Nacre and Beyond: Highly parallel crystallization of nanoparticles to their superstructures

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Agenda:

a) MeO nanoparticles and their self-assembly

b) Nanocasting:Mesoporous crystalline layers and Soft Epitaxy

c) Nacre and beyond: Polymer controlled Crystallization of Minerals

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A New Synthesis of Metal Oxides Nanoparticles

General Synthesis Protocol:

All procedures were carried out in the glovebox.

1) Dissolve Alkali Metal (Li) or Alkaline Earth Metals (Sr,Ba) in Benzyl Alcohol ($C_6H_5CH_2OH$)
2) Addition of Metal Alkoxides: $Ti(O^iPr)_4$, $Zr(O^iPr)_4$ or $Nb(OEt)_5$ $VO(O^iPr)_3$, $Nb(OEt)_5$, $Hf(OEt)_4$, $Ta(OEt)_5$, $Sn(O^tBu)_4$, $In(O^iPr)_3$
3) Heat treatment in autoclave at 200°C-250°C

(Boiling point of benzyl alcohol is 205°C)

No water, no halide precursors, no surfactants!

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Which materials are new as nanoparticles ?

$$Ba + \text{Benzyl Alcohol} + Ti(O\textit{i}Pr)_4 \xrightarrow{200°C} BaTiO_3$$

$$Sr + \text{Benzyl Alcohol} + Ti(O\textit{i}Pr)_4 \xrightarrow{200°C} SrTiO_3$$

$$Ba,Sr + \text{Benzyl Alcohol} + Ti(O\textit{i}Pr)_4 \xrightarrow{200°C} (Ba,Sr)TiO_3$$

$$Ba + \text{Benzyl Alcohol} + Zr(O\textit{i}Pr)_4 \xrightarrow{220°C} BaZrO_3$$

$$Li + \text{Benzyl Alcohol} + Nb(OEt)_5 \xrightarrow{220°C} LiNbO_3$$

Angew. Chem. Int. Ed. **2004**, *43*, 2270-2273 – JACS 2004, 126, 9120 – German Patent Nr. 103 38 465.0

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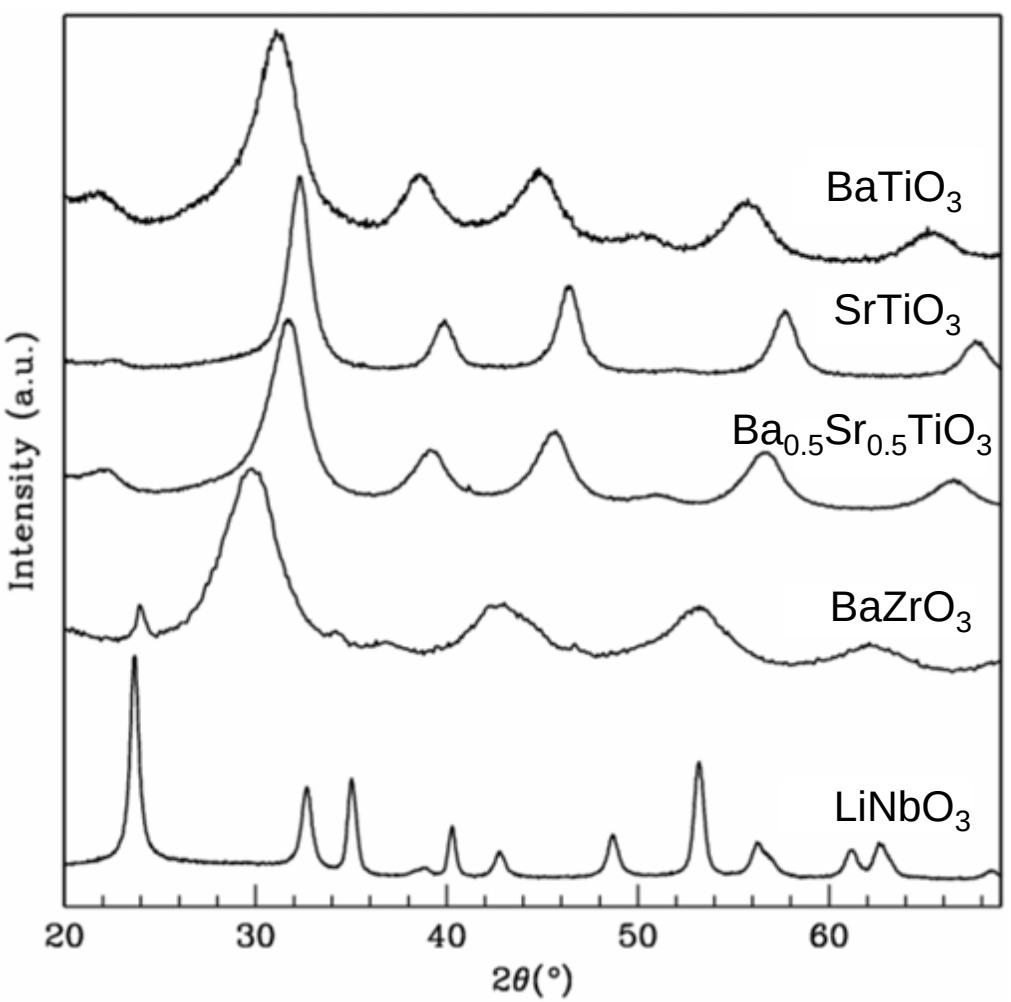
Characterization: X-ray Powder Diffraction



Titanates:

- Phase-pure
- Broad peaks
- Discrimination cubic-tetragonal impossible

Bariumzirconate:

- $BaZrO_3$ + $BaCO_3$

Lithiumniobate:

- Sharper reflections
- Phase-pure

Characterization: TEM

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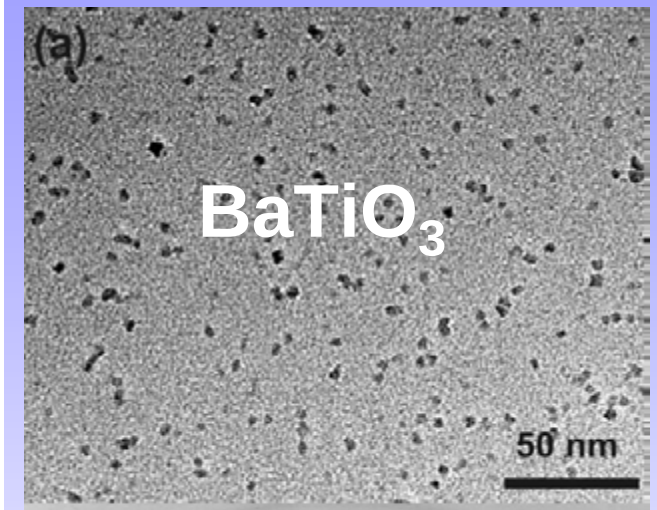
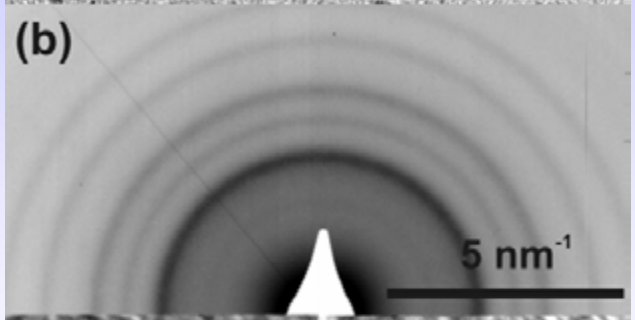
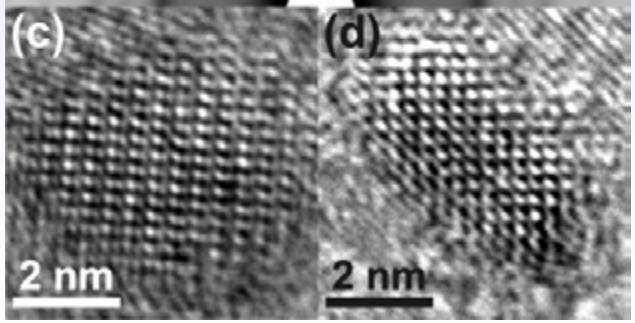
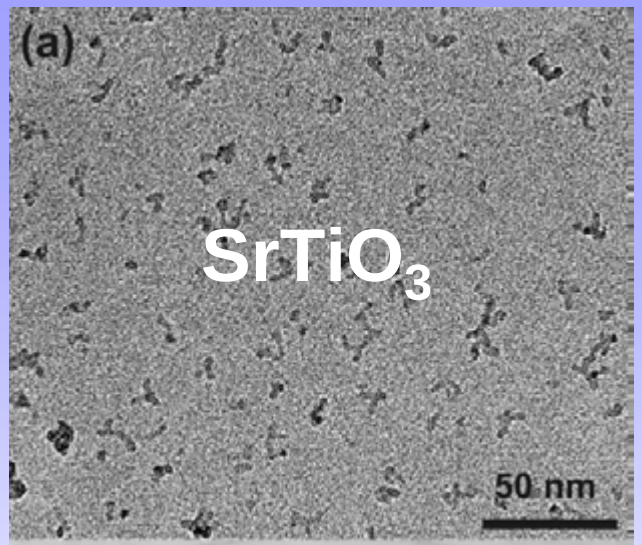
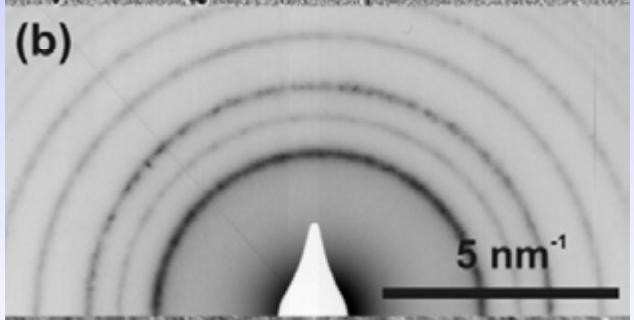
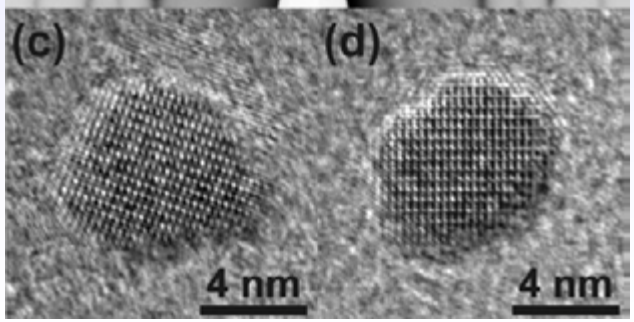


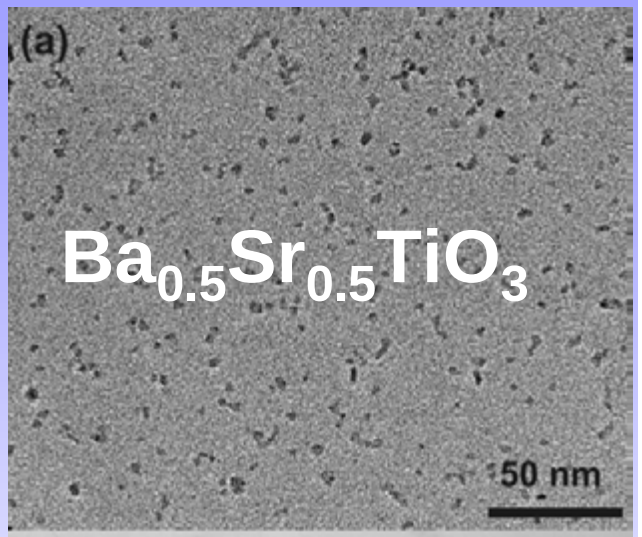


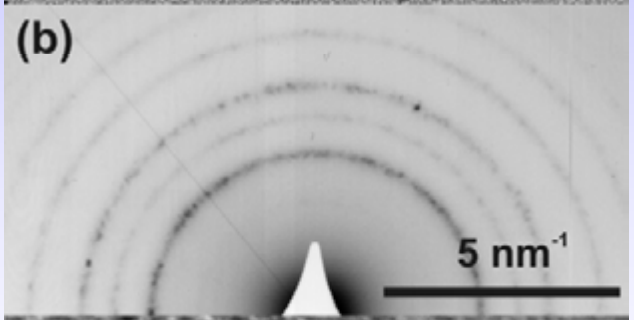


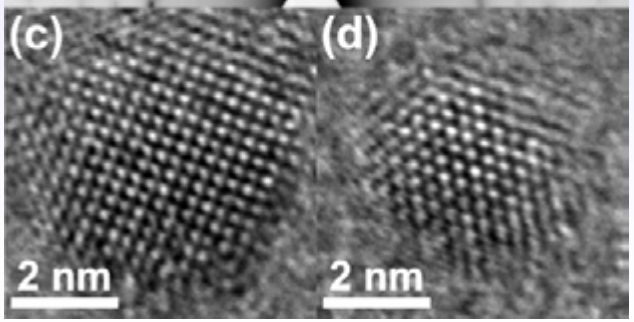






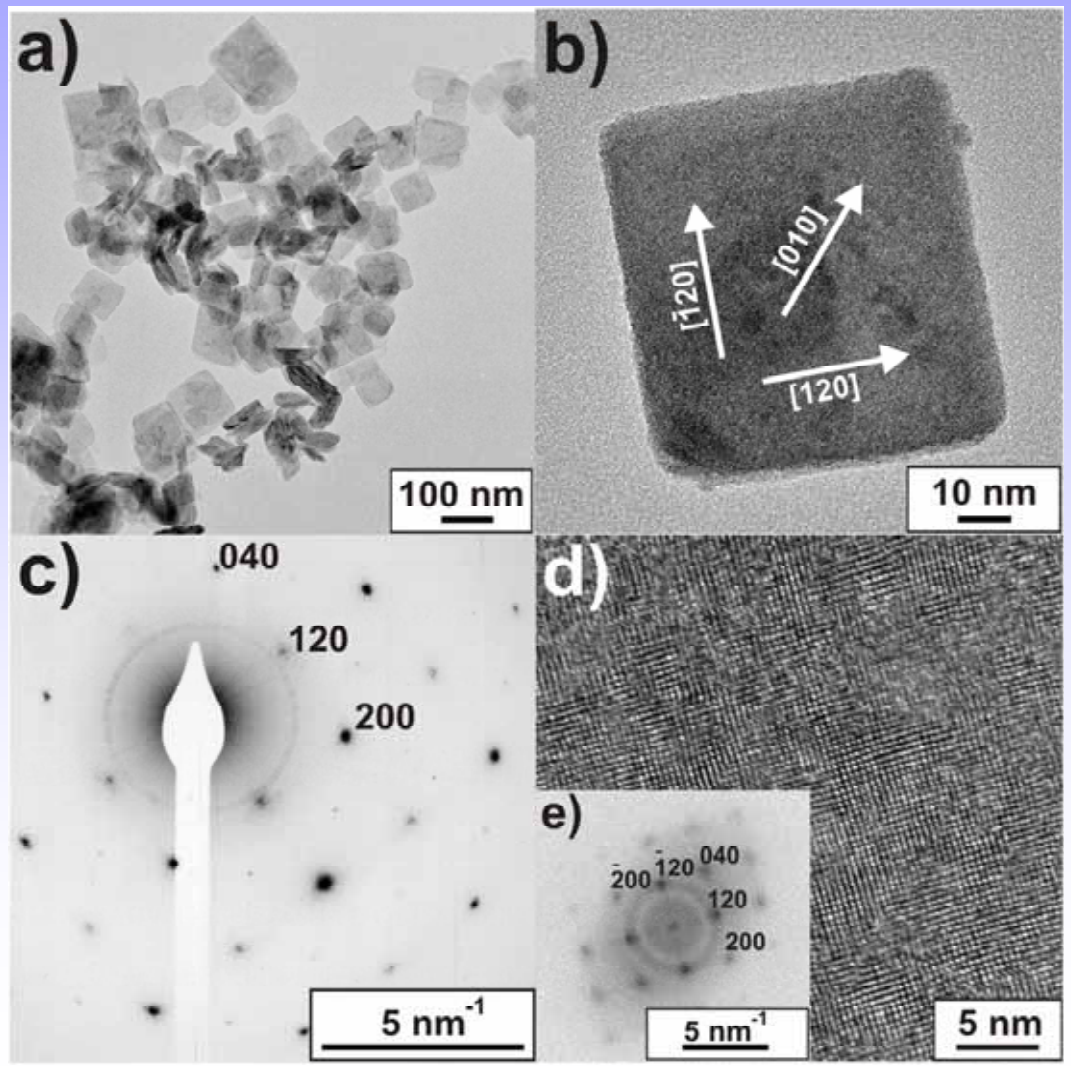






Organized Nanoparticles: WO_3-plates

Reaction of WCl_6 with Benzyl Alcohol: Without DFOM



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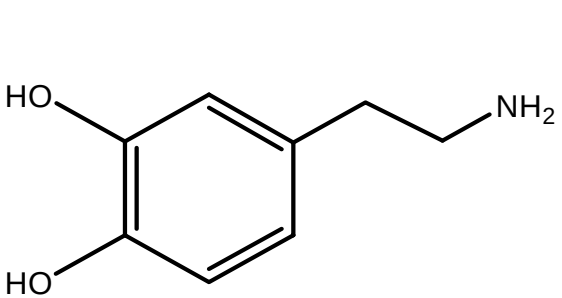
In situ - Surface Functionalization:

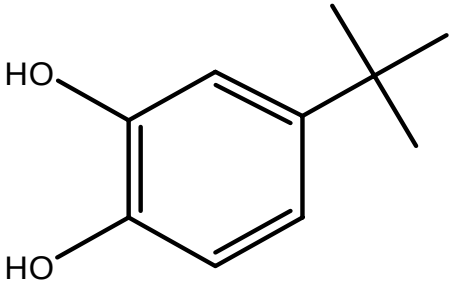
Addition of chelating ligands:

1) Nanoparticles + enediol ligands

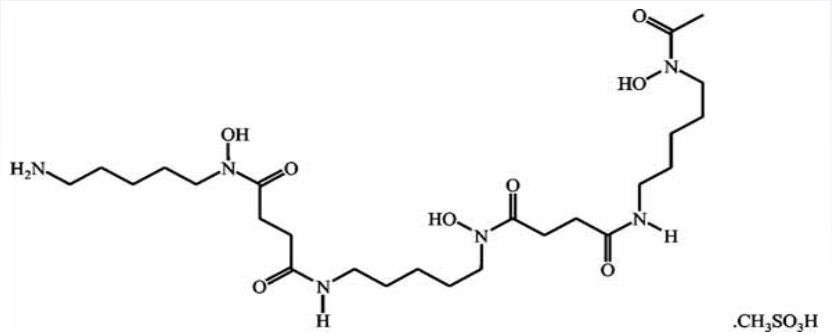
   [dopamine $(HO)_2C_6H_3CH_2CH_2NH_2 \cdot HCl$; 4-*tert*-butylcatechol $(CH_3)_3CC_6H_3(OH)_2$]



dopamine

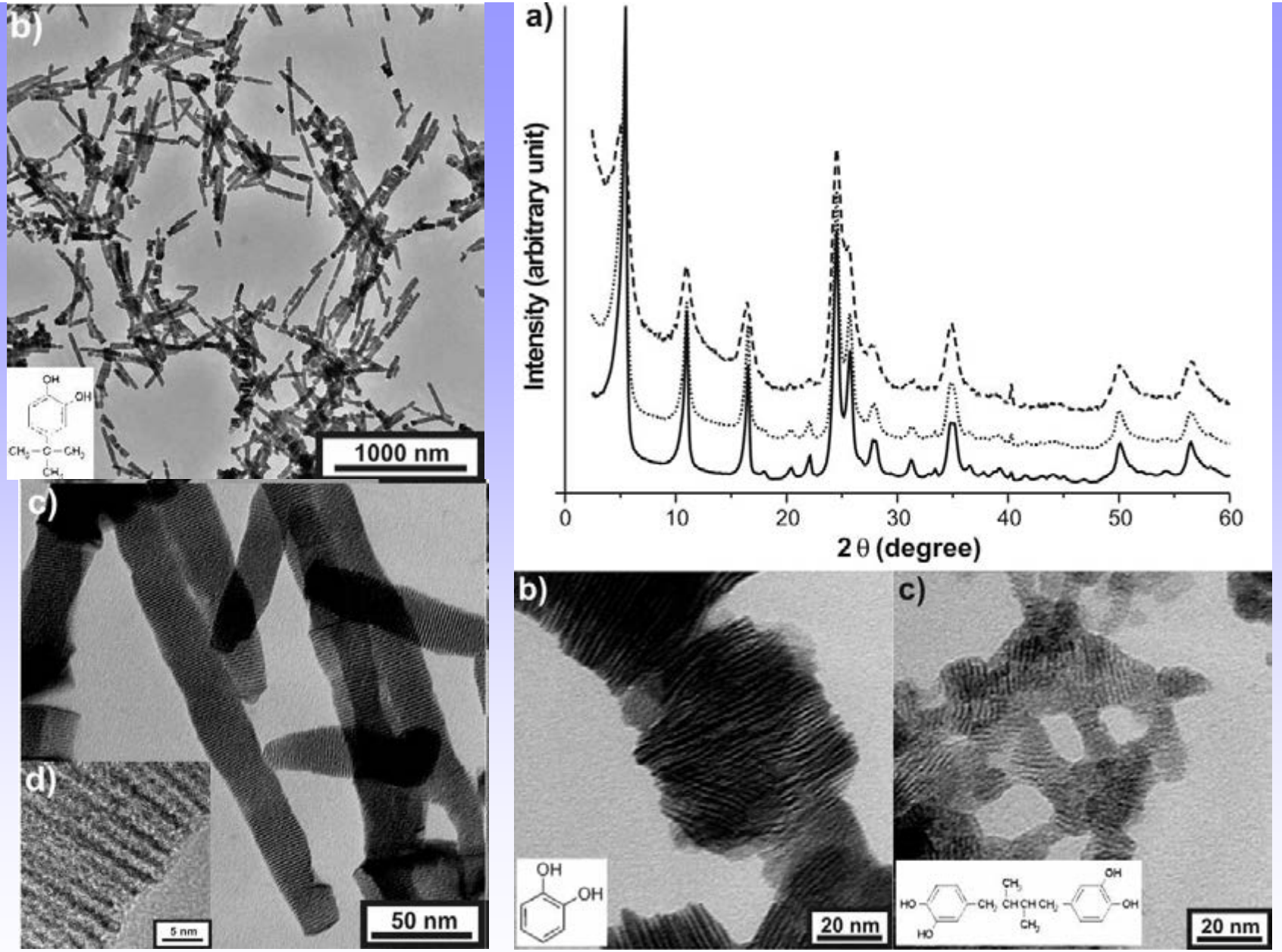


4-*tert*-butyl catechol

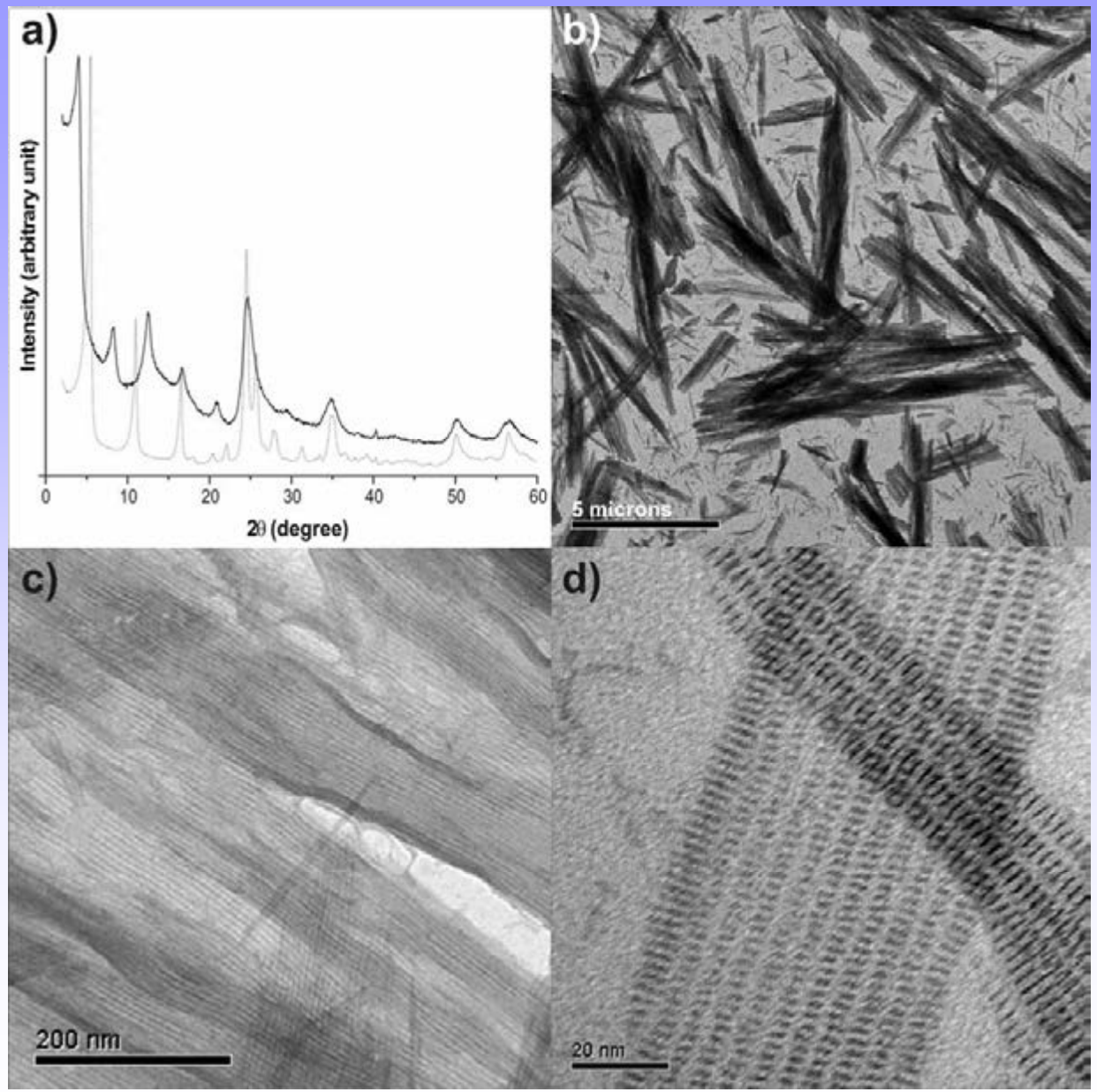


Deferoxamine (siderofore)

Chem. Mater. **2004**, *16*, 1202-1208

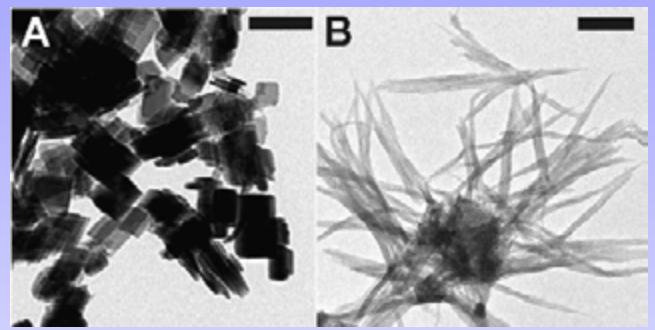


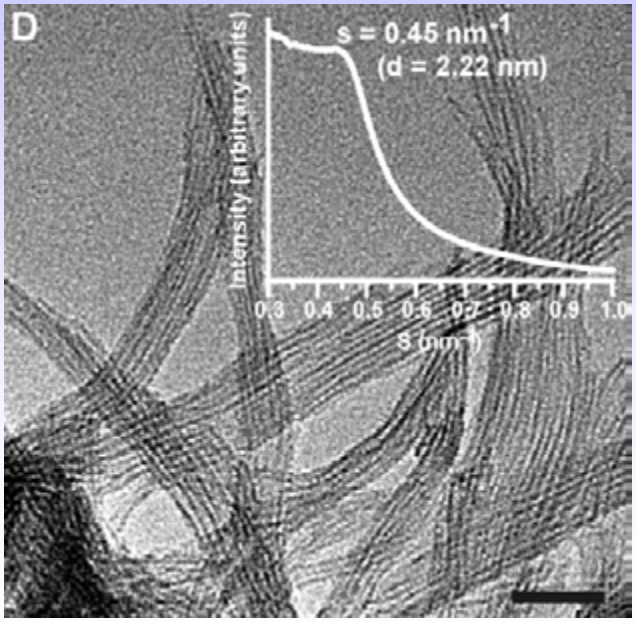
4-tert-butylcatechol (solid line), pyrocatechol (dotted line) and nordihydroguaiaretic acid (dashed line).

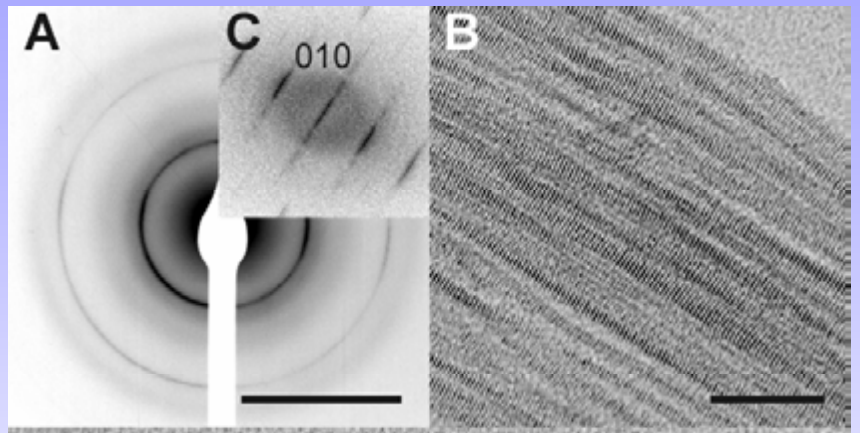


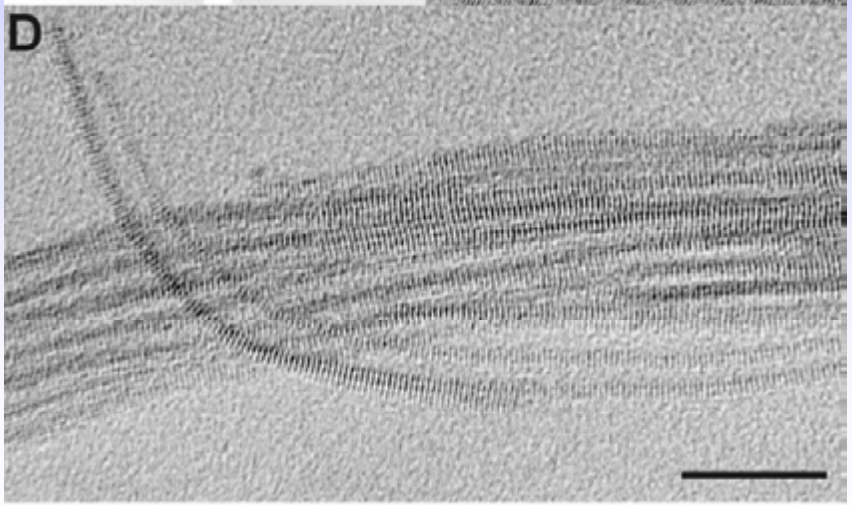
Special structures at the correct stoichiometry of BA and t-butylCA

With DFO ligands: spontaneous formation of WO_x - nanofibres









$W_{18}O_{49}$

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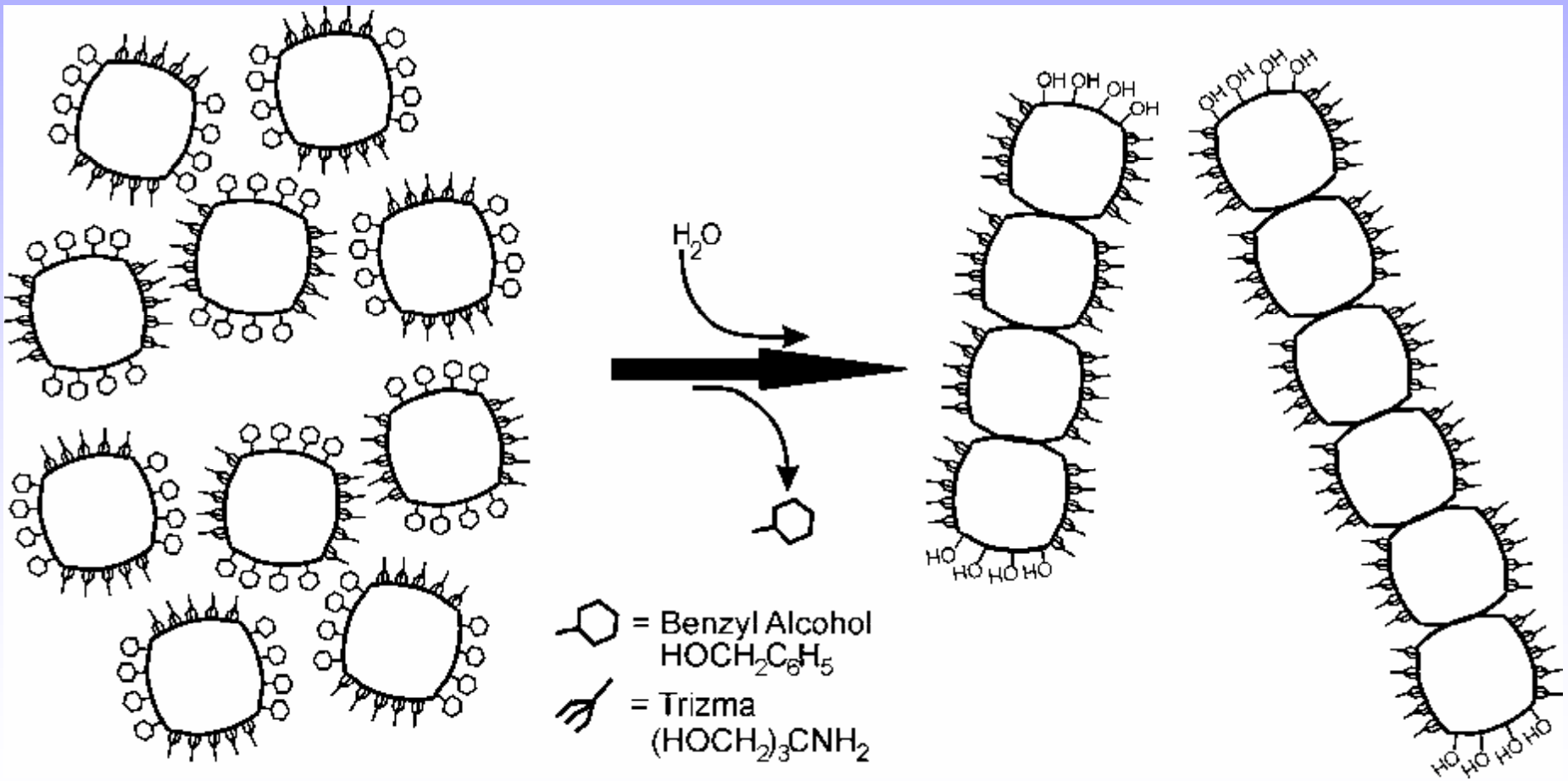
Assembly of Nanoparticles into Nanowires

Concept - Idea



Polydentate ligands expected to provide best selectivity!

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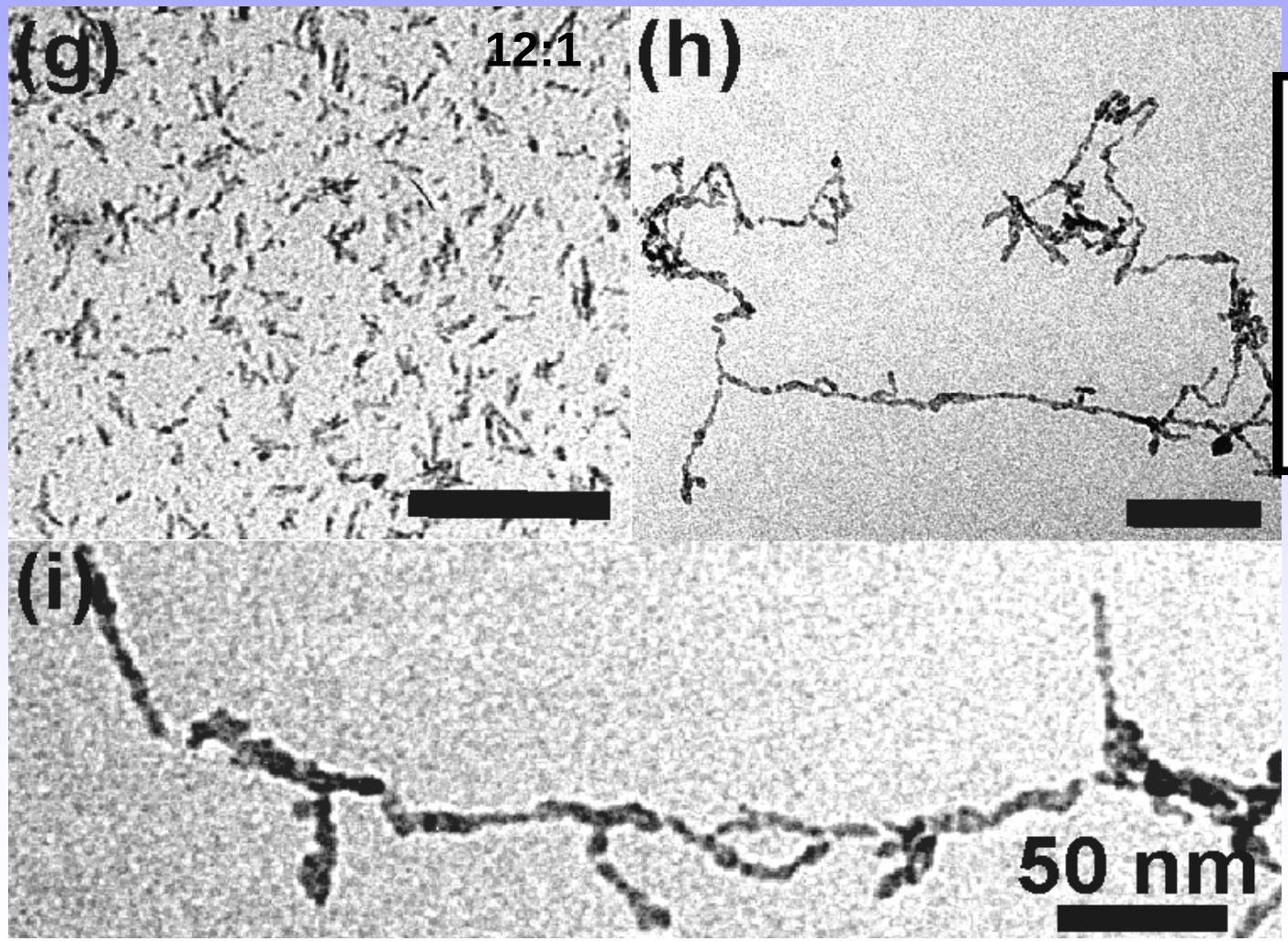
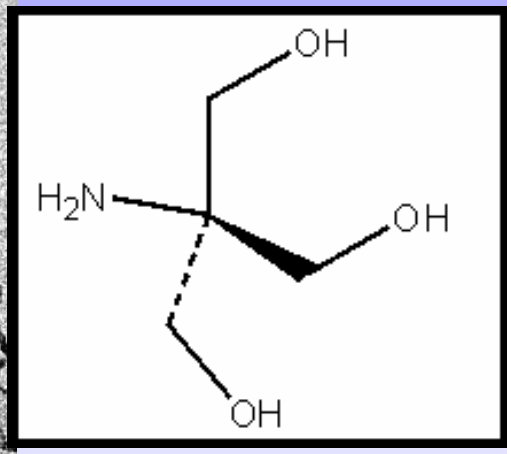
Assembly of Nanoparticles into Nanowires



Scale bar: 100 nm



Structures up to 1μm: 200 particles and more arranged!

Bottom-up approach for small nanostructures!

Adv. Mater. **2004**, *16*, 436

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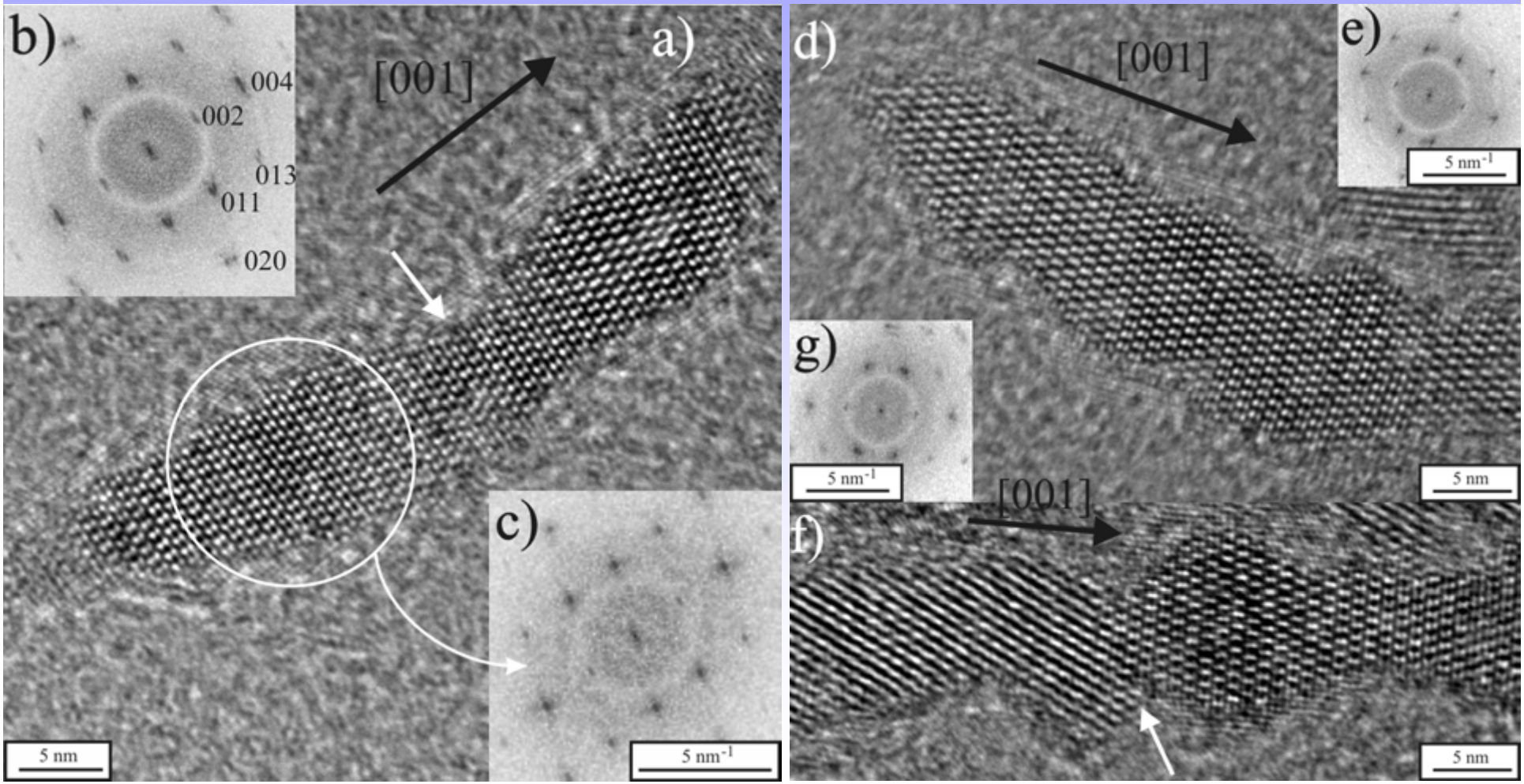
Assembly of Nanoparticles into Nanowires



Adv. Mater. **2004**, *16*, 436

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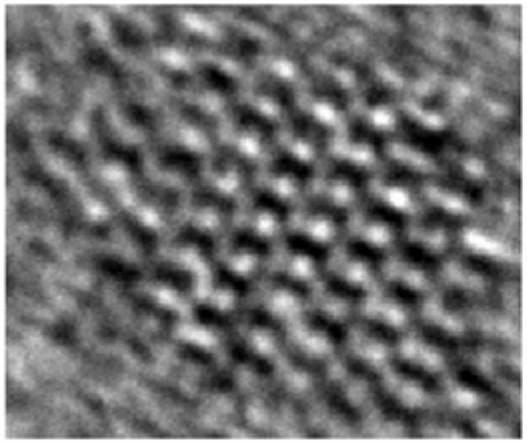
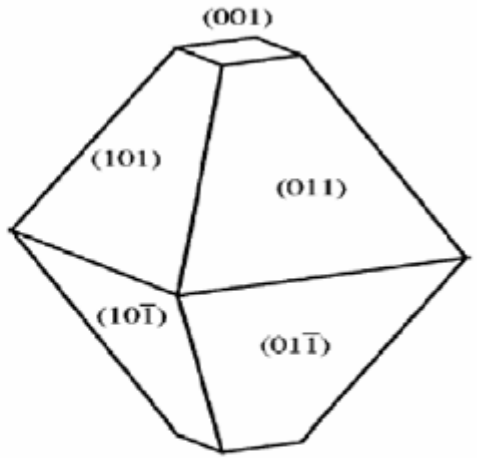
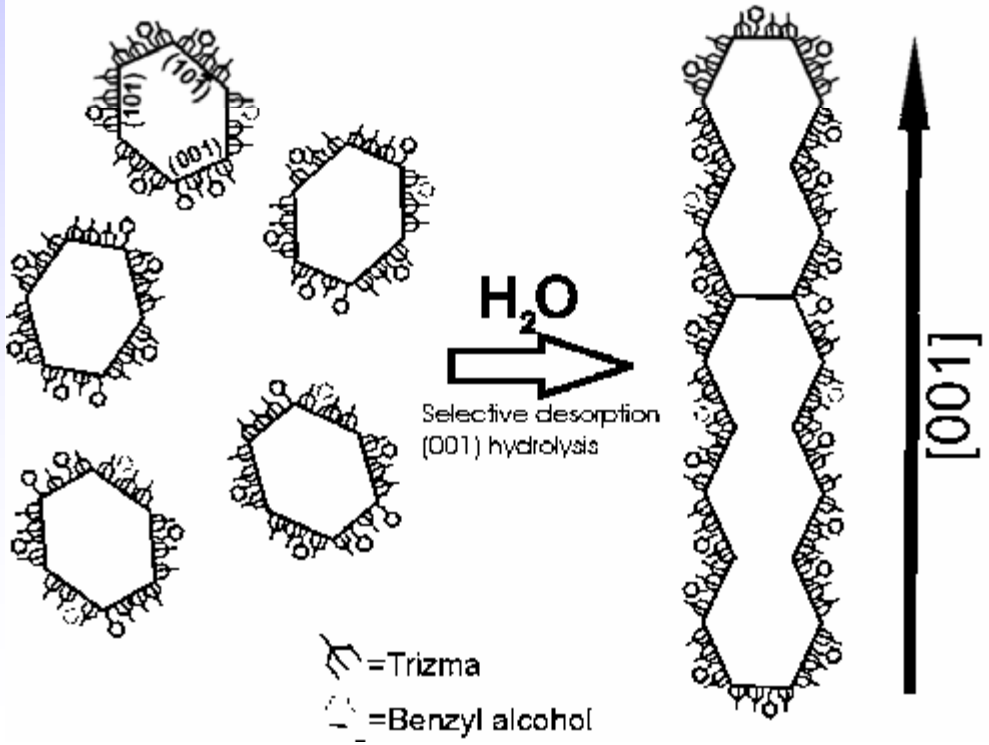
Possible explanation:

- (001) has the highest surface free energy
- (001) shows a different reactivity towards water
- Trizma binds to all crystal faces during synthesis
- Trizma desorbs faster from the (001) face during reflux

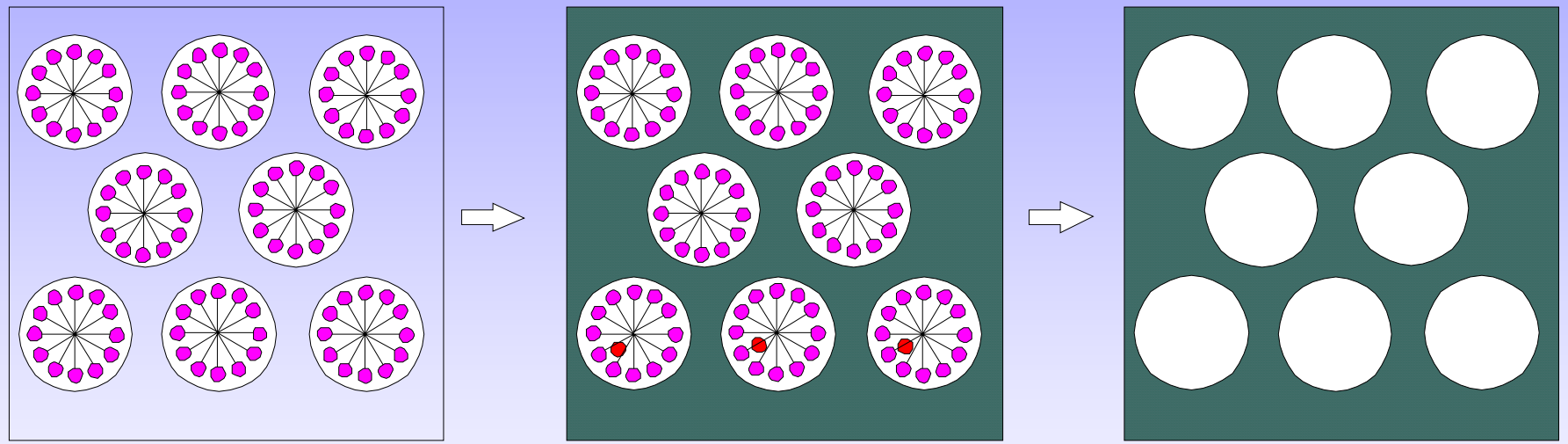






Chem. Eur. J. **2005**, *11*, 3541

B):Nanocasting



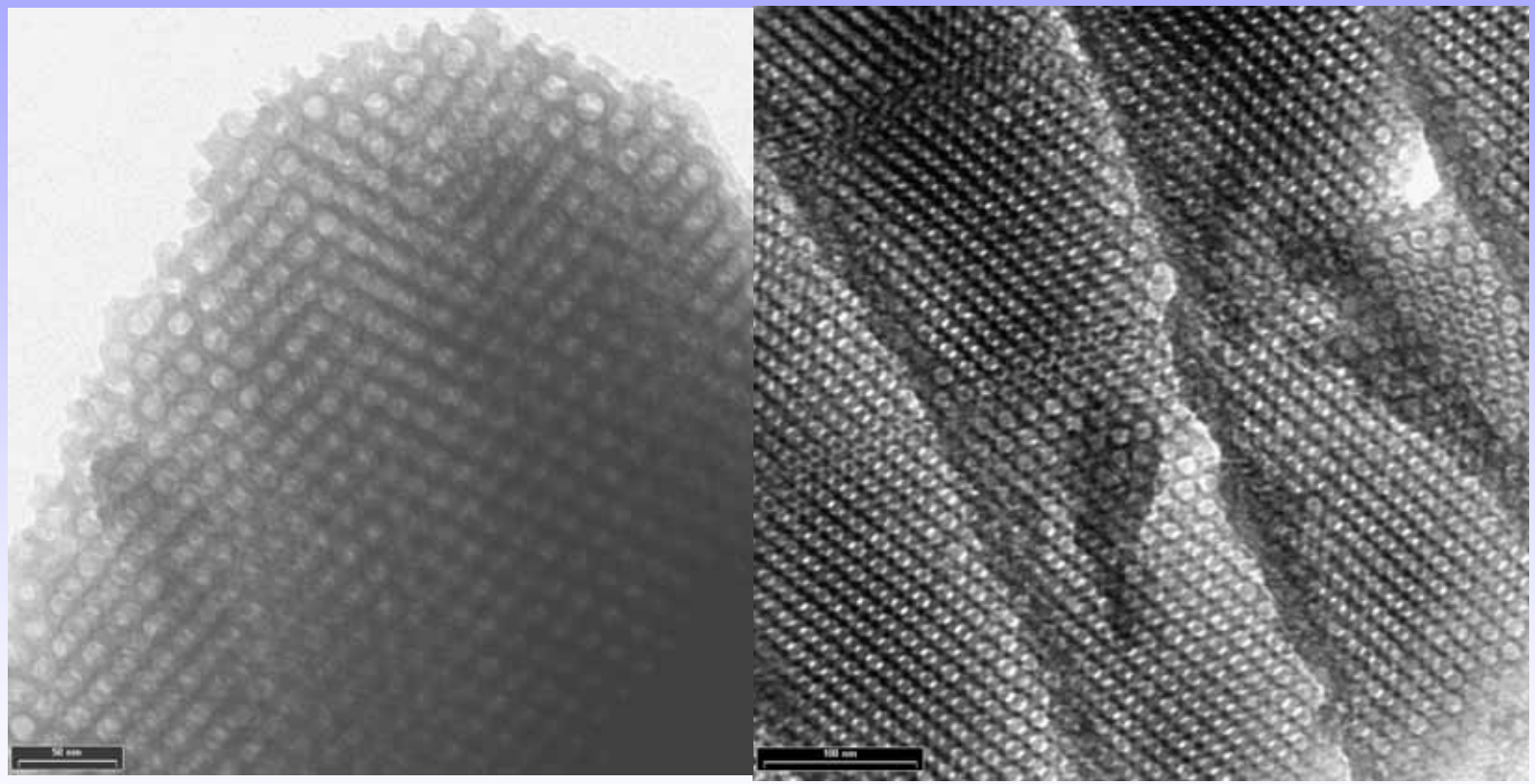
Sol-gel

Calcination

"TLCT"

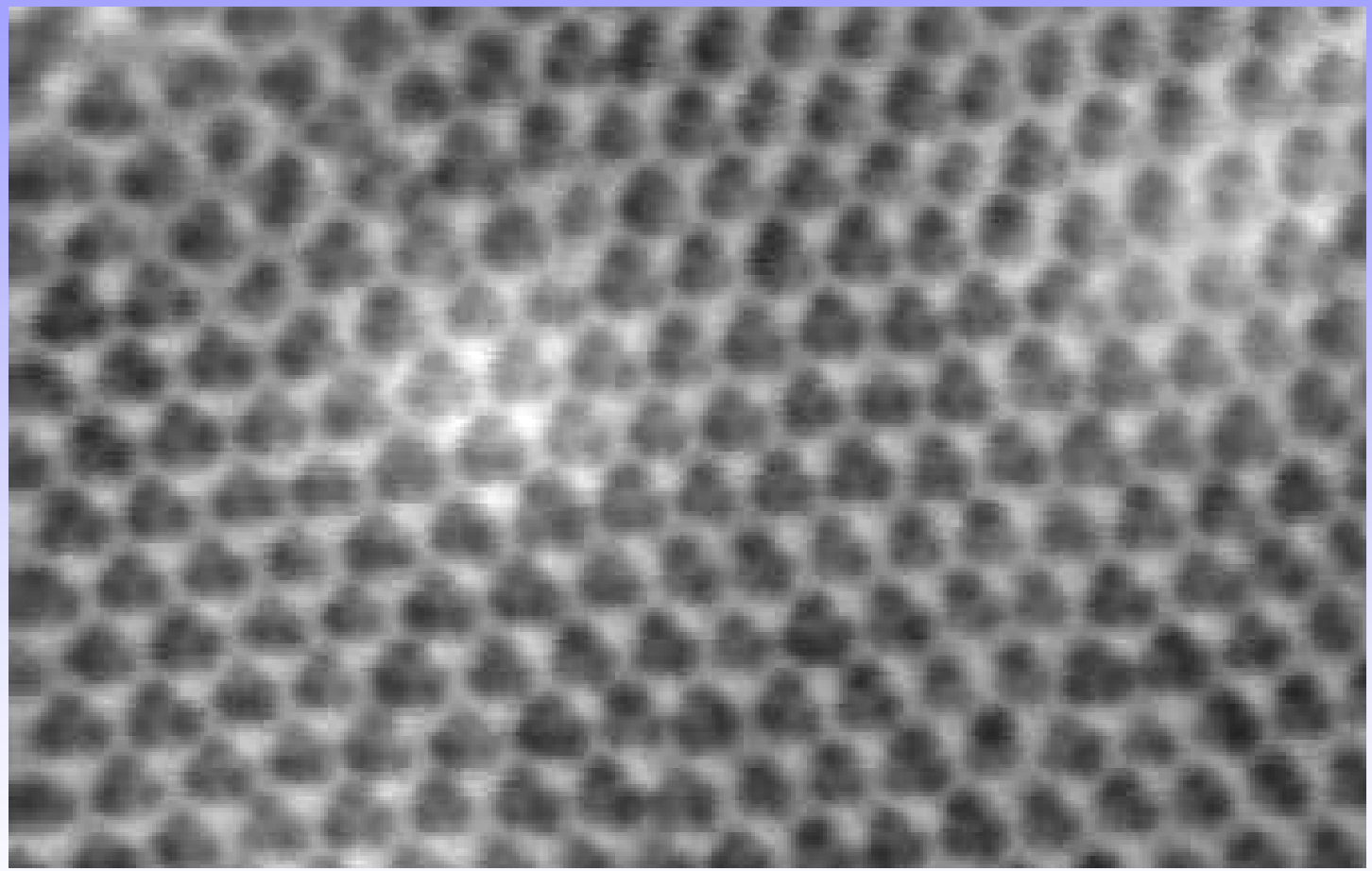
"1:1"-copy of
starting situation

Regularity of block copolymer silica



Template PHB-b-PEO = KLE-Type

Investigations of film after calcination

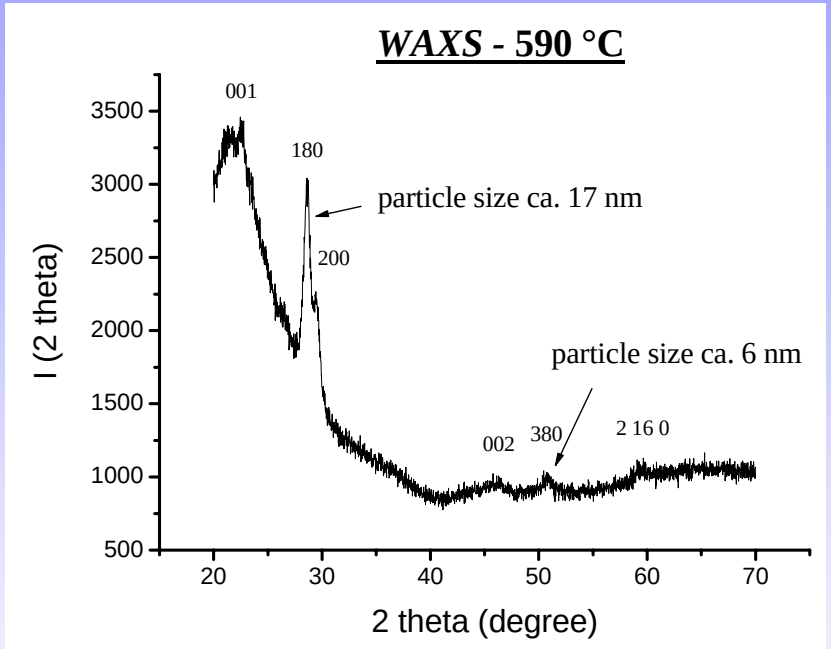


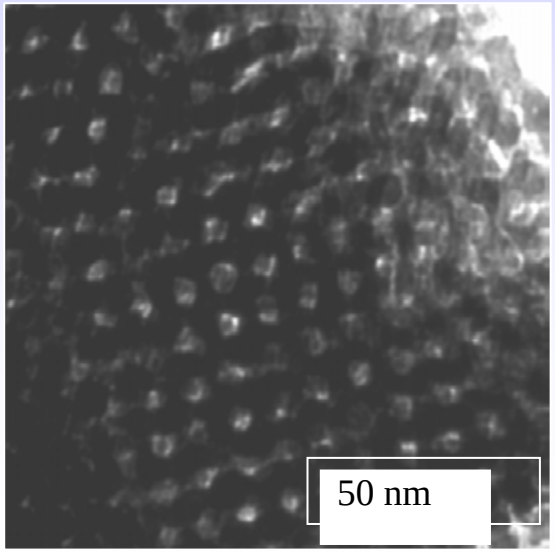
HR-SEM without contrasting: inverse opal structure with d ≈ 15 nm

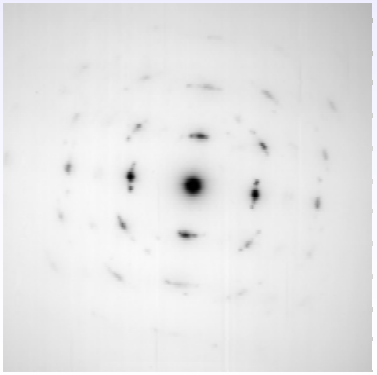
Mesoporous Nb_2O_5 films: “soft epitaxy”

WAXS evaluation of the structure shows the characteristic orthorhombic structure

- The system reveals an interesting ***nano-meso-effect***, since the crystallites are not randomly oriented.
  Therefore one peak in the WAXS pattern is more pronounced than the others.

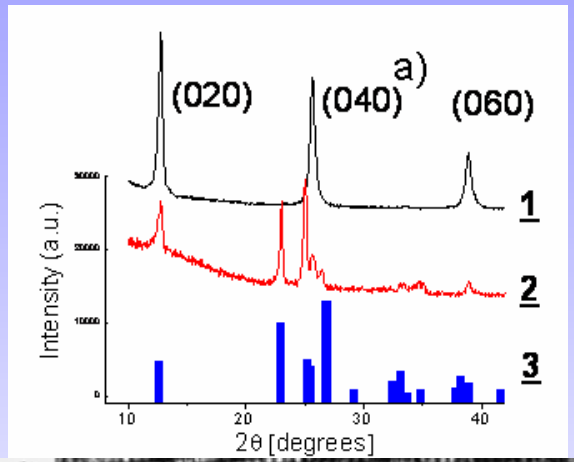


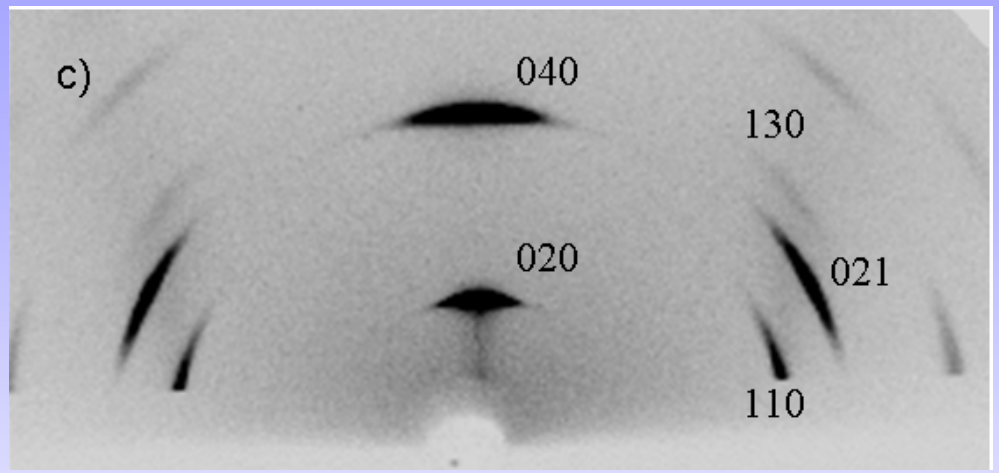


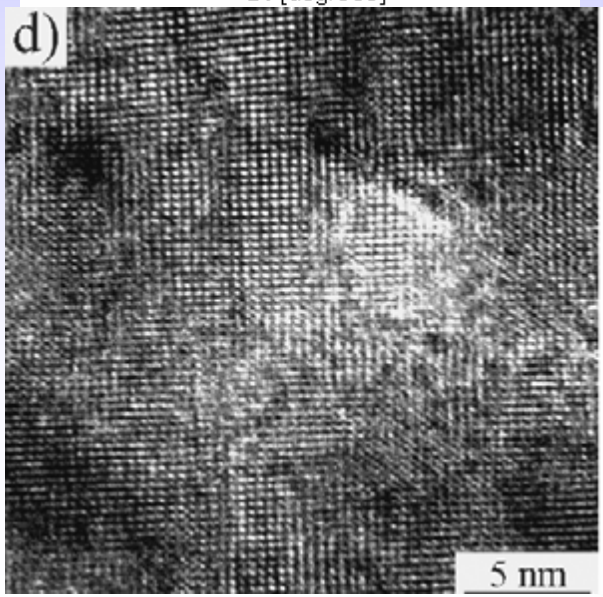


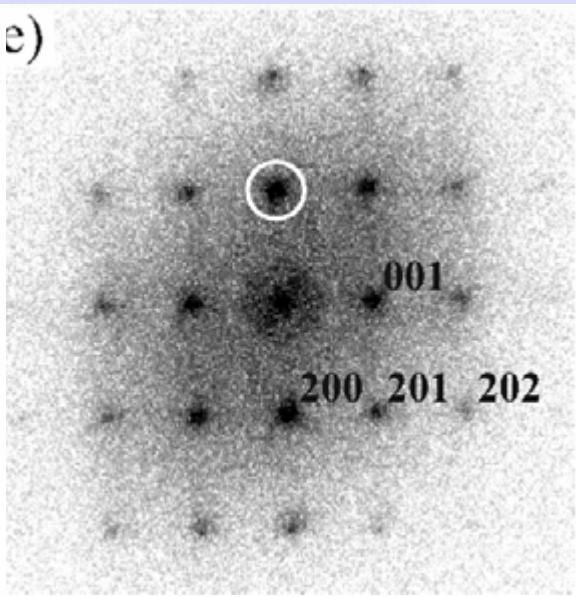
- Electron diffraction pattern of a 10000 nm^2 array

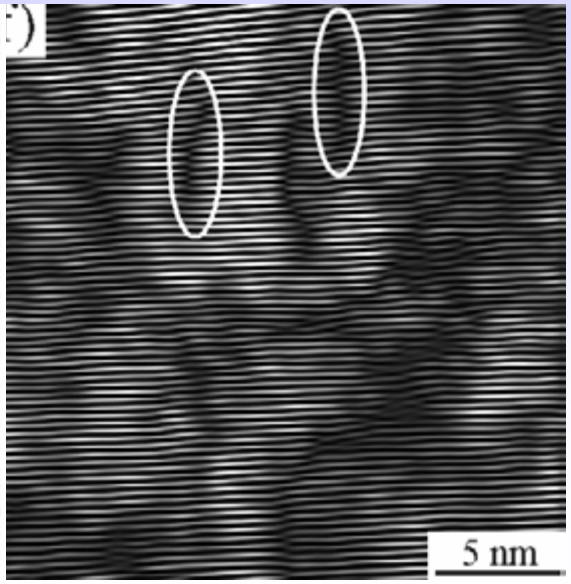
„Soft Epitaxy“ to generate oriented crystalline films (here WO_3)









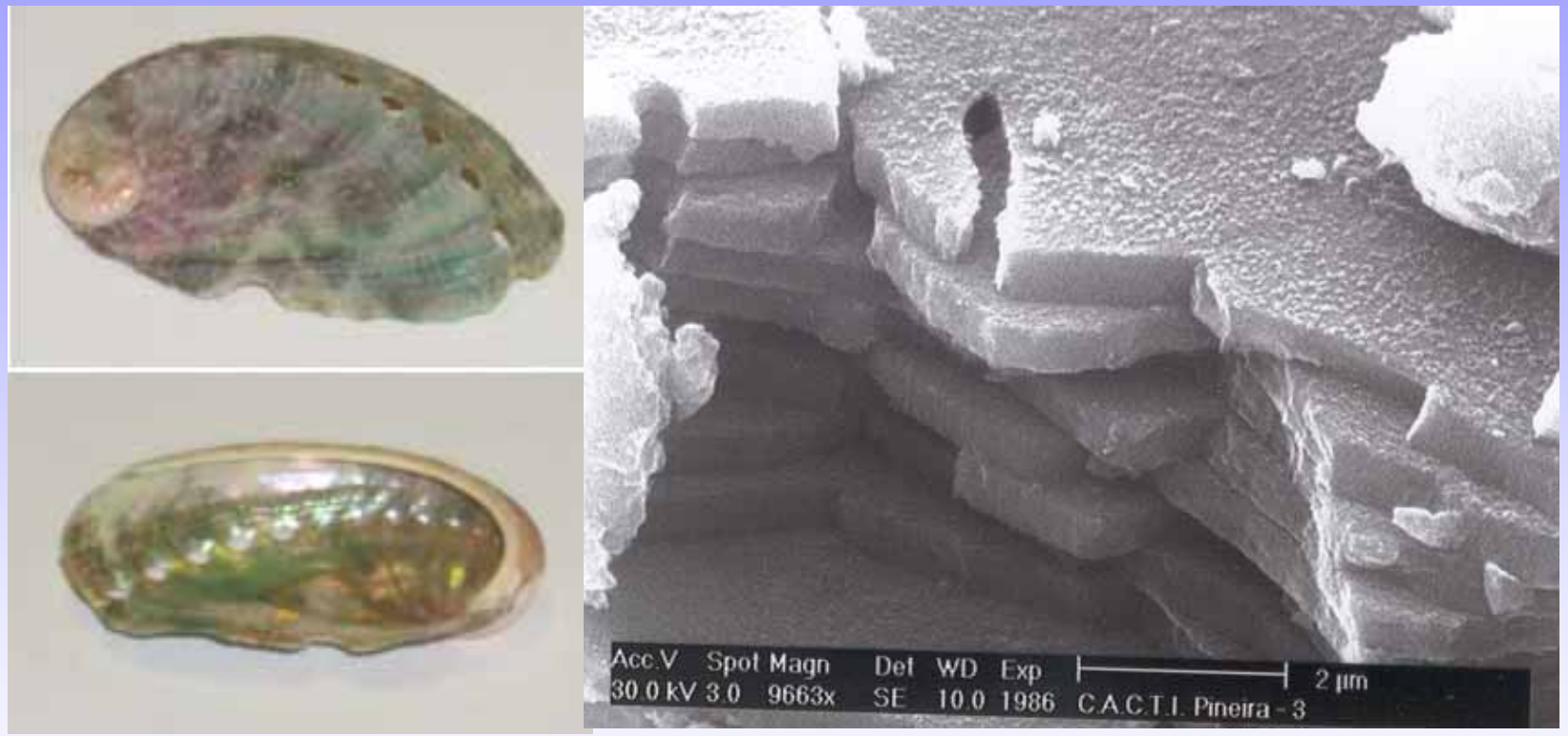


Bernd Smarsly, MA et al., submitted

C): dynamic templates

polymer controlled crystallization

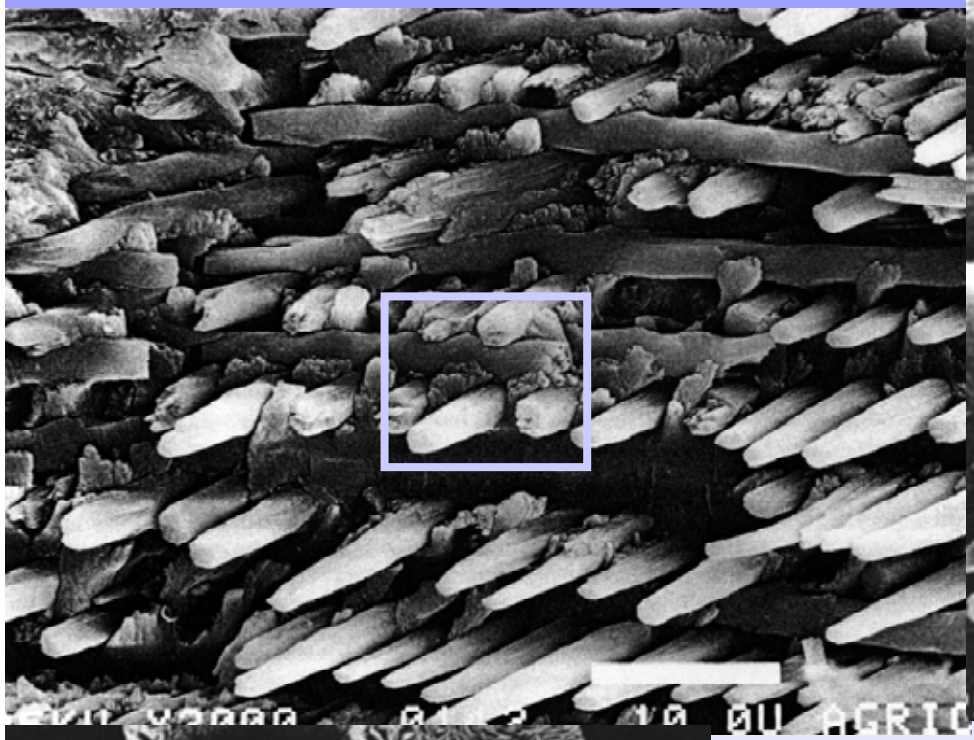
Motivation: Biominerals

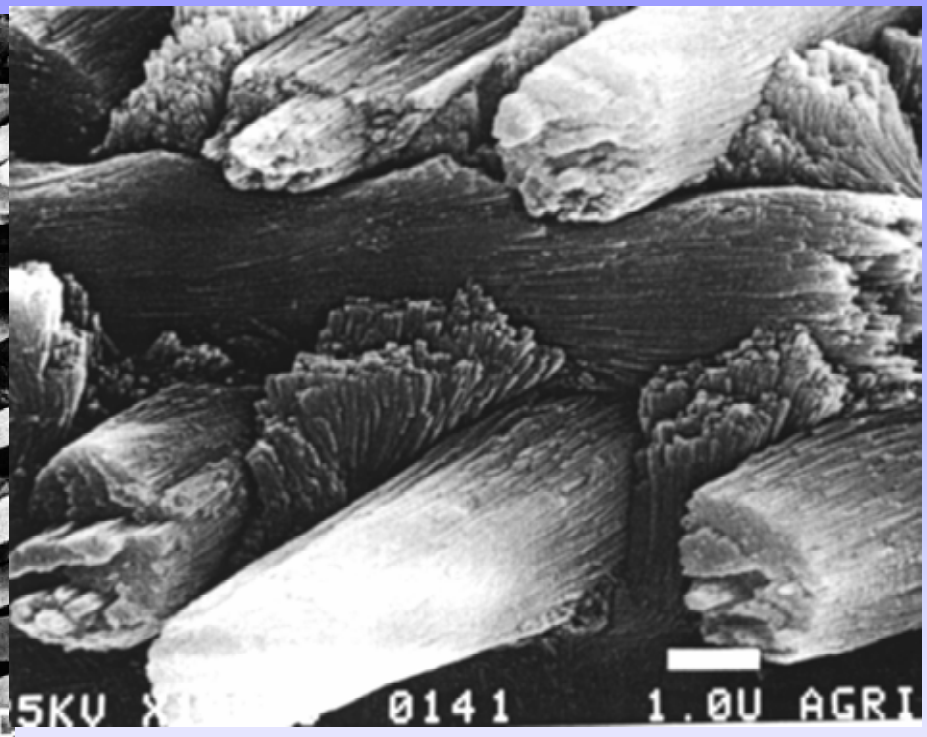


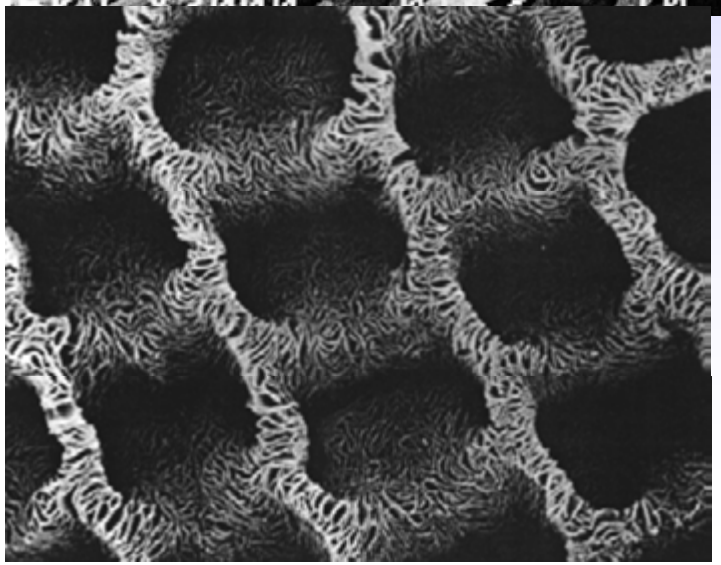
Crystal structure: Aragonite

Abalonia: mechanical properties / non-sticky !

Tooth enamel

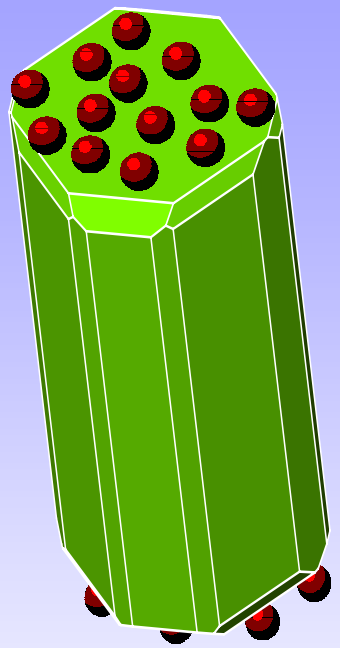






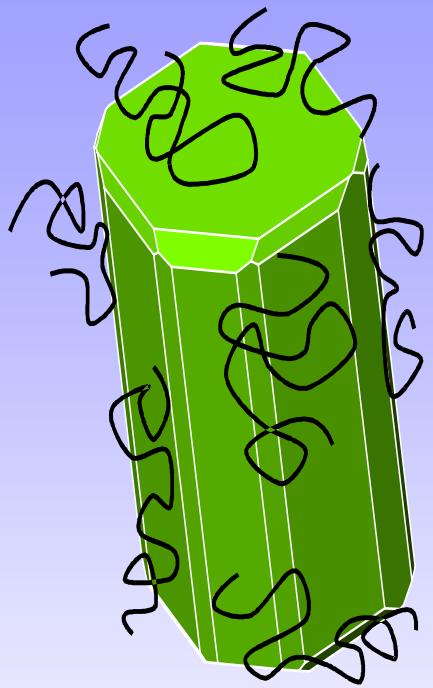
- Crystallization and assembly of fibers into rods on the μm scale
- Ordered layer structure of rods provides mechanical strength
- Permanent further crystallization and density increase up to 95 wt.-% mineral

Concepts



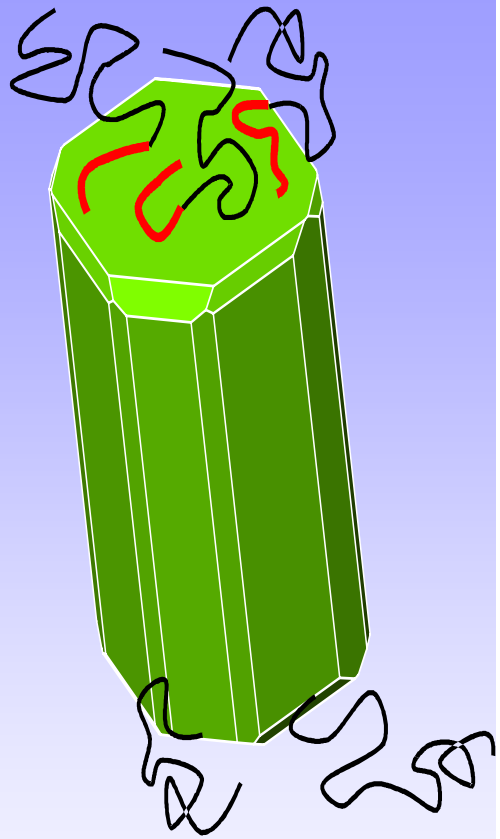
Selective absorption of ions or low molar mass additives

Directed crystal growth but no stabilization



Stabilization by polymers

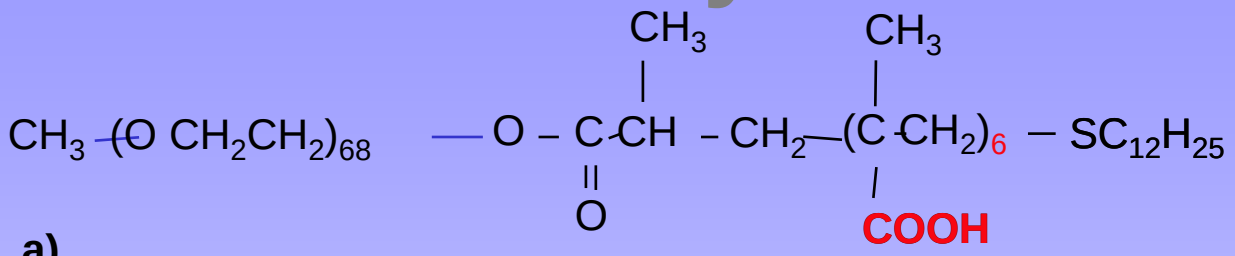
Stabilization but no directed crystal growth



Selective absorption of hydrophilic block copolymer with functional & stabilizing block

Directed crystal growth and stabilization

Syntheses



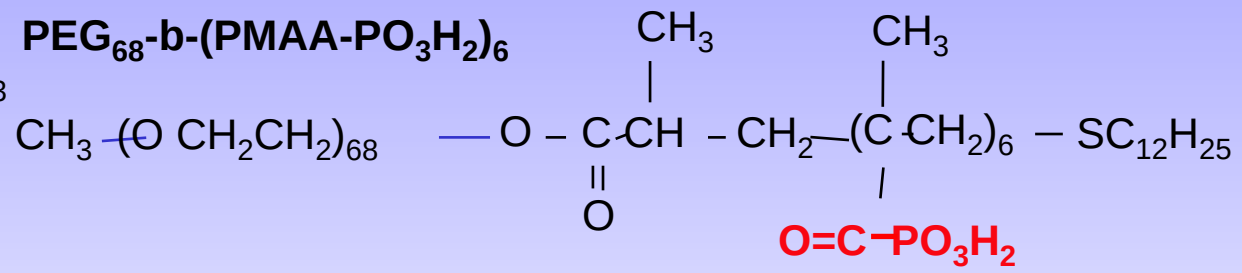
PEG-b-PMAA

a)

PCl_3 / H_3PO_3

CH_3SO_3H

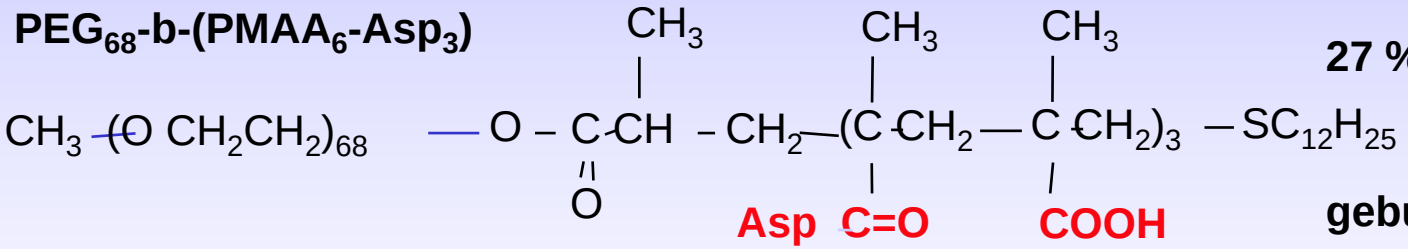
PEG_{68}-b-$(PMAA\text{-}PO_3H_2)_6$



b)

1) $SOCl_2$
2) Asp

PEG_{68}-b-$(PMAA_6\text{-}Asp_3)$



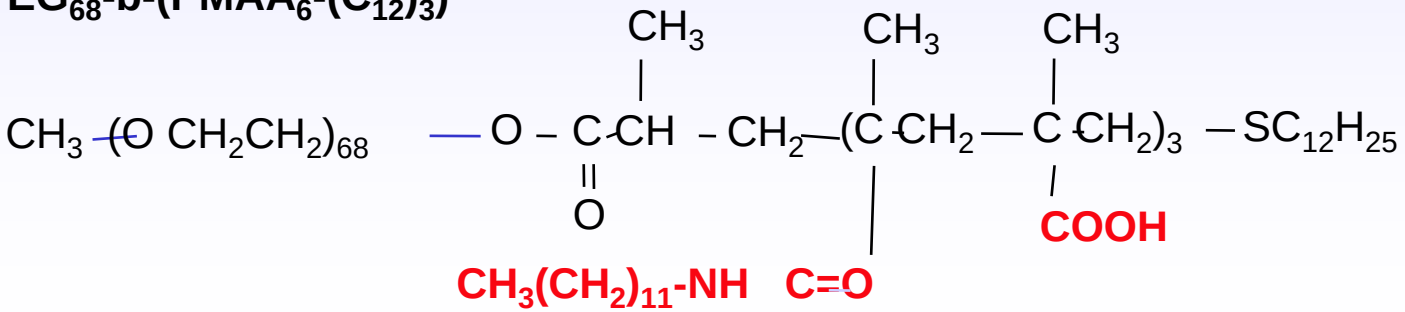
27 %Asp

gebunden

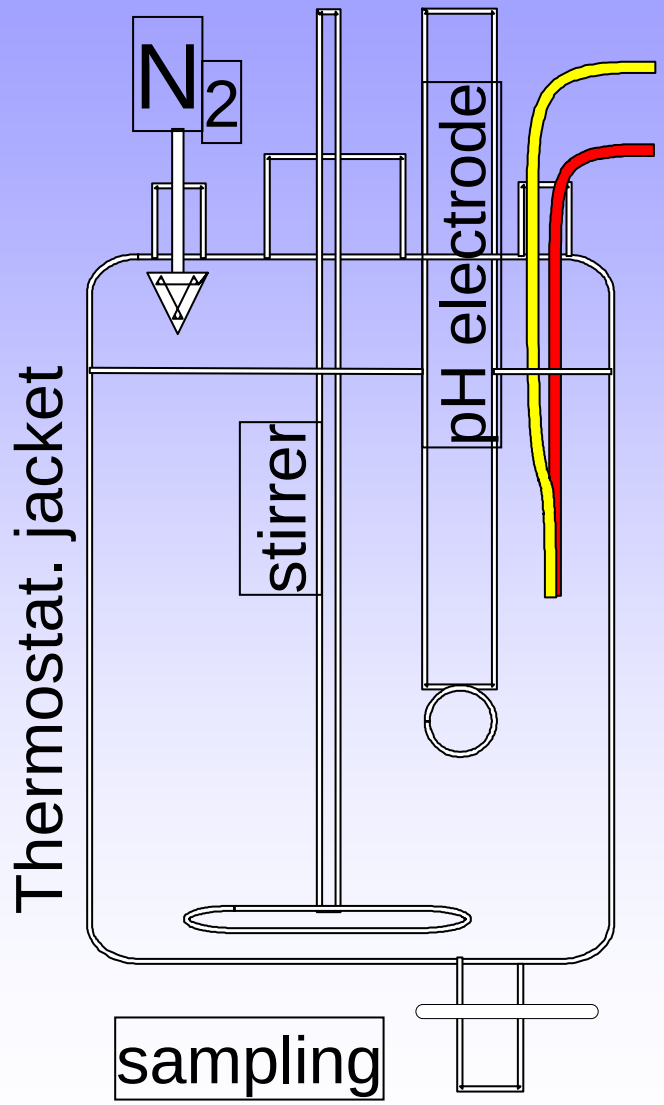
c)

1) $SOCl_2$
2) $CH_3(CH_2)_{11}$-NH_2

PEG_{68}-b-$(PMAA_6\text{-}(C_{12})_3)$



$CaCO_3$ formation in the double jet reactor



$CaCl_2$

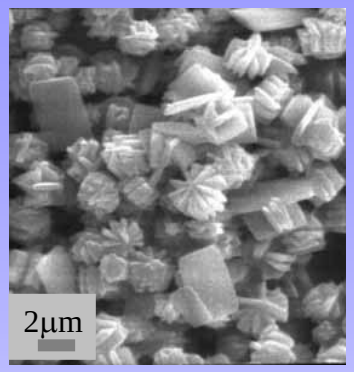
Na_2CO_3

0.5 mol/l Na_2CO_3

0.5 mol/l $CaCl_2$, pH 8.5

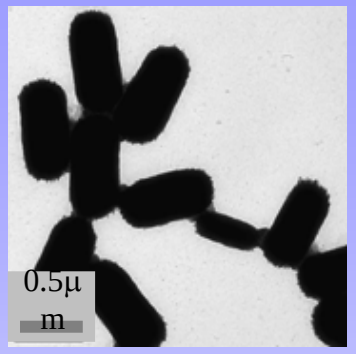
- 300 ml aqueous polymer solution, (0.1 - 1 mmol) , pH 8.5, 25 °C
- 10 ml/h Na_2CO_3 & $CaCl_2$ (83.3 μmol/min $CaCO_3$ formation
- pH is recorded

$BaSO_4$ formation with different polymers

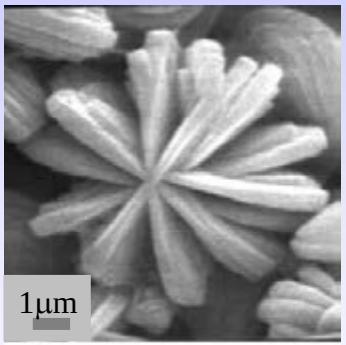


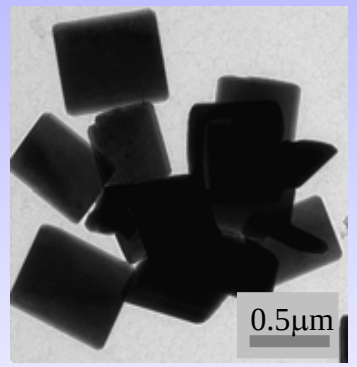
PEG

PMAA

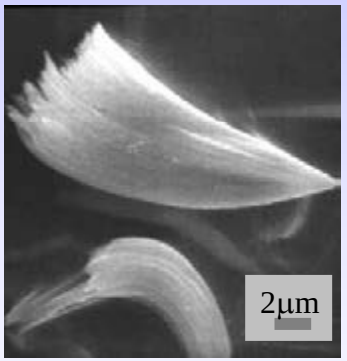


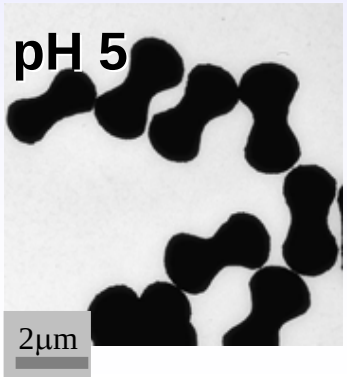
PEG-b-PEIPSA

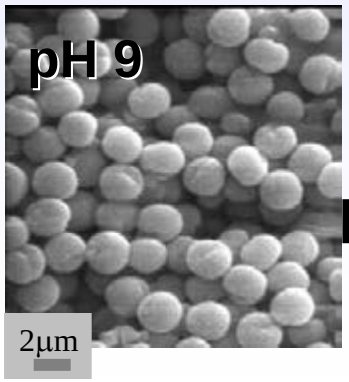




PEG-b-PMAA-PO_3H_2



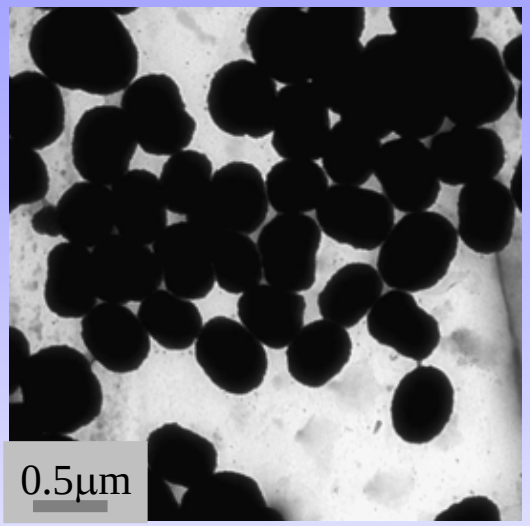


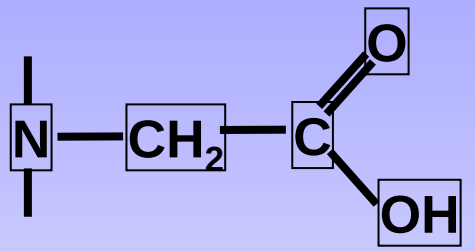


PEG-b-PMAA-Asp

Inner structure of $BaSO_4$ peanuts

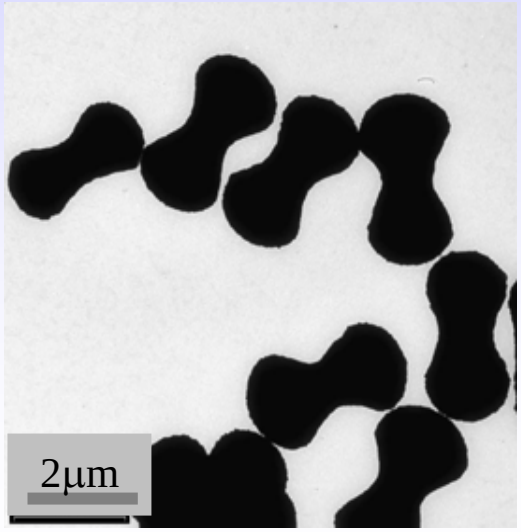
pH = 9

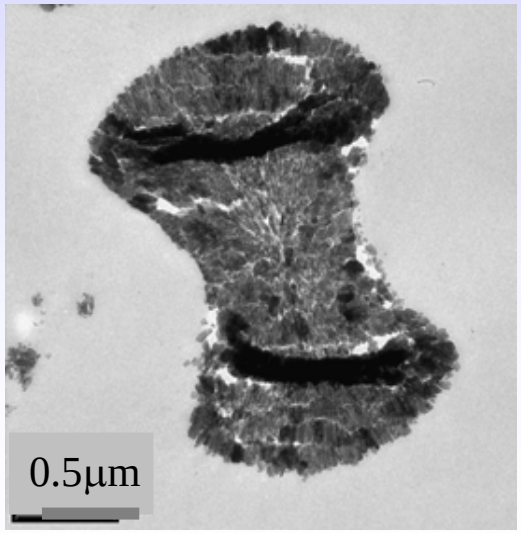


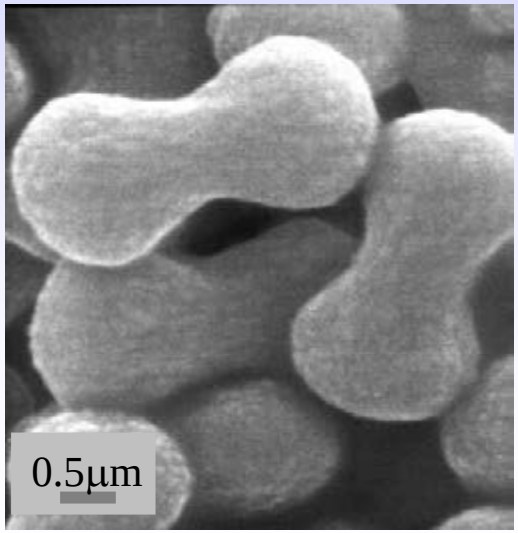


PEG-*b*-PEDTA

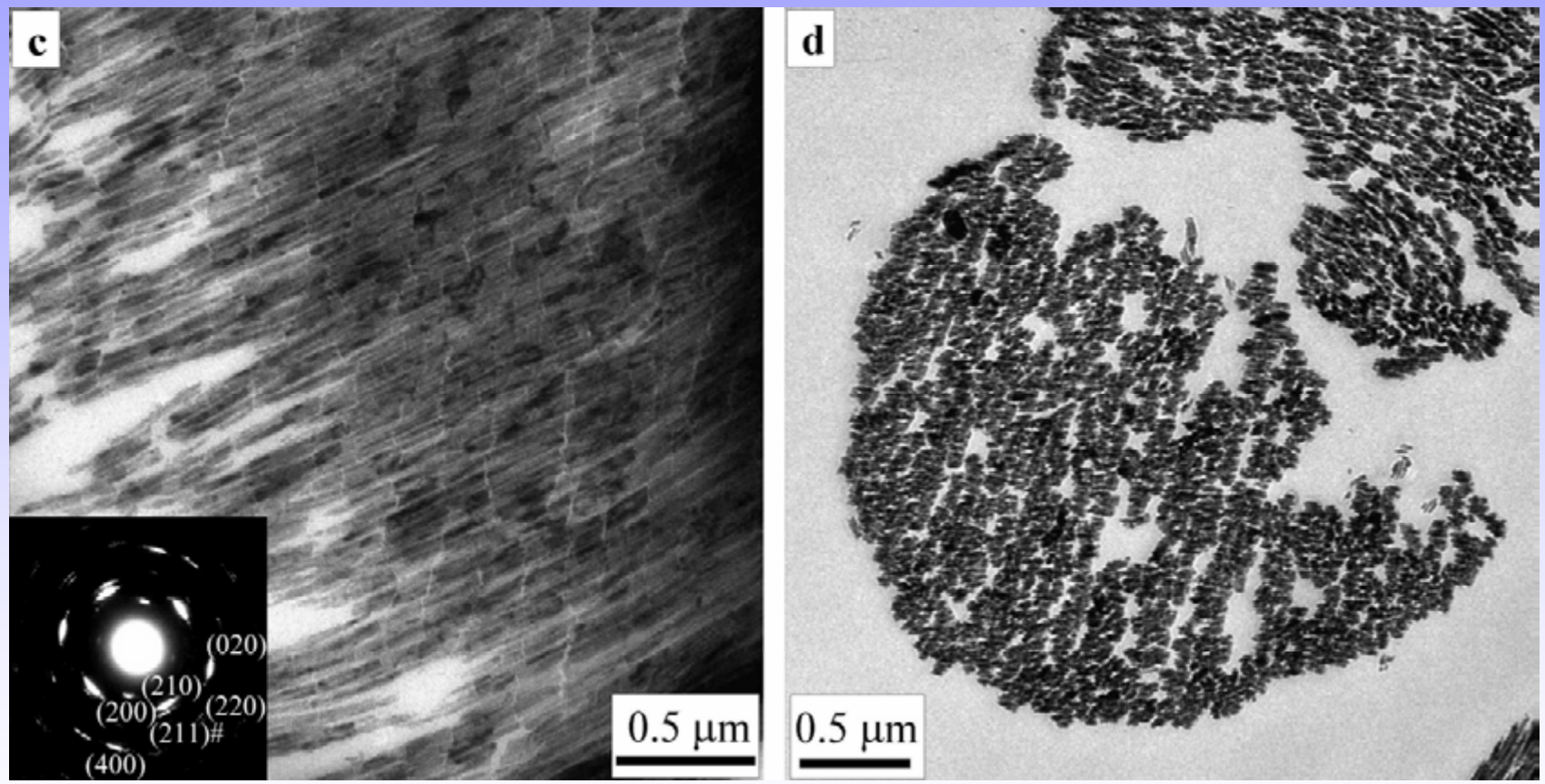
pH = 5







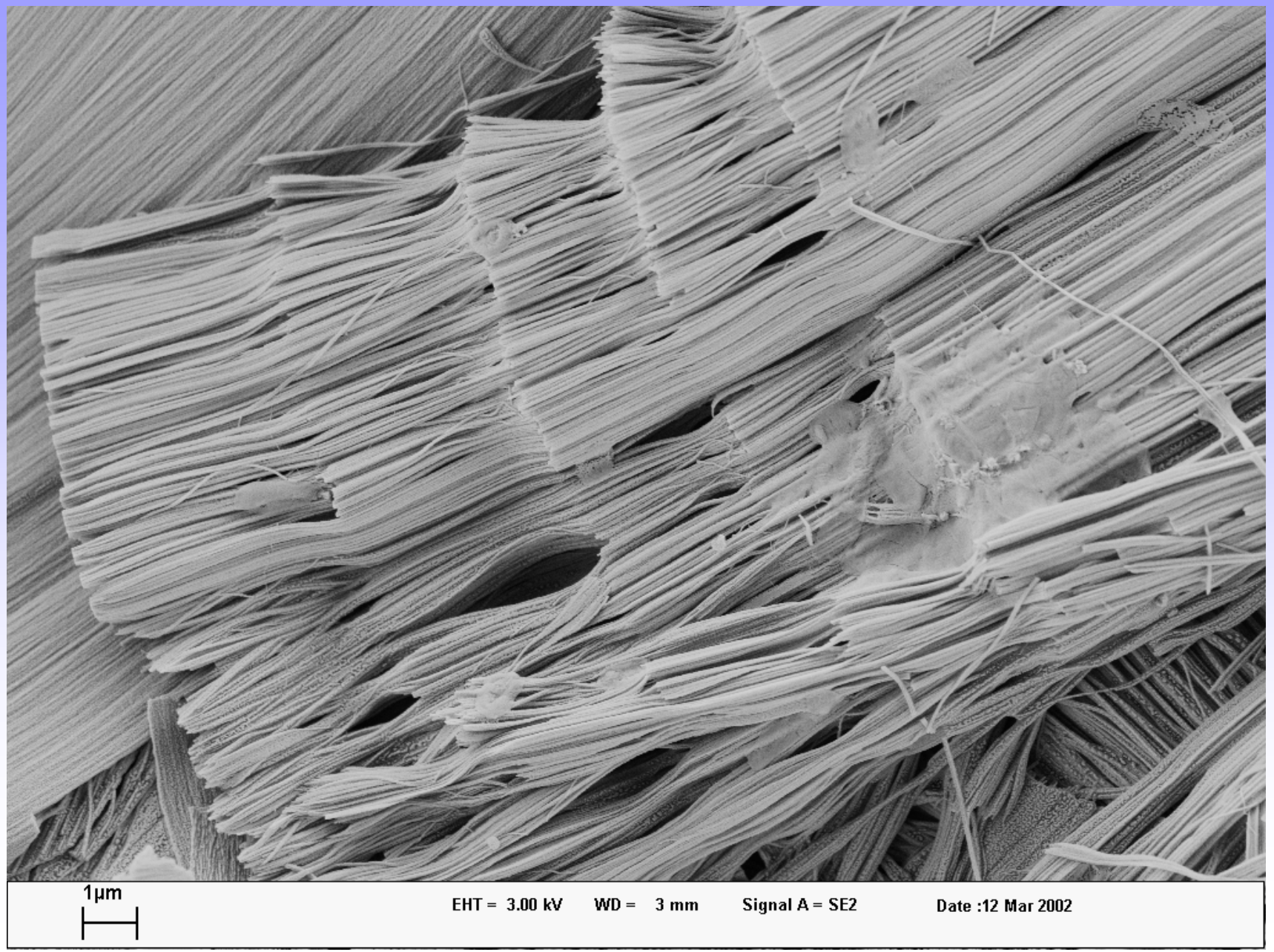
$BaSO_4$ fibre formation, pH 5



Parallel cut to to fiber axis
Fiber axis is [120]

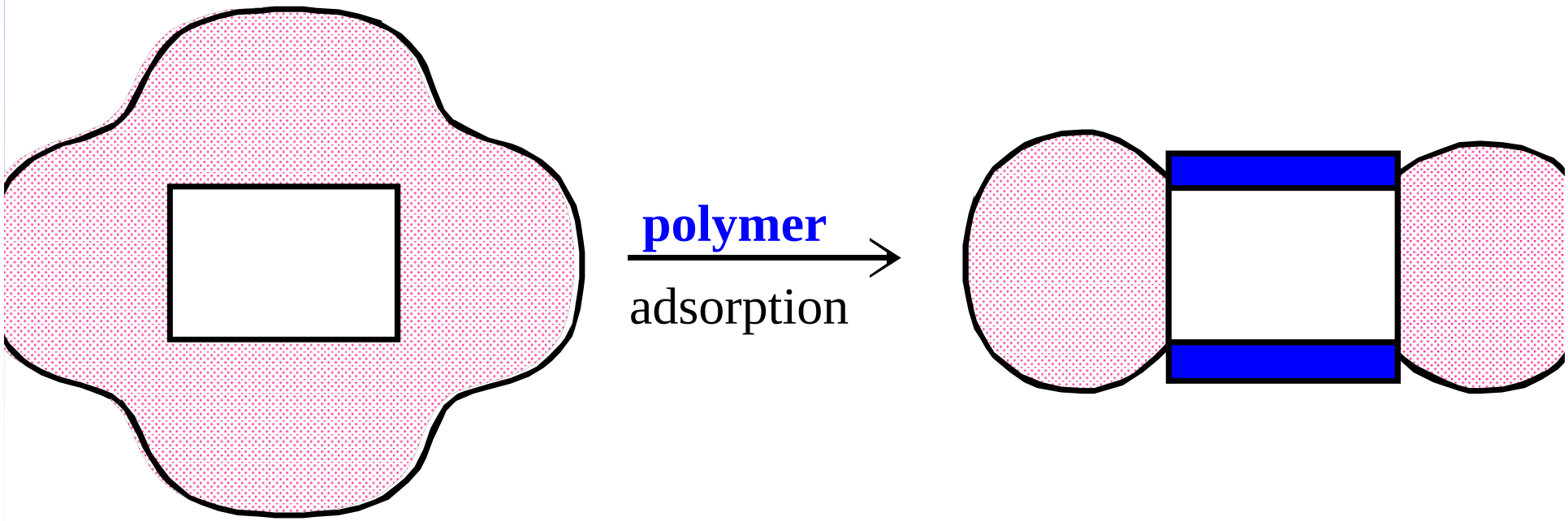
Perpendicular cut to fiber axis
Diameter 20 - 30 nm

Figure 2: BaSO4, 2 mM, polyacrylate (Mn = 5100) 0.11mM, pH = 5.5, Room temperature



obviously something got „wrong“: not only particle shape control, but superstructure at the same time !

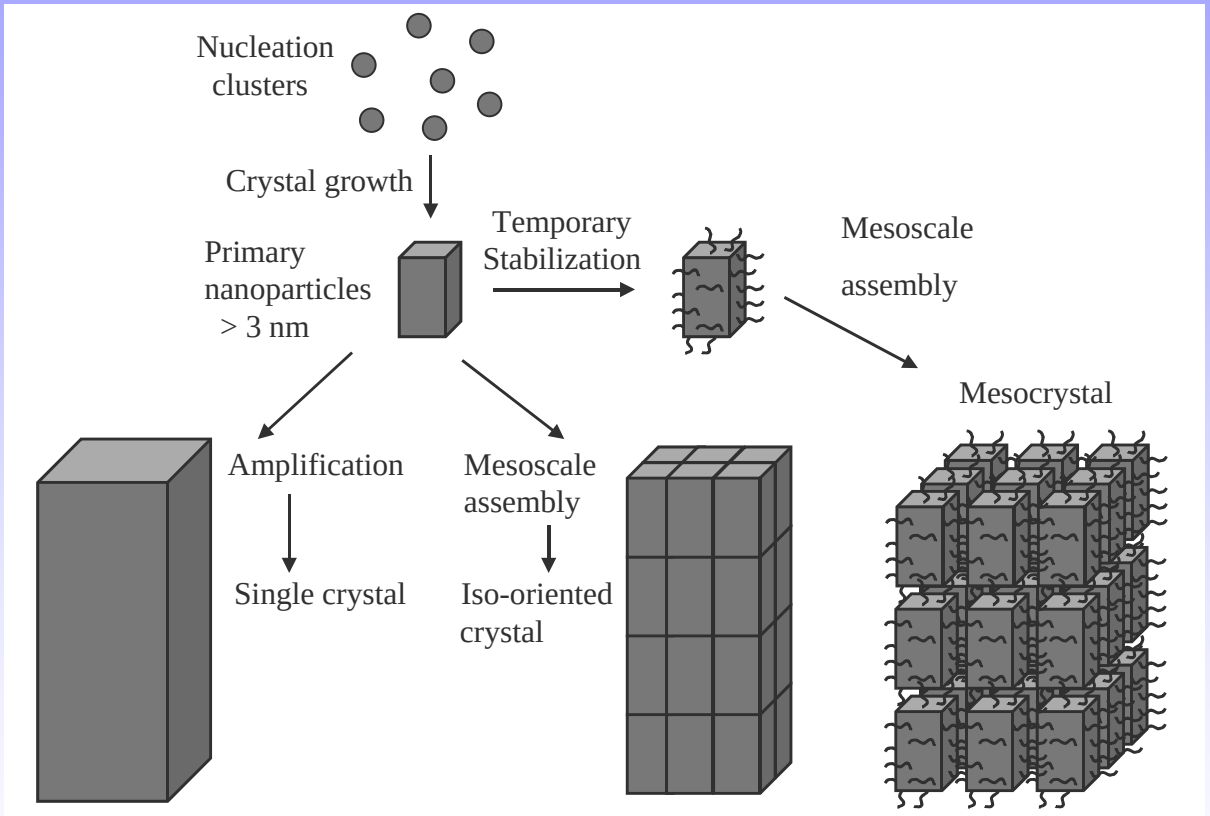
→ These are coupled processes, also in nature !



This is the base for vectorial alignment of nano-blocks in a vectorial fashion

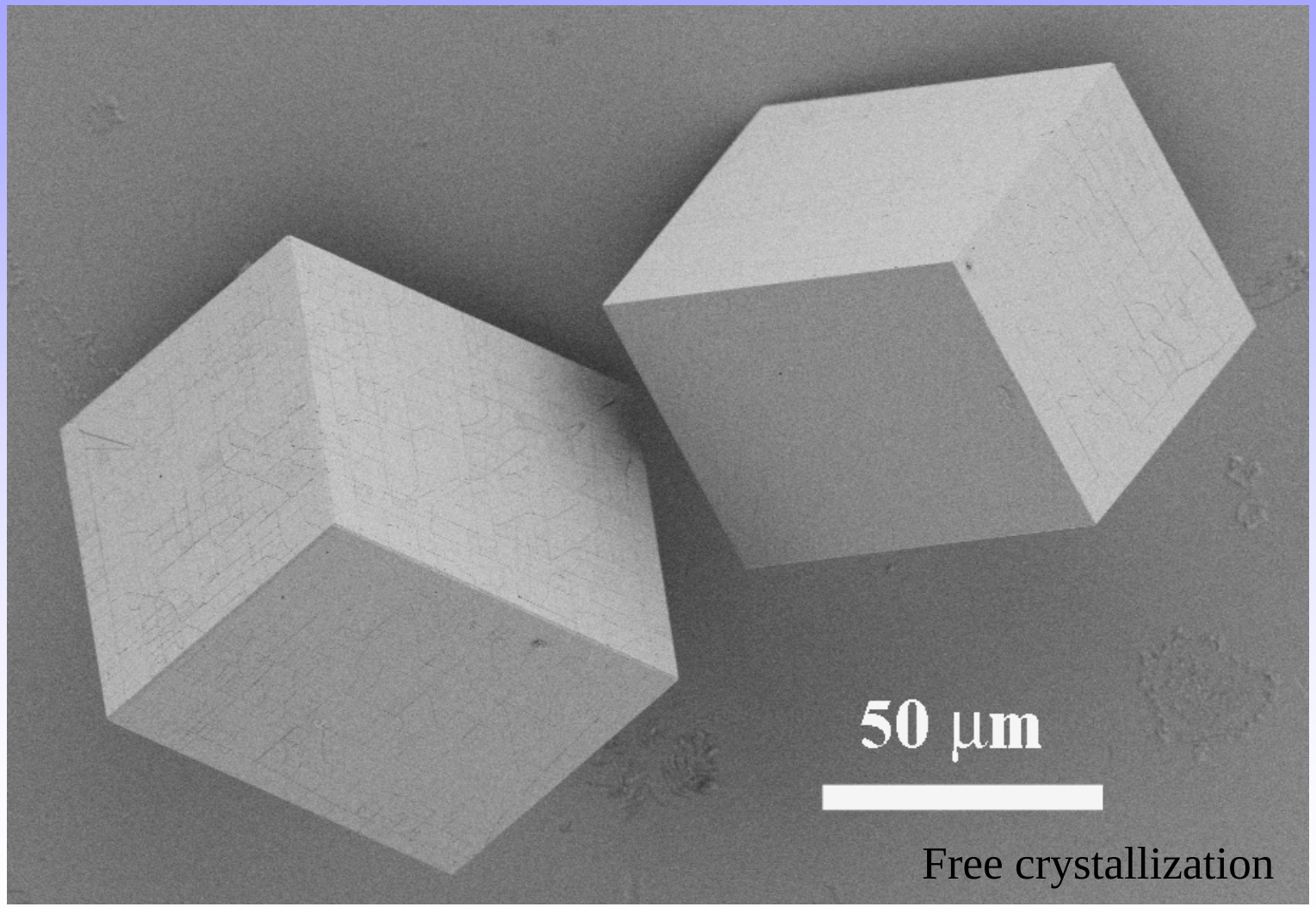
“self assembly can go 3d”

The „mesocrystal“ concept

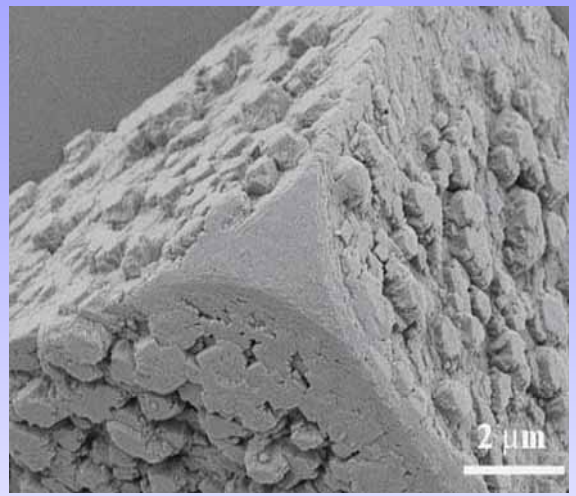


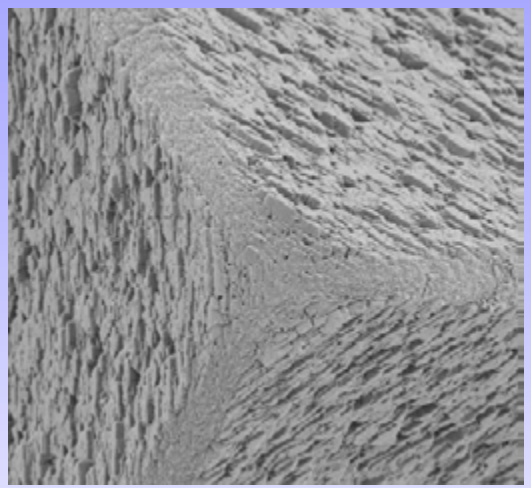
Statement (& overwhelming literature evidence): most „real“ crystallization events (high supersaturation) undergo „mesocrystallization“

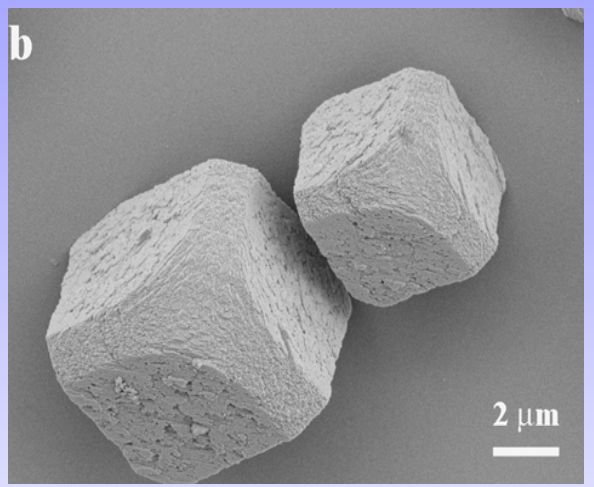
$CaCO_3$: The model biomineral (the drosophila of biomins)



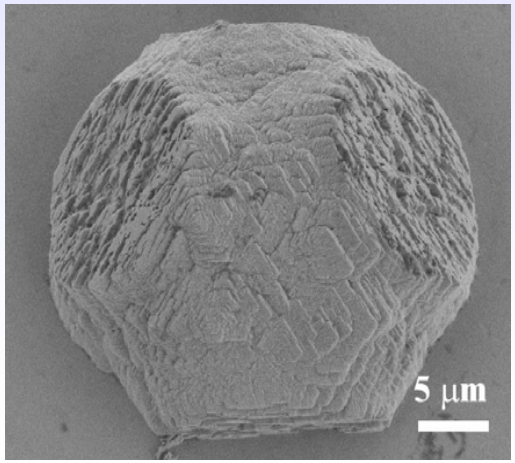
$CaCO_3$ superstructures I: the suppression of corners

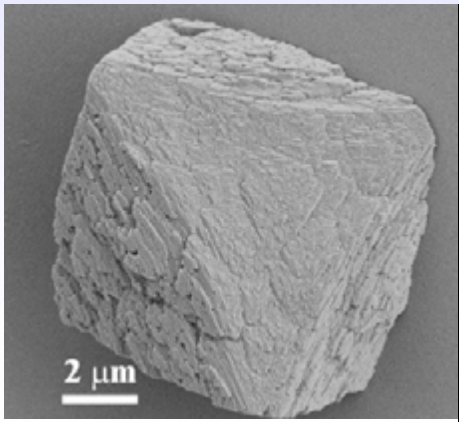


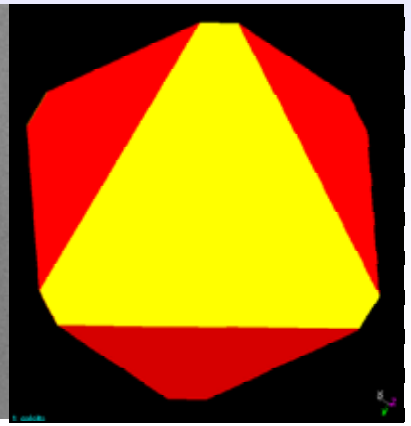




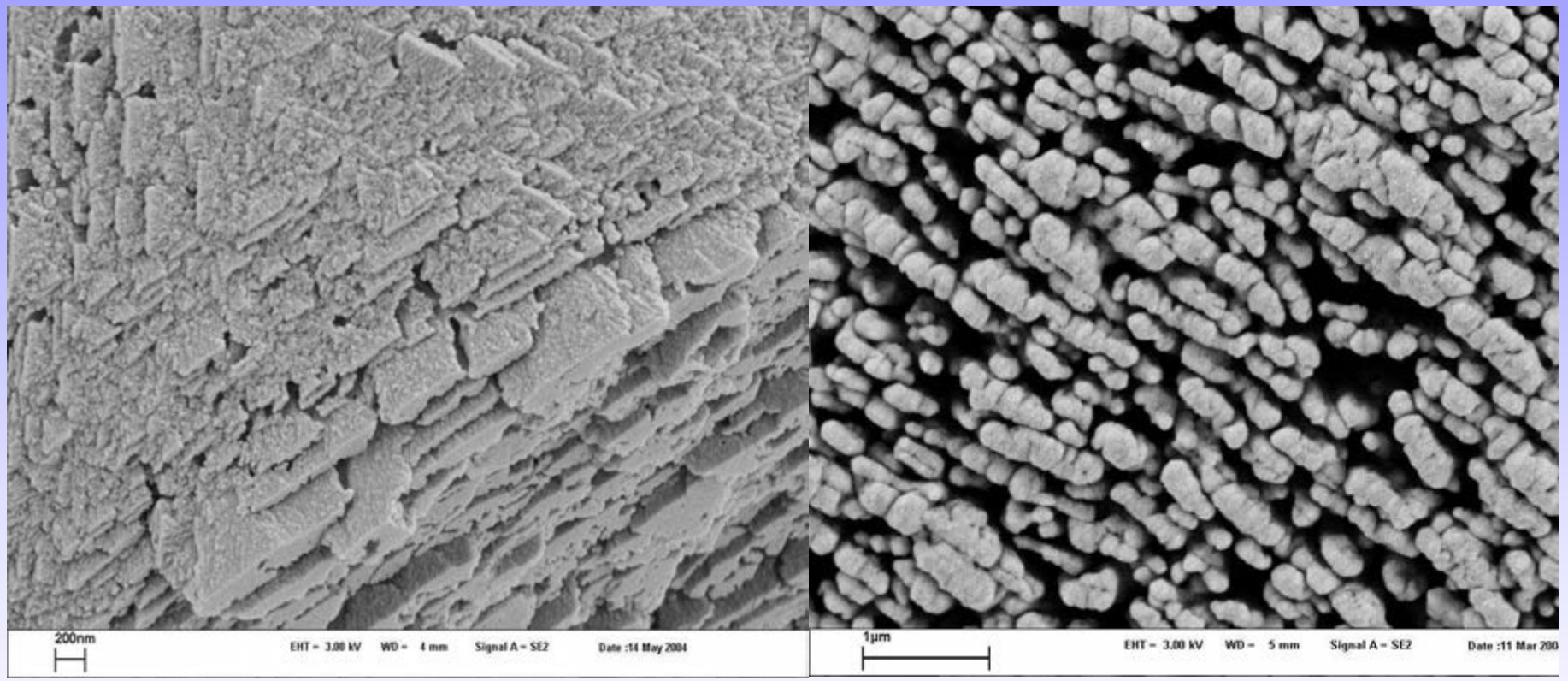
Successive addition of polystyrenesulfonate







Structural porosity of $CaCO_3$:

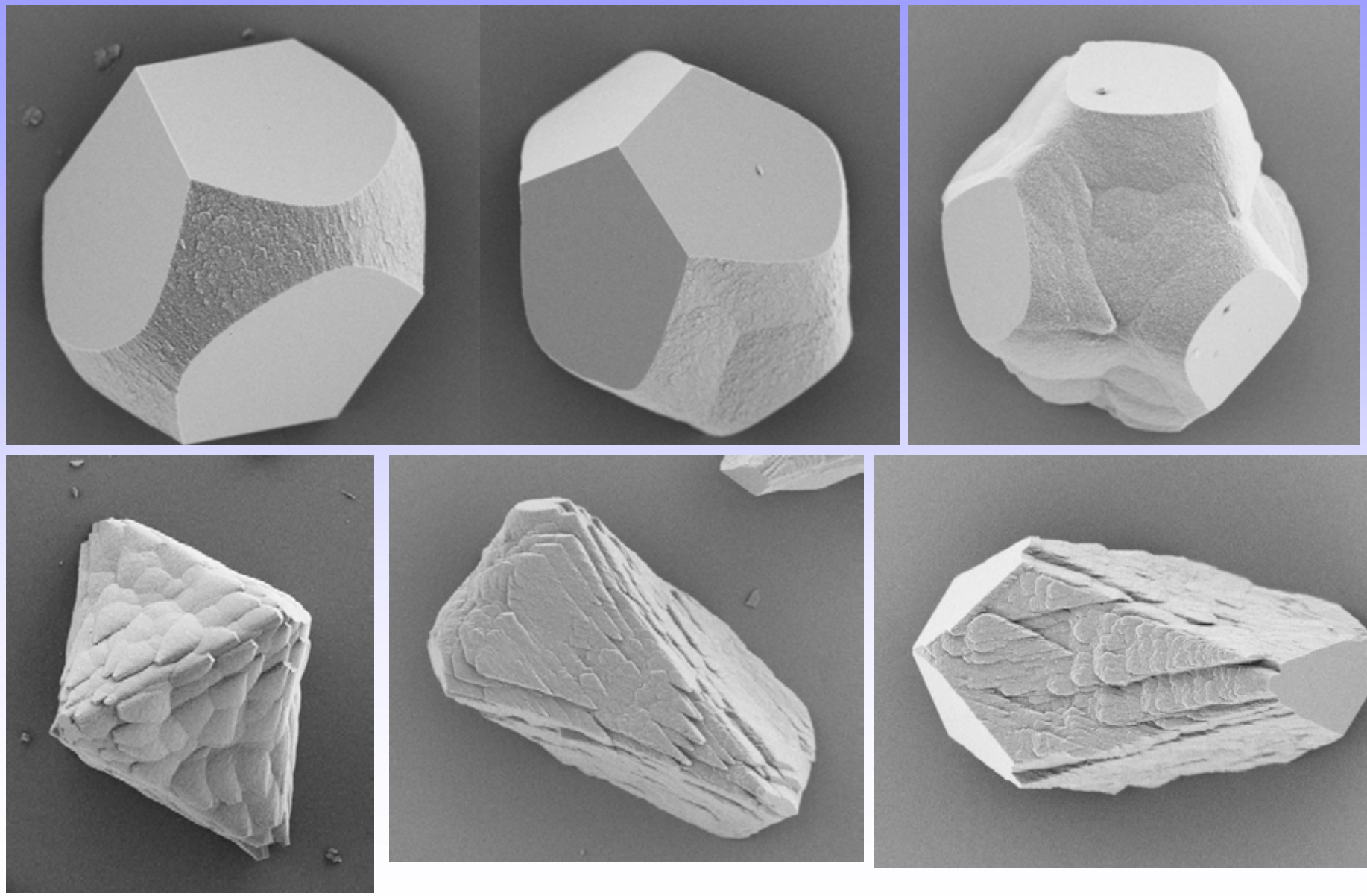


BET surface area: 280 – 400 m^2 /g !

Absorbants, printing technology

remind: polymerization of nanoparticles !!

„MORPHING“



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