Definierte Porositäten - Mögliche positive Beeinflussung des Zellwachstums (?)

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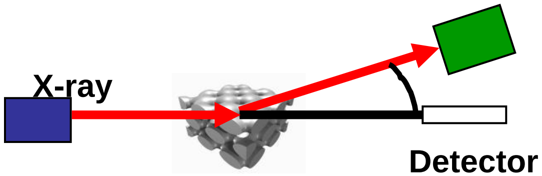
Overview

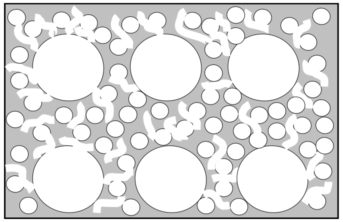
- Principles of the generation of mesoporous metal oxides
- Studies on the bioactivity of mesoporous materials (literature)
- The diversity of porosity and morphologies

Research topics AG Smarsly

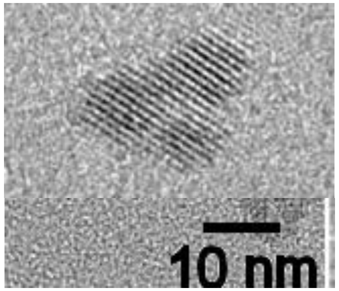
Characterization of nanostructures



Multimodal pore strucures

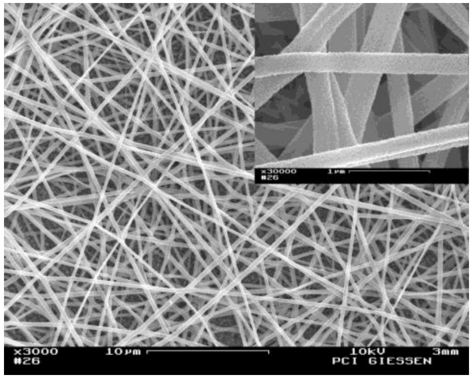


Nanoparticles

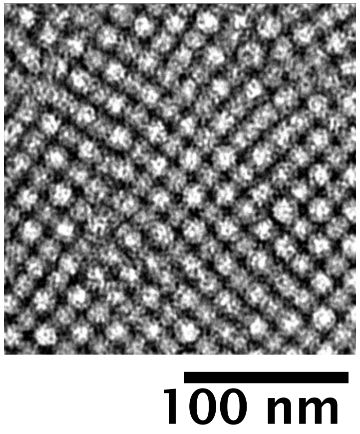


HPLC

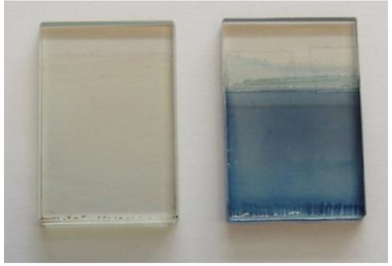
Electrospinning of inorganic nanofibers



Ordered nanoporous metal oxides



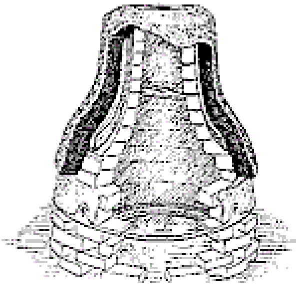
Applied electrochemistry



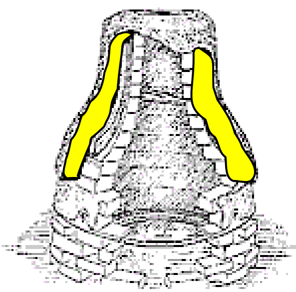
Relationship between self-assembled nanostructures and Physicochemical properties?

The principle of nanocasting

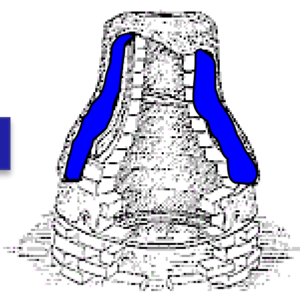
Petrified wood (Arizona, USA):



Wood



Infiltration with alumosilicate ions



Condensation to 3D alumosilicates (= mineral)

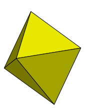
Sol-Gel-Chemistry

M-OR + H_2O	⟶	M-OH + ROH	Hydrolysis: „SOL“
M-OH + M-OH	⟶	M-O-M + H_2O	Condensation: „GELIERUNG“
M-OH + M-OR	⟶	M-O-M + ROH	

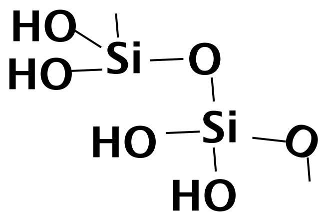
M-OR: z.B. $Si(OMe)_4$

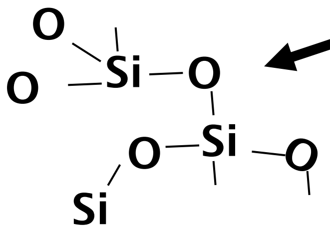
Hydrolysis

Condensed oxide (Glas)



$Si(OR)_4$ $\xrightarrow{H_3O^+}$ $Si(OH)_xMe_y$ ⟶





ΔT

Metal oxide
(e.g. SiO_2 or TiO_2, etc.)

Structure of sol-gel derived SiO_2 networks

J. Chem. Soc., Dalton Trans., 2001, 97–108 **97**

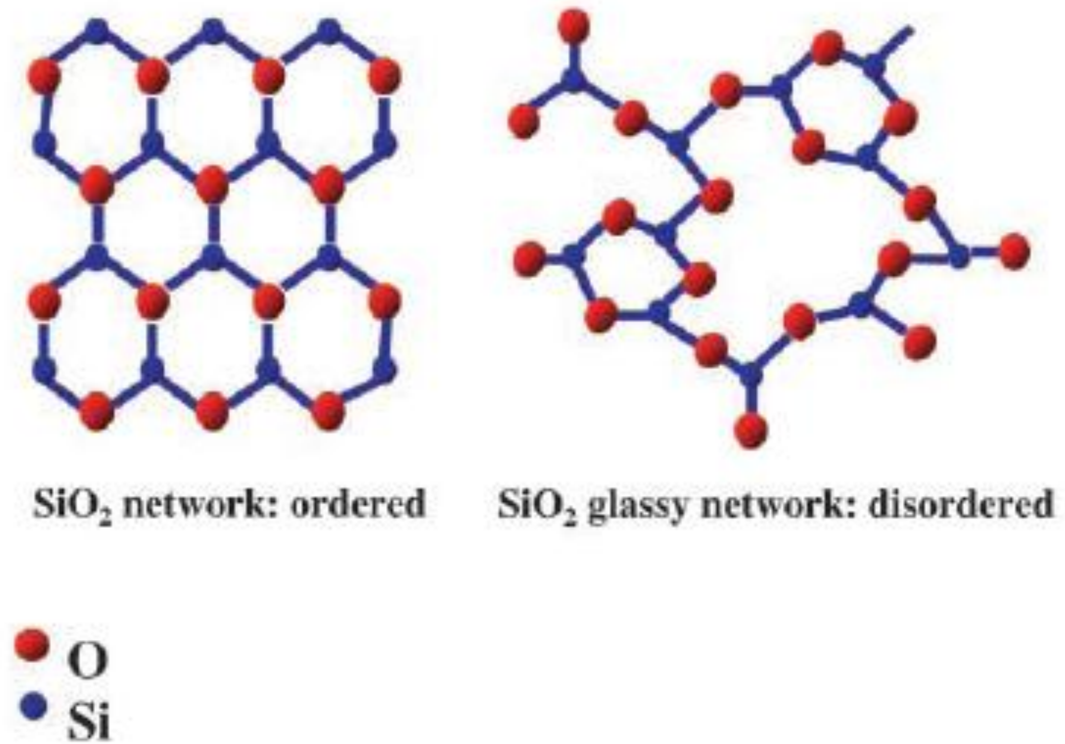
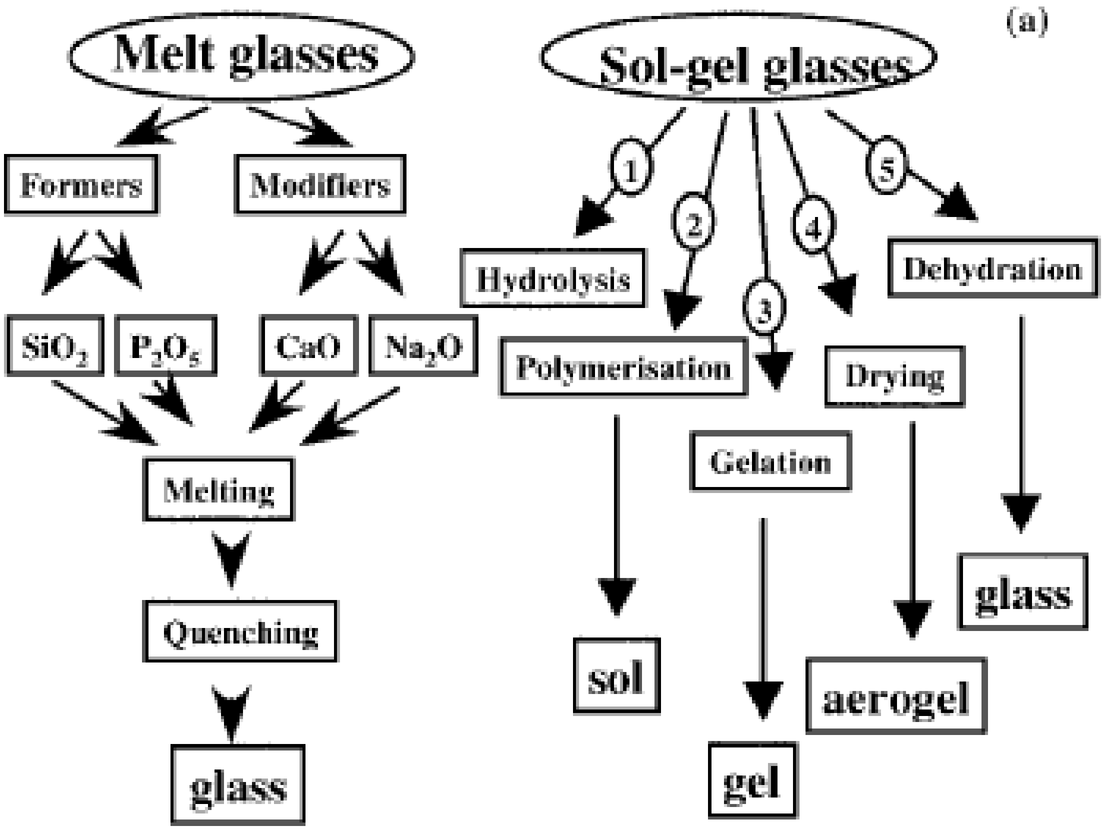


Fig. 7 Two very different structural situations for an identical chemical composition, SiO_2, namely ordered and disordered structure, thus giving rise to a crystalline ceramic and a glass, respectively.

Structure of sol-gel derived SiO_2 networks

J. Chem. Soc., Dalton Trans., 2001, 97–108 97



Structure of common glass

J. Chem. Soc., Dalton Trans., 2001, 97–108 **97**

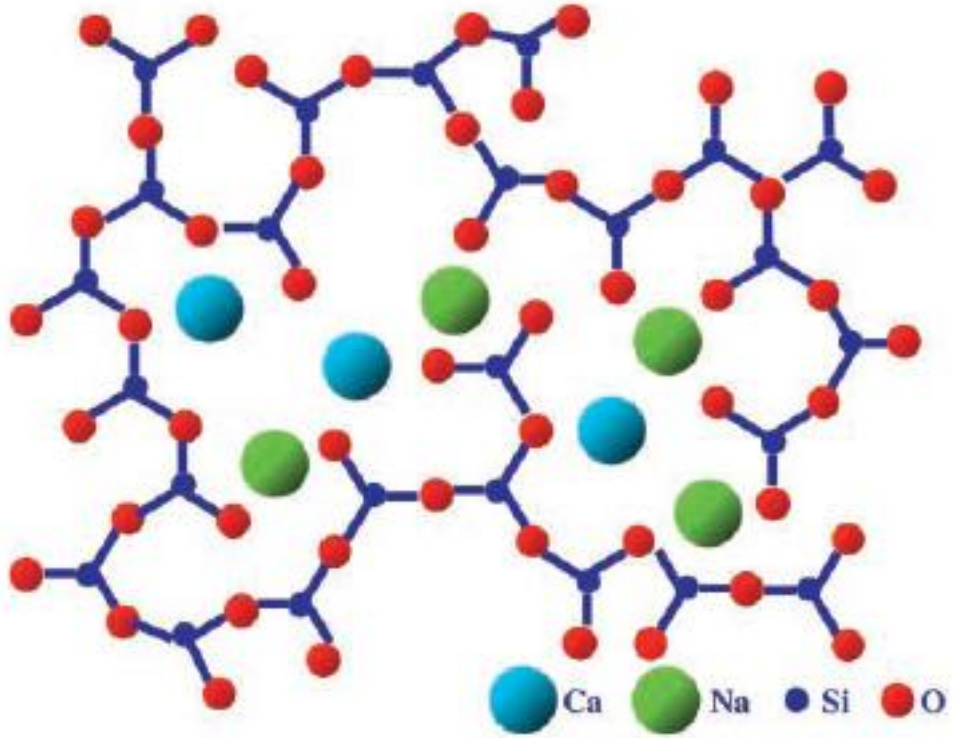
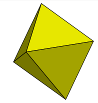


Fig. 9 Disordered structure of a glass in the SiO_2–CaO–Na_2O system.

„Bottom-up“ principle for producing nanoscaled porosity

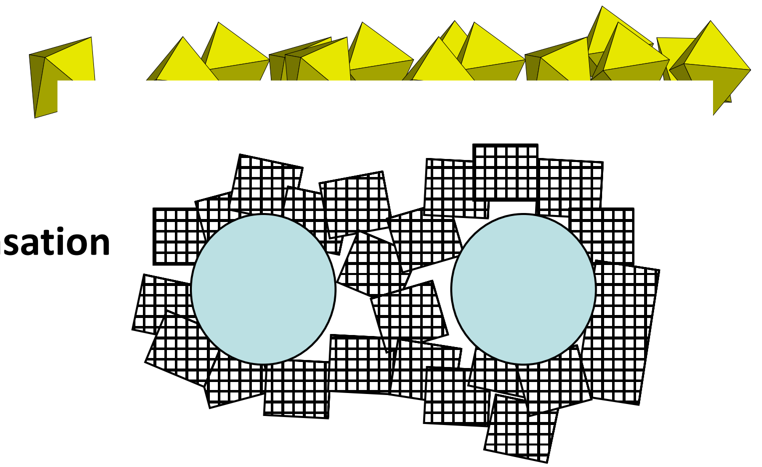
Building blocks



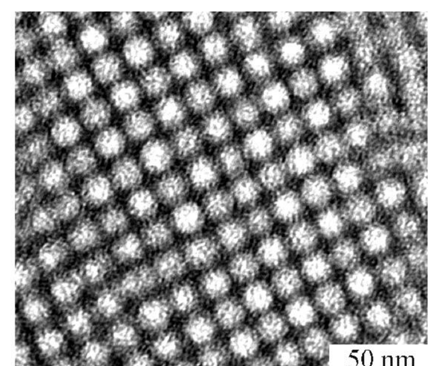
= **Molecular Precursor or nanoparticle**

Construction („Architect“)

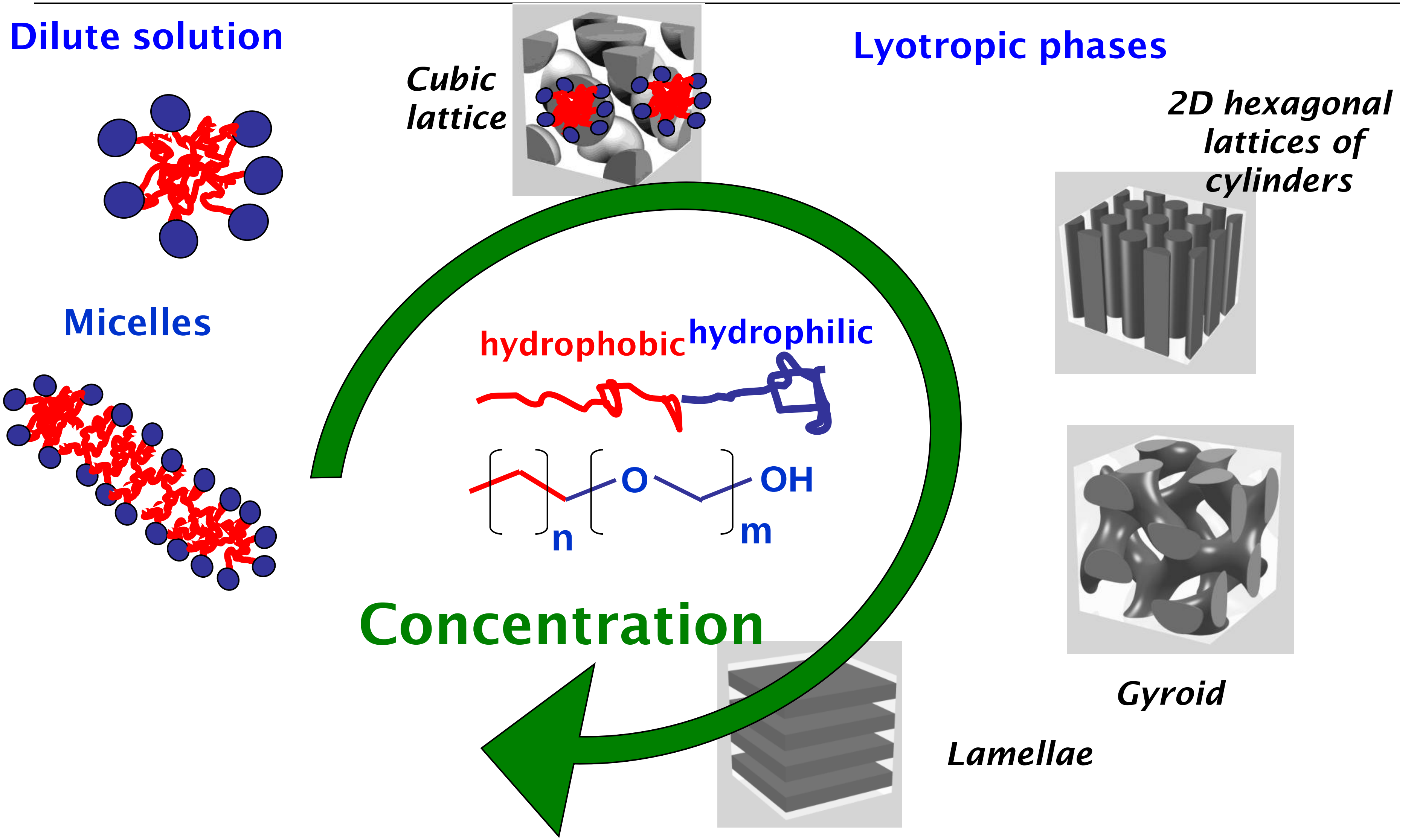
condensation



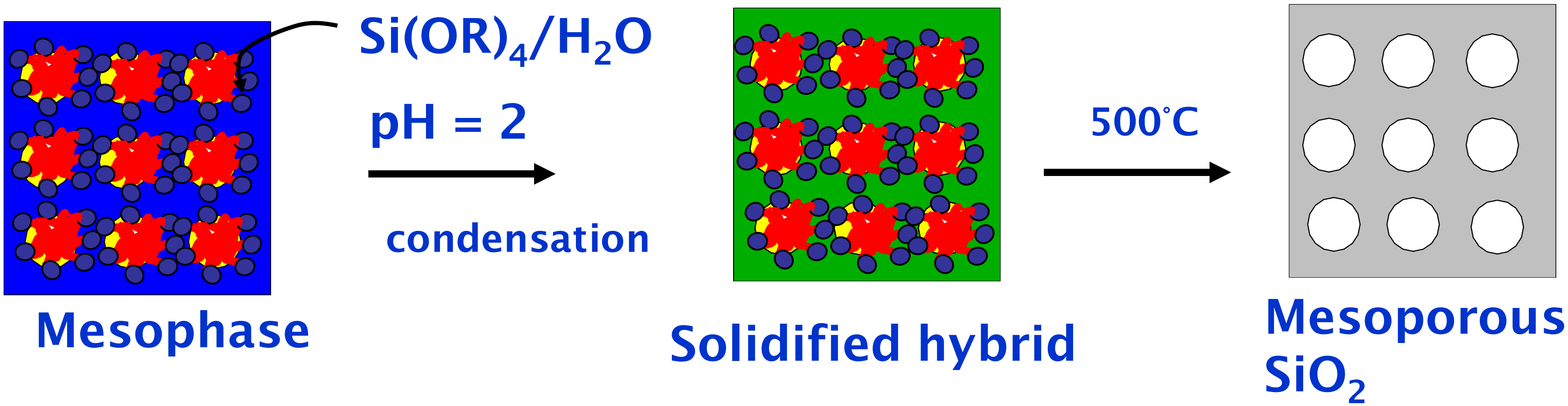
Building

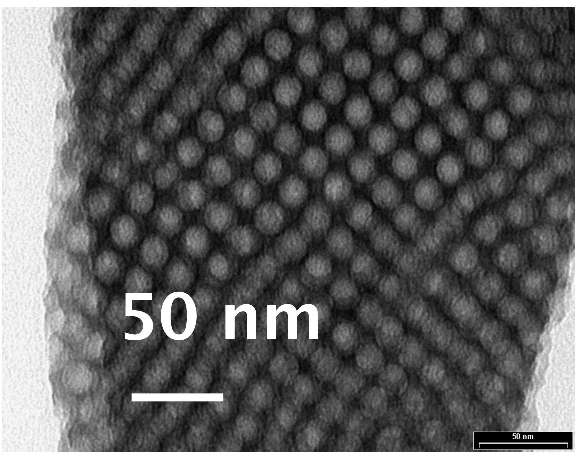


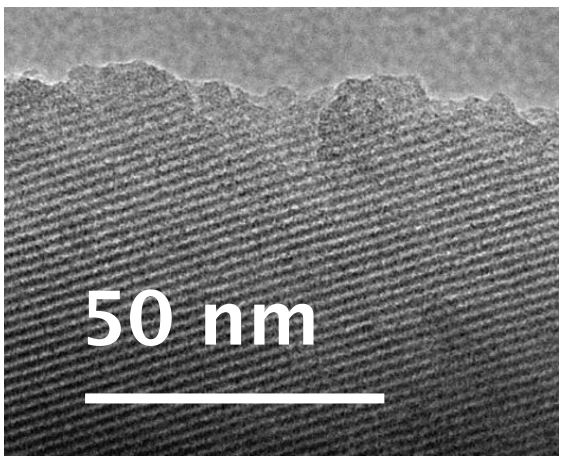
Template: Mesostructures of surfactants/block copolymers in solution



Nanocasting with block copolymers







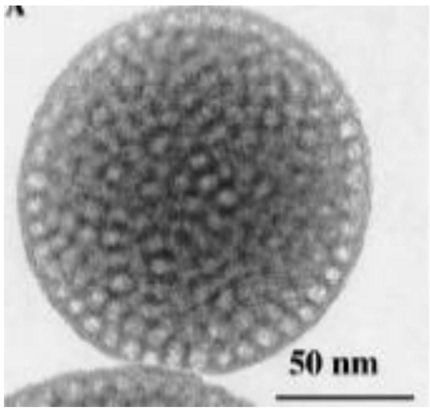
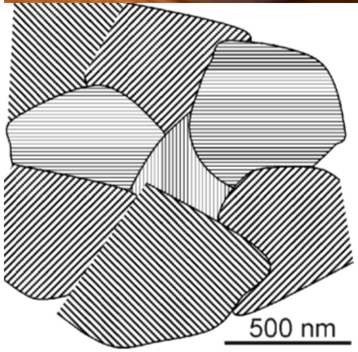
AG Smarsly:

Large variability of shape and size (3 nm – 40 nm)

Spherical mesopores (14-40 nm)
Surface area ca. 90 – 200 m²/g

Cylindrical mesopores (3 nm – 8 nm)
Surface area ca. 500 – 900 m²/g

Possible morphologies

Thin films (50 – 1000 nm)	Mesoporous microparticles	Mesoporous powders
		 

Mesoporous SiO_2 for bone tissue regeneration - 1

Vallet-Regi et al., J. Mater. Chem, 2006, 16, 26-31

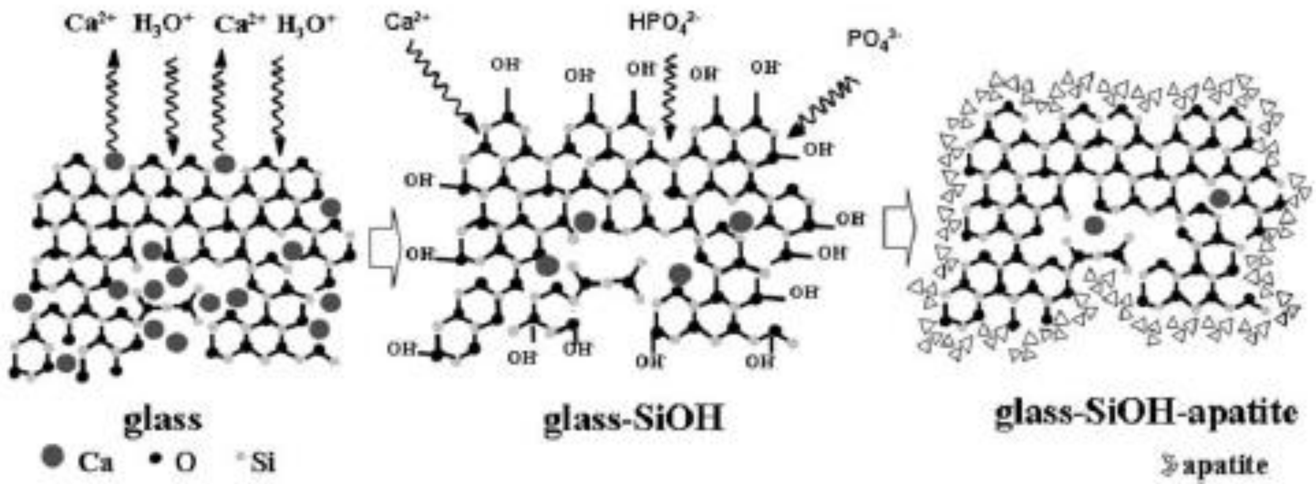
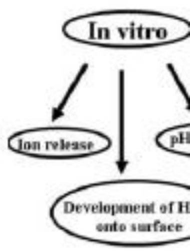


Fig. 2 Hydroxyapatite formation mechanism in bioactive glasses when soaked in physiological fluids.



Ionic co

	Na
SBF	142
plasma	142

Mesoporous SiO_2 for bone tissue regeneration - 1

J. Chem. Soc., Dalton Trans., 2001, 97–108 **97**

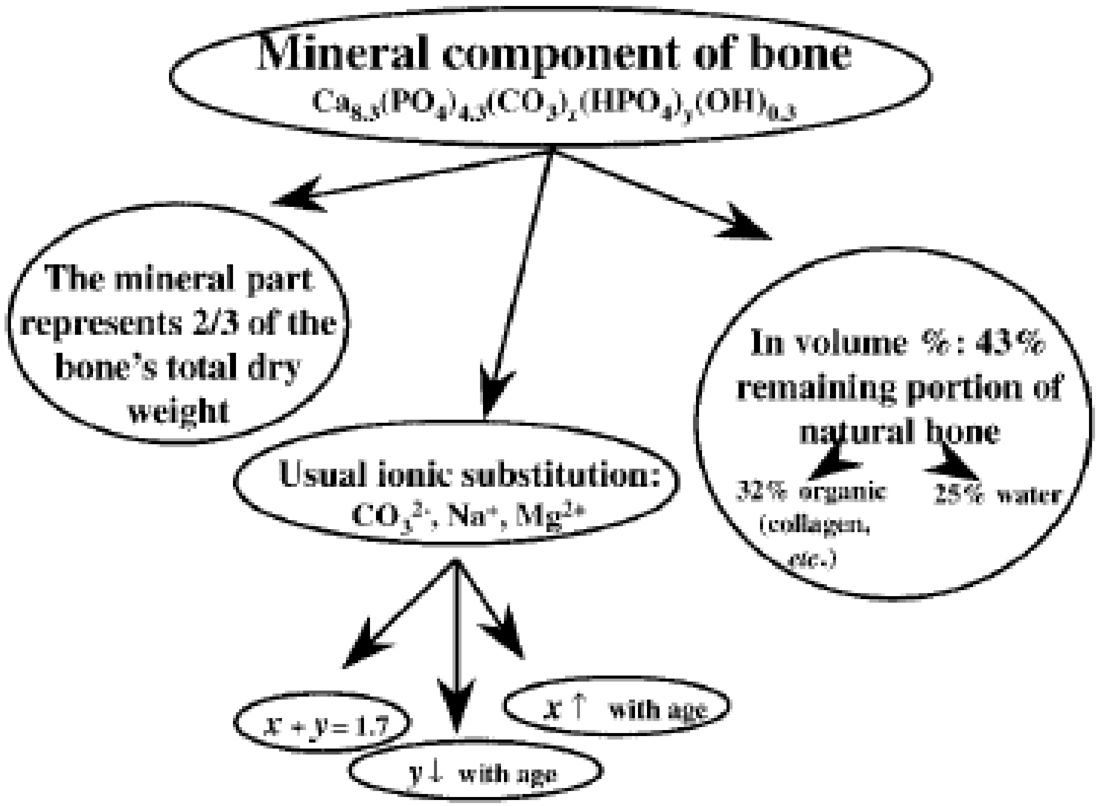


Fig. 6 Composition of the mineral component of bones.

Mesoporous SiO_2 for bone tissue regeneration - 1

Vallet-Regi et al., J. Mater. Chem, 2006, 16, 26-31

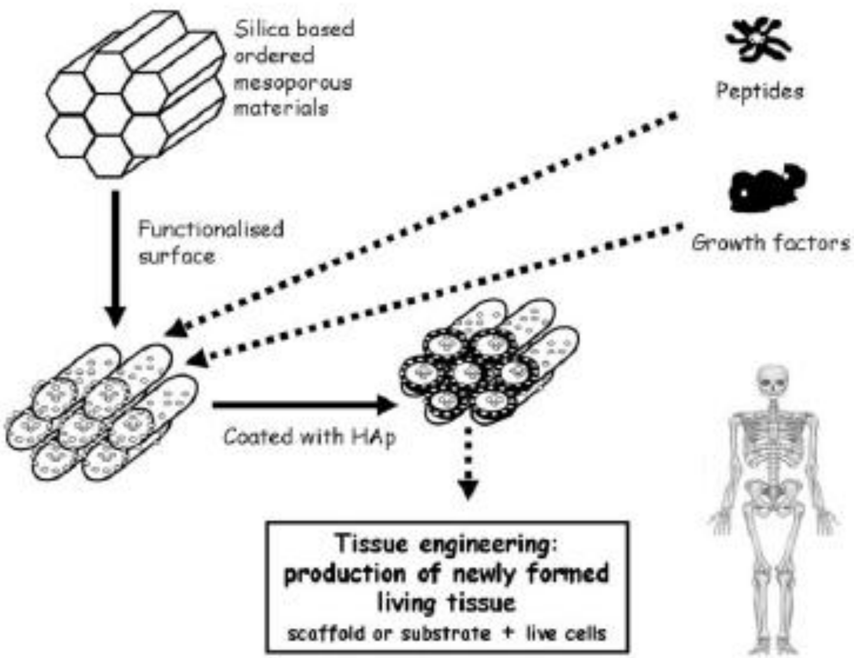
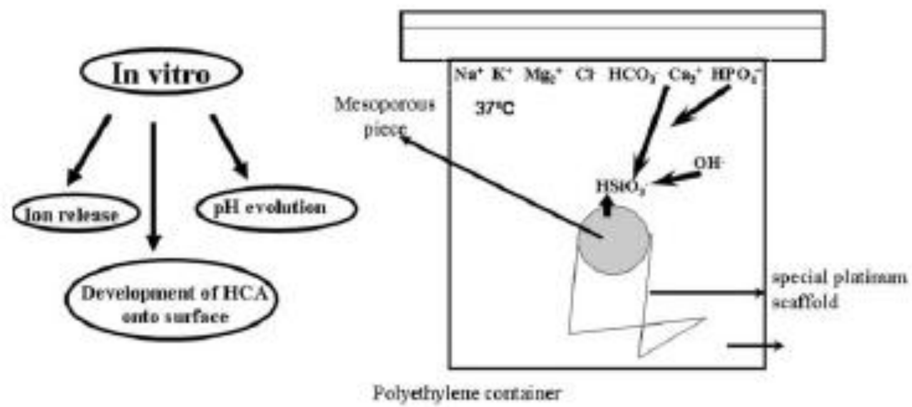


Fig. 7 Schematic illustration of tissue engineering technique promoted by bioactive ordered mesoporous materials which can be functionalized with organic groups and release different growth factors for tissue regeneration.



Ionic composition of SBF and human plasma (mM)

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5
plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

SBF: simulated body fluid

Mesoporous SiO_2 for bone tissue regeneration - 1

J. Mater. Chem, 2006, 16, 26-31

TEM analysis

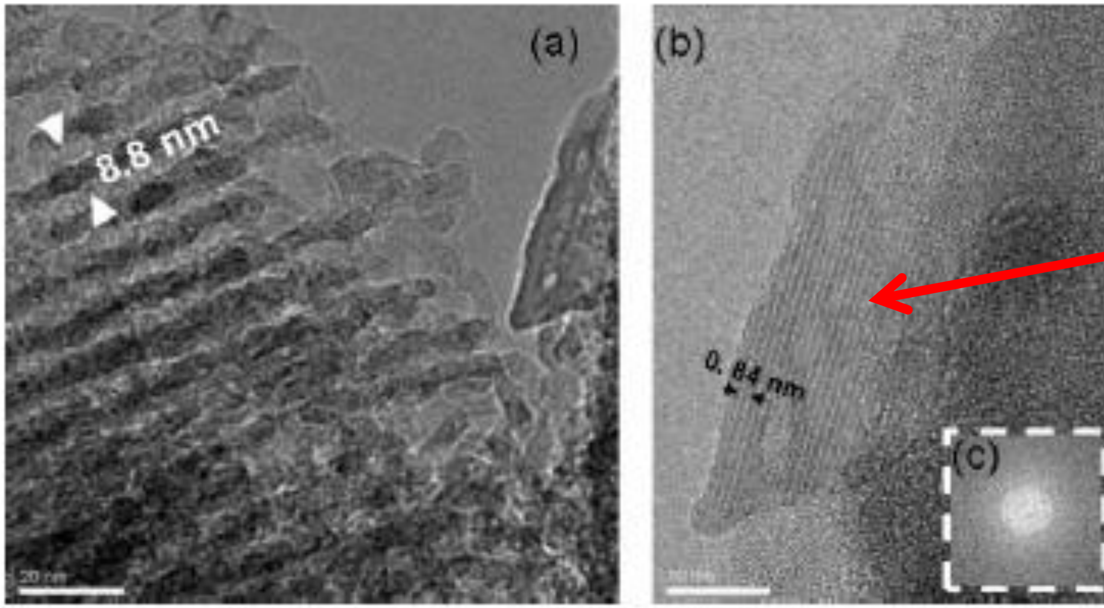


Fig. 6 TEM micrographs showing different features of SBA-15 after treatment: (a) area where the original mesoporous material is not completely transformed; features of both raw material and apatite are evident; (b) enhanced image reflecting the fact that apatite appears over the modified mesoporous material; (c) FT performed at the amorphous area in b.

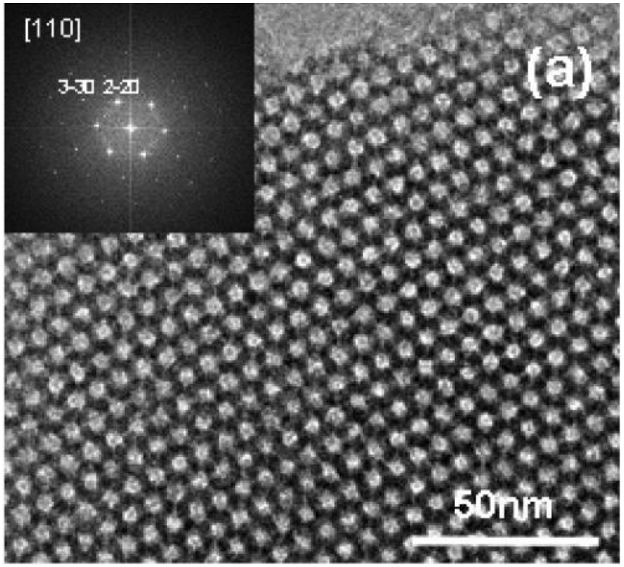
apatite

Mesoporous SiO_2 for bone tissue regeneration - 2

Chem. Mater. 2006, 18, 3137−3144

Ordered Mesoporous Bioactive Glasses for Bone Tissue Regeneration

López-Noriega,† D. Arcos,*,† I. Izquierdo-Barba,‡,§ Y. Sakamoto,‡ O. Terasaki, M. Vallet-Regí*,†



S85m: 3D mesopore structure

Recipe:
Tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), and calcium nitrate, $Ca(NO3)_2$, 4H2O, (Aldrich) were used as SiO2, P2O5, and CaO sources,

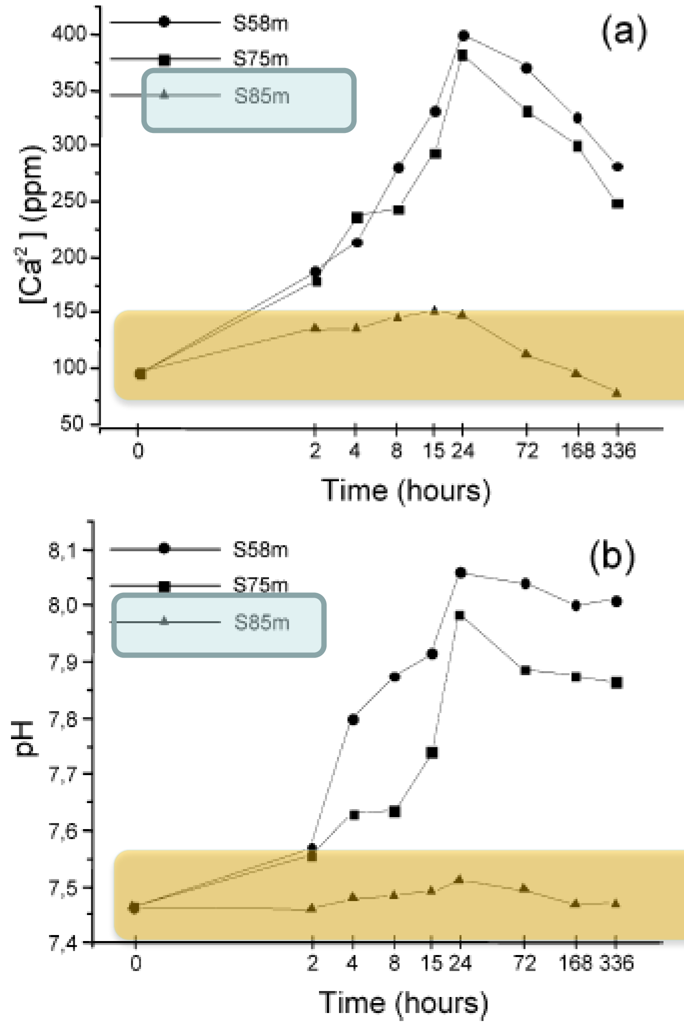


Figure 6. Variations of (a) calcium content and (b) pH values of the SB after soaking the mesoporous $SiO_2-CaO-P_2O_5$ glasses.

Mesoporous SiO_2 microspheres for bone grafting

Chem. Mater. 2009, *21*, 1000–1009

Porous SiO_2 microspheres

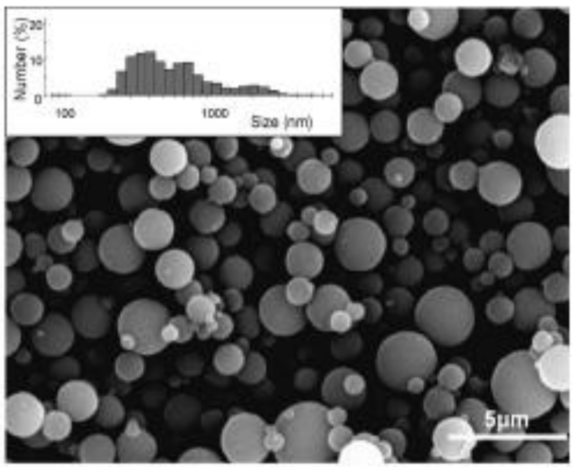


Figure 1. SEM micrograph of BMS85P. Magnification 5000×. Inset shows particle size distribution determined by DLS measurements.

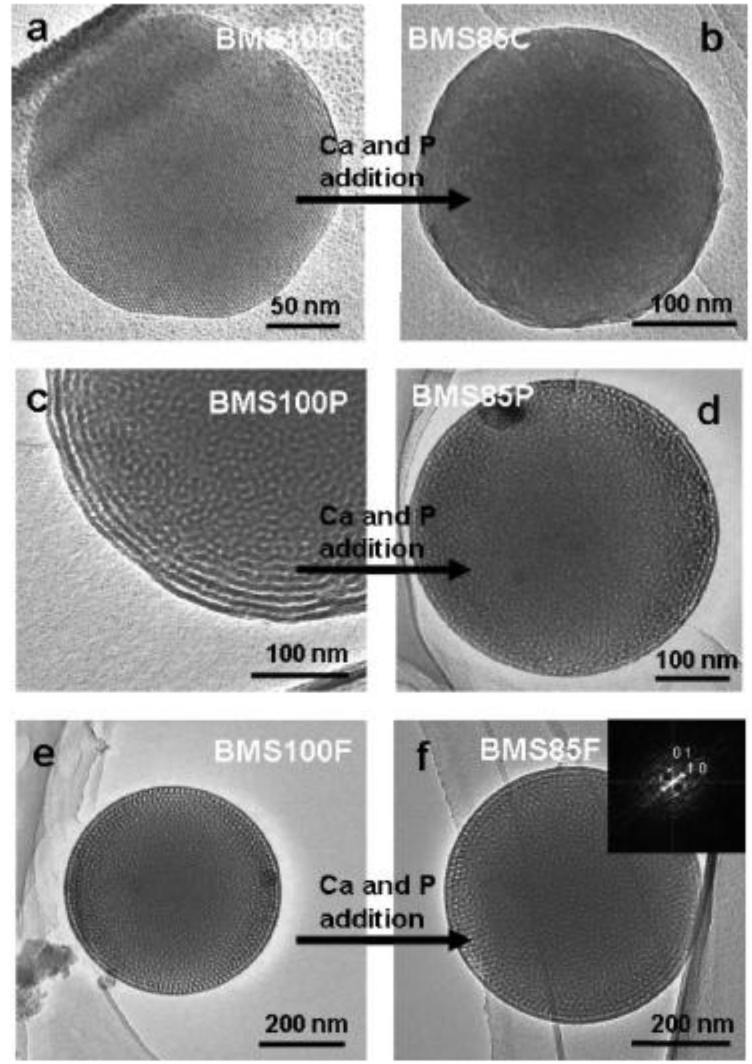
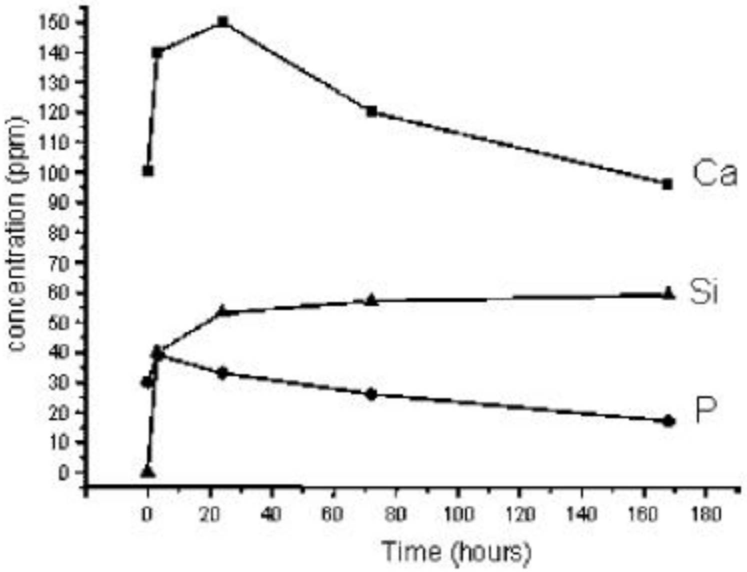


Figure 3. TEM images of BMS100x and BMS85x microspheres synthesized with CTAB, P123, and F127. Magnification 30 000×. Fourier transform pattern for BMS85F is shown, demonstrating the hexagonal mesoporous ordering remaining in this sample.

Mesoporous SiO_2 microspheres for bone grafting

Chem. Mater. **2009**, *21*, 1000–1009

Dissolution behavior



Spheres covered by apatite

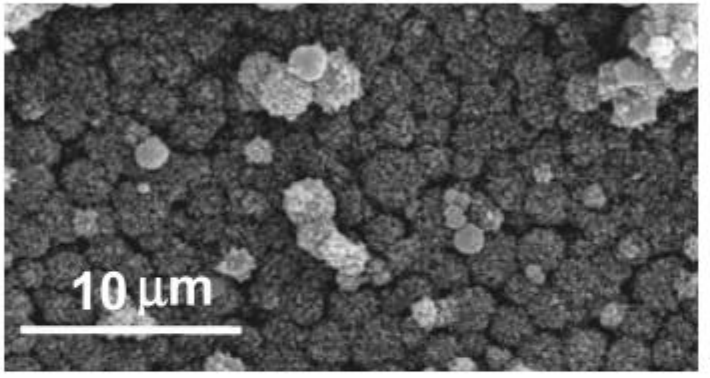


Figure 7. SEM micrographs of BMS85P after soaking in SBF for 3 days.

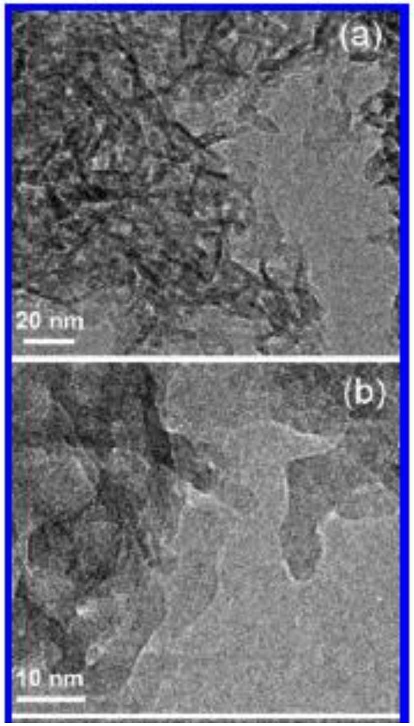
Modifications of apatite

High Specific Surface Area in Nanometric Carbonated Hydroxyapatite

Chem. Mater. 2008, *20*, 5942–5944

S. Padilla,† I. Izquierdo-Barba,†,‡ and M. Vallet-Regí*,†,‡

Synthesis of nanocrystalline, carbonated hydroxyapatite (CHA)



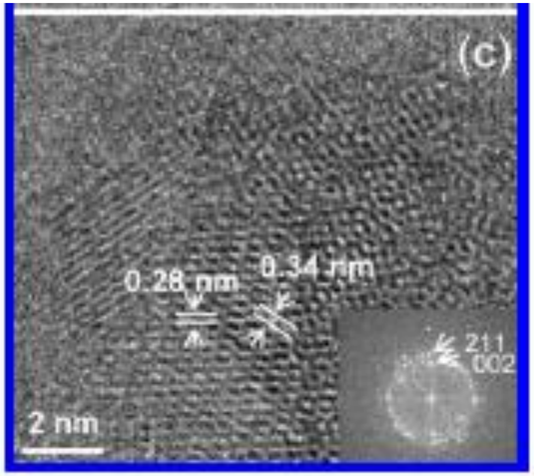
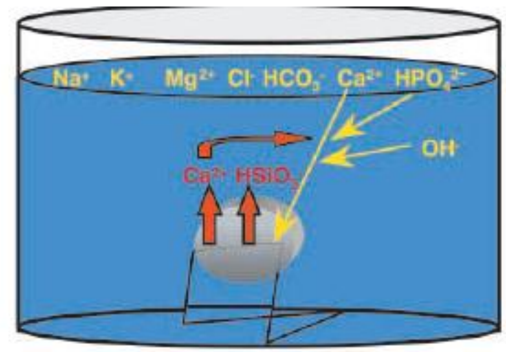


Figure 3. TEM images of CHA taken at different magnification (60 000, 300 000 and 600 000 K, respectively). (a, b) Low-magnification images show the small size and the needle-like shape of the nanoparticles. (c) HRTEM image and its corresponding Fourier diffractogram show the *d*-spacing corresponding to the 002 and 211 reflections of an apatite phase.

SiO$_2$ Aerogels for bone grafting

Fig. 10 Description of the synthesis process for bioactive glasses.



Ionic composition of SBF and Human Blood Plasma (mM)

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plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

Fig. 15 Chemical process taking place between a bioactive glass and a solution of SBF.

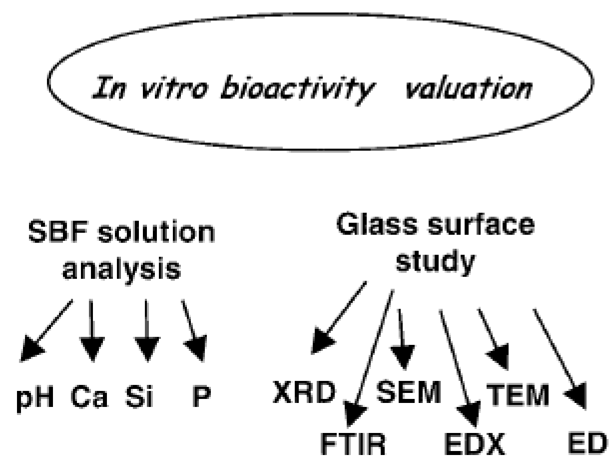
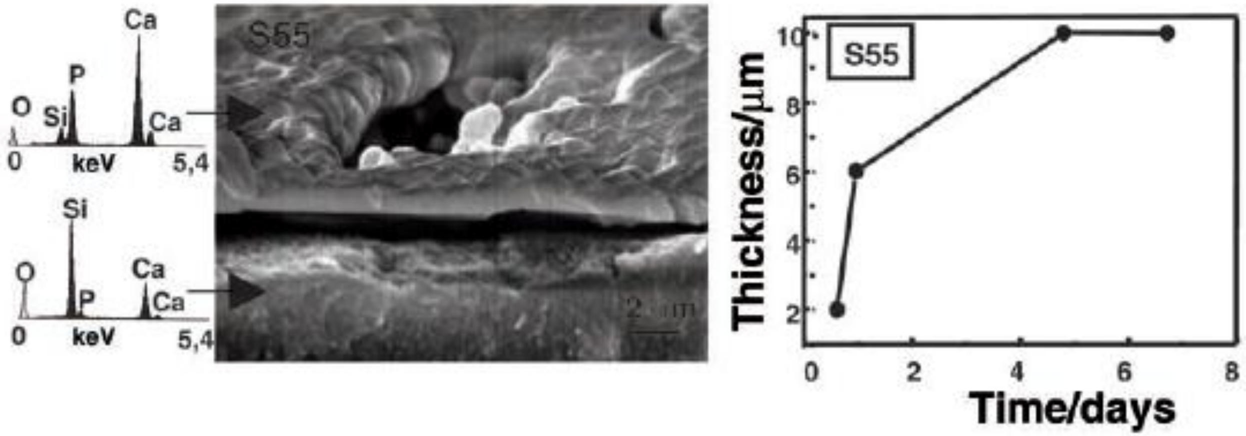


Fig. 14 Techniques employed in characterisation of bioactive glasses.

Modifications of apatite



. 20 Evolution with time of the apatite-like layer thickness on a bioactive glass. SEM and EDS techniques have been used.

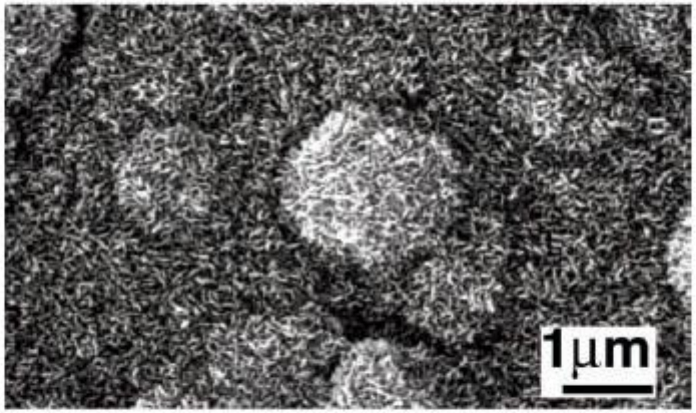


Fig. 18 Micrograph of a bioactive glass after soaking in SBF for one week.

Are nanoporous SiO_2 materials suitable?

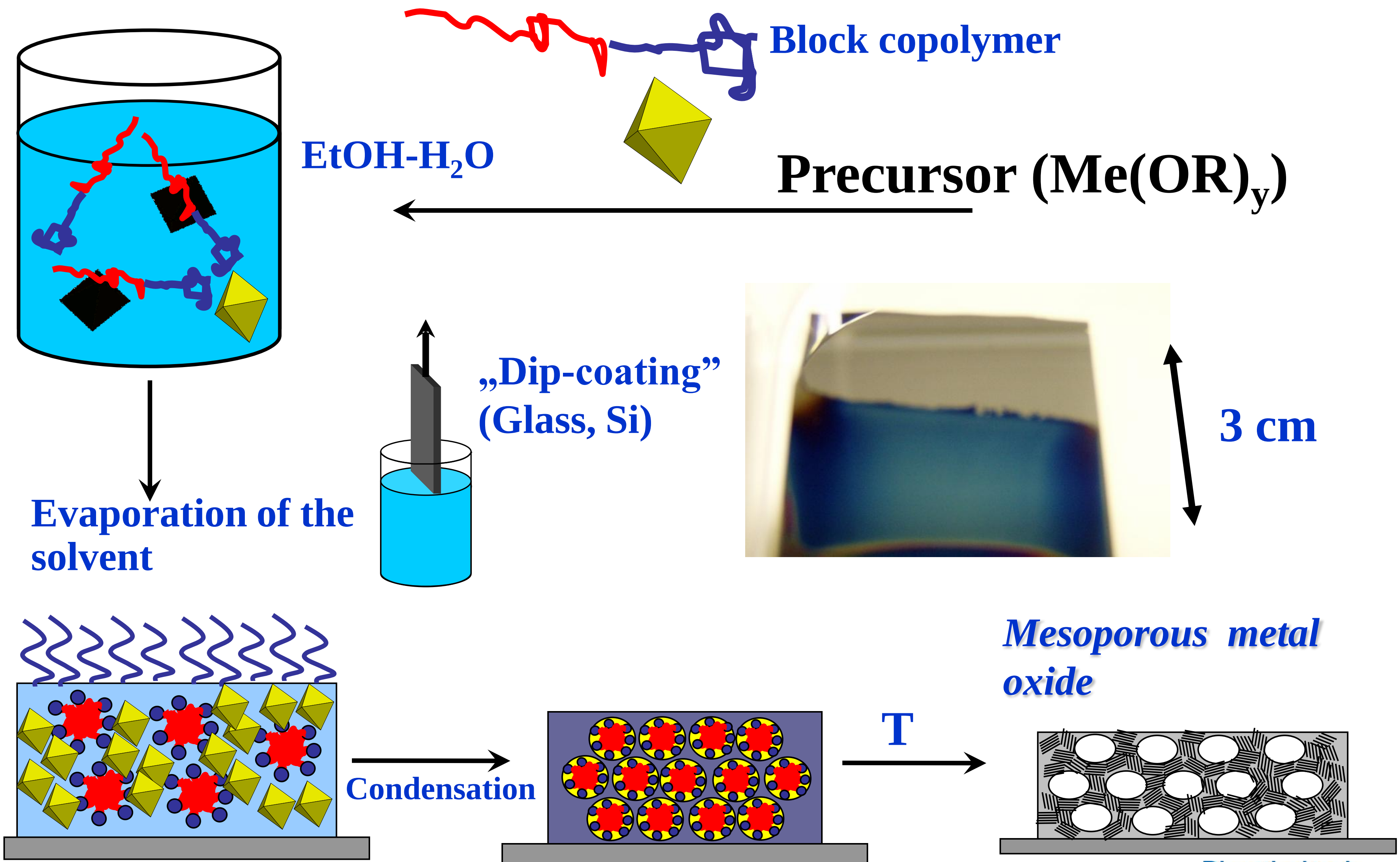
Problems of using porous SiO_2 as bioactive glass

- Mesoporous powders do not possess macroscopic shape, thus produce „ill-defined“ apatite layers
- The influence of the macroscopic shape is not understood
- Small mesopores (< 8 nm) can be easily blocked

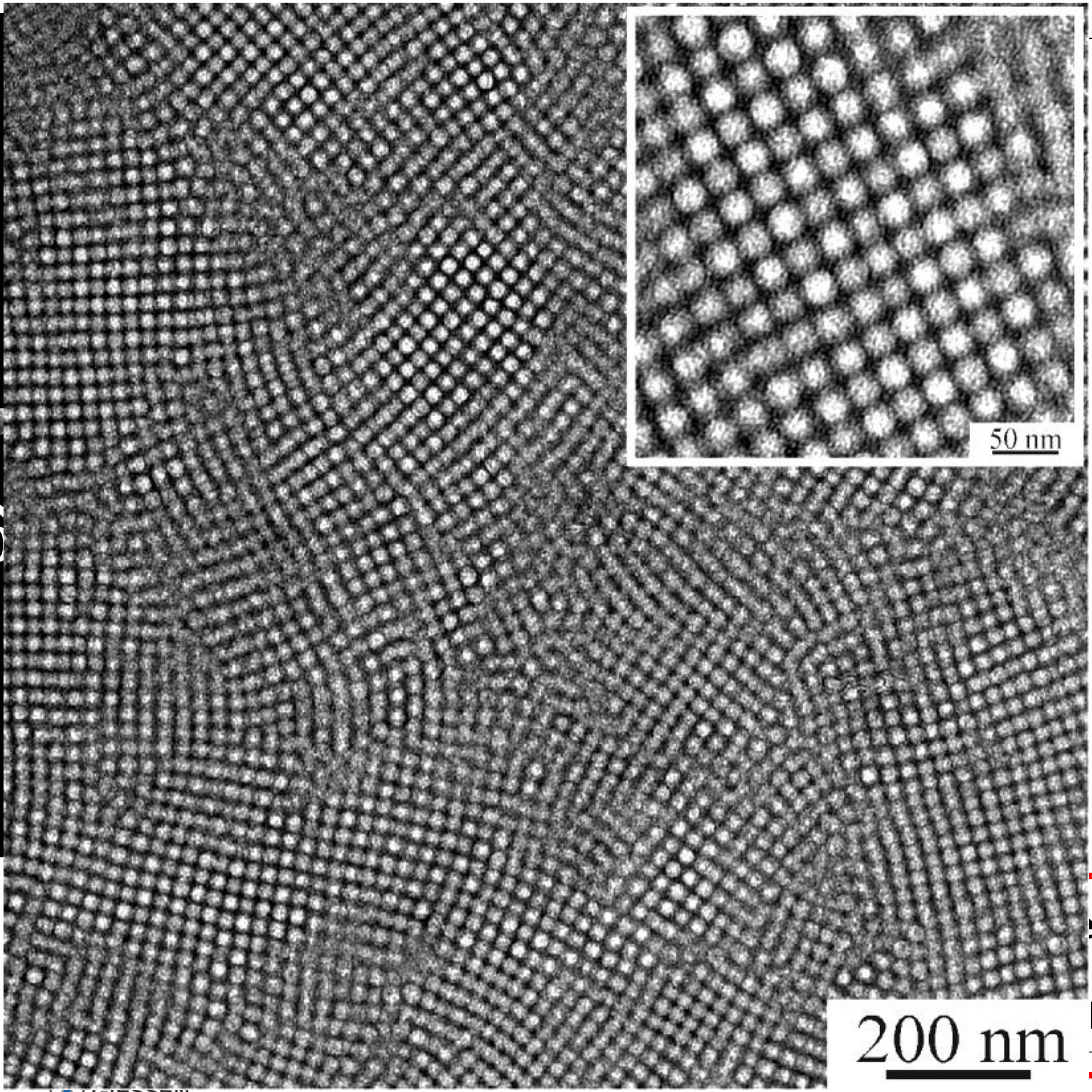
Possible requirements for the materials

- Well-defined shape (monoliths)
- Ideally: as little amount of SiO_2 as possible
- Combination of high surface area and high porosity

Mesoporous metal oxide films by „Evaporation-induced self-assembly" (EISA)



Macroscopic homogeneity



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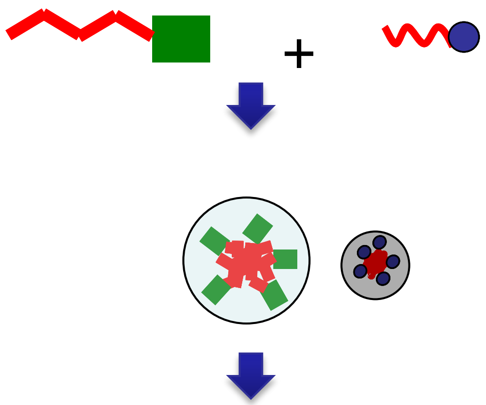
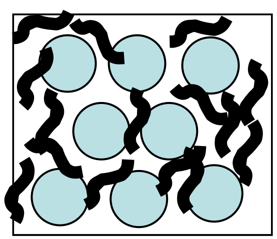
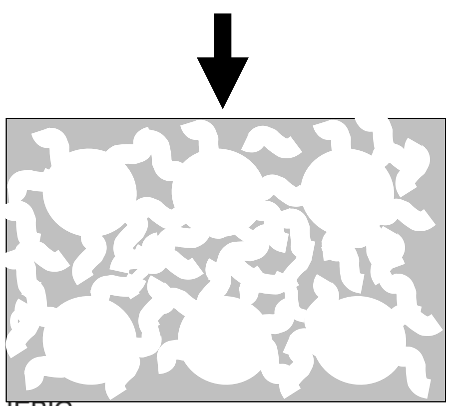
Porosimetry)

Dual micellar templating

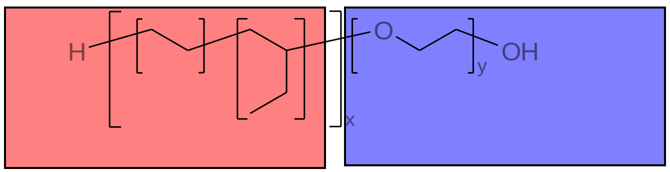




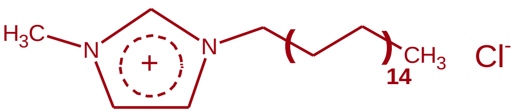
"Micellar mixing"/
micellar "alloys"



Large pores:
block copolymers or colloid particles

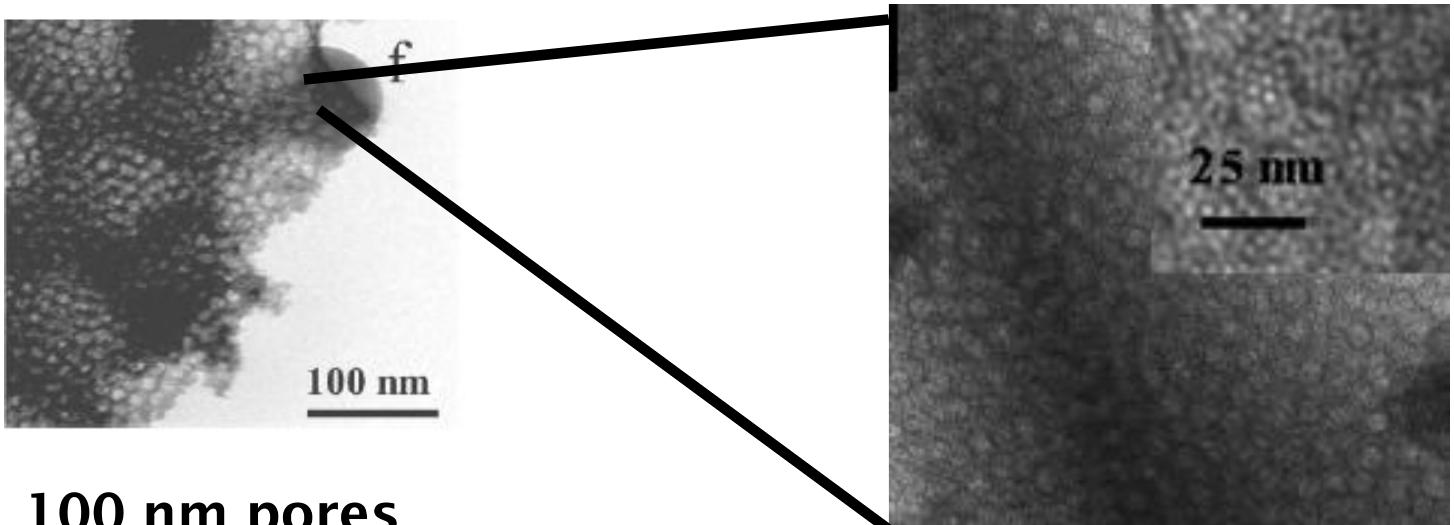


Small mesopores:
Small surfactants



Hierarchical pore structures

Combination of a large pore volume with large surface area

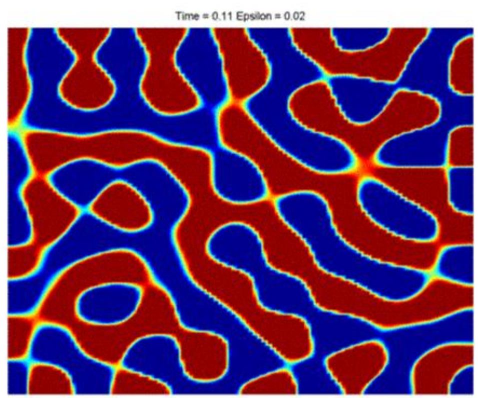


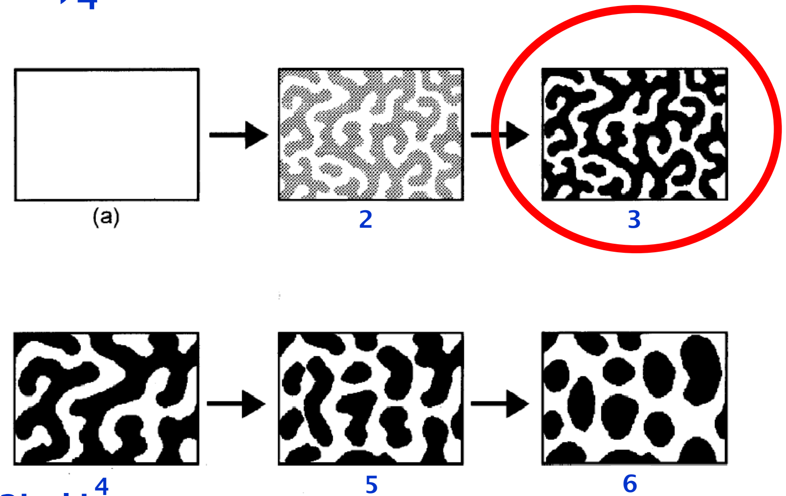
100 nm pores
+ 14 nm pores
+ 3 nm pores

Surface area: 600 m^2/g
Pore volume: 1.3 ml/g

Generation of monolith pore structures: Nakanishi process

Sol-Gel-Prozess: PEO + "$Si(OH)_4$"+ EtOH

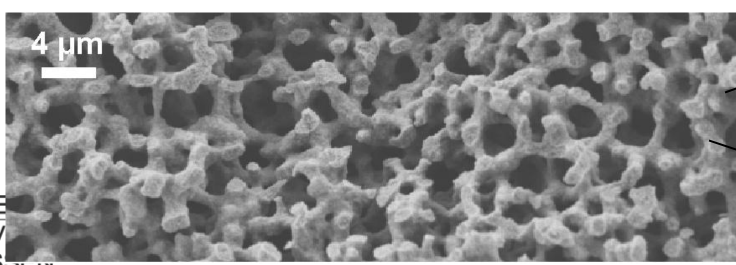


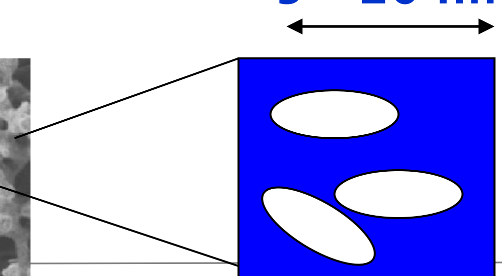


http://complex.gmu.edu/images/gallery/thumb/spinnum2ind.jpg

N. Ishizuka et al. (1998)

Meso- and macroporous SiO_2

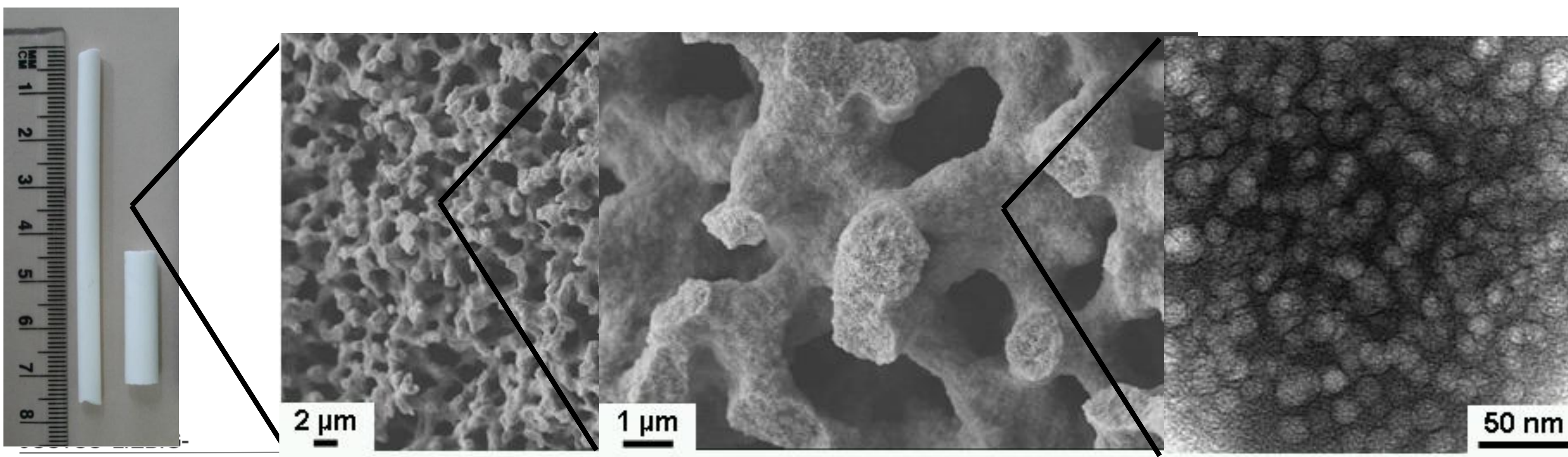




Structure of monolithic SiO_2 with hierarchical pore structure

- Shape control
- Large pores: 2-4 micrometer
- Mesopores: 13 nm
- Surface area: Ca. 250 m^2/g
- Pore volume = ca. 0.8 ml/g

Electron microscopy

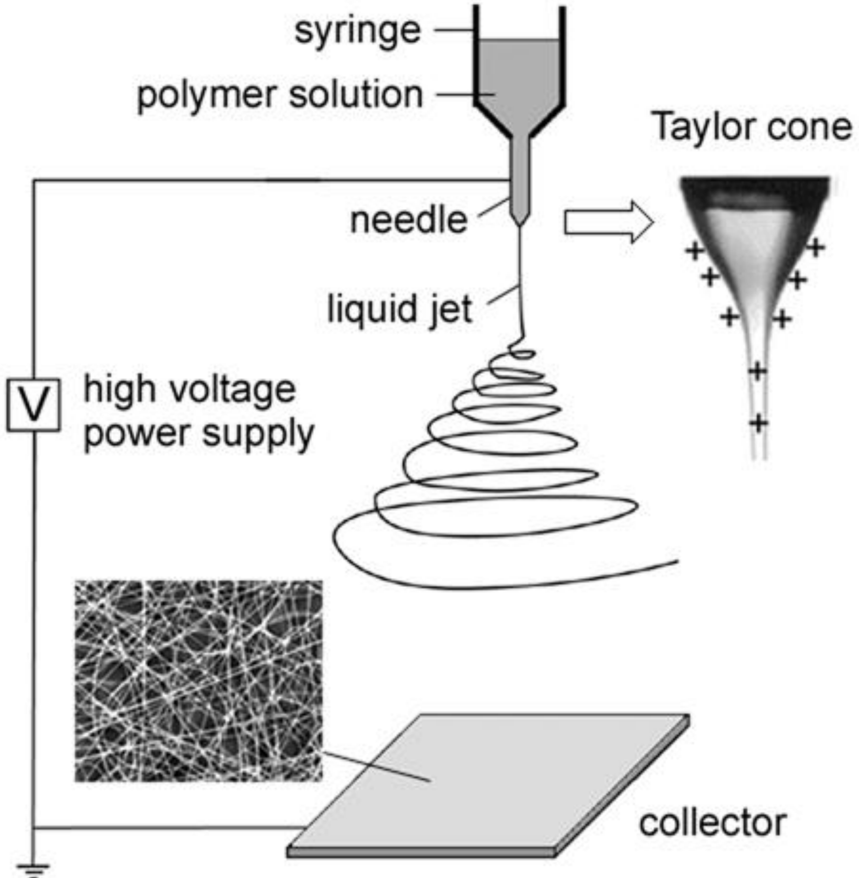


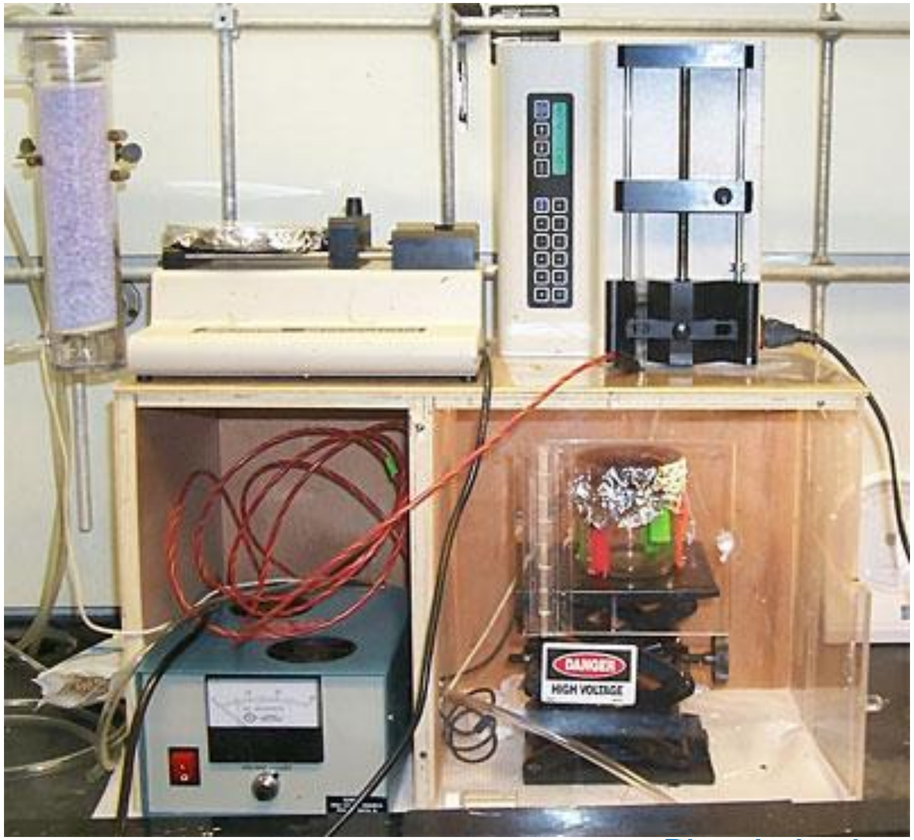
Application of monolithic SiO_2 in HPLC

HPLC setup
AG Smarsly

Electrospinning

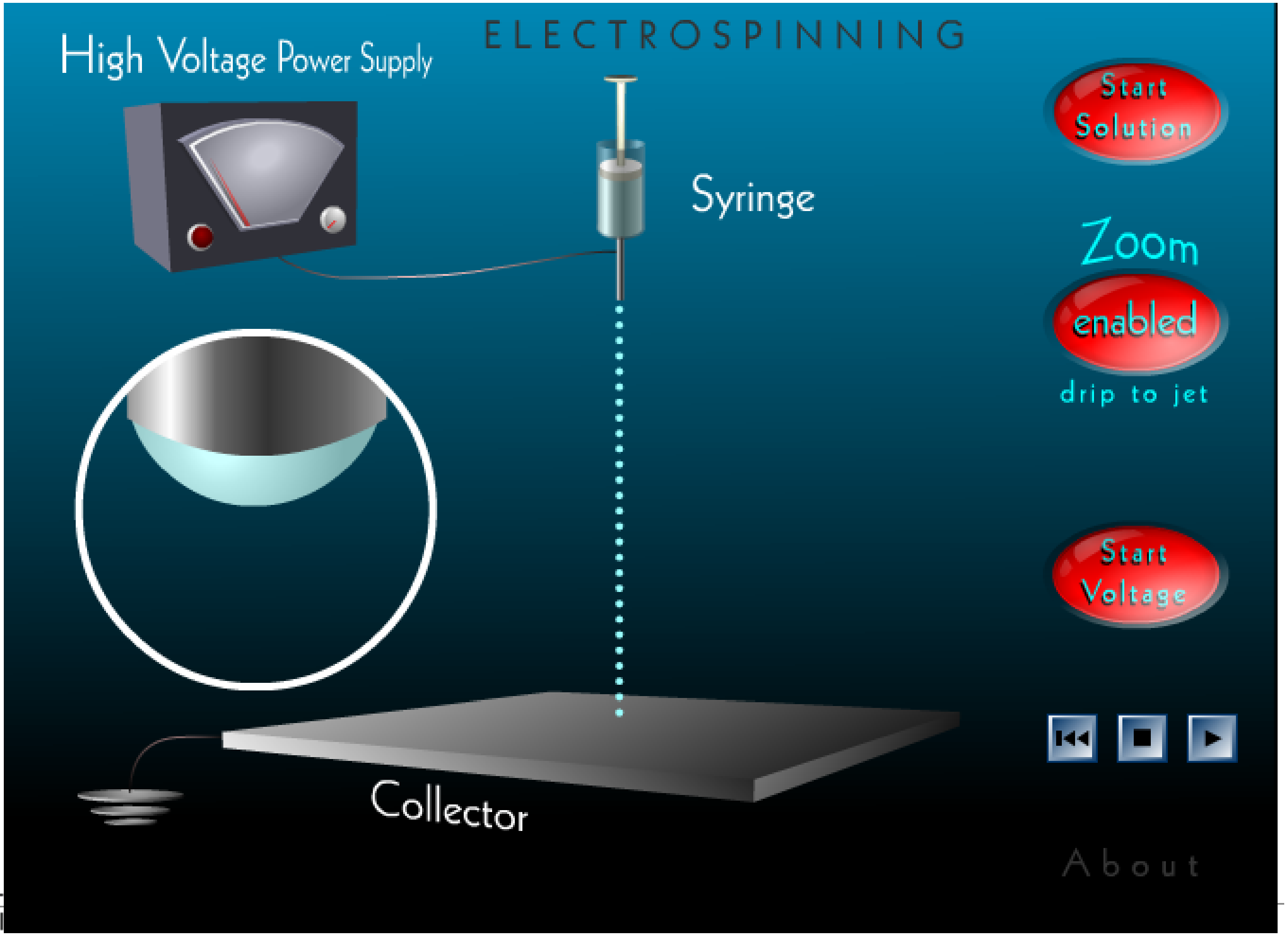
Basics and Setup





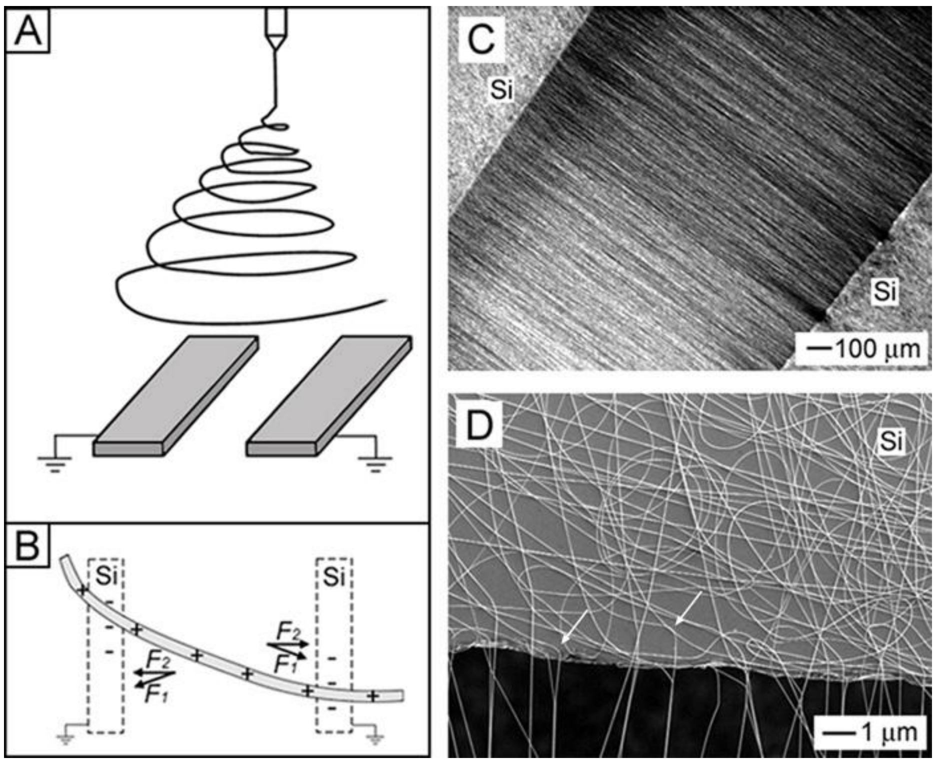
Electrospinning

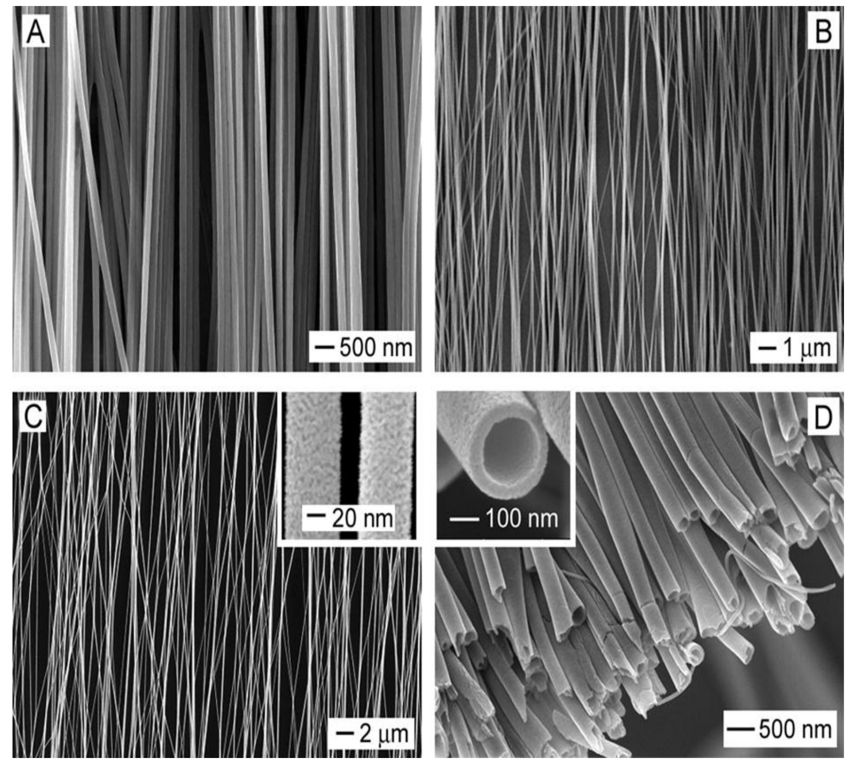
How does it work?



Courtesy of Dr.S.Hill, MichiganTech University

Alignment of Fibers





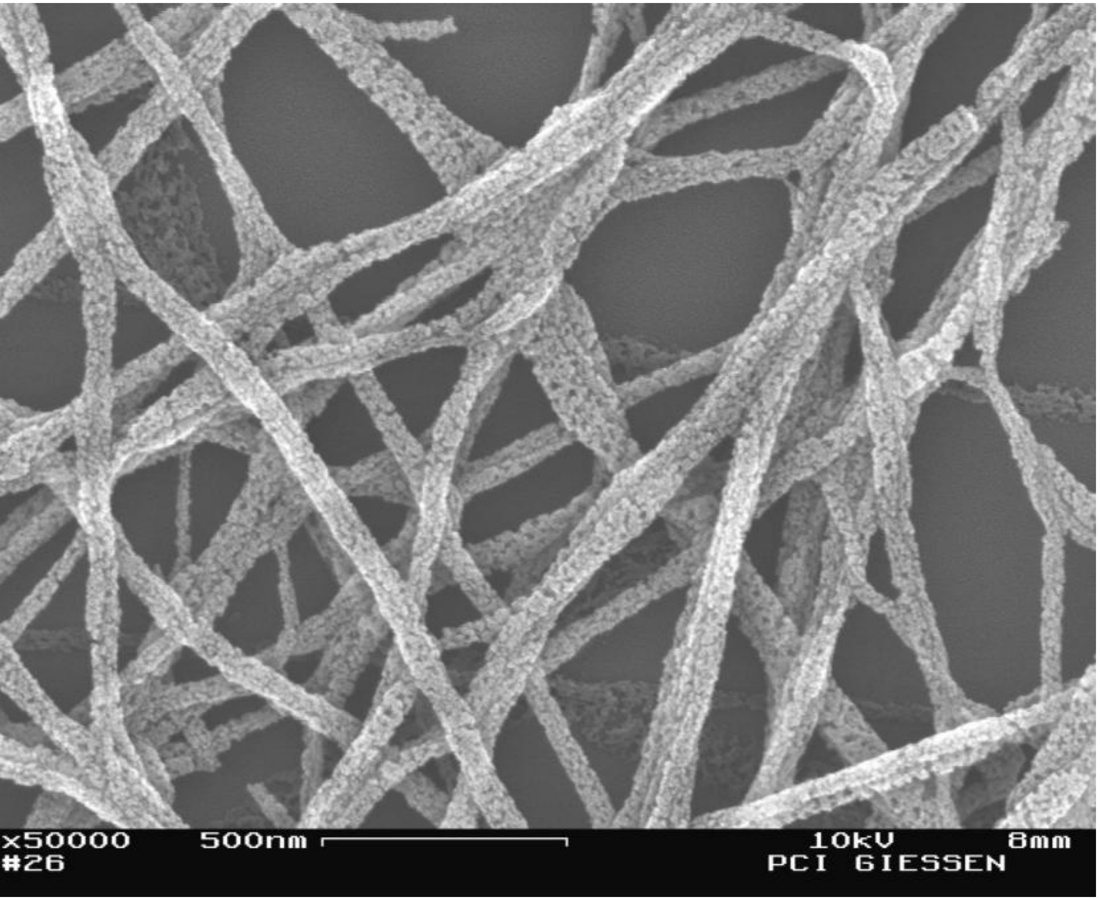
Li, Wang & Xia, *Nano Lett.* 2003, 3, 1167

Versatile materials by electrospinning

Thick mats

Thin coatings

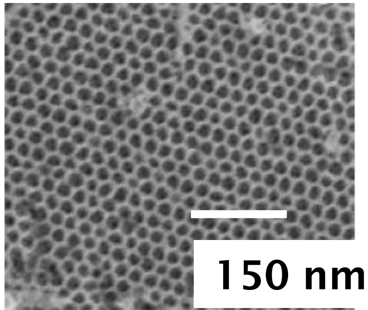
Possible benefits for medical applications



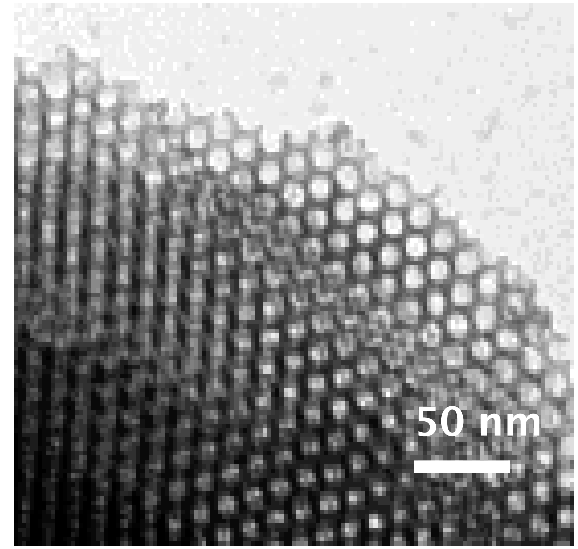
- Electrospinning allows the generation of mats of reasonable mechanical stability
- Generation of internal porosity possible

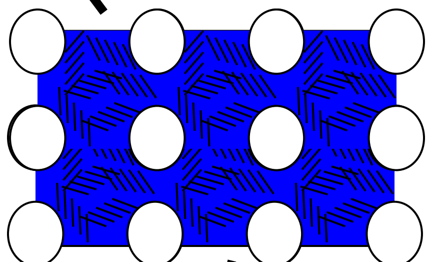
Generation of diverse pore structures

SMALL
polymer-colloids
(30 nm)

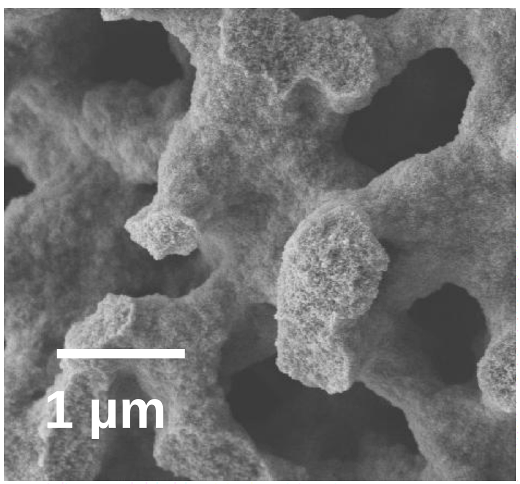


Lyotropic Blockcopolymer-
Mesophases

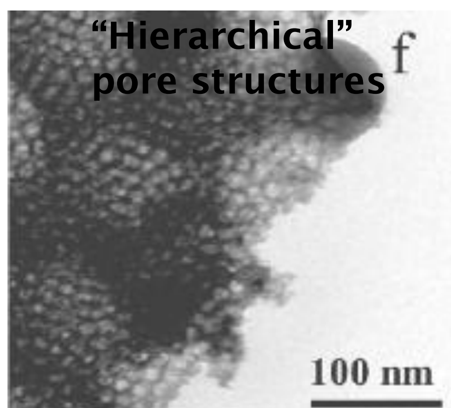


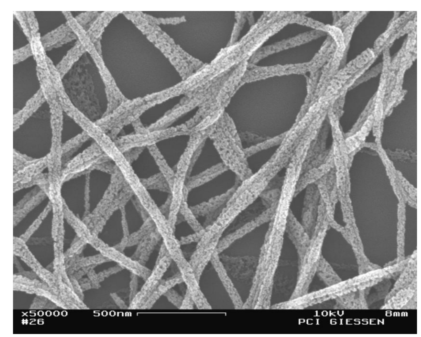


Polymer-
“sponge phases”



“Hierarchical”
pore structures

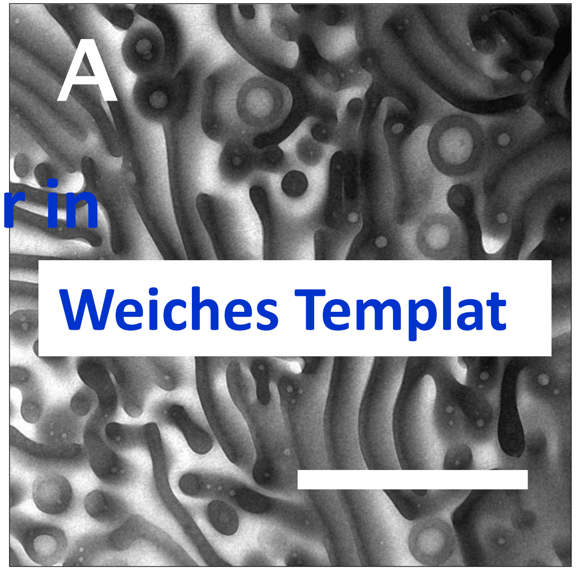




The principle of nanocasting

Elektronenmikroskopische Aufnahmen

Polymer in Wasser



Nanoporöses SiO_2

Skala:
1 Mikromete