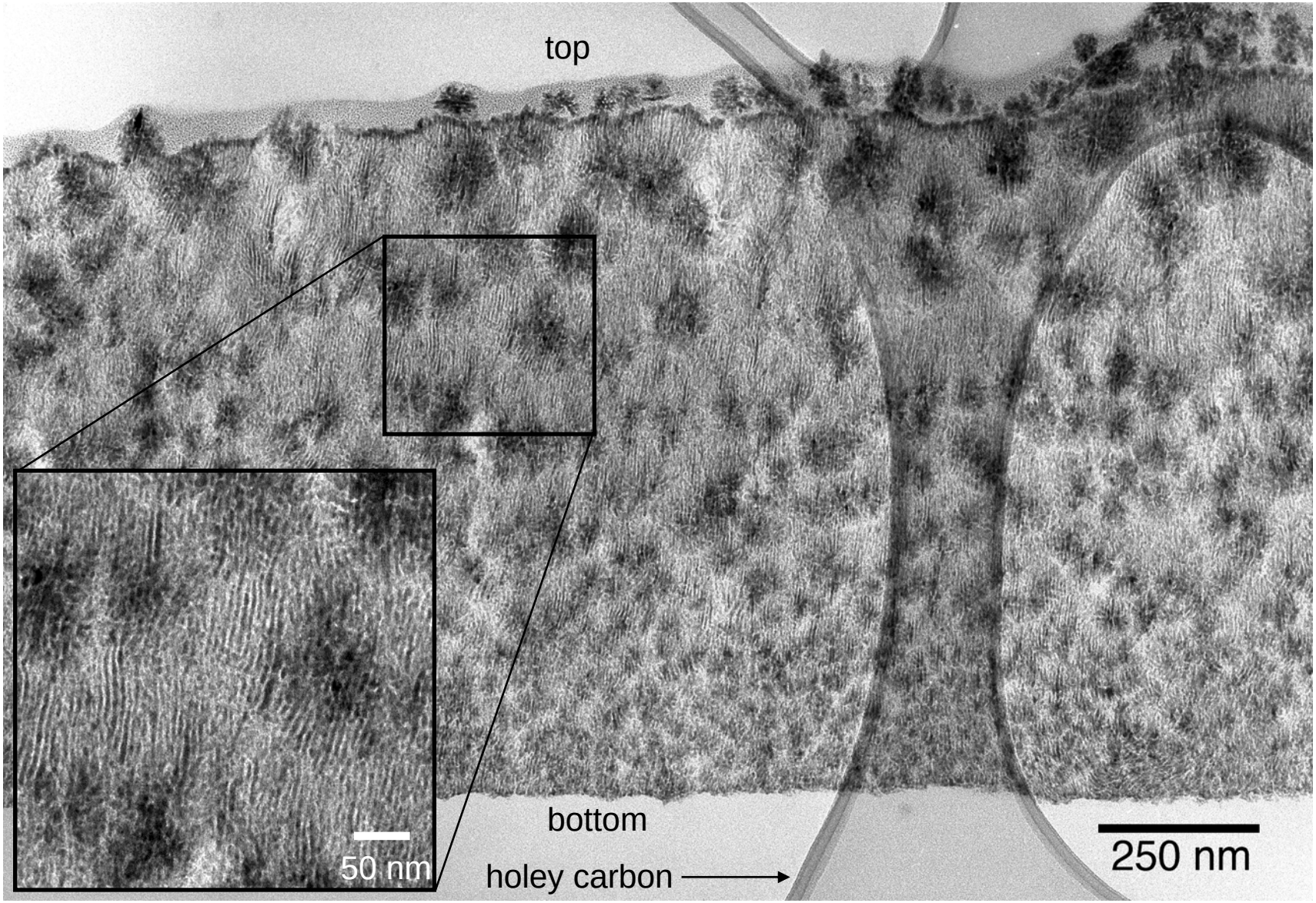
polyol based lyotropic liquid crystal directly templates the growing CdS film as H_2S diffuses through the polymer substrate



TEM of the CdS film, after removal of the organic template. Inset is a small angle electron diffraction from the film

Braun, unpublished

CdS Thick Film Growth

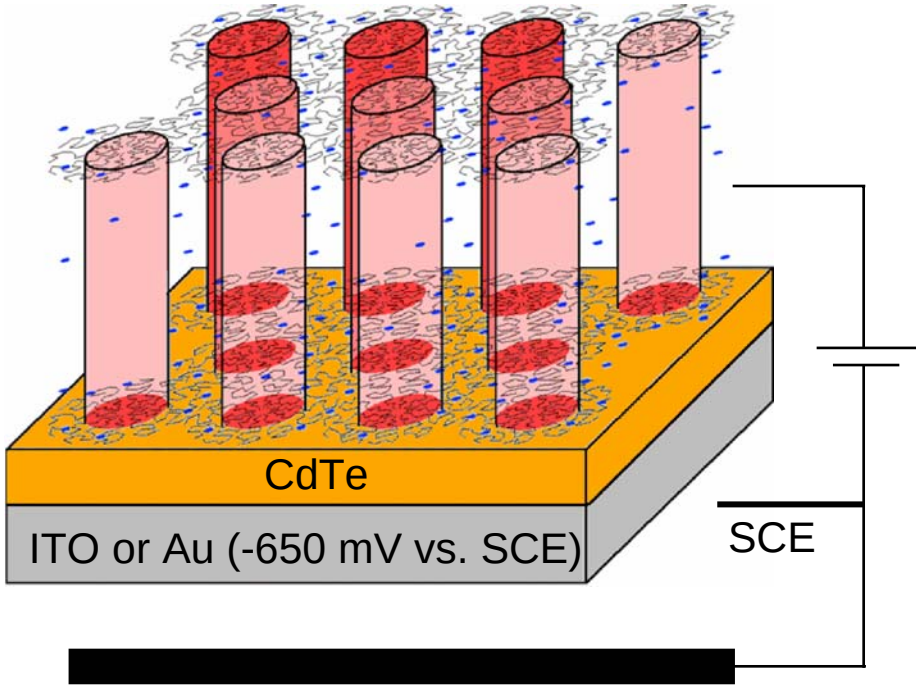


microtomed cross-section of a templated CdS film grown with 15 min. H_2S exposure, note mesopores running entirely through the film, as required by the growth mechanism

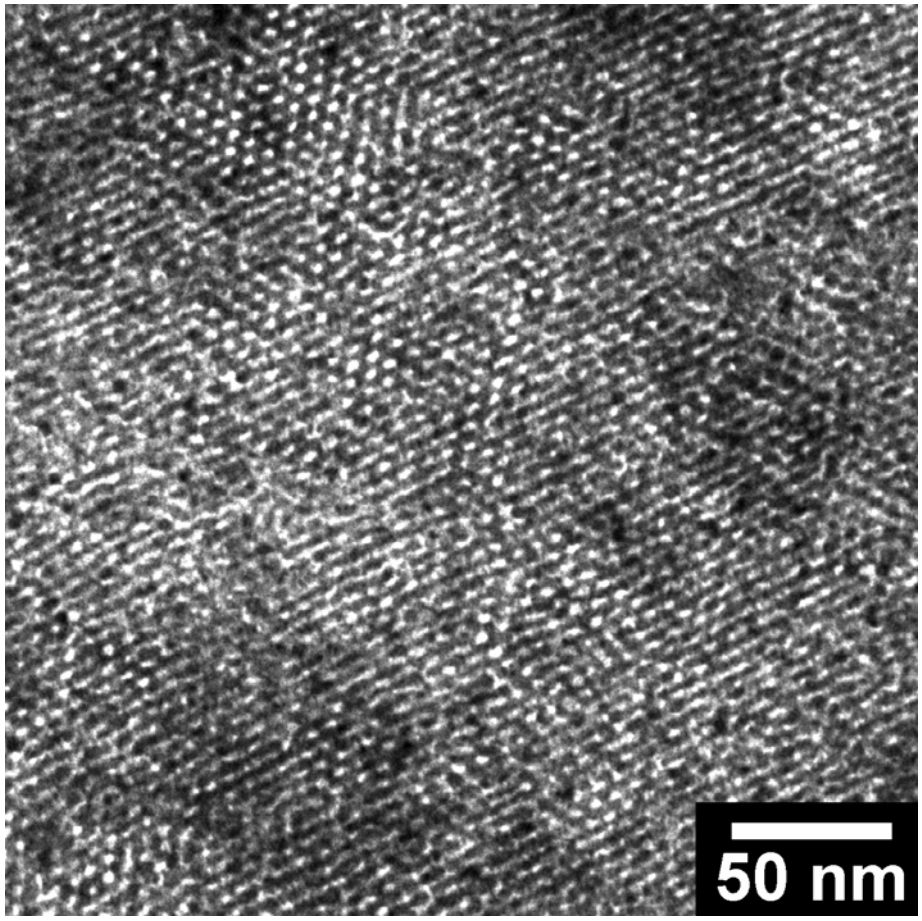
Braun, unpublished

Electrodeposition of CdTe Film

Direct Templating by Hexagonal Liquid Crystal



Bias substrate to -650 mV vs. SCE resulting in CdTe growth

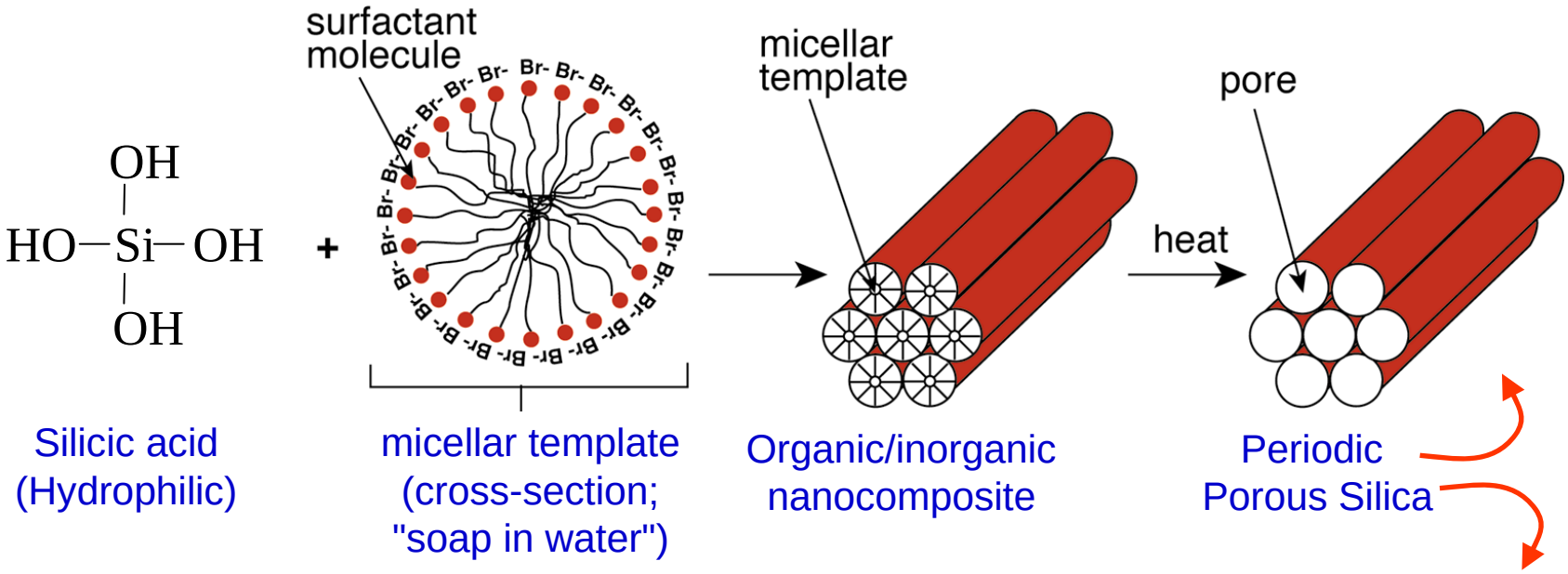


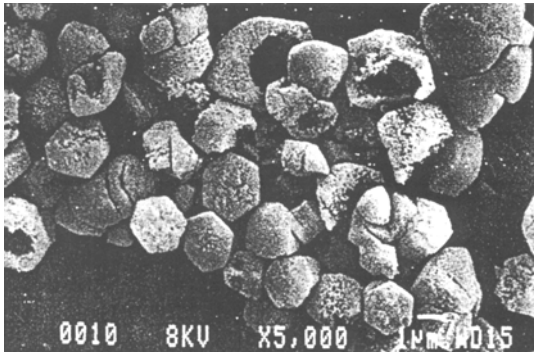
TEM of periodically nanoporous CdTe film

Potential for chemical sensors and solar energy conversion

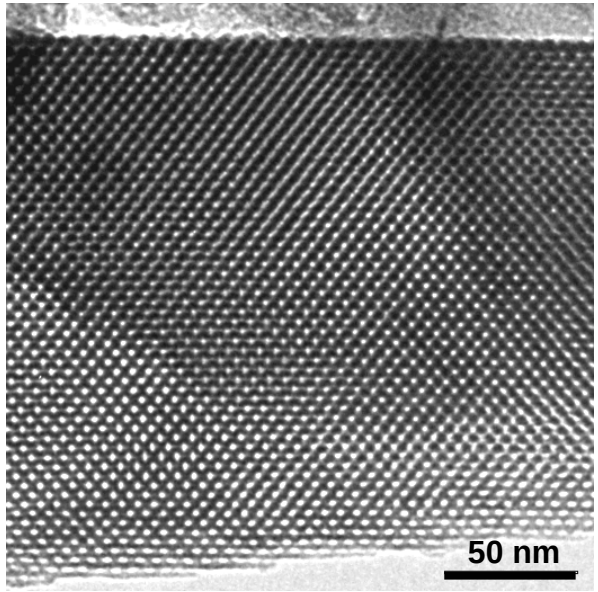
Braun, unpublished

Combine Sol-Gel Processing + Molecular Self-Assembly (Mobil)



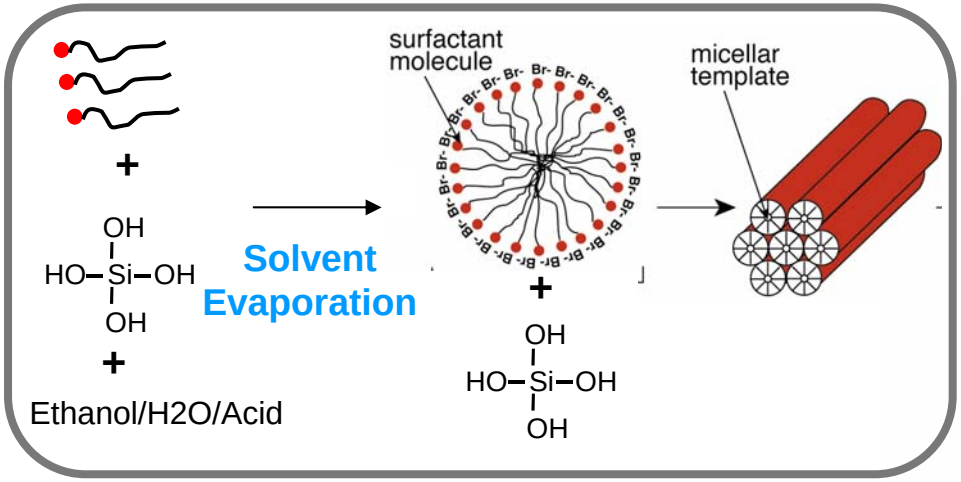


Kresge, C.T. et al.,
Nature, 359, 710-712, 1992

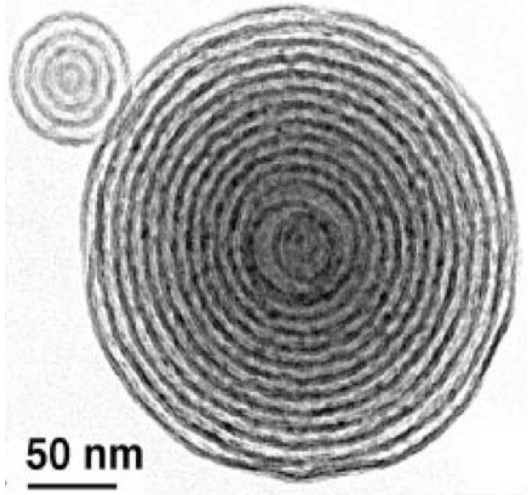


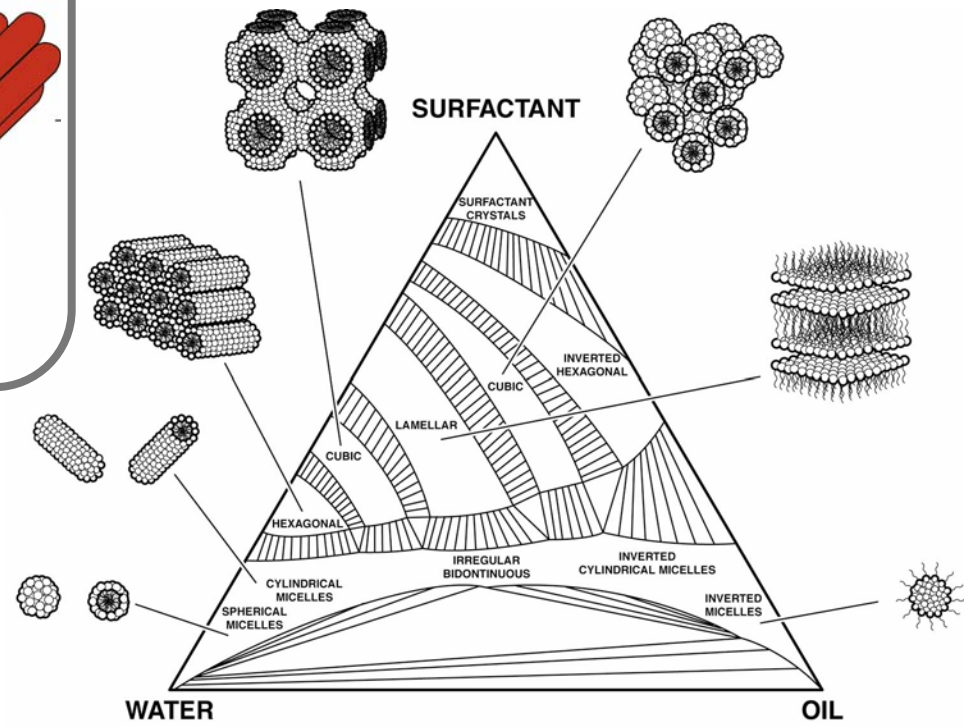
Brinker et al., Adv. Mater. 1999

Evaporation Induced Self-Assembly of Mesoporous Silica



Formed by spray drying

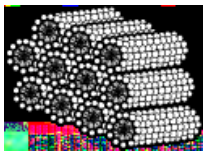


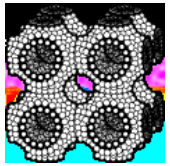


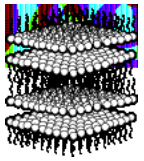
Silicic Acid, Hydrophilic precusor

Ethanol Co-Solvent

Monomers, PhotoInitiators, Hydrophobic Precursors



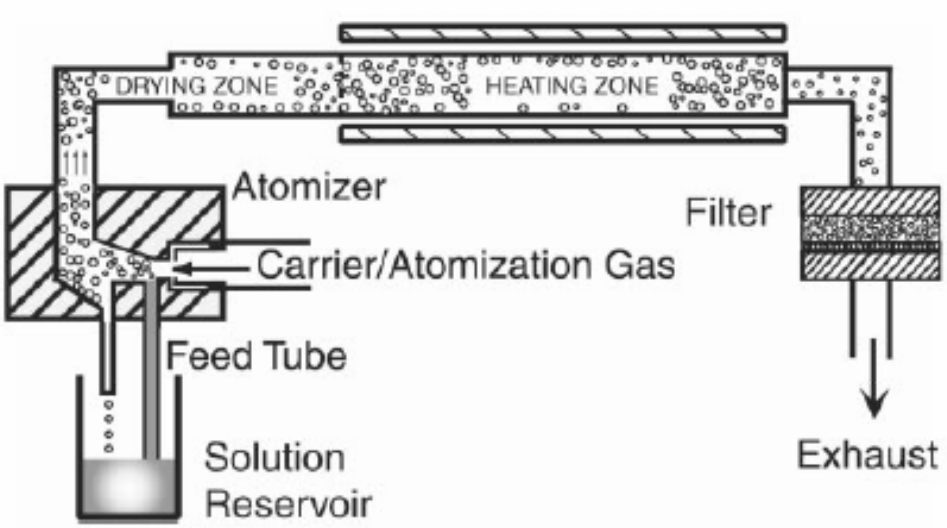


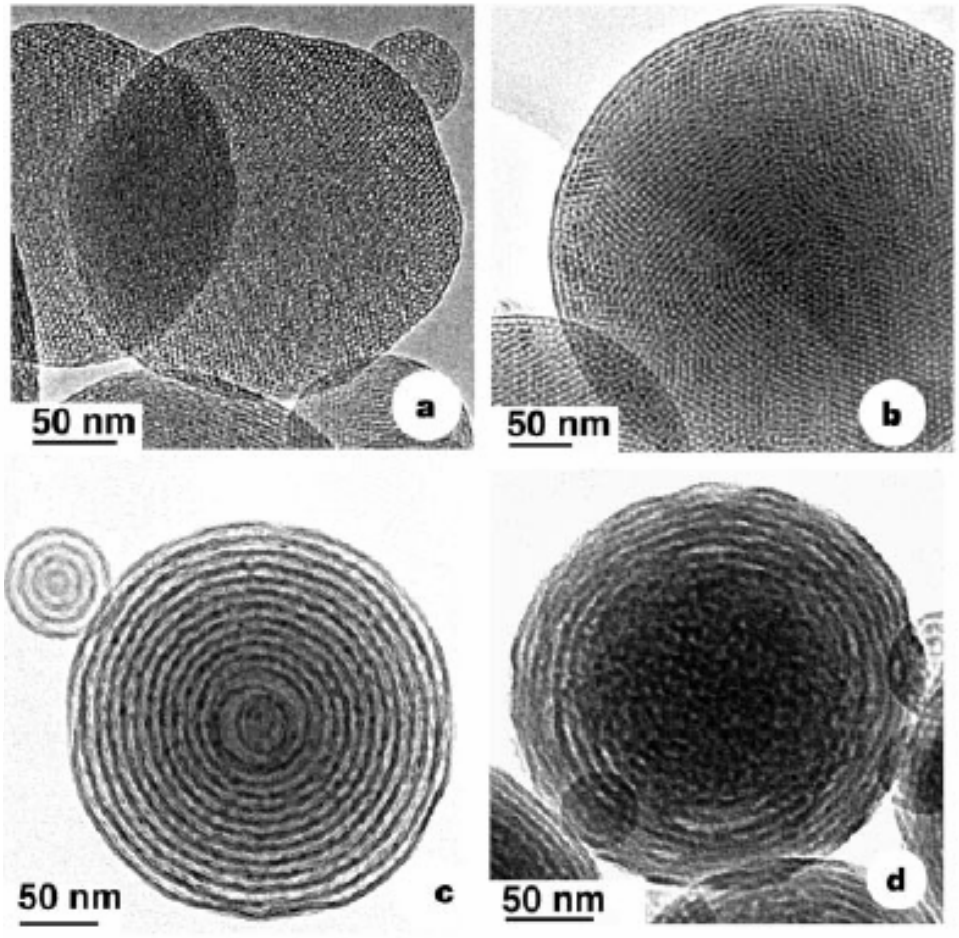


Sphere **Cylinder** **Hexagonal** **Cubic** **Lamellar**

C. J. Brinker, *et al.*
multiple publications

Evaporation Induced Self-Assembly of Mesoporous Silica

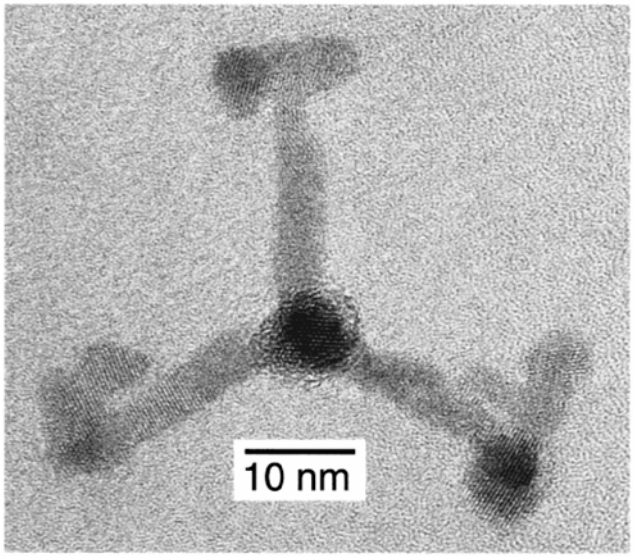


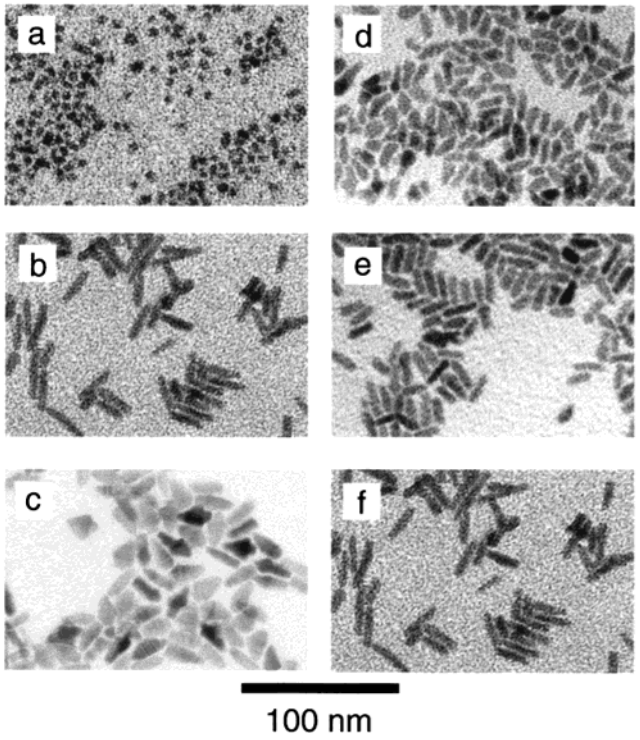


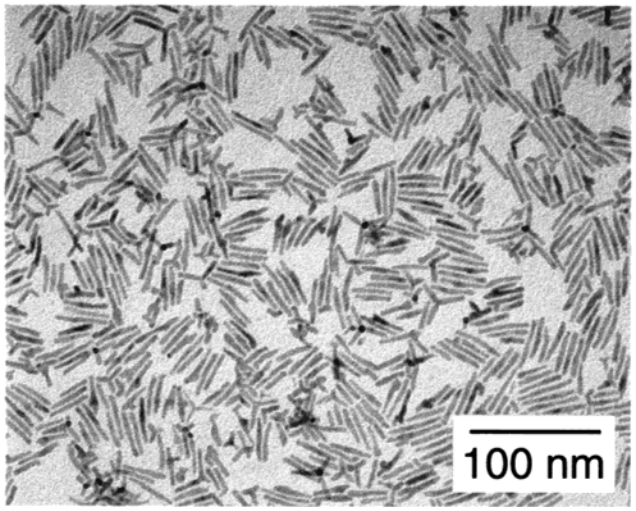
C. J. Brinker, *et al.*
Nature, 1999

Semiconductor Nanostructure – Surface Control

Semiconductor nanorods







Alivisatos, *J. Am. Chem. Soc.* 2000
Also, see similar work by M. P. Pileni

Products include extremely high aspect ratio CdSe nanorods (30:1), as well as arrow-, teardrop-, tetrapod-, and branched tetrapod-shaped nanocrystals of CdSe.

Solvent: mixture of hexylphosphonic acid and trioctylphosphine oxide

Important parameters: ratio of surfactants, injection volume, and monomer concentration.