Overview of Nanoparticle Materials

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Particle Synthesis, Particle Modification
Particle Characterization
Particle-Based Materials
**Synthesis and Modification**  
*Gas Phase (Pratsinis)*

<table>
<thead>
<tr>
<th>Product Particles</th>
<th>Volume t/y</th>
<th>Value $/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>8 M</td>
<td>8 B</td>
</tr>
<tr>
<td>Titania</td>
<td>2 M</td>
<td>4 B</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>0.2 M</td>
<td>2 B</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>0.6 M</td>
<td>0.7 B</td>
</tr>
<tr>
<td>Filamentary Ni</td>
<td>0.04 M</td>
<td>~0.1 B</td>
</tr>
<tr>
<td>Fe, Pt, Zn$_2$SiO$_4$/Mn</td>
<td>~0.02 M</td>
<td>~0.3 B</td>
</tr>
</tbody>
</table>
Synthesis and Modification

Gas Phase (Pratsinis)

Mixing of reactant gases ==> product size-shape

Synthesis and Modification

**Liquid Feed Flame-Spray Pyrolysis**

*Laine*
Synthesis and Modification

Segmented Flow Tube Reactor

(Hoffman)
Synthesis and Modification

Hydrothermal (Matijevic)
Synthesis and Modification

**Binary Metal Oxides - Nonaqueous Sol-Gel (Niederberger)**

**General Synthesis Protocol:**

1) Metal Alkoxide + Benzyl Alcohol 
   \((C_6H_5CH_2OH)\)
   
   Metal Alkoxides:
   
   \(VO(OiPr)_3, Nb(OEt)_5, Hf(OEt)_4,\)
   \(Ta(OEt)_5, Sn(OtBu)_4, In(OiPr)_3\)

2) Heat Treatment in Autoclave at 
   \(200°C-250°C\)

\(Ta_2O_5\)
Synthesis and Modification

Monodisperse Particles from Aggregation of Nanoparticles (Matijevic)
Synthesis and Modification

Monodisperse Emulsions (Pine)

1. Monomer liquid
2. Polymer particles
3. Polar fluid + surfactant
4. Swell with monomer
5. Polymerize monomers $M_w$ small
6. Add solvent (oil) for polymer
7. Swell with oil
Synthesis and Modification

Barium Sulfate Morphogenesis (Coelfen, Qi)

PEG-b-PEI-SO$_3$H

PEG-b-PMAA-Asp

PEG-b-PEI-COOH

No additive

PEG-b-PMAA-PO$_3$H$_2$
Synthesis and Modification
SIP (Advincula)

Igepal (nonionic surfactant) + Cd(NO$_3$)$_2$ then (NH$_4$)$_2$S
H$_2$O / Cyclohexane $\xrightarrow{\text{Si(OEt)$_4$}}$ NiBr$_2$(PPh$_3$)$_2$
MMA, 100 ºC

Silica $\xrightarrow{\text{Bromoisobutyrate-based siloxane}}$ Ethanol 20 ºC $\xrightarrow{\text{Cu(I)X : bipy (1:2.5)}}$ H$_2$O, 20 ºC, 3 h
Synthesis and Modification

Block Copolymers as Nanoreactors (Advincula)

Cationic polyelectrolytes

Amphiphilic block copolymers (PS-\(b\)-P2VP)

Dendrimers (PAMAM)
Synthesis and Modification

*Microgels by Dispersion Polymerization (Lyon)*

\[ \text{Oligoradical} \quad \rightarrow \quad \text{Precursor Particle} \quad \rightarrow \quad \text{Growing Particle} \quad \rightarrow \quad \text{Microgel} \]

\[ \text{Precipitation Polymerization} \]

\[ \text{SDS} \quad \text{APS} \quad 70 \, ^\circ\text{C} \quad >4 \, \text{hrs.} \]
Synthesis and Modification
Functionalization (Hoffman)
Synthesis and Modification

**Ligand Coated Metal Nanoparticles**

*(Stellacci)*

Metal Salt ($\text{AuHCl}_4$) + Reducing Agent ($\text{NaBH}_4$)

Direct mixed ligands reaction**

Ligand exchange reaction*
Synthesis and Modification
Quantum Dots in Frogs (Norris)

- Me$_2$Cd
- Se
- CdSe NCs
- 320 °C
- diameters between 2nm to 12nm
- size distributions <3-5%

- hydrophilic shell
- hydrophobic core
- micelle

Thickness of micelle core, $R_c$
Synthesis and Modification in Reverse Micelles (Pinna)

1. 60% Ag(AOT) - 40% Na(AOT) 0.1 M - W=2
2. Na(AOT) 0.1 M - N₂H₄ - 4.1 < [N₂H₄]/[AOT] < 16.5

\[ 2 \text{N}_2\text{H}_4 + 4\text{Ag}^+ \rightarrow \text{N}_2 + 4\text{H}^+ + 4\text{Ag}^{0} \]
Synthesis and Modification

Microemulsion Polymerization (Kaler)

Initiation by IM•

Propagation

Chain Transfer

PM•

Initiation by M•

# Micelle \approx 10^3

# Particles

5 nm
Synthesis and Modification

Templating in Matrices (Braun)
Synthesis and Modification

Replacement of Ag by Au (Xia)
Synthesis and Modification

Stretching Polymer Beads (Xia)
Synthesis and Modification

**Dimeric Colloids (Xia)**
Synthesis and Modification
Geometrical Clusters (Pine)

silica spheres

silica-coated PMMA spheres
Synthesis and Modification
Colloidal Molecules (Pine)
Synthesis and Modification
Encapsulation (Velev)
Characterization

Confocal Microscopy (Wiltzius)

- photomultiplier tube
- objective lens, e.g. 100x
- illuminating aperture
- dichroic beamsplitter
- confocal aperture
- sample
- focal plane
- in focus
- out of focus
Characterization

**Surface Charge in Heterocoagulation**

*(Matijevic)*

![Image of surface charge in heterocoagulation](image.png)
Characterization

Analytical Ultracentrifugation (Coelfen)
Characterization

HRTEM (Pinna)
Characterization

TEM Image Analysis (Coelfen)
Characterization

Particle Interaction Potentials (Yodh)

Scan Position

Scan Rate - 180Hz

~ 50 mW

\[ k = 10 \, k_B T/\mu m^2 \]

\[ k = 40 \, fN/\mu m \]

The interaction potential for a single 1.2\mu m PMMA sphere along the x direction.
Characterization
SANS (Kaler)
Characterization

Rheology (Weitz)
Particle-Based Materials

Particle Assembly

Thermodynamics

Functional Materials

Devices
Particle Assembly

Thermodynamics (Wiltzius)

[Diagram showing a graph with axes labeled 'Volume Fraction, $\phi$' and 'Pressure, $p$'. The graph includes points labeled 'Freezing', 'Metastable branch', 'To RCP', 'Melting', and 'To FCC (Close Packed)' with values 0.494, 0.545, 0.64, and 0.74.]
Particle Assembly

**Entropy Drives Growth (Weitz)**

Entropy $\Rightarrow$ Free Volume

\[ F = \psi - TS \]

**Disordered:**
- Higher configurational entropy
- Lower local entropy
- Higher Energy

maximum packing $\phi_{RCP} \approx 0.63$

**Ordered:**
- Lower configurational entropy
- Higher local entropy
- Lower Energy

maximum packing $\phi_{HCP} = 0.74$
Particle Assembly

Entropy and Other Forces (Yodh)
Particle Assembly
Dielectrophoretic Microwire Assembly (Velev)
Particle Assembly
2D Epitaxy (Yodh)
Particle Assembly
Template Assisted Assembly (Niederberger)
Particle Assembly
Templated Clusters (Xia)
Particle Assembly
2D Dielectrophoretic Assembly (Velev)

Optical micrograph  Fourier transform  Diffraction pattern

5 s

15 s
Particle Assembly

Domain sizes too small (Wiltzius)
Particle Assembly
Convective Crystallization (Xia)
Particle Assembly
Convective Assembly (Velev)

- Ambient light
- Low angle
  Light transmission

$1 \text{cm}^2$ coatings from $\mu \text{L}$ drops in minutes

1.1 $\mu \text{m}$ latex crystal viewed with:

1 cm
Particle Assembly
CCAs to close-packed photonic xtals (Wiltzius)

Charge Stabilized

Screened

Electrostatics dominate

Screened electrostatics

VdW’s attraction “guide” adhesion

Charge Stabilized u(r)

electrostatic repulsion

van der Waals attraction

Screened u(r)

screening

$u(r)$

$\text{no salt}$

$salt$

$salt$

Particle Assembly

Modifying interactions and annealing in microgel photonic materials (Lyon)
Particle Assembly
Strategies for Assembling Anisotropic Structures (Niederberger)
Particle Assembly
Self-Assembly of Nanoparticles (Niederberger)
Particle Assembly

Chains with Given Handedness (Xia)
Particle Assembly
**Colloidal Crystalline Arrays (Asher)**

Dialysis / Ion Exchange Resin

Self-assembly

FCC

~ $10^{13}$ spheres/cm$^3$

- spacing dependent only upon particle number density and crystalline structure

Crystalline Colloidal Array
Particle Assembly
Mechanism of Convective Crystallization (Norris)

800nm spheres

immersion oil

microscope objective

100X

CCD

video camera

real time video
Particle Assembly

Biomineralization (Coelfen)

SEM of broken mussel shell
SEM of broken mussel shell after protein removal
SEM of broken mussel shell after CaCO₃ removal
TEM thin cut of developing mussel shell
SEM of developing mussel shell
SEM mature mussel shell
Particle Assembly

Magnetically Driven Assembly (Asher)
Particle Assembly

Balancing Interfacial Interactions (Coelfen)

Nucleation clusters

Crystal growth

Primary nanoparticles > 3 nm

Amplification

Single crystal

Temporary Stabilization

Mesoscale assembly

Mesoscale assembly

Mesocrystal
Particle Assembly

Balancing Interfacial Interactions (Hoffman)
Particle Assembly
Copper Oxalate Assembly (Hoffman)
Functional Materials

Flame Pyrolysis (Laine)

- Pure nano α-Al2O3
- Abrasives
  - Chemical mechanical polishing
- Transparent ceramics
  - Sodium vapor lamps
  - Ti:Sapphire lasers among other things.
- Coatings
- High strength monoliths
  - Ceramic prosthetics for example
- Catalyst supports that do not sinter
- Catalysts
Functional Materials

Microporous and Mesoporous Materials (Stein)

Synthesis of Macroporous Metal Oxides

- Metal Alkoxide $M(OR)_4$ (Solvent)
- Colloidal Crystal
- Metal Salt Solution
- Oxalate Precipitation
- Vacuum
- Calcination or Solvent Extraction
- Macroporous Metal Oxide

(Holland, Stein, 1998) (Yan, Stein, 2000)
Functional Materials

Inorganic Pigments (Stein)

**Industrial Pigments**

- CeAl₂O₄
- Cr₂O₃
- ZnCo₂O₄
- Ti₁₀₅N⁰₅Nb₁₀O₂
- α-Fe₂O₃

*Feldmann, C. Adv Mater. 2001, 13, 1301-1303*

**3D Ordered Macroporous ZrO₂**

- 201 nm
- 252 nm
- 283 nm

*In 3DOM solids: Wavelength of maximum reflection is proportional to pore size:*

\[
\lambda = \frac{2d_{hk\ell}}{m} n_{avg}
\]
Functional Materials

*Photonic Crystals (Norris)*

![Graph showing wavevector and reflectance against frequency and wavelength](image)
PDMS Master (10 µm structures)
Place on substrate
Place a drop of suspension of polystyrene spheres at one end (1 µm structures)

Fill channels by capillary flow; evaporate solvent.
Place sol droplet; fill space between latex particles by capillary flow.
Allow to gel. Remove PDMS master. Calcine.
Functional Materials

_two photon fab (braun)_
Functional Materials

**Metal Cation Sensors (Asher)**

![Graph showing diffraction intensity vs. wavelength with various concentrations of metal cations.](image-url)
Functional Materials

Glucose Sensing (Braun)

PBA (phenylboronic acid)

Glucose-PBA complex

Inflow from syringe pump

Outflow

Flow cell

Hydrogel

10x Objective

Beamsplitter

Photodiode Array Detector

Optical fiber

Pinhole

Light source

SEM of templated hydrogel

0 mM glucose

1 mM glucose

0 mM 100 mM

Reflection (%)

[Glucose]

0 mM → 100 mM

Wavelength (nm)

600 650 700 750

1 μm

100 μm
Functional Materials

Gyricon Display (Morrison)

**Functional Materials**

**Electrophoretic Display (Morrison)**

Negatively charged pigment particles.

Positively charged pigment particles.

Suspended in a clear oil.

Addressed with electrodes.

Sony’s LIBRie EBR-1000EP from E Ink and Phillips Electronics
Functional Materials

Electrochromic Devices (Kotov)
Functional Materials

Donor-Acceptor Tagging (Kotov)

Two different CdTe nanowires

2.5 nm in diameter
+ Biotin
(short and thin)

6 nm in diameter
+ Streptavidin
(long and thick)

Gap between wires

NPgr-biotin:STV-NPred

Fluorescence intensity (cps)

Green emission of thin nanowires decreases

Red emission of thick nanowires increases

Wavelength (nm)
**Functional Materials**

*Insulin Incorporation and Release (Lyon)*

Linear increase in insulin content with particle layer number.
Functional Materials
Glucose Sensing (Asher)
Functional Materials

Lab on a Chip (Velev)

gold nanoparticles $\rightarrow$
sulfate latex $\rightarrow$
Functional Materials
Quantum Dots in Frogs (Norris)
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Overview of Nanoparticle Materials

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