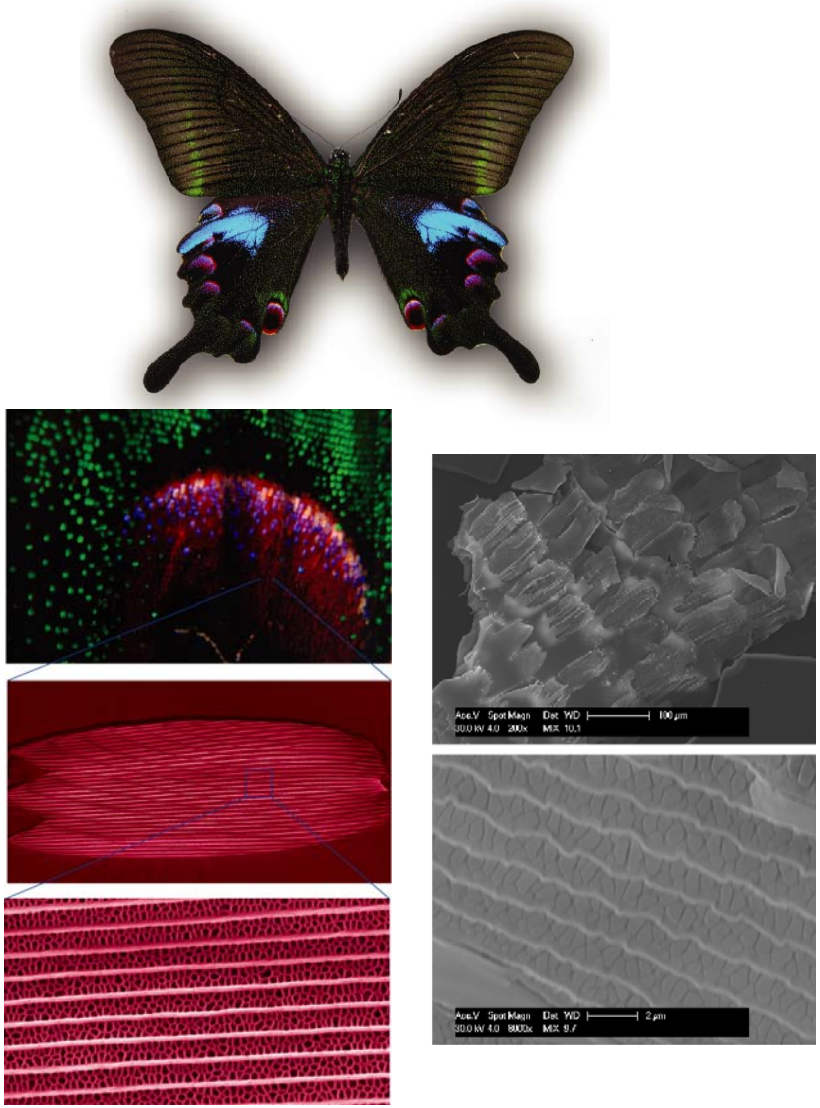
Surface Chemistry and Nanotechnology

Bruce Lyne

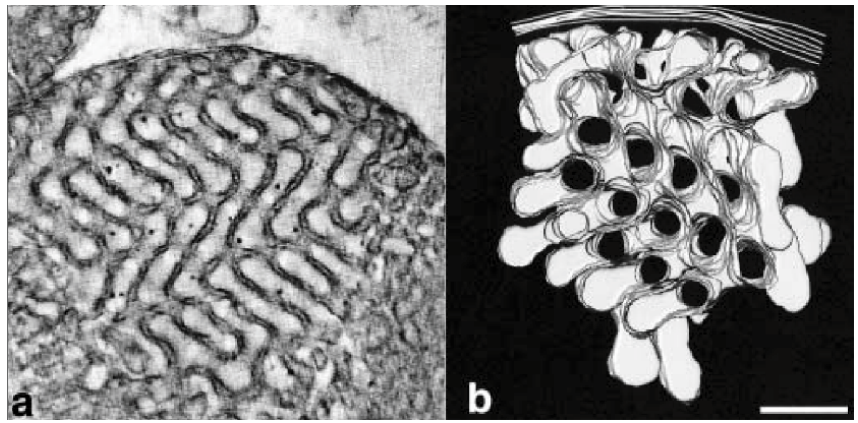
KTH Dept. of Surface and Corrosion Science

Biological porous materials – Q-membranes

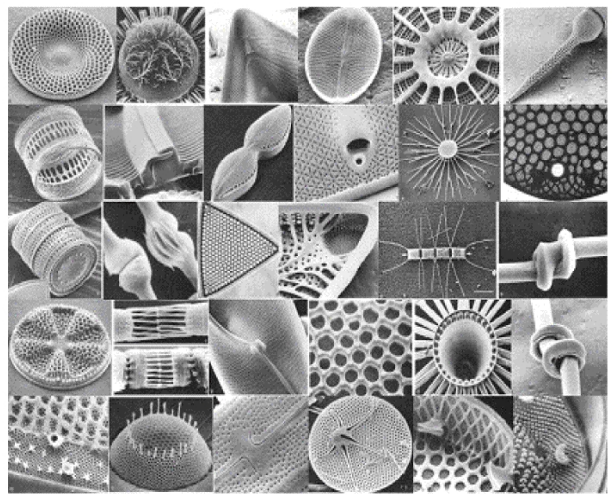
Silica template from wing scales

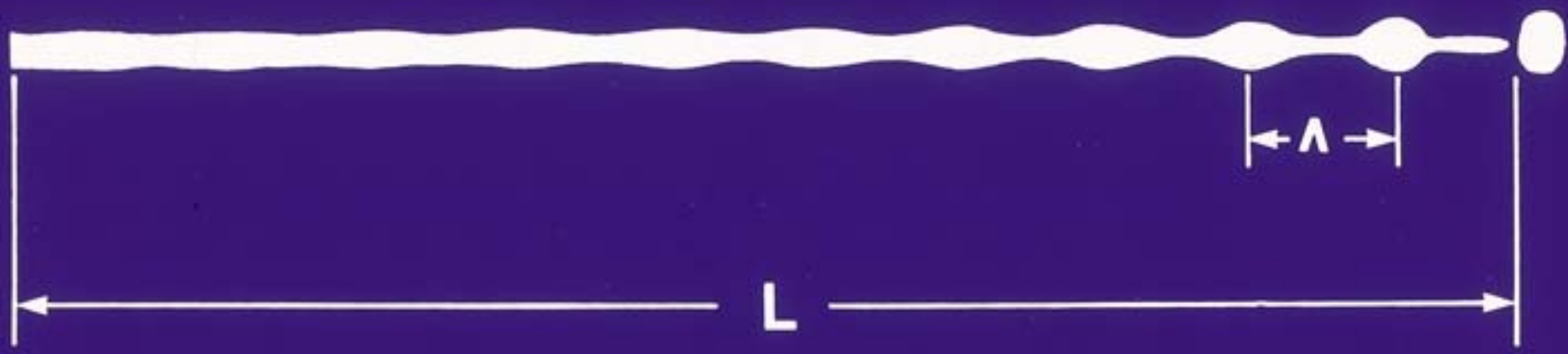


Porous membranes in Amoeba



Plankton biostructures

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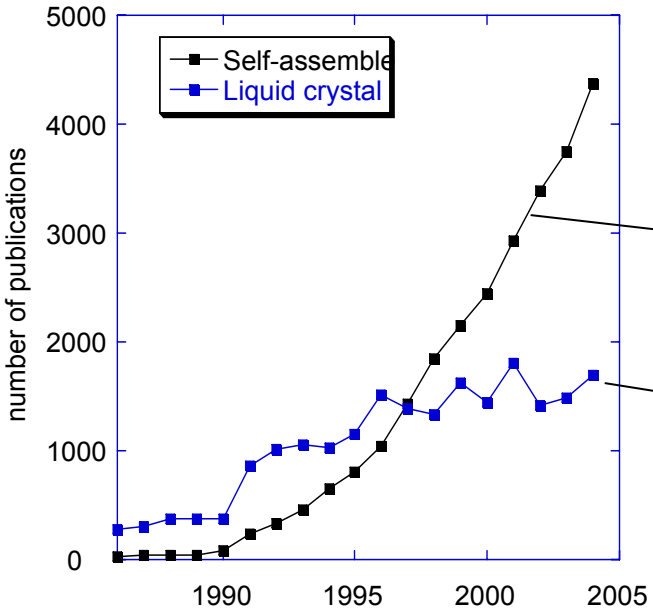
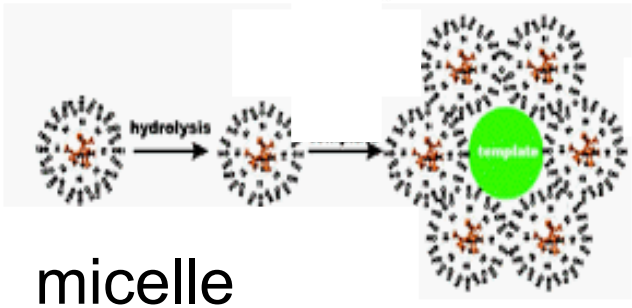
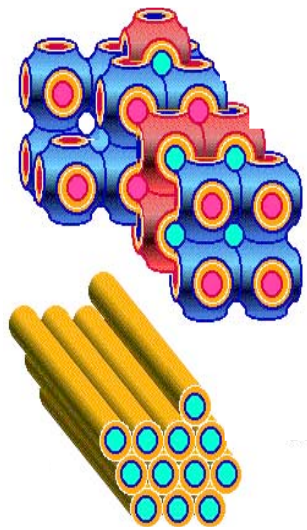
Nanostructured materials





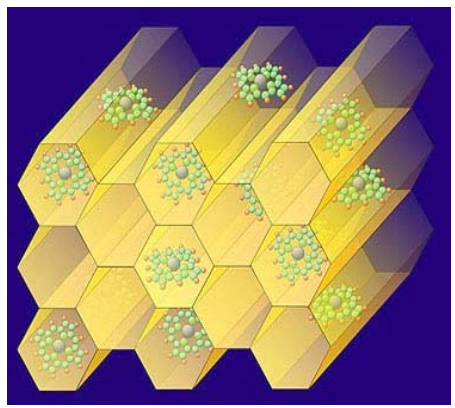
micelle

Self-assembly

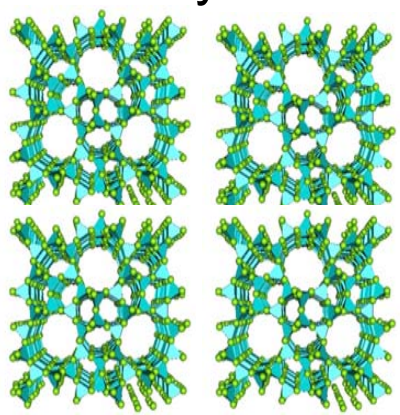


Liquid crystals

Self-assembly is one of the most important concepts for building nanostructured material templates e.g. Zeolites and mesoporous silica

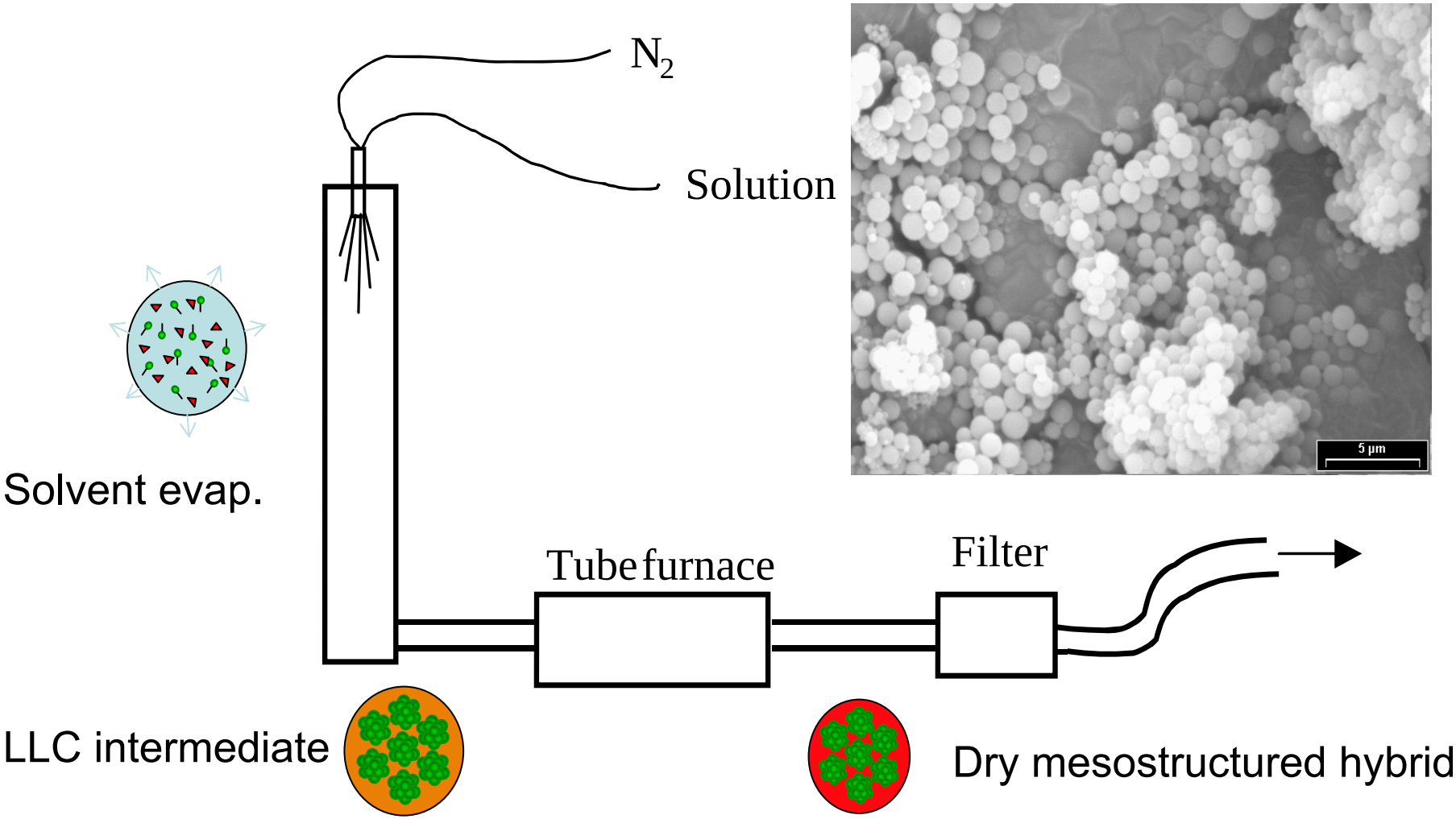


Mesoporous silicates



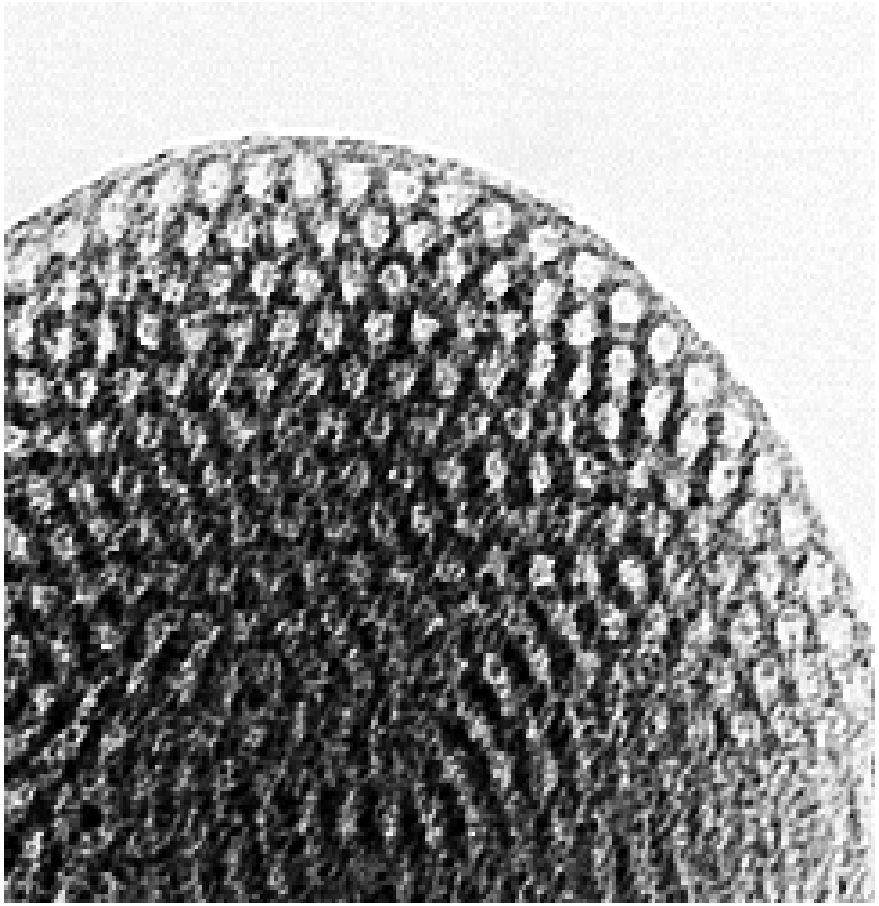
Zeolites

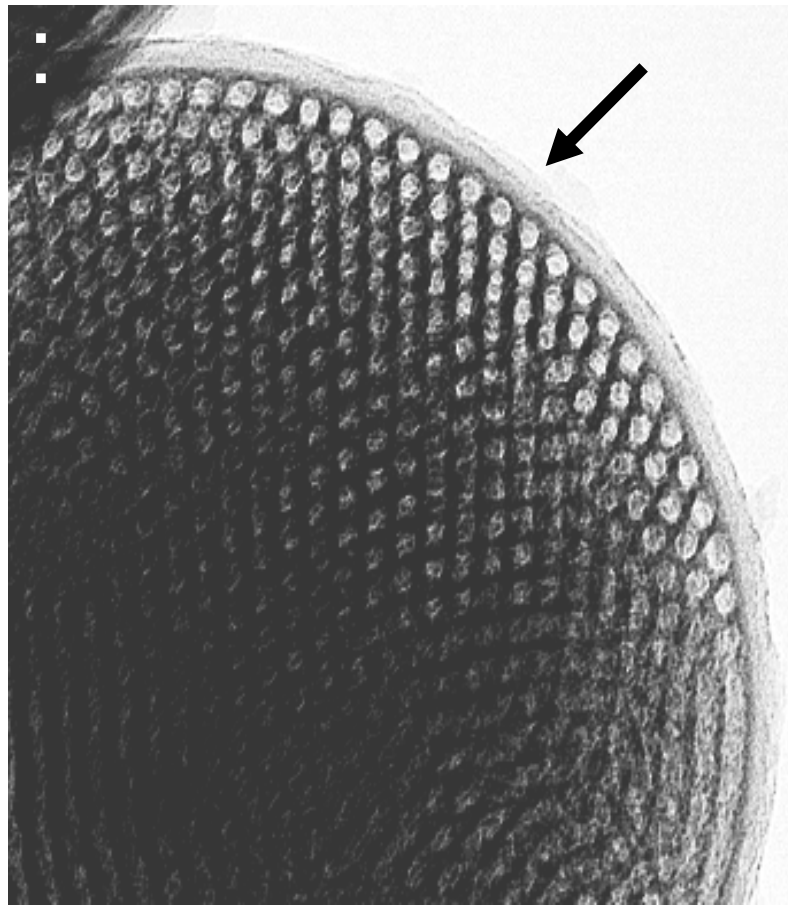
Micellar templating at YKI



Micr. Mesop. Mater. 2004, 72, 175

Uncoated: Coated



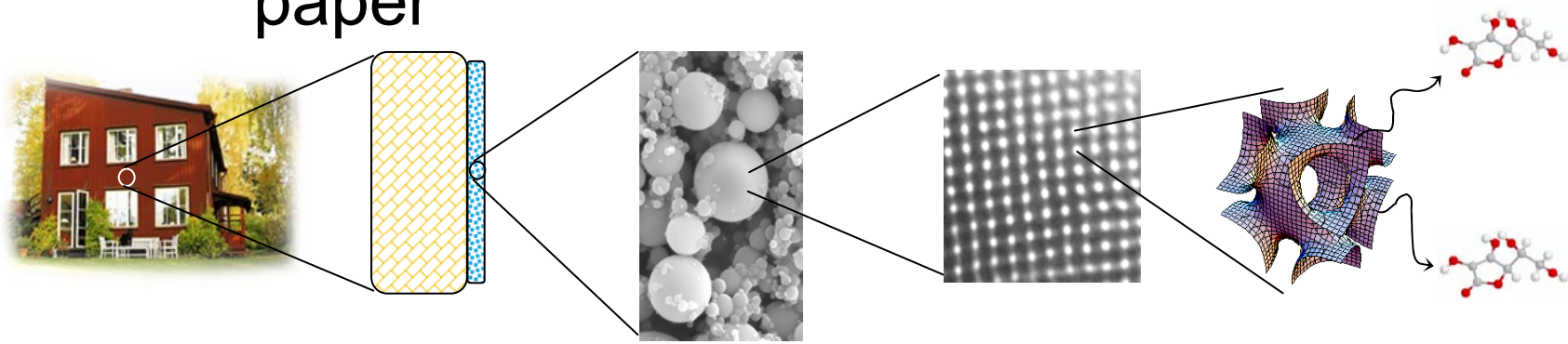


TEM pictures

9 nm thick film

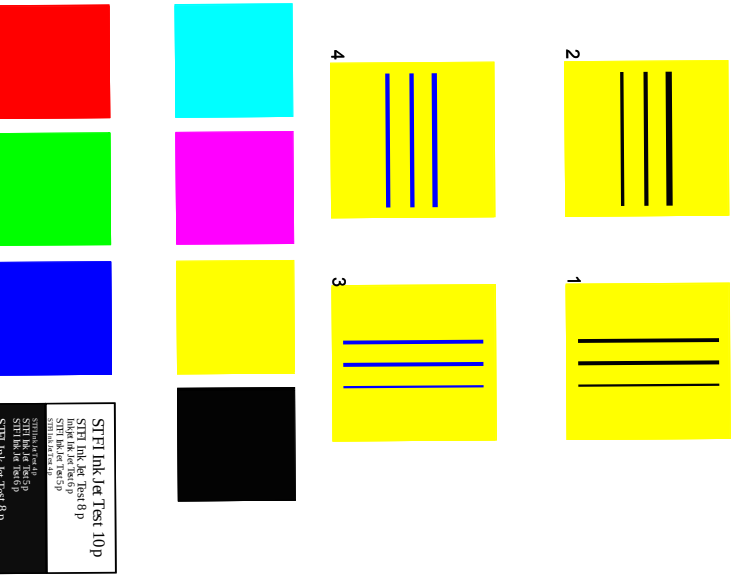
Application Projects

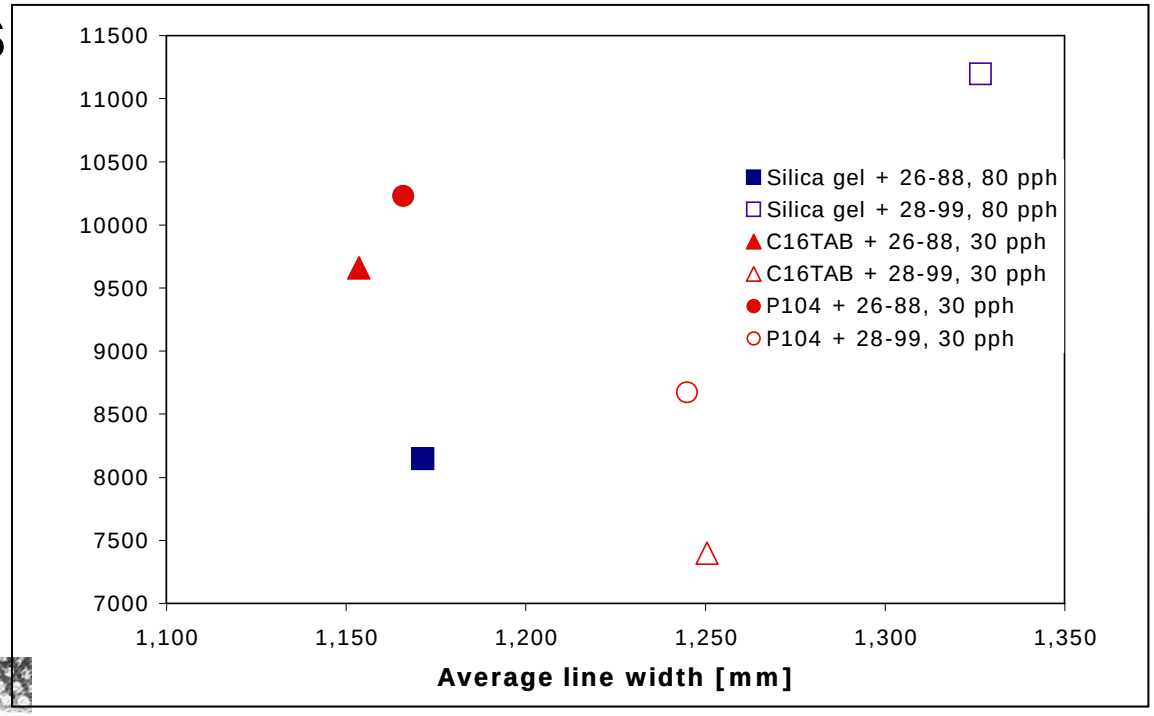
- Fragrance delivery
- Flavour delivery
- Biocide delivery in paints and coatings
- Drug delivery
- Immobilization of sensor liquids
- Carriers in ink jet inks
- Pigment coating for high quality ink jet paper

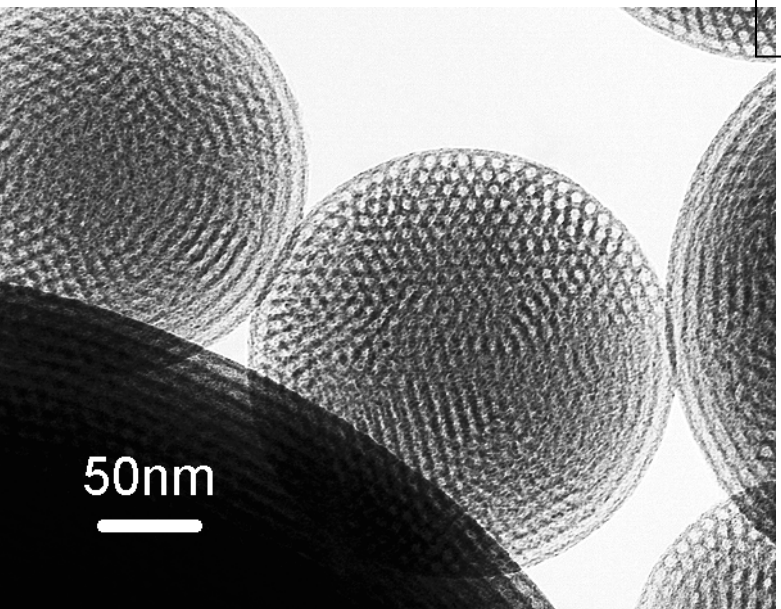


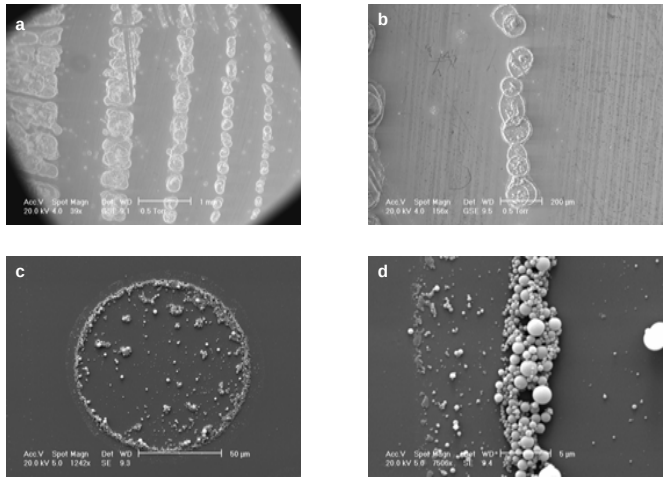
Mesoporous silica for inkjet paper

Paper coatings









Carriers for sensor liquids

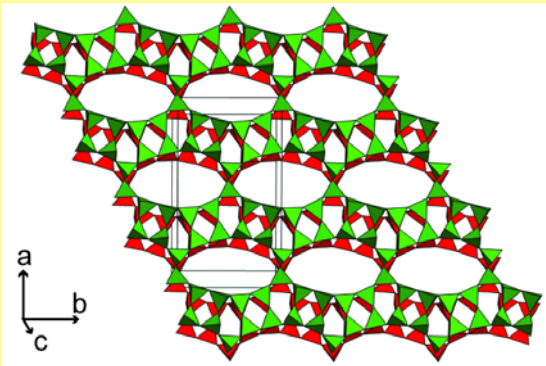
Berzelii Centre EXSELENT on Porous Materials

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

Nobel Biocare AstraZeneca Perstorp biovitrum.

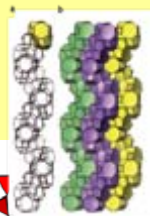
Novel porous materials

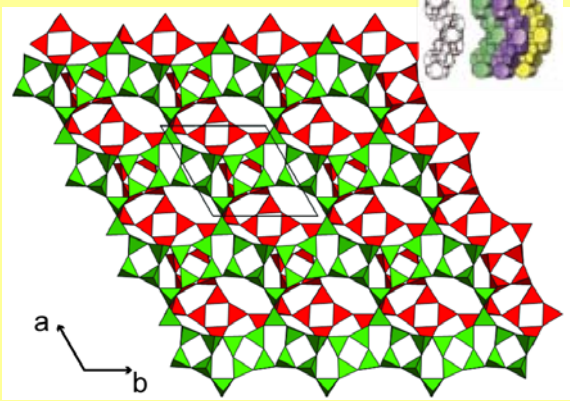
Zeolites



SU-15, achiral

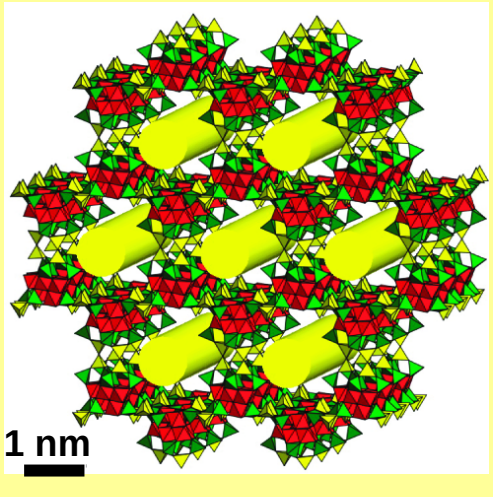
1 nm



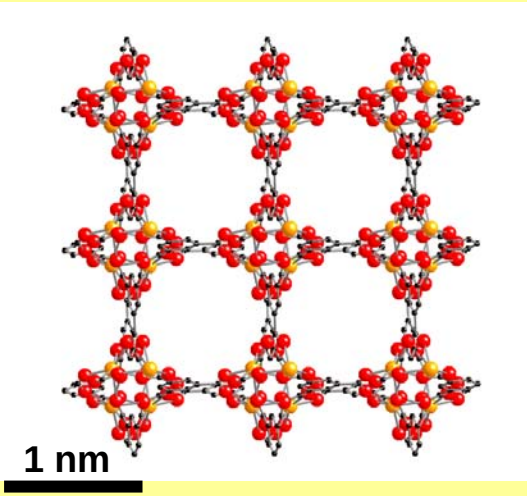


SU-32, chiral

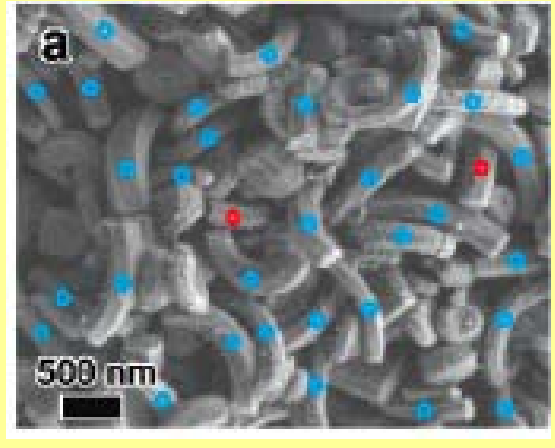
Open-framework



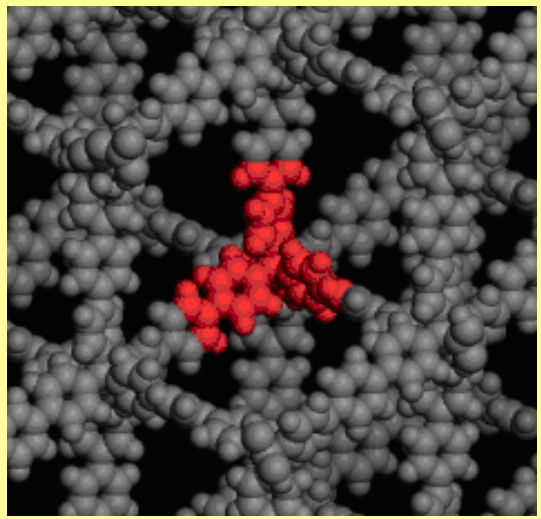
Metal-organic framework

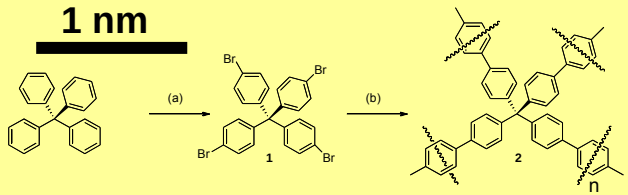


Chiral mesoporous silica



Covalent organic networks





CO_2 adsorption – approach and results

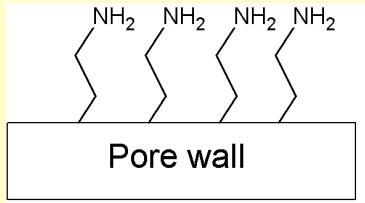
- APPROACH: Realization via synthesis, property measurements, theoretical analyses

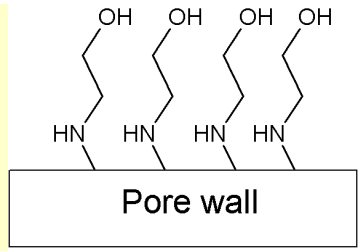
E.g. : mesoporous silica modified with amine-like moieties

+ CO_2/ N_2 selectivity ~ 30

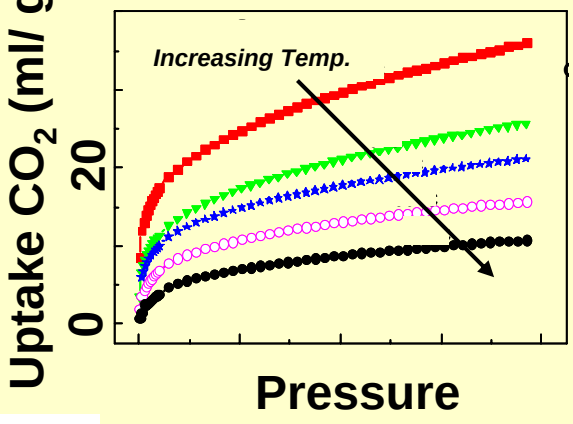
+ Significant uptake

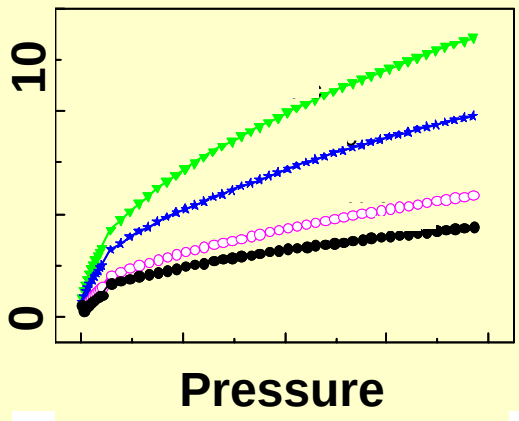
Picture of experimental set up



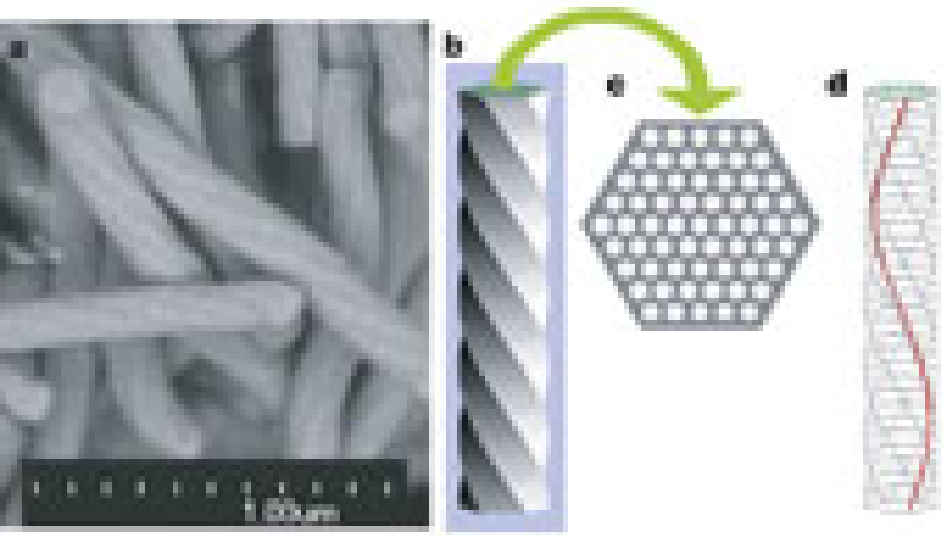


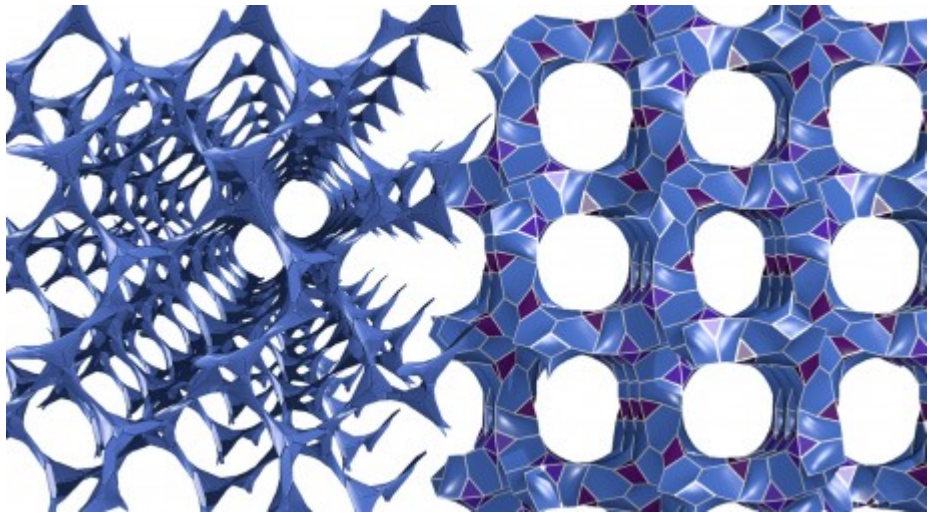
Experimental CO_2 uptake





Enantioselective catalysis





The ITQ-37 mesoporous chiral zeolite

Nature **458**, 1154-1157 (30 April 2009)

Junliang Sun1, Charlotte Bonneau1, Ángel Cantín2, Avelino Corma2, María J. Díaz-Cabañas2, Manuel Moliner2, Daliang Zhang1, Mingrun Li1 & Xiaodong Zou1

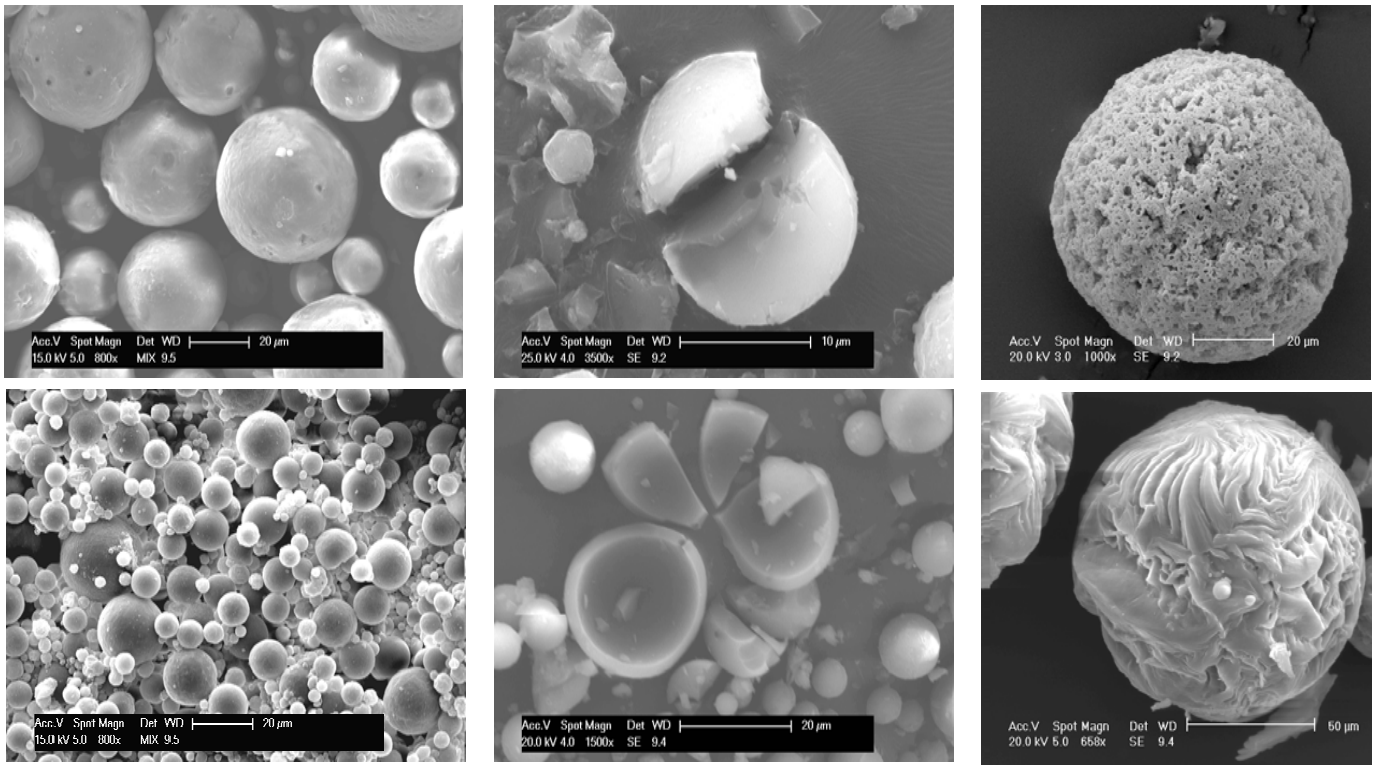
1. Berzelii Centre, EXSELENT on Porous Materials, Stockholm University
2. Instituto de Tecnología Química, Valencia, Spain

New YKI emulsion based method!

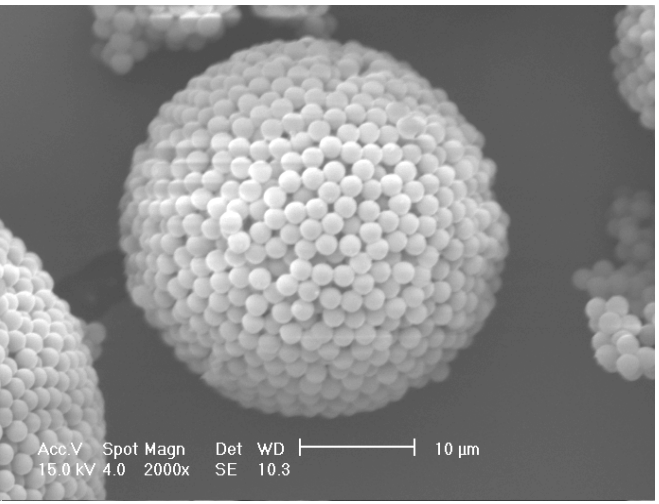
Particle size

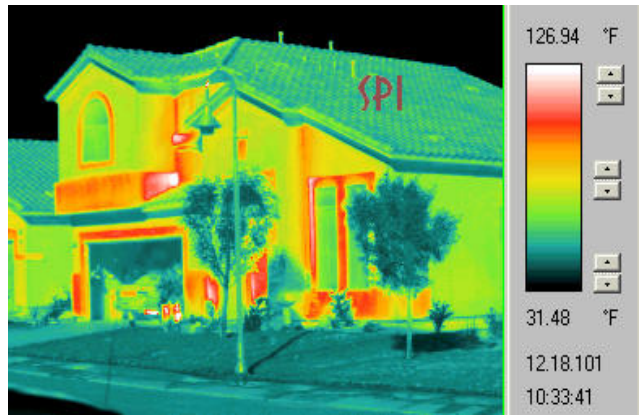
Solid or hollow

Macro / meso



New photonic bandgap pigments



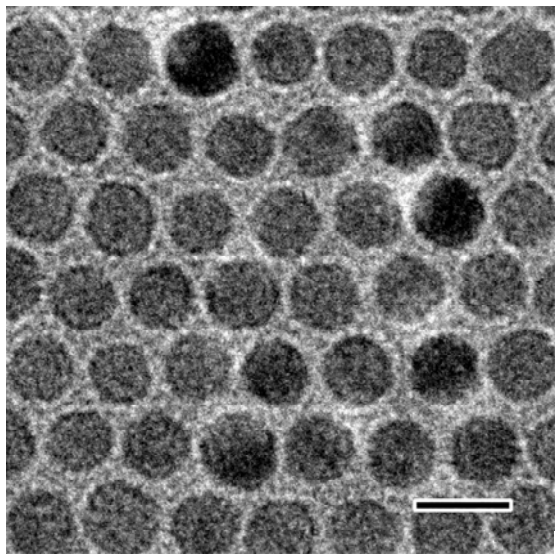


Applications in
- camouflage
- IR reflection
- cosmetics
-novel paper coatings and colorants?

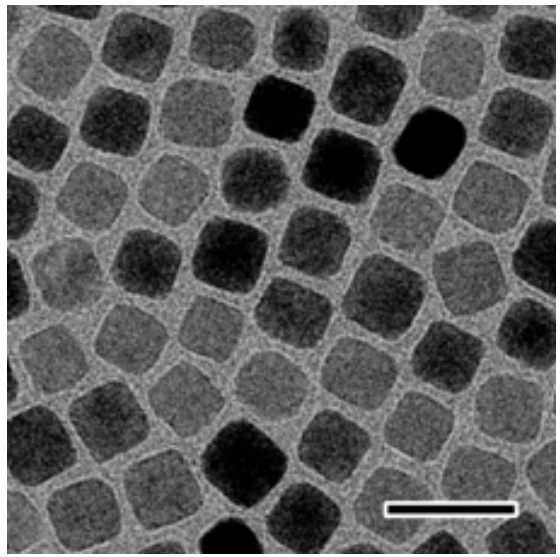
New pigments by trapping dyes in silica

Controlling the shape of nanoparticles with surfactants

rod **sphere** **platelet**



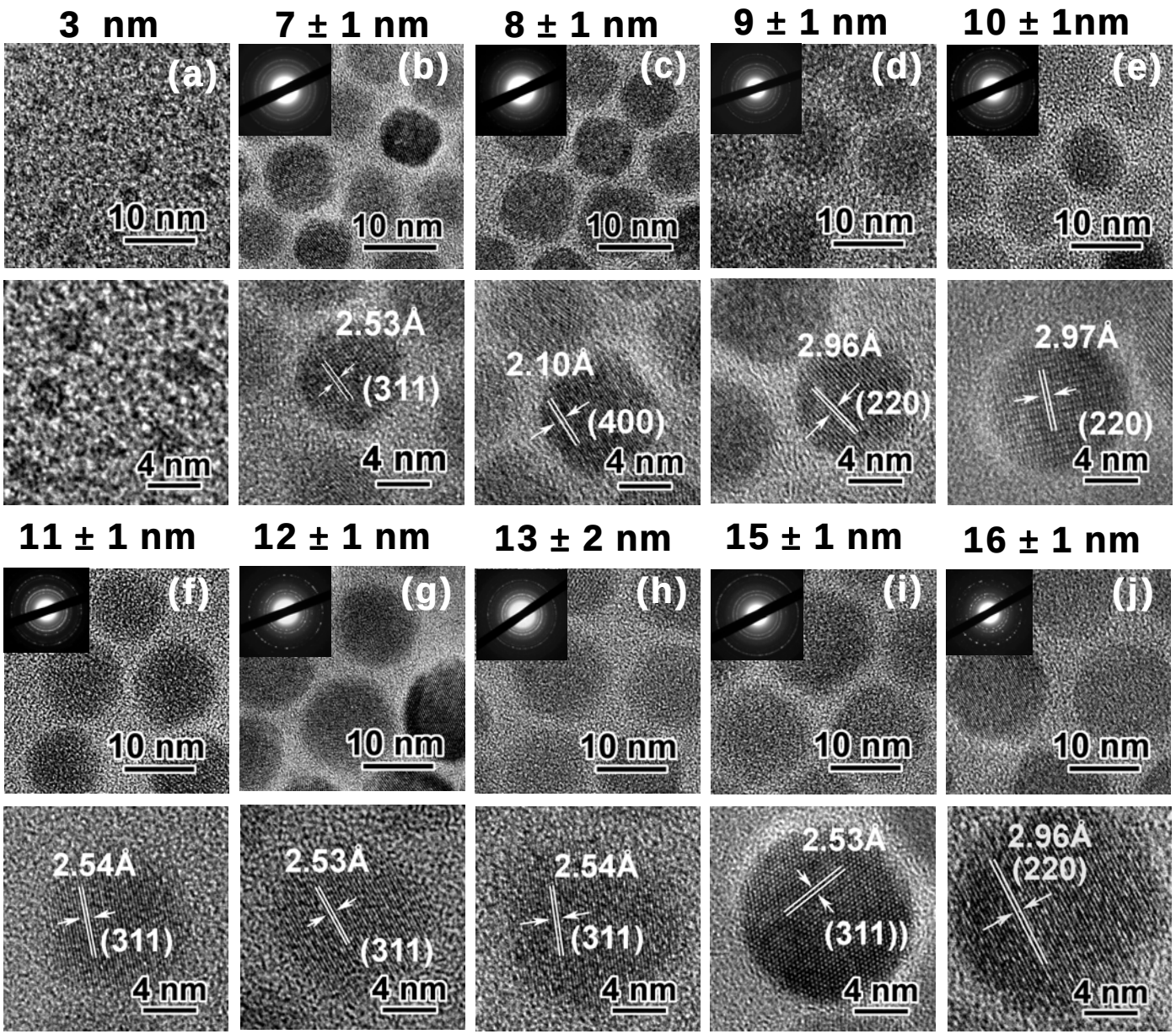
12nm iron oxide nanocubes
(Scale bar is 20nm)



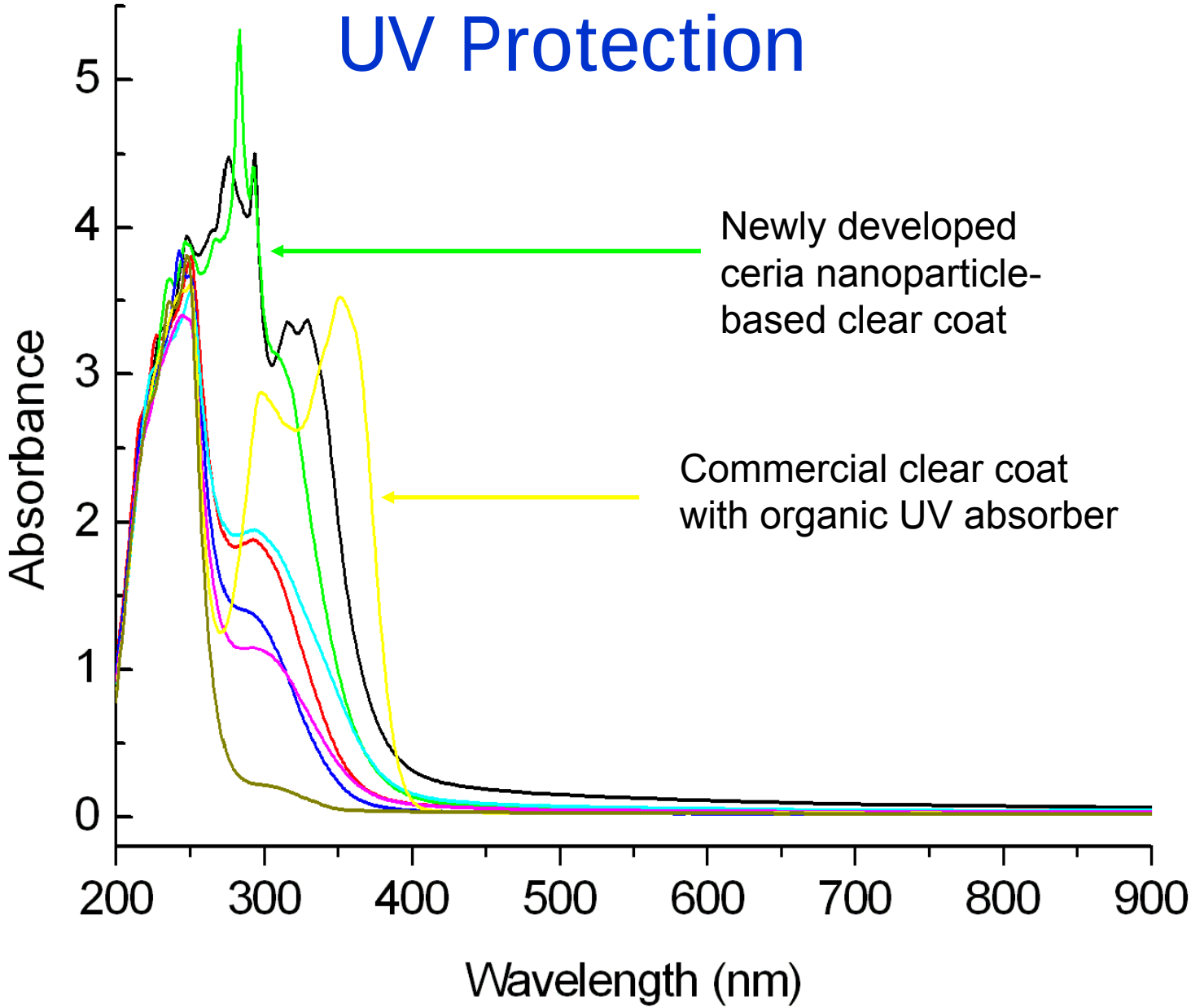
13 nm iron oxide nanospheres
(Scale bar is 20nm)

Courtesy of Anwar Ahniyaz, YKI

Seeded Growth of iron oxide nanocrystals



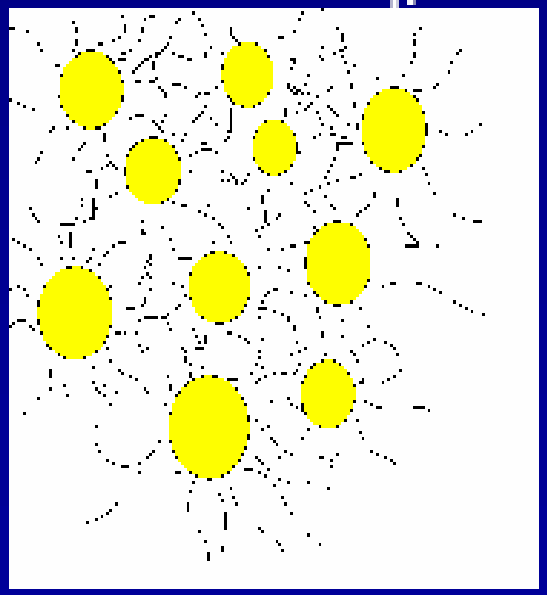
Nanoparticle-based Clear Coat for UV Protection

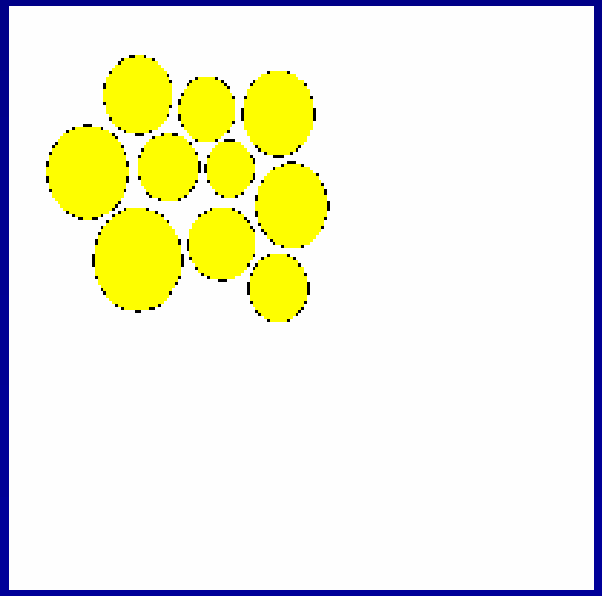


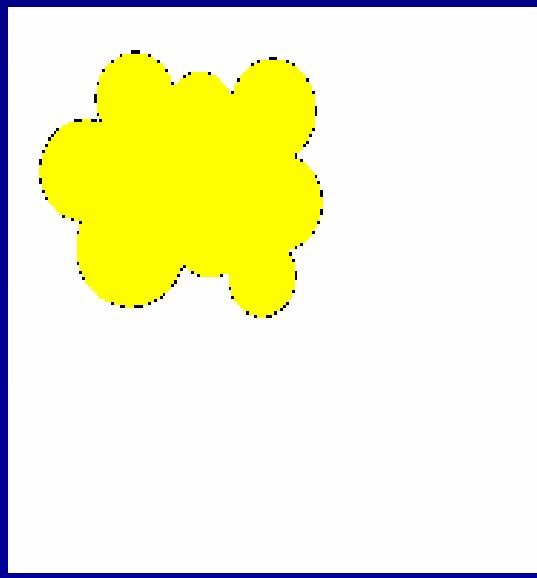
- Nanoparticles generally show a reduction in melting point relative to bulk counterparts

$$T_{melt}(R) = T_m^{bulk}(1 - \sigma / R)$$

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



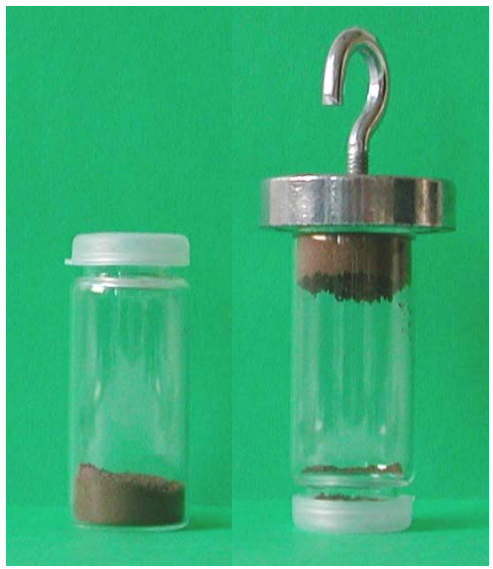




uang *et al*, J. Electrochem. Soc, 150, 2003

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

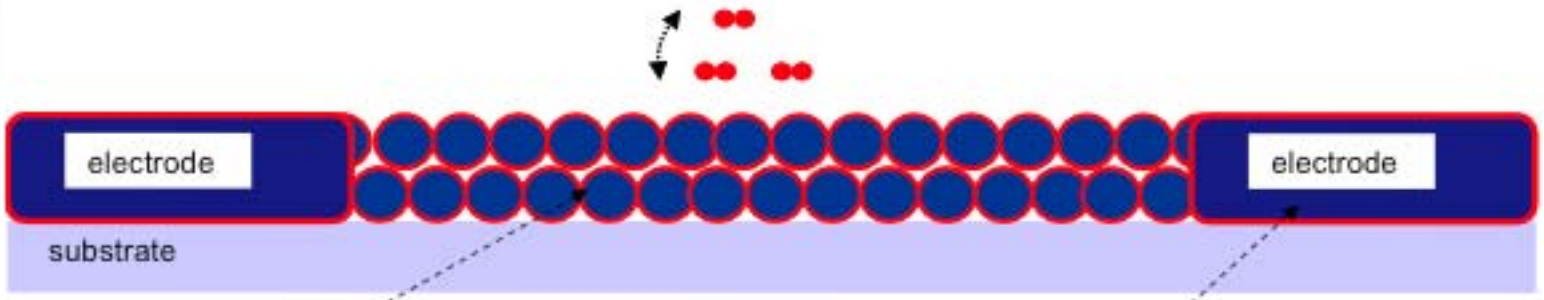


Courtesy of Prof. Hans-Erik Nilsson

Mittuniversitetet
MID SWEDEN UNIVERSITY

Nanoparticle Sensors

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



nanoparticle array (e.g. metal nanoparticles coated with polymer)

electrode can be of the same material (metal nanoparticle array) but created using electrical patterning

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

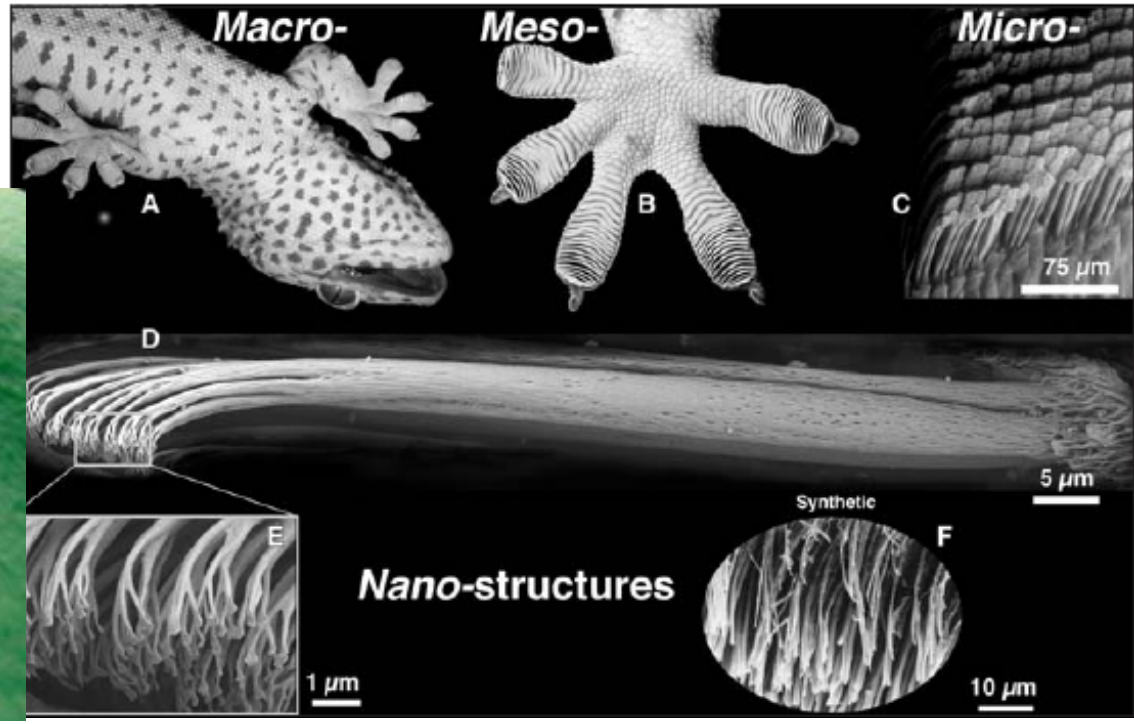
KTH VETENSKAP OCH KONST

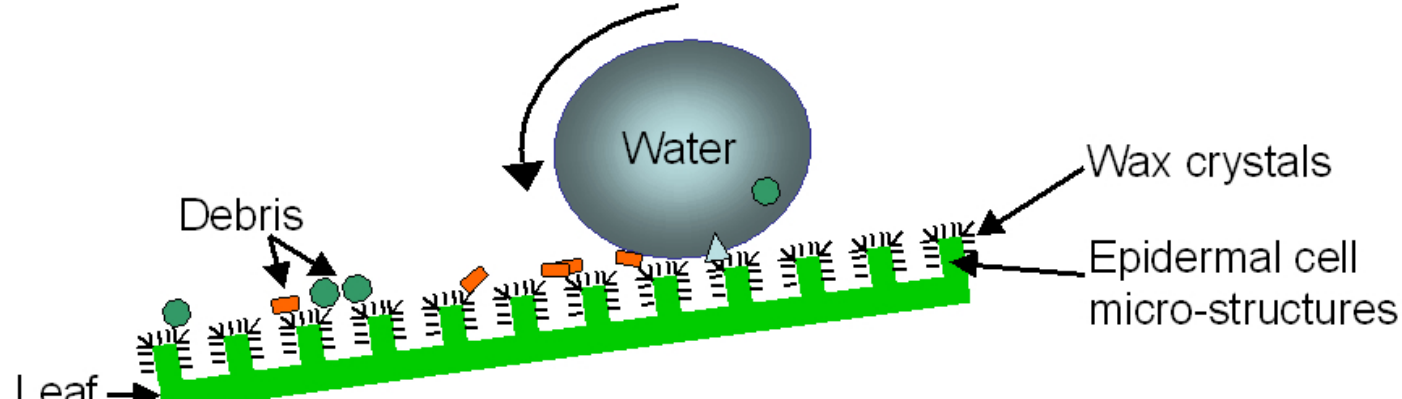
VTT

Nano Surface Design in Nature

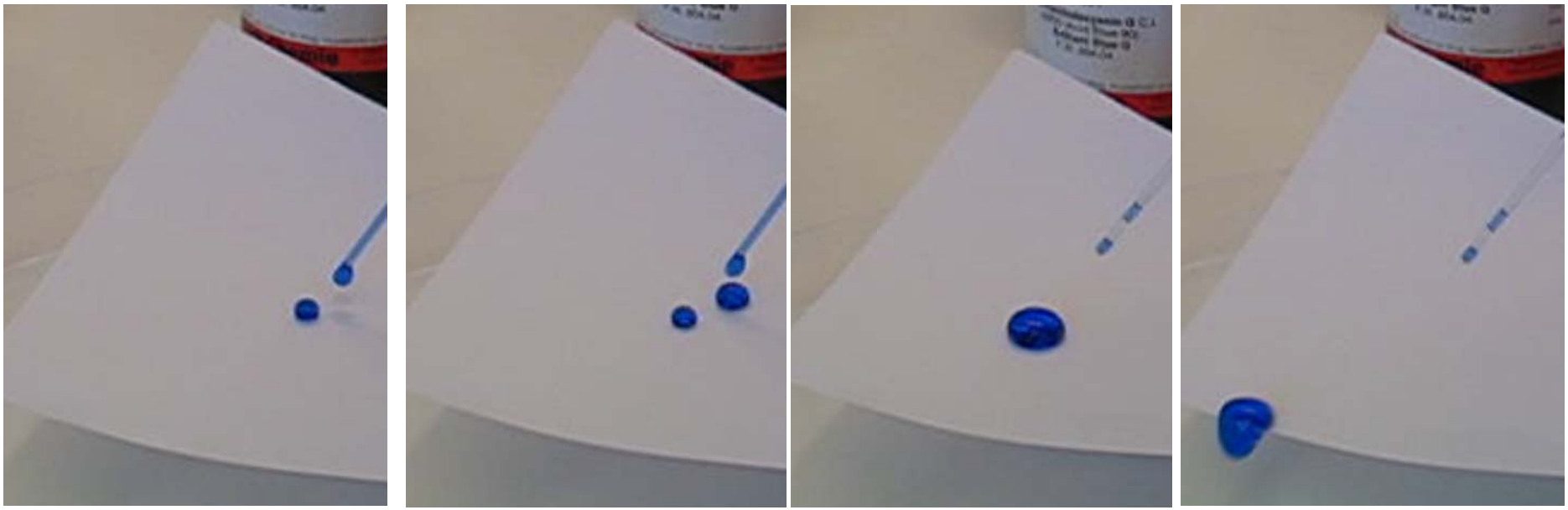
Gecko Feet

- Lotus leaf effect





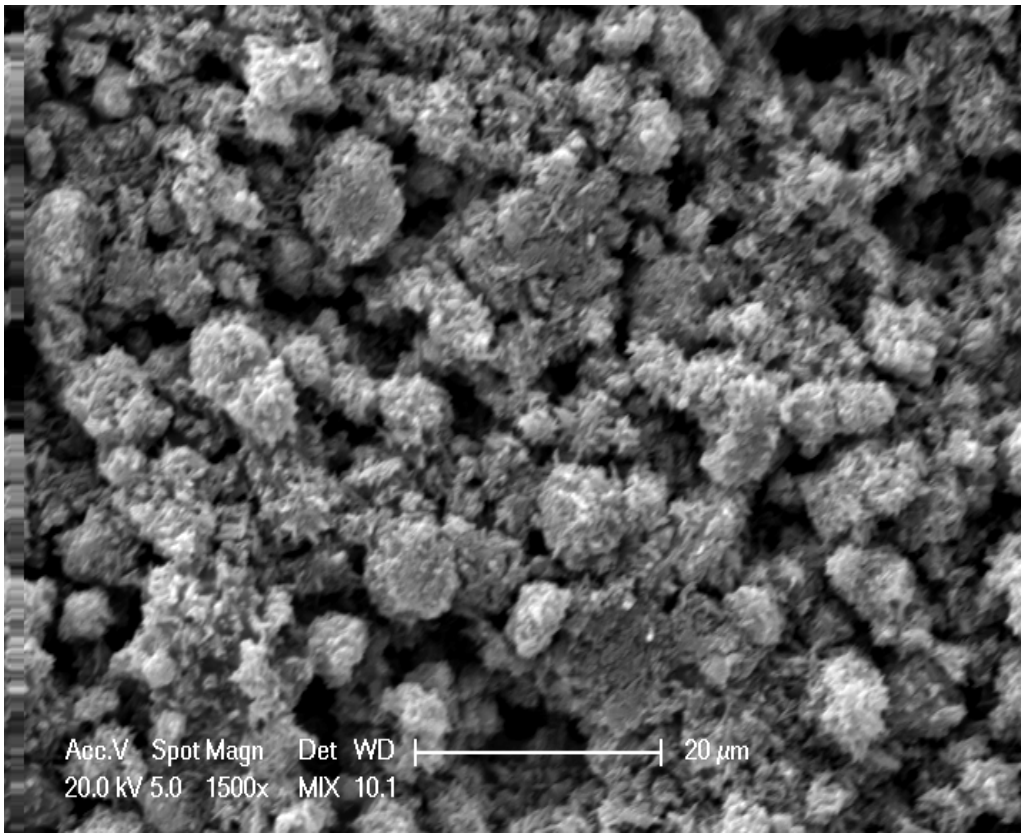
Superhydrophobic surfaces

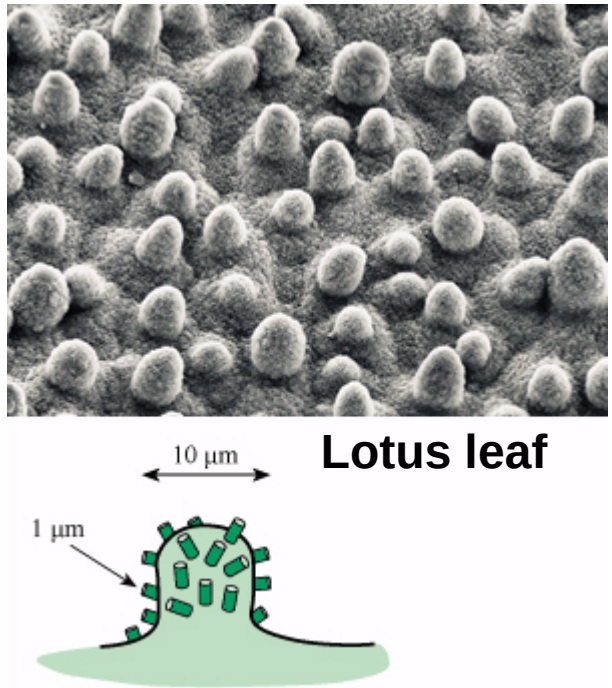


Water repellency and self-cleaning via patented self assembly coatings

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

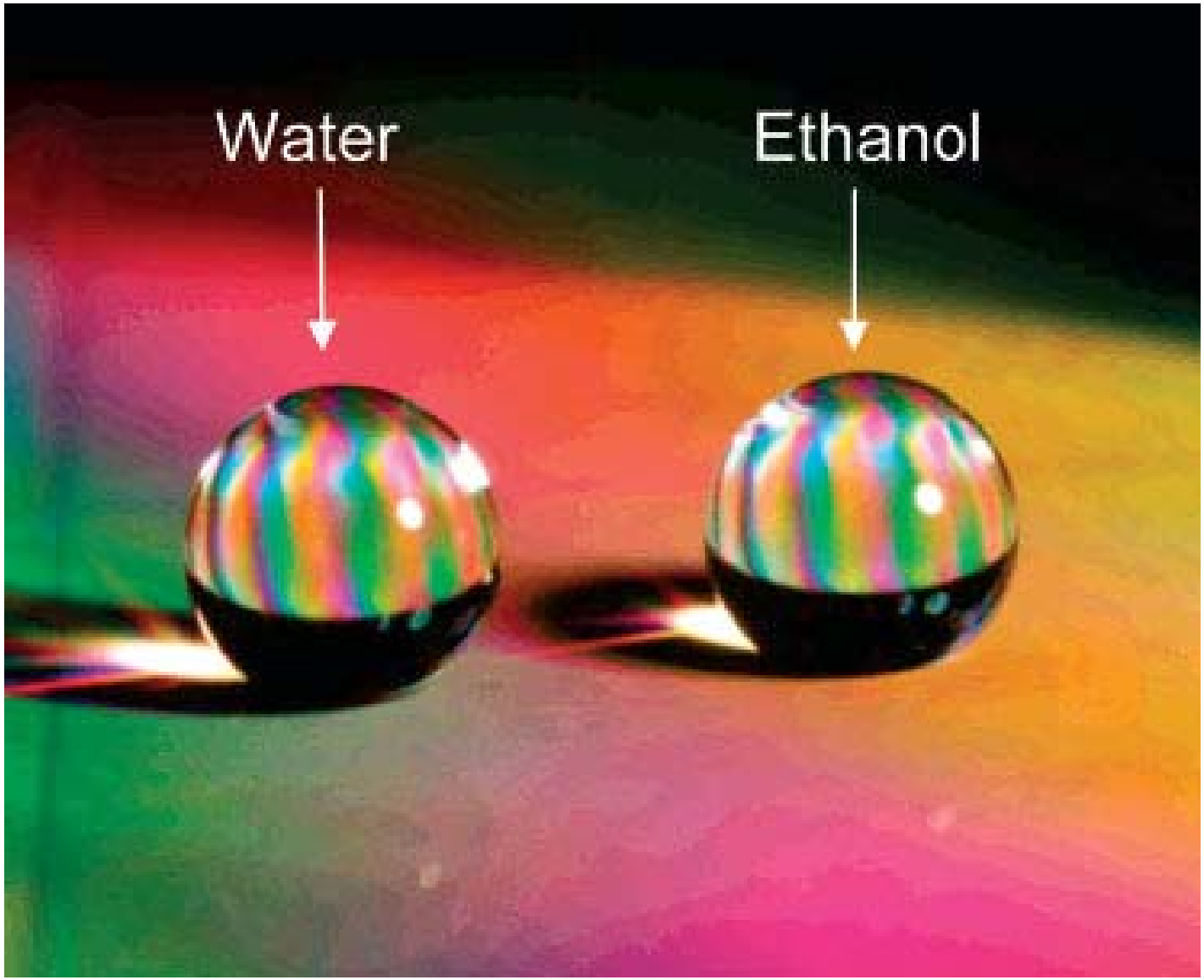
Superhydrophobic coatings

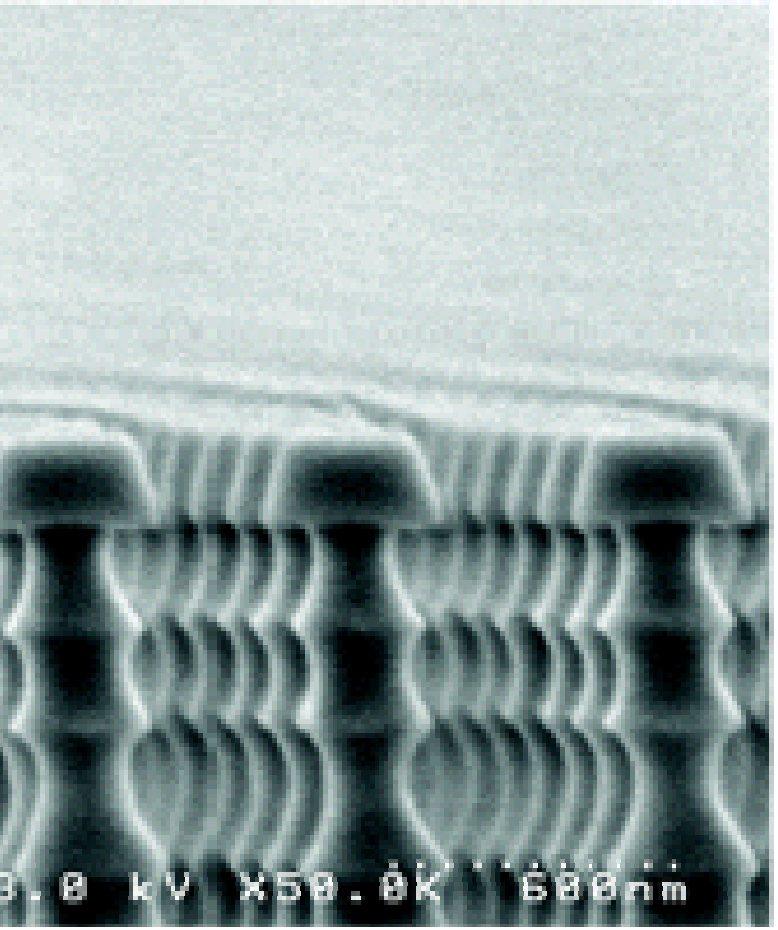


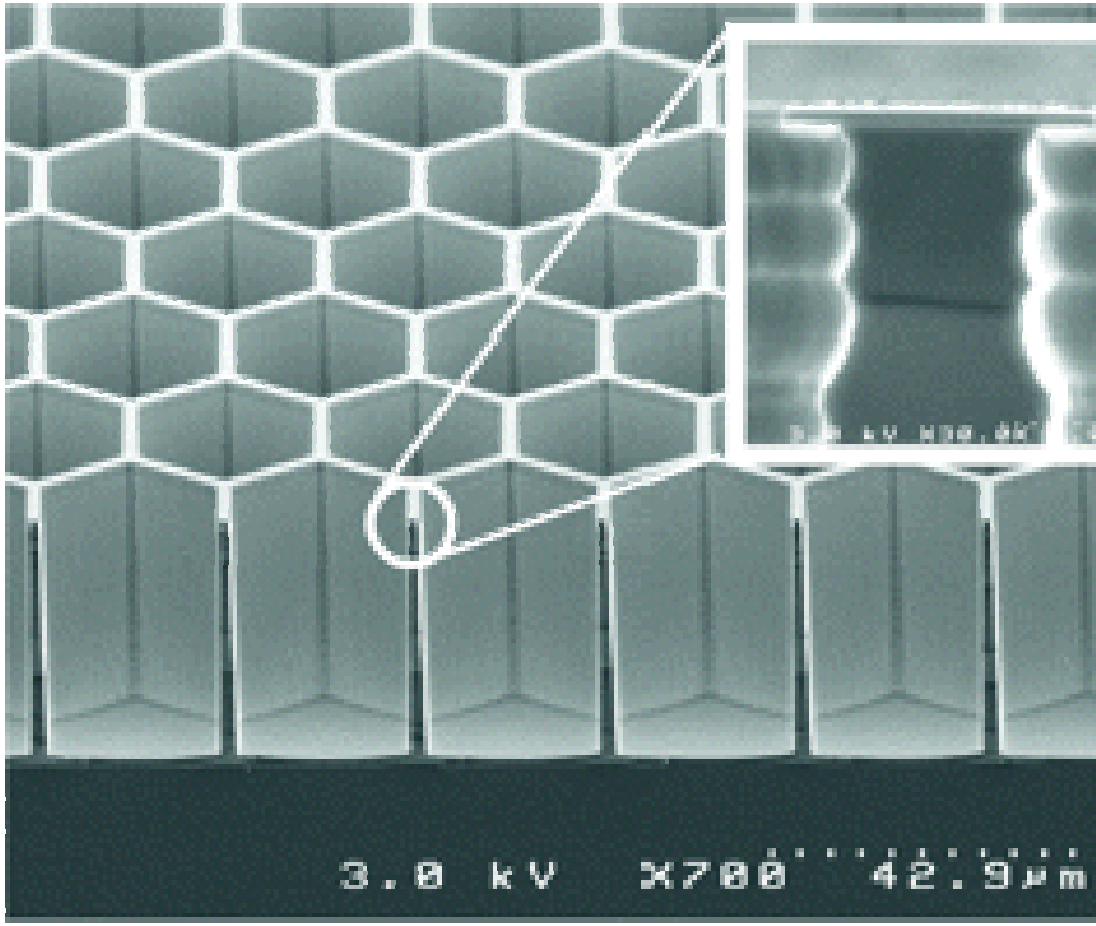


- One-step coating procedure to produce required hydrophobicity and roughness to achieve a contact angle of 150°
- Both macro and microscale roughness important (scale bar 20 µm)

Superlyophobic Surfaces

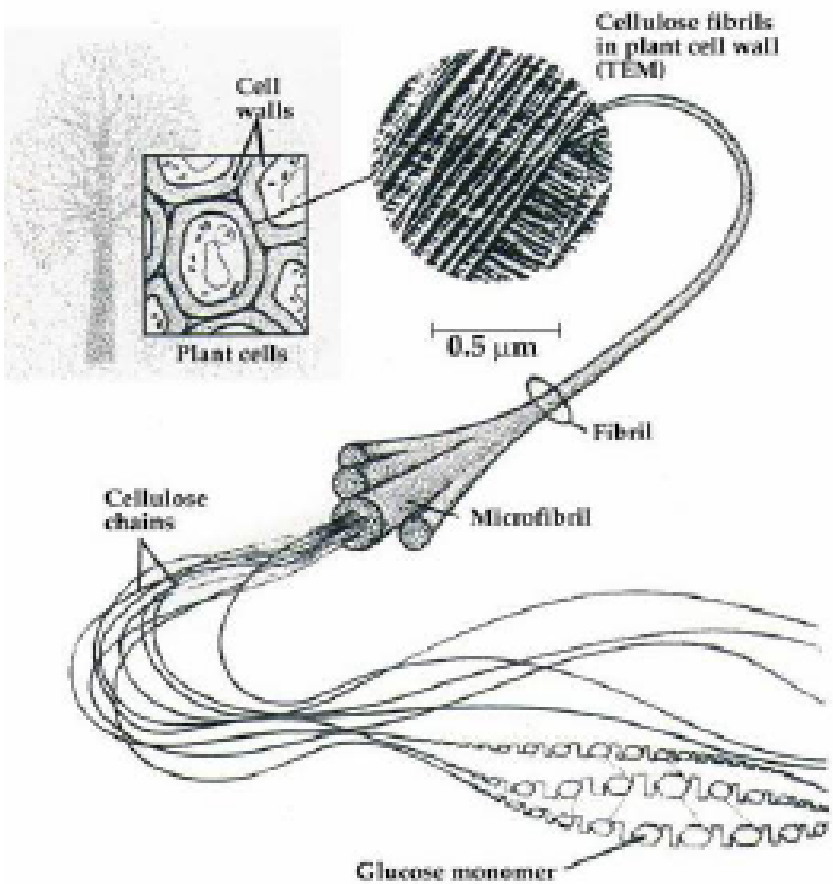


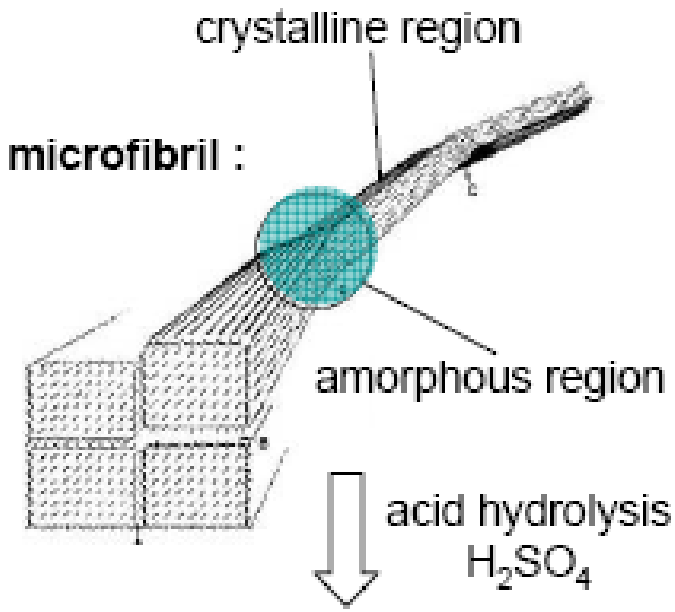


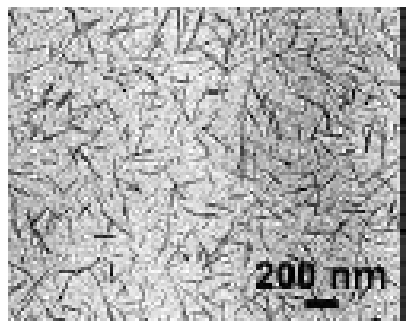


Nanonails: A Simple Geometric Approach to Electrically Tunable Superlyophobic Surfaces *Krupenkin et al, Bell Labs ACS 2008*

Isolation of crystalline cellulose







TEM image of cotton nanocrystals

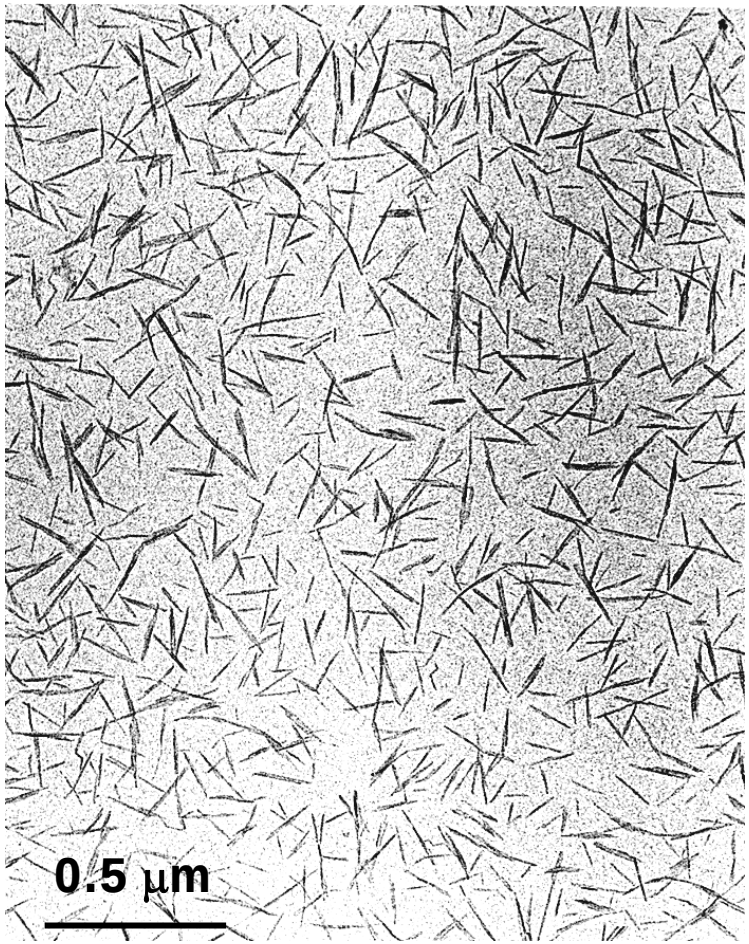
Chemistry
McGill University

Paprican

Research on Nano Crystalline Cellulose

- **Preparation techniques:**
  - H_2SO_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



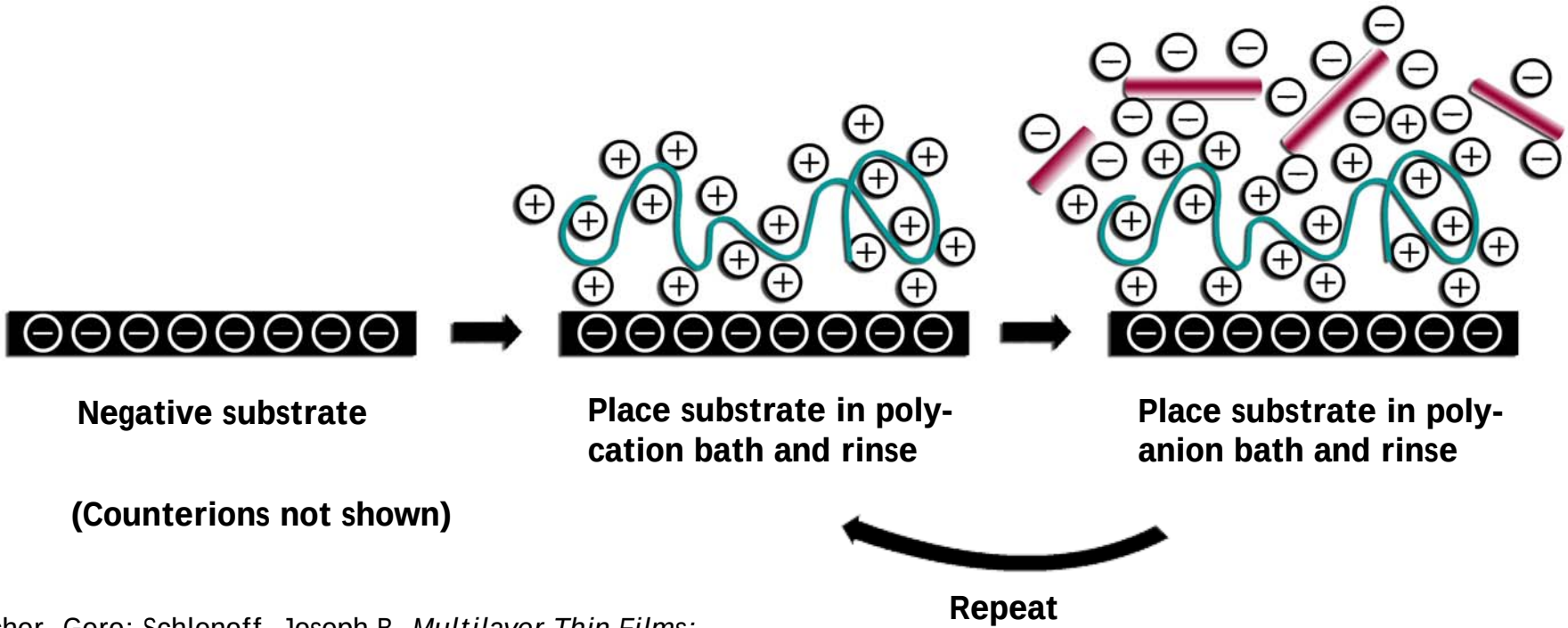
TEM image of dilute suspension on carbon grid

- 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/nm^2 (and hydrophilic)
- Optically birefringent

Revol, J-F; Godbout, L.; Gray, Derek G. *J. Pulp and Paper Sci.*, **1998**, 24,146.

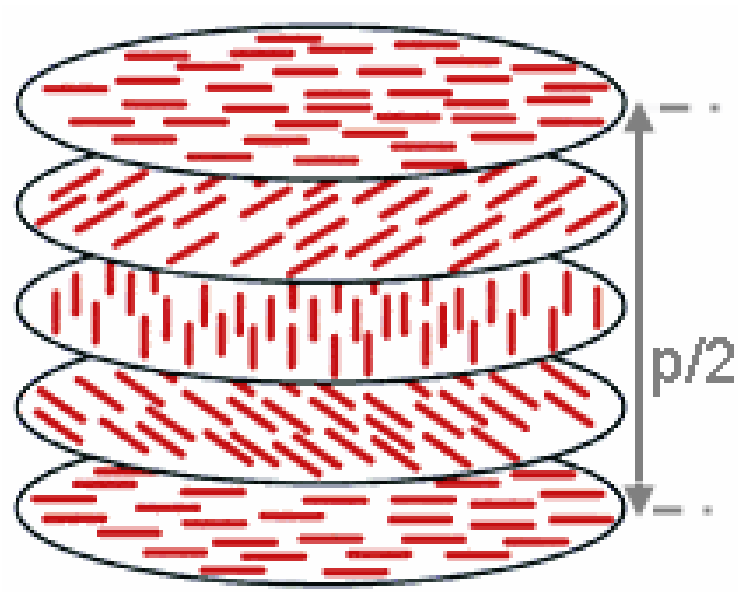
Electrostatic Multilayering

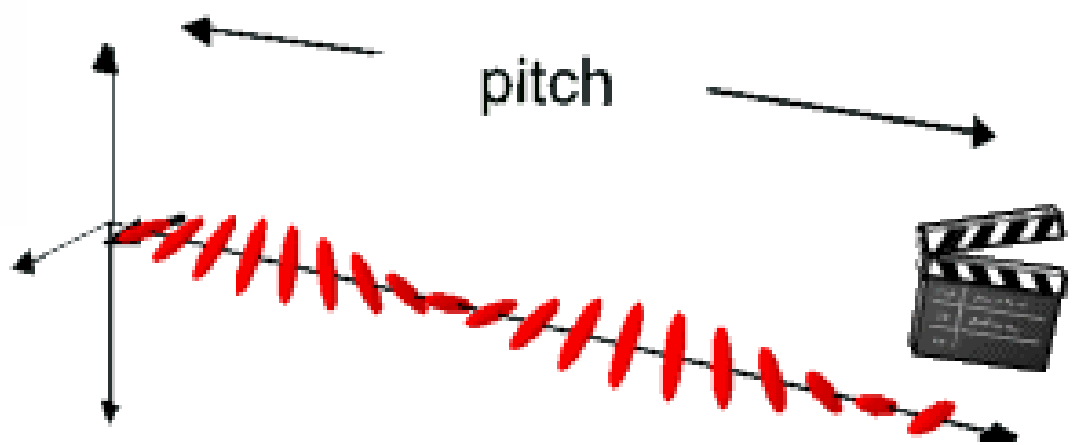
- Multilayered thin films are prepared by sequential electrostatic adsorption of oppositely charged polymers
    - Physisorption onto charged substrate from dilute solution
    - Self-assembly is driven by electrostatics and entropy



Decher, Gero; Schlenoff, Joseph B. *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*; Wiley-VCH: Weinheim, **2003**.

Chiral nematic structure



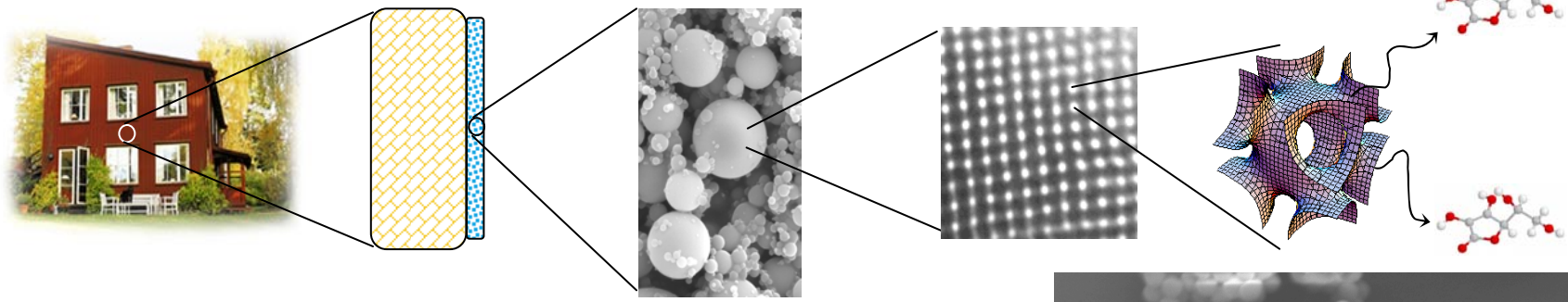


Film Morphology

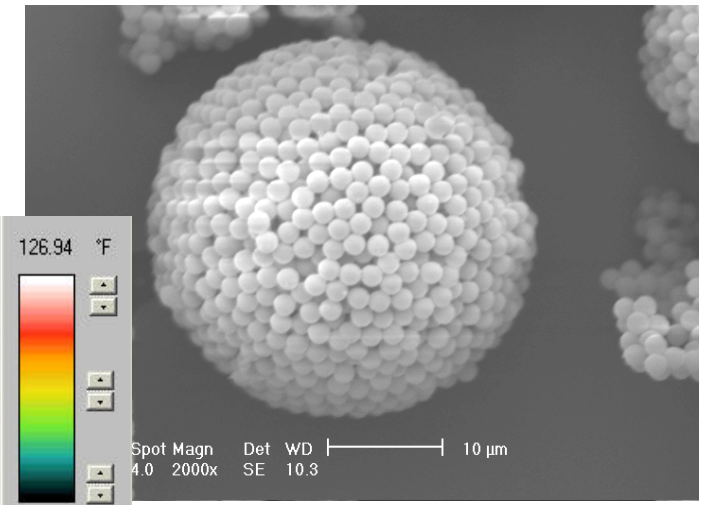
- Films are stable in water due to ionic crosslinking
- Full surface coverage after 5 layers
- Thicker films are uniformly and brightly coloured (nematic order)

5 layers **10 layers** **20 layers** **30 layers** **50 layers**

Slide courtesy of Emily Cranston

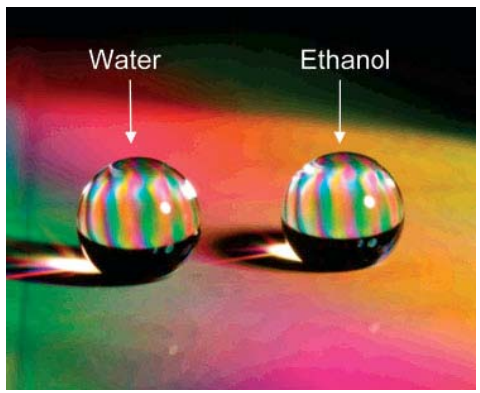


- **Nanostructured materials**
  - Surfactant templated mesostructured materials and controlled release
  - Photonic materials and IR-reflective pigments
  - LC NCC coatings
  - Selective catalysis



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

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



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