Templating Nanoparticles with Self-Assembled Matrices

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Biological Self-Assembly

- Invertebrates
  - Single crystal spine
  - Spongy single crystal

- Mammals
  - Composite fibrils
  - Bacteria
  - Ca^{2+} + SO_4^{2-}
  - Mineral cross-ply
  - Protein template
  - Mineralized membrane

Figures courtesy of:
L. Addadi
C. C. Harrison
S. Schultze-Lam
Bone – Mineral Grown in (with?) a Biomolecular Template

mineral - collagen nanocomposite.

Direct Templating of Semiconductor Nanostructures

“liquid crystal lithography”

Motivation

quantum dots  
antidots  
photoactive zeolites  
filter membranes  
LEDs  
nanocomposites

Braun, various publications 1995-2000
Lyotropic Liquid Crystals

Cubic packing of micelles

4-20 nm

Bicontinuous
lyotropic liquid crystal

Nature 1996
Science 1997
JACS 1999


semiconductor nanostructures

P. V. Braun et al.
“Best Case”

\[ \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} \]
H₂S 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

Mineralization of a Cubic Liquid Crystal

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

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

Mineralization of a Cubic Liquid Crystal

Tilt series confirms hollow sphere morphology

BiOCl synthesized in lyotropic liquid crystals

- Potential precursor for nanostructured thermoelectric materials

- BiCl₃ stabilized in HCl(aq), diffuse in NH₄OH gas → BiOCl

- Water
- Hexagonal phase (50% amphiphile, 50% water)
- Lamellar phase (78% amphiphile, 22% water)

- 250 nm disks
- 250 by 100 nm arrowheads
- 5 nm nanoparticles

Dellinger, Braun, Scripta Materialia, 2001
Biological Templating of CdS in DNA-membrane complexes

Organization of ion precursors using DNA-membrane complexes

Biopolymer

Cationic Lipid

Neutral Lipid

Cadmium ion Cd\textsuperscript{2+}

(precursor to CdS)

Biopolymer

Cationic Lipid

Neutral Lipid

Cadmium ion Cd\textsuperscript{2+}

(precursor to CdS)

DNA

DOTAP

DOPC

Crystallographic control via biomolecular architecture: Templated nanorods have (002) directions tilted by $60^\circ$ 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

hydropobic core

hydrophilic ‘sea’

dissolved metal salt (Cd(NO$_3$)$_2$)

lyotropic liquid crystal

polymer substrate

reactive gas (H$_2$S)

“liquid crystal lithography”

Braun, unpublished
Polyol Amphiphiles—properties

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

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

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Braun, unpublished
Direct Templating of CdS Films

polyol based lyotropic liquid crystal directly templates the growing CdS film as $\text{H}_2\text{S}$ 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
microtomed cross-section of a templated CdS film grown with 15 min. H₂S 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)

Silicic acid (Hydrophilic)

Micellar template (cross-section; "soap in water")

Organic/inorganic nanocomposite

Periodic Porous Silica


Brinker et al., Adv. Mater. 1999
Evaporation Induced Self-Assembly of Mesoporous Silica

**Formed by spray drying**

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

**Solvent Evaporation**

Ethanol/H2O/Acid

**Surfactant**

Silicic Acid, Hydrophilic precursor

**Ethanol Co-Solvent**

Monomers, Photoinitiators, Hydrophobic Precursors

**Drying**

Sphere  Cylinder  Hexagonal  Cubic  Lamellar
Evaporation Induced Self-Assembly of Mesoporous Silica

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