Surface Chemistry and Nanotechnology

Bruce Lyne
KTH Dept. of Surface and Corrosion Science
Biological porous materials – Q-membranes

Silica template from wing scales

Porous membranes in Amoeba

Plankton biostructures
Self-assembly is one of the most important concepts for building nanostructured material templates e.g. Zeolites and mesoporous silica.
Micellar templating at YKI

Solvent evap.

N₂

Solution

Tube furnace

Filter

LLC intermediate

Dry mesostructured hybrid

Micr. Mesop. Mater. 2004, 72, 175
Uncoated: Coated

TEM pictures

9 nm thick film
Application Projects

• Fragrance delivery
• Flavour delivery
• Biocide delivery in paints and coatings
• Drug delivery
• Immobilization of sensor liquids
• Carriers in ink jet inks
• Pigment coating for high quality ink jet paper
Mesoporous silica for inkjet paper

Paper coatings

![Graph showing average line width vs. coating type and concentration]

- Silica gel + 26-88, 80 pph
- Silica gel + 28-99, 80 pph
- C16TAB + 26-88, 30 pph
- C16TAB + 28-99, 30 pph
- P104 + 26-88, 30 pph
- P104 + 28-99, 30 pph

Carriers for sensor liquids

50nm
Berzelii Centre EXSELENT on Porous Materials

Department of Physical, Inorganic and Structural Chemistry, SU
Department of Organic Chemistry, SU
Institute for Surface Chemistry (YKI)
Novel porous materials

Zeolites
- SU-15, achiral
- SU-32, chiral

Open-framework

Metal-organic framework

Covalent organic networks

Chiral mesoporous silica
CO₂ adsorption - approach and results

- APPROACH: Realization via synthesis, property measurements, theoretical analyses
  
  E.g.: mesoporous silica modified with amine-like moieties
  
  + CO₂/ N₂ selectivity ~ 30
  
  + Significant uptake
Enantioselective catalysis

The ITQ-37 mesoporous chiral zeolite


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New YKI emulsion based method!

Particle size | Solid or hollow | Macro / meso

![Image 1](image1.png)  ![Image 2](image2.png)  ![Image 3](image3.png)

![Image 4](image4.png)  ![Image 5](image5.png)  ![Image 6](image6.png)
New photonic bandgap pigments

New pigments by trapping dyes in silica

Applications in
- camouflage
- IR reflection
- cosmetics
- novel paper coatings and colorants?
Controlling the shape of nanoparticles with surfactants

Rod → Sphere → Platelet

12nm iron oxide nanocubes (Scale bar is 20nm)

13 nm iron oxide nanospheres (Scale bar is 20nm)

Courtesy of Anwar Ahniyaz, YKI
Seeded Growth of iron oxide nanocrystals

3 nm (a)
7 ± 1 nm (b)
8 ± 1 nm (c)
9 ± 1 nm (d)
10 ± 1 nm (e)

11 ± 1 nm (f)
12 ± 1 nm (g)
13 ± 2 nm (h)
15 ± 1 nm (i)
16 ± 1 nm (j)
Newly developed ceria nanoparticle-based clear coat

Commercial clear coat with organic UV absorber
Nanoparticles generally show a reduction in melting point relative to bulk counterparts

\[ T_{m_{\text{melt}}} (R) = T_{m_{\text{bulk}}} (1 - \sigma / R) \]

Additionally, nanoparticles may be stabilized in solution by encapsulating them in organic ligands, which may be removed after printing by subsequent annealing.

Superparamagnetic mesoporous silica

- Powder with large surface area
- Dispersible in different solutions and media
- Magnetic only in the presence of a magnetic field
- Good for recycling applications
Nanoparticle Sensors

- Charge tunneling through the thin insulating layer between nanoparticles.
- Gas adsorption in the tunnel barrier affects the electrical conductivity dramatically.

Schematic representation of a sensor based on the sensed molecules (e.g., moisture) affecting the tunneling current in the nanoparticle assembly.

Linear sensors for packaging surveillance
Nano Surface Design in Nature

- Lotus leaf effect
Superhydrophobic surfaces

Water repellency and self-cleaning via patented self assembly coatings

Next step is oil repellency through advanced surface chemistry – avoiding the use of fluorocarbons.
Superhydrophobic coatings

- One-step coating procedure to produce required hydrophobicity and roughness to achieve a contact angle of 150°
- Both macro and microscale roughness important (scale bar 20 μm)
Superlyophobic Surfaces
Nanonails: A Simple Geometric Approach to Electrically Tunable Superlyophobic Surfaces  *Krupenkin et al, Bell Labs*  *ACS 2008*
Isolation of crystalline cellulose
Research on Nano Crystalline Cellulose

• **Preparation techniques:**
  – $\text{H}_2\text{SO}_4$ hydrolysis degrades amorphous regions
  – Cellulose nanocrystals form stable aqueous suspension
  – Electrostatic multilayering
  – Spin coating

• **Novel optical properties**
  – NCC bi-refringent
  – NCC shows nematic order in spin coatings
  – Exhibits chiral nematic ordering in dip coating (electrostatic multilayering)
  – RMS roughness of 5nm possible
• The nanocrystals are made up of ~25 chains of 13000 glucose units

• Whisker shaped particles 100-200 nm x 5-10 nm

• Highly crystalline cellulose I can be used to prepare flat model surfaces

• Average nanocrystal anionic charge of ~0.5 e/nm² (and hydrophilic)

• Optically birefringent

Electrostatic Multilayering

- Multilayered thin films are prepared by sequential electrostatic adsorption of oppositely charged polymers
  - Physisorption onto charged substrate from dilute solution
  - Self-assembly is driven by electrostatics and entropy

Chiral nematic structure
Film Morphology

- Films are stable in water due to ionic crosslinking
- Full surface coverage after 5 layers
- Thicker films are uniformly and brightly coloured (nematic order)

Slide courtesy of Emily Cranston
• **Nanostructured materials**
  - Surfactant templated mesostructured materials and controlled release
  - Photonic materials and IR-reflective pigments
  - LC NCC coatings
  - Selective catalysis

• **Bio-Nano**
  - Biomimetics
  - Biocomposites

• **Non-wetting surfaces**
  - Self assembly superhydrophobic coatings
  - Superlyphobic surfaces

• **Nanoparticulate Metals and Metal Oxides**
  - UV blockers
  - Oxygen storage and catalysis