

# Synthesis of Nano Particles

## 1. Spheroids, Clusters and Spheroidal Holoids

Insulators: Halides, Oxides, Nitrides

Hard/Strong Matter: Carbons, BN, etc.

Semiconductors: Chalcogenides

Metals: Noble Metals, Magnetic Metals

Organic Matter: Polymers, Biopolymers

## 2. Anisotropic Particles

Insulators: Halides, Oxides, Nitrides

Hard/Strong Matter: Carbons, BN, etc.

Semiconductors: Chalcogenides

Metals: Noble Metals, Magnetic Metals

Organic Matter: Polymers, Biopolymers

31.10.2007

Nanochemistry UIO

1

# Synthesis Routes - Spheroids

1. Natural (Opal)
2. Sol-Gel
3. Solvothermal
4. Templated
5. Hydrolysis
6. Extraction
7. Flame&Gas Phase
8. Phase Transitions
9. Corrosion
10. Block Structures
11. Intercalations

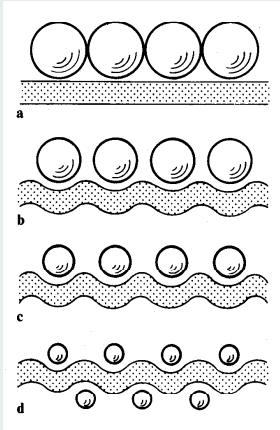
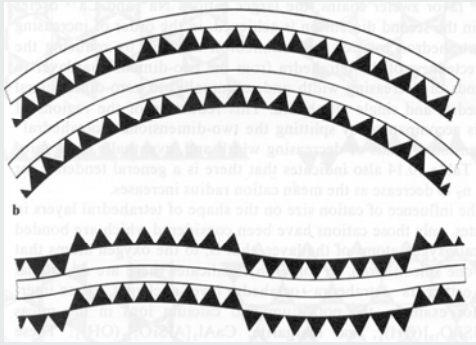


31.10.2007

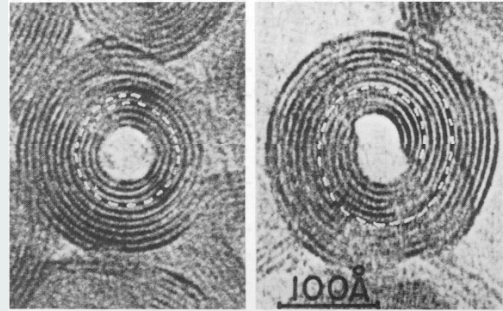
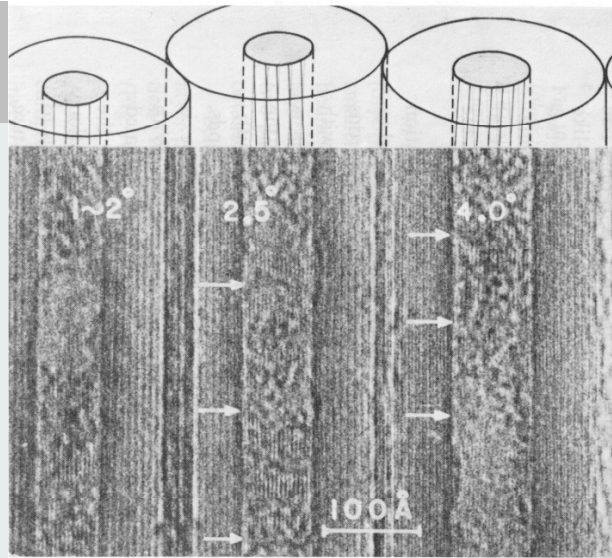
Nanochemistry UIO

2

# Bending of a layer



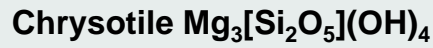
31.10.2007



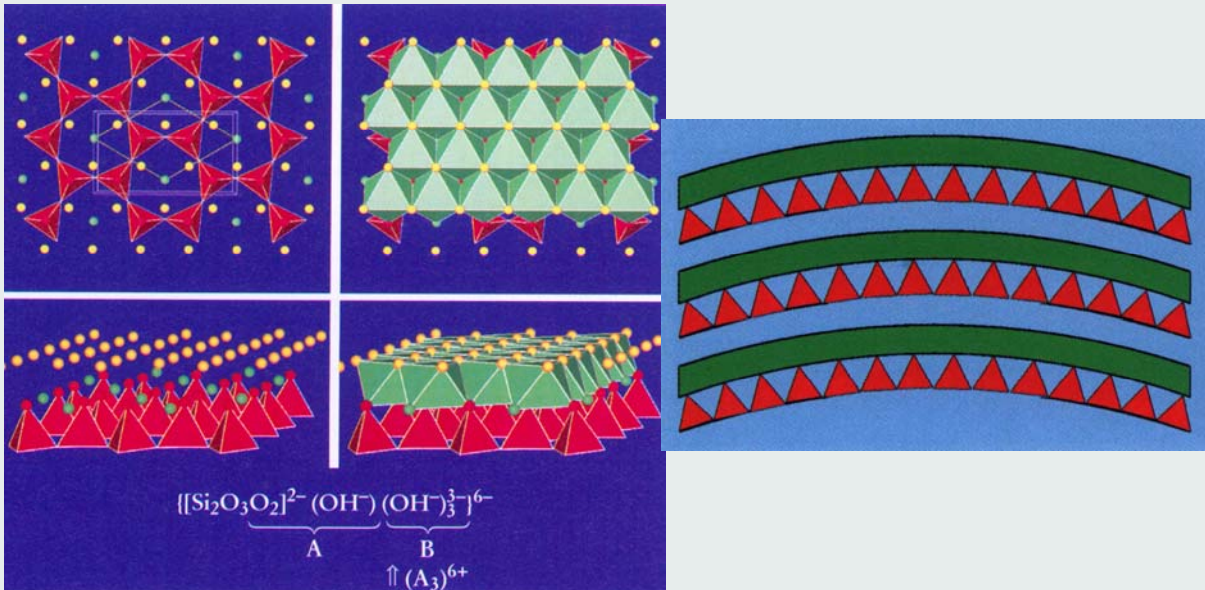
Nanochemistry UIO

3

# Single Layer Misfits - Silicate Minerals



Anisotropic structure inside layers causes bending of the double layers



Structure models reproduced from: Röhr, *ChiuZ* 32 (1988) 64

31.10.2007

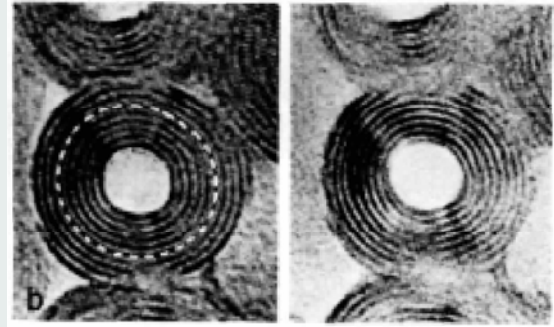
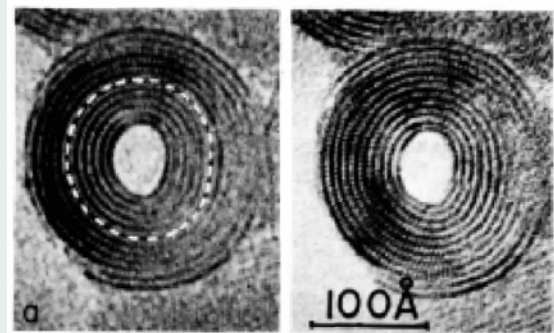
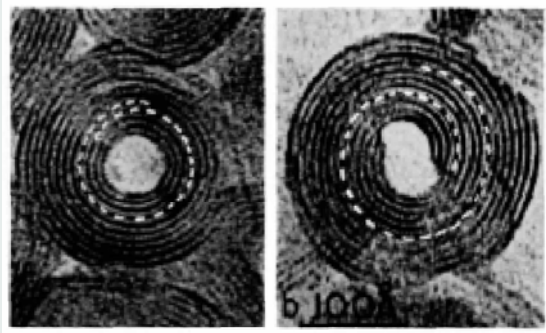
Nanochemistry UIO

4



# Tubular Silicate Minerals

## TEM investigation of the cross-sections of Chrysotile

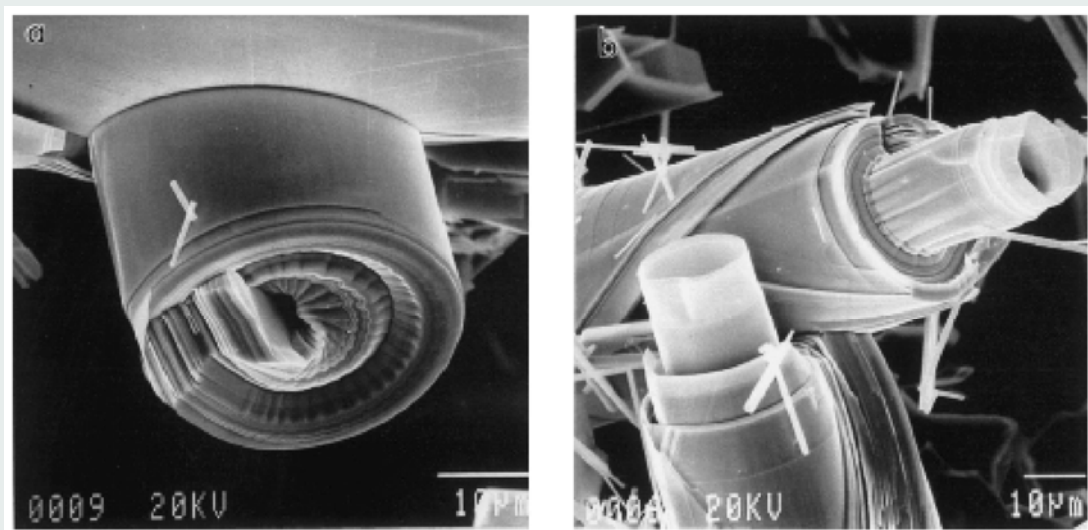


Scrolls of one or more layers

But: also closed, concentric cylinders

Yada, *Acta Crystallogr. A* 27 (1971) 659

## Misfit Layer Structures in Ternary Chalcogenides



SEM images of tubular crystals in the system Bi-Nb-S

Landa-Cánovas, Gómez-Herrero, Otero-Díaz, *Micron* 32 (2001) 491

# Starting from Solids

1. Topotactic reactions
2. Surface reactions
3. Phase widths
4. Intercalations & Ionic exchange

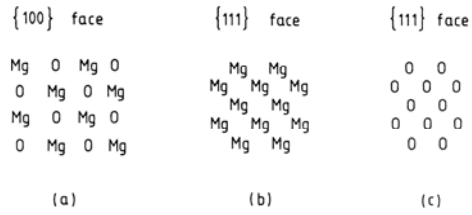
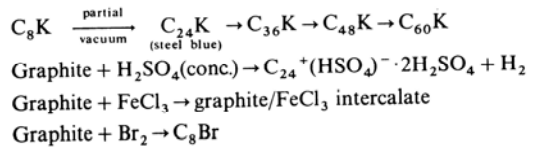
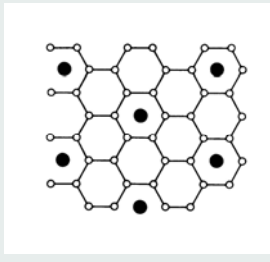
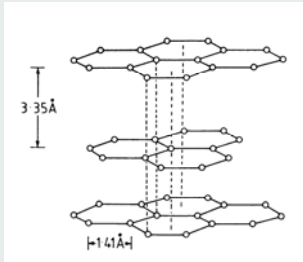
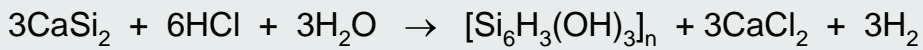


Fig. 2.3 Surface structures of a MgO crystal displaying (a) (100) and (b, c) (111) faces



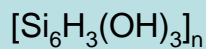
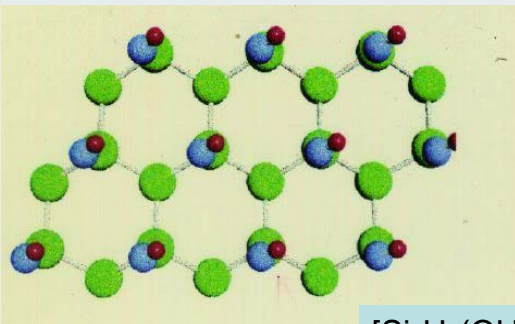
## Topochemical Reactions

### Siloxenes

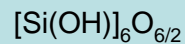
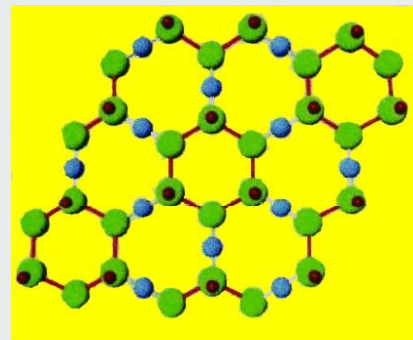


Wöhler 1863

Kautzky 1924



2D-poly  
[1,3,5-tri  
hydroxy  
cyclohexa  
silan]



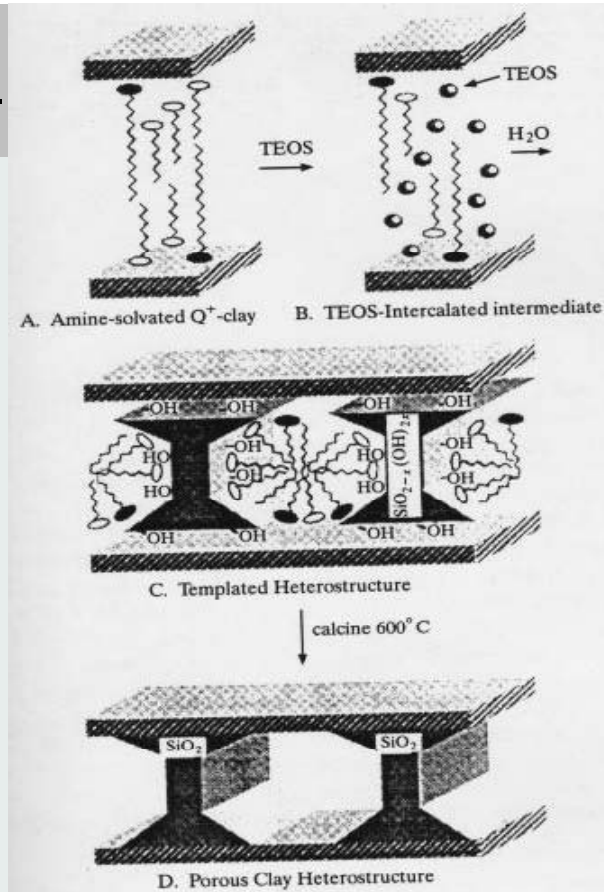
"Das Silicon (= Siloxen) ist lebhaft orangegebl; es besteht aus durchscheinenden gelben Blättchen[...]. Es ist unlöslich in Wasser, in Alkohol, in Kieselchlorid, in Phosphorchlorid, in Schwefelkohlenstoff. Beim Erwärmen wird es vorübergehend tiefer orangegebl. Stärker erhitzt entzündet es sich und verbrennt mit schwacher Verpuffung und Funkensprühen unter Zurücklassung von Kieselsäure, die durch amorphes Silicium braungefärbt ist. Ohne Luftzutritt erhitzt, entwickelt es Wasserstoffgas und hinterläßt ein Gemenge von Kieselsäure und amorphem Silicium in Gestalt glänzender, schwarzbrauner Blättchen. Erst nach vollem Glühen hört die Wasserstoffentwicklung auf. War es mit einer nicht ganz konzentrierten Säure bereitet, so enthält es die weiter unten beschriebene Verbindung beigemengt; es ist dann heller an Farbe und zeigt beim Erhitzen auch in einer Röhre eine Art Verpuffung, unter gleichzeitiger Entwicklung von selbstentzündlichen Kieselwasserstoffgas. Diese Zersetzung des Silicons in der Wärme beginnt schon bei 100 °C[...]."

Sehr merkwürdig ist sein Verhalten im Licht. Im Dunkeln bleibt es, selbst im feuchten Zustand, ganz unverändert; im zerstreuten Licht wird es zunehmend blasser und im direkten Sonnenlicht wird es nach kurzer Zeit vollkommen weiß, und zwar unter Entwicklung von Wasserstoffgas. Stellt man es unter Wasser in den Sonnenschein, so fängt es augenblicklich an Wasserstoffgas zu entwickeln, was gleich einer Gährungserscheinung fort dauert, bis es ganz weiß geworden ist [...]. Das Silicon wird weder von Chlor noch rauchender Salpetersäure oder von konzentrierte Schwefelsäure angegriffen, selbst nicht beim Erhitzen damit. Flußsäure erhitzt sich damit; es erhebt sich darin zugleich an die Oberfläche, wird allmählich heller, zuletzt weiß und verschwindet endlich ganz [...]."

Re-detected ~ 1989 !

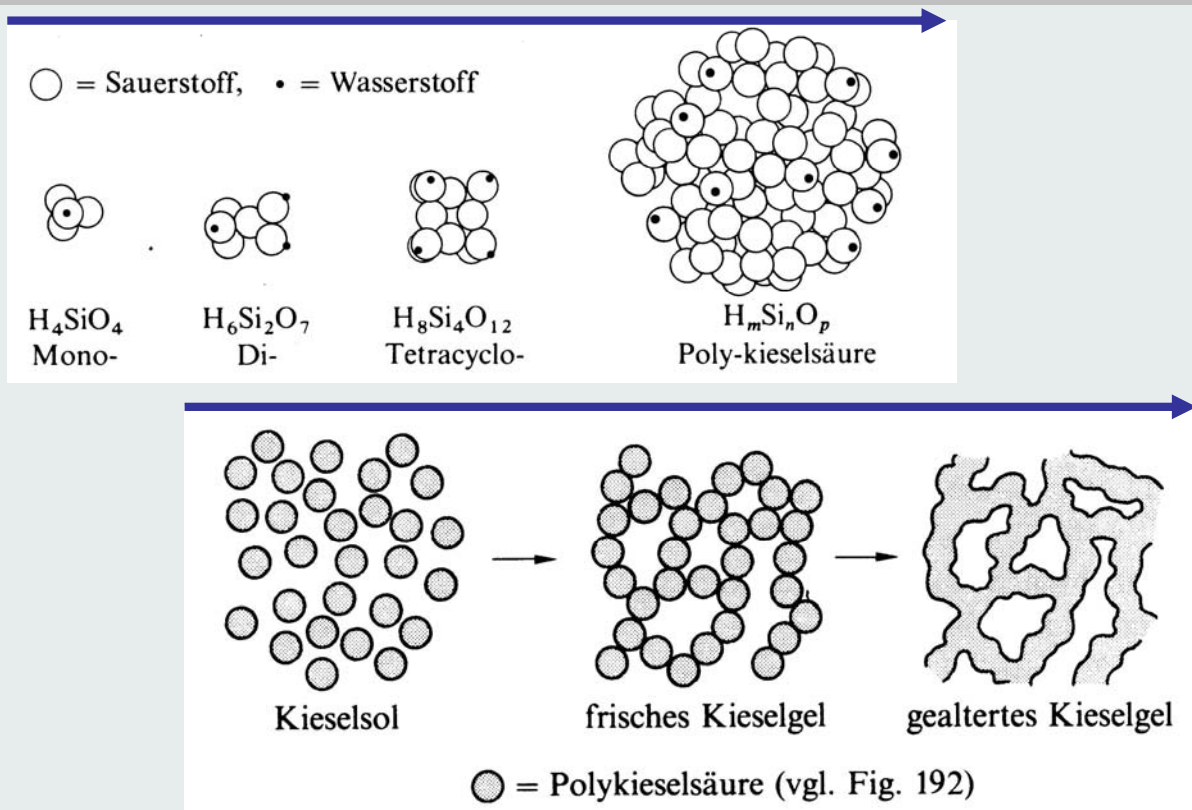
## Intercalation and Delamination

Layered Materials





# Sol-Gel- Route



31.10.2007

Nanochemistry UIO

11



# Sol-Gel – Templates as Space Holders and Structure Directors

hydrophobic hydration

soluble silicate species

1) nucleation

2) crystal growth

a)

b)

Model II: Elektronen- und Photonen-Transfer

31.10.2007

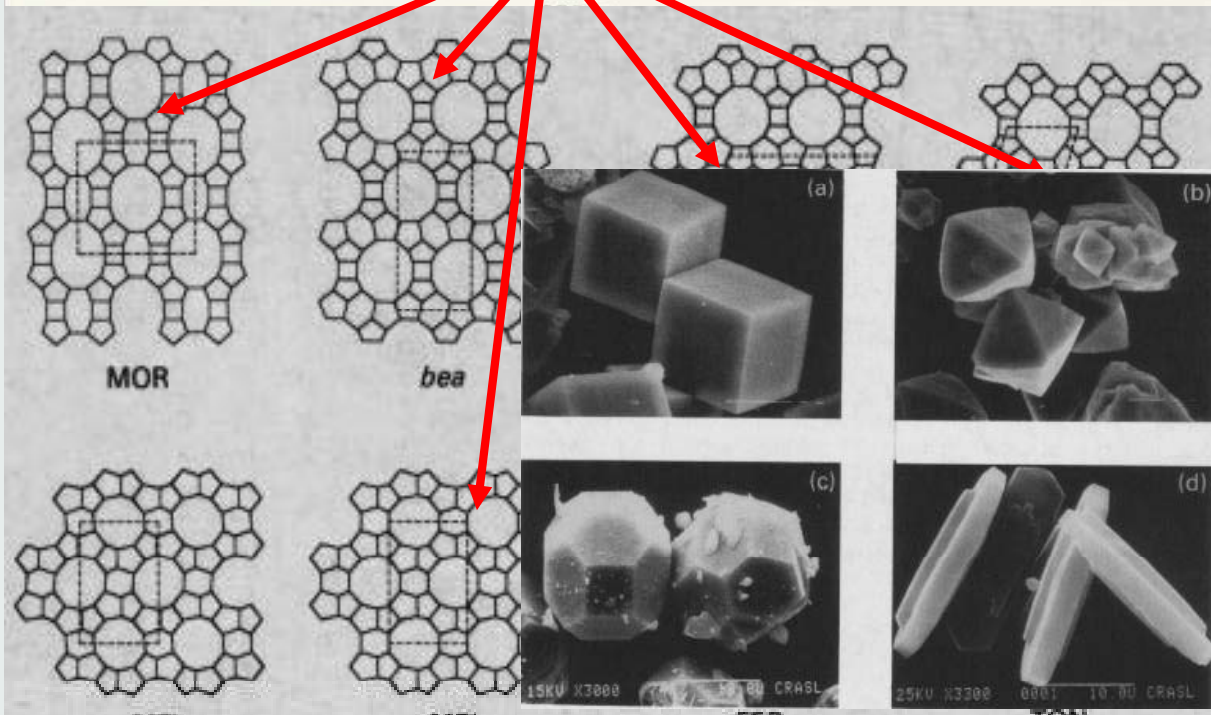
Nanochemistry UIO

12



# Zeolites (boiling stones)

concentrations + template + temperature + time + ??

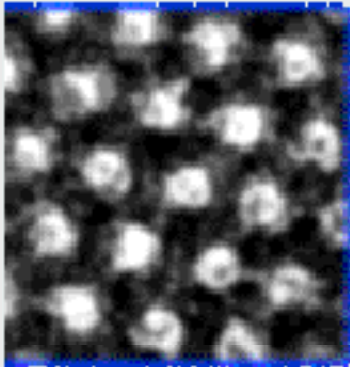


31.10.2007

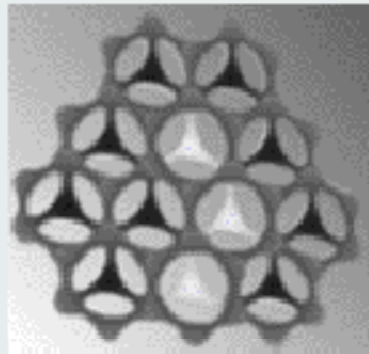
Nanochemistry UIO

13

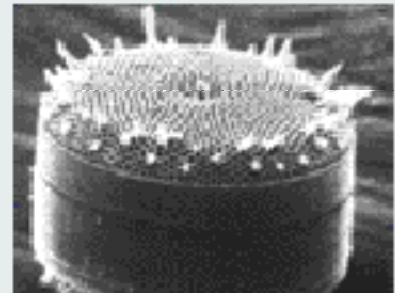
## Mesoporous Materials



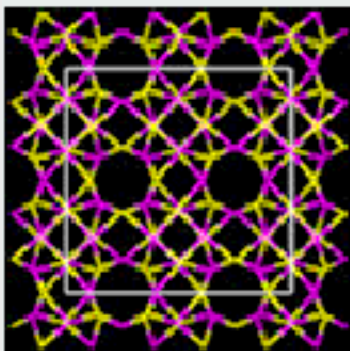
## Mesocellular Foams



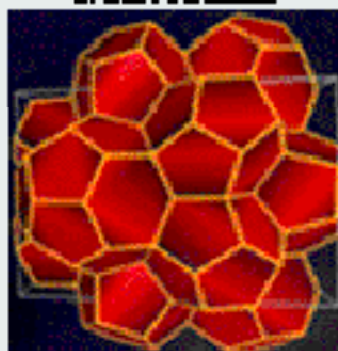
## Biomimetic Mineralization of Silica



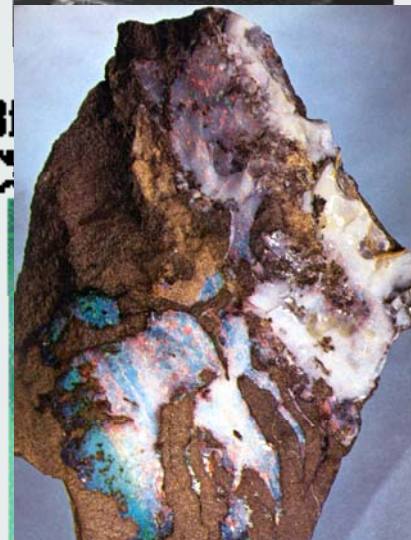
## Microporous Materials



## Thermoelectric Materials



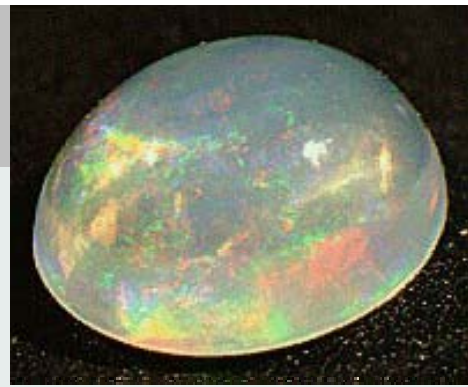
## Bio



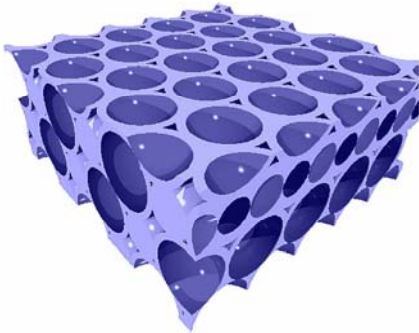


# Opals and Photonic Crystals

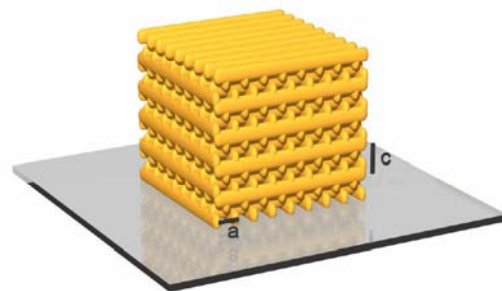
- (styrene) nanobeads + TEOS  $\rightarrow$  SiO<sub>2</sub> coated beads
- thermalize beads



3D Photonic Crystals - the **inverse opal**



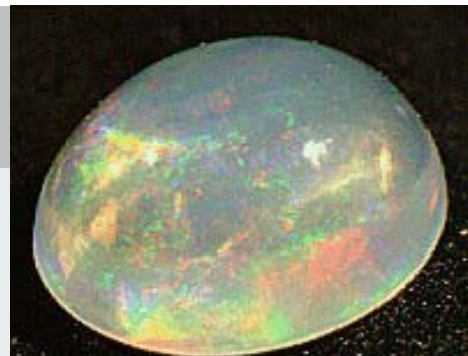
3D Photonic Crystals - the **Woodpile (Layer-by-Layer structure)**



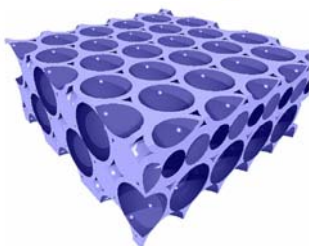
fcc for  $(c/a)^2=2$ , full gap for index contrast  $> 1.9$ , 25% gap for holes in Si

# Opals and Photonic Crystals

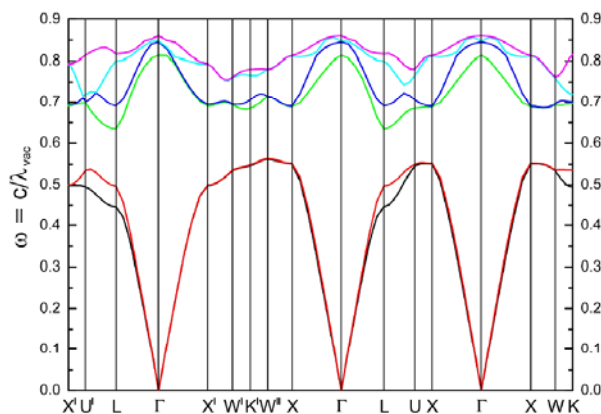
- (styrene) nanobeads + TEOS  $\rightarrow$  SiO<sub>2</sub> coated beads
- thermalize beads



3D Photonic Crystals - the **inverse opal**



3D Photonic Crystals - the **Woodpile (Layer-by-Layer structure)**

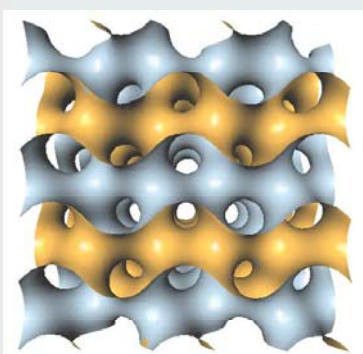
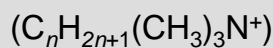
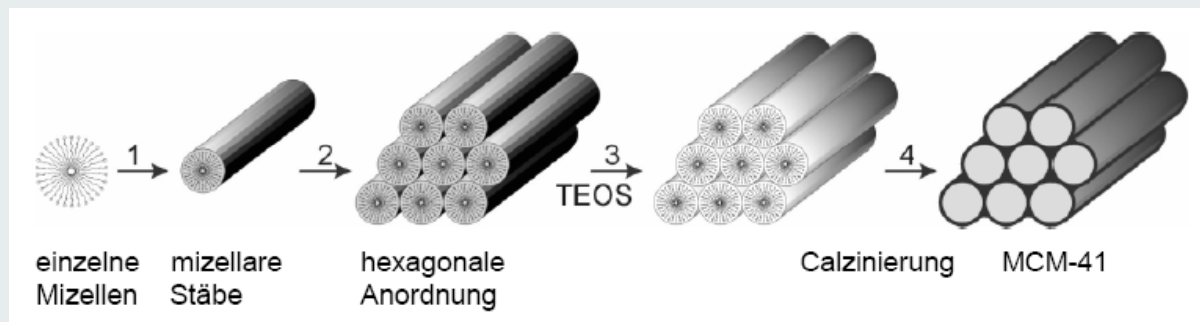


**Band structure of a woodpile composed of Si-rods**

Proposal: C.M. Soukoulis et al., Solid State Commun. 89, 413 (1994)



# Mesoporous Silicates: MCM41 / MCM48

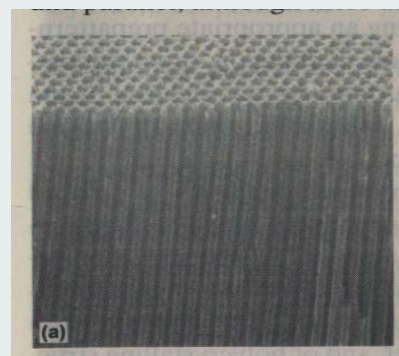


31.10.2007

Tetraethoxysilan, TEOS

MCM 41 – hexagonal Porengrößen 3-8nm

MCM 48 – cubisch 3D-Kanalstruktur



Nanochemistry UIO

17

# Ionic Liquids

Characteristic properties:

- low vapour pressure
- thermischal stability
- elektric conductivity
- Phasenseparation from products
- high thermal capacity
- non burning

These liquids are – in contrast to salt melts – not corrosive and thus are used to replace ordinary organic solvents

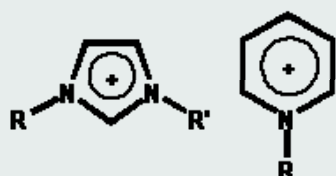
fields of applications

- head carrier
- Elektrolyte
- Analytics
- separator
- Membran etechniques



**P. Wasserscheid und W. Keim.**  
*Angew. Chem.* 2000, 112, 3926-3945.

Kationen und Anionen in Ionischen Flüssigkeiten: Ausgewählte Beispiele



Cl<sup>-</sup> BF<sub>4</sub><sup>-</sup> Br<sup>-</sup> AlCl<sub>4</sub><sup>-</sup>  
 PF<sub>6</sub><sup>-</sup> SbF<sub>6</sub><sup>-</sup> CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>



31.10.2007

Nanochemistry UIO

18

# Controlled Precursor Hydrolysis

## Polyolate-Route

(ionic liquids)

$Cu_2O$	$ZnO$	$Mn_3O_4$	$Al_2O_3$	$SiO_2$	$V_2O_5$	$MoO_3$
	$CdO$		$Bi_2O_3$	$SnO_2$	$Nb_2O_5$	$WO_3$
	$CoO$		$Y_2O_3$	$CeO_2$	$Ta_2O_5$	
			$La_2O_3$	$TiO_2$		
			$Cr_2O_3$	$ZrO_2$		
			$Fe_2O_3$			
	$Zn_2SiO_4$	$CaTiO_3$	$YVO_4$	$MgAl_2O_4$	$ZrNb_2O_6$	
			$MnWO_4$	$BaAl_2O_4$		
				$CoAl_2O_4$		
				$ZnCo_2O_4$		

(als Ausgangsverbindungen wurden verwendet:  $Al(sec-OC_4H_9)_3$ ,  $Al(OC_3H_7)_3$ ,  $Ba(CH_3COO)_2$ ,  $Bi(CH_3COO)_3$ ,  $Ca(CH_3COO)_2 \cdot xH_2O$ ,  $Cd(CH_3COO)_2 \cdot xH_2O$ ,  $Ce(CH_3COO)_3 \cdot xH_2O$ ,  $Co(CH_3COO)_2 \cdot 4H_2O$ ,  $CrCl_3 \cdot 6H_2O$ ,  $Cu(CH_3COO)_2 \cdot H_2O$ ,  $Fe(CH_3COO)_2$ ,  $La(CH_3COO)_3 \cdot xH_2O$ ,  $Mg(CH_3COO)_2 \cdot 4H_2O$ ,  $Mn(CH_3COO)_2 \cdot 4H_2O$ ,  $Mo(i-OC_3H_7)_5$ ,  $Nb(OC_2H_5)_5$ ,  $Si(OC_2H_5)_4$ ,  $Sn(C_2H_5)_4$ ,  $Ta(OC_2H_5)_5$ ,  $Ti(OC_2H_5)_4$ ,  $VO(i-OC_3H_7)_3$ ,  $W(OC_2H_5)_5$ ,  $Y_3O(i-OC_3H_7)_3$ ,  $Y(i-OC_3H_7)_3$ ,  $Zn(CH_3COO)_2 \cdot 2H_2O$ ,  $Zr(OC_4H_9)_4$ )

nanoskaligem $VO(i-OC_3H_7)_3$			Reaktions-	Reaktions-	mittlerer Partikel-
$VO(i-OC_3H_7)_3$	$H_2O$	DEG	temperatur [°C]	dauer [h]	durchmesser [nm]
[mmol]	[ml]	[ml]			
0,5	1	50	180	1	30 bis 40
2,3	2	50	180	2	60 bis 70
5,5	2	50	180	2	90 bis 100
10,6	2	50	190	8	160 bis 180



31.10.2007

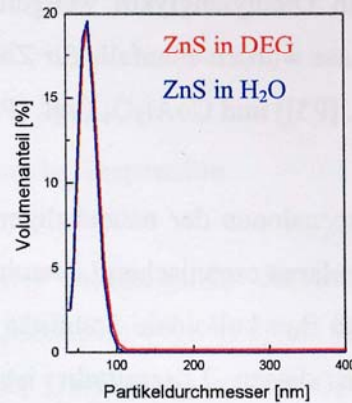
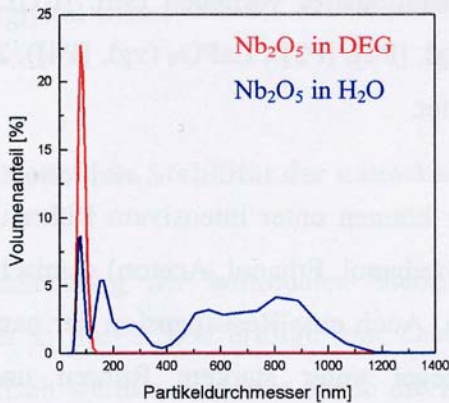
Nanochemistry UIO

19

# Controlled Precursor Hydrolysis

## Polyolate-Route – Particle Size Distribution

Solvent: DEG ( $Et(OH)_2$ ) Metal source : Alkoxides, Halides, T ~ 200 °C



**Abb. 4:** Partikelgrößenverteilung von nanoskaligem  $Nb_2O_5$  und  $ZnS$  in Diethylenglykol sowie nach dem Mischen der DEG-Suspensionen mit Wasser

31.10.2007

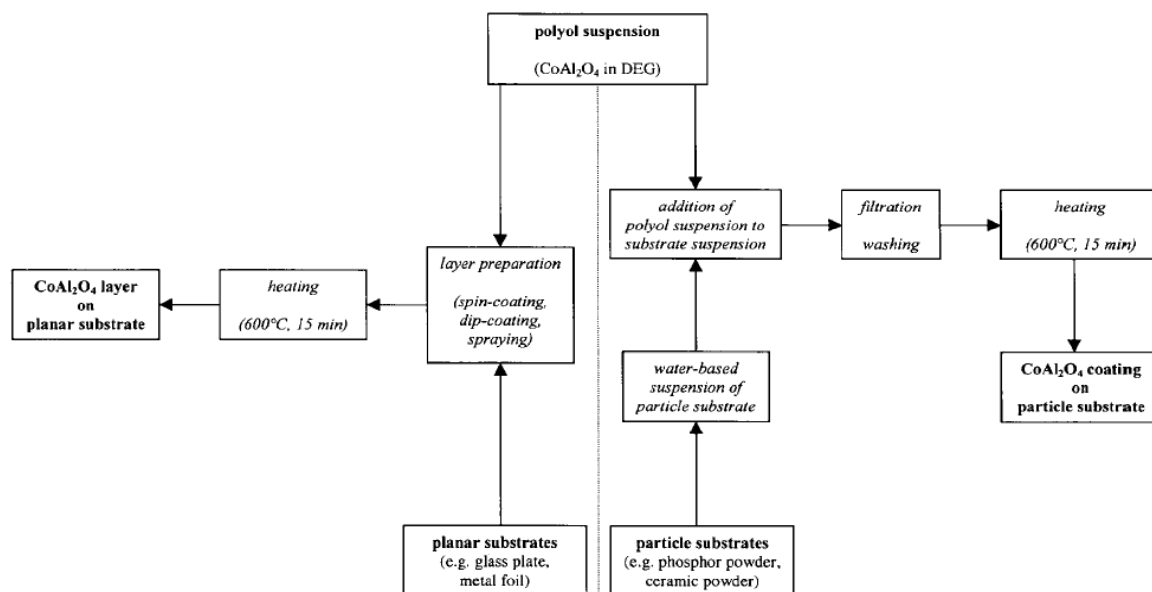
Nanochemistry UIO

20



# Polyolate Route – Magnetic Particles – Coating Recipe

Co(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O/g	Al(CH <sub>3</sub> COO) <sub>2</sub> OH/g	H <sub>2</sub> O/ml	DEG/ml	d <sub>50</sub> /nm
0.50	0.72	1	50	56
2.00	2.86	1	50	96
2.00	2.86	3	50	143



31.10.2007

Nanochemistry UIO

21

## Controlled Precursor Hydrolysis

## Metal Organic Precursors

### Room-Temperature Organometallic Synthesis of Soluble and Crystalline ZnO Nanoparticles of Controlled Size and Shape

Miguel Monge, Myrtil L. Kahn, André Maisonnat, and Bruno Chaudret\*

Angew. Chem. 2003, 115, 5479–5482

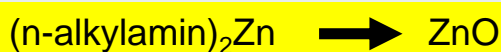
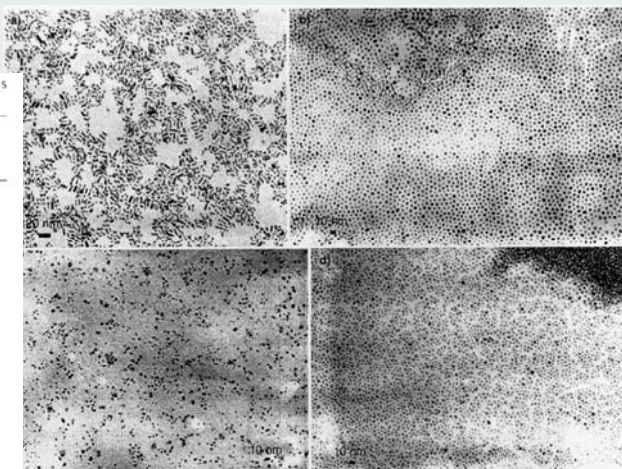


Table 1: Summary of the results obtained after oxidation of the [Zn(*n*-C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>)] precursor under various reaction conditions.

Ligand added	Solvent	Time	Overall concentration [M]	Temperature	Size [nm] <sup>[a]</sup>	Morphology
–	THF	Standard <sup>[a]</sup>	0.042	RT	–	Agglomerated nanoparticles
HDA	THF	Standard	0.042	RT	8.1 ± 3.3 × 2.6 ± 0.4	Nanorods
HDA	THF	Standard	0.125	RT	11.4 ± 5.7 × 2.8 ± 0.7	Nanorods
HDA	THF	2 weeks	0.042	RT	4.1 ± 0.9	Nanodisks
HDA	THF	Standard	0.042	45 °C	4.8 ± 0.3	Nanodisks
HDA	THF	Standard	0.01	RT	< 3.0 after 1 day 4.3 ± 0.5 after 4 days	Nanodisks
HDA	THF	5 min under Ar	0.042	RT	5.8 ± 1.3 × 2.7 ± 0.3	Nanorods
DDA	THF	Standard	0.042	RT	3.0 ± 0.5	Nanodisks
OA	THF	Standard	0.042	RT	4.0 ± 0.7	Nanodisks
HDA	Toluene	Standard	0.042	RT	4.6 ± 0.9	Nanodisks
HDA	Heptane	Standard	0.042	RT	2.4 ± 0.5	Nanodisks
HDA	–	Standard	–	RT	10.7 ± 1.2 × 1.6 ± 0.3	Nanorods
DDA	–	Standard	–	RT	9.2 ± 2.0 × 3.7 ± 1.8	Nanorods
OA	–	Standard	–	RT	7.4 ± 1.4 × 2.8 ± 0.6	Nanorods
2HDA	–	Standard	–	RT	–5	Not homogeneous
2DDA	–	Standard	–	RT	17.1 ± 3.4 × 3.0 ± 0.4	Nanorods
2OA	–	Standard	–	RT	36.9 ± 10.8 × 2.8 ± 0.3	Nanorods

[a] Standard reaction time is 17 h under Ar and 1 or 2 days of oxidation/evaporation. [b] The values indicate the diameter of nanodisks or the length and width for nanorods; size dispersion is given after the mean size.



31.10.2007

Nanochemistry UIO

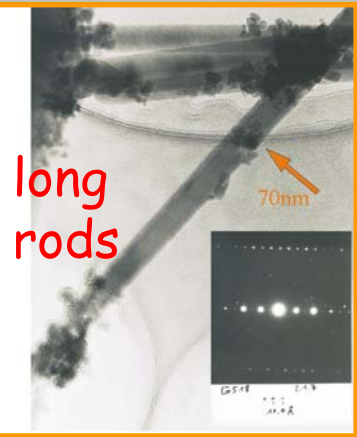
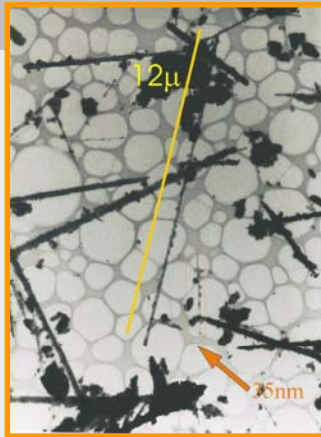
22

# Alkoxide Hydrolysis

R. NESPER, ETH ZÜRICH & COLLEGIUM HELVETICUM



small needles



long rods

## FeO<sub>x</sub> NPs



small rods



large needles



small lenses



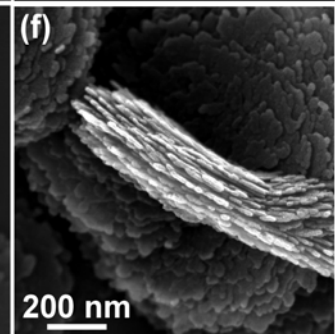
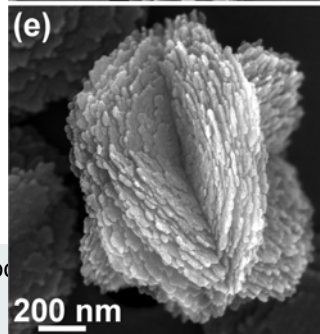
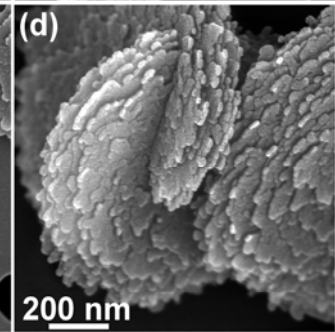
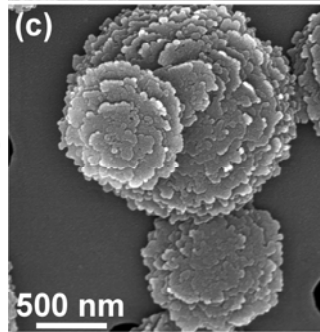
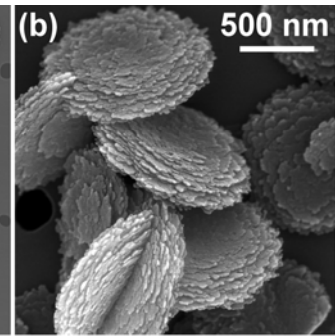
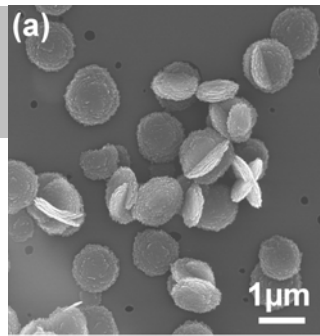
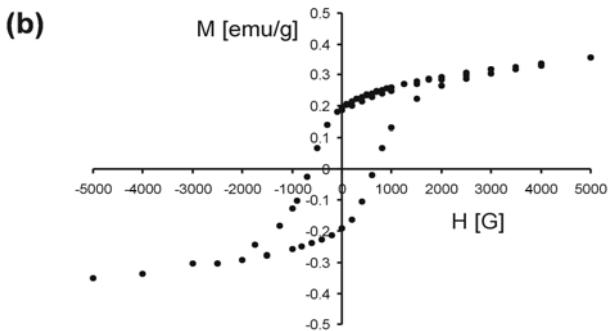
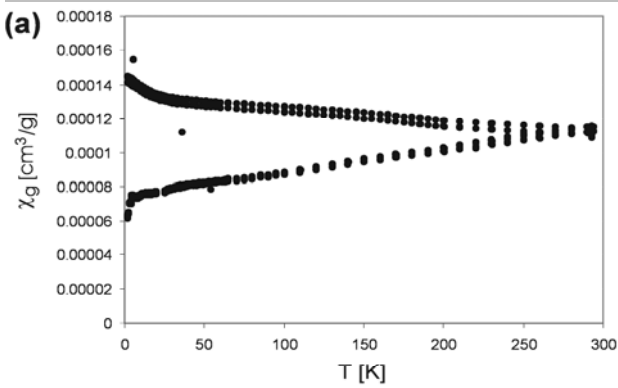
large cubes

31.10.2007

Nanochemistry UIO

23

# Hematite-Discs

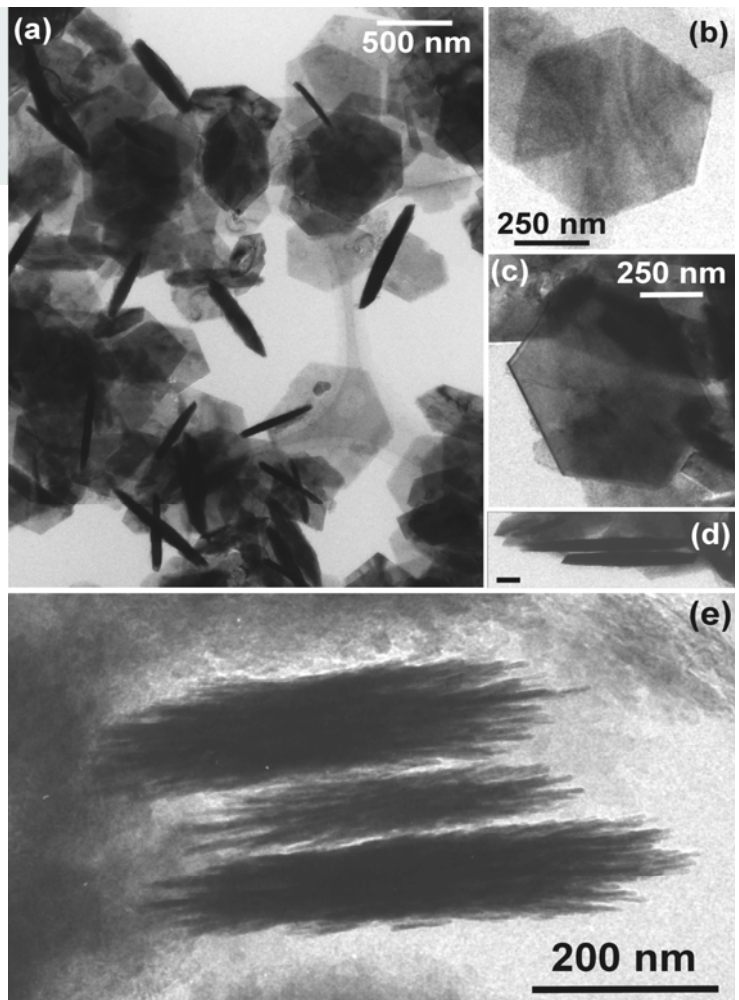
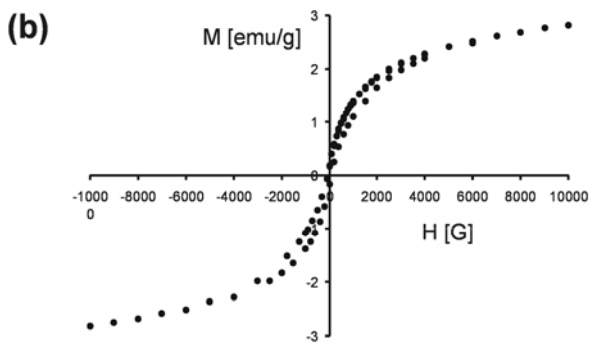
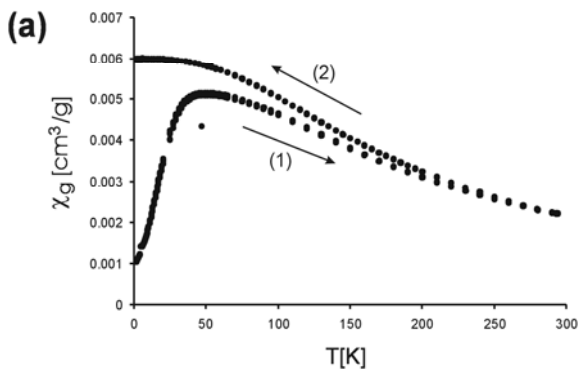


31.10.2007

Nano



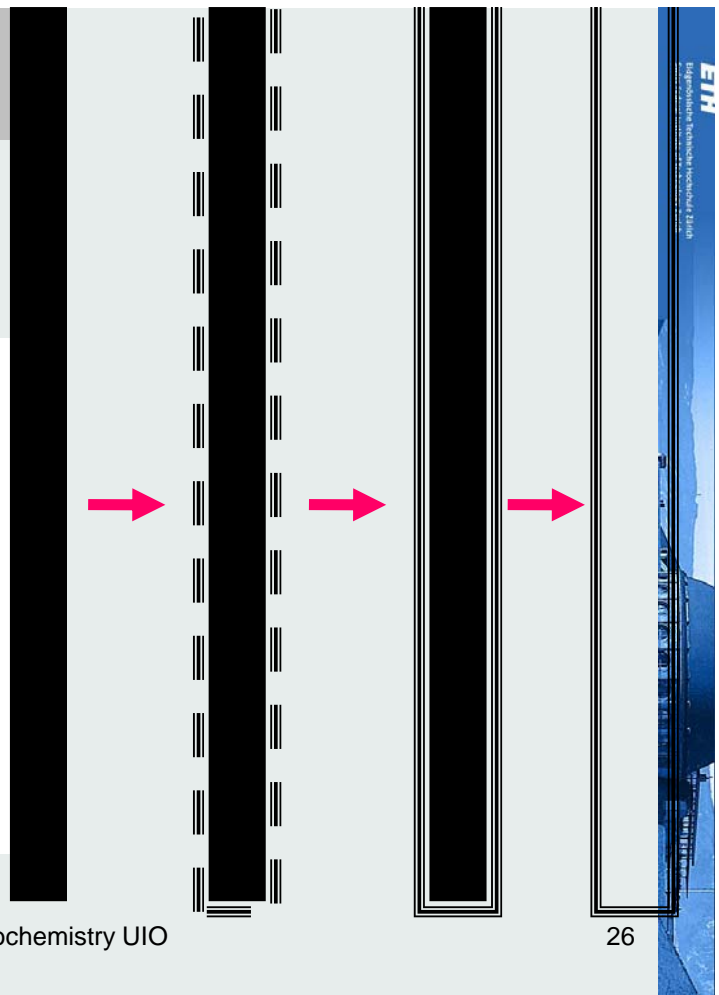
# Hematite-Discs



# Secondary Nanoparticles

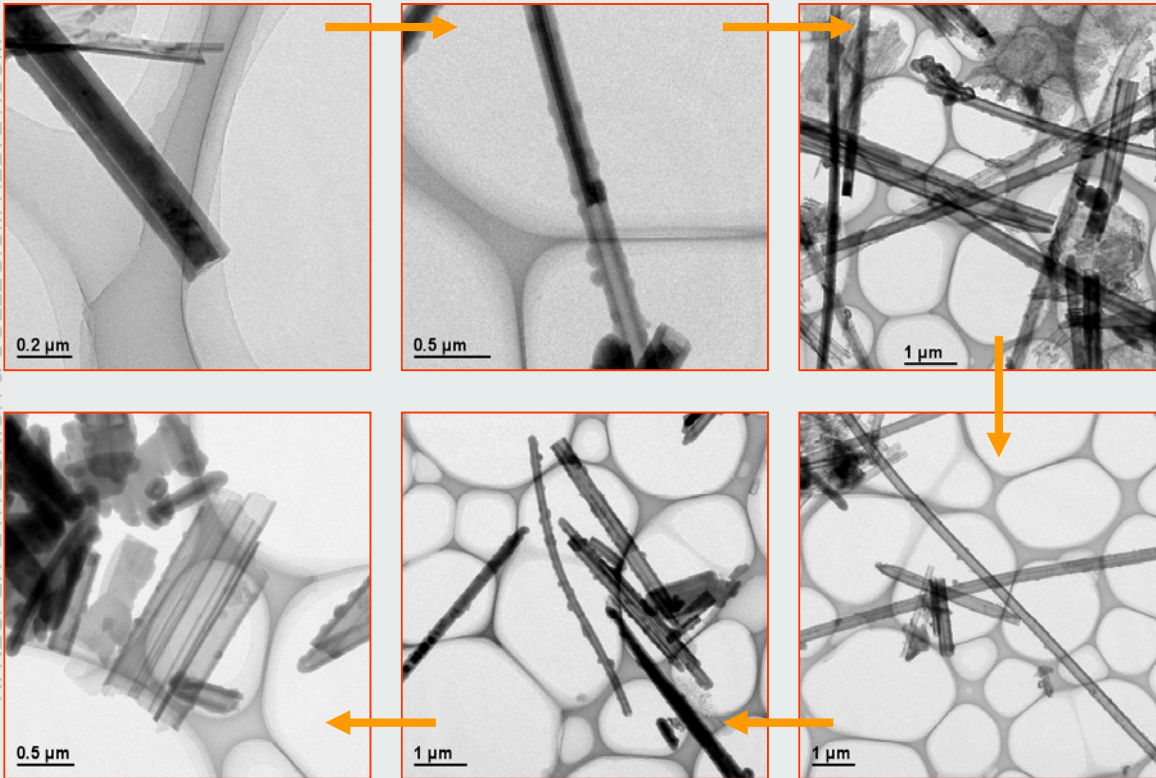
R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM

1.  $V_2O_5$  nanofibers
2. Coating utilizing TEOS
3. Calcination
4. Emptying
5.  $SiO_2$  secondary nanotubes



# Nanotubular SiO<sub>2</sub>

R. NESPER, ETH ZÜRICH & COLLEGIUM HELVETICUM



31.10.2007

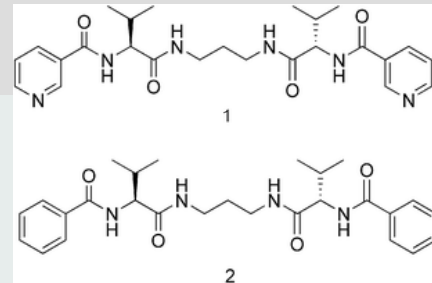
Nanochemistry UIO

27

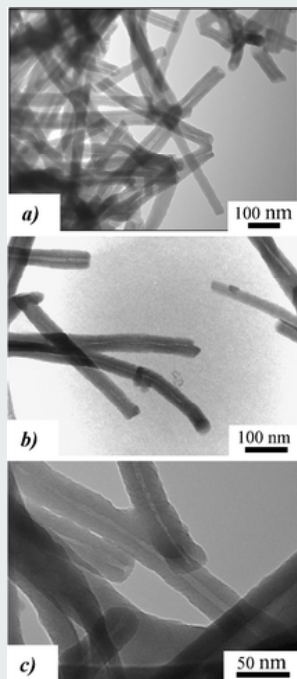


# Applying Organogels

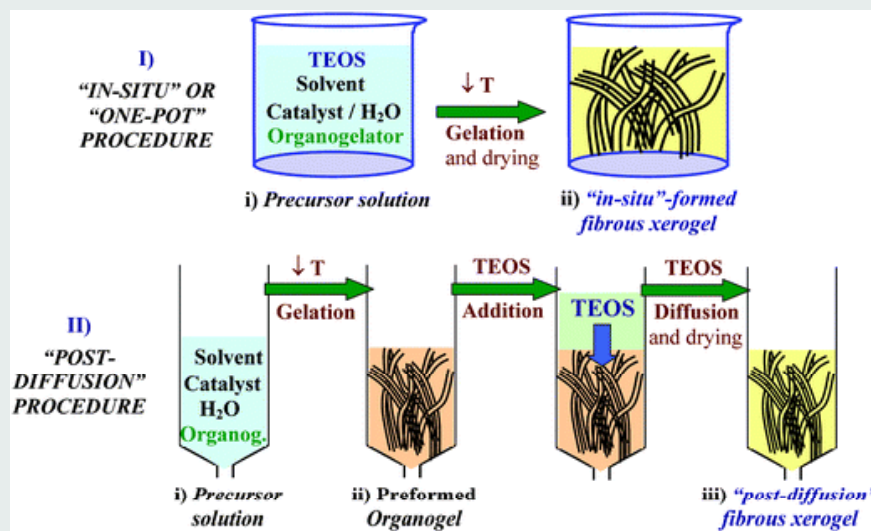
*J. Mater. Chem.*, 2006,



R. NESPER, ETH ZÜRICH & COLLEGIUM HELVETICUM



31.10.2007



Nanochemistry UIO

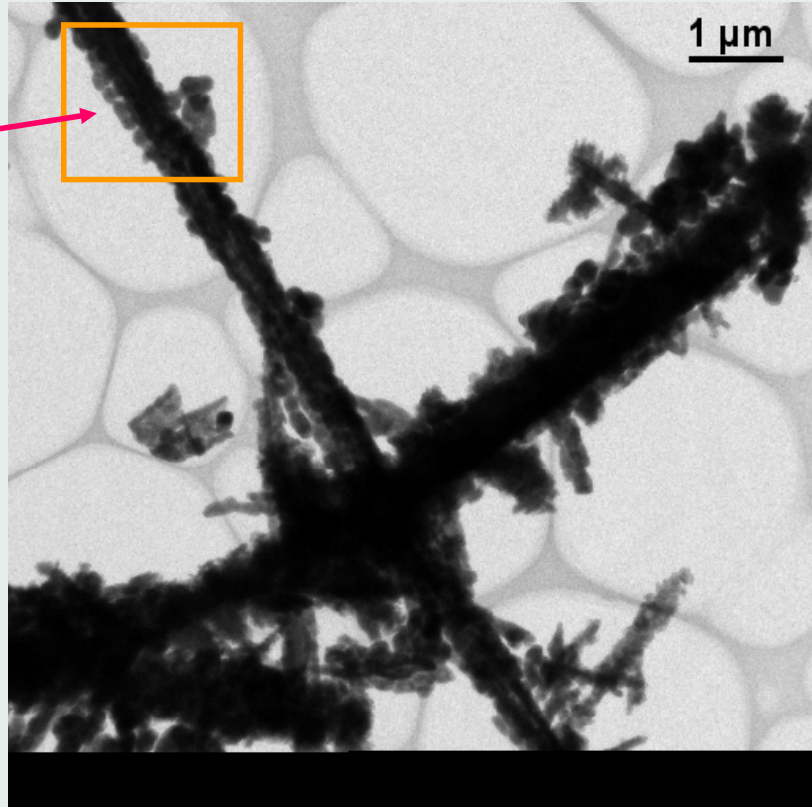
28





# Surface Growth on Nanorods

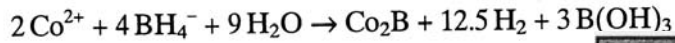
MnO<sub>2</sub>  
on  
TiO<sub>2</sub>



31.10.2007

## Controlled Precursor Hydrolysis

## Metal + Hydride Reaction



**Magnetic Fluids: Fabrication, Magnetic Properties, and Organization of Nanocrystals\*\***

By Marie-Paule Pileni\*

*Adv. Funct. Mater.* **2001**, *11*, No. 5, October

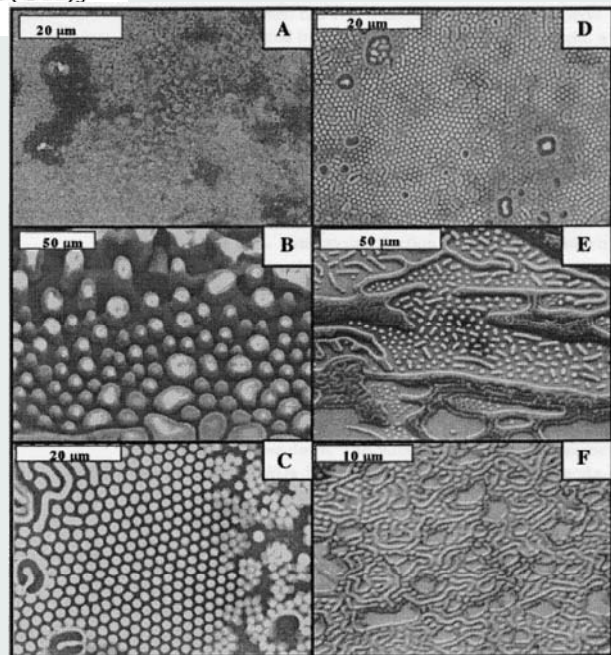


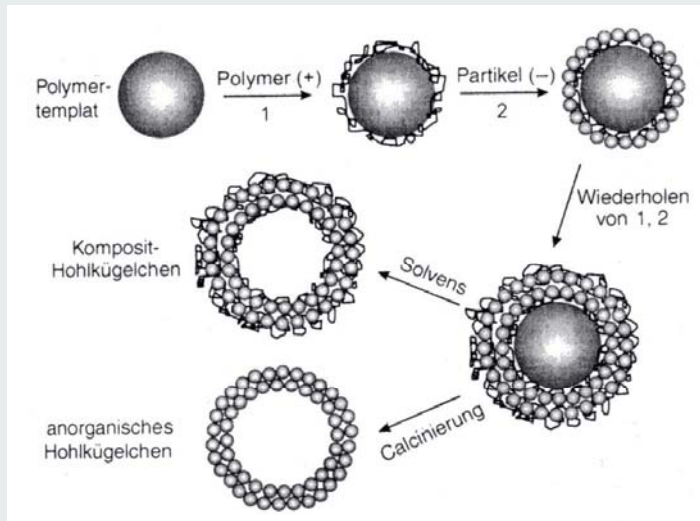
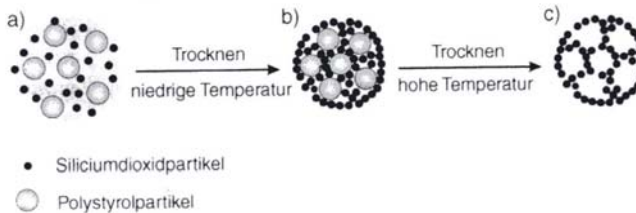
Fig. 14. SEM patterns obtained by evaporating 200 μL of a concentrated solution of cobalt nanocrystals ( $4 \times 10^{-7}$  M in particles) deposited in a magnetic field perpendicular to the HOPG substrate. The evaporation time is 12 h. The strength of the applied field is 0 (A); 0.01 T (B); 0.27 T (C); 0.45 T (D); 0.60 T (E); and 0.78 T (F).

31.10.2007

### Organische Template zur Formgebung anorganischer Materialien\*\*

Kjeld J. C. van Bommel, Arianna Friggeri und Seiji Shinkai\*

Adv. Funct. Mater. 2003, 13, No. 1, January



**important route towards photonic crystals**

31.10.2007

Nanochemistry UIO

31

# Micelles/Vesicles as Nano Templates

### Emergent Nanostructures: Water-Induced Mesoscale Transformation of Surfactant-Stabilized Amorphous Calcium Carbonate Nanoparticles in Reverse Microemulsions\*\*

By Mei Li and Stephen Mann\*

**Nano Calcite**  
**Bio Mineralization**

Adv. Funct. Mater. 2002, 12, No. 11-12, I

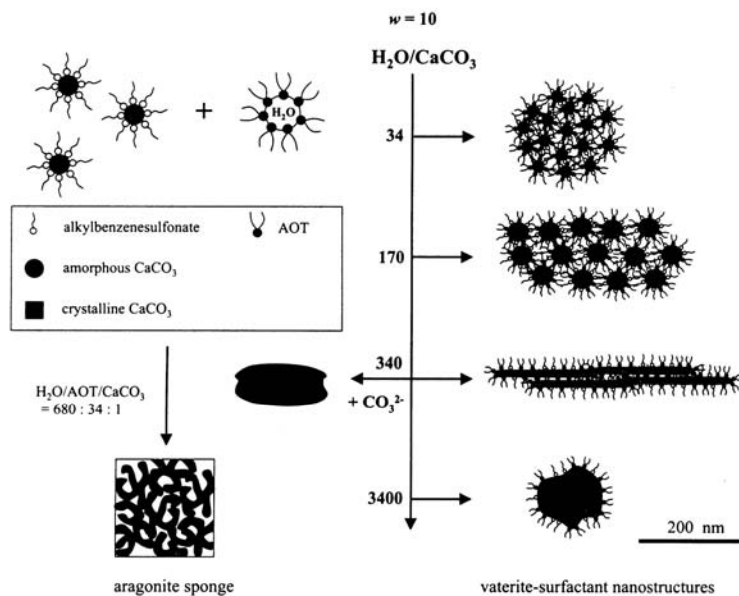


Fig. 8. General scheme showing experimental conditions and types of hybrid surfactant-vaterite nanostructures synthesized by microemulsion-mediated phase transformation of surfactant-stabilized ACC nanoparticles. Reactants are shown top/middle left. Nanostructures produced at  $w = 10$  using different water droplet/amorphous  $\text{CaCO}_3$  nanoparticle ratios are shown on the right. The aggregated structures are drawn approximately to scale (bar = 200 nm).

31.10.2007



# Loaded Micelles and Dendrimers

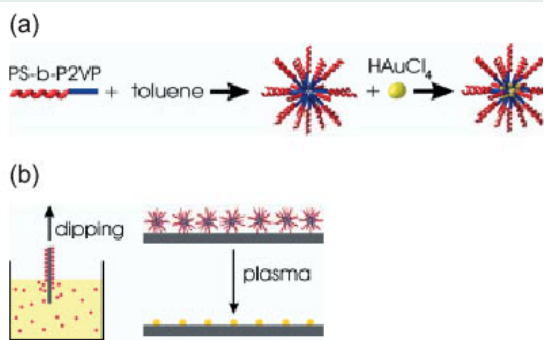


Fig. 1. a) Sketch of the formation of reverse micelles within PS-P2VP diblock copolymer solutions. The core of the micelle can be loaded with a metal precursor (e.g., HAuCl<sub>4</sub>). b) The reverse micelles in solution are transferred onto substrates by dip coating. The polymer is removed and, simultaneously, the metal salt is reduced by applying either an oxygen plasma followed by a hydrogen plasma or by a single hydrogen plasma step (more details are given below).

31.10.2007

Nanochemistry UIO

33

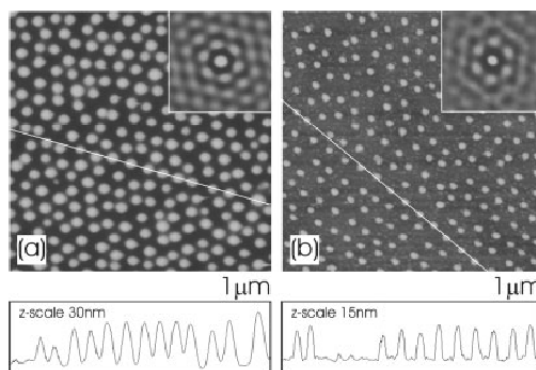


Fig. 2. Gold-loaded micelles on a silicon substrate before (a), z-scale 30 nm) and after (b), z-scale 15 nm) removal of the polymer matrix. Clearly, the order of the resulting nanoparticles reflects the order of the original micellar array. Local order is reasonably good as proven by the autocorrelation functions in the insets. The bottom panels show the results of line scans measured along the white lines shown.

# Loaded Micelles and Dendrimers

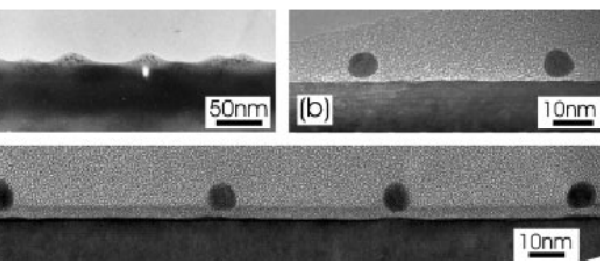
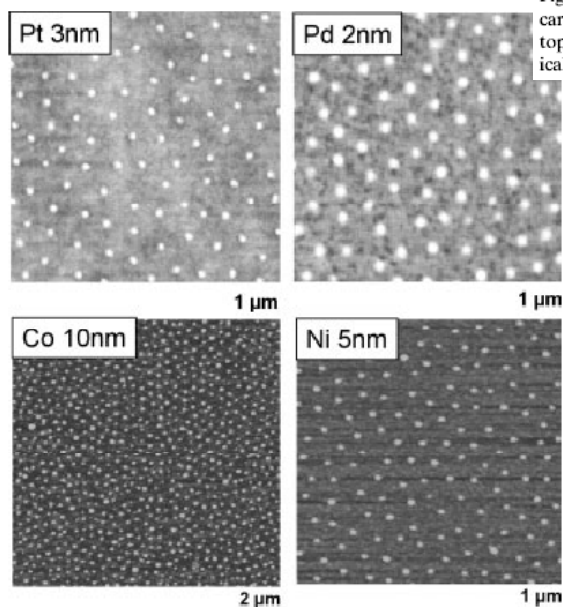


Fig. 10. TEM cross-section images of Au-salt-loaded micelles deposited onto a carbon-coated copper grid (a) and of the final array of Au nanodots prepared on top of a sapphire substrate (b) and on silicon (c), demonstrating the nearly spherical shape of the resulting particles.

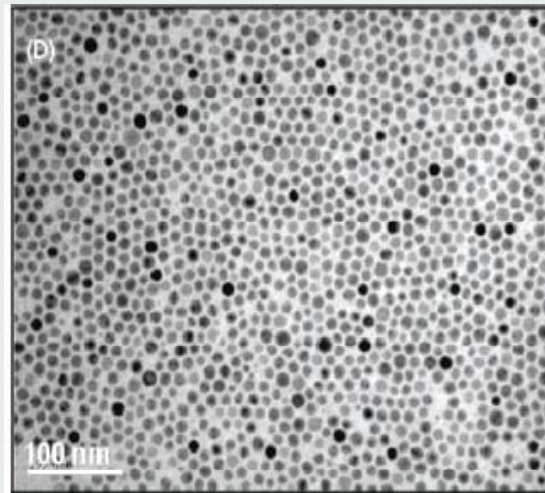
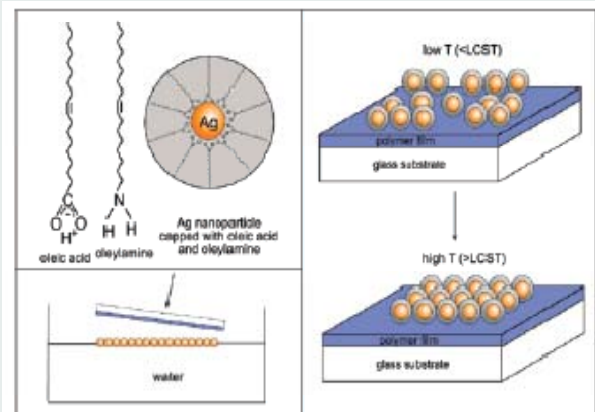
Fig. 11. AFM images of nanoparticles prepared from different elements. The universality of the micellar approach allows a wide variety of metallic, magnetic, or oxide particles to be prepared.

31.10.2007

Nanochemistry UIO

34

# Silver Nanospheres from Oleic Acid Emulsions



31.10.2007

Nanochemistry UIO

35

# Nano Templates

## Noble-Metal Nanotubes (Pt, Pd, Ag) from Lyotropic Mixed-Surfactant Liquid-Crystal Templates\*\*

Tsuyoshi Kijima,\* Takumi Yoshimura, Masafumi Uota, Takayuki Ikeda, Daisuke Fujikawa, Shinji Mouri, and Shinji Uoyama

Angew. Chem. 2004, 116, 230–234

## Noble Metal Nano Tubes

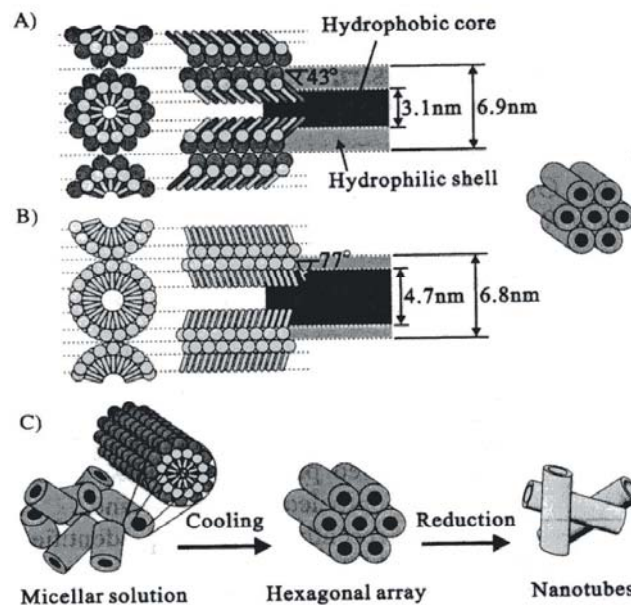
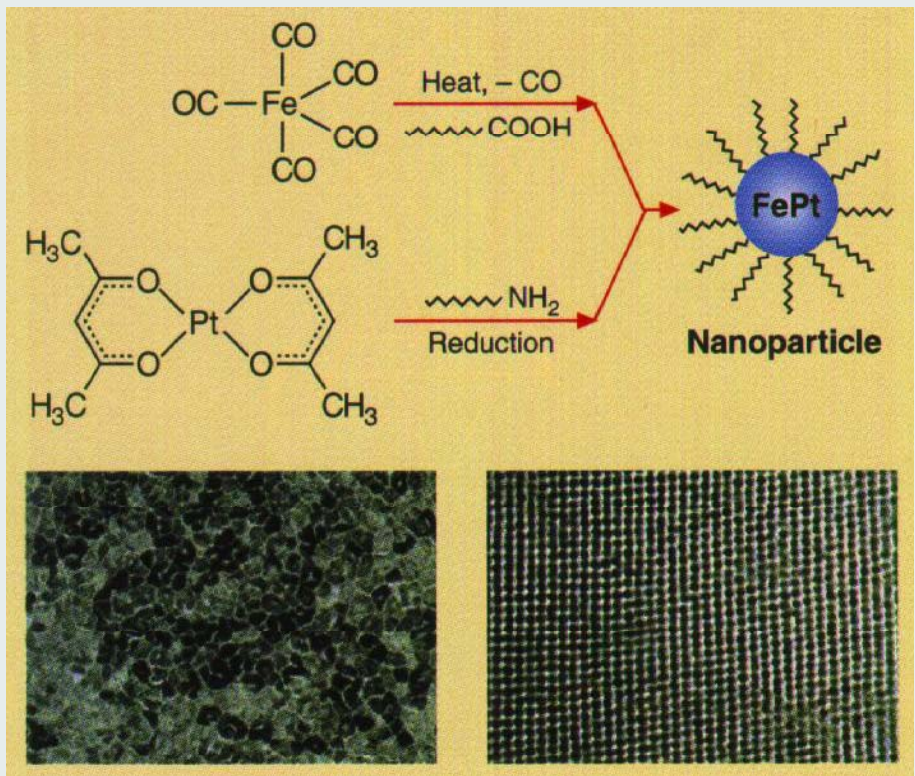


Figure 4. Schematic models for the formation of platinum nanotubes in the mixed surfactant templating system: A) Mixed ( $C_{12}EO_9$ /Tween 60) and B) single ( $C_{12}EO_9$ ) surfactant cylindrical rodlike micelles. C) Pathway from micellar solution to metal nanotubes by the reduction of metals salts confined to the aqueous shell of mixed-surfactant cylindrical micelles. The metal salts and water molecules are omitted from the models.

31.10.2007



# Composite and Multimetallic Particles

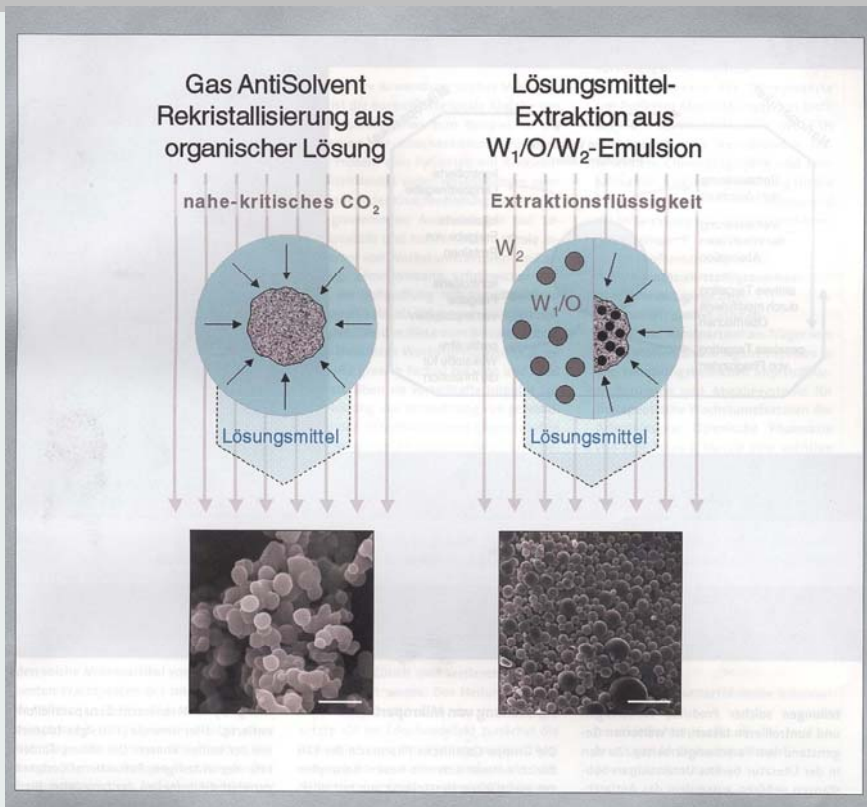


31.10.2007

Nanochemistry UIO

37

# Extraction Methods



31.10.2007

Nanochemistry UIO

38



# Spray Pyrolysis + Fly Ashes

## An experimental and modeling investigation of particle production by spray pyrolysis using a laminar flow aerosol reactor

I. Wuled Lenggoro, Takeshi Hata, and Ferry Iskandar  
 Department of Chemical Engineering, Hiroshima University, Kagamiyama 1-4-1,  
 Higashi-Hiroshima 739-8527 Japan

Melissa M. Lunden  
 Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory,  
 1 Cyclotron Road, Berkeley, California 94720

Kikuo Okuyama<sup>\*)</sup>  
 Department of Chemical Engineering, Hiroshima University, Kagamiyama 1-4-1,  
 Higashi-Hiroshima 739-8527 Japan

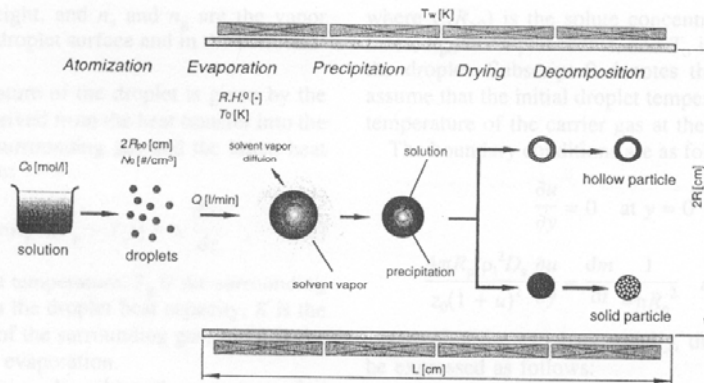


FIG. 3. Description of the simulation model.

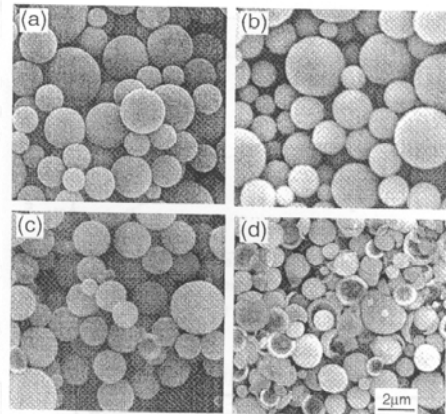
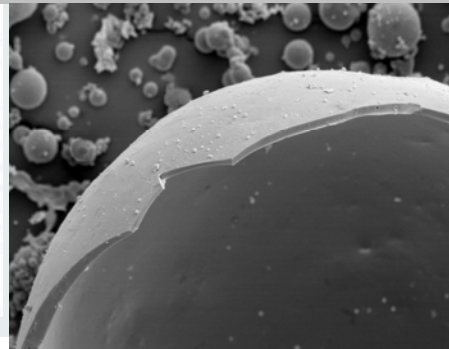


FIG. 6. Effect of furnace temperature on the morphology of zirconia particles: (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 500 °C. Other experiment conditions:  $C_0 = 2 \text{ mol/l}$ ;  $Q = 2 \text{ l/min}$ .

31.10.2007

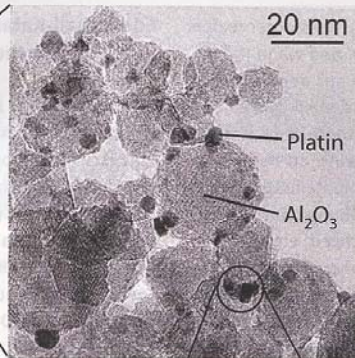
Nanochemistry UIO

# Gas Phase Reactions

## Flame Synthesis



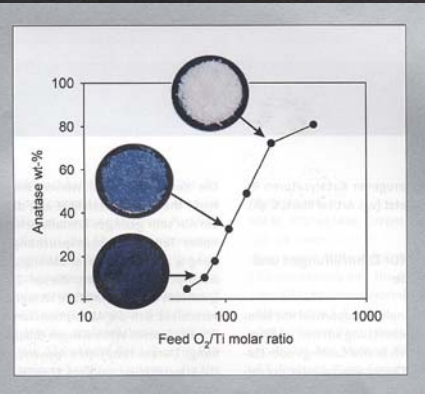
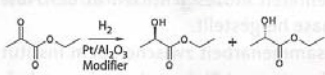
Flammensynthese



20 nm

Platin

Al<sub>2</sub>O<sub>3</sub>



31.10.2007

Nanochemistry UIO

**Large industrial importance**

40



# Gas Phase Reactions

## Oxide Evaporation

### Novel Nanostructures of Functional Oxides Synthesized by Thermal Evaporation\*\*

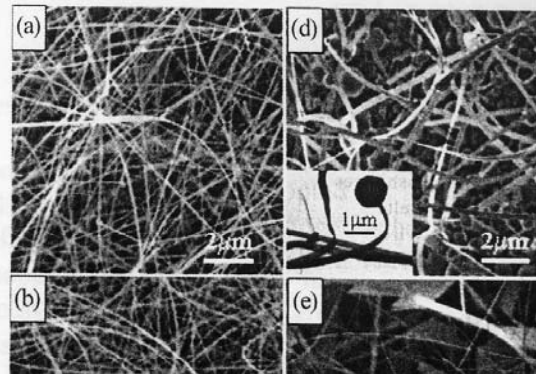
By Zu Rong Dai, Zheng Wei Pan,  
and Zhong L. Wang\*



*Adv. Funct. Mater.* 2003, 13, No. 1, January

Table 2. Synthesis conditions and morphology characteristics of oxide nanostructures.

Nano-structure	Source materials	Evaporation temperature [°C]	Pressure [torr]	Substrate temperature [°C]	Length [μm]	Width or diameter [nm]	Width-to-thickness ratio
ZnO belt	ZnO	1400	200–300	800–1100	>500	50–300	5–10
t-SnO <sub>2</sub> belt [a]	SnO	1050	200–300	800–950	>500	30–200	5–10
	SnO <sub>2</sub>	1350					
In <sub>2</sub> O <sub>3</sub> belt	In <sub>2</sub> O <sub>3</sub>	1400	200–300	800–1100	50–300	50–150	5–10
CdO belt	CdO	1000	200–300	700–800	<100	100–500	>10
CdO sheet	CdO	1000	200–300	700–800	5–10 μm	5–10 μm	20–60 nm (thickness)
Ga <sub>2</sub> O <sub>3</sub> belt	Ga <sub>2</sub> O <sub>3</sub>	1400	200–300	800–1100	50–500	20–100	5–10
	GaN	950		700–850			
Ga <sub>2</sub> O <sub>3</sub> sheet	GaN	950	200–300	700–850	5–10 μm	5–10 μm	20–60 nm (thickness)
PbO <sub>2</sub> belt	PbO	950	200–300	600–800	50–200	50–300	5–10
t-SnO <sub>2</sub> wire [a]	SnO	1050	250–700	25–40	>500	30–100	2–5
o-SnO <sub>2</sub> wire [b]	Sn+SnO	1050	200	25–40	>500	100–600	2–3
SnO diskette	SnO	1050	500–600	200–400		100 nm–10 μm	15
	SnO <sub>2</sub>	1350					



R. NESPER, ETH ZÜRICH & COLLEGIUM HELVETICUM

EiH  
Eidgenössische Technische Hochschule Zürich  
Swiss Federal Institute of Technology Zurich

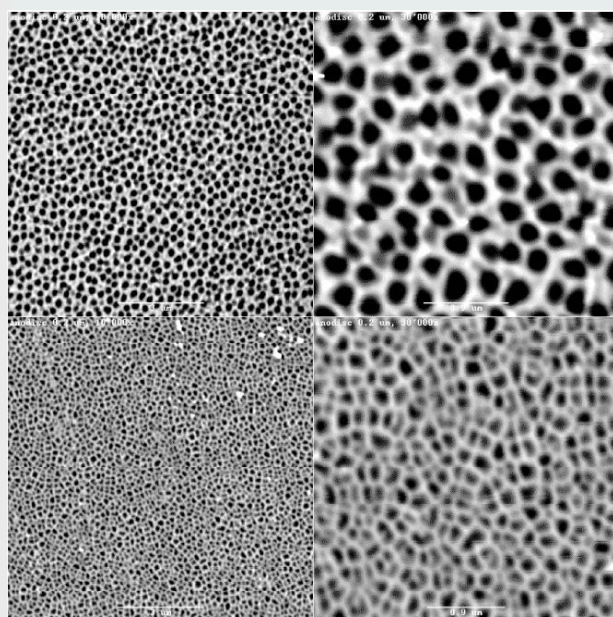
31.10.2007

Nanochemistry UIO

41

# Corrosion Methods and Phase Transitions

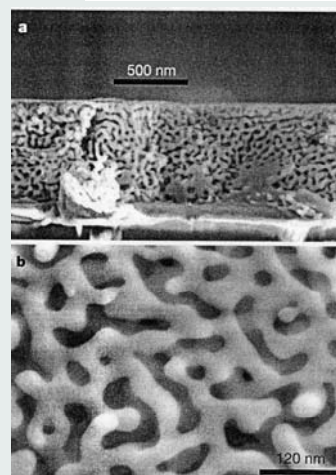
## Porous alumina (V, I, t, T + solv. characteristics)



## Evolution of nanoporosity in dealloying

Jonah Eriebacher\*†, Michael J. Aziz\*, Alain Karma†, Nikolay Dimitrov‡ & Karl Sterzadki§

Nature, 2001, 410, 450



**Figure 1** Scanning electron micrographs of nanoporous gold made by selective dissolution of silver from Ag-Au alloys immersed in nitric acid under free corrosion conditions. **a**, Cross-section of dealloyed Au<sub>32</sub>Ag<sub>68</sub> (atom%) thin film. **b**, Plan view of dealloyed Au<sub>26</sub>Ag<sub>74</sub> (atom%). The porosity is open, and the ligament spacings shown in **b** are of the order of 10 nm; spacings as small as 5 nm have been observed. Measurements of the surface area of nanoporous gold are of the order of order 2 m<sup>2</sup> g<sup>-1</sup> (refs 24, 25), comparable to commercial supported catalysts.

R. NESPER, ETH ZÜRICH & COLLEGIUM HELVETICUM

EiH  
Eidgenössische Technische Hochschule Zürich  
Swiss Federal Institute of Technology Zurich

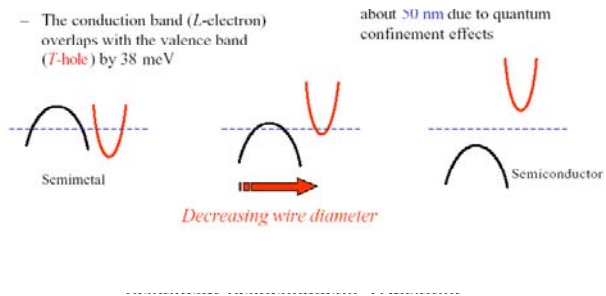
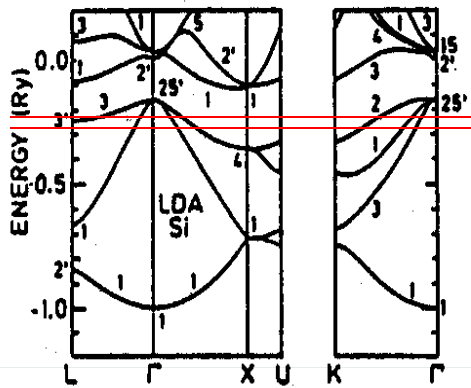
31.10.2007

Nanochemistry UIO

42

# Corrosion Methods and Phase Transitions

- |                              |  |
|------------------------------|--|
| 1. Porous alumina            | anodization  |
| 2. Porous silicon            | HF etching   |
| 3. Porous metals evaporating | dealloying / etching /   |
| 4. Amorphization of metals   | reconstructive phase transitions,<br>hydriding/dehydr.<br>Precipitation (Raney metals) |



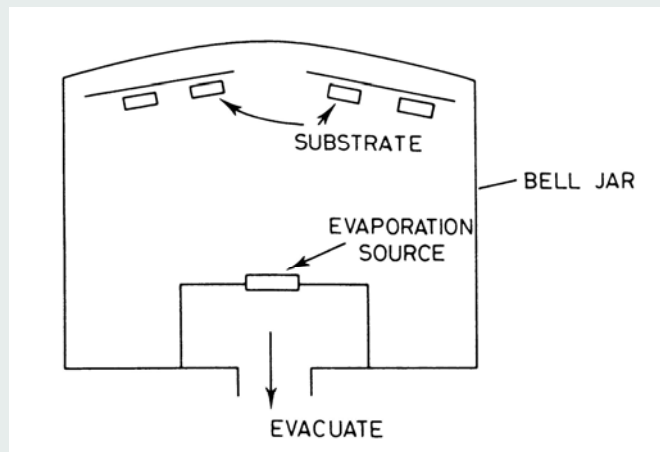
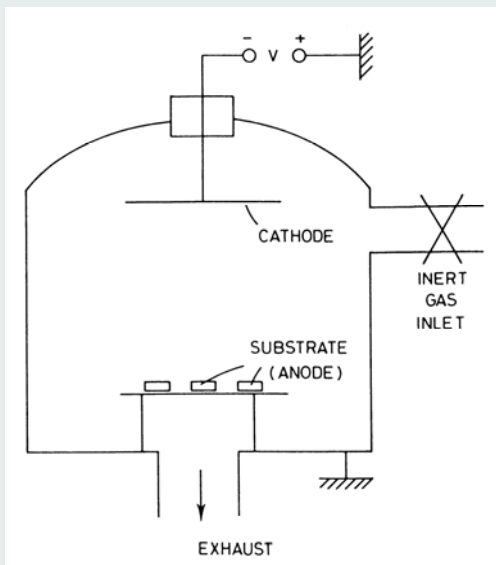
31.10.2007

Nanochemistry UIO

43

# Thin films

## Sputter technique



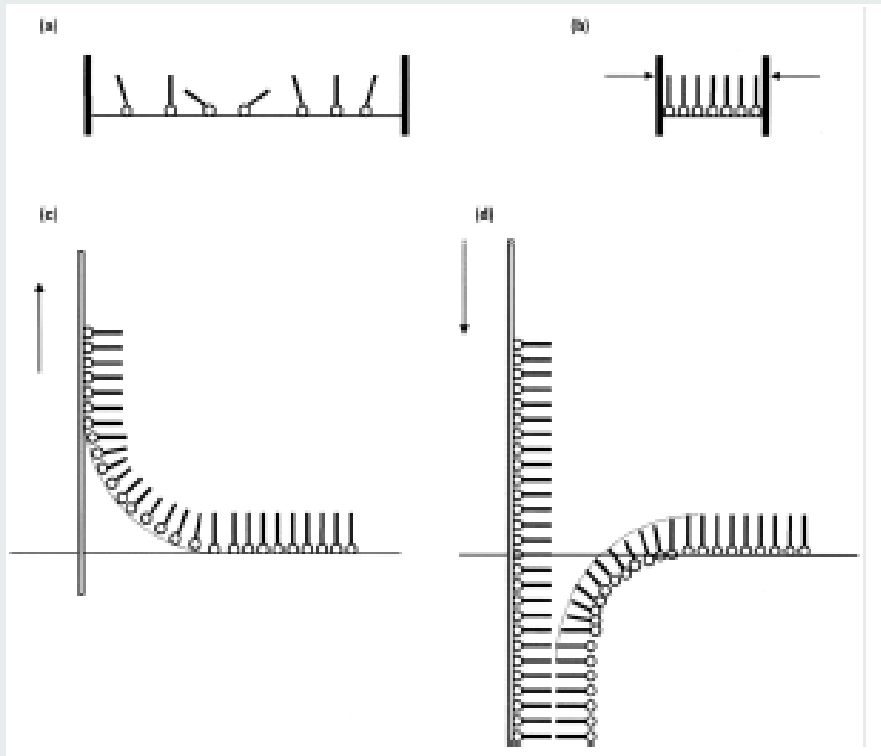
31.10.2007

Nanochemistry UIO

44



# Langmuir Blodgett Films



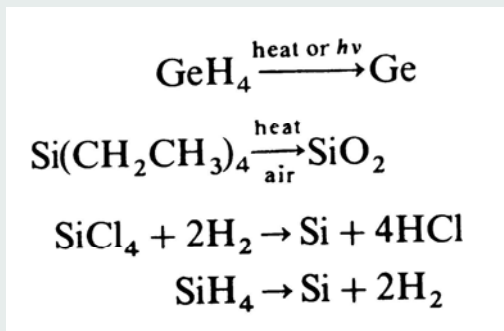
31.10.2007

Nanochemistry UIO

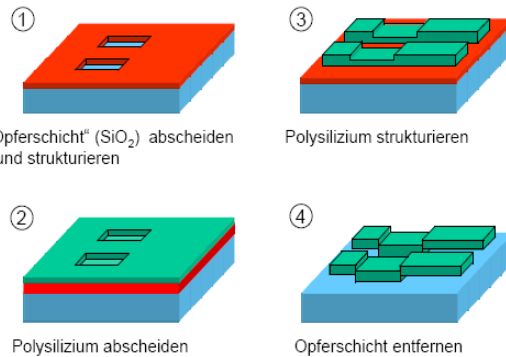
45

# Thin Films

## 1. Chemical Vapor Deposition –CVD und MOCVD



### Polysilizium - Oberflächenmikromechanik



TMA ---> Trimethylaluminium Al(CH<sub>3</sub>)<sub>3</sub>  
 TMG ---> Trimethylgallium, Ga(CH<sub>3</sub>)<sub>3</sub>  
 GaAs (3-5 - semiconductor) + PH<sub>3</sub>, AsH<sub>3</sub>

31.10.2007

Nanochemistry UIO

46

1. Chemical Twinning
2. Double Salts of Zintl Phases
3. Layered Compounds
4. Intercalated Layered Compounds
5. Exfoliated Layered Compounds

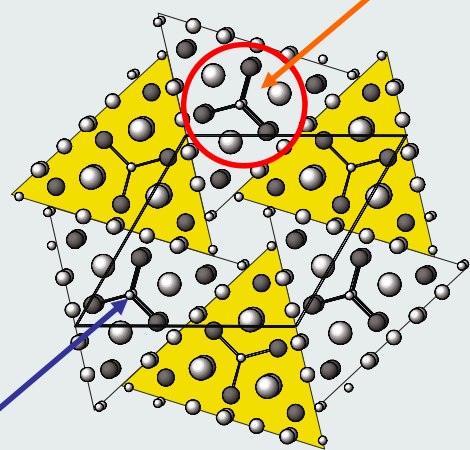
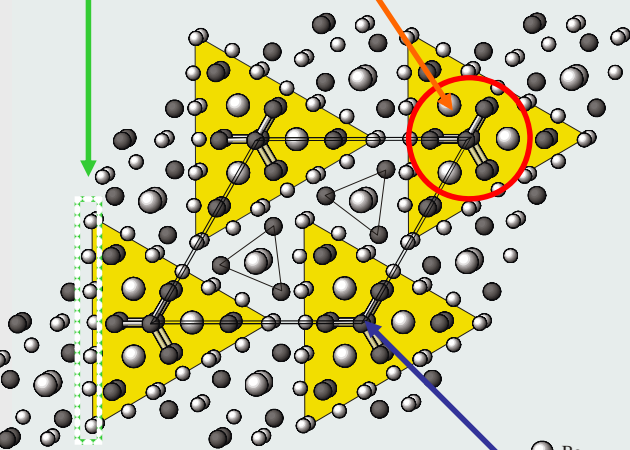
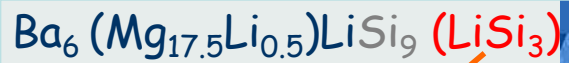
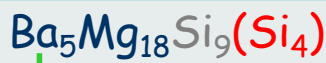
31.10.2007

Nanochemistry UIO

47

Direct Synthesis – Chemical Twinning - Intergrowth

S. Andersson; E. Parthe



(a)  $Ba_5Mg_{18}Si_{13}$

(b)  $Ba_6Mg_{17.5}Li_{2.5}Si_{12}$

● Ba  
● Si  
● Mg  
● Li

31.10.2007

Nanochemistry UIO

48



# Double Salts - Ordered Quantum Layers

R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM

**metallic**

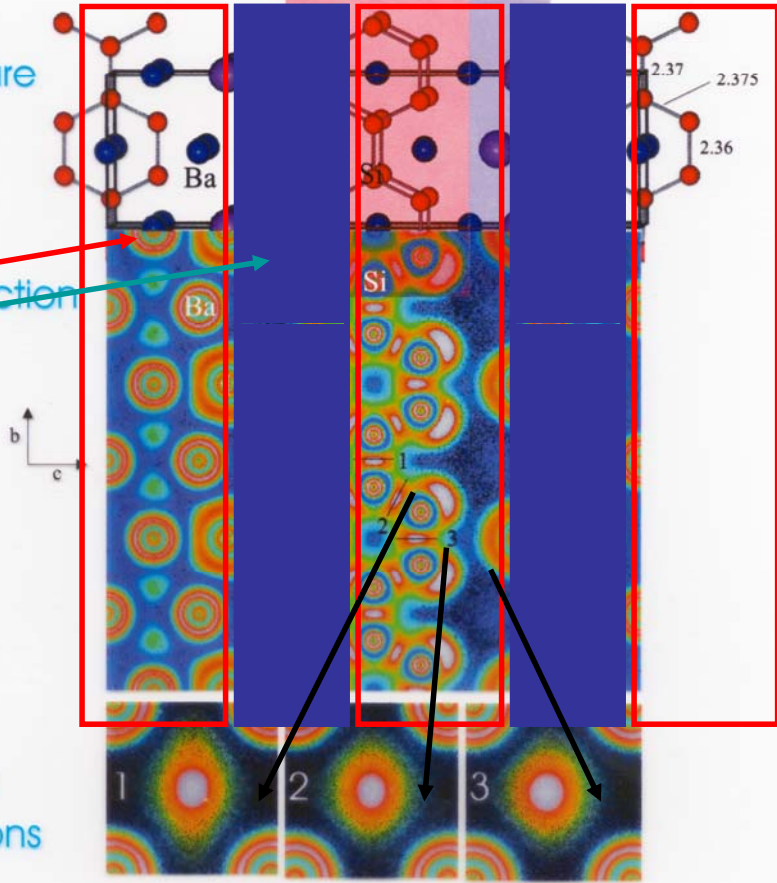
$[Ba_2Si_3]$   $[BaI_2]$

**insulating**

Structure

ELF section

Elf  
bond  
sections



31.10.2007