Self-Assembly of Colloidal Particles
Colloidal Epitaxy for Colloidal Single Crystals

Before e-field: 30s; after e-field: Several hours

Proposed Mechanism: Electrohydrodynamic Flow

(Science 272, 706, 1996)

(Langmuir 13, 6375, 1997)
Optically Tunable Electrohydrodynamic Assembly

Higher current density in the light regions induces electrohydrodynamic assembly

( *Nature* 404, 56, 2000)
Galvanic Cell Induced Colloidal Assembly

- Aggregation is confined to Cu.
- Multiple sites aggregation.
  "Galvanography"

Localized Electroosmotic Flow (EOF) Induced Colloidal Crystallization
Template Chemistry: Steps Toward Full 3D Gaps

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Absorption Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>1.48</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.4</td>
</tr>
<tr>
<td>TiO2- rutile</td>
<td>2.8-3.0</td>
</tr>
<tr>
<td>Metals (visible)</td>
<td>very large</td>
</tr>
</tbody>
</table>

Template Chemistry Strategy:
1. Form template
2. Fill template
3. Remove template

Self-assembling System
Polymers, Ceramics, Semiconductor, Metal...
Thermal/Chemical treatments
“Lost-Wax” Method – Extending the Availability of Artificial Opals

1. Form a clay figure.
2. Cast a hollow wax replica.
3. Embed in external mold, remove wax through heating.
4. Pour bronze into the mold.

(From the *Fire of Hephaistos*, ed. C. C. Mattusch, Harvard University Press, 1996)
Nanoscale Lost-Wax Method

The “Clay” Figure – Silica Template

The “Wax” Mold – Polymer Template

Colloidal crystals from every major class of functional materials. 

(Science 291, 453, 2001)
Macroporous Silicon with Full Bandgaps

Band Structure of Si Inverse Opal

Macroporous Si Inverse Opal

(Nature 405, 437, 2000)
Template Chemistry: Structured Porous Materials

Glass slide
SiO₂ colloidal array
Monomer
Photo/Thermal Polymerization

Fill interstitials
Polymer
Remove templates
HF solution
Macroporous Polymer

Polystyrene
PMMA

2 μm
2 μm
Macroporous Metals from “Seeded” Electroless Plating

Electroless plating:

\[ \text{Mn}^+ + \text{reductant} \rightarrow \text{M} \text{O} + \text{by-product} \]

Catalytic Surface

Convective Self-Assembly

Dip in nano-Au solution and dry

Nanocrystal gold attaches to silica surfaces.

(J. Am. Chem. Soc. 121, 7957, 1999)
Monolithic Macroporous Metals

Pt

Cu
Break the Symmetry – Elliptical Spheres

Macroporous polymer \( T > T_g \)

\( \text{TiO}_2 \)

\( \text{TiO}_2 \)
Nature is the Ultimate Nanotechnologist
Displays & Vapor Detectors
Desert Spider Beetle
Butterfly Wings
Circularly Polarized Wave Metamaterials

Bragg's Diffraction

**Bragg's Law**
\[
\lambda = 2n_{avg}d \sin \theta \\
\lambda_{max} = 2n_{avg}d
\]

- **n**: Refractive index
- **d**: Distance between planes

**Key Requirements:**
1. Particle Spacing < 1 µm
2. Long-Range Periodic Structure

**Clay/ TiO₂ Composite Convective Assembly Spin-Coating**

Color Tunable Displays

Solvent Swelling  Electrochemical Reaction  Magnetic Force

Butterfly Wings in Chemical Vapors

\[ \Delta R = 100\% \times \left( \frac{R}{R_o} - 1 \right) \]

Polymeric Photonic Crystals
Photonic Crystals in Chemical Vapors

Kelvin’s Equation

\[
\ln \frac{P}{P_0} = -\frac{2\gamma V_m}{rRT}
\]

- \( P \) - Vapor Pressure
- \( P_0 \) - Saturated Vapor Pressure
- \( \gamma \) - Surface Tension
- \( V_m \) - Molar Volume
- \( R \) - Gas Constant
- \( r \) - Radius of the Cavity
- \( T \) - Temperature (K)
Silica Colloidal Crystals
Colloidal Crystal-Based Vapor Detectors

Ethanol

Water

Toluene

Vapor Detector Applications

- Alcohol breath analyzer
- Worker with vapor detector
- Vapor detection chart: DI water, Methanol, Ethanol, Isopropyl alcohol, Diethyl ether, Hexane, Control