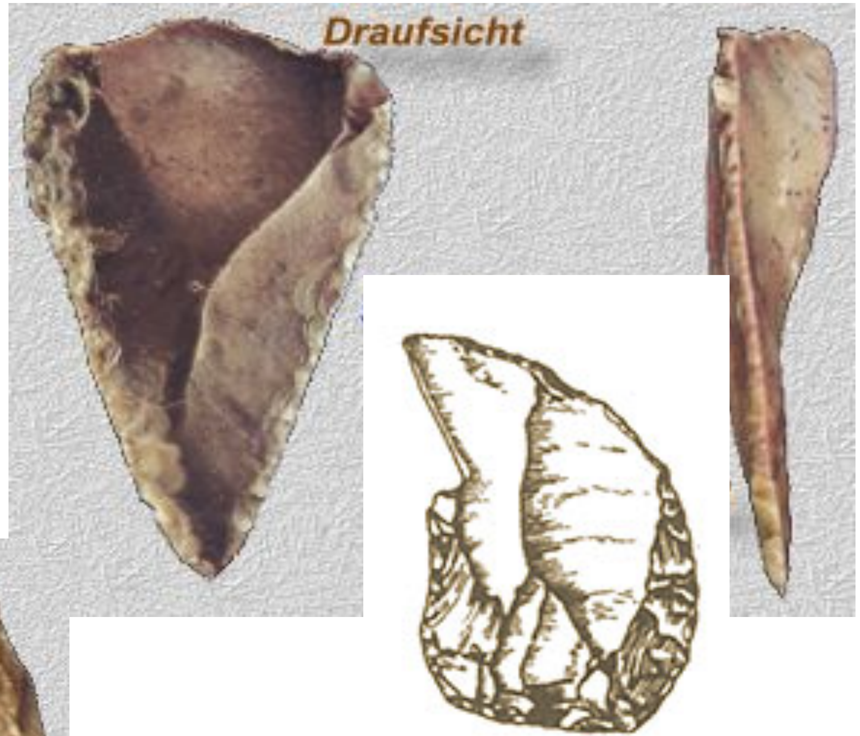
New materials: Where chemistry and materials science meet

Ulrich Schubert
Institute of Materials Chemistry

Stone Age Technology

Clovis point

needle
(from bone)

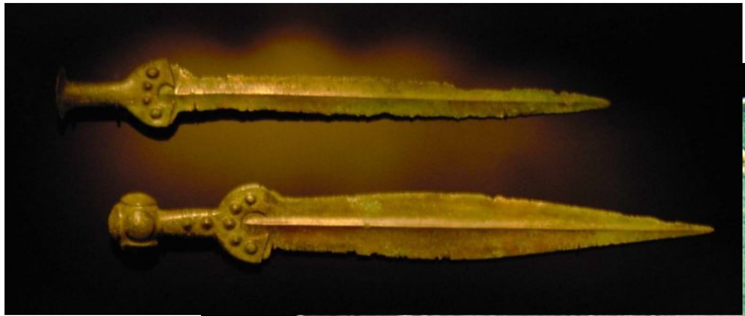


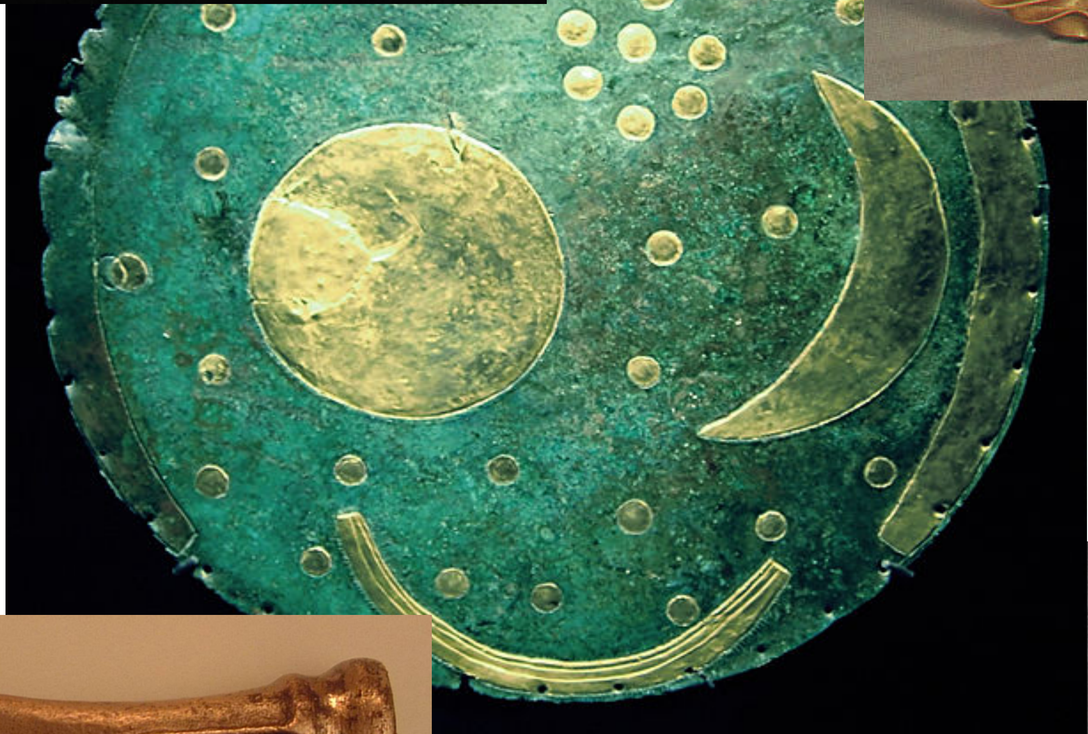
burin

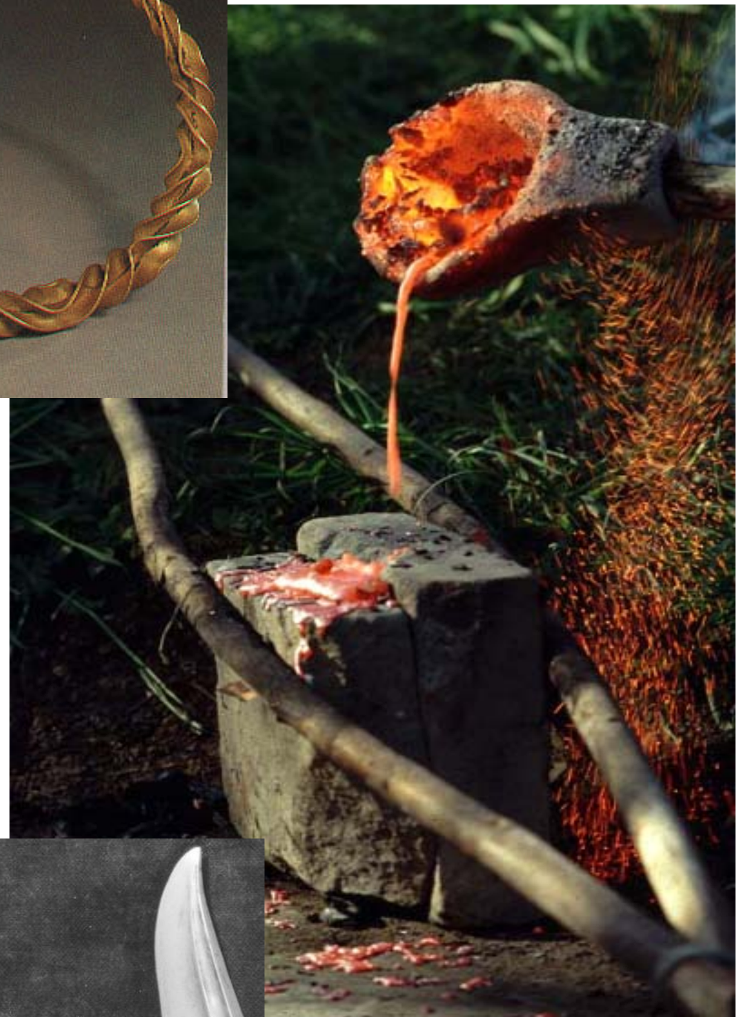
scraper

Pottery Technology

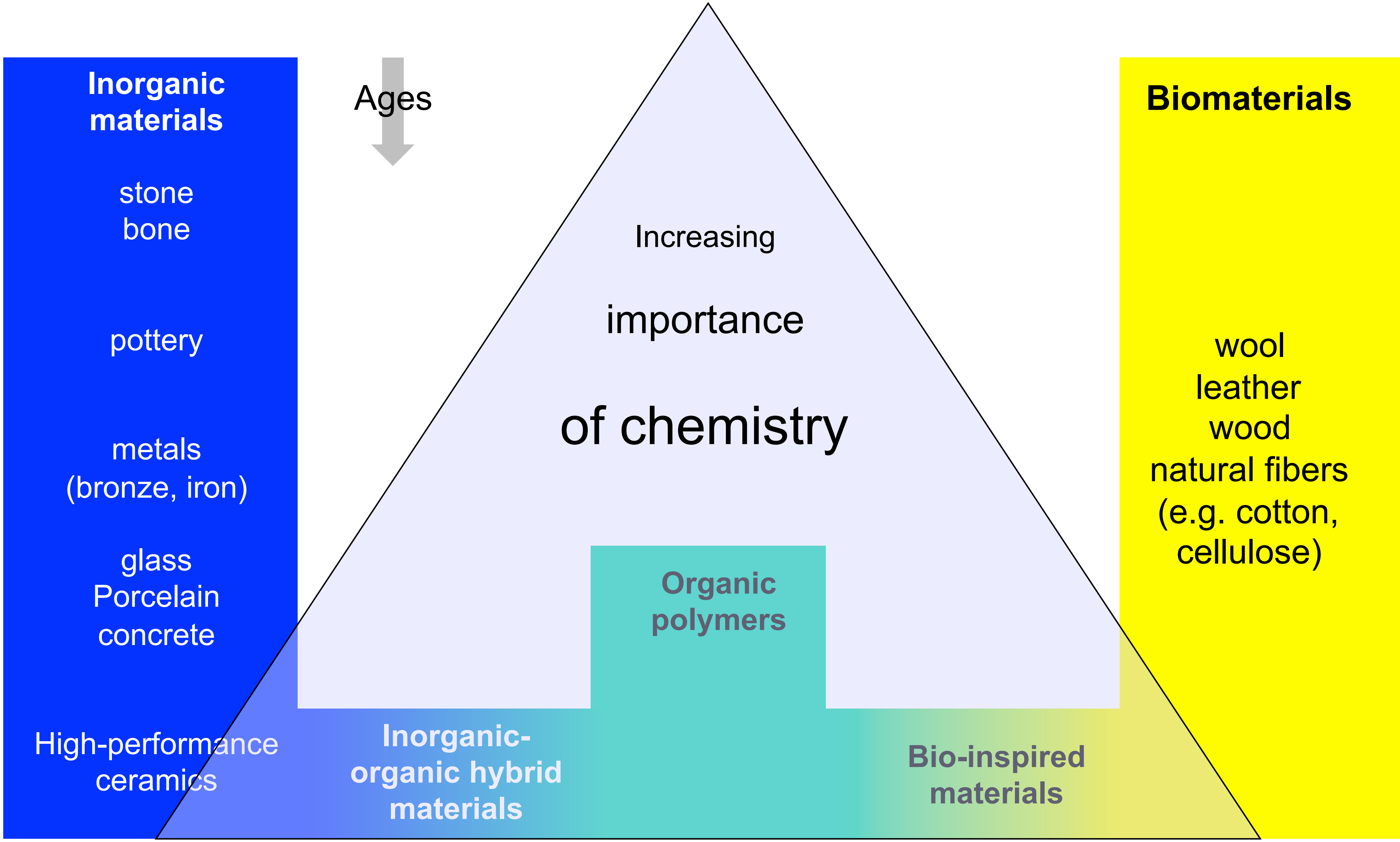
Bronze Age Technology



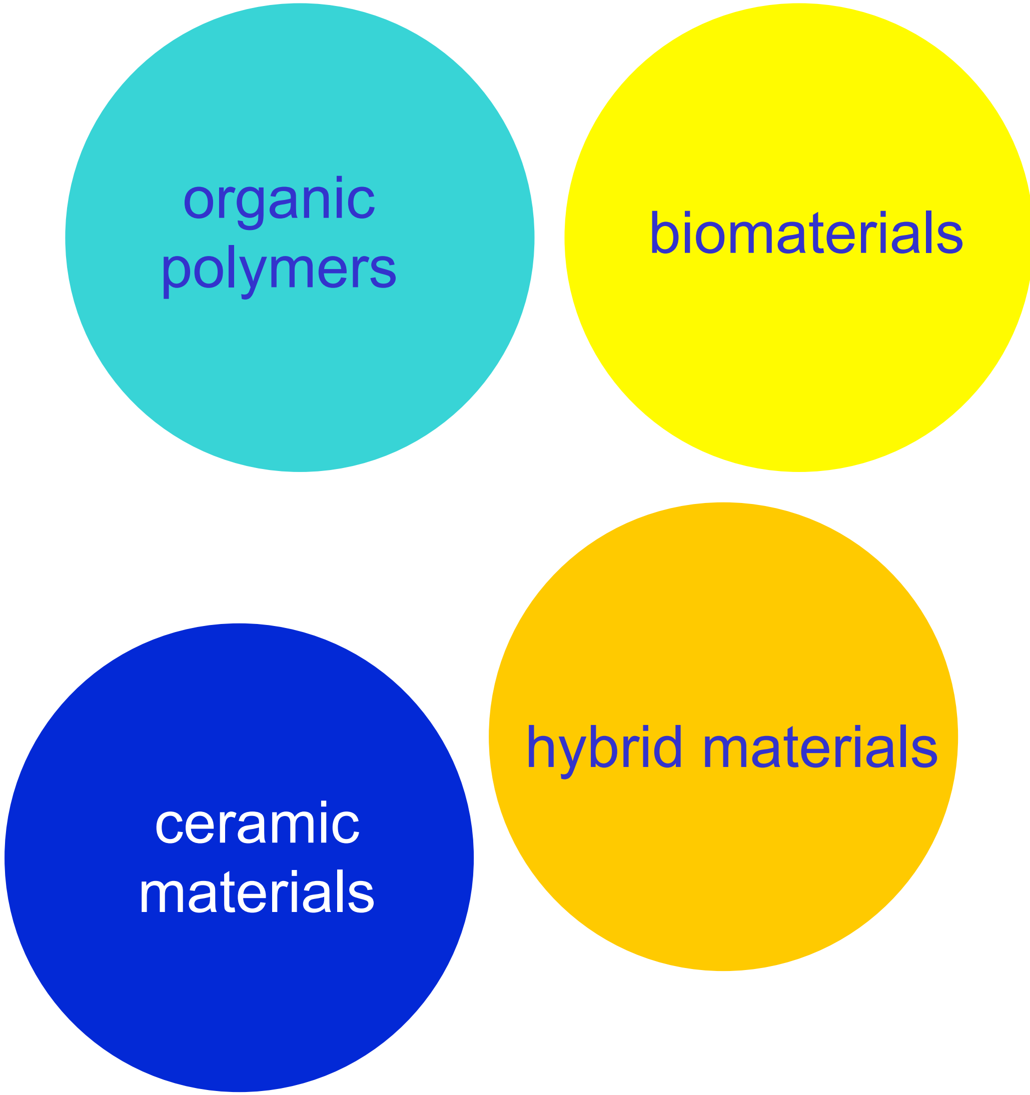




Evolution of Materials

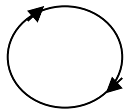


Evolution of Materials



„New Materials“

New technologies require new materials, e.g. no progress in microelectronics without new materials.



New materials enable new technologies, e.g. polymers, molecular materials, polymers etc. for development of plastic solar cells.

What renders a material “new”

New forms (for a given chemical composition)

- amorphous vs. crystalline
- dense vs. porous (tailoring of porosity)
- crystal size and shape
- nanomaterials (nanoscale or nanostructured)

New chemical compositions

- alloys (metals, semiconductors)
- doping of crystalline solids
- hybrid materials

Systems

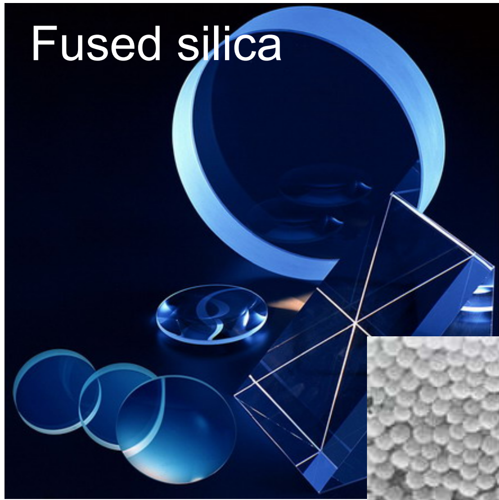
- separation of bulk and surface properties
- hierachically structured materials
- composites (and the role of interfaces)

„New Materials“ – New Forms

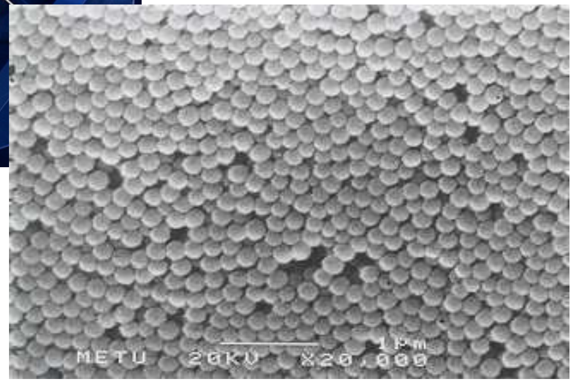
- Amorphous materials
- Porous materials (aerogels, ordered mesoporous materials)
- Nanostructures

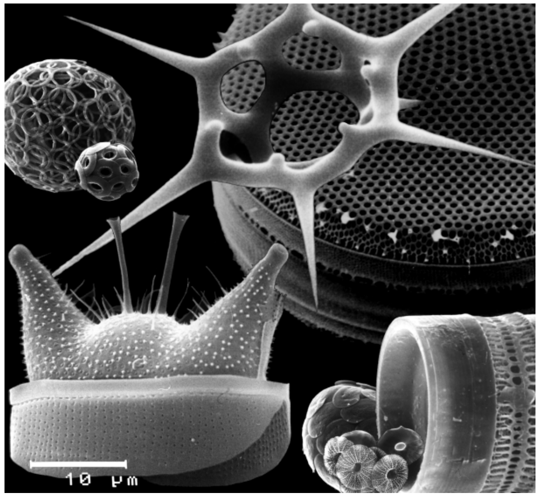
The Many Appearances (and Uses) of Silica (SiO_2)

Fumed silica

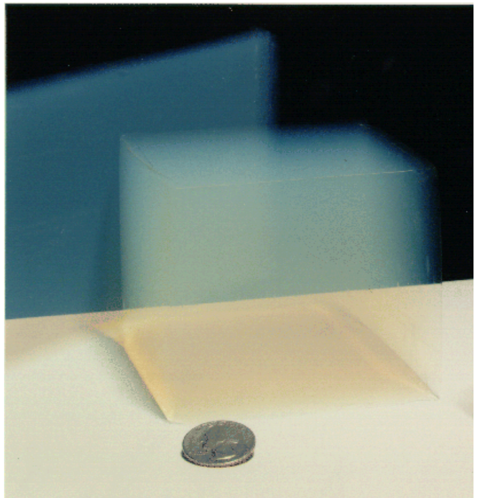


Stöber particles

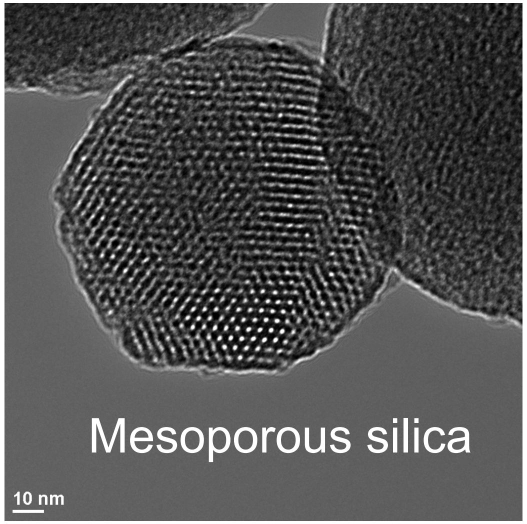


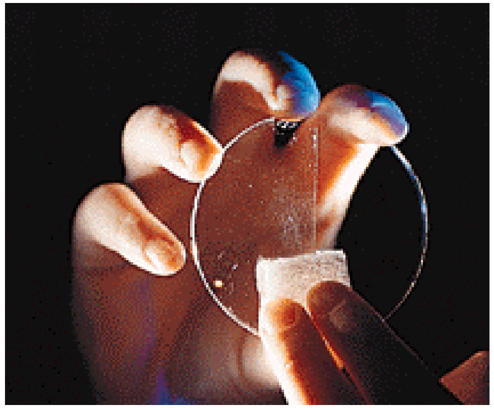


Diatoms



Silica aerogel





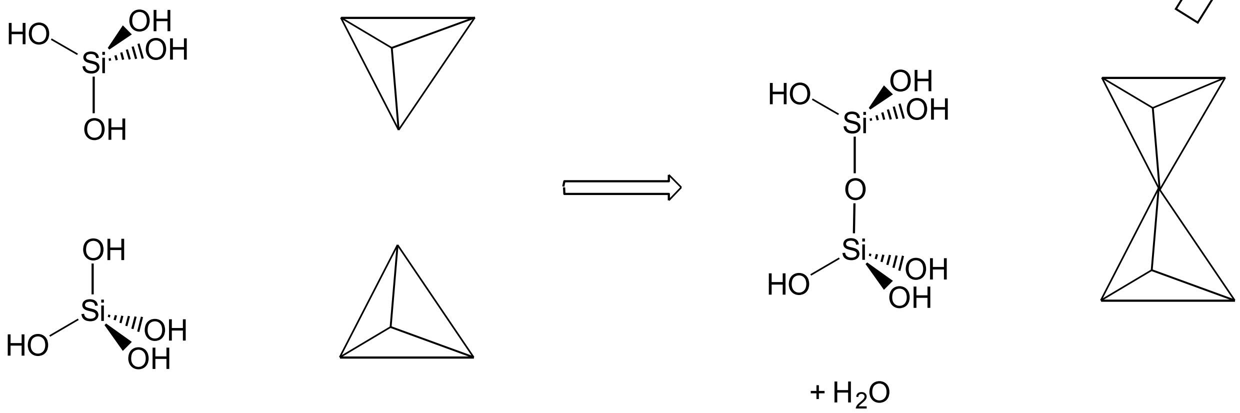
Silica film

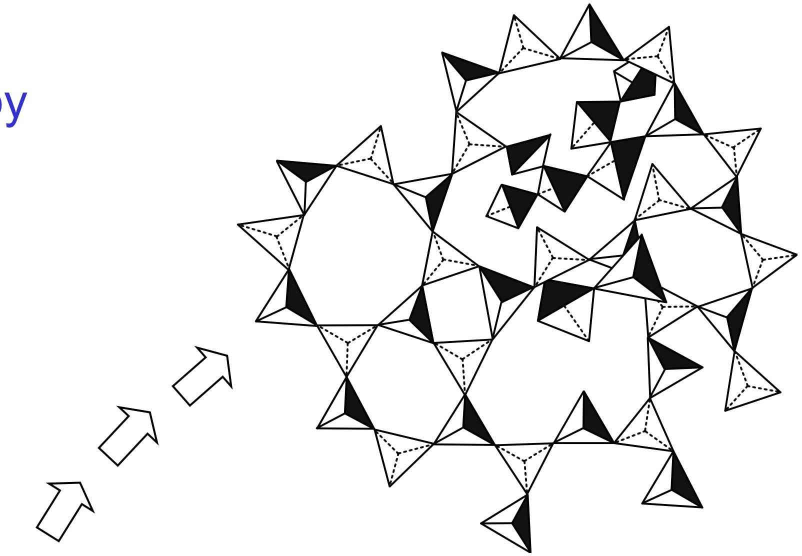
Amorphous Networks by Sol-Gel Processing

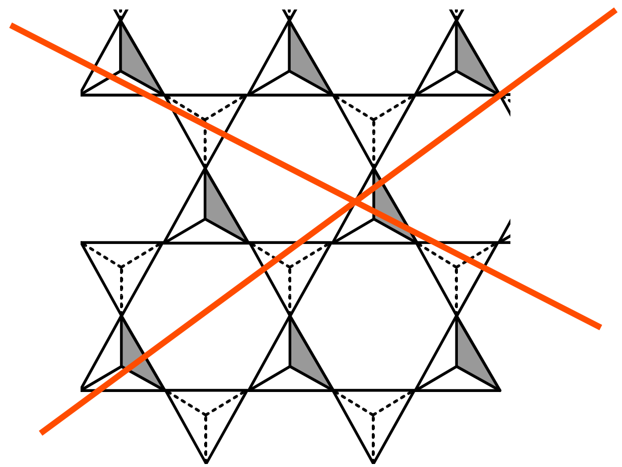
Gels are amorphous (= non-crystalline) solids
⇒ structures and properties are decisively influenced by the reaction conditions (kinetic reaction control)

Network formation by stepwise condensation reactions

2 ≡Si-OH ⟶ ≡Si-O-Si≡ + H_2O

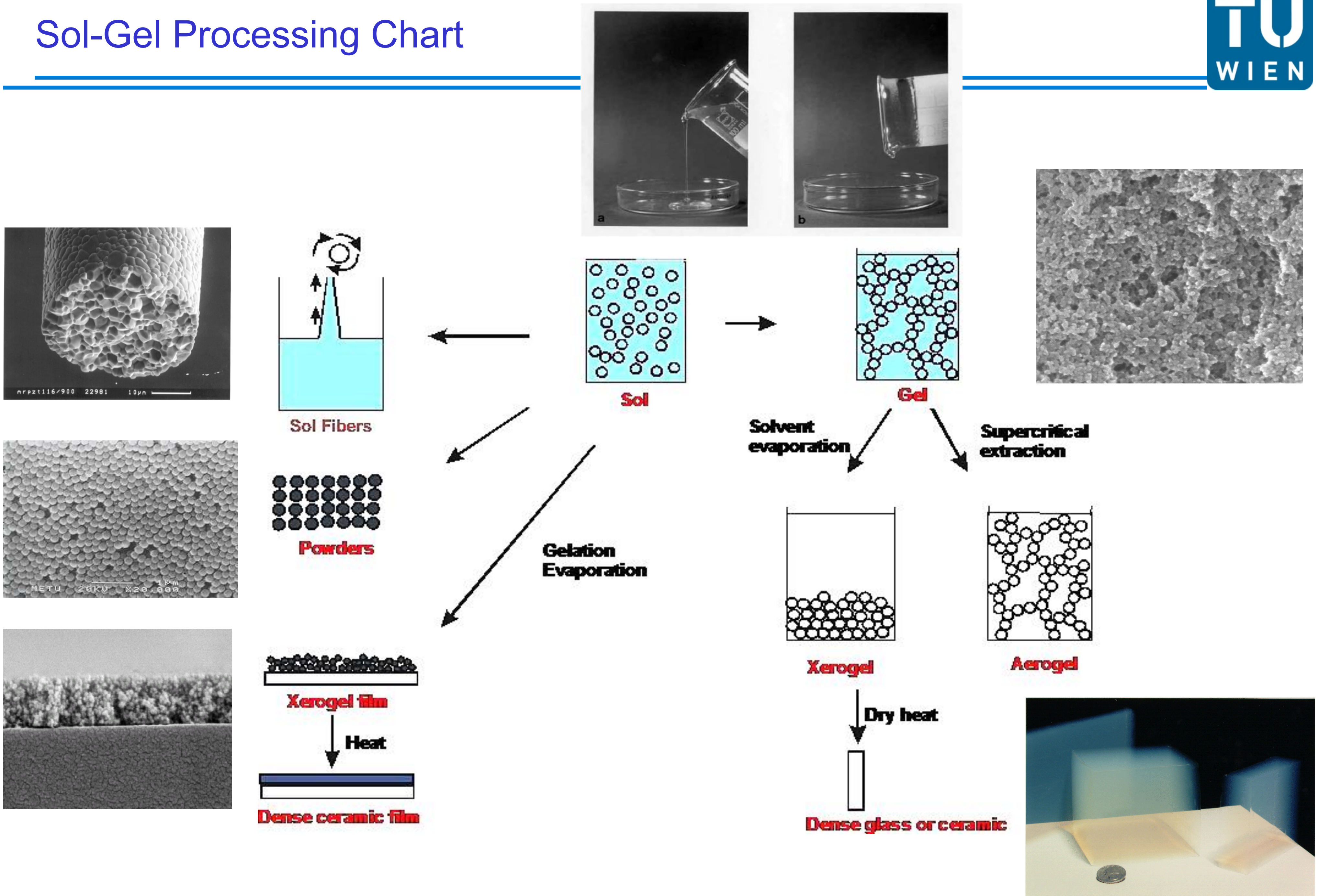






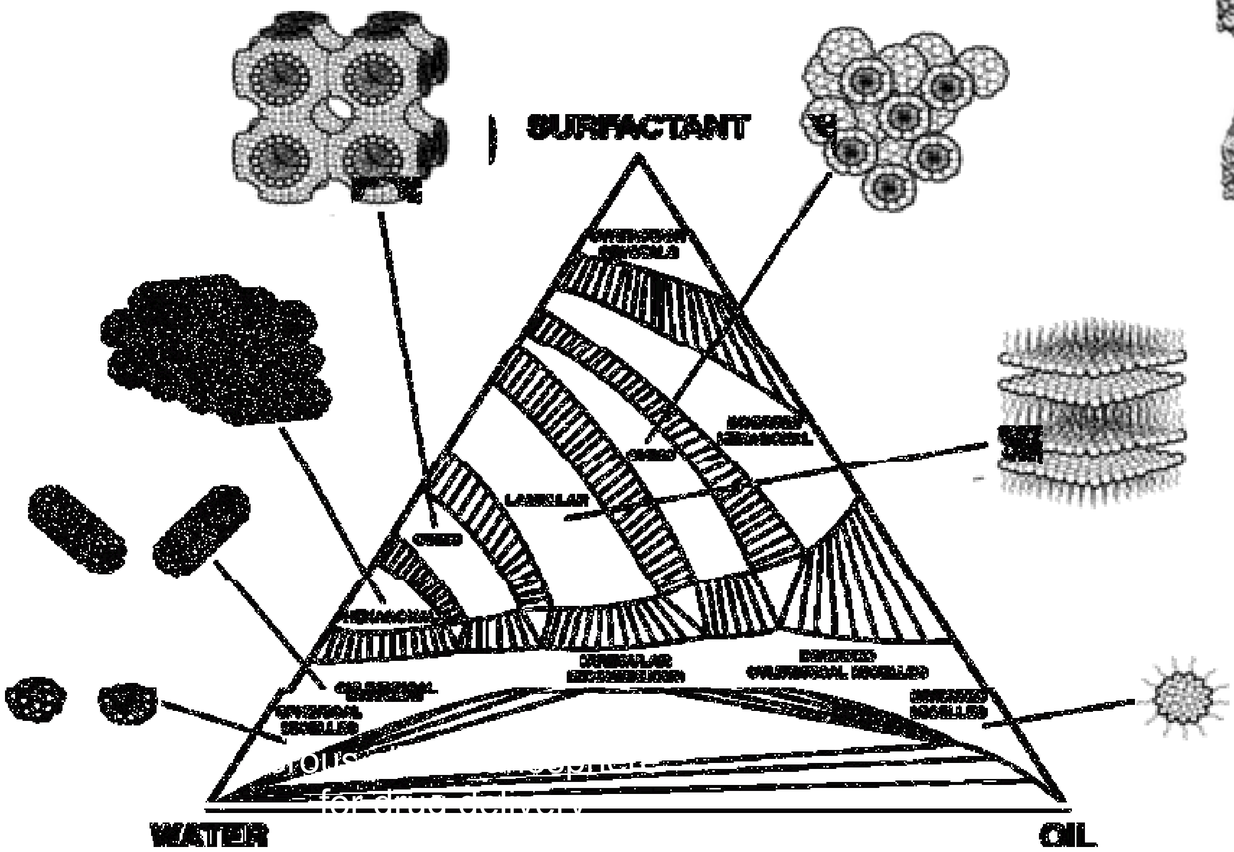
Very similar for metal compounds
→ amorphous or microcrystalline gels

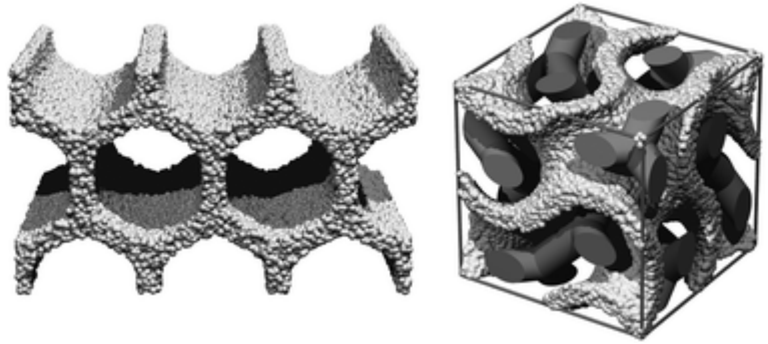
Sol-Gel Processing Chart

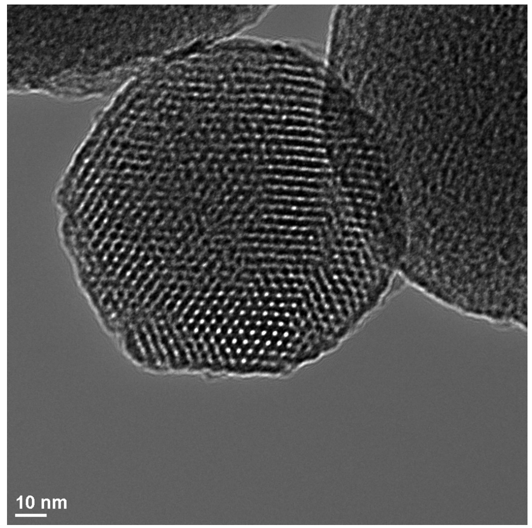


Silica with Ordered Porosity

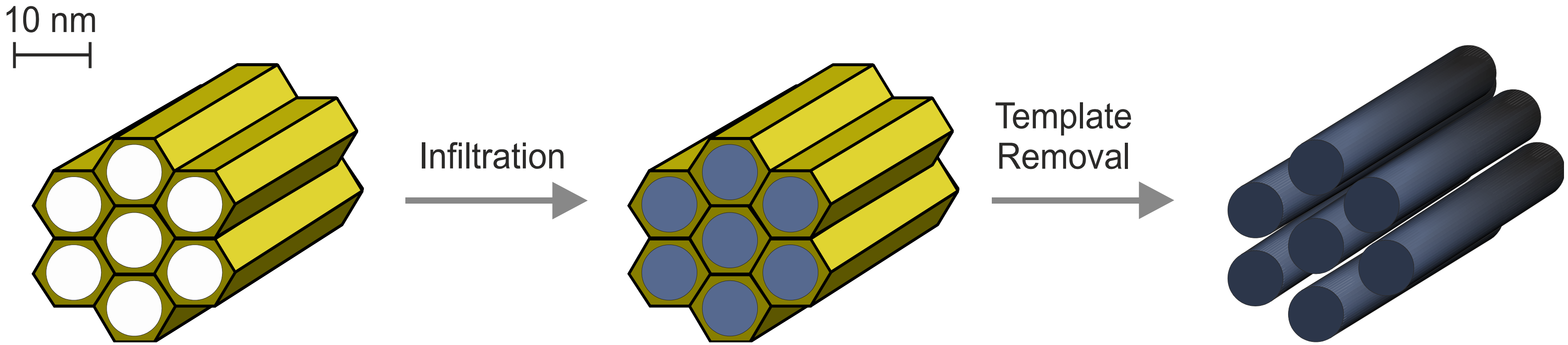
Self-assembled surfactant structures as template





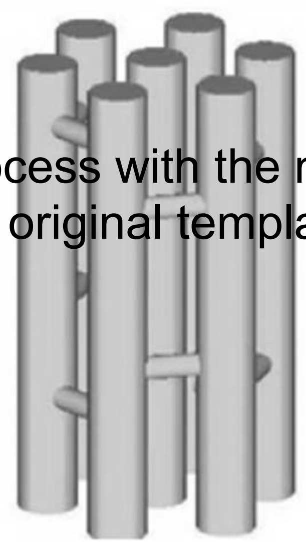


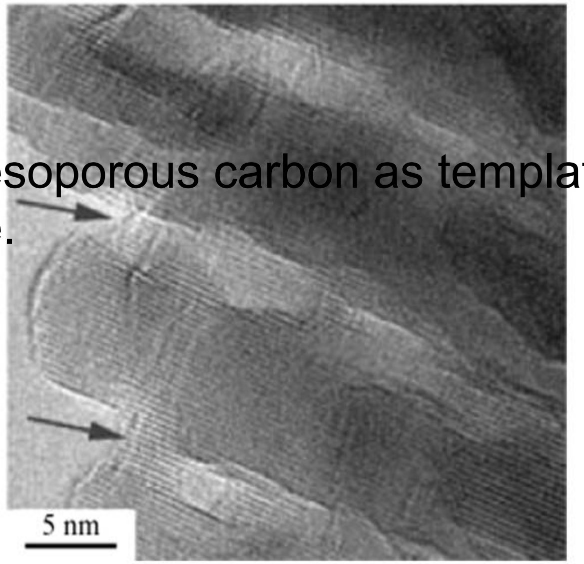
Nanocasting: Mesoporous Silica as Template



Mesoporous carbon

Templated mesoporous Cr_2O_3:

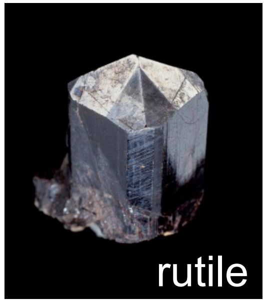




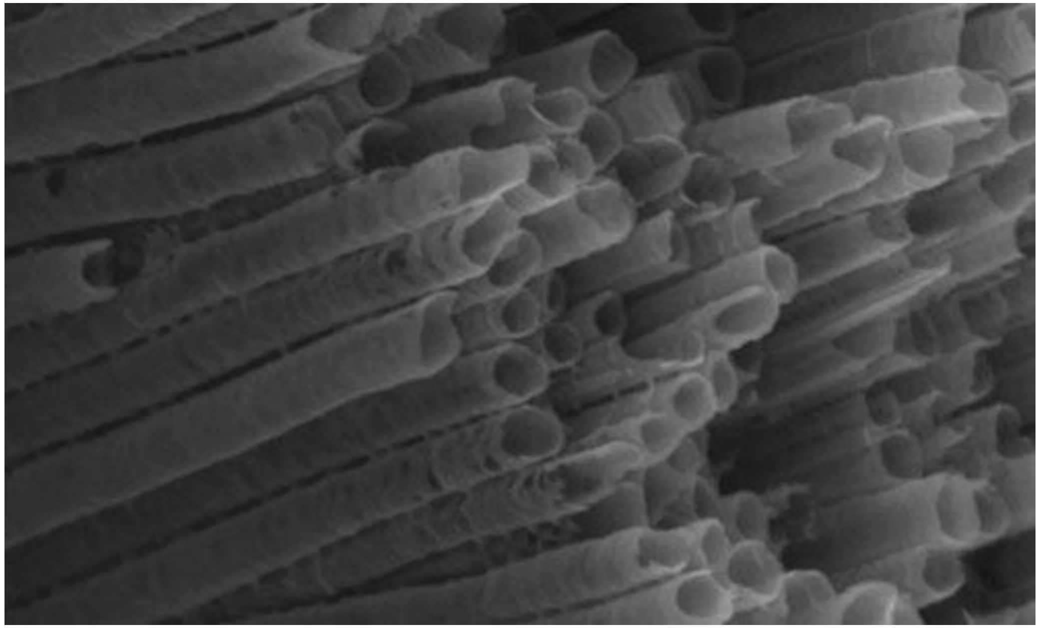
Repetition of the nanocasting process with the mesoporous carbon as template results in a positive replica of the original template.

K. Zhu et al., Chem. Comm. 2003

New Forms of Titania

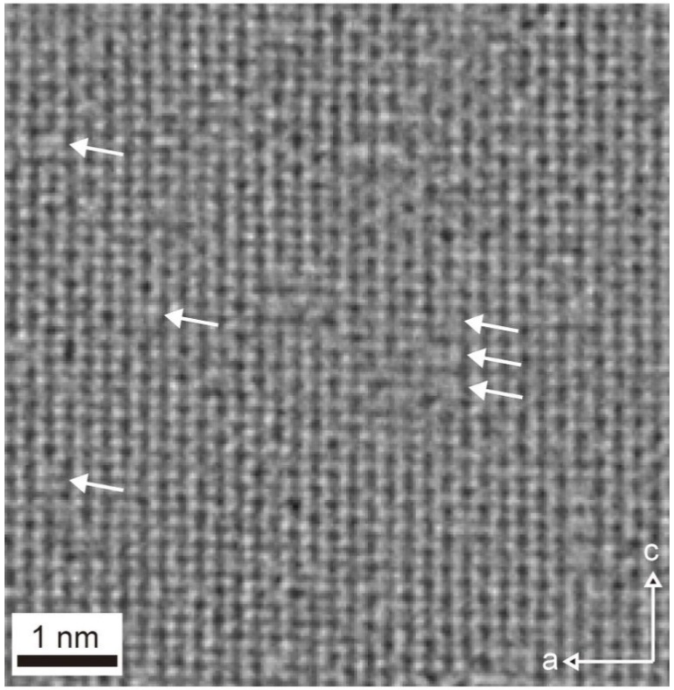


Unusual forms of easily crystallizing metal compounds can be created by other methods as well: titania as an example



Titania nanotubes by anodic oxidation of titania

I.V. S. Yashwanth, I. Gurrappa, 2004



Titania nanoheet by delamination of layered $K_{0.8}Ti_{1.73}Li_{0.27}O_4$

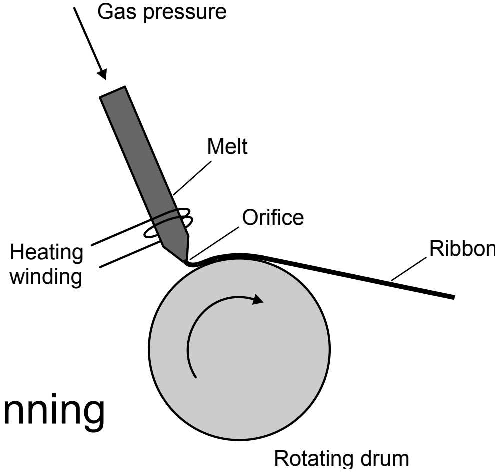
M. Ohwada et al, 2013

„New Materials“ – New Chemical Compositions

- Alloys (metals, semiconductors)
- Metal-organic frameworks
- Hybrid materials by sol-gel processing

Alloys – the Case of Bulk Metallic Glasses

The glassmakers‘ traditional approach: rapid cooling



chill-block melt-spinning

https://www.physik.unibas.ch

Bulk metallic glasses: confusion principle

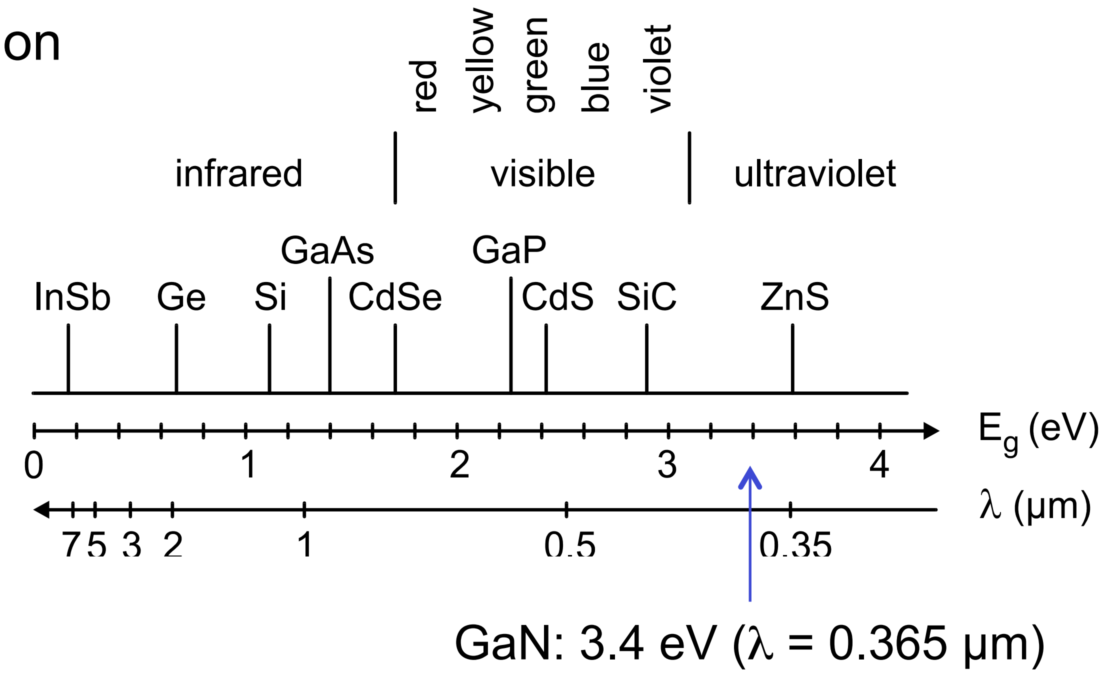
http://thefutureofthings.com/

Example: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vitreloy 1®)

- Alloy with ≥ three elements.
- Significant difference in atomic size ratios (>12%) among the three main constituents (→ higher packing density).
- The three main elements should exhibit negative heats of mixing (→ retards local atomic rearrangements).

Semiconductor Alloys – the Case of Blue LEDs

Band gaps of some common semiconductors



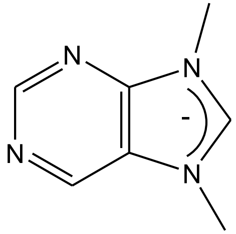
Increasing the In proportion in $In_{1-x}Ga_xN$ shifts emission maximum to higher wavelengths (up to 0.57 µm) → blue and green LEDs (blue [0.440 µm] at ca. 30% InN)

Chemical Vapor Deposition (CVD)

$$GaMe_3/InMe_3 + NH_3 \longrightarrow In_{1-x}Ga_xN + 3\ CH_4$$

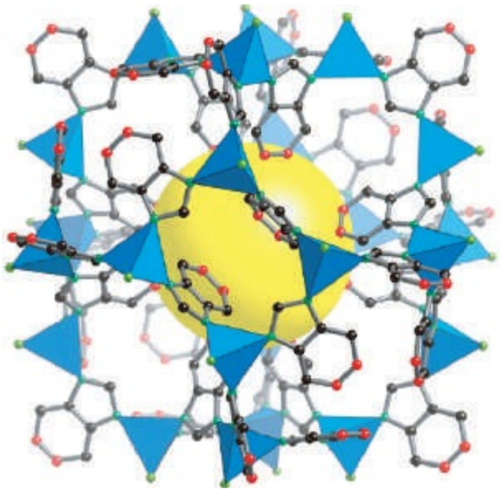
Metal-organic Frameworks (MOF)

Replace Si^{4+} (Al^{3+}) by Zn^{2+}, and O^{2-} by

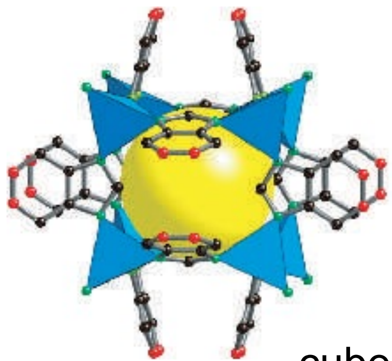


Zeolith A Topology

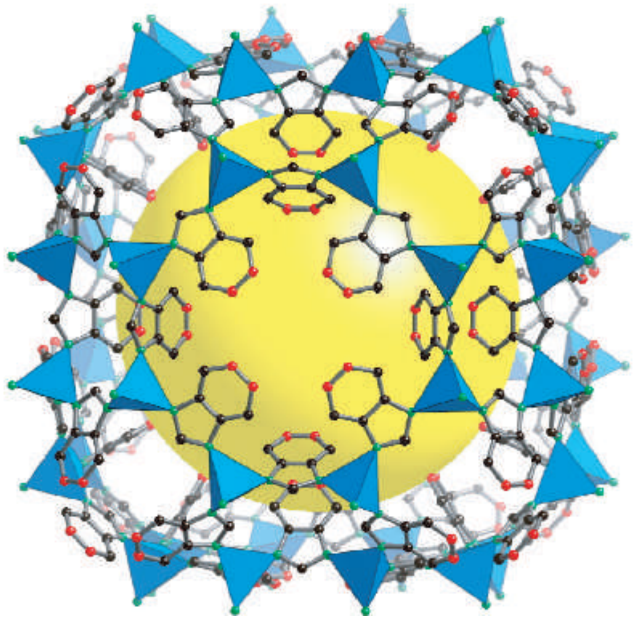
= Si-O-Si or Si-O-Al



ß-cage



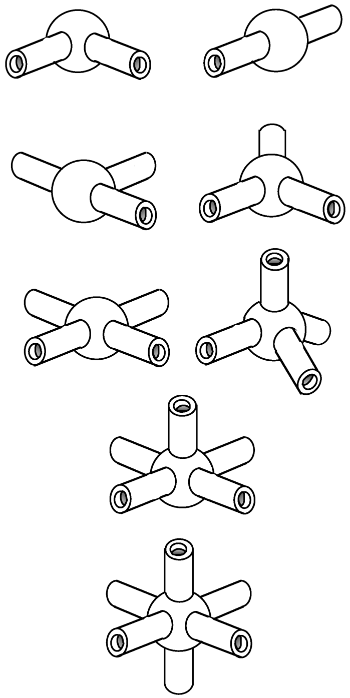
cube



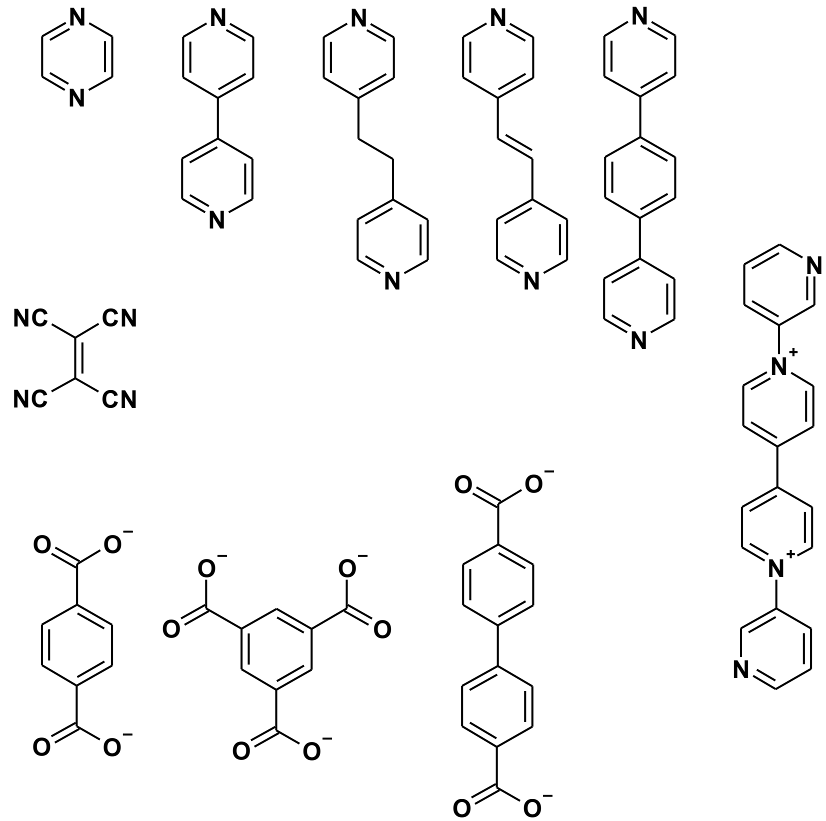
α-cage

Metal-organic Frameworks (MOF)

Metal node
(ions or clusters)

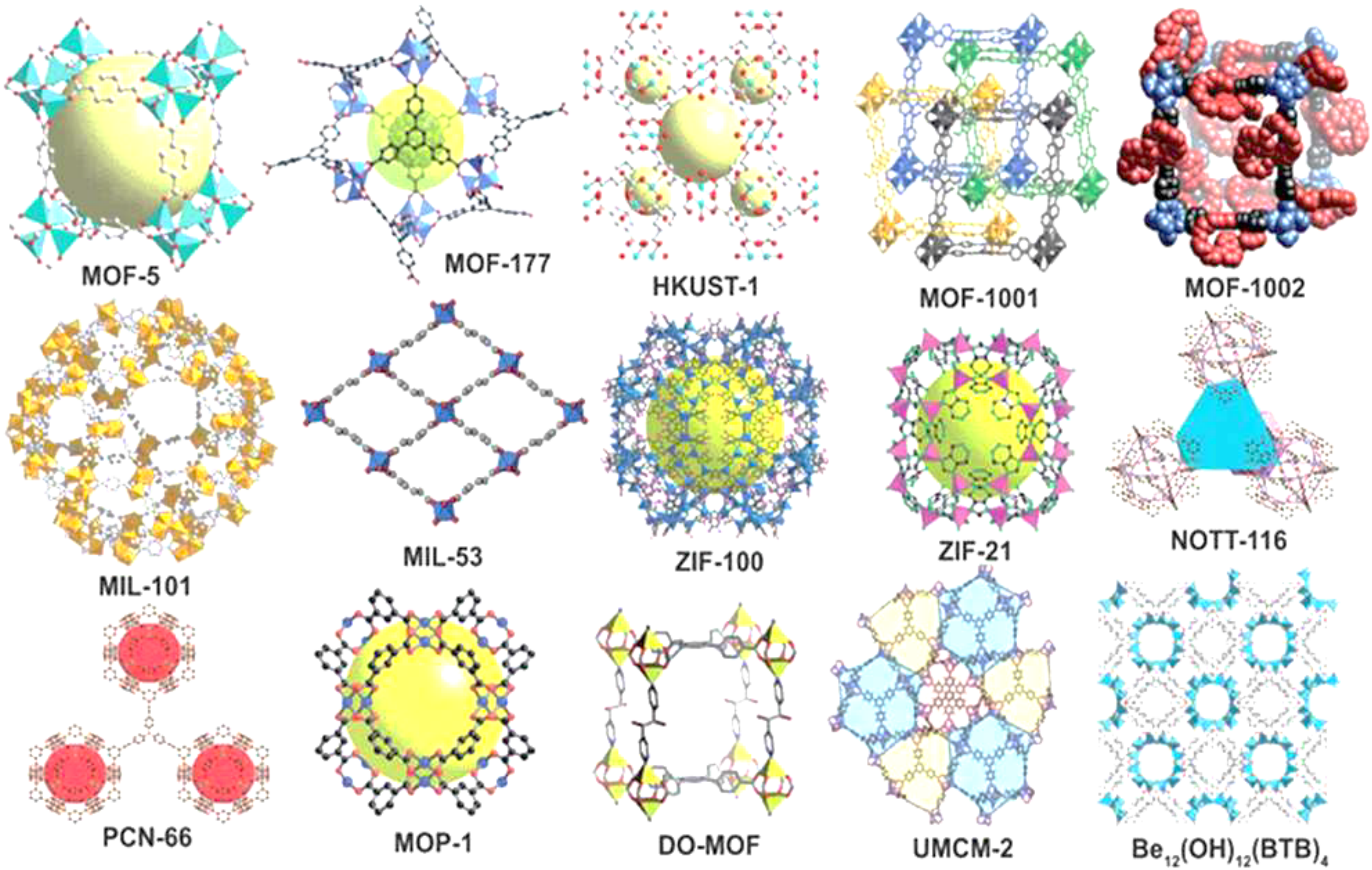


Linker



(Linkers can be functionalized)

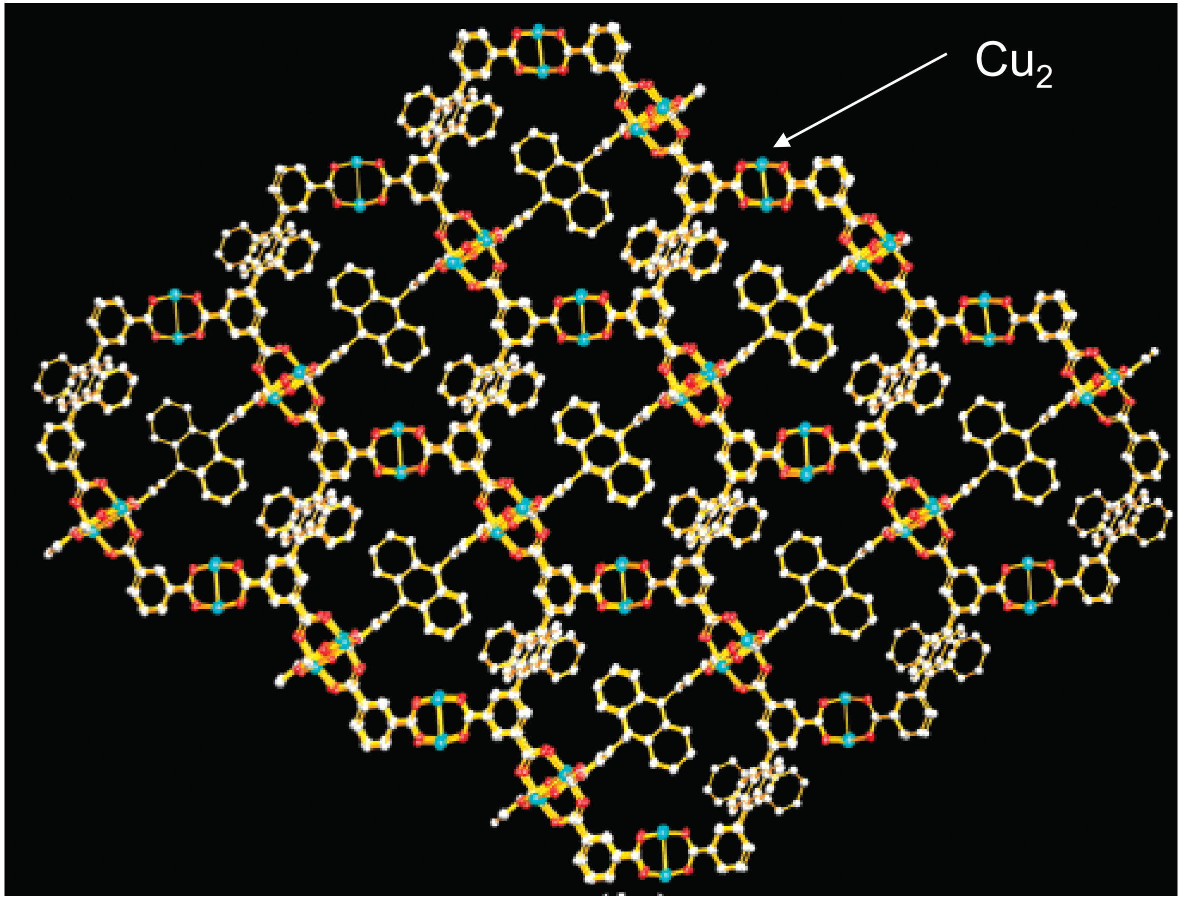
Metal-organic Frameworks (MOF)



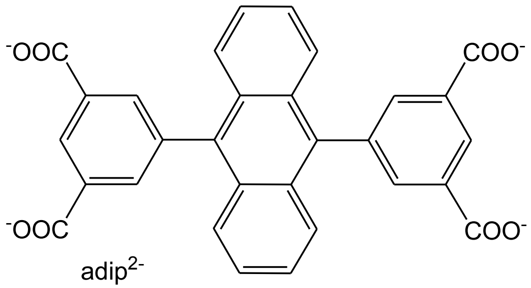
Xiang, et al. *Energy Environ. Sci*. (2010), **3**, 1469.

Metal-organic Frameworks (MOF)

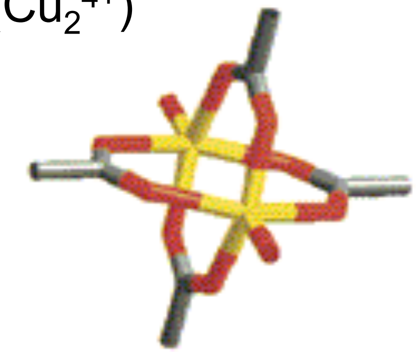
$Cu_2(adip) \cdot 2\ H_2O$ (PCN-14)



Linker



Metal node (Cu_2^{4+})



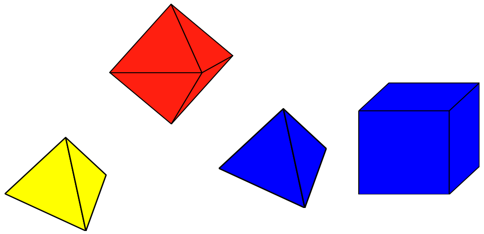
$S = 1753\ m^2/g$
Storage capacity for CH_4 at 125 K:
434 vol CH_4 / vol PCN-14
= 73.4% of the density of liquid CH_4

H.-C. Zhou et al. JACS 2008

Inorganic-Organic Hybrid Materials – Molecular Lego

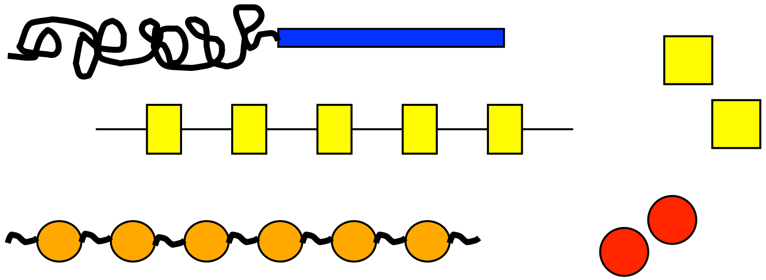
One of the advantages of amorphous materials (obtained by sol-gel processing): deliberate combination of (molecular or nanoscale) **building blocks**

- Combination of two or more inorganic building blocks → bi- and multimetallic oxides with any metal ratio
- Combination of organic and inorganic building blocks → inorganic-organic hybrid materials



Inorganic building blocks

+



Monomeric, oligomeric or polymeric organic building blocks

The goal is to create materials with specific combinations of properties by combining variable proportions of organic and inorganic building blocks. Molecular precursors play a decisive role since they become part of the final material. This requires their careful selection and chemical „design“.

An Example: Corrosion-Protection Coating for Mg Alloys

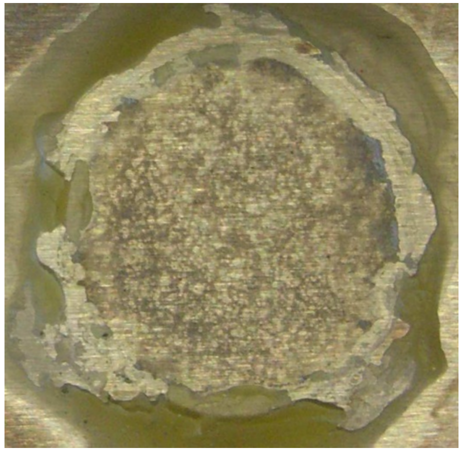
Optimized composition / conditions *:

(1) Cleaning of the Mg substrate by pickling with an aqueous solution of 20% acetic acid and 5% $NaNO_3$.

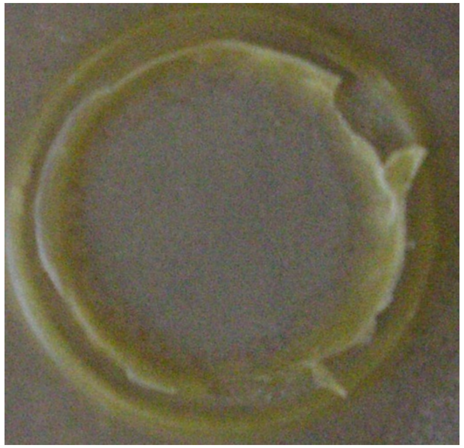
(2) Coating sol from $MeSi(OEt)_3$, $Si(OEt)_4$, $(MeO)_3SiCH_2CH_2CH_2X$ (X = N-heterocyclic group), water, H_3PO_4, alcohol and a metal-organic compound as adhesion promotor

Corrosion test (WE34, 5% NaCl solution) after 24 h

untreated



only pickling

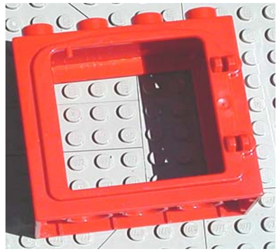


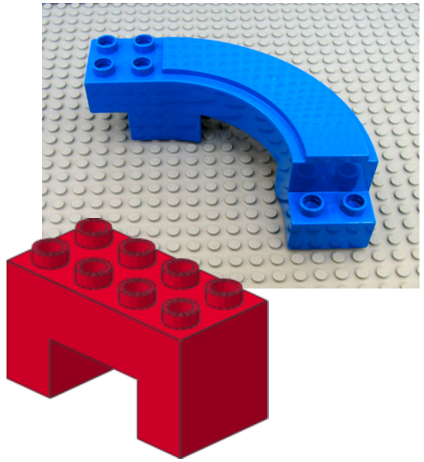
with sol-gel coating

* DE 10 2009 005 105; PCT/EP2010/050090

From Molecular Building Blocks to Preformed Modules

and arrangement “by chance”

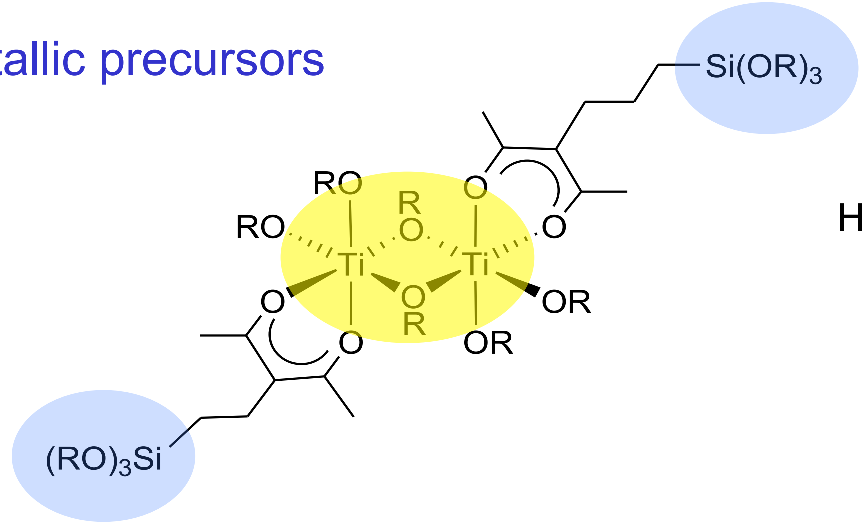


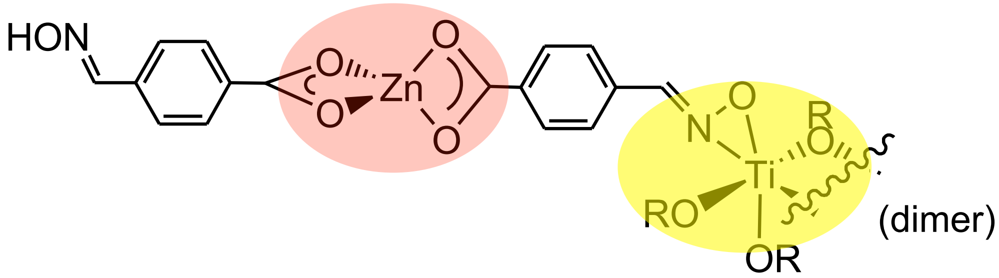


and arrangement according to a master plan

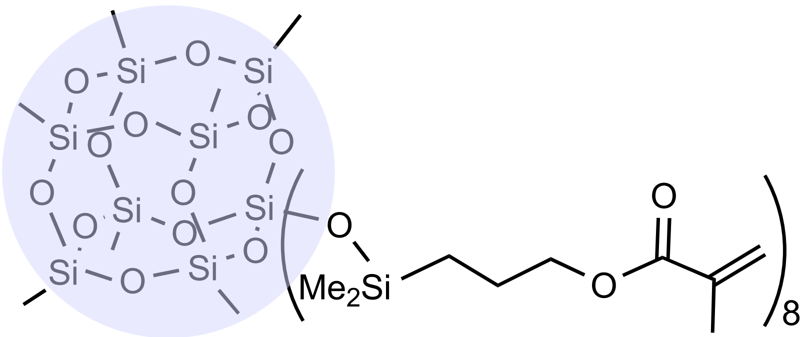
From Simple Molecular Building Blocks to Modules

Bimetallic precursors

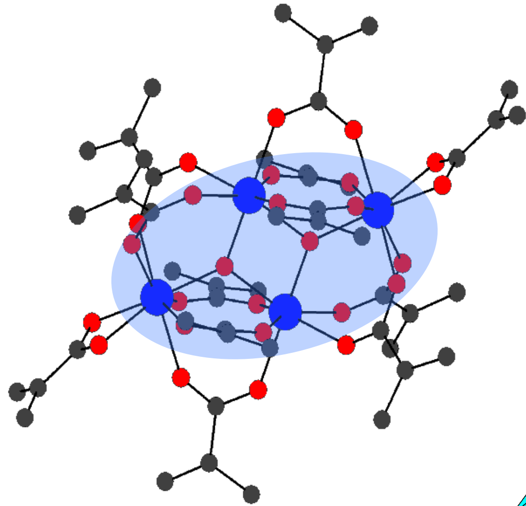


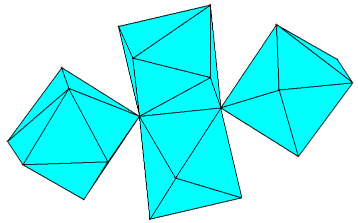


Inorganic nano building blocks (NBB)



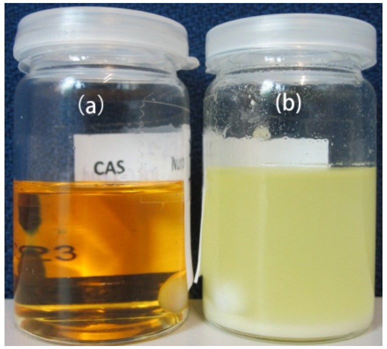
Spherosilicates or POSS



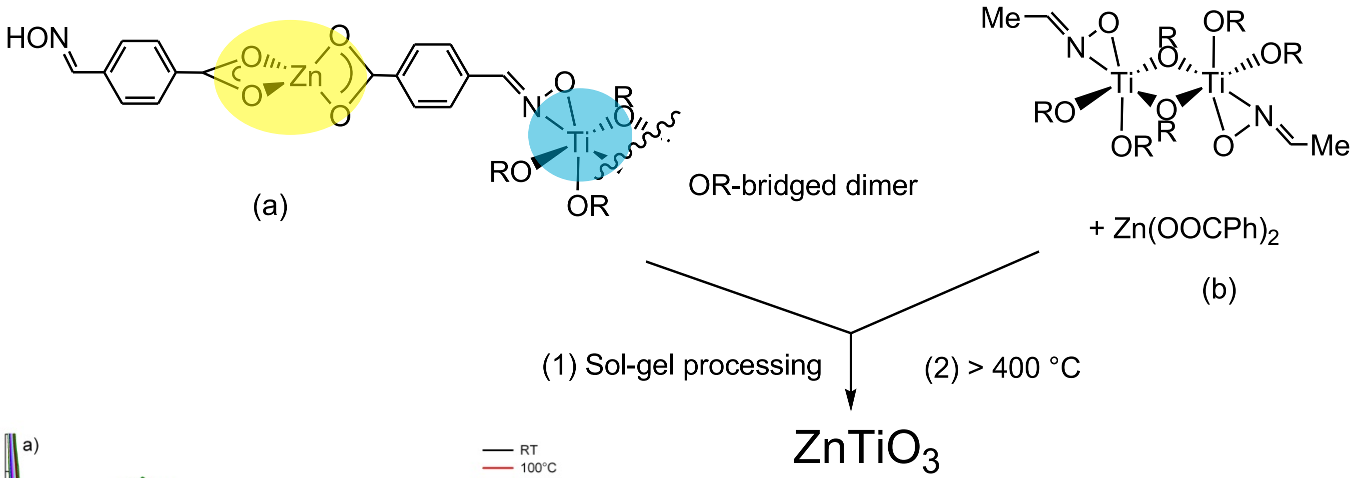


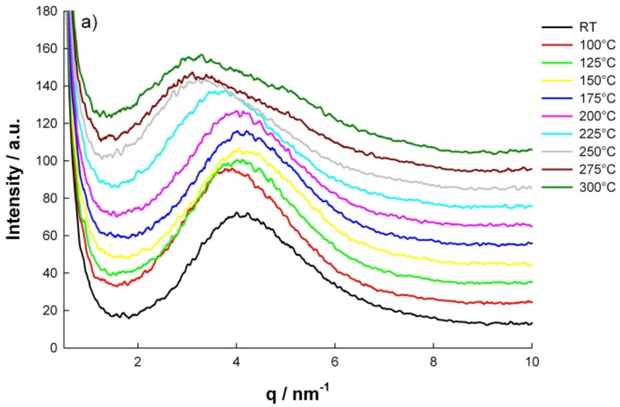
$Zr_4O_4(methacrylate)_{12}$

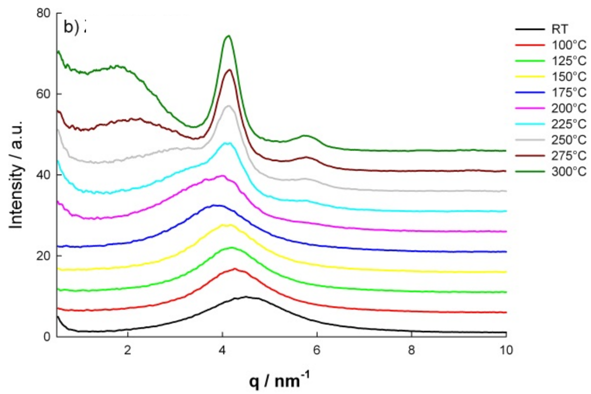
$ZnTiO_3$ from Ti-Zn Mixed-Metal Precursor

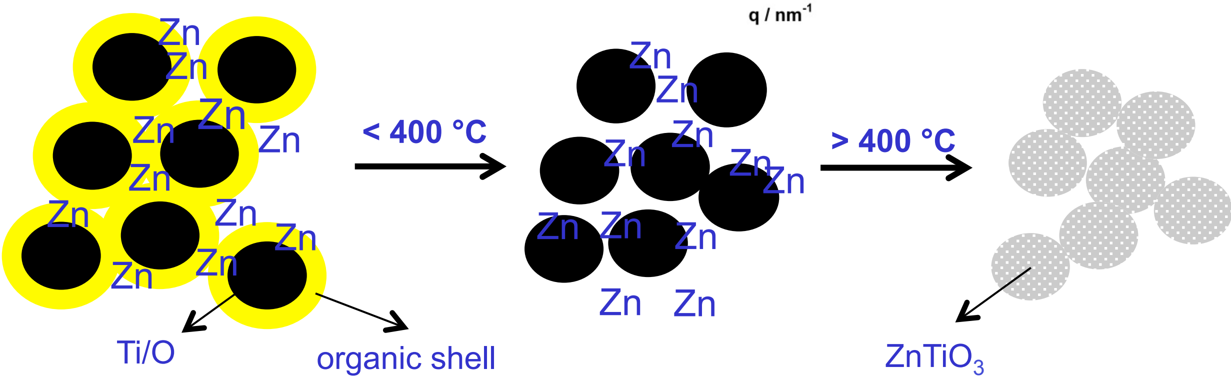


After sol-gel processing









J. Yang; SAXS: H. Peterlik, Univ. of Vienna

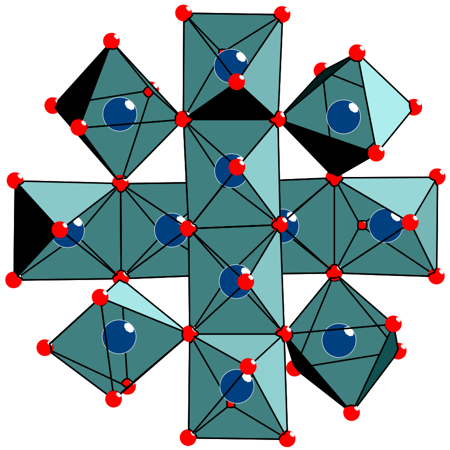
Magnetic Polymers

$$Mn_{12}O_{12}(OOC\text{-}CH_3)_{16} \xrightarrow[- n\ CH_3COOH]{+ n\ CH_2=CH\text{-}COOH} Mn_{12}O_{12}(OOC\text{-}CH_3)_{16}$$

Radical polymerization | + CH_2=CMe-COOMe

↓

PMMA crosslinked by Mn_{12}



„Mn_{12}“: total cluster spin S = 10
(4 Mn^{IV}, S = $^3/_2$ + 8 Mn^{III}, S = 2)

Material combines the properties of organic polymers (processibility, flexibility, etc.) with that of the inorganic cluster (superparamagnetism)

I.Mijatovic. Magnetic measurements F.Palacio et al.

„New Materials“ – Systems

- Composite (and related materials) where the properties of the components are additive
- Composite (and related materials) where the properties of the components are synergetic
- Hierarchical structures

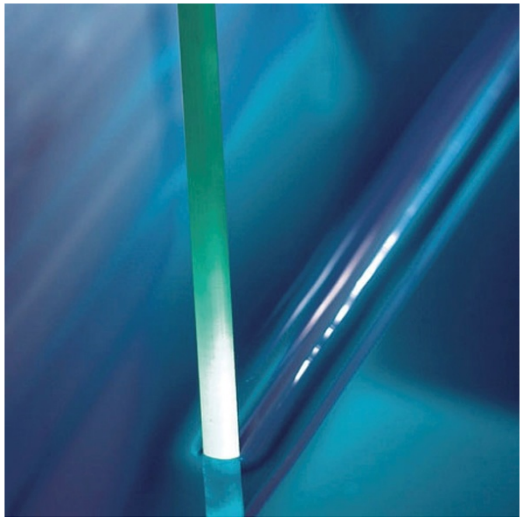
Functional Coating on a Substrate

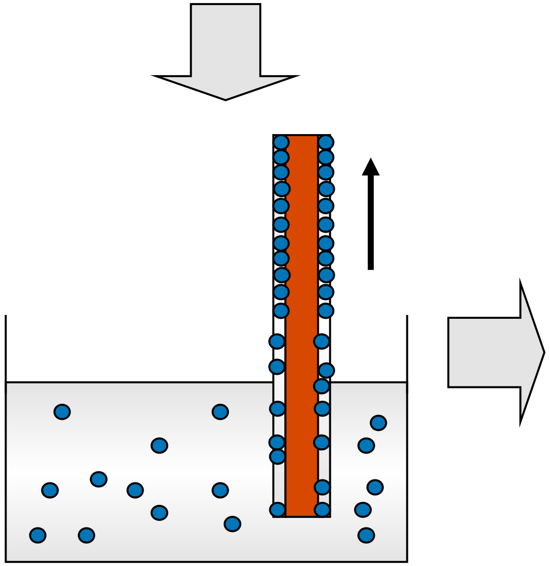
Antireflective coating on glass

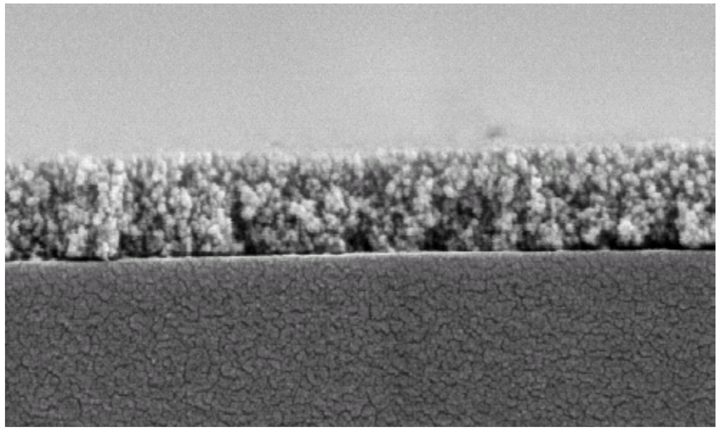
Glass: inexpensive, transparent, mechanically stable
Coating: antireflective

$Si(OR)_4$

hydrolysis/ condensation





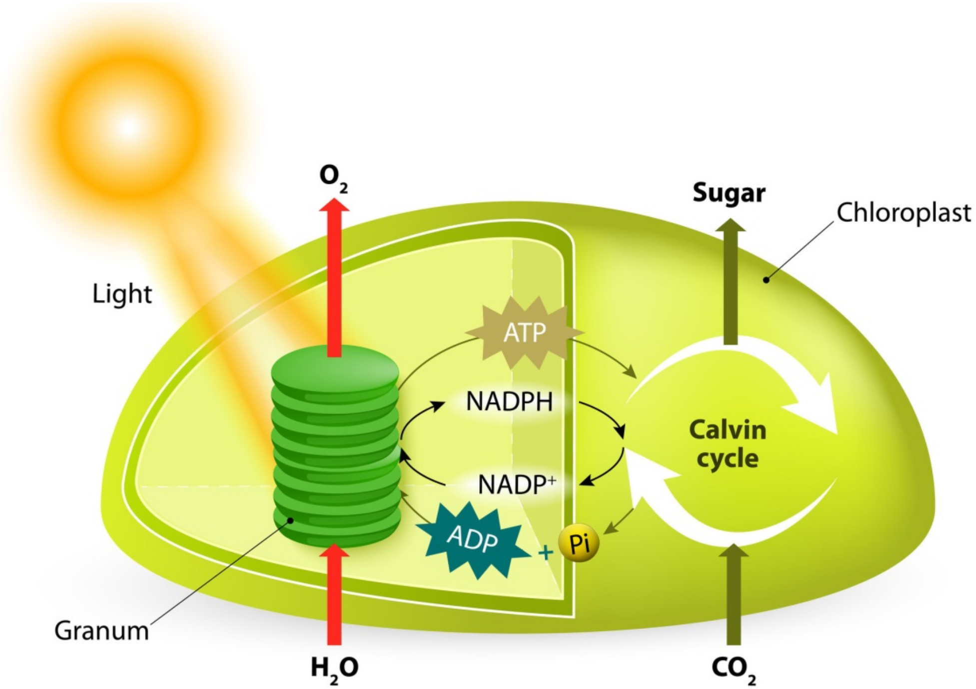


MERCK, FhG-ISE

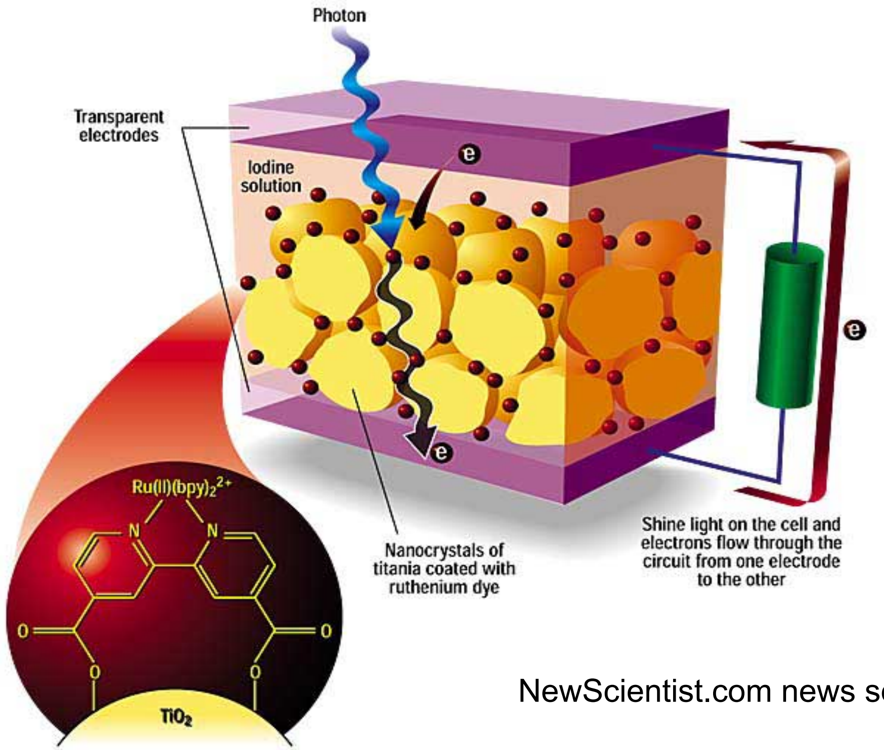
nanoporous SiO_2 layer (interparticle porosity)

Thermal annealing (400-550°C) ⇒ smear- and weather-proof porous SiO_2 layer

Natural photosynthesis



Dye-sensitized solar cell (Grätzel Cell)

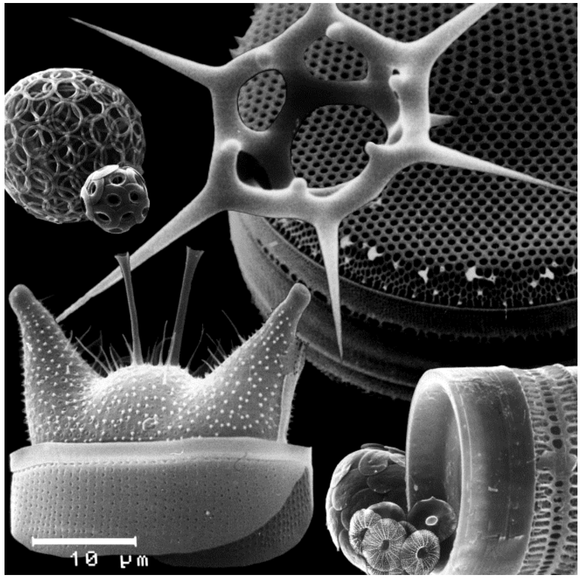


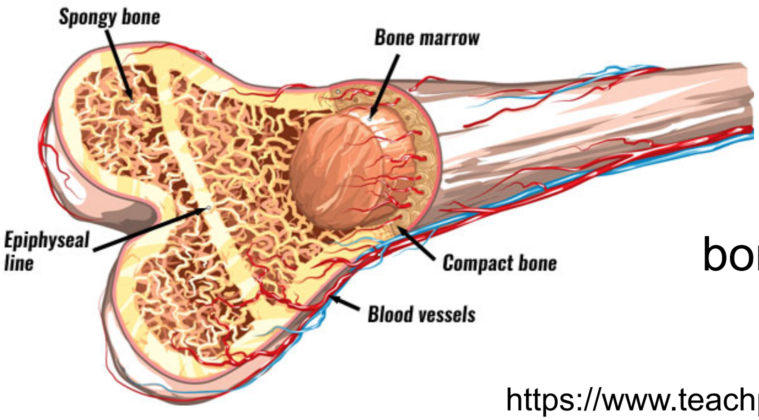
NewScientist.com news service

Hierarchical Structures

Hierarchical structures in nature

diatoms

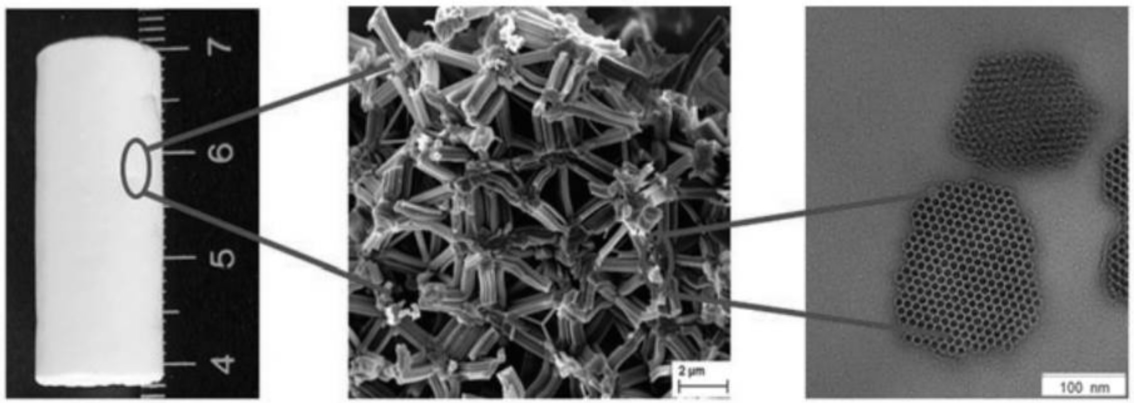




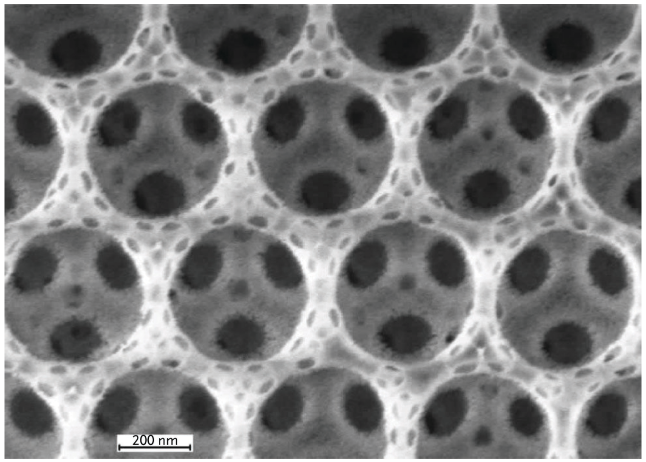
bone

https://www.teachpe.com

Man-made hierarchical structures (silica)



N. Hüsing



J. Wang et al., JACS, 2006

"During the past century, science developed a limited capability to design materials, but we are still too dependent on serendipity."

M.E.Eberhart, D.P.Clougherty, Nature 2004

More chemistry would possibly help!