Mineral Morphologies

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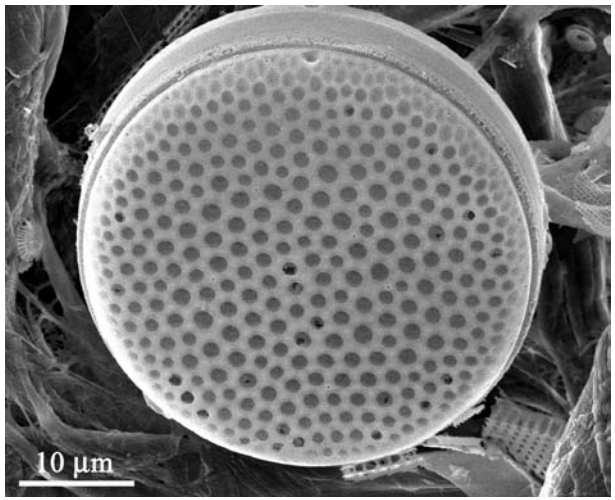
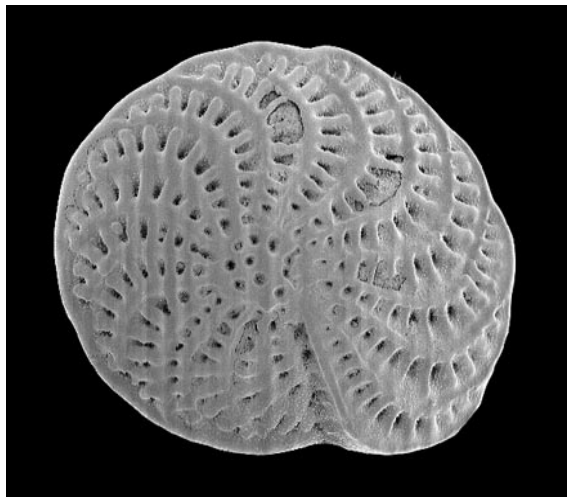
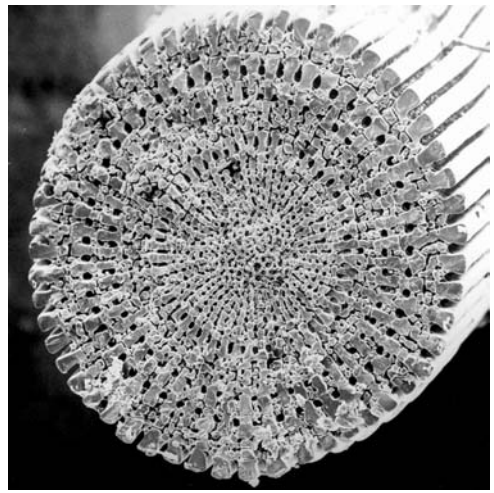
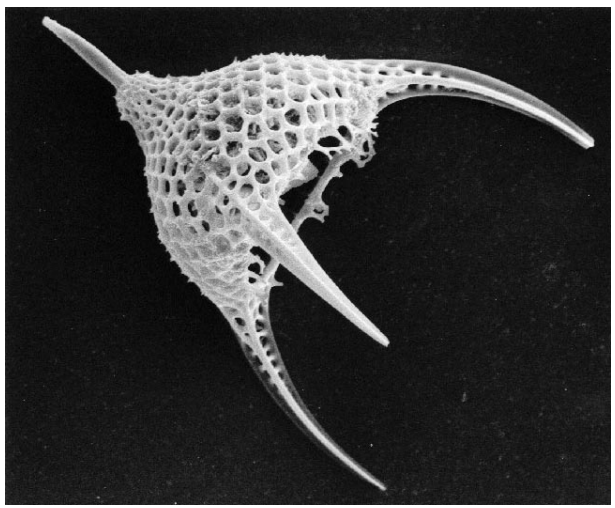
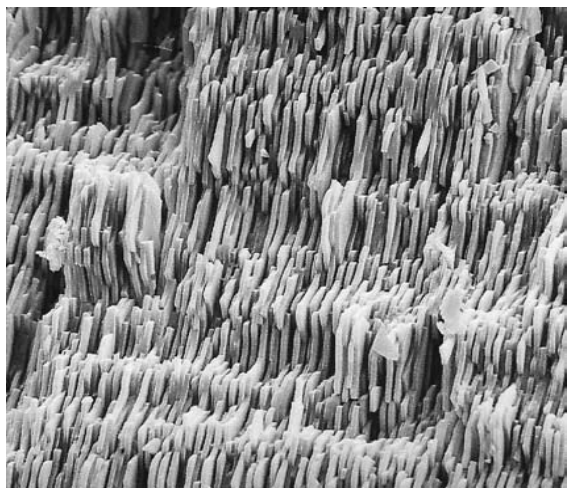
Biomineralisation

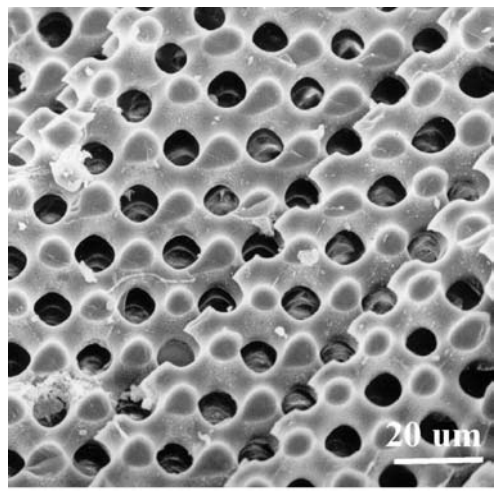












AMORPHOUS

POLYCRYSTALLINE

SINGLE CRYSTAL

Introduction

Routes to Controlling Crystal Morphologies:

- Additives to control single crystal morphologies
- Additives to produce polycrystalline structures

  ⇒ Oriented and non-oriented

- Templating to control production :

⇒ Nanoparticles

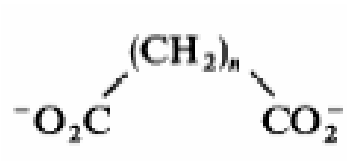
⇒ Polycrystalline structures with complex morphologies

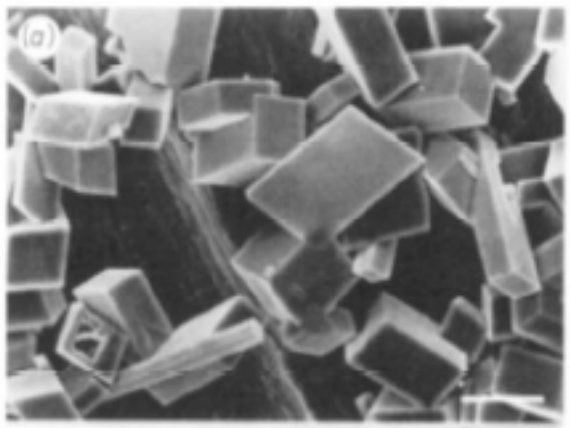
⇒ Single crystals with complex morphologies

Additives to Control Single Crystal Morphologies

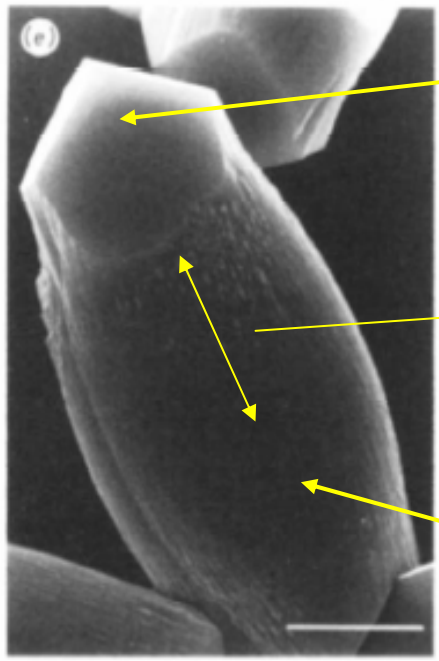
Calcite Precipitation in the Presence of α,ω-Dicarboxylates

- Influence of subtle changes in additive structure studied
- Malonic acid (n = 1) was the most effective ⇒ effect reduced with increasing chain length





Control



Ca/malonate 1:3

capped with rhombohedral {104} end faces

elongated parallel to the *c*-axis

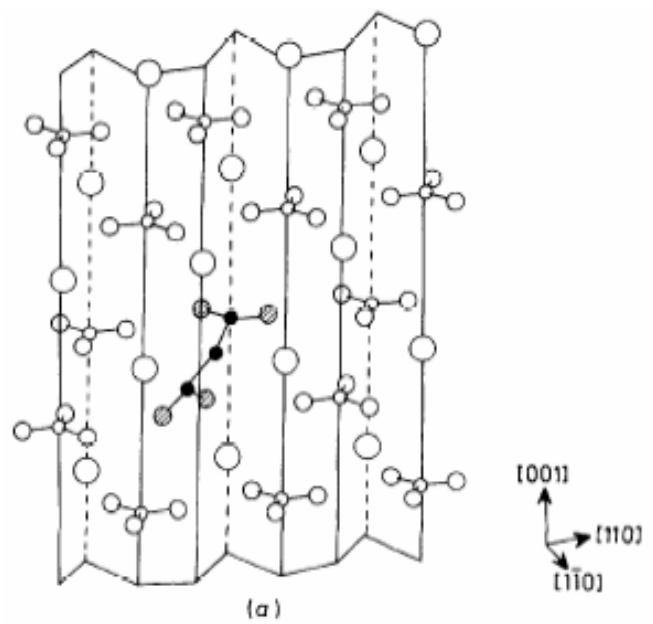
curved {1–10} faces

Mann, Didymus, et al *J. Chem. Soc. Faraday Trans.*, 1990, 86, 1873-1880

- Morphological changes were considered in terms of molecular recognition between the crystal face and additive

- Calcite crystal faces parallel to the *c*-axis have carbonate groups oriented perpendicular to the face

- These faces may be stabilised via stereoselective adsorption of the acids via bidentate binding of the carboxylate groups



(l-10) face of calcite showing possible malonate binding site

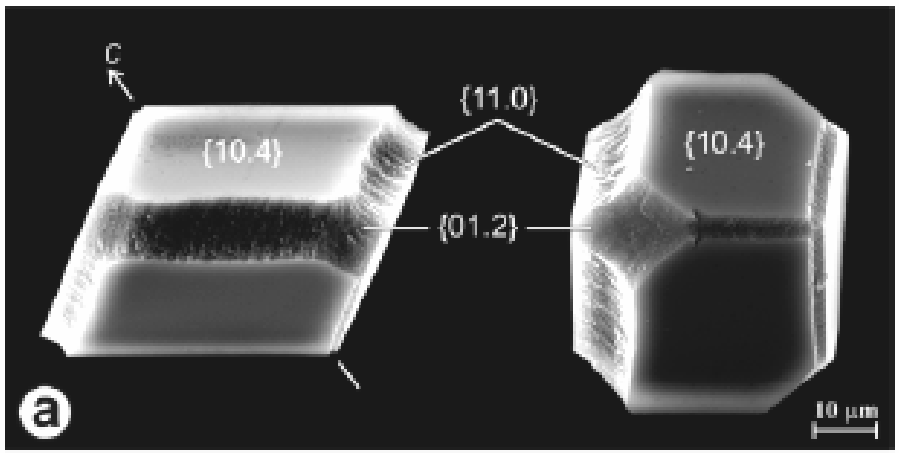
Cooperative binding of the carboxylate groups may occur in the case of the short-chain additives

The carboxylate groups in the longer-chain additives behave independently

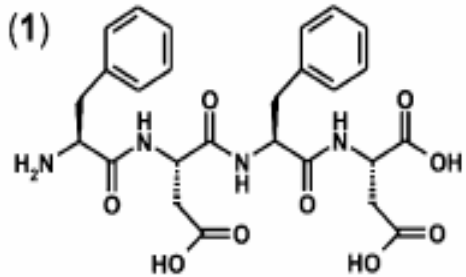
Acidic Peptides as Growth Modifiers

Acidic proteins extracted from biogenic $CaCO_3$ often comprise alternating Asp or Glu residues and more hydrophobic residues.

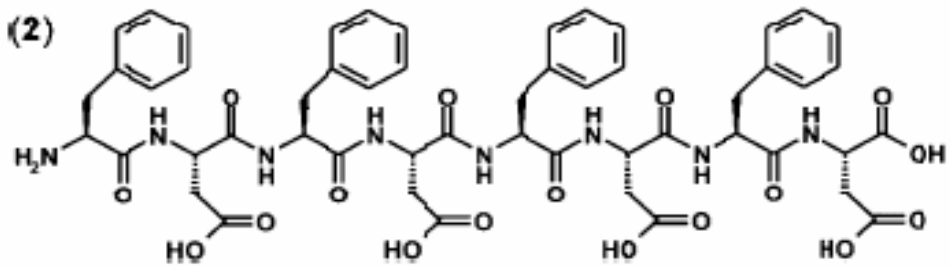
⇒ Mimic this structure / use as calcite growth modifier



H-(Phe-Asp)$_2$-OH



H-(Phe-Asp)$_4$-OH

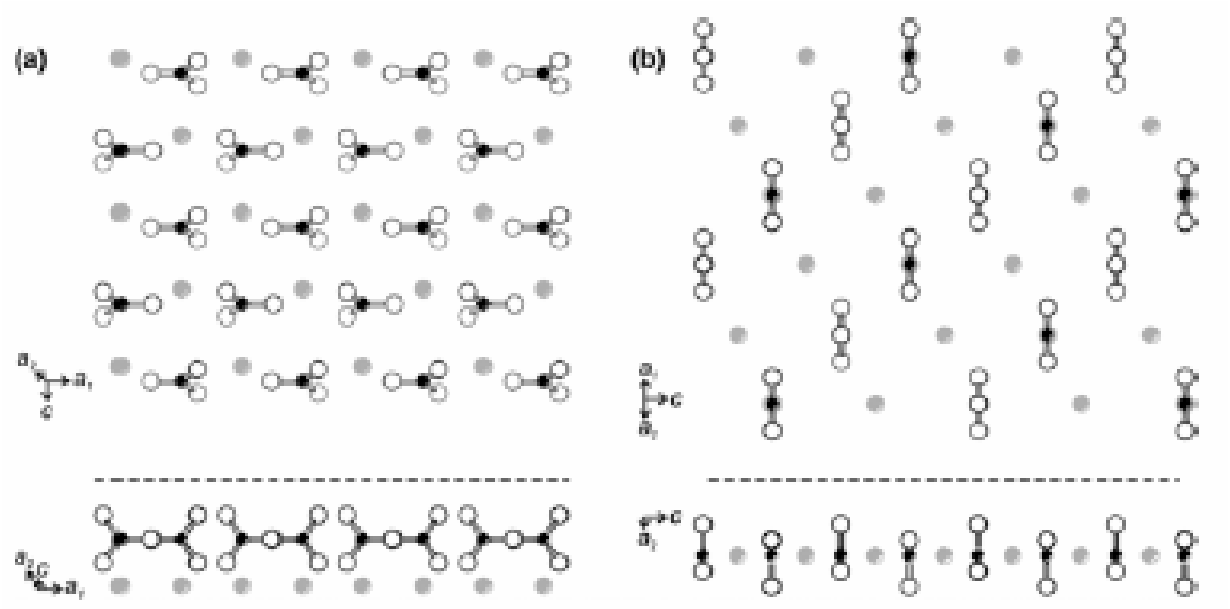


Observe NEW {01.2} and {11.0} faces

Volkmer, Fricke, Huber, Sewald *Chem. Commun.* (2004), 1872-1873

{01.2} and {11.0} faces have few common features in terms of symmetry or electrostatics

Also, polymer additives very flexible



{01.2} {11.0}

⇒ Seems unlikely these faces are selected on the basis of stereochemical or geometrical recognition

Additives to Control Polycrystalline Particle Morphologies

Higher concentration of additives

⇒ Observe transition from single crystal to polycrystalline structure

⇒ Can obtain unusual morphologies

Polycrystalline particles frequently form by aggregation

⇒ Can be disordered or oriented

⇒ Aggregation can be mediated by additives

Aggregation-Based Crystal Growth

In natural systems (biology, geology), crystal growth traditionally considered to occur by:

1 Atom-by-atom addition

2 Dissolution of unstable phases and reprecipitation as more stable phases

However…

There is growing evidence that self-assembly based mechanisms may also be very widespread

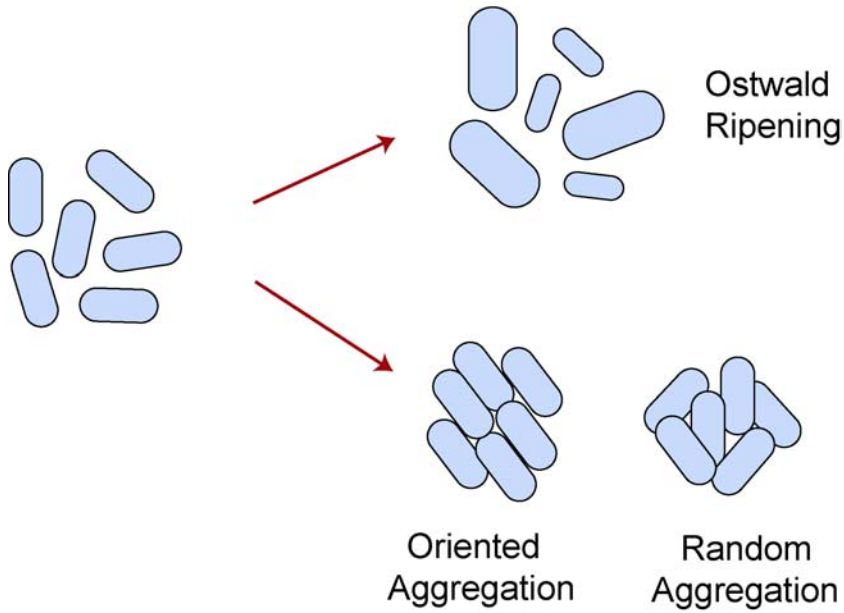
Nanosized particles can also provide the building blocks for the growth of ordered solids

Alivisatos *Science* 2000, 289, 736-737.

Growth by Aggregation

Nanocrystal growth in solution typically involves the **fast nucleation** of primary particles, followed by **growth** by:

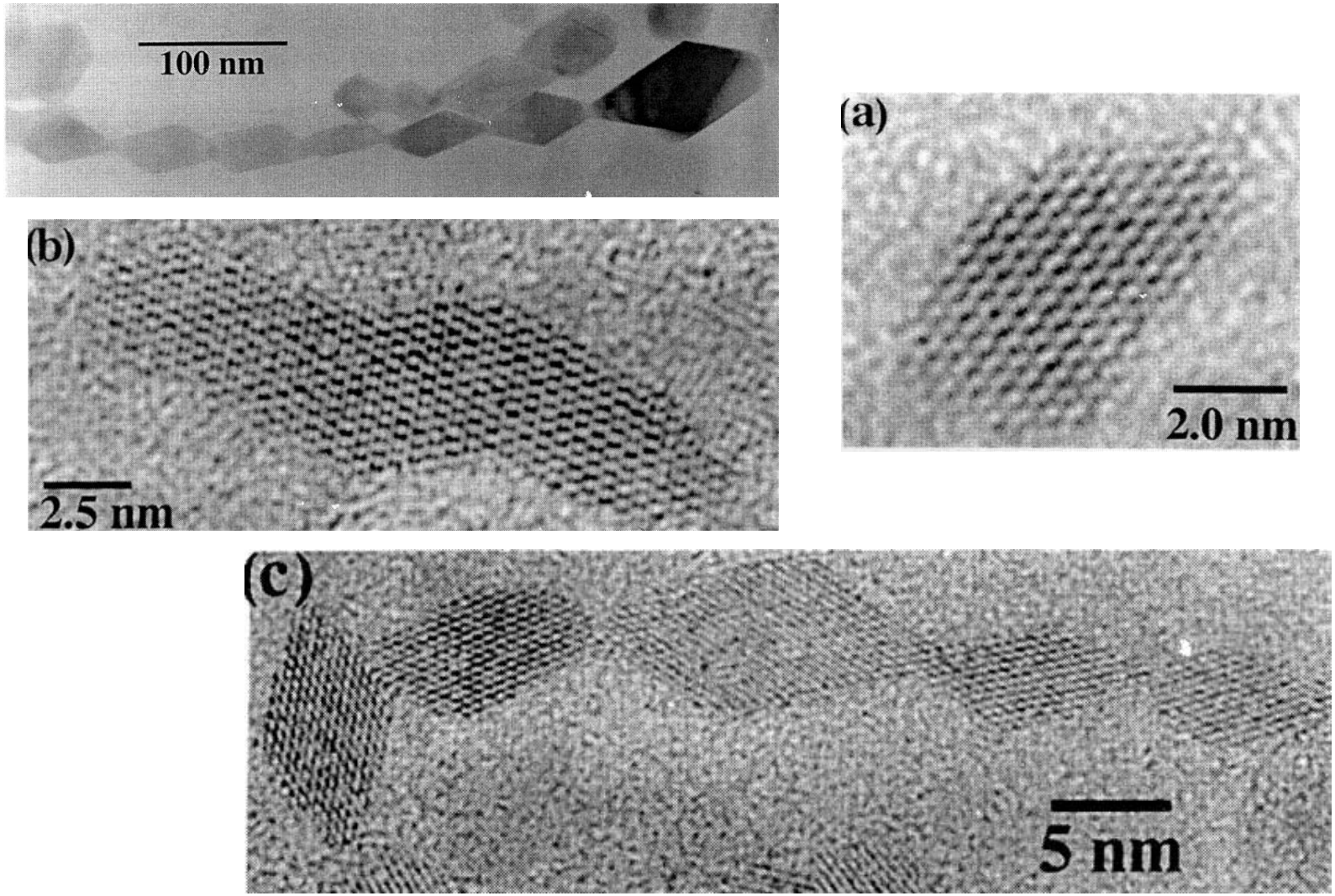
- ***Coarsening***
- ***Aggregation***



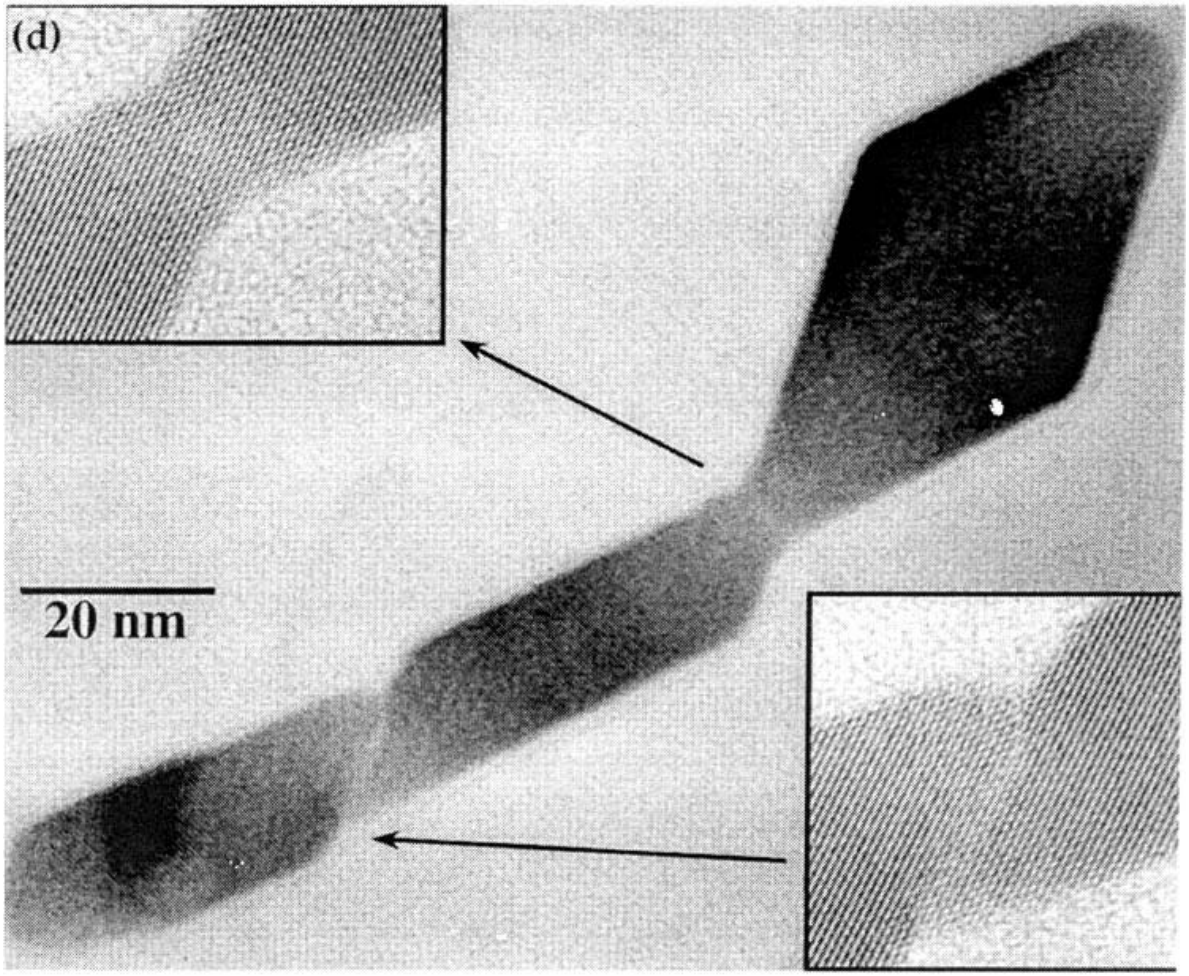
Oriented aggregation provides a special case

RL Penn *J Phys Chem B* 2004, 108, 12707-12712.

Nanocrystalline Titania Aggregates



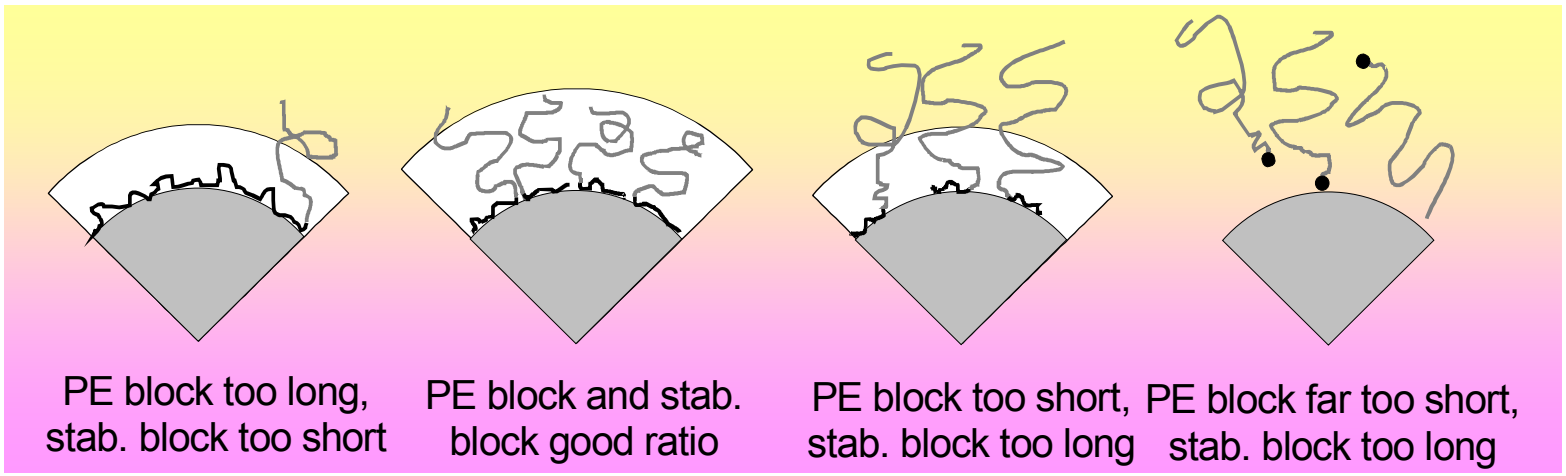
Penn and Banfield *Geochim Cosmochim Acta* 1999, 63(10), 1549-1557.



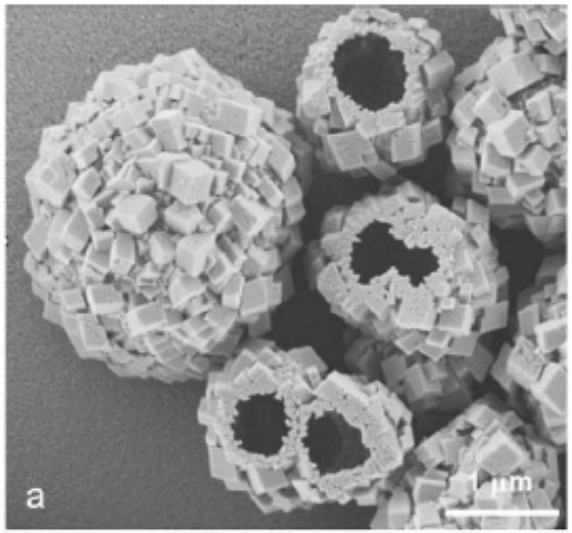
TiO_2 particles aggregate on high energy faces to produce elongated single crystals

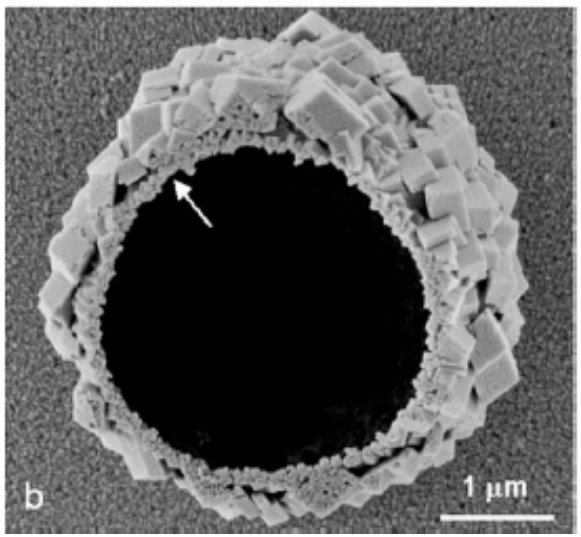
Diblock Copolymers as Growth Additives

- Highly versatile in controlling crystal growth
- Used to produce homogeneous particle populations
- Particles of controlled morphologies
- Unusual highly-ordered polycrystalline structures
- Hierarchically ordered structures

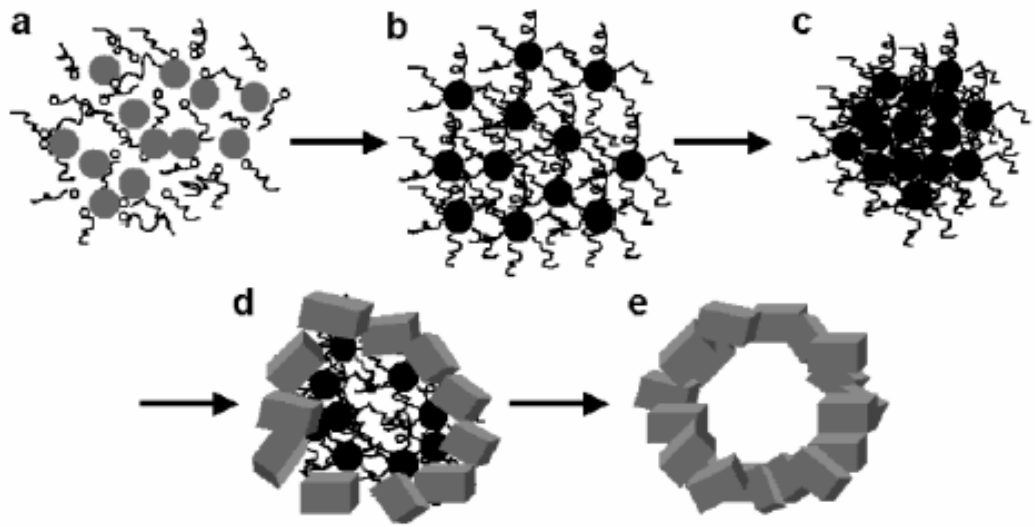


$CaCO_3$ Hollow Spheres





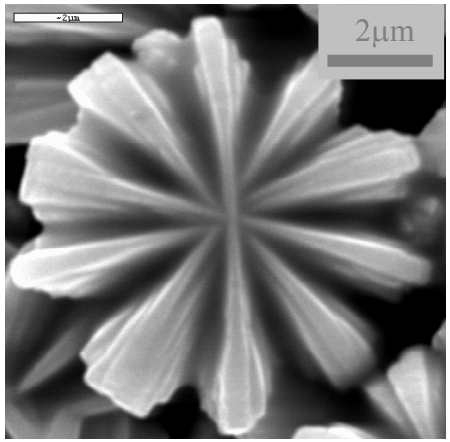
PEG-*b*-PMAA, ammonia diffusion



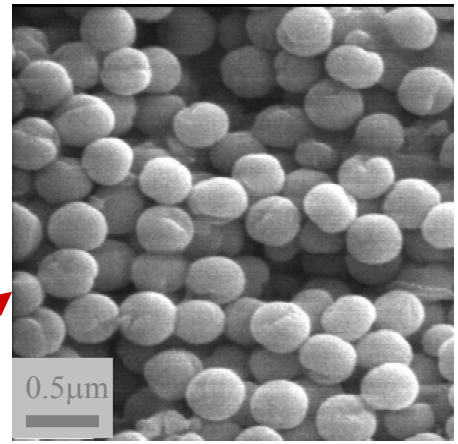
- Vaterite nanospheres aggregate
- Transformation to calcite starts on the surface – calcite rhombohedra form on particle surface
- Continue to grow at expense of dissolving vaterite

Yu, Cölfen, Hartmann, Antonietti, *Adv. Mater.* 2002, 12, 541.

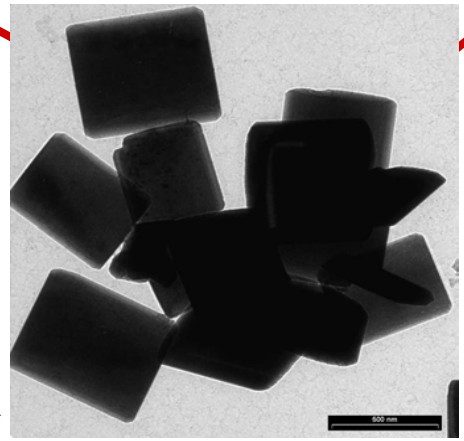
Control of $BaSO_4$ Precipitation



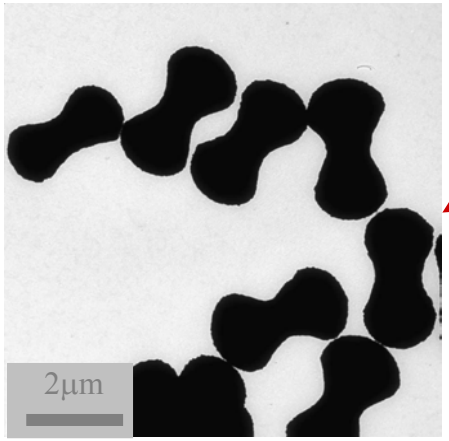
PEG-*b*-PEI-SO_3H



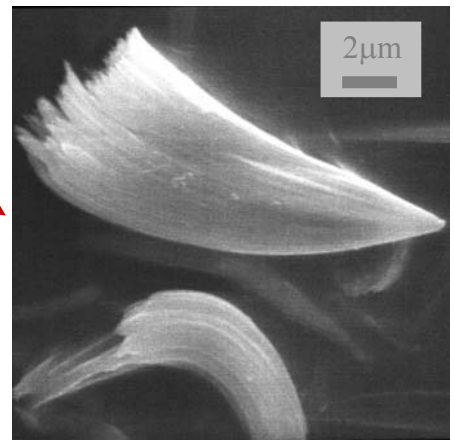
PEG-*b*-PMAA-Asp



No additive



PEG-*b*-PEI-COOH

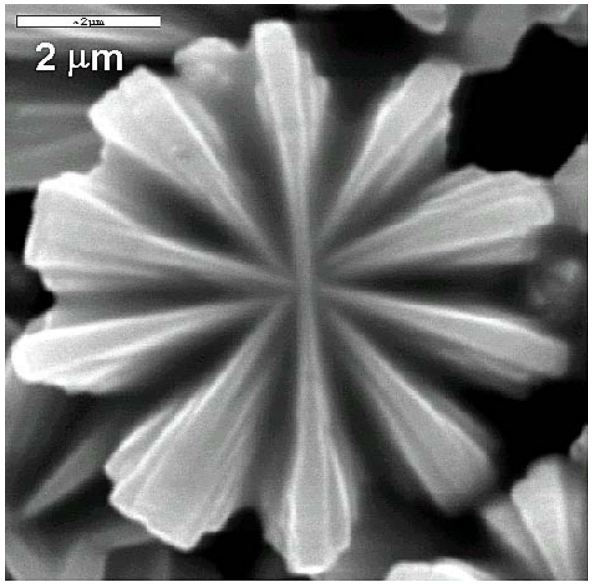


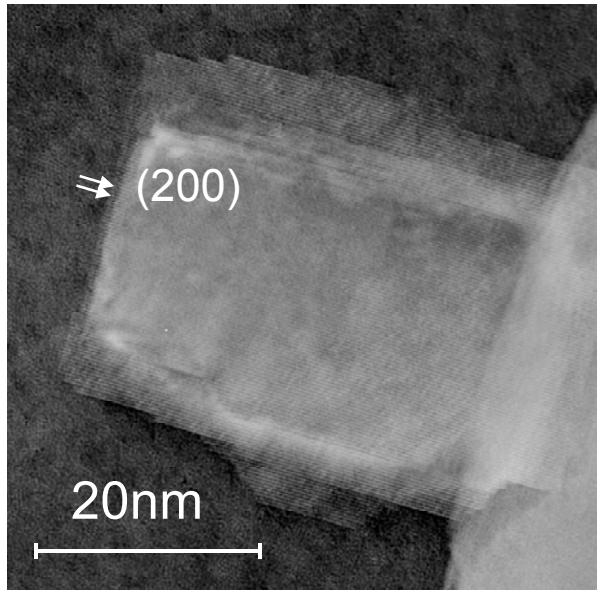
PEG-*b*-PMAA-PO_3H_2

Qi, Cölfen, Antonietti, *Chem. Mater.* 2000, 12, 2392-2403

Formation of $BaSO_4$ "Flowers"

$BaSO_4$ with PEG-*b*-PEI-SO_3H additive, pH 5

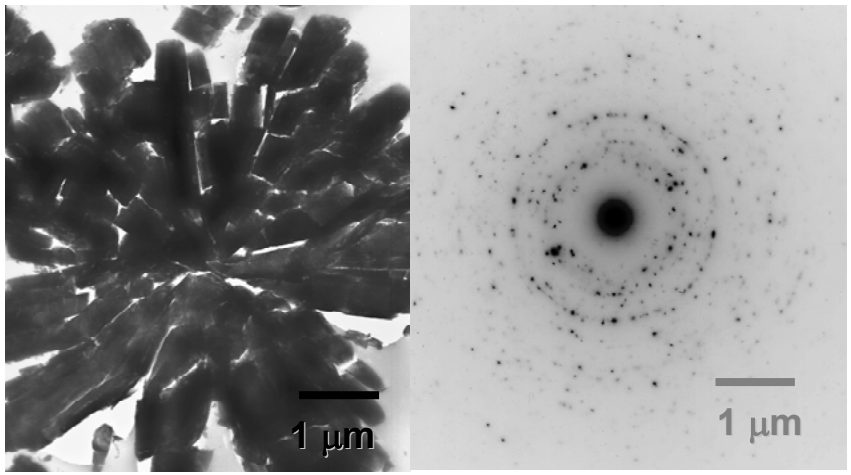




- Flower-like structures with 10 petals
- Angles between petals almost equal
- Petals are overgrown
- Petals are single crystals with the same faces

Cölfen, Qi, Mastai, Börger, *Cryst. Growth Des.* (2002), 2(3), 191-196.

Mechanism of Formation

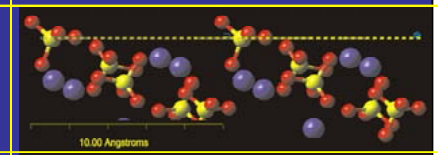
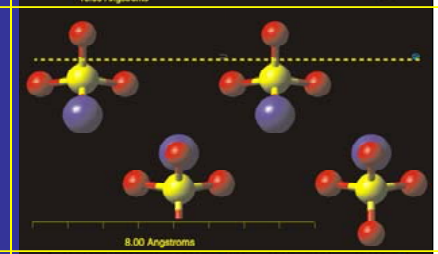
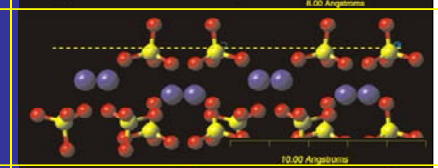
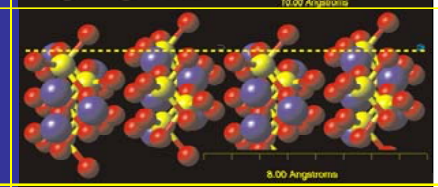
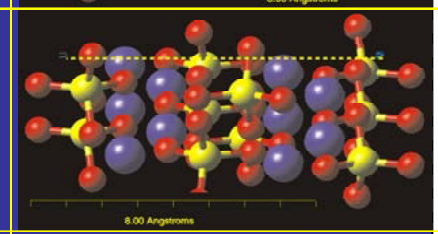


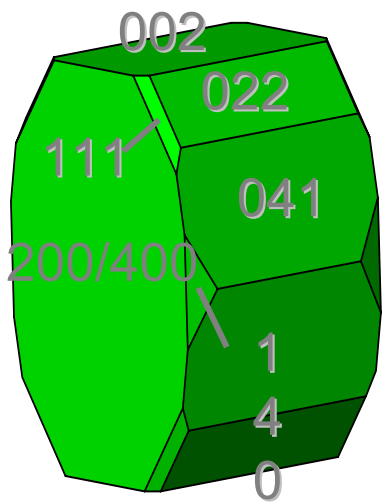
ED of thin section

⇒(400) reflection much more intense than expected

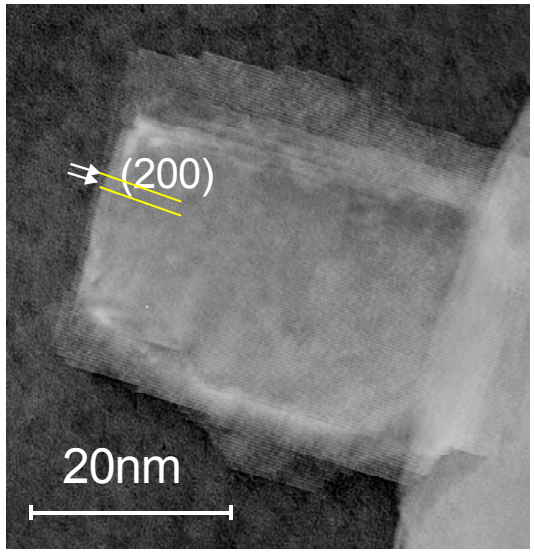
⇒ suggests possible exposed (200)/(400) faces

Polymer adsorption preferred on (200)/(400) faces

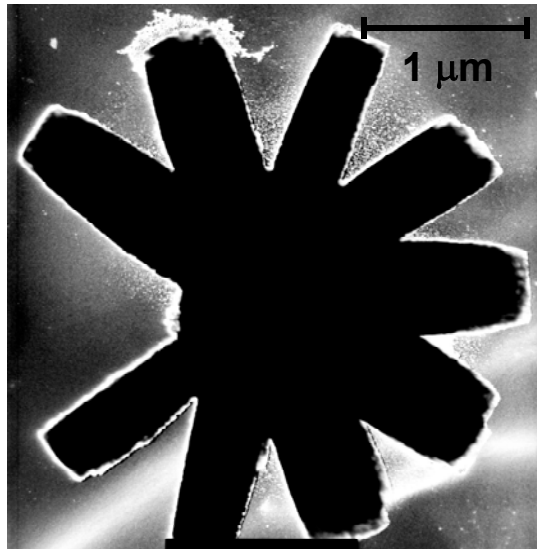
Ring	d (Å)	Plane	Atomar surface structure
1	3.852	111	
2	3.510	200	
3	2.772	002	
4	2.340	022	
5	2.170	140	
6	2.106	041	
7	1.769	400	As 200



Possible morphology of barite crystal



ED of single crystal "petal"
⇒ elongated along c-axis

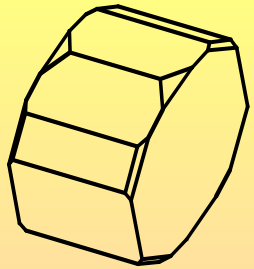


Dark field image constructed using (200) reflection

Petals do not grow epitaxially on underlying crystal

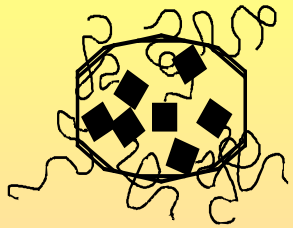
⇒ Dark field TEM

⇒ Equal separation of petals

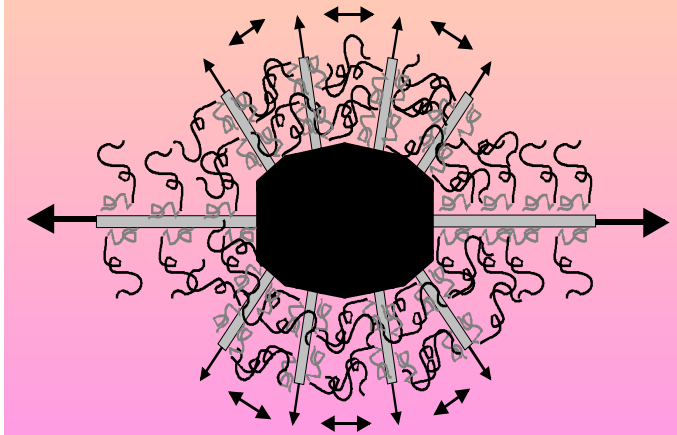


Formation of primary nanocrystal

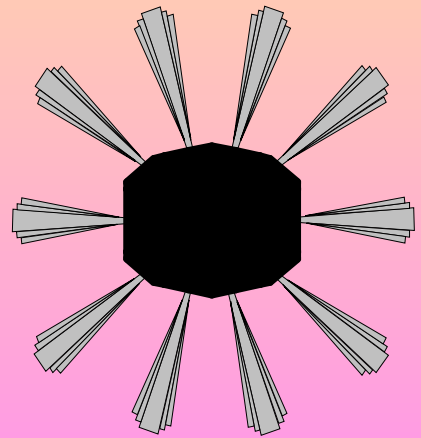
2D pro-jection →



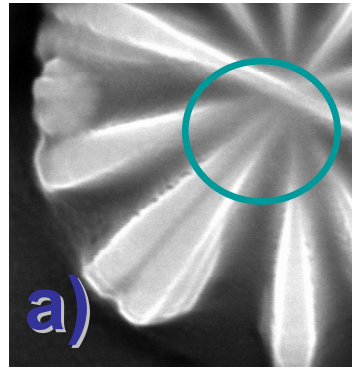
Polymers are adsorbed at 200/400 onto primary nanocrystal

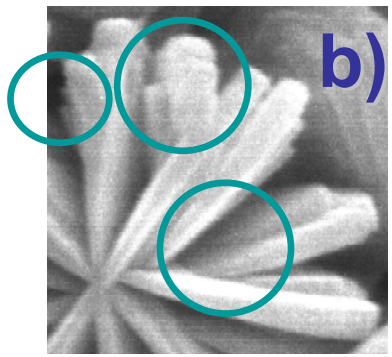


Heterogeneous secondary growth at remaining 10 faces, Initial steric repulsion between petals, Reorientation to maximum distance



Overgrowth of petals



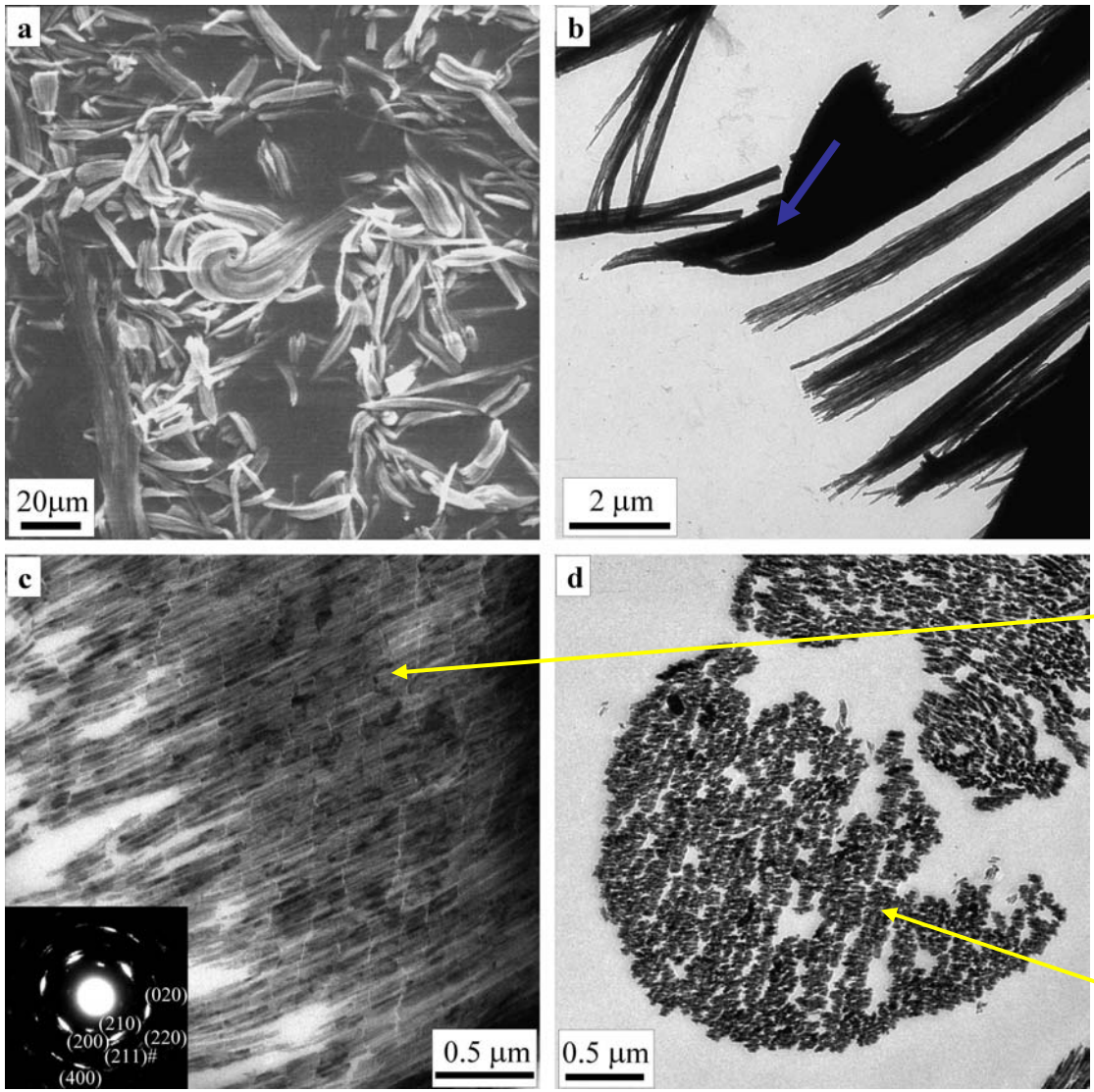


Observed defects:

a) Nucleation of two petals on one side

b) Crystallization at defects on petals

$BaSO_4$ Fibres



pH = 5

PEG-*b*-PMAA-PO_3H_2

Bundles of single crystalline fibers

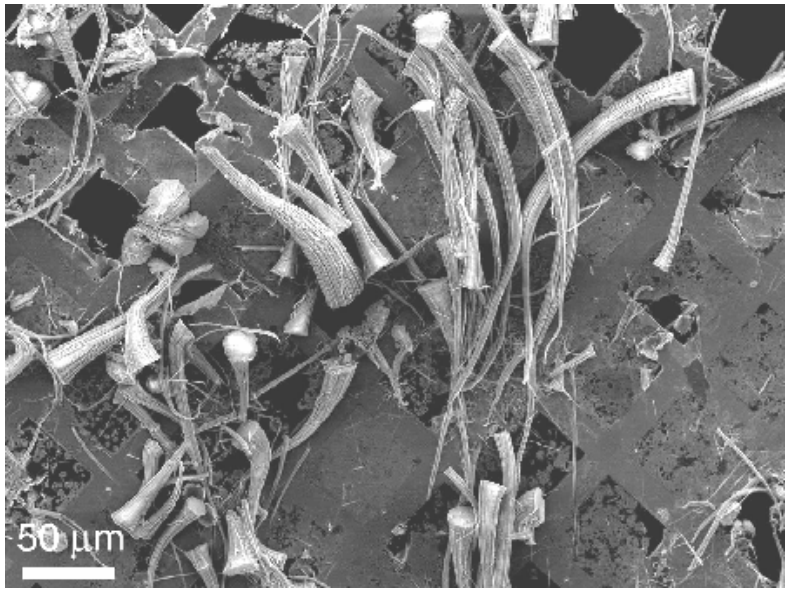
Parallel cut to fibre axis ⇒ [210]

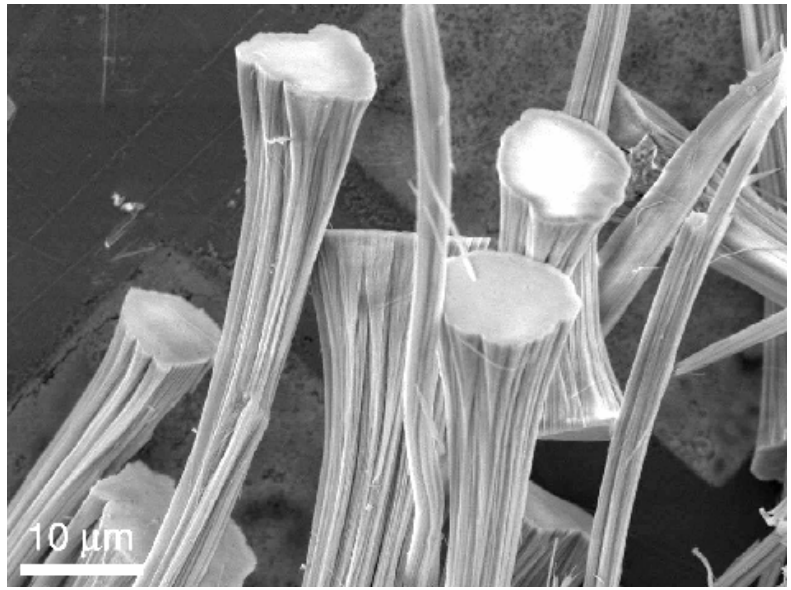
Perpendicular cut to fibre axis
Diameter 20 - 30 nm

Qi, Cölfen, Antonietti, *Chem. Mater.* 2000, 12, 2392-2403

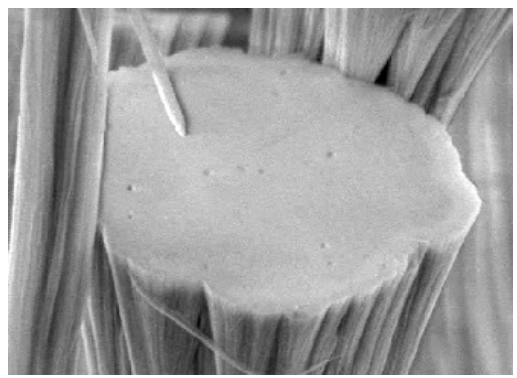
$BaSO_4$ Fibers Obtained on Carbon Films

PEG-*b*-PMAA-PO_3H_2, 5 days, pH = 5





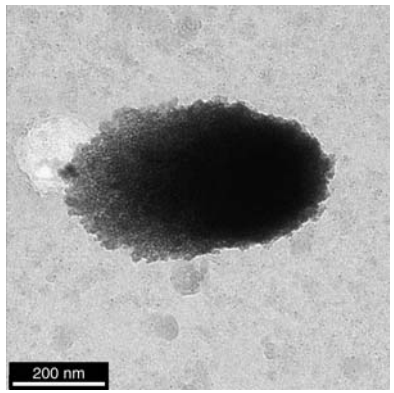
- Heterogeneous nucleation on carbon films
- Perfectly flat surface of growth edge

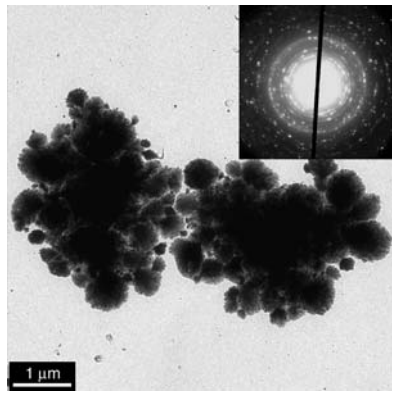


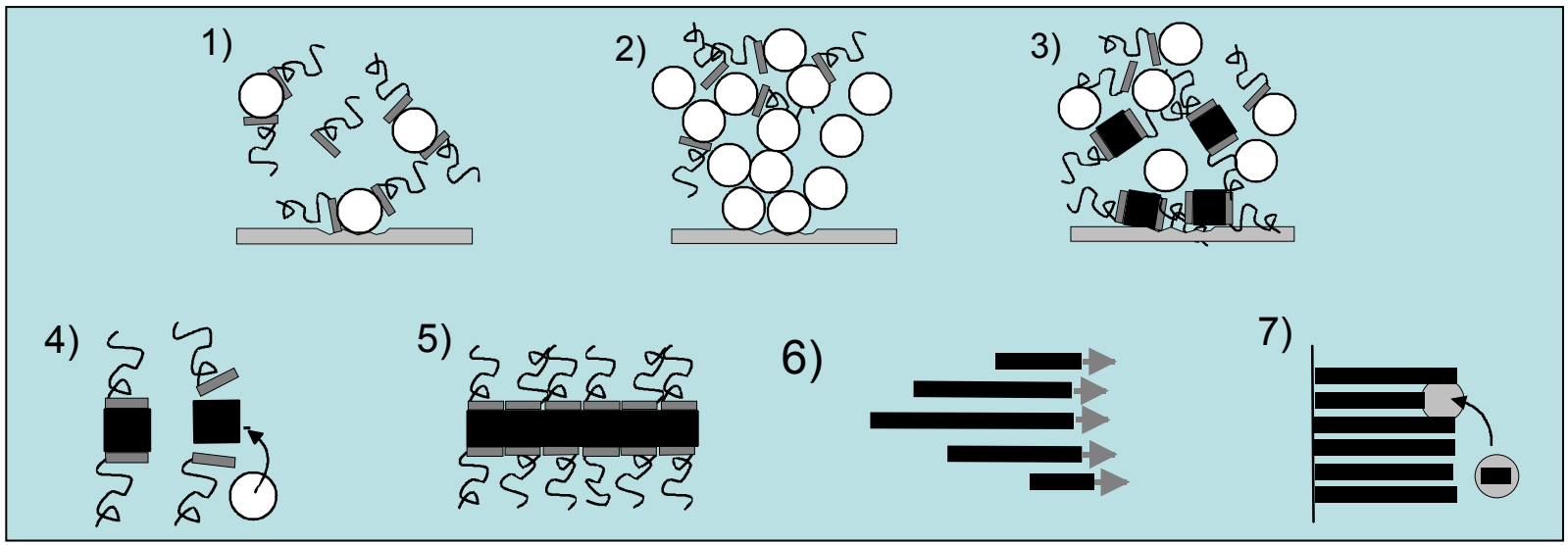
Qi et al *Chem. Eur. J.* (2001) 7(16), 3526-3532.

Mechanism of Fibre-Formation

- Form via amorphous $BaSO_4$ precursor particles
- Aggregate to form clusters ⇒ start to crystallise
- Anionic polymer chains absorb to positively charged crystal faces







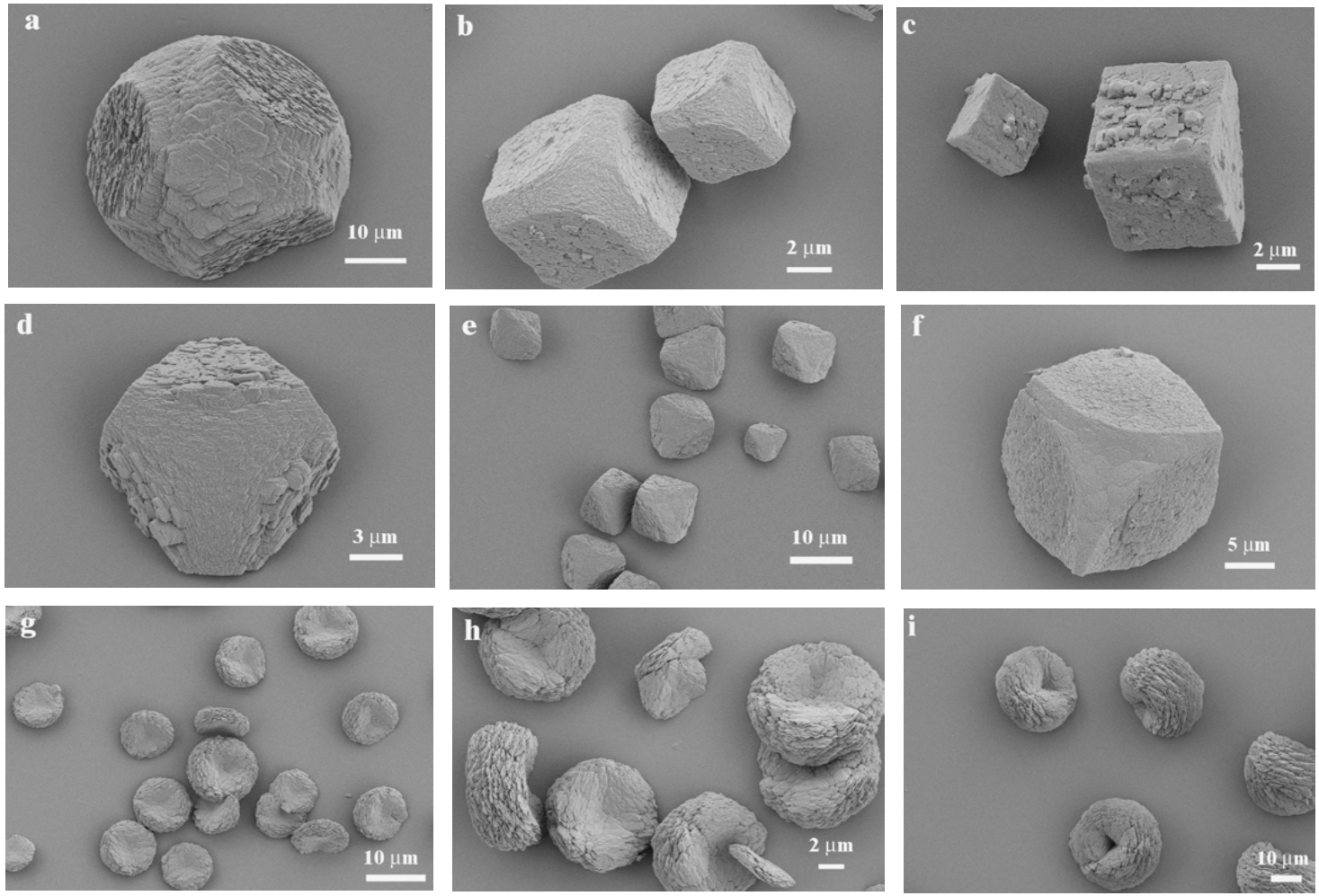
Different charges on different faces, and different shielding due to polymer adsorption may cause directional aggregation

$CaCO_3$ Mesocrystals

$[Ca^{2+}]$ 1.25 mM

$[Ca^{2+}]$ 2.5 mM

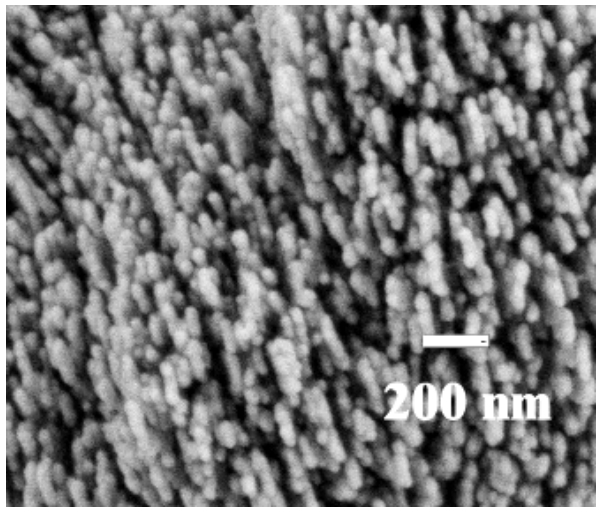
$[Ca^{2+}]$ 5.0 mM



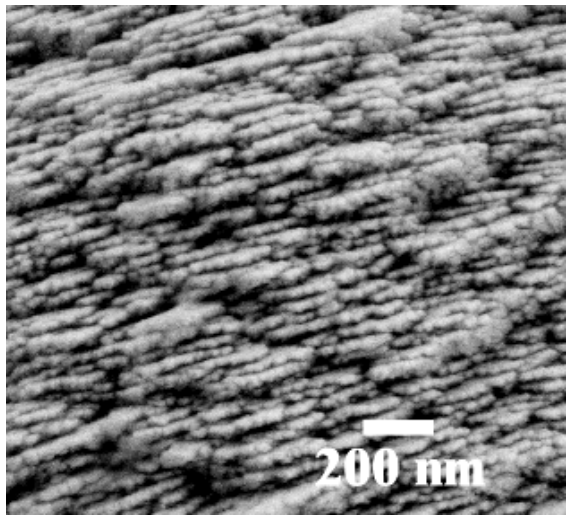
[PSS] = 1.0 g/L [PSS] = 0.5 g/L [PSS] = 0.1 g/L

Wang, Cölfen, Antionetti, *J. Am. Chem. Soc* (2005), 127, 3246-3247.

$CaCO_3$ Mesocrystals

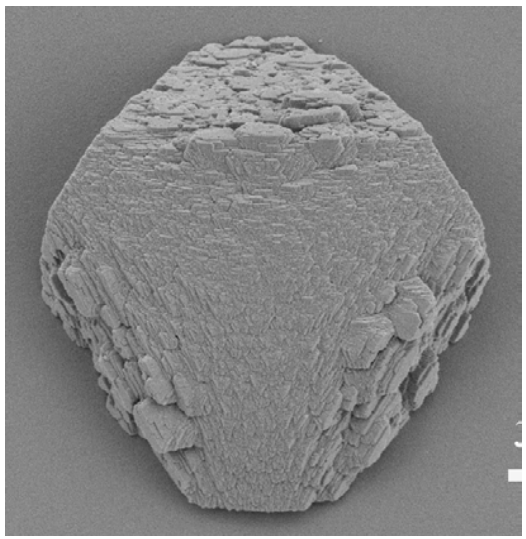


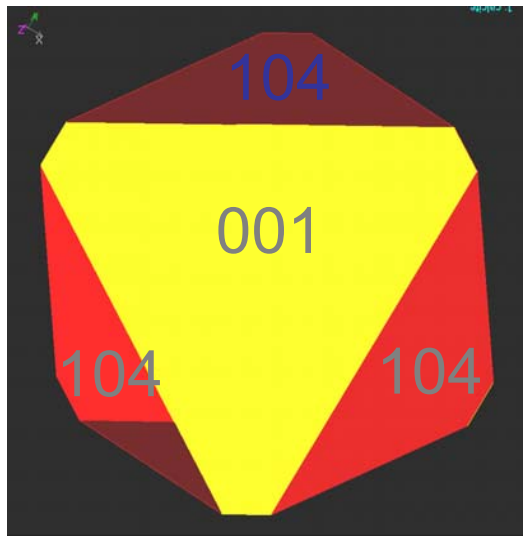
[PSS] = 1 g/L



[PSS] = 0.1 g/L

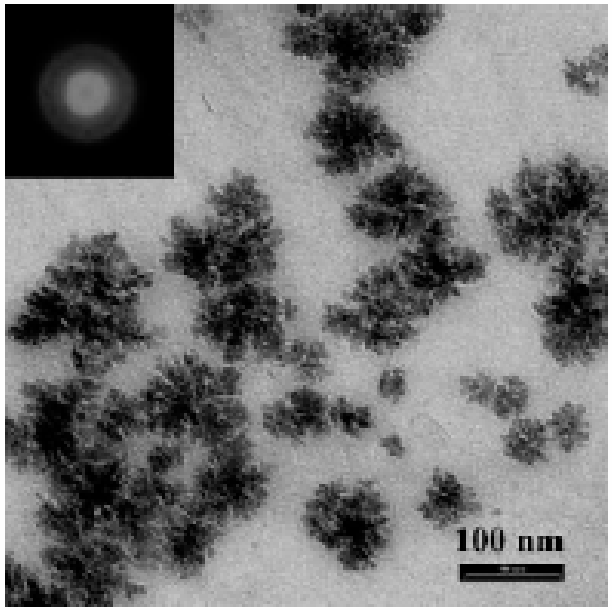
$[Ca^{2+}]$ = 5 mM
7 hr





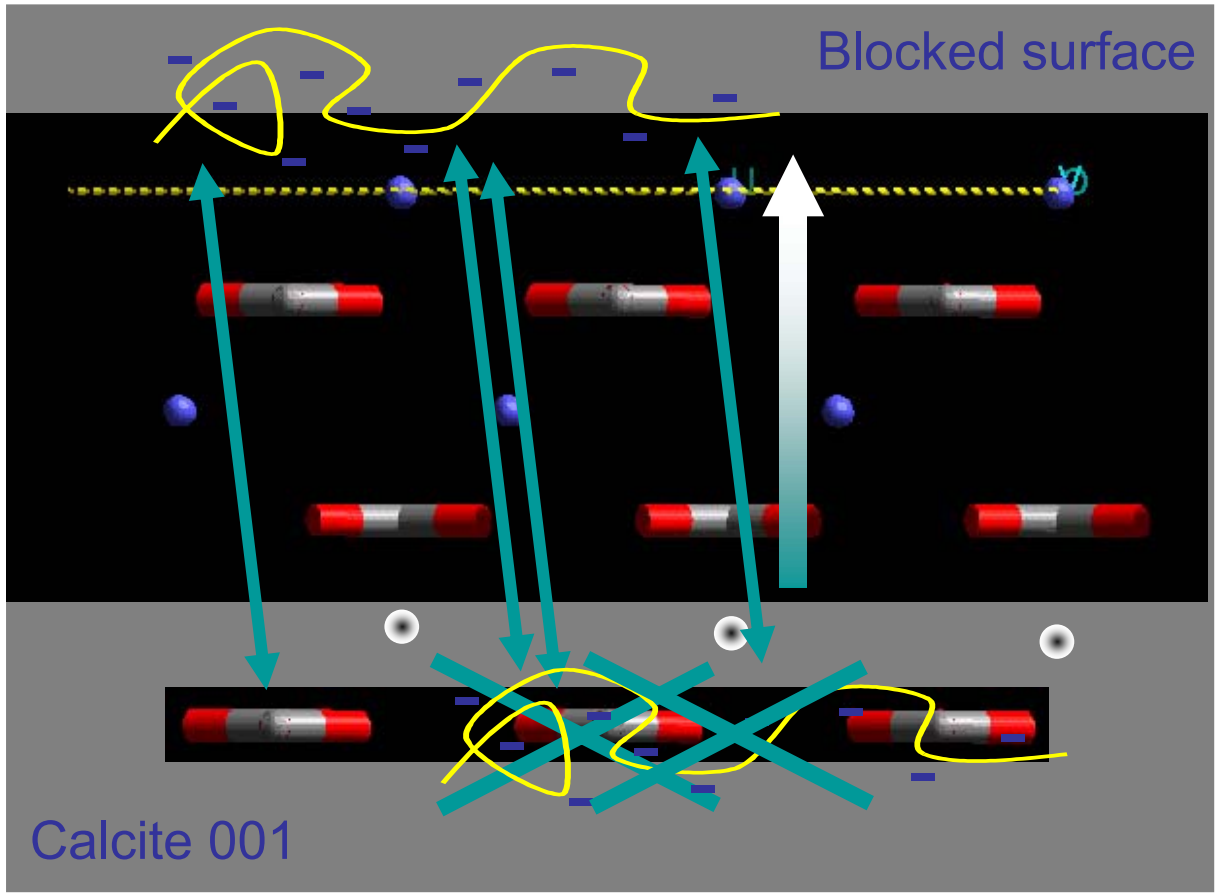
- Morphology like single crystal
- Extinguish under crossed polars as single crystal

Mechanism



- Amorphous $CaCO_3$ precursor particles
- ACC particles aggregate and crystallise
- Crystal units assemble to form "mesocrystals"

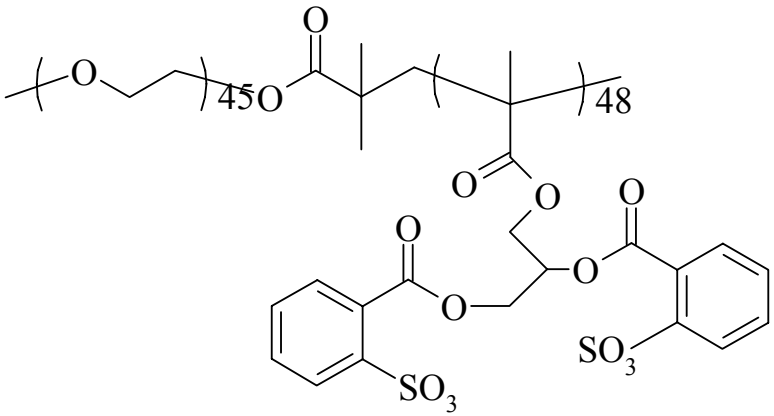
- PSS is selectively adsorbed on positive (001) faces of nanocrystals
- Adsorption of negative species to opposite surface is prevented by dielectric interaction throughout the crystal
- Resulting dipole along the *c*-axis drives nanoparticle assembly

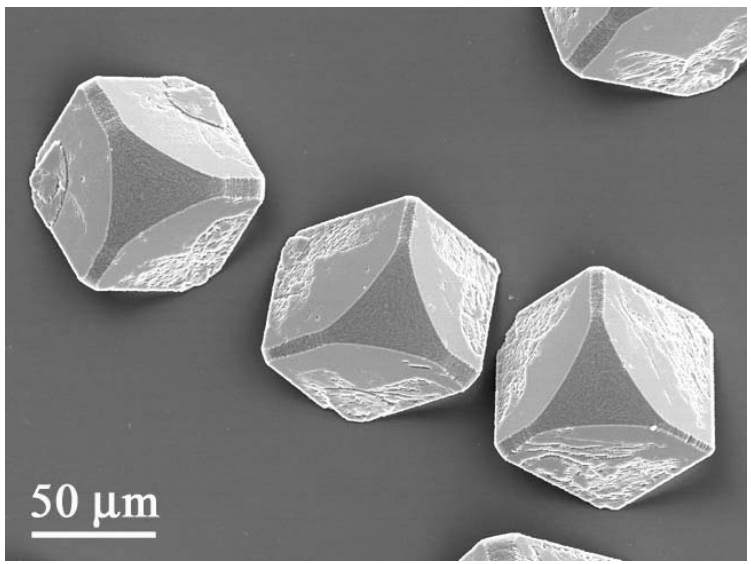


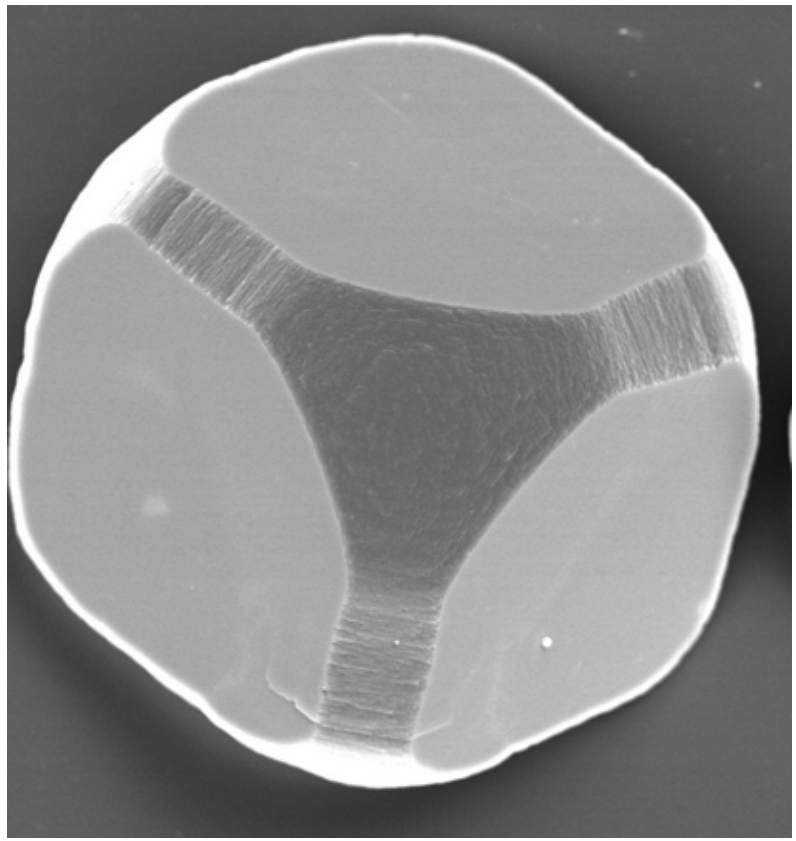
A dipole is induced in the very thin platelets which have exposed (001) faces

⇒ Two oppositely charged faces produced, which drives aggregation

Sulphonate Functionalised Copolymers



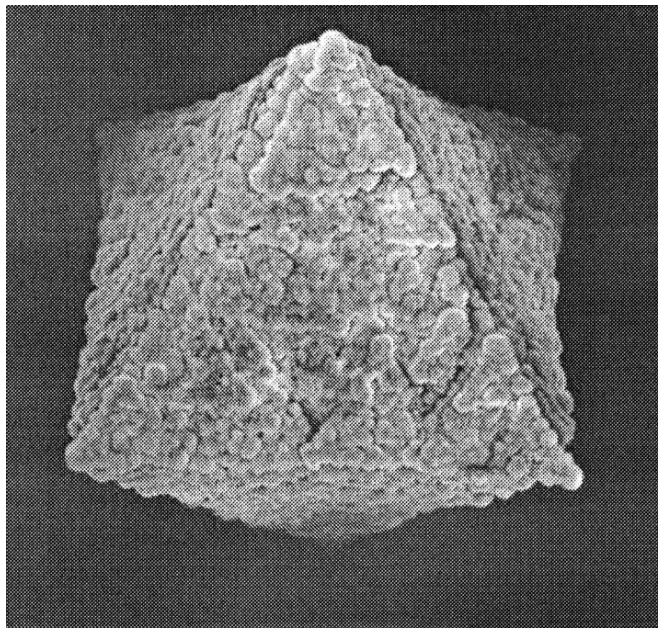


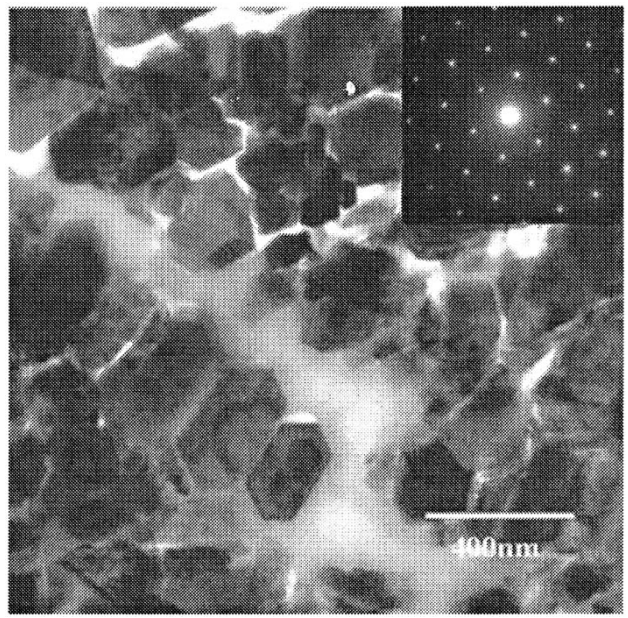


Gel-Grown Calcite Aggregates

Calcite crystals grown in pol-acrylamide hydrogels using double diffusion ⇒ Remarkable crystal aggregates formed

Pseudo octahedral morphology





Diffraction shows entire aggregate behaves as a single crystal !

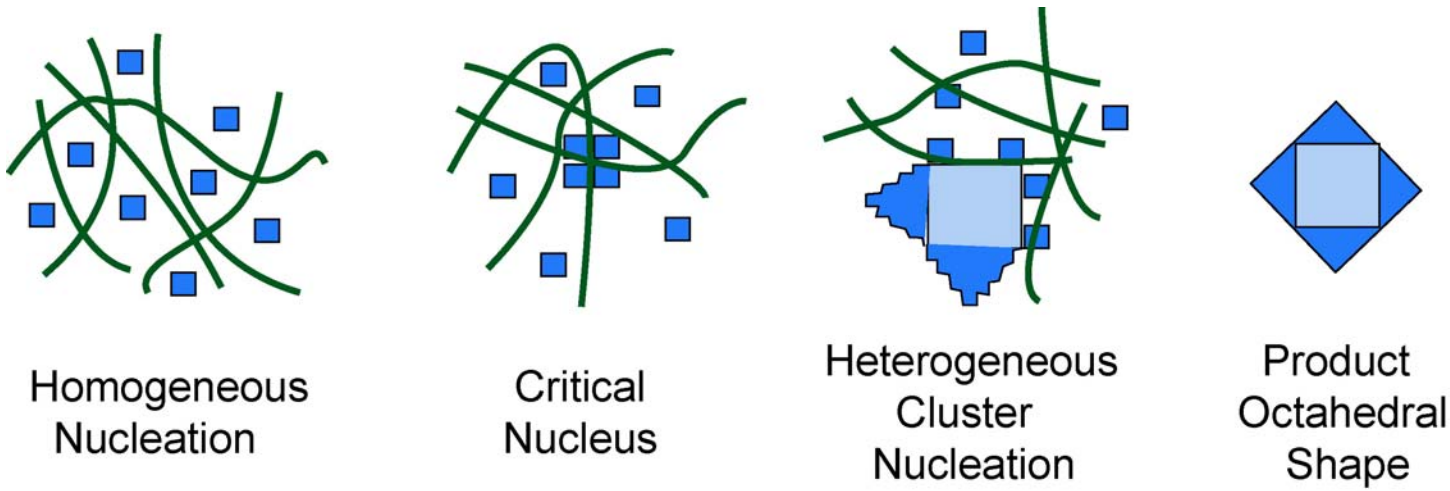
Grassman et al, *Am. Mineral.* 2003, 88, 647-652.

Mechanism

- Supersaturation is high in the gel ⇒ nucleation burst occurs

- Some nuclei grow by adsorption of ions to reach a supercritical size

- Further growth can then occur by adsorption of clusters to the large faces of the particle ⇒ reduces the surface energy of the face



⇒ Pseudo-octahedral morphology results

Templating Routes to Nanoparticles

Many examples:

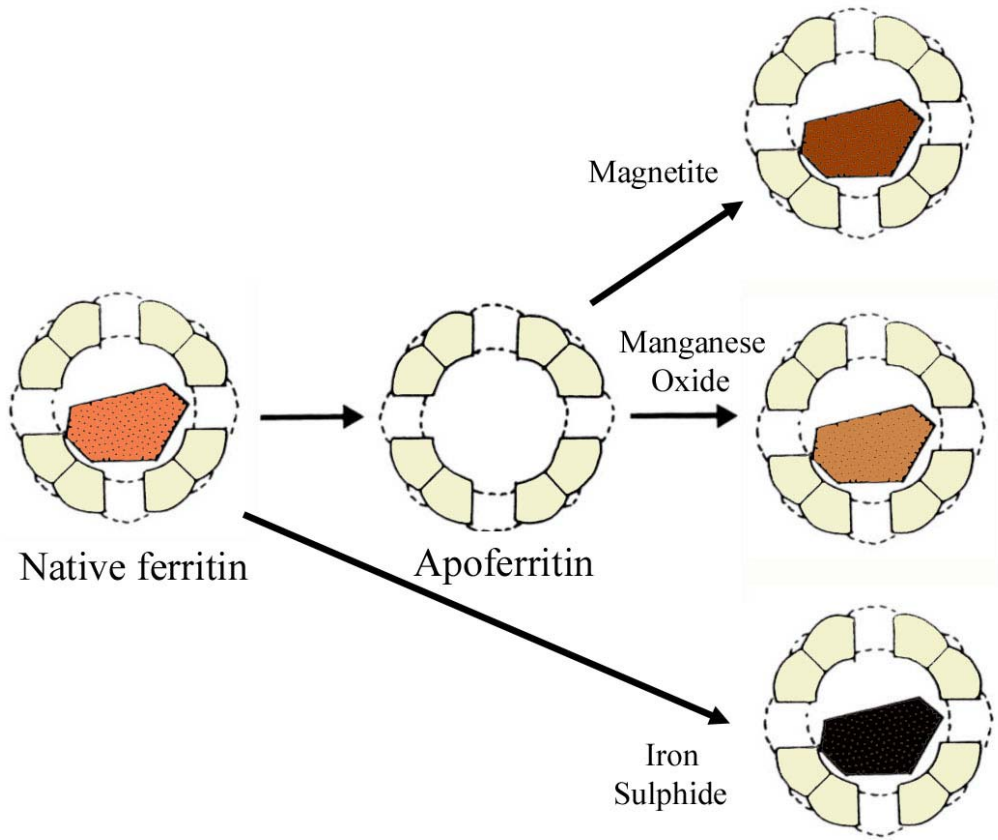
- Crystallisation in micelles
- Crystallisation in vesicles
- Polymer capsules

Look at two examples profiting from biological structures:

- Crystallisation in ferritin
- Crystallisation in viruses

Synthesis of Nanoparticles within Ferritin

Ferritin is a uniquely stable protein ⇒ can be used as a reaction vessel in which to synthesise a range of inorganic particles

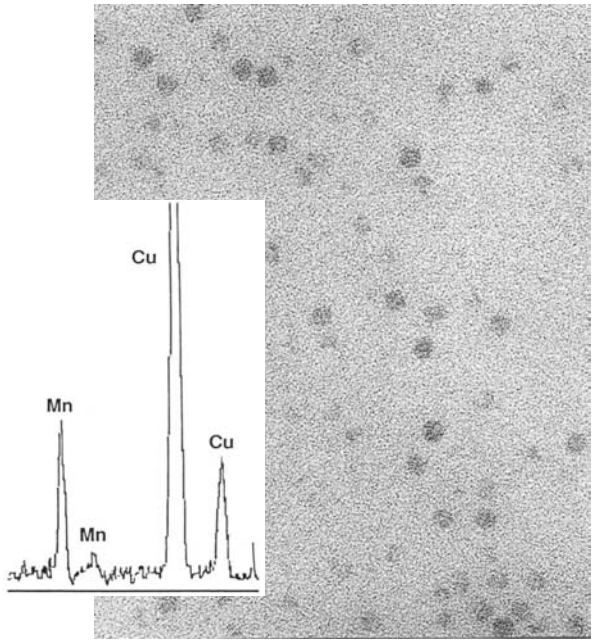


Meldrum, Wade, Nimmo, Heywood, Mann (1991) *Nature* 349, 684-687.

Formation of MnOOH Cores

Reconstitution of apoferritin with Mn(II)
⇒ alternative redox active metal

pH 8.9 – poorly ordered Mn oxide core formed over weeks



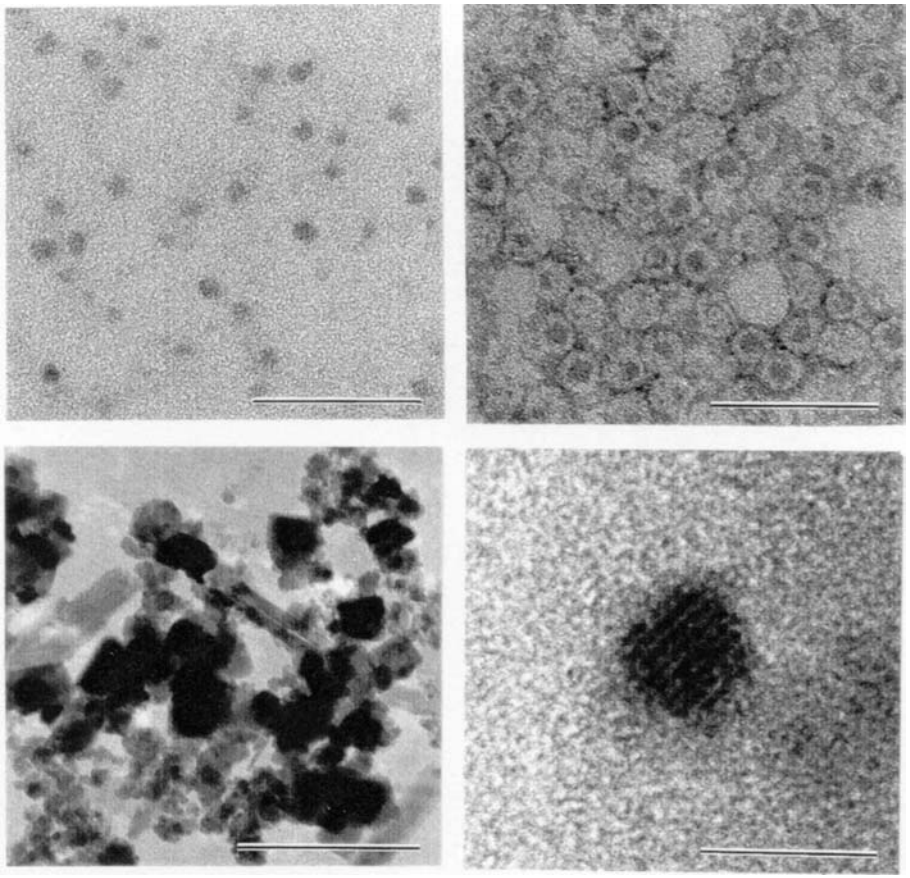
- Significantly more non-specific precipitation than in Fe(II) reconstitutions

- Cores always large, but only present in a proportion of ferritin molecules.

- Ferritin provides a nucleation site for MnOOH, but shows poor catalytic activity towards the oxidation of Mn(II)

Magnetite – "Magnetoferritin"

Modify reconstitution conditions with Fe(II) ⇒ magnetite



- pH8.5
- slow oxidation
- 60°C

⇒ Magnetite rather than ferrihydrite

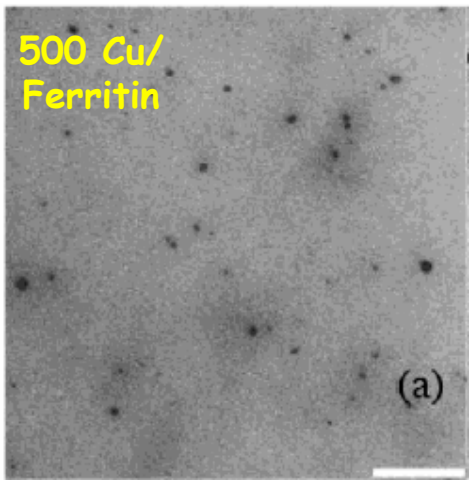
Meldrum F.C., Heywood B.R., Mann S. (1992) *Science* 257, 522-523.

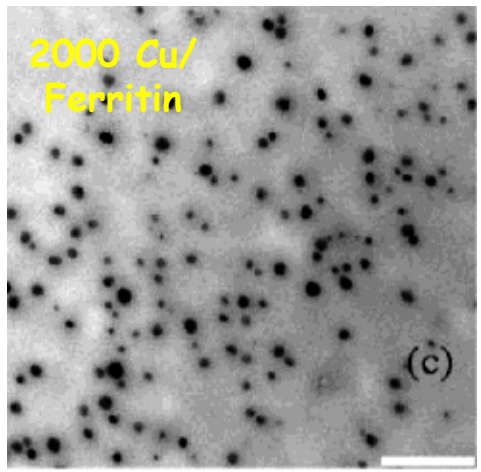
Photocatalytic Synthesis of Copper Colloids in Ferritin

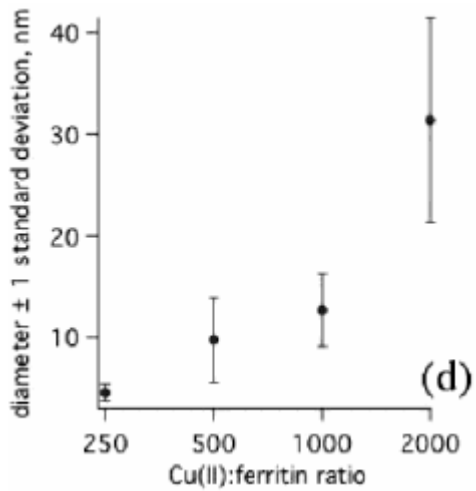
Mineralised ferritin can act as a photocatalyst for redox reactions

⇒ Ferrihydrite core may act a visible-band-gap semiconductor

Form Cu nanoparticles on photocatalytic reduction of Cu(II) in the presence of mineralised ferritin in the presence of a sacrificial reductant (citrate)

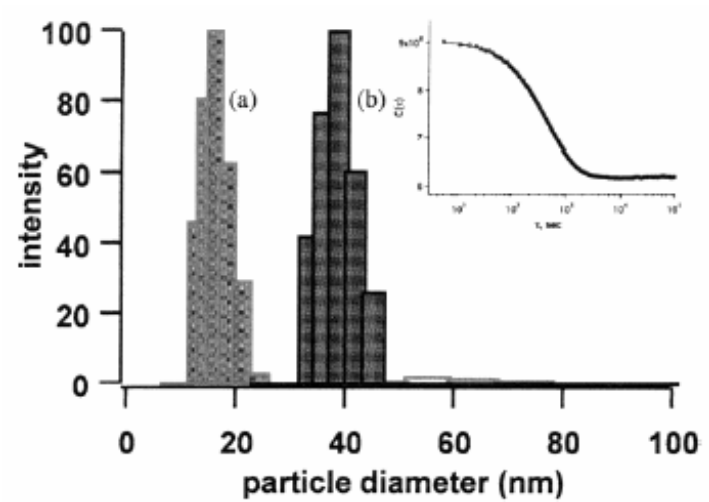


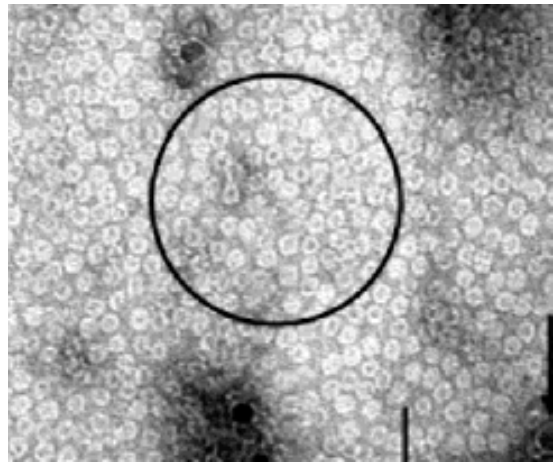




Ensign, Young, and Douglas *Inorganic Chemistry*, 2004, 43(11), 3441-3446

Mechanism





DLS indicates DISCRETE particles, sizes 36nm for 2000-Cu, 28nm for 1000-Cu and 16nm for 500-Cu

⇒ All LARGER than protein shell ⇒ DISRUPTION

⇒ Images suggest particles formed within protein shell

$Cu^{2+}_{(inside)} \rightarrow Cu^{o}_{(s)}$ (1)

$Cu^{2+}_{(inside)} + Cu^{o}_{(s)} \rightarrow Cu_{n}^{o}{}_{(s)}$ (2)

Slow nucleation is followed by fast growth

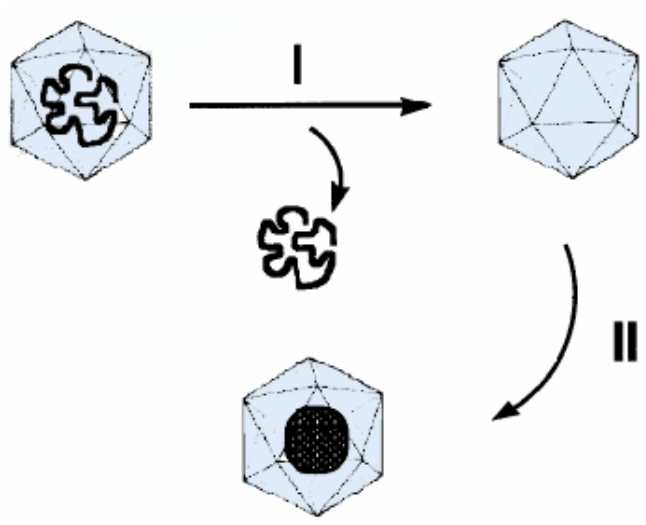
Nanoparticle Synthesis in Virus Protein Cages

Viruses act as host containers for nucleic acid storage and transport

Occur in wide range of sizes and morphologies

⇒ offer more versatile "protein reaction vessel" than ferritin

⇒ use virus cage in formation and entrapment of inorganic and organic polymer species



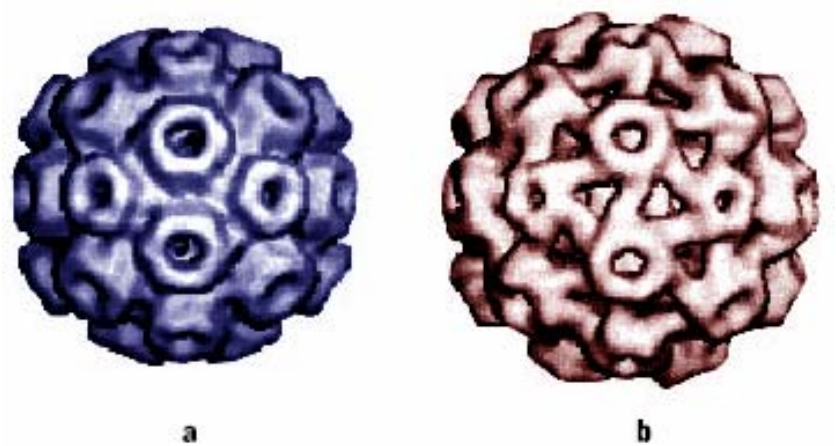
I Removal of viral RNA and purification of the empty virus particle

II Selective mineralization within the confines of the virus particle

Douglas and Young, *Nature*, 1998, 393, 152-154.

Synthesis of Paratungstate Particles in Cowpea Chlorotic Mottle Virus (CCMV)

Many virions undergo reversible structural changes, that open up pores in the structure, giving access to the cage interior



CCMV in
(a) Unswollen condition at low pH
(b) Swollen condition at high pH.

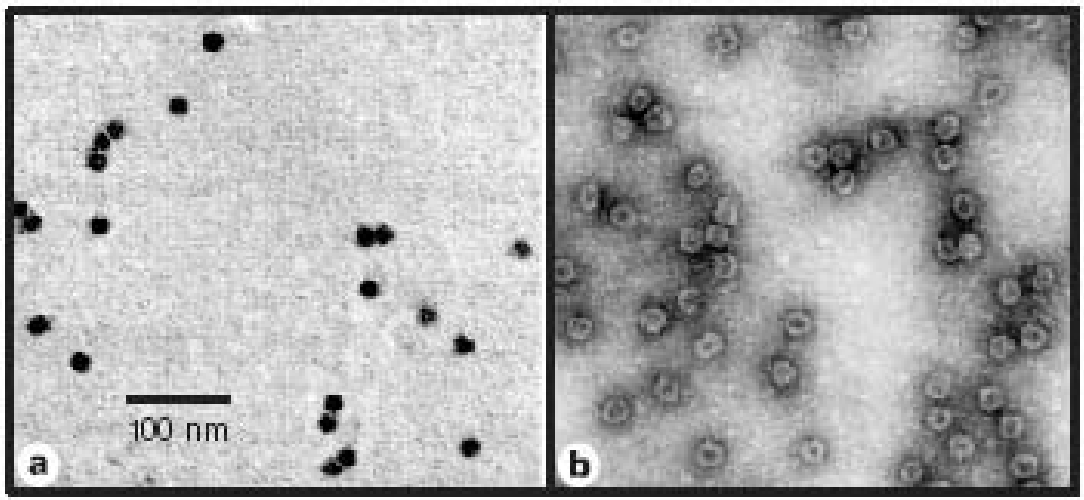
Swelling causes formation of 60, 2nm pores

- CCMV ⇒ 28 nm outer, 18 nm inner diameter
- Positively charged interior/ outer surface not highly charged
- Inner surface provides unique chemical environment
- CCMV – Swells pH > 6.5, reverses pH < 6.5

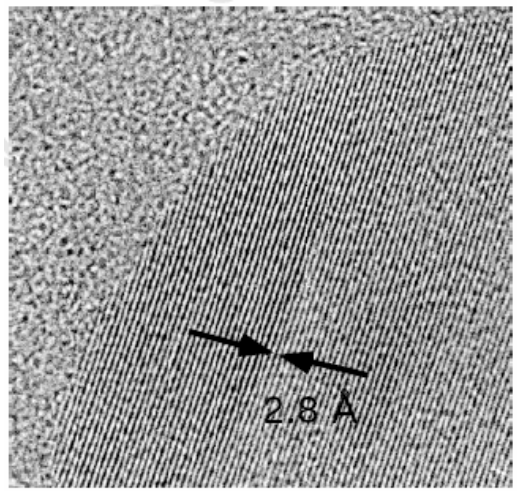
Douglas and Young, *Nature*, 1998, 393, 152-154.

Paratungstate particles ($H_2W_{12}O_{42}^{10-}$) formed in virus host cage

- Aqueous molecular tungstate (WO_4^{2-}) species incubated with virus cage > pH 6.5
- Polymerisation induced by reduction in pH < 6.5

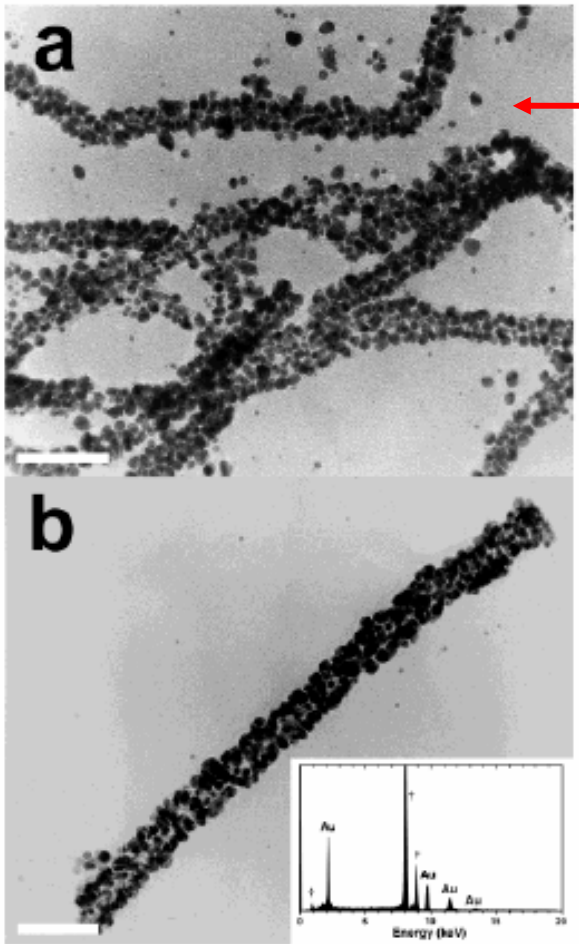


TEM images of paratungstate-mineralized virus particles (a) unstained (b) negatively stained



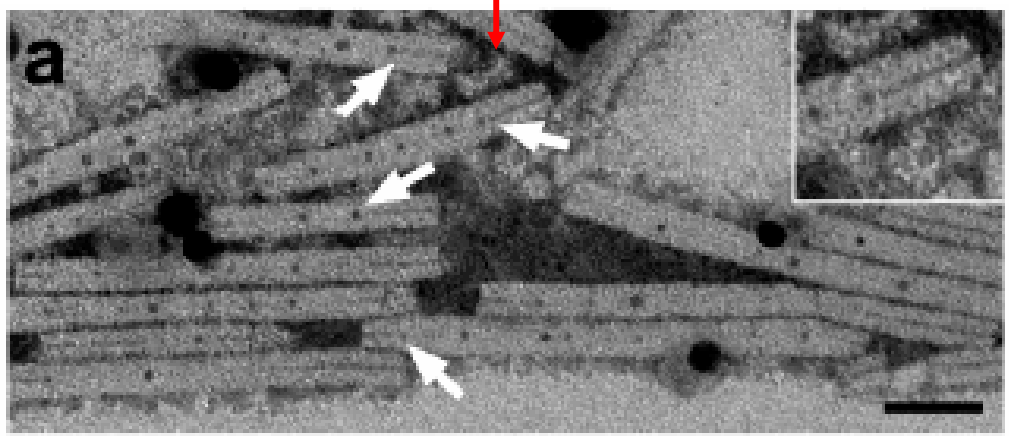
HRTEM image of part of a paratungstate core

Organization of Metallic Nanoparticles using Tobacco Mosaic Virus



External surfaces of TMV rods decorated with metal nonoparticles on chemical reduction of $[PtCl_6]^{2-}$ or $[AuCl_4]^-$ at low pH

Photochemical reduction of Ag(I) salts at pH 7 resulted in nucleation of Ag nanoparticles within the internal channel



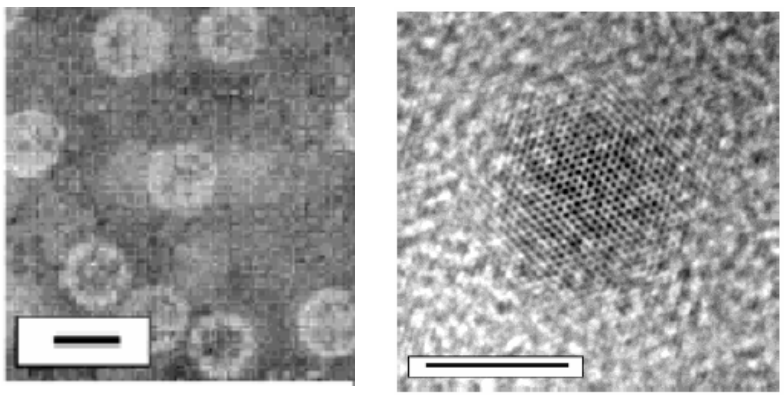
Dujardin, Peet, Stubbs, Culver, and Mann *Nano Lett.* 3(3), (2003), 413-417.

Protein Engineering of Viral Cage

CCMV offers cationic cage interior ⇒ alter to provide a more versatile reaction vessel

CCMV protein coat genetically modified by replacing 9 basic residues at N-terminus with glutamic acid

⇒ Does not affect assembly, and interior surface becomes anionic



Iron oxide particles formed in modified CCMV protein shells

⇒ Lepidocrocite (γ-FeOOH)

Douglas, Strable, Willits, Aitouchen, Libera, Young *Adv. Mater.* 2002, 14 (6), 415-418.

Mechanism

- Lepidocrocite (γ-FeOOH) formed – same as in control reactions

- Negatively charged interior accumulate Fe(II) ions

$\Rightarrow$ Aggregation may change the redox potential of Fe(II)

$\Rightarrow$ Interior surface acts as a nucleation site by clustering Fe(II)/Fe(II) ions at the interface

- After nucleation, the initially formed crystallite can act as a catalytic site for further oxidative hydrolysis

Can form up to 24 nm cores – upper limit of virus cage

Templating Polycrystalline Structures

Large complex structures ⇒ currently cannot be produced via self-assembly techniques

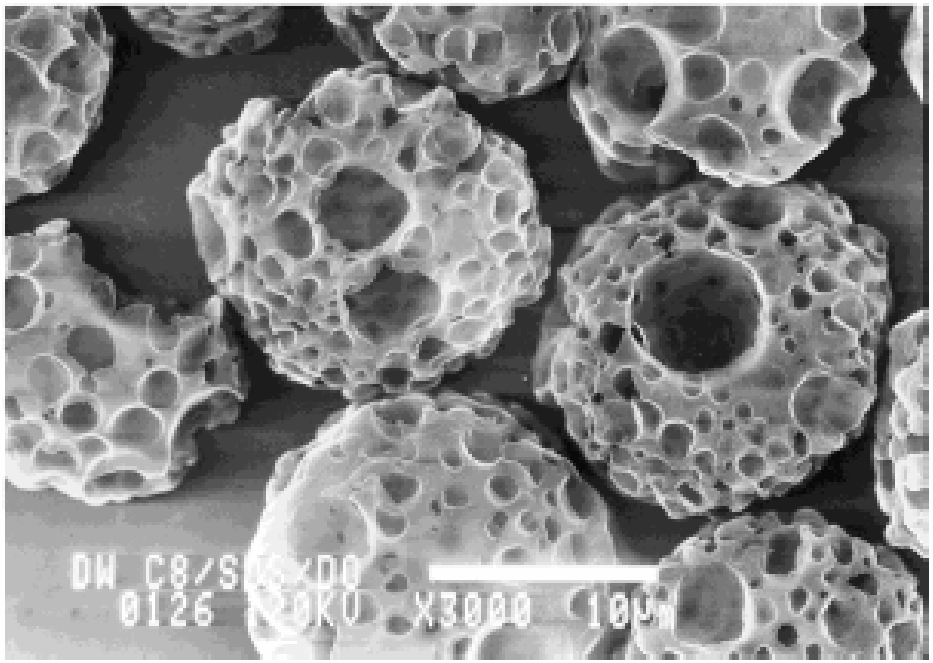
Alternative method ⇒ Templating

Soft templates	eg microemulsions
Rigid organic templates	eg. pollen grains
Inorganic templates	eg. sea urchin skeletal plates
	eg diatoms

Templating Microemulsions

Spherical vaterite particles with sponge-like microstructures

⇒ Produced by evaporation of SDS/octane/supersaturated calcium bicarbonate solution water-in-oil microemulsions



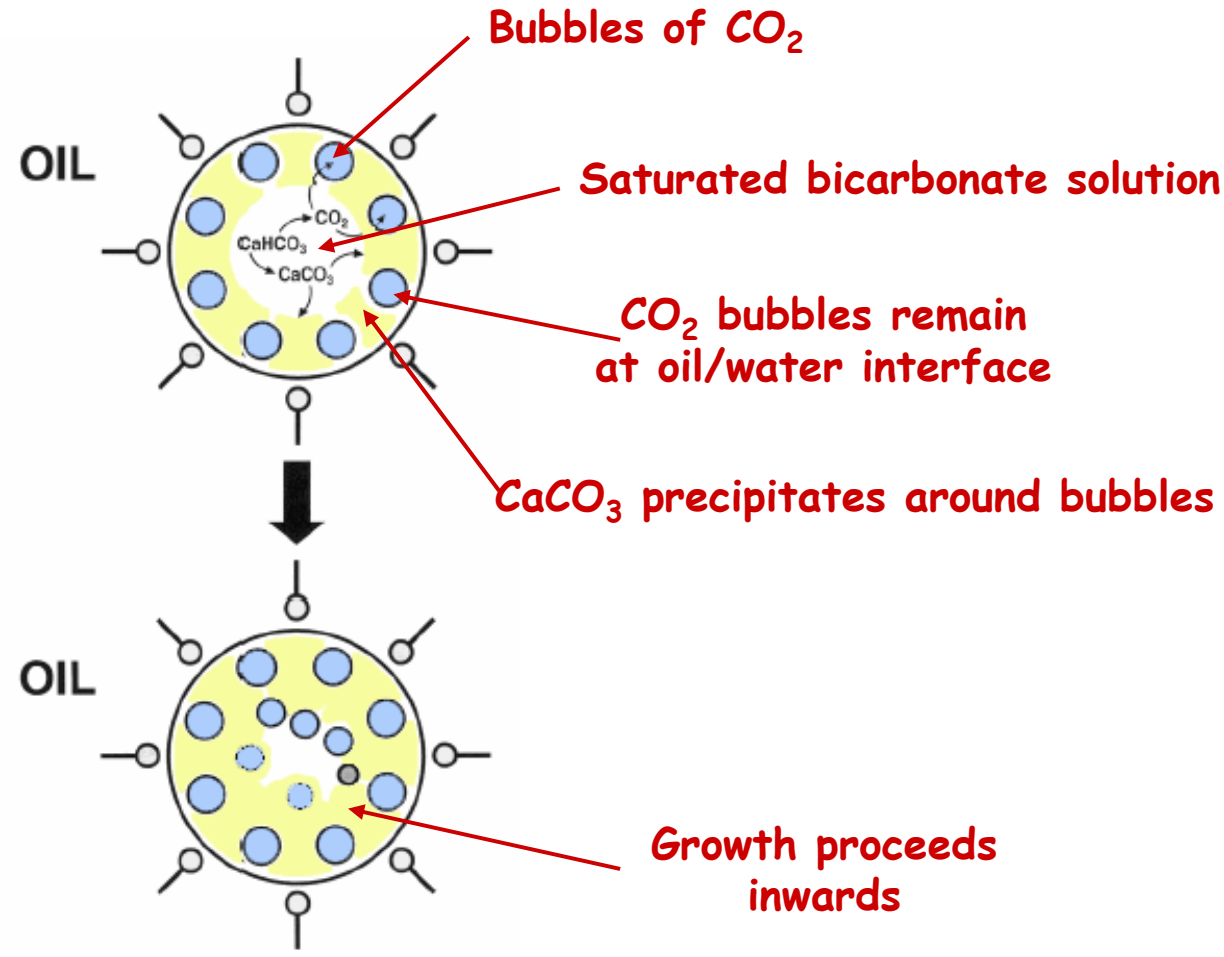
- Typically show irregular surface depressions and pores

- Many highly porous with a perforated outer shell and a partially hollow centre,

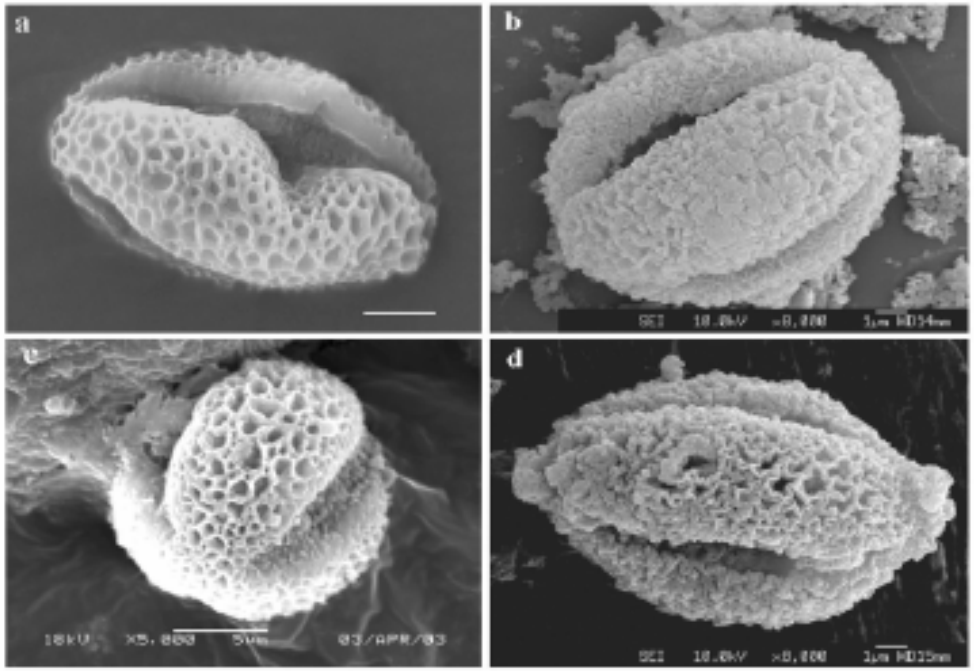
Walsh, Lebeau, Mann, *Adv. Mater.* (1999), 11(4), 324-328

- Micro-emulsion solution contains micron-sized water droplets

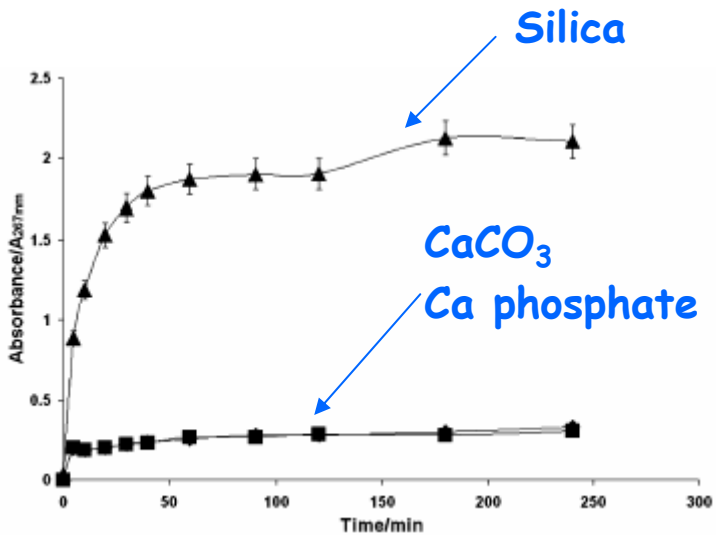
- Mineral aggregates initially form along the surface of water droplets ⇒ form perforated hollow shells with smooth surfaces



Complex Morphologies using Pollen Grain Templates



(a) Uncoated pollen grain
(b) Calcium phosphate
(c) Calcium carbonate
(d) Silica



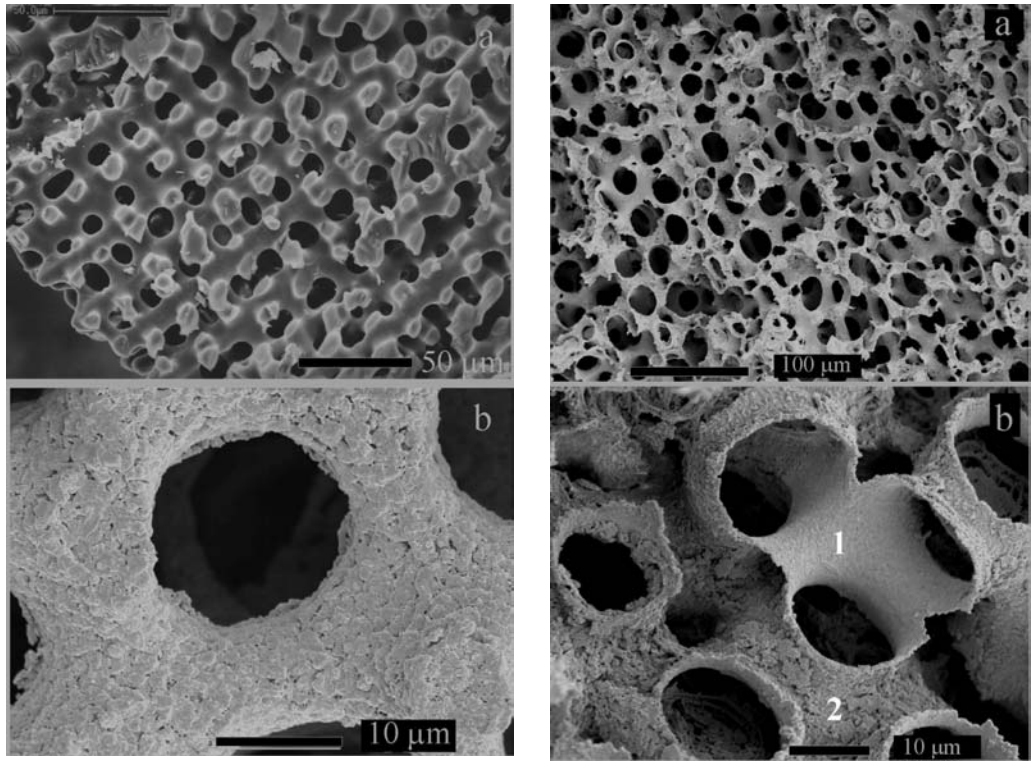
Replicas investigated for drug release

⇒ release of ibuprofen

Hall SR, Bolger H, Mann S *Chem. Commun.*(22): 2784-2785 2003

Templating Sea Urchin Skeletal Plates

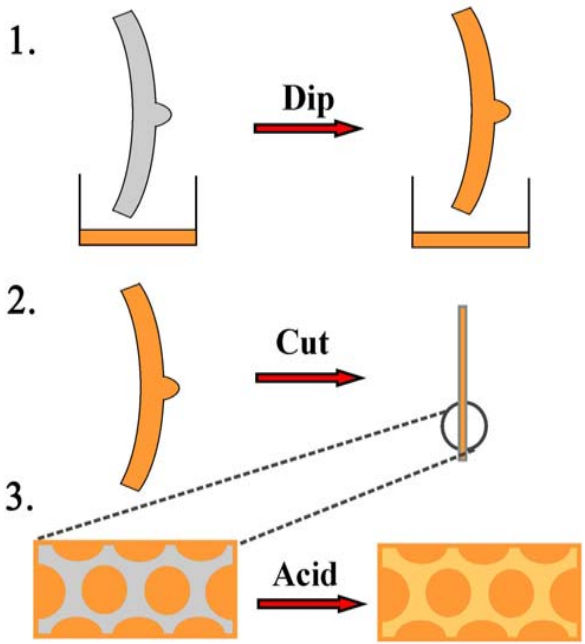
Sea urchin plates have a remarkable morphology - use as template for synthesis macroporous solids

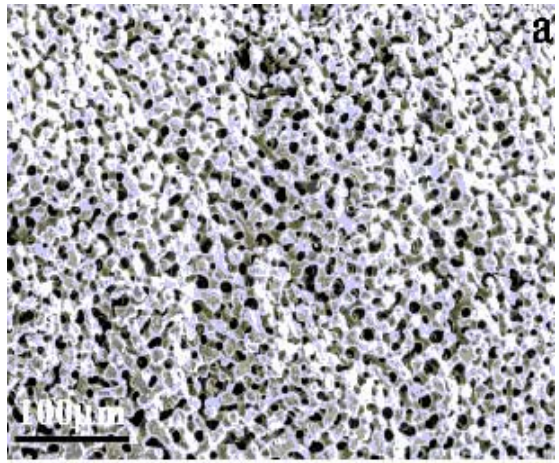


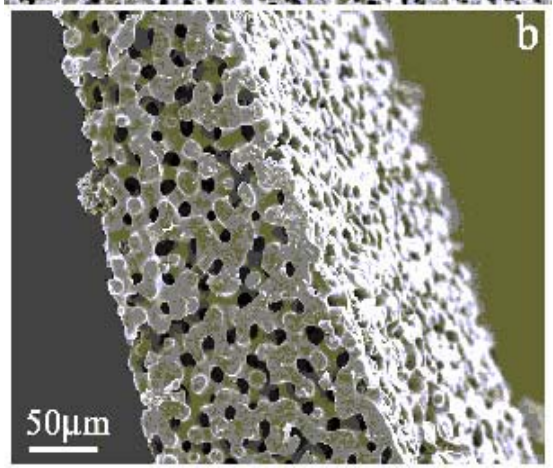
- Urchin plate dipped in a solution of stabilised gold particles
- Annealed • $CaCO_3$ dissolved $\Rightarrow$ POROUS GOLD

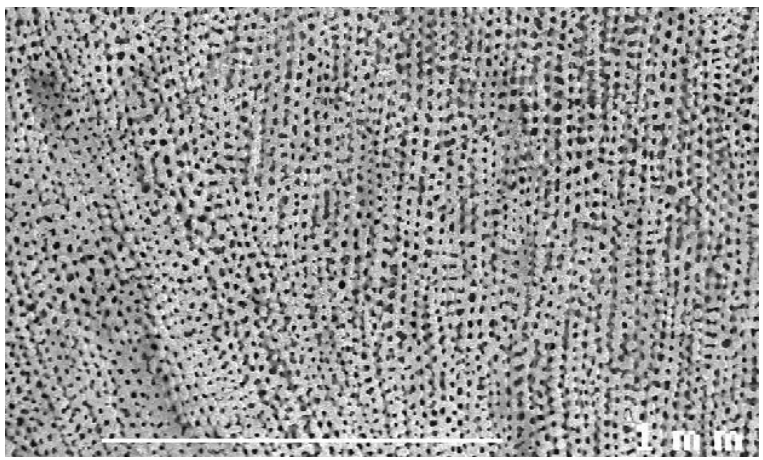
Meldrum F.C., Seshadri R. *Chem. Comm.* (2000) 29-30.

Polymer Replica



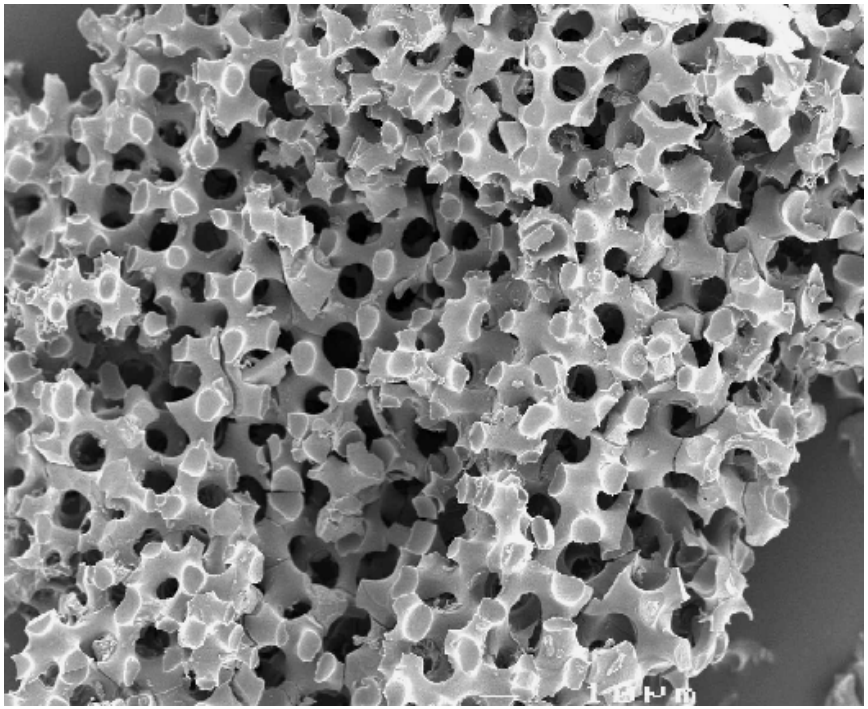






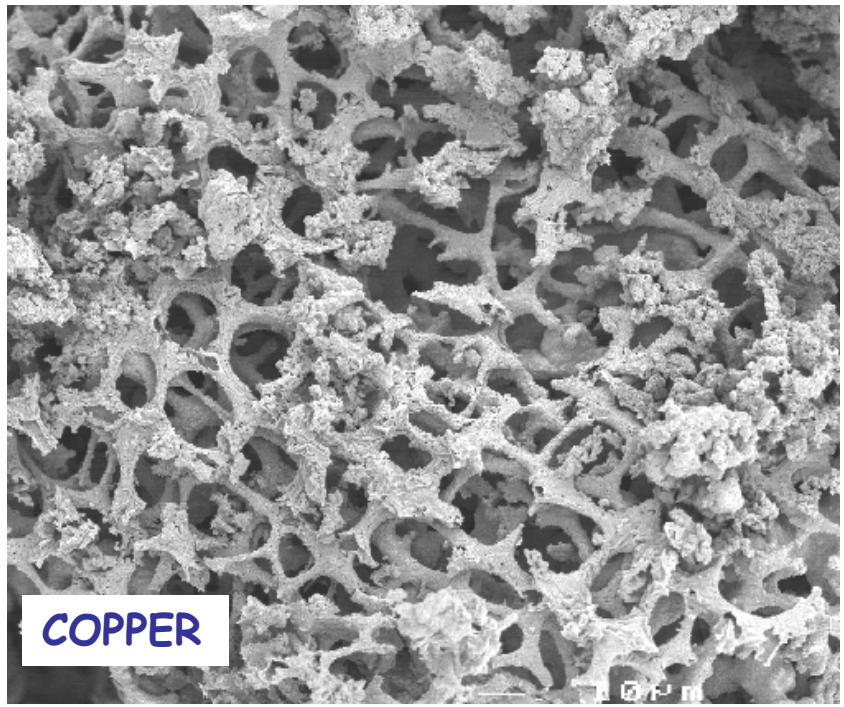
Polymer template is readily dissolved in chloroform

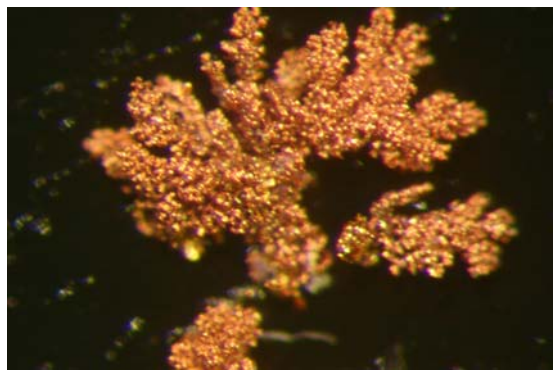
Templating of TiO_2



$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

Electrochemical Deposition



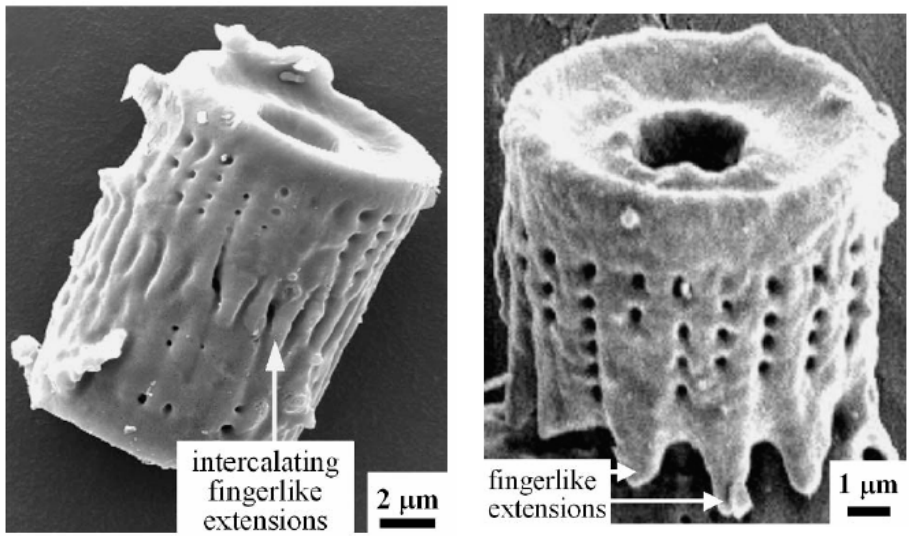


Profiting from Biominerals .... Chemical Convertion of Diatoms

Shape-preserving conversion of SiO_2-based diatom frustrules into new structured materials

Diatoms ⇒ unique 3D morphologies, specific patterns of fine features

⇒ no synthetic analogues

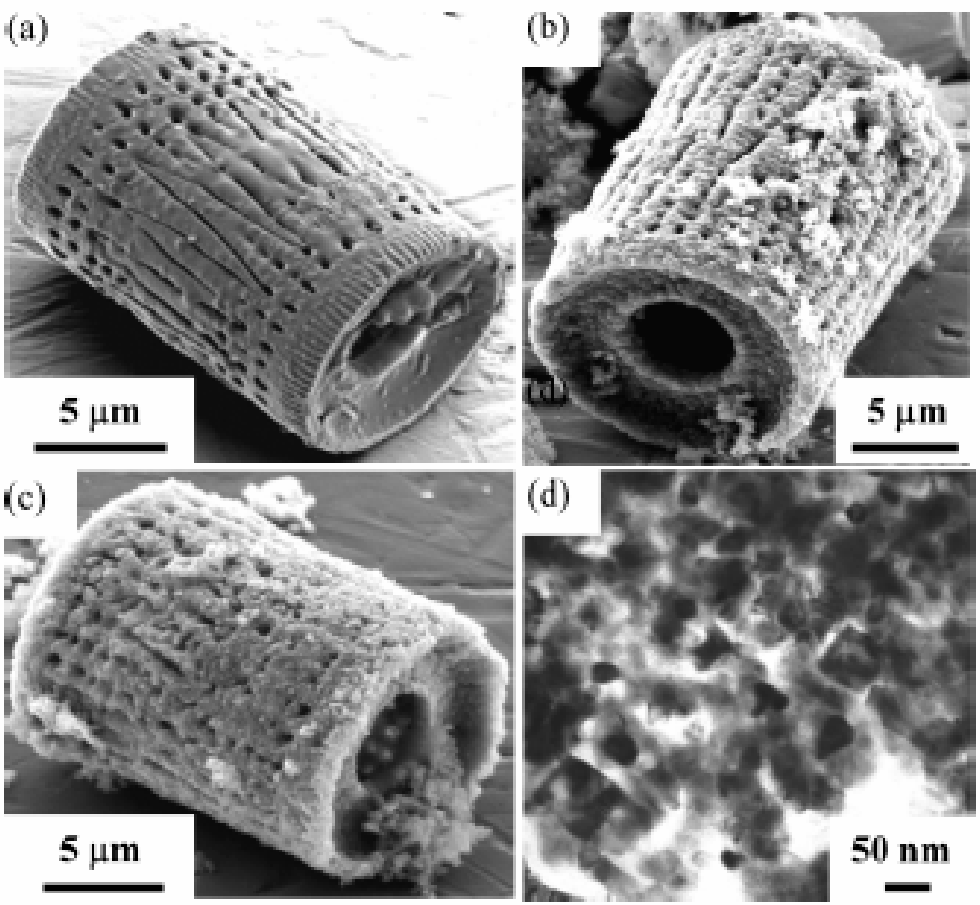


Silica-based *Aulacoseira* diatom

Used as precursors to a range of ceramics including:

TiO_2, ZrO_2, $BaTiO_3$

3-D Nanoparticle Structures from Anatase



(a) Untreated diatom

(b) Exposure to $TiF_4(g)$ 2h, 350°C

$TiF_4(g) + 2/3\ SiO_2\ (s) \rightarrow TiOF_2(s) + SiOF_2\ (g)$

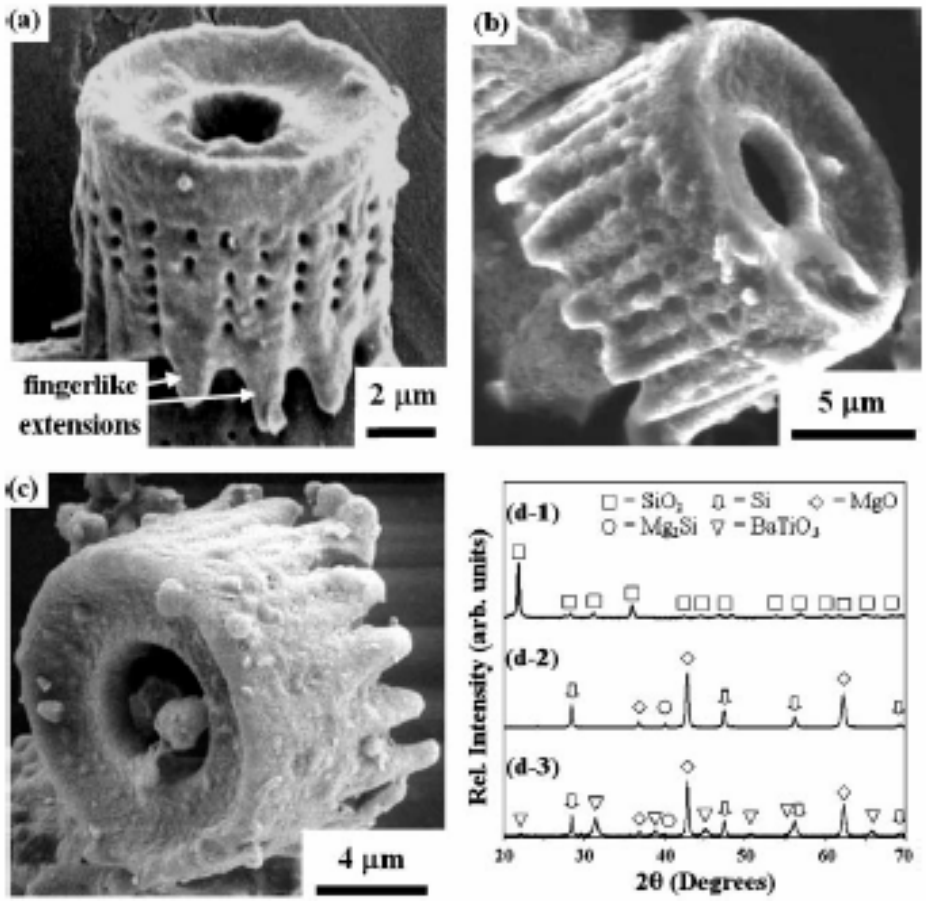
(c) Exposure to $TiF_4(g)$ 2h at 350°C then pure O_2 for 2h at 350 °C.

$TiOF_2(s) + \frac{1}{2}\ O_2(g) \rightarrow TiO_2(s) + F_2(g)$

(d) TEM image of cross-section of frustule after exposure to $TiF_4(g)$ for 2 h, 350 °C and then to O_2 for 2h at 350°C.

Unocic, Zalar, Sarosi, Cai, Sandhage Chem. Commun (2004), 796-797.

Replication of Diatom Structure in $BaTiO_3$



(a) Diatom frustule

(b) After reaction with Mg(g) for 1.5 h at 900 °C

$2Mg(g) + SiO_2\ (s) \rightarrow 2MgO(s) + \{Si\}$

(c) A MgO-bearing frustule coated with a $BaTiO_3$ sol-gel precursor and fired at 700 °C for 1.5 h.

Layer of tetragonal $BaTiO_3$ formed on underlying scaffold containing MgO, Si, Mg_2Si

(d) XRD analyses of (a) (b) and (c)

Weatherspoon, Allan, Hunt, Cai, Sandhage, *Chem. Commun.* (2005), 651–653.

Templating Routes to Single Crystals with Complex Morphologies

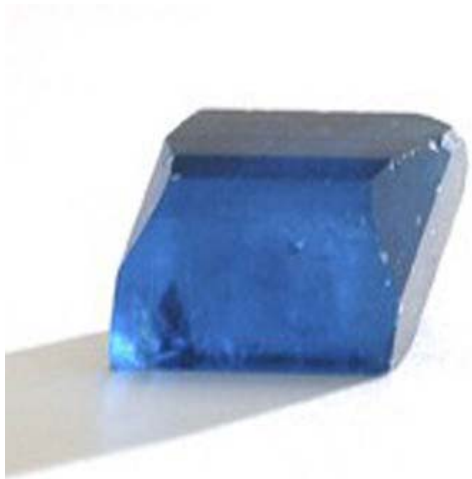
- Nature shows it is possible to produce calcite single crystals with complex morphologies (eg. sea urchin plates)

- Clearly cannot use simple additives to produce such morphologies

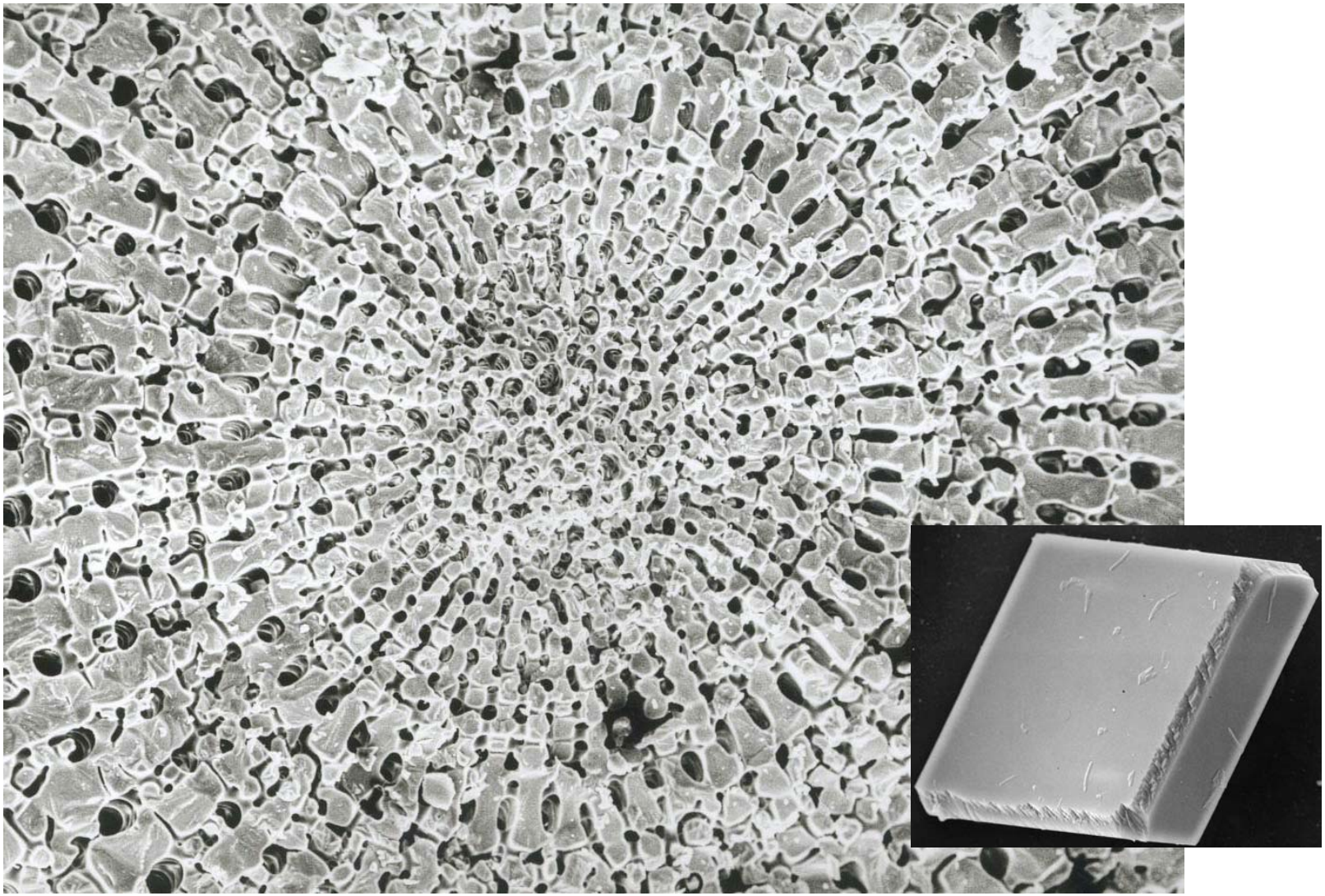
⇒ biology forms such complex forms within structured environments

- Is it possible to produce remarkable morphologies in the absence of complex biological mechanisms by shape constraint only ?

Consider a "Single Crystal"....

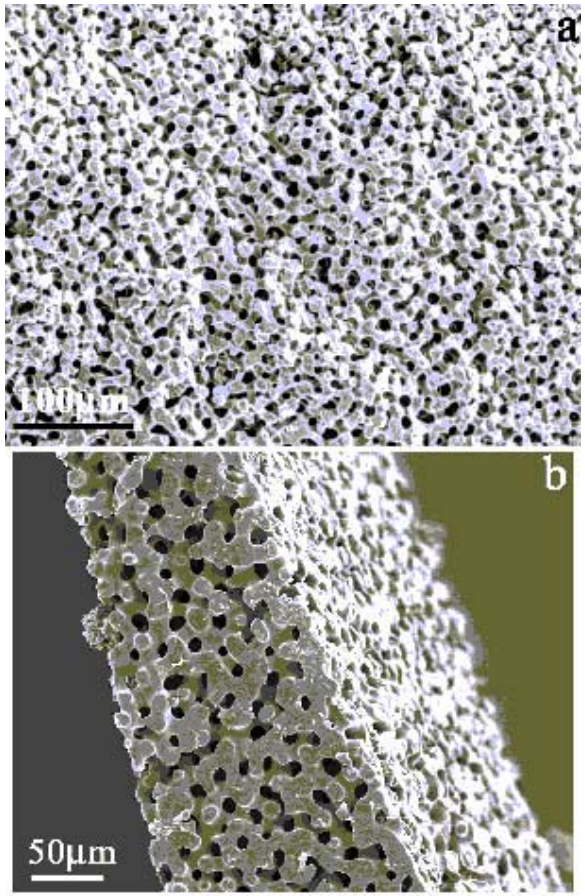


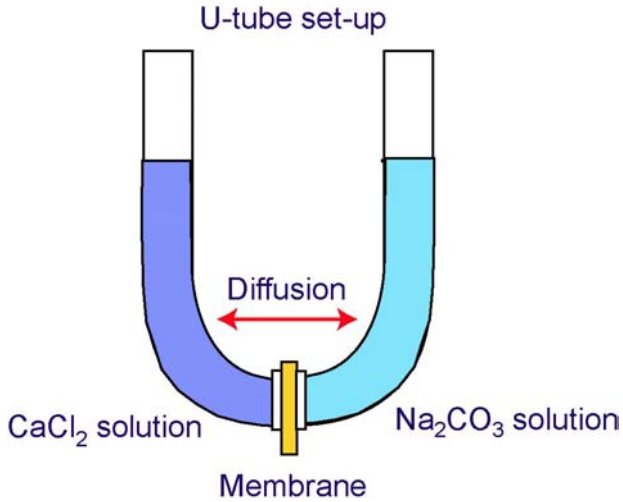
Now look at Biology…



Calcium Carbonate Precipitation in Sponge-Like Polymer Membrane

$CaCO_3$ precipitation in sponge-like "sea urchin" membranes

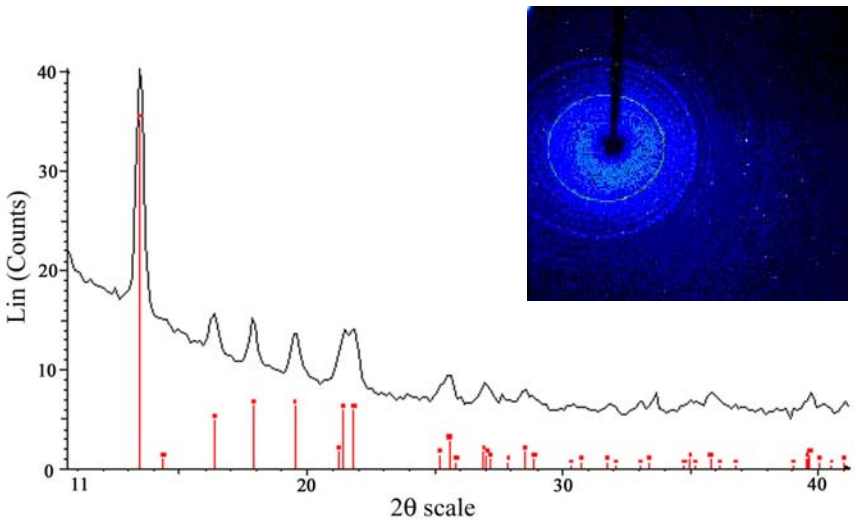


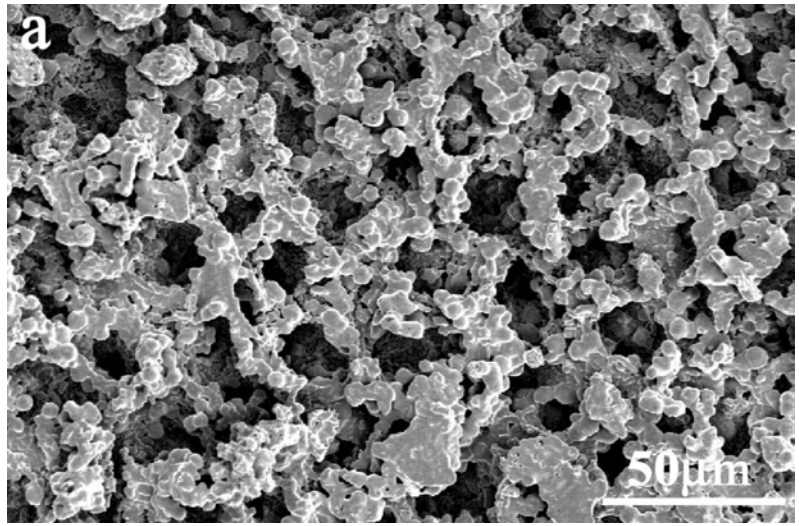


- Double-diffusion method
- Mixing of Ca^{2+} and CO_3^{2-} in membrane results in precipitation of $CaCO_3$
- Product highly concentration-dependent

Park R.J., Meldrum F.C. (2002) *Adv. Mater*, 14, 1167-1169.

Polycrystalline Product





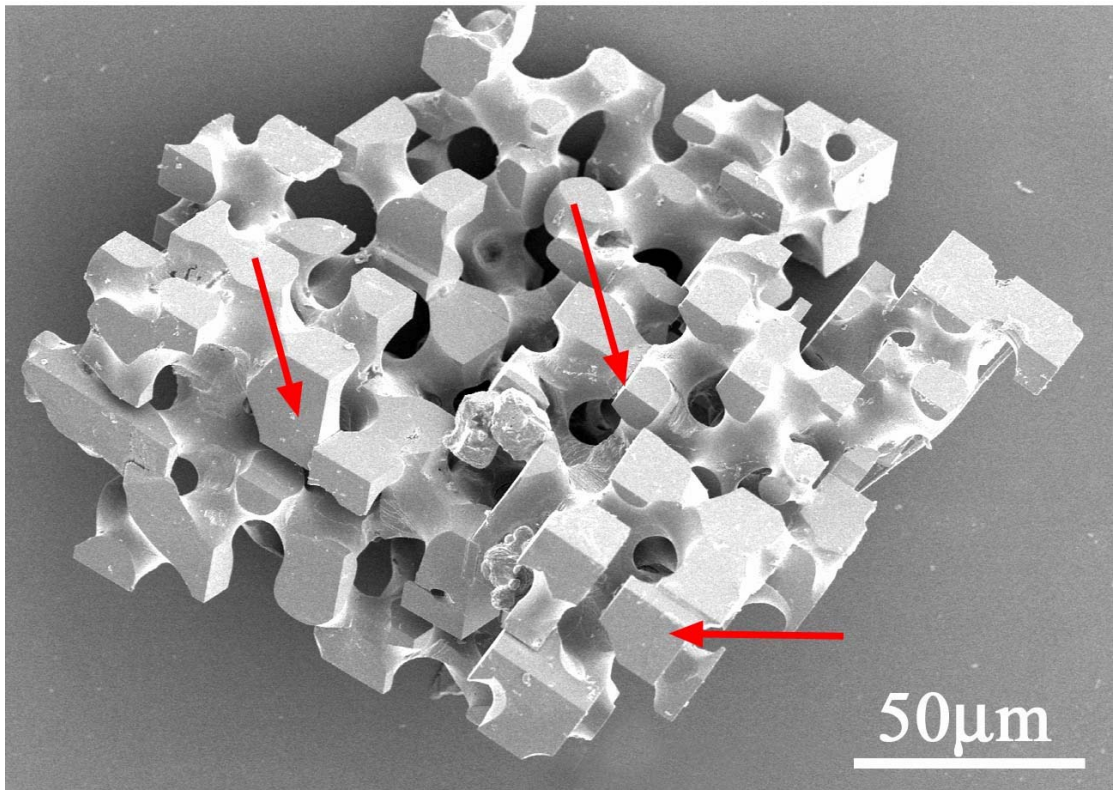
Reagents 0.1 M ⇒ **evidence of templating**

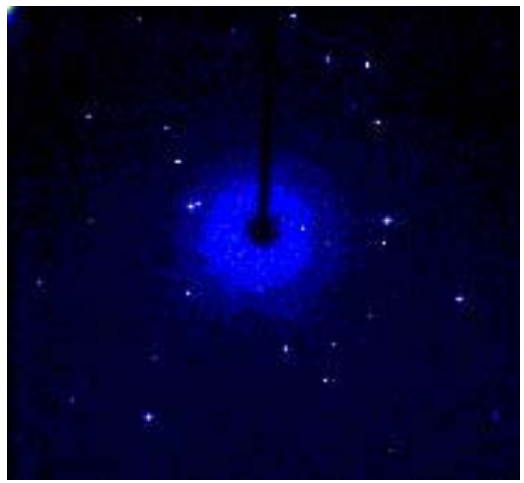
⇒ **Product polycrystalline**

Single Crystal Product

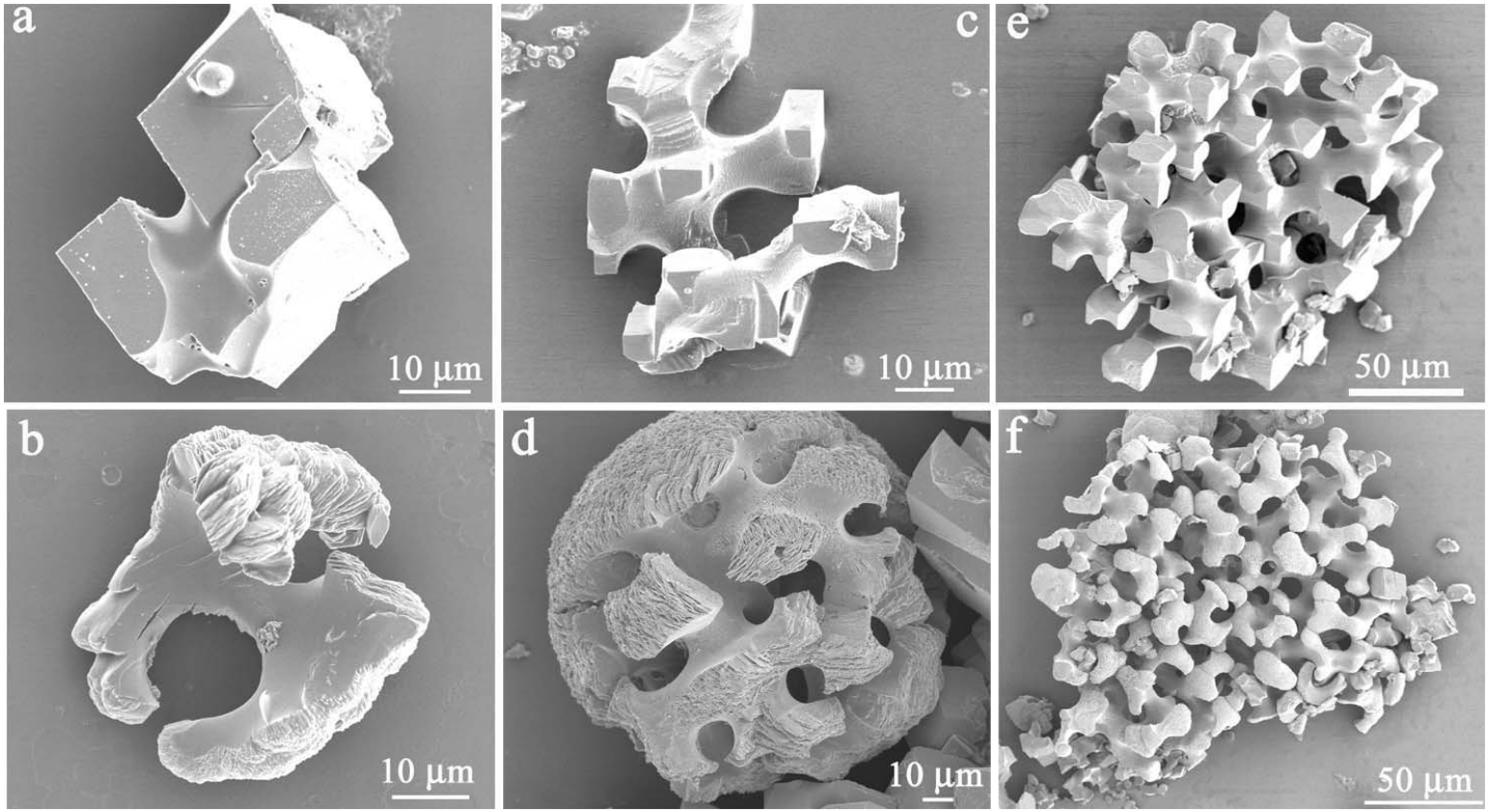
Low concentration reagents (0.02 M)

⇒ single crystals formed !!





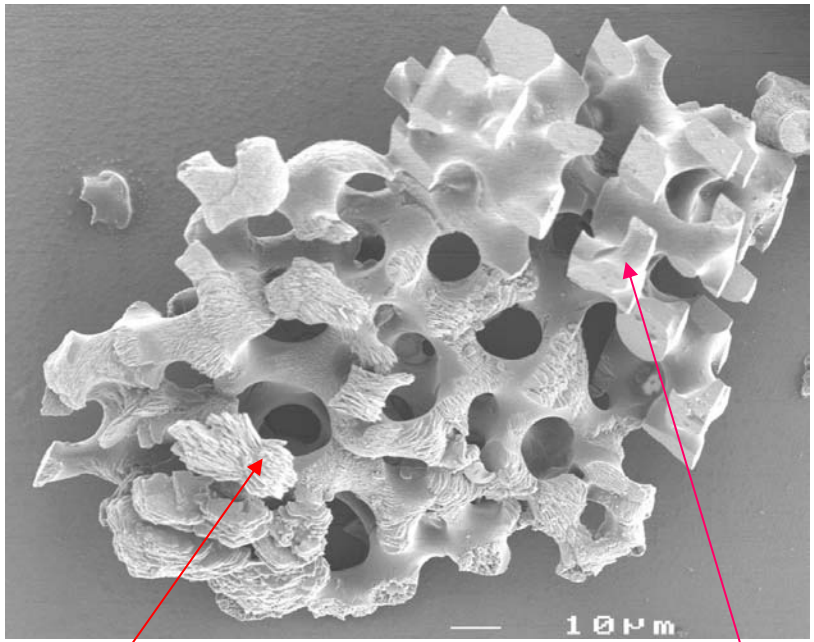
Growth Mechanism



Calcite and vaterite particles precipitated initially in 1:1 ratio

24 hrs ⇒ 75% particles calcite

Park R.J., Meldrum F.C. (2004) *J. Mater. Chem.* 14, 2291-2296.



Vaterite

Calcite

Incubation Time	C : V Ratio	Particle Size µm
20 min	50%	20 - 30
1 hour	50%	60 - 80
2 hours	60%	90 - 110
1 day	75%	> 120
3 days	> 80%	> 120

- Proportion of calcite to vaterite increases with time
- Dissolution of vaterite ⇒ reprecipitation as calcite
- Larger particles ⇒ transformation of vaterite to calcite

Summary

- Experiments demonstrate it is possible to produce calcite single crystals with complex morphologies synthetically

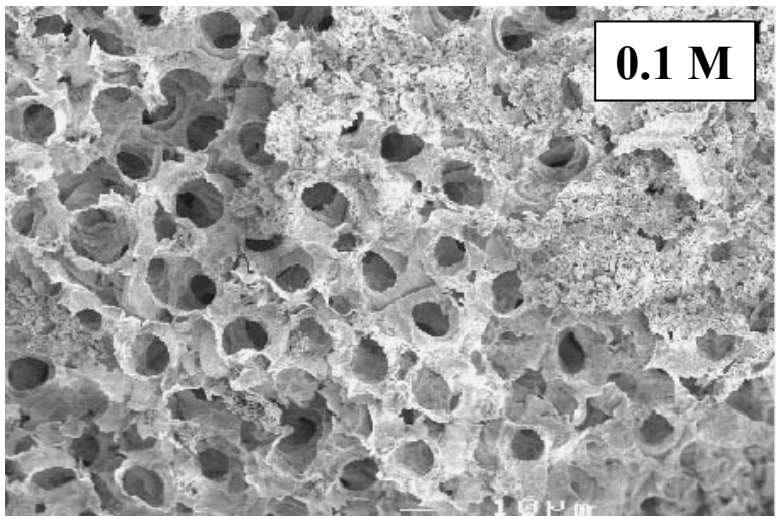
⇒ no elaborate control mechanisms are required

CONSTRAINT OF MORPHOLOGY IS SUFFICIENT

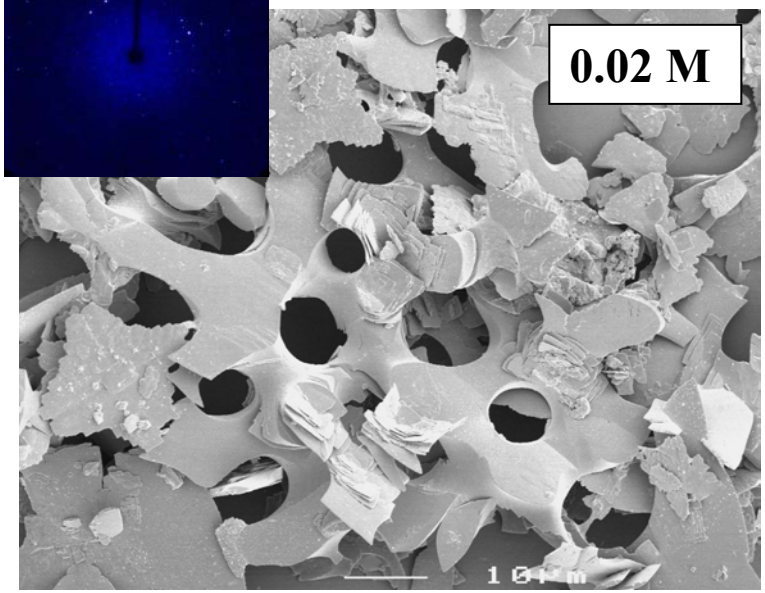
Can A Similar Route Be Used To Template Other Single Crystals ?

Barium Sulphate

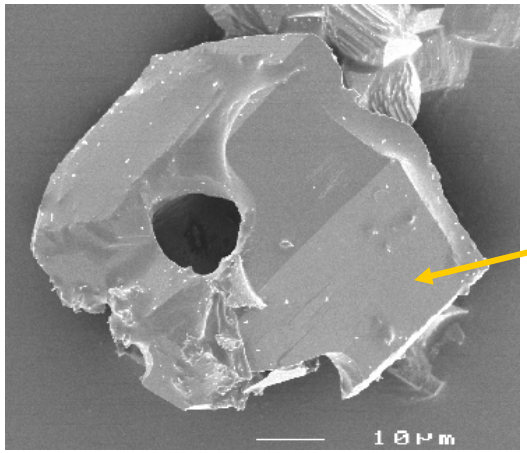
- Product concentration dependent
- High conc (0.1 M) clearly polycrystalline
- Low conc (0.02 M) tends to templated single crystals



Single/twinned crystal?

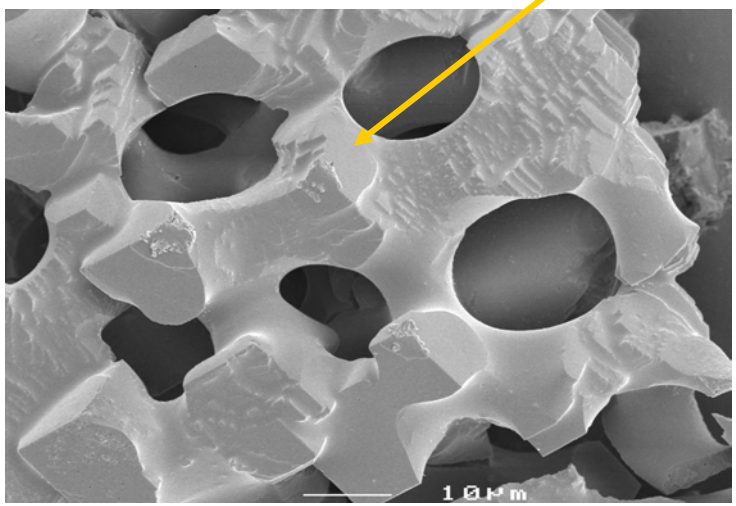


Strontium Sulphate

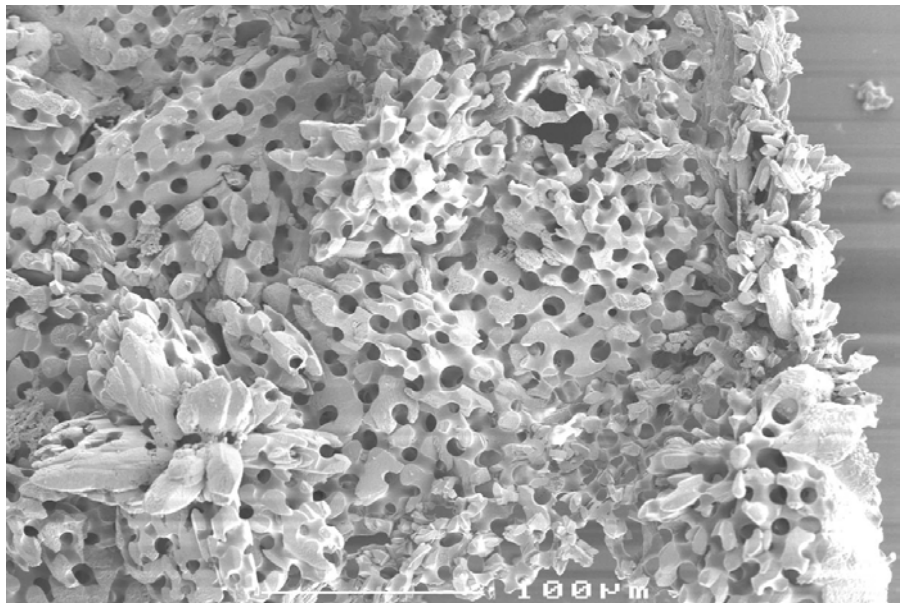


0.1M $SrCl_2$ for 4hr

Well-defined crystal faces indicate single crystal character



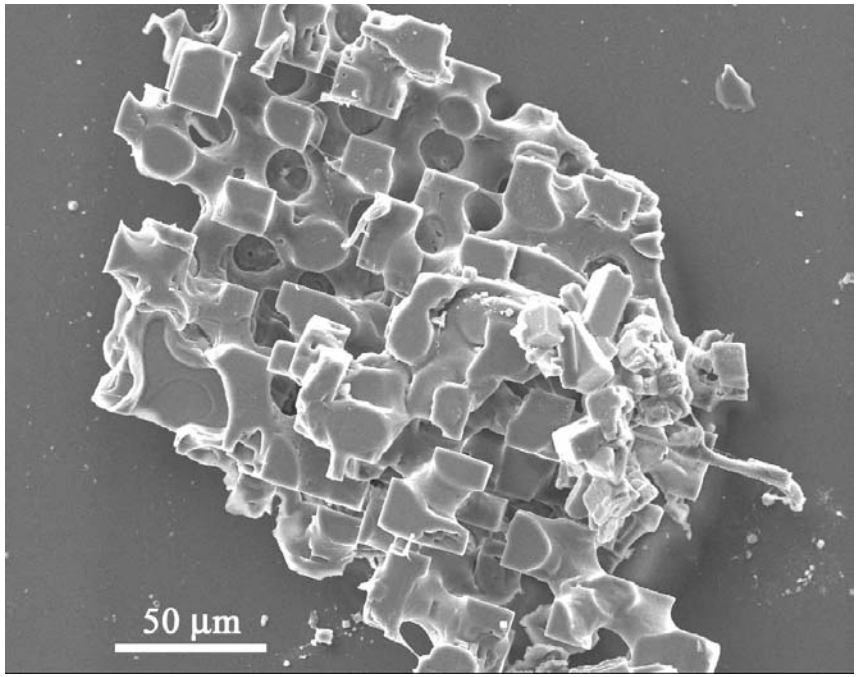
0.02 M $SrCl_2$ for 24 hr

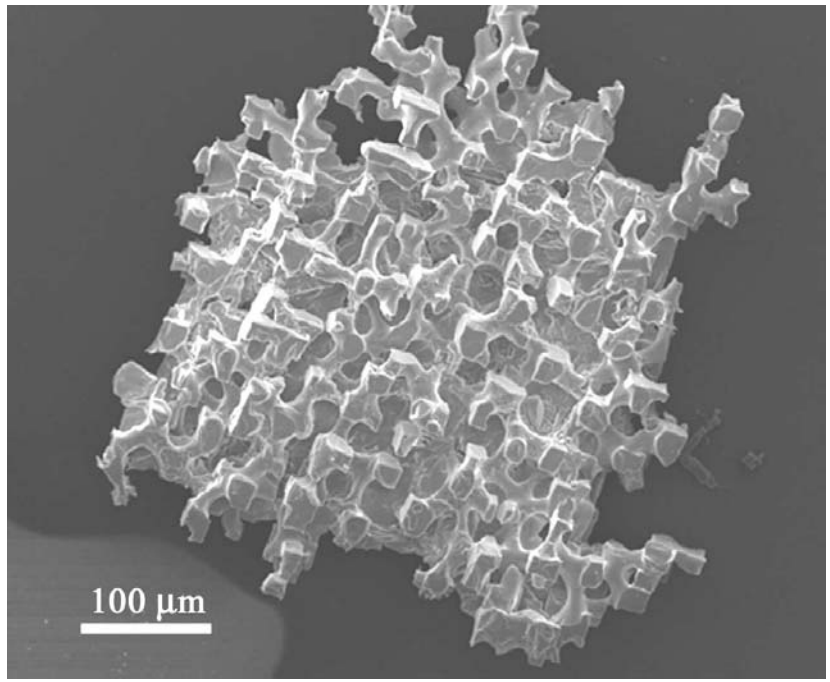


0.1M $SrCl_2$ for 24 hrs

MANY SINGLE CRYSTALS

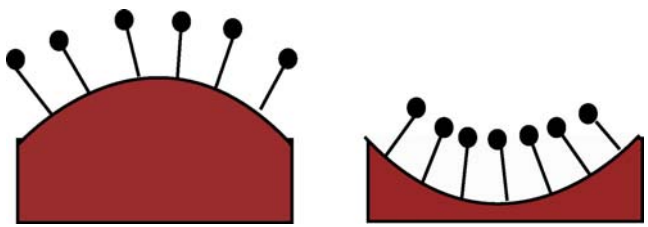
Sodium Chloride



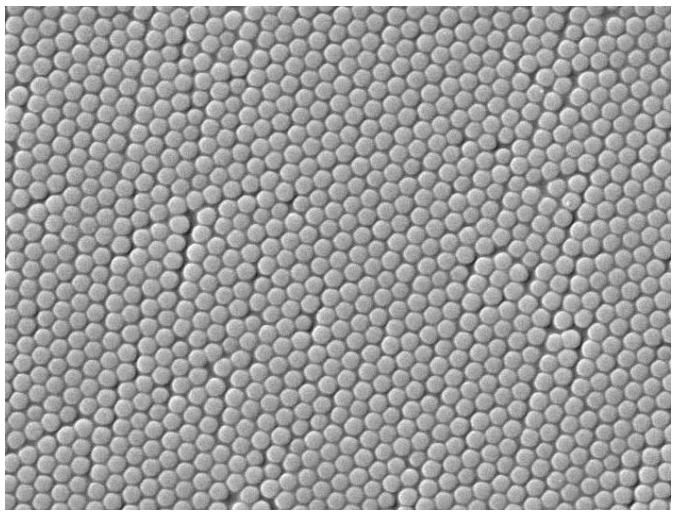


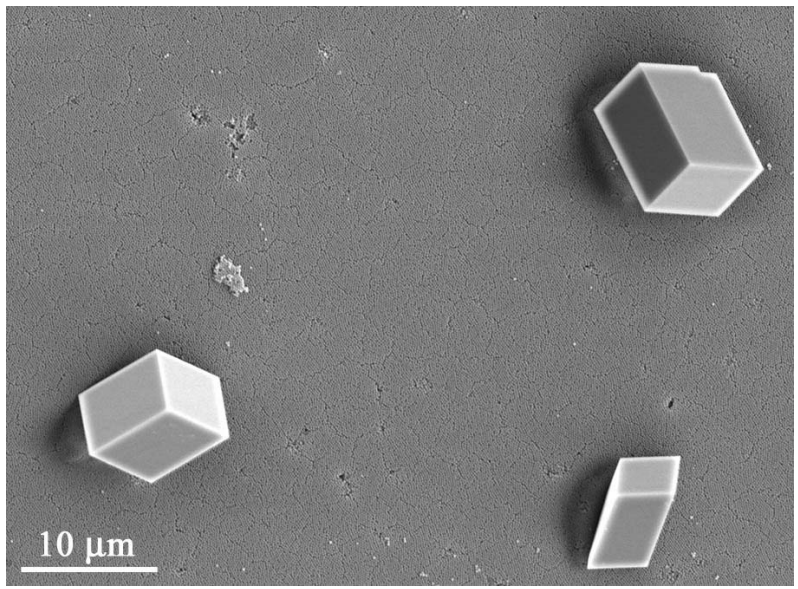
NaCl crystals formed by evaporation of a saturated solution

Surfaces with Well-Defined Topography

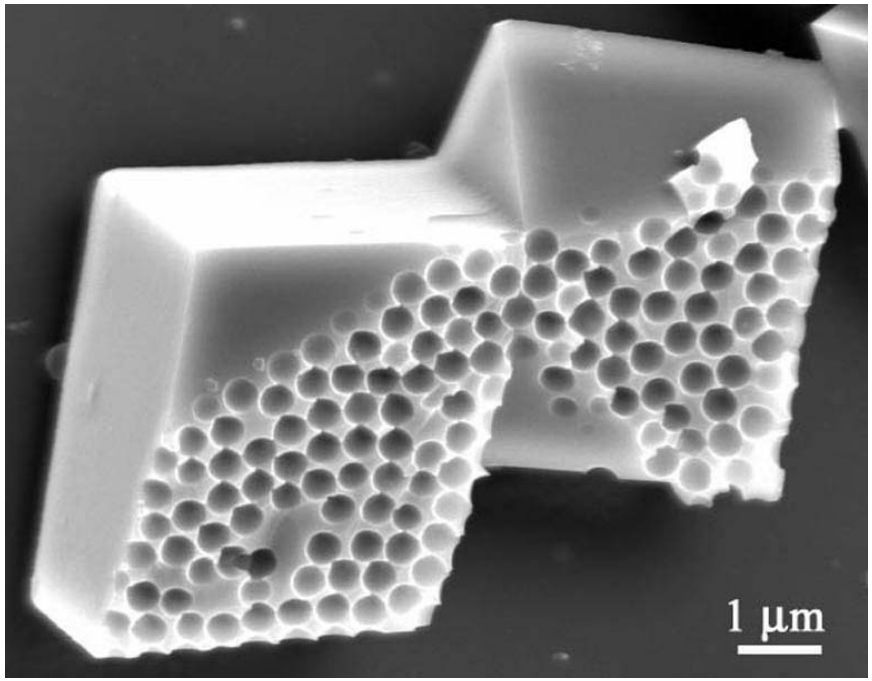


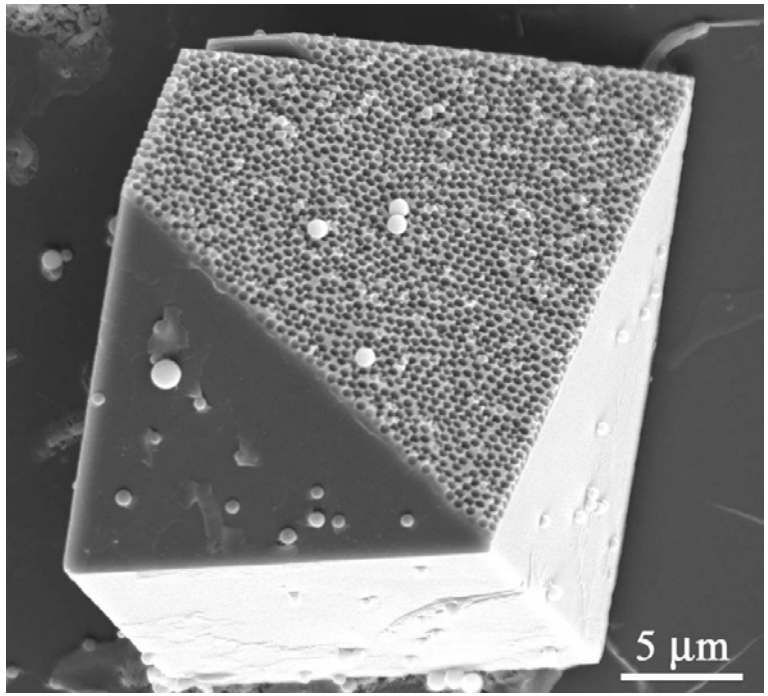
- Construct SiO_2 or polystyrene particle monolayers
- $CaCO_3$ grown on monolayers





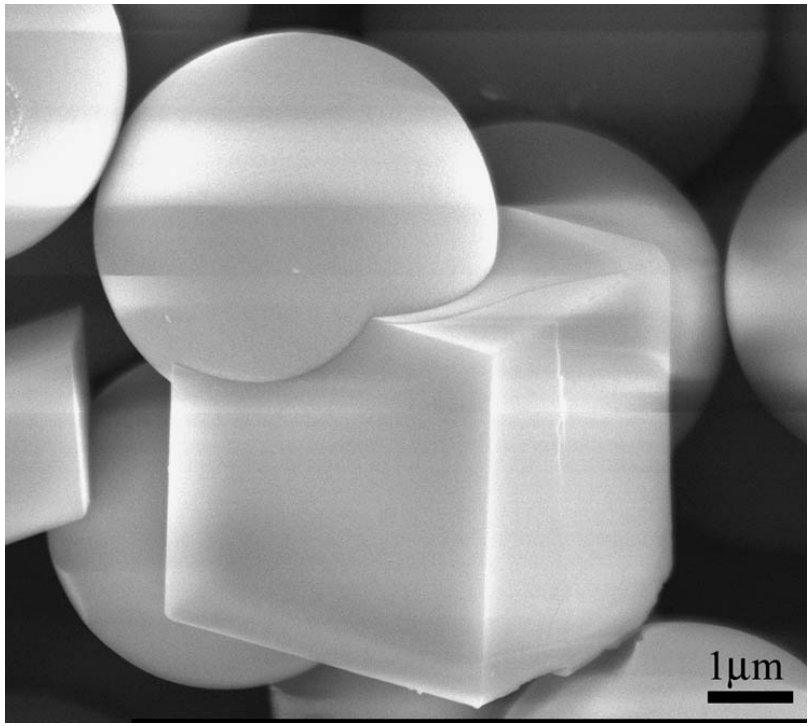
Nucleating Crystal Face Templated by Monolayer

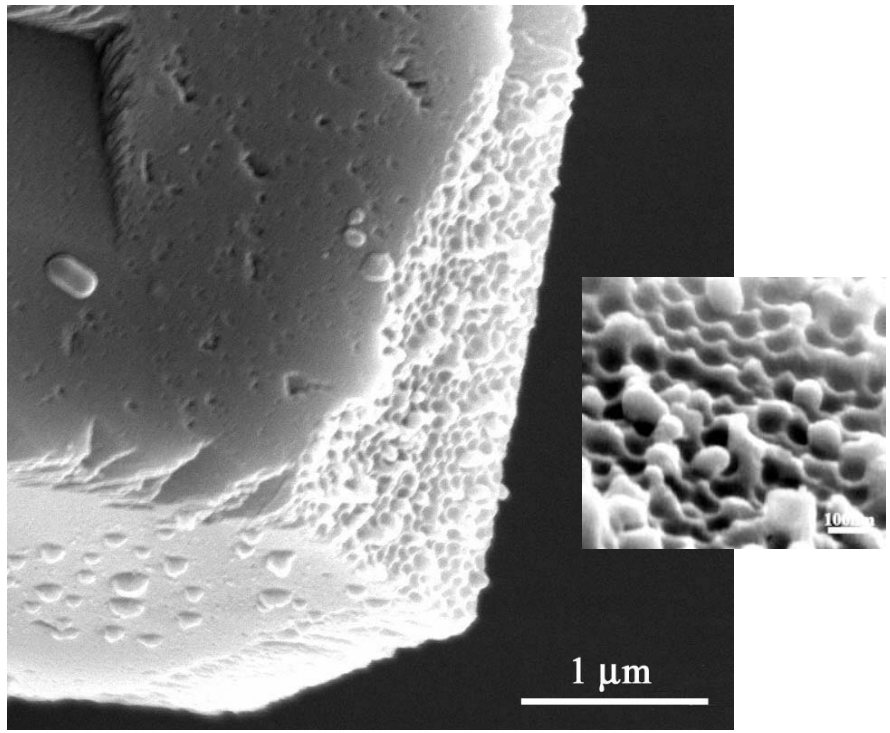




Calcite crystals grow around particles → shape of particles perfectly reproduced in single crystal

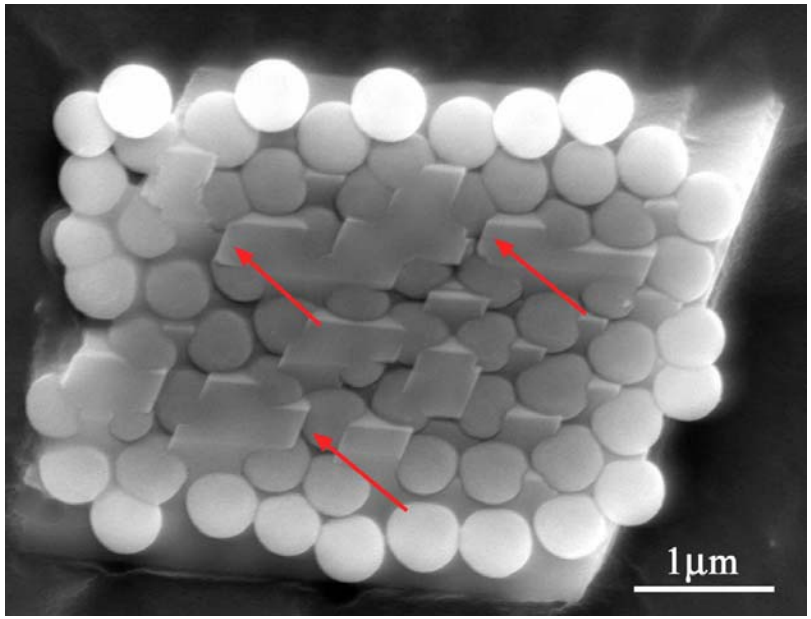
Influence of Particle Size ….

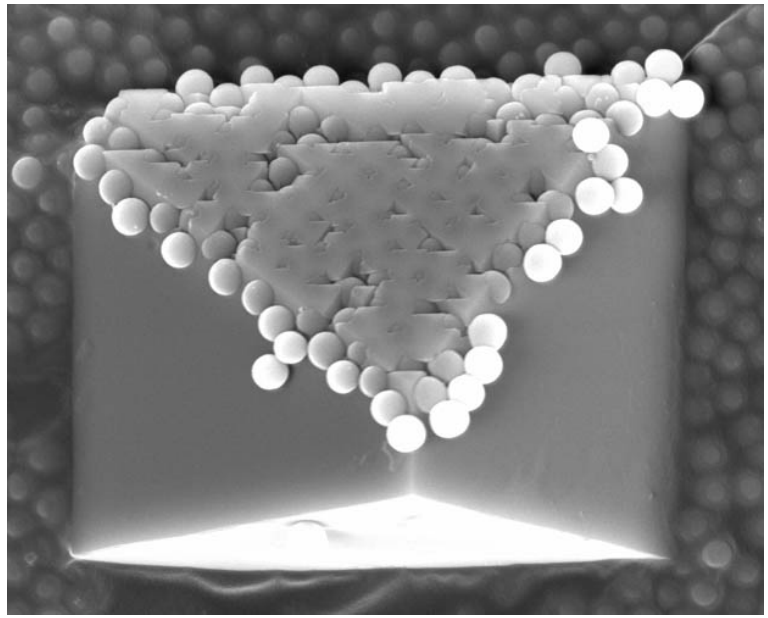




Templating successful in particle size range 5 μm to 50 nm

Continued Growth..

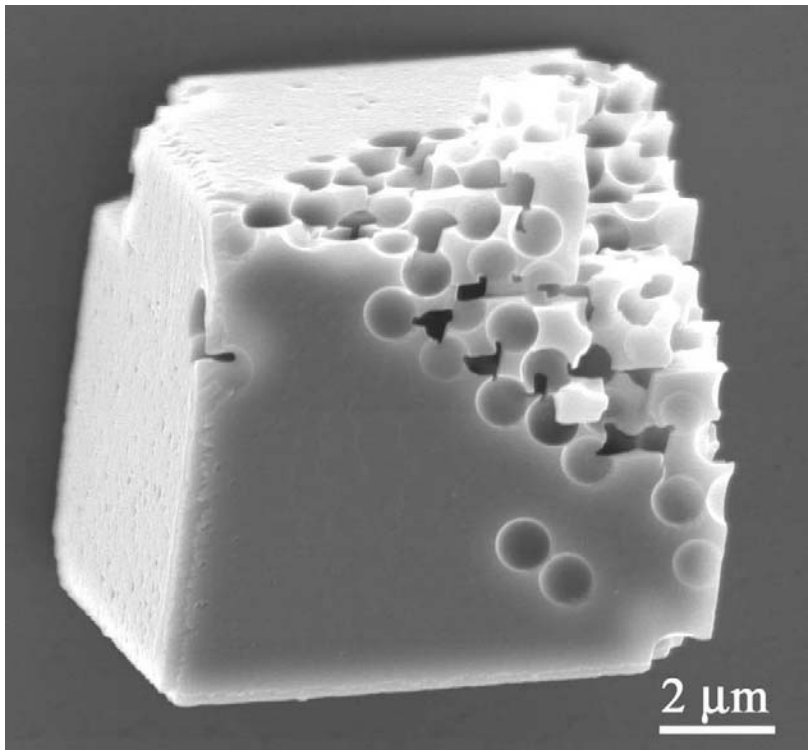


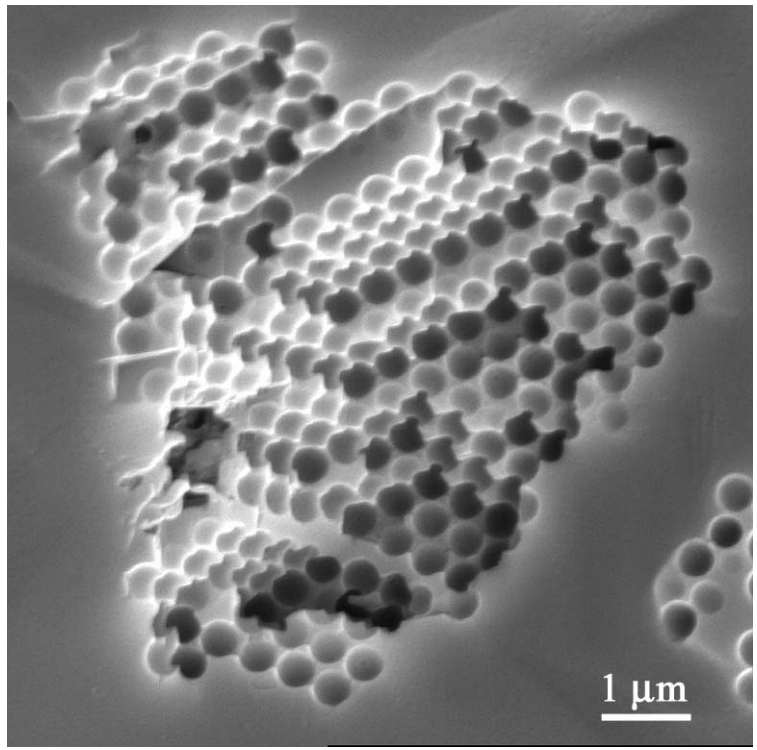


- Allow crystal growth to continue – see growth *through* the colloidal monolayer

- Particles become encapsulated within single crystals

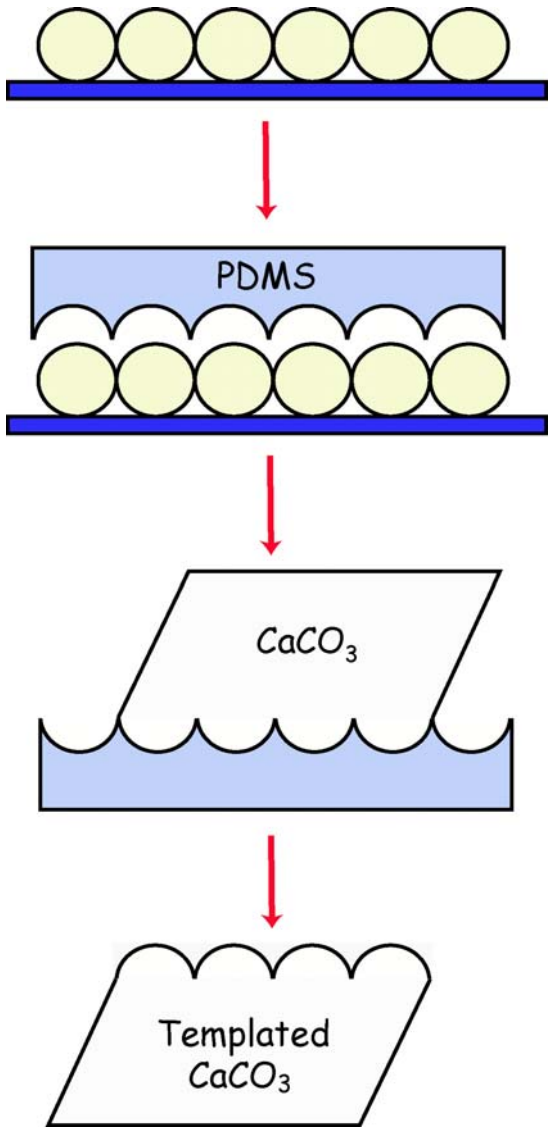
Crystal Growth on Colloidal Multilayers





Can extend methodology to use colloidal multilayers and form crystals templated in 3D

Surfaces with Positive Curvature

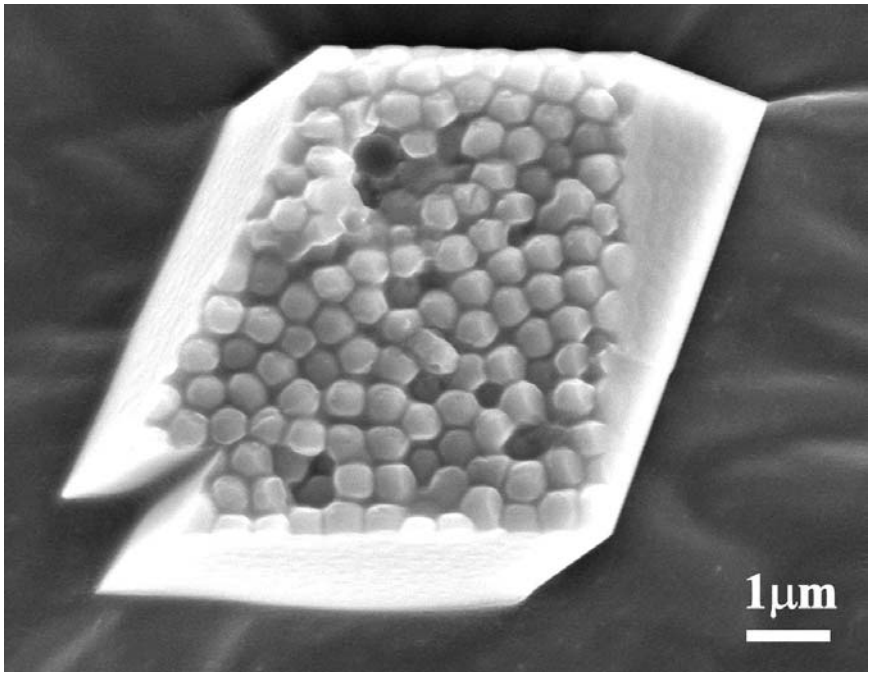


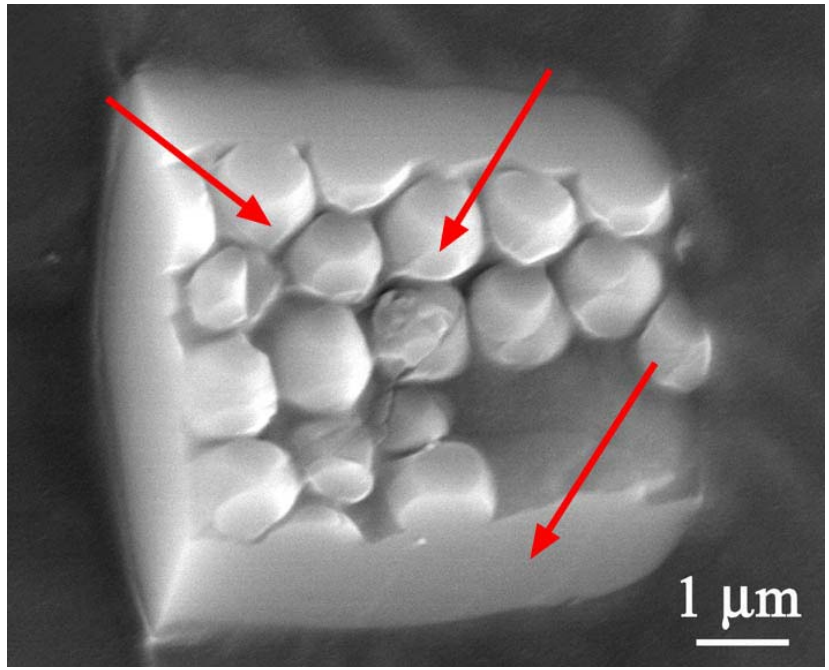
- Surfaces of opposite curvature created by generating PDMS replica of particle monolayer

- $CaCO_3$ precipitated on PDMS replica

... Templated Crystals Produced

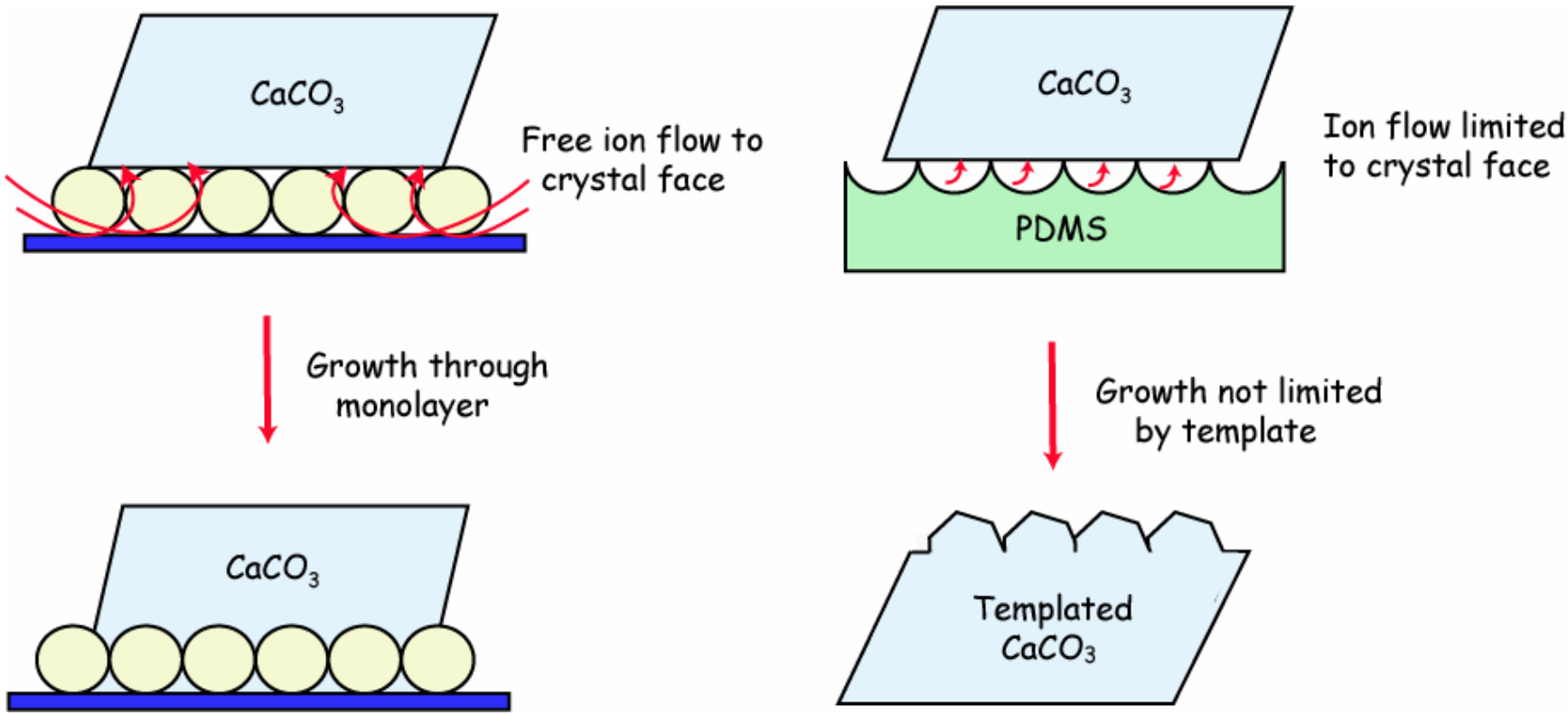
- Again see replication of template pattern in crystal face



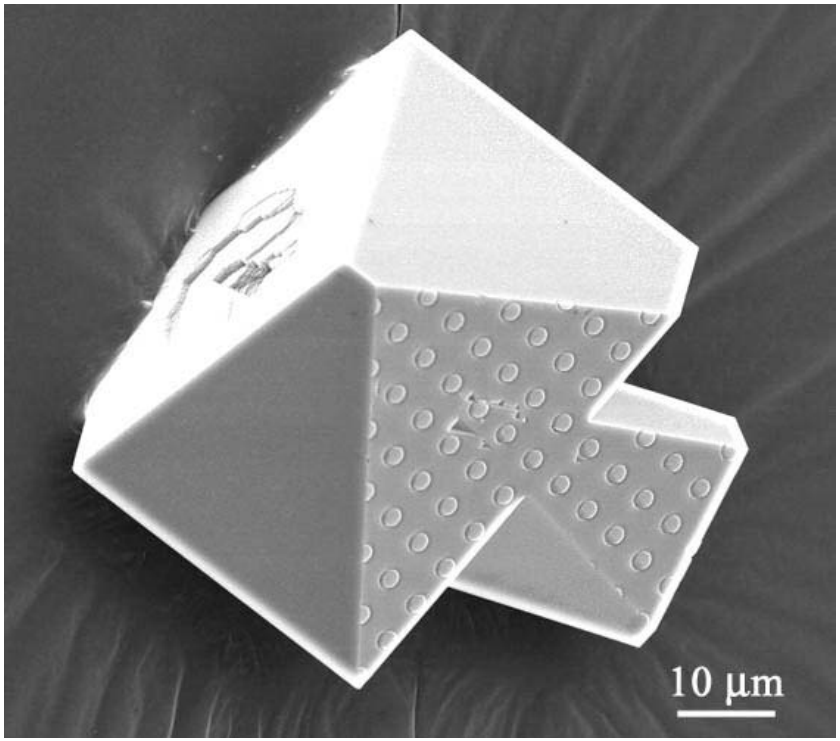


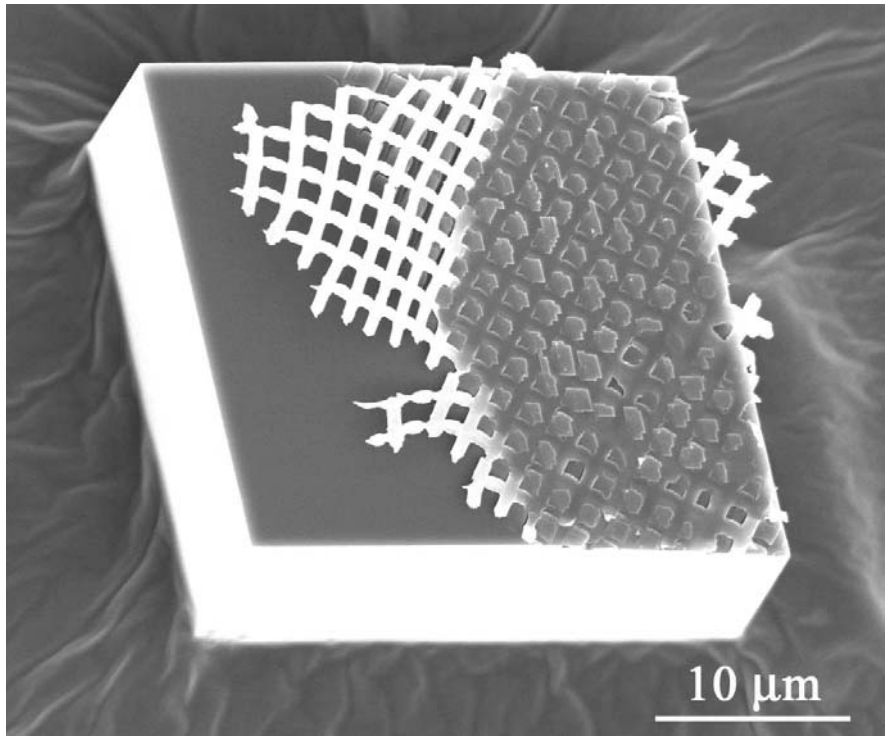
- As opposed to perfectly smooth surfaces, see evidence of defined crystal faces

... Mechanism


$CaCO_3$
Free ion flow to crystal face
Growth through monolayer
$CaCO_3$
$CaCO_3$
PDMS
Ion flow limited to crystal face
Growth not limited by template
Templated $CaCO_3$

Polymer Film Templates





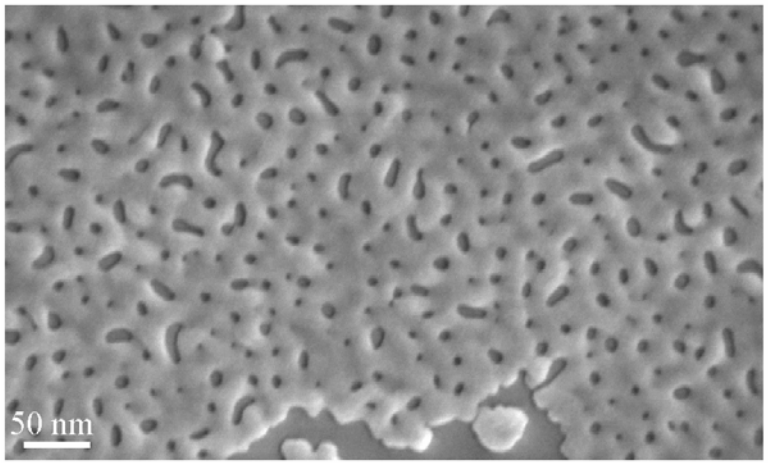
Using patterned polymer films to template crystal surfaces

⇒ Potential for structuring surfaces at small length scales

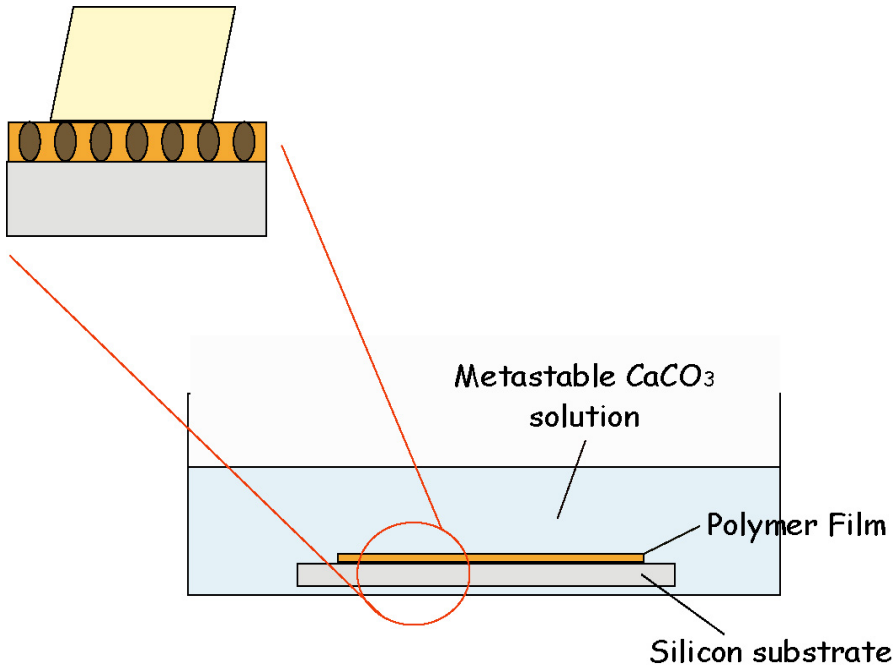
Sabine Ludwigs, Ulli Steiner, University of Cambridge

Patterning at Small Length Scales

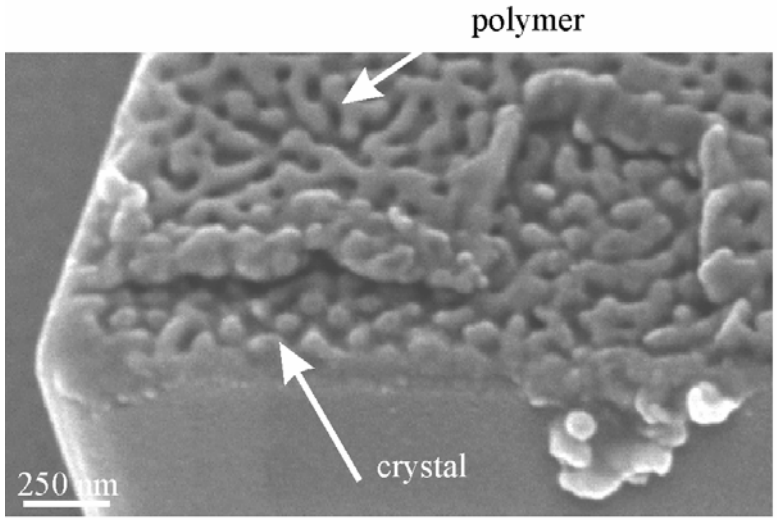
Demixing of polymer blends and subsequent removal of one component polymer templates yields patterned films with structure sizes from 100 nm - 10 nm prepared.

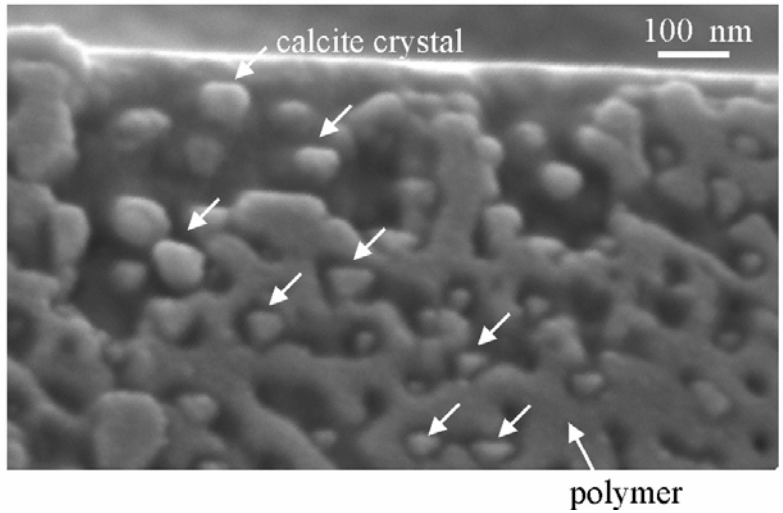


porous polystyrene film prepared via spontaneous phase separation of a polystyrene / polymethylmethacrylate blend and selective removal of PMMA



Crystal Growth on Polymer Film

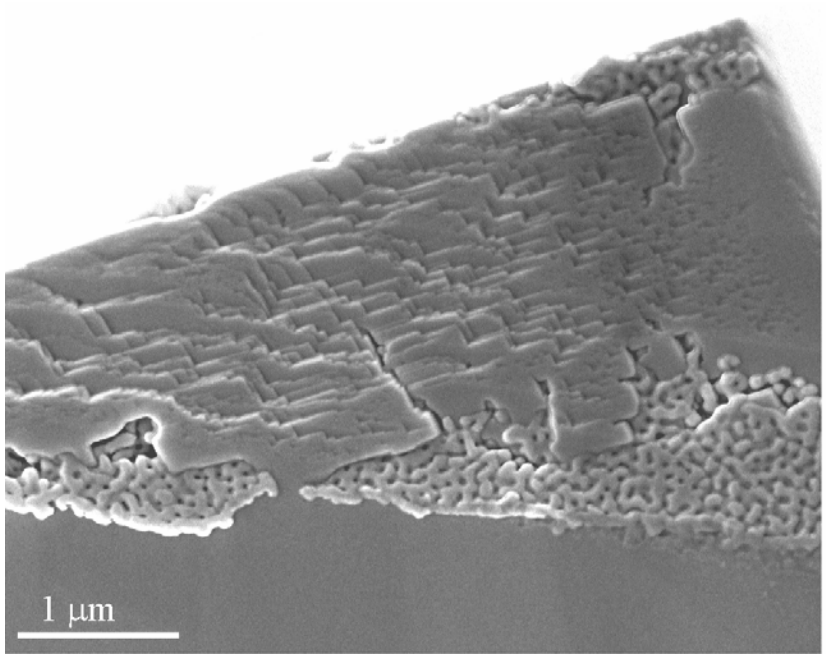


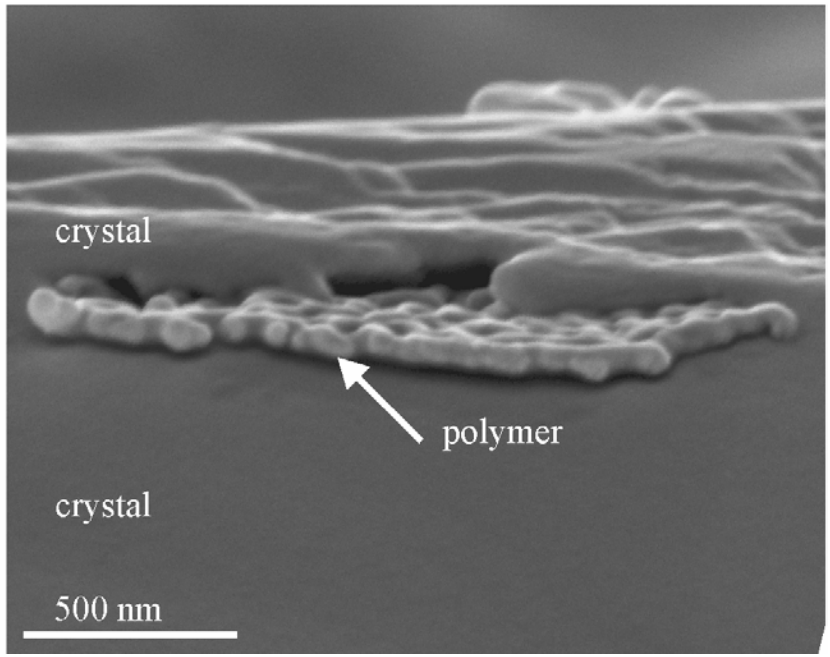


- Crystals nucleate on the surface of the polymer film
- Removal of the crystals from the substrate reveals the crystal face which nucleated on the polymer film
- Separation of the polymer shows the crystal morphology to be templated by the polymer film

Continued Growth ...

Through Pores in Polymer Film



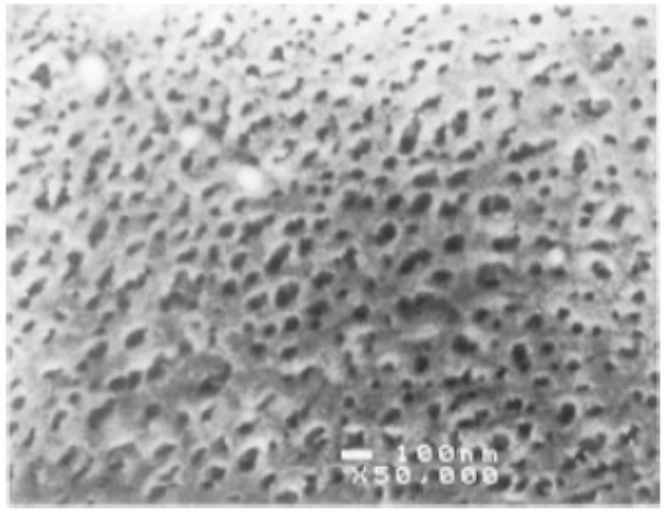


Further crystal growth results in growth *through* the pores

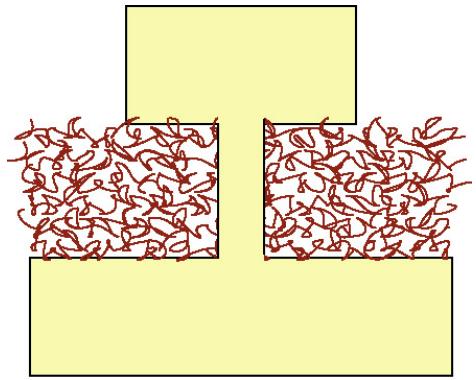
⇒ Continued on other side of polymer film

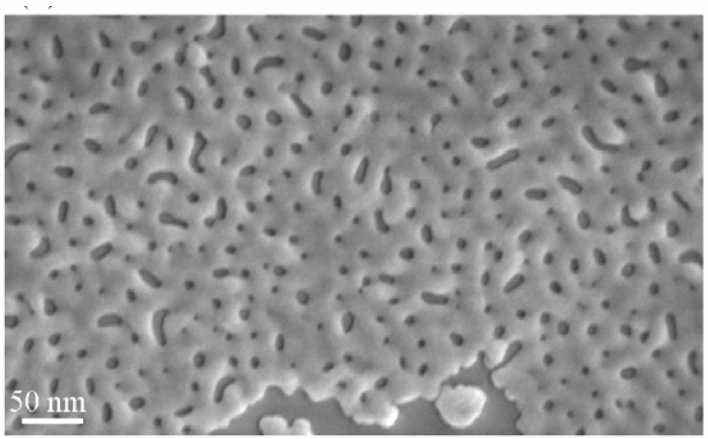
⇒ Polymer film becomes incorporated in the crystal

Reminiscent of Abalone Nacre ?



Abalone polymer film



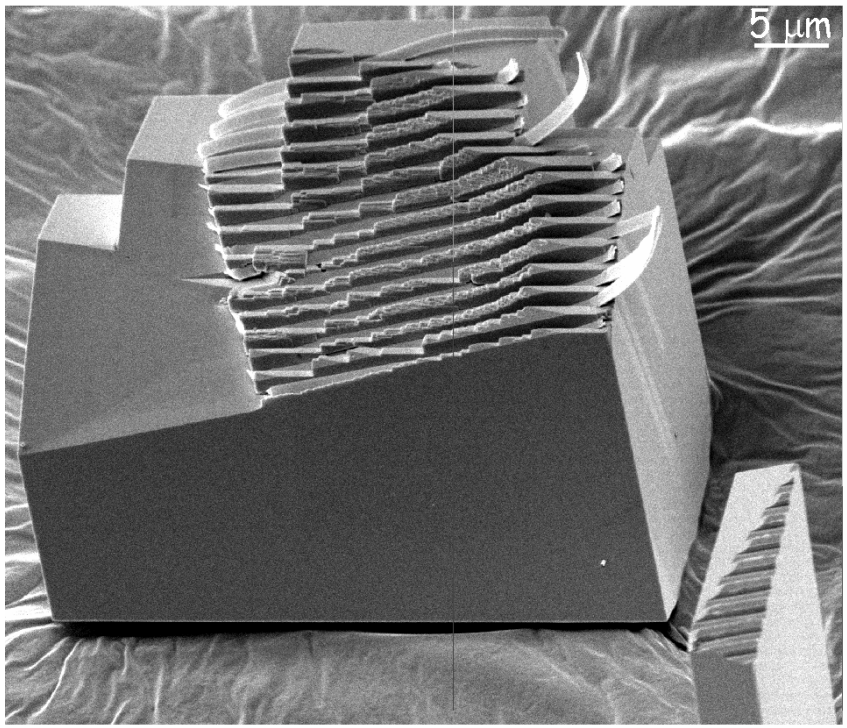


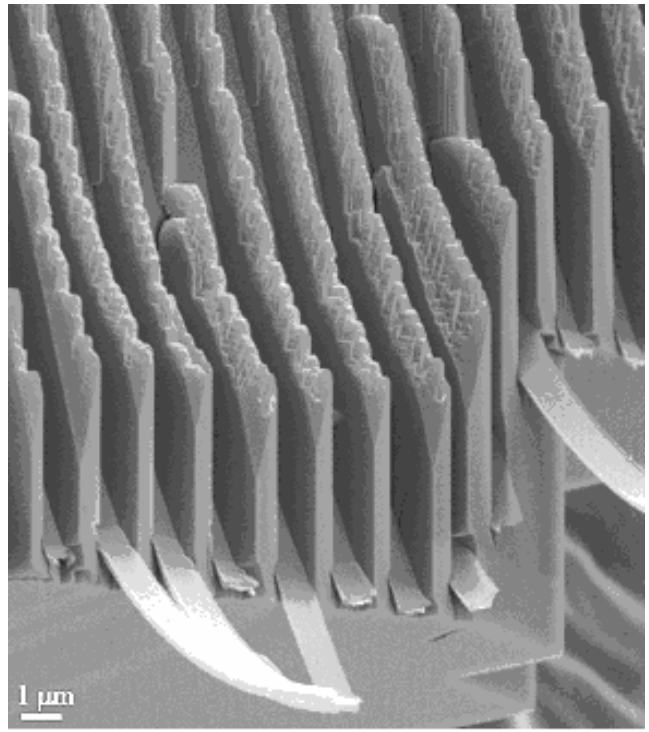
Synthetic polymer film

Structure of nanoporous polymer thin film and crystal growth through strongly resemble abalone nacre

⇒ Further vindication for this model?

High Aspect Ratio Crystal via Patterning with Polymer Thin Film





Control of crystal growth using a polymer mask. Directional growth in the area not covered by the polymer (thin stripes), giving rise to a high aspect ratio morphology of the crystal.

Summary

Controlling Crystal Morphologies:

- Additives to control single crystal morphologies

⇒ Subtle changes in morphology/ mechanism controversial

- Additives to produce polycrystalline structures

⇒ Oriented and non-oriented structures

⇒ Block copolymers extremely versatile

- Templating to control production :

⇒ Nanoparticles / ferritin and virus cages

⇒ Polycrystalline structures with complex morphologies

⇒ Single crystals with complex morphologies

/ simple templating sufficient!