TECNOLOGIA DOS MATERIAIS CERÂMICOS

II – SPECIAL CERAMIC PRODUCTS

Colloidal particles design

Nucleation and crystal growth (revisited)

Powders from chemical solution techniques

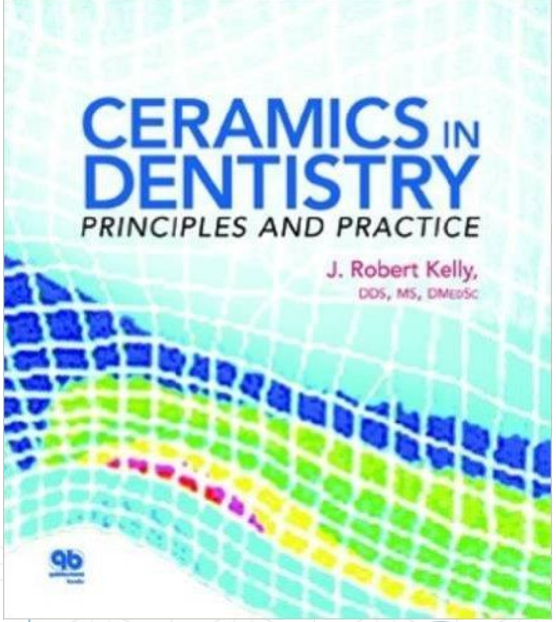
Powders from vapor phase reactions

Objective

The quest for a knowledge-based economy in Europe-strategy aims to consolidate the major European advantages in the biomedical, healthcare and pharmaceutical areas. Towards the *medicine research agenda*, in alignment with Horizon 2020, the development of *nanomedicine procedures* for a wide range of serious and debilitating disorders play a central role.

Personalized nanomedicine is based on *nanocarriers* i.e. nanosystems/platforms capable of delivering distinct drugs with different pharmacokinetics/pharmacodynamics, to elaborate optimized treatment tailored to each patient.

The **European Ceramic Roadmap** targets the consolidation of the European leading position in **nanomedicine, pharmaceutic** and **healthcare** areas.



CERAMICS IN DENTISTRY

PRINCIPLES AND PRACTICE

J. Robert Kelly, DDS, MS, DMedSc

Esthetic Nano Ceramic Restorative

Fusion Ceramfil

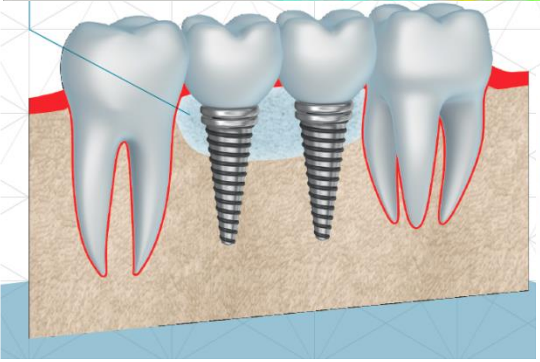
Aesthetic sculptable, radiopaque, highly filled nano-hybrid universal composite for the restoration of anterior and posterior teeth

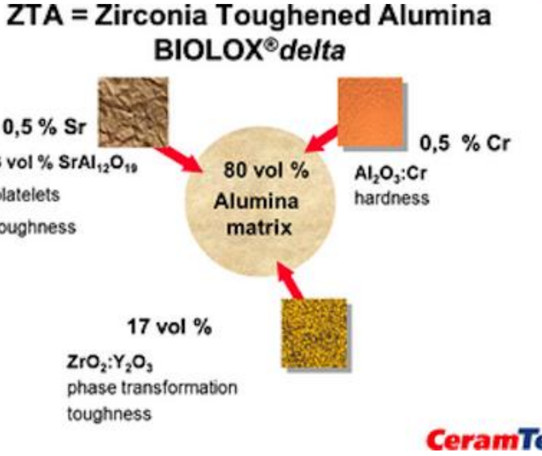
QUALITY MADE IN GERMANY

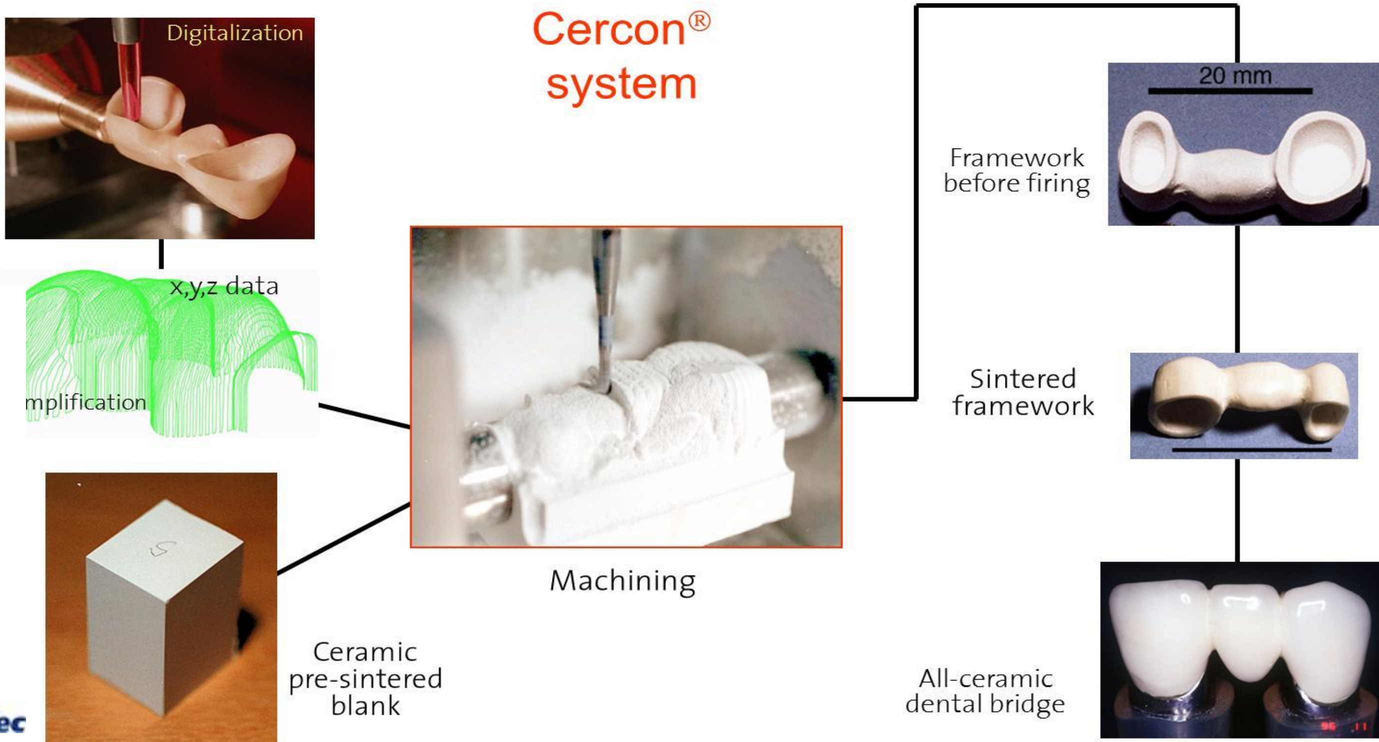
Available 12 VITA Shades

A1,A2,A3,A3.5,A4,B1,B2,B3,C2,D3,UO,Incisal

Clinical images provided by:
Dr Anja Ulpins, Germany

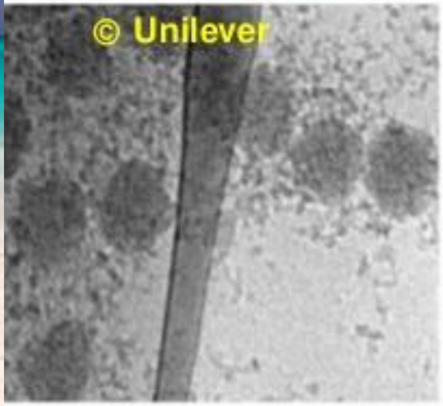






Nano-TiO_2 for Cosmetics

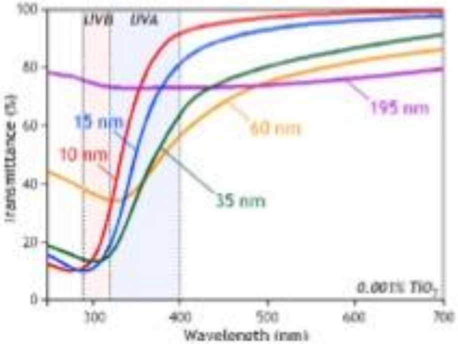
TiO_2 USED AS NANOPIGMENT & NANOEMULSION



Milky TiO_2 (nanoemulsion)

NanoTiO_2 cluster (nanopigment)

Transmittance varies with respect to the particle size of TiO_2



smetics-europe/products-and-ingredients/nanotechnology-.html

UV-protection

How to improve UV protection factor (UPF) of textiles

Fabric design
-Tighter weaving or knitting
-Higher weight

Textile finishing
-Organic dyes absorbing UV light
- Optical brighteners (in detergents)
- Dark coloration

Fibermodification
-TiO_2, ZnO nano pigments for dulling of chemical fibers
-Coating – to prevent photocatalytic reactions

Fiber Raw Materials:
1) Polyester (PET, PPT, PBT)
2) Polyamide (PA 6, PA 6,6)
3) Natural fibers (CO, WO, LI)

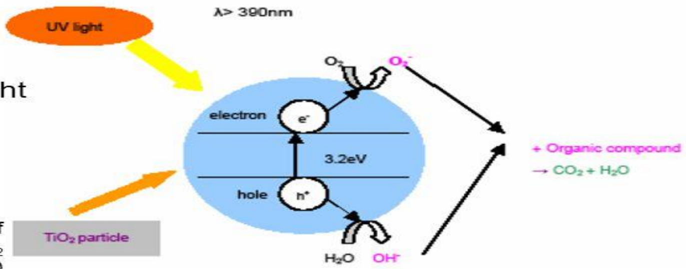
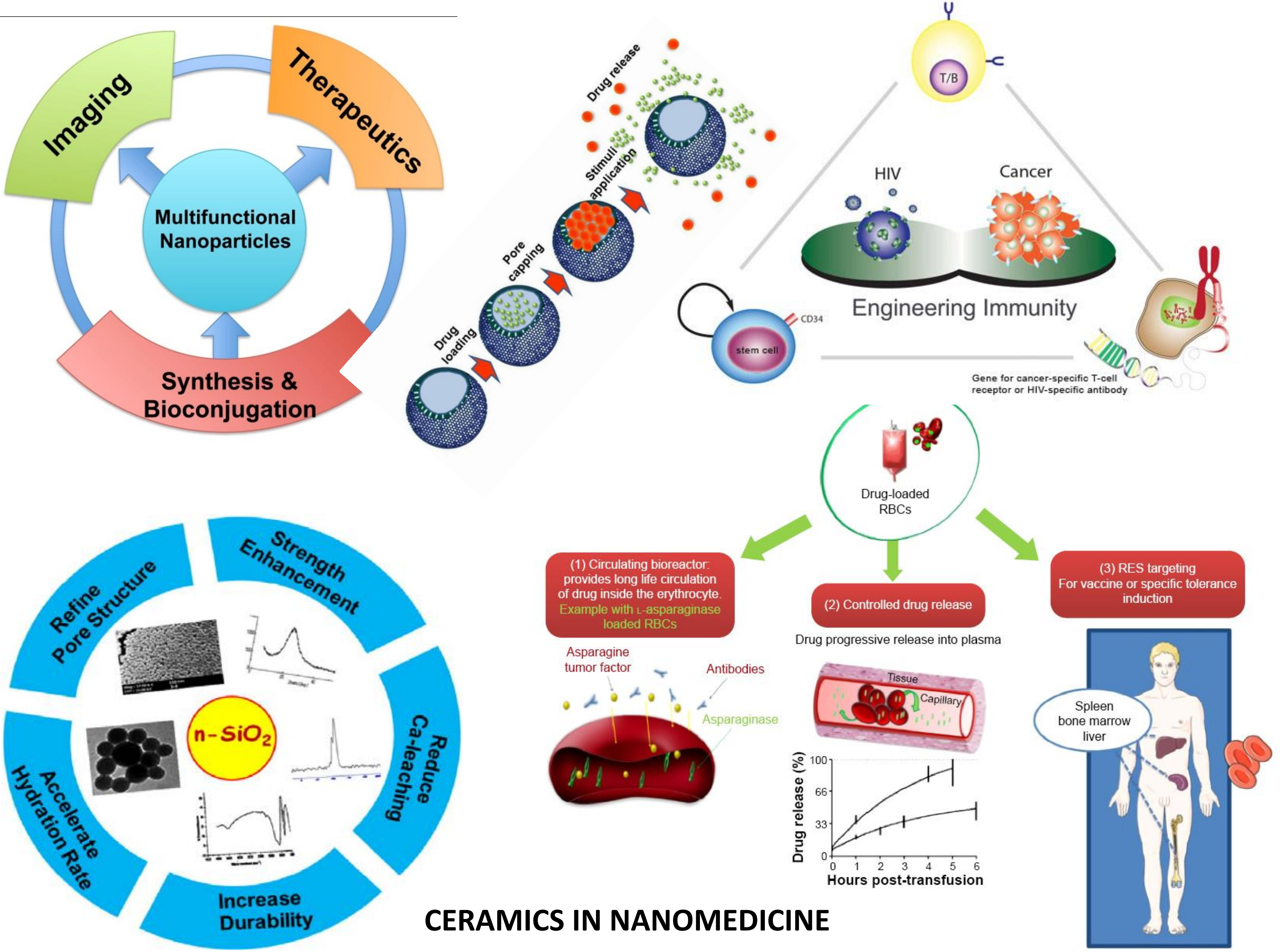


Photo catalysis mechanism of TiO_2
(Source: Samal *et al.*, 2010)

CERAMICS IN NANOMEDICINE



CERAMICS IN TEXTILES

Nanotechnology applications in Textiles

- Self-cleaning fabric
- Antistatic
- Odor fight finish
- Anti-pollen finish
- Flame retardant
- Functional finishes wrinkle, stain & static resistant
- Protection against chemical & biological threats
- Spinning of functional nano-fibers/yarns
- Smart, comfort & medical textiles
- Functionalized fabrics for UV protection & de-odorizing

V-protection

How to improve UV protection factor (UPF) of textiles

Fabric design
-Tighter weaving or knitting
-Higher weight

Textile finishing
-Organic dyes absorbing UV light
- Optical brighteners (in detergents)
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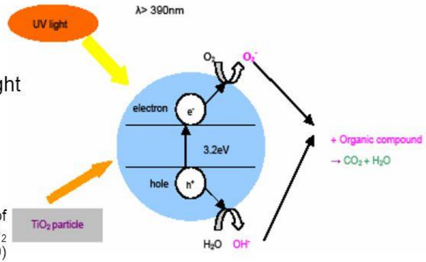


Photo catalysis mechanism of TiO_2
(Source: Samal *et al.*, 2010)

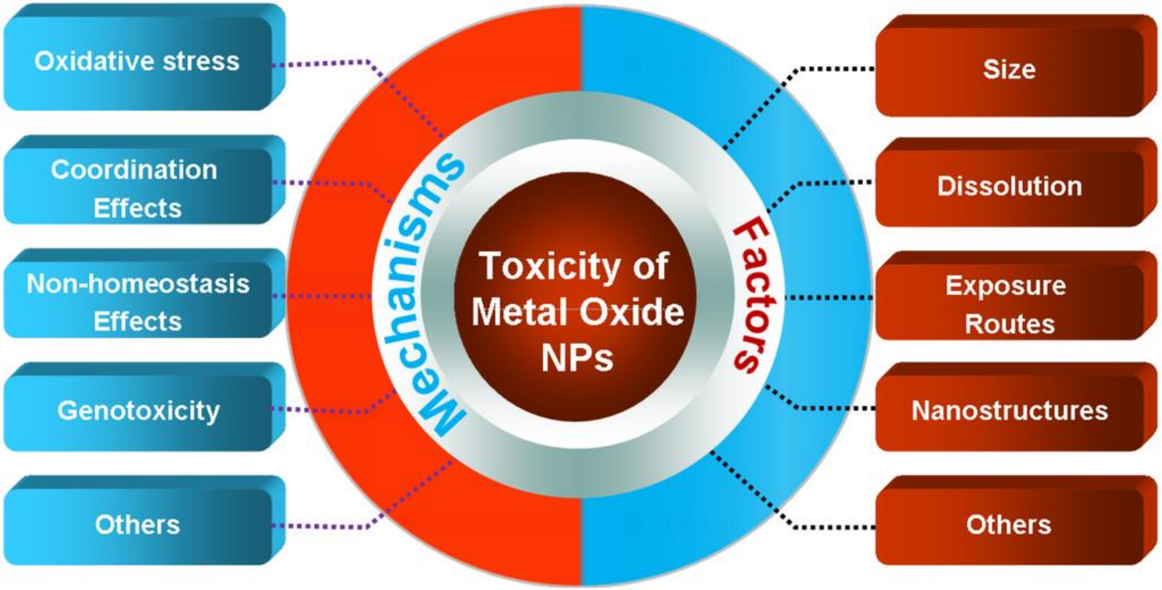
How does WoundEx® work?

Anti-adhesive surface of the **WoundEx®** non- woven pad fabric.

Patented **zeolite-iodine complex** absorbs exudate from the wound

Bioactive iodine reduces the risk of infection and accelerates the healing process.

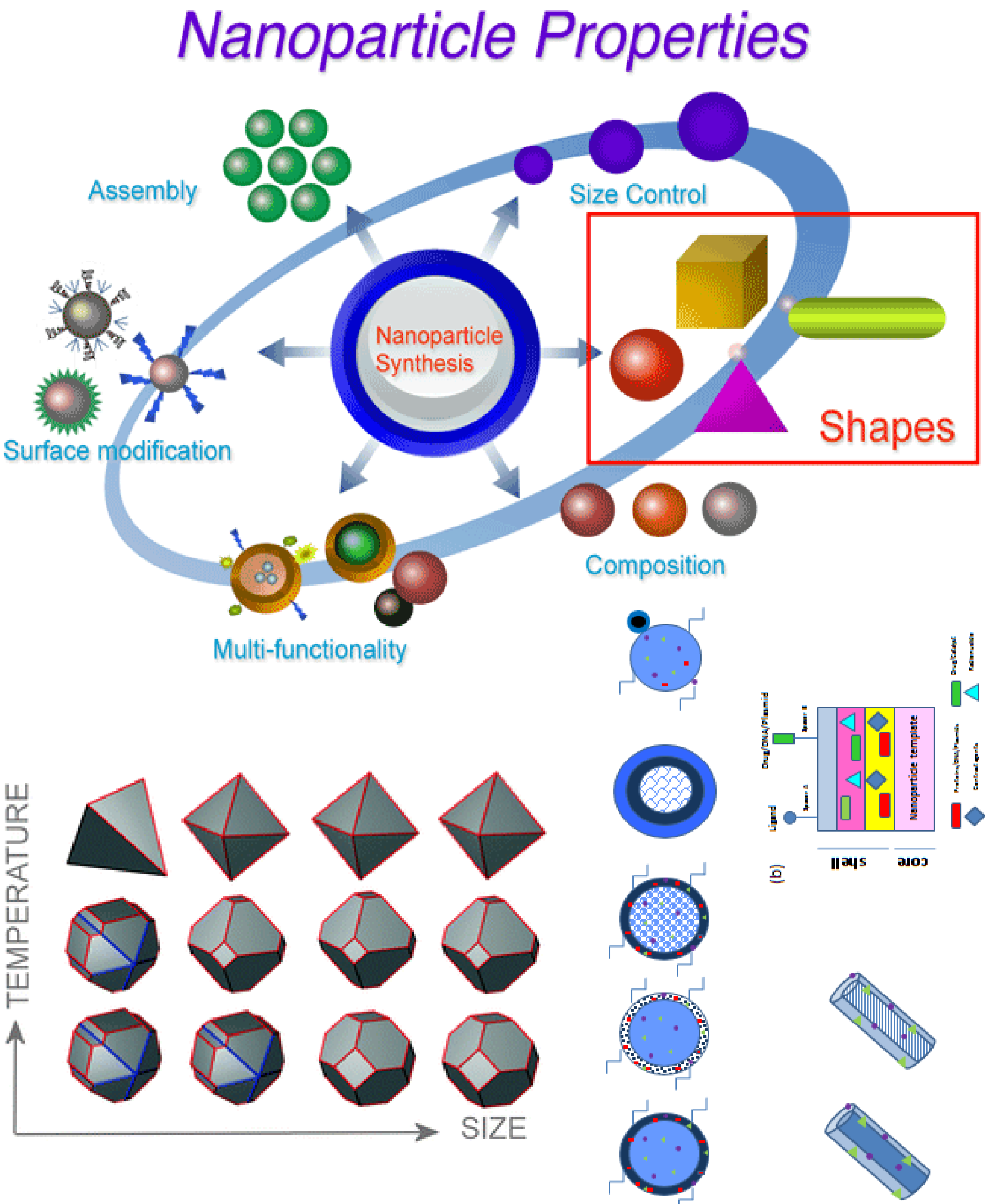
Removal of bacteria and physical cleaning support faster wound healing.




WHAT ARE
{ POTENTIALLY }
DANGEROUS
NANOPARTICLES DOING
IN BABY FORMULA

-KELLYSTHOUGHTSONTHINGS.COM

Why nanoparticles?



- **size** (actual and hydrodynamic diameter) and **size distribution**
- **angle of curvature**, **shape** and **shape distribution**
- **surface area** and **smoothness/roughness**
- **surface charge**, **surface chemistry/reactivity** (hydrophobicity/hydrophilicity)
- **coating thickness** (in core-shell structures)
- **chemical composition** of both core and shell
- **crystallinity** of both core and shell
- **porosity** (porous size and porous size distribution)
- identification and **levels** of any **impurities**

1.1 Special Ceramic Powders

Introduction: Colloidal Particles design

→ Various types of **colloidal ceramic particles** have been developed in outstanding efforts between academia and industry, in the last decades. Colloidal particles benchmarket demands **an accurate particles characterization** which absence has been one of the main drawbacks in technological applications. The following set of properties needs to be addressed:

size (actual and hydrodynamic diameter) **and size distribution**

shape and **surface curvature**

surface area and **smoothness/roughness**

surface charge, **surface chemistry/reactivity**, **hydrophobicity/hydrophilicity**

coating thickness

chemical composition of both **core** and **shell**

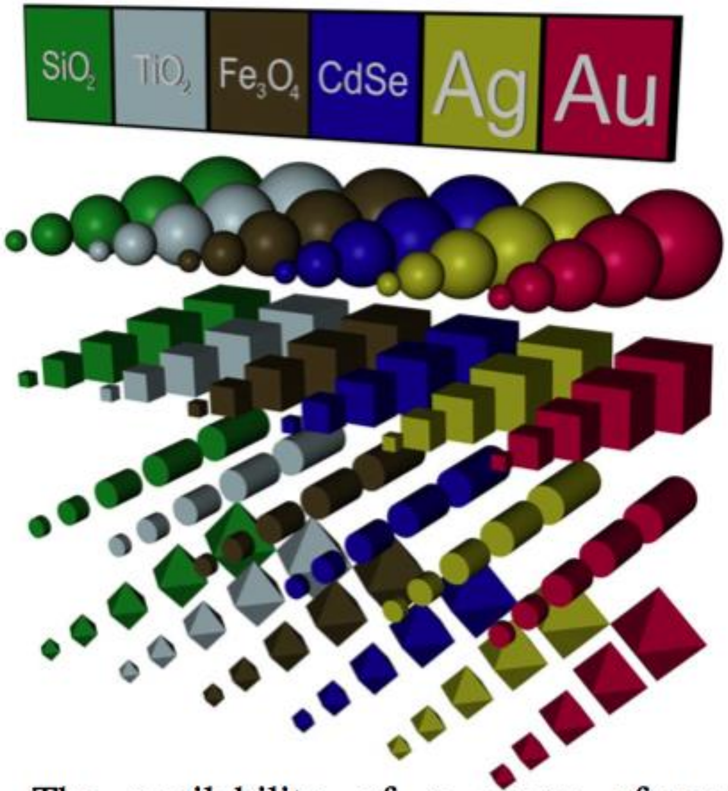
crystallinity of both **core** and **shell**

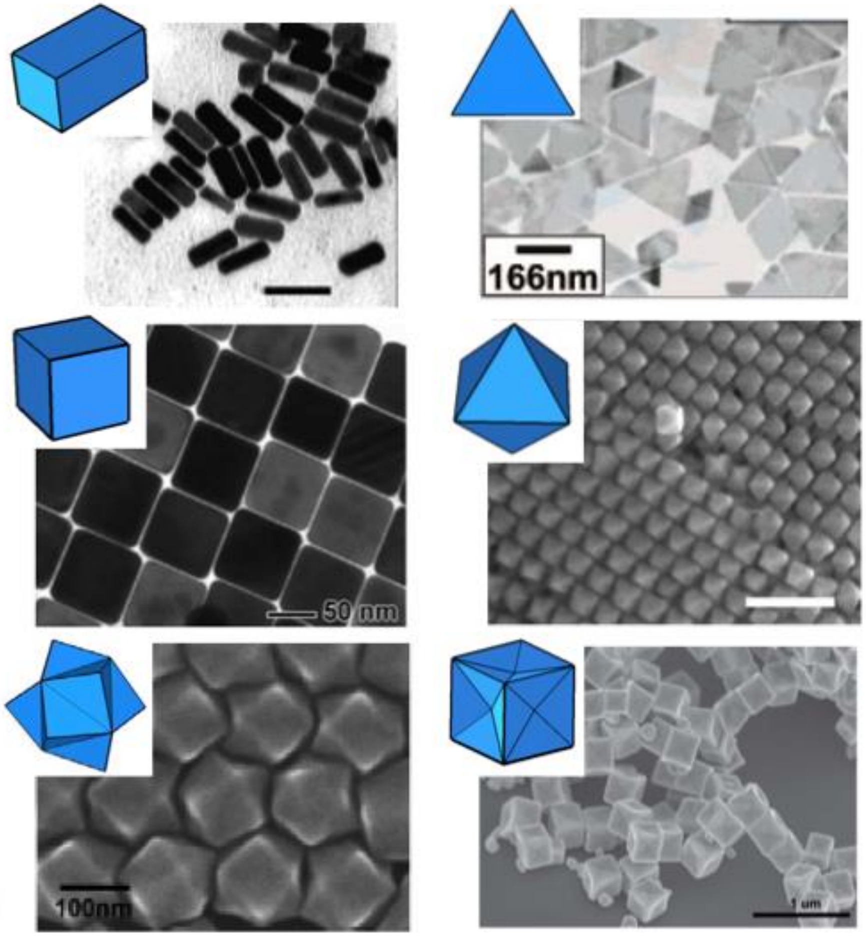
porosity (**size** and **size distribution**)

identification and **levels** of any **impurities**

1.1 Special Ceramic Powders

Introduction: Colloidal Particles design





The availability of a range of new nanostructures has been facilitated by synthetic control over composition, size and shape.

Nano2

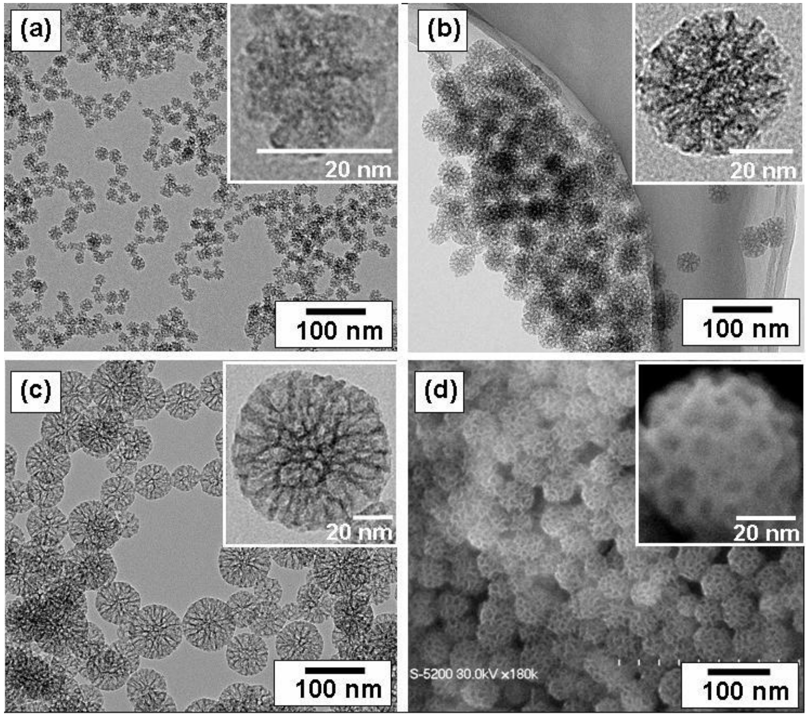
Nikoobakht, B. et al. *Chem. Mater.* 2003. **15,** 1957.
Xia, Y. et al. *Angew. Chem. Int. Ed.* 2009. **48,** 60.
Yu, Y. et al. *J. Phys Chem. C.* 2010. **114,** 11119.

Millstone, J. E. et al. *J. Am. Chem. Soc.* 2005. **127,** 5312.
Niu, W. et al. *J. Am. Chem. Soc.* 2009. **131,** 697.
Zhang, J. et al. *J. Am. Chem. Soc.* 2010. ASAP.

1.1 Special Ceramic Powders

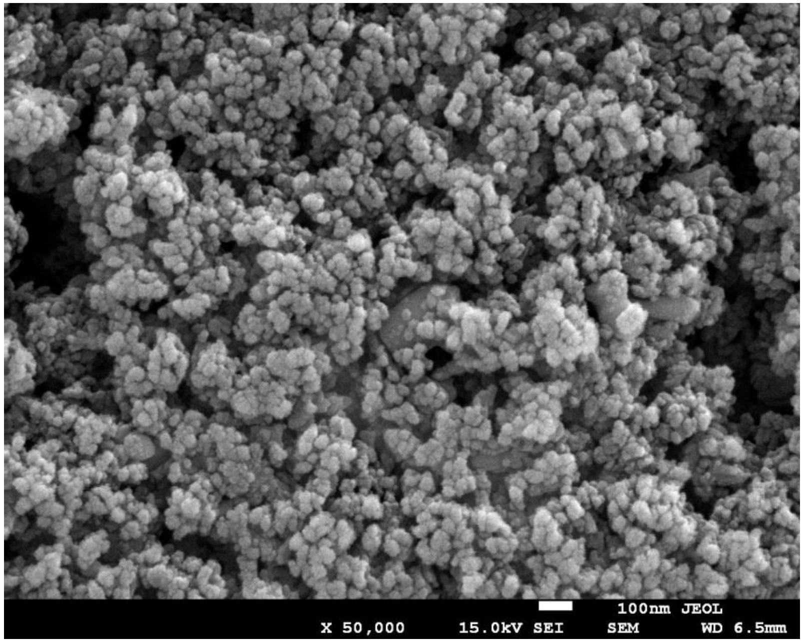
Introduction: Colloidal Particles design

https://en.wikipedia.org/wiki/Nanoparticle



TEM (a, b, and c) images of prepared mesoporous **SiO_2** nanoparticles with mean outer diameter:
(a) 20 nm, (b) 45 nm, and (c) 80 nm.

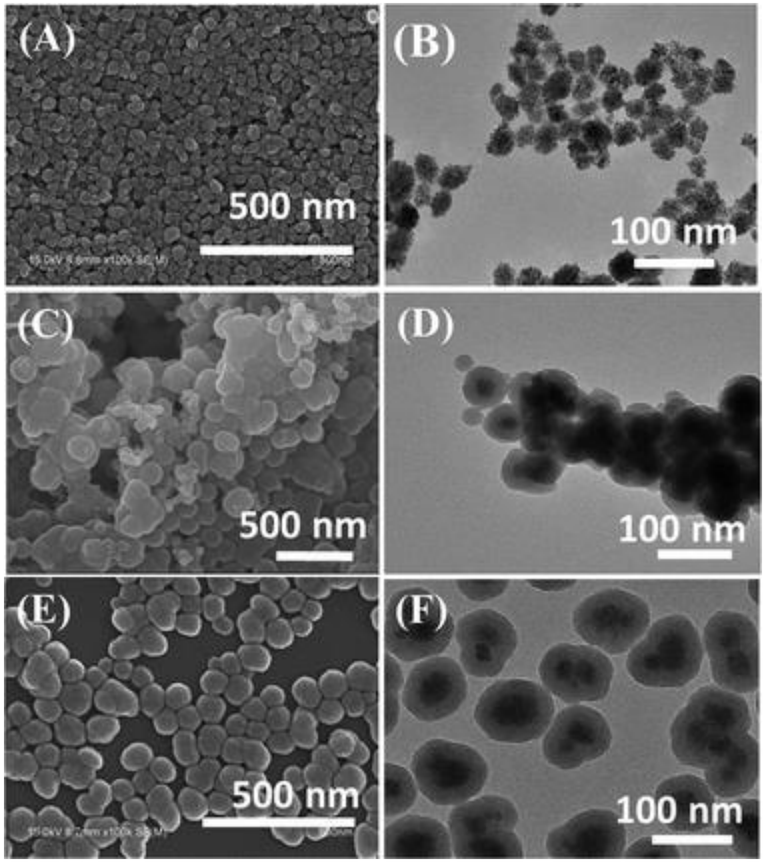
http://www.us-nano.com/oxides?cmx=185&start=120



SEM images of **Al_2O_3** nanoparticles

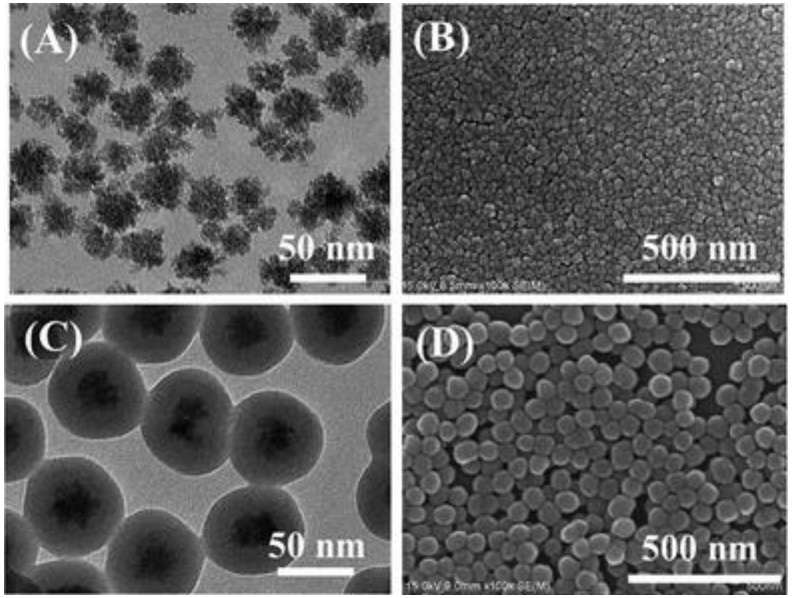
1.1 Special Ceramic Powders

Introduction: Colloidal Particles design



SEM and TEM images of ZrO_2 nanoparticles

http://pubs.rsc.org/en/content/articlehtml/2013/tc/c3tc30324a



Morphology of the prepared ZrO_2 nanoparticles and $ZrO_2@SiO_2$ CSNs

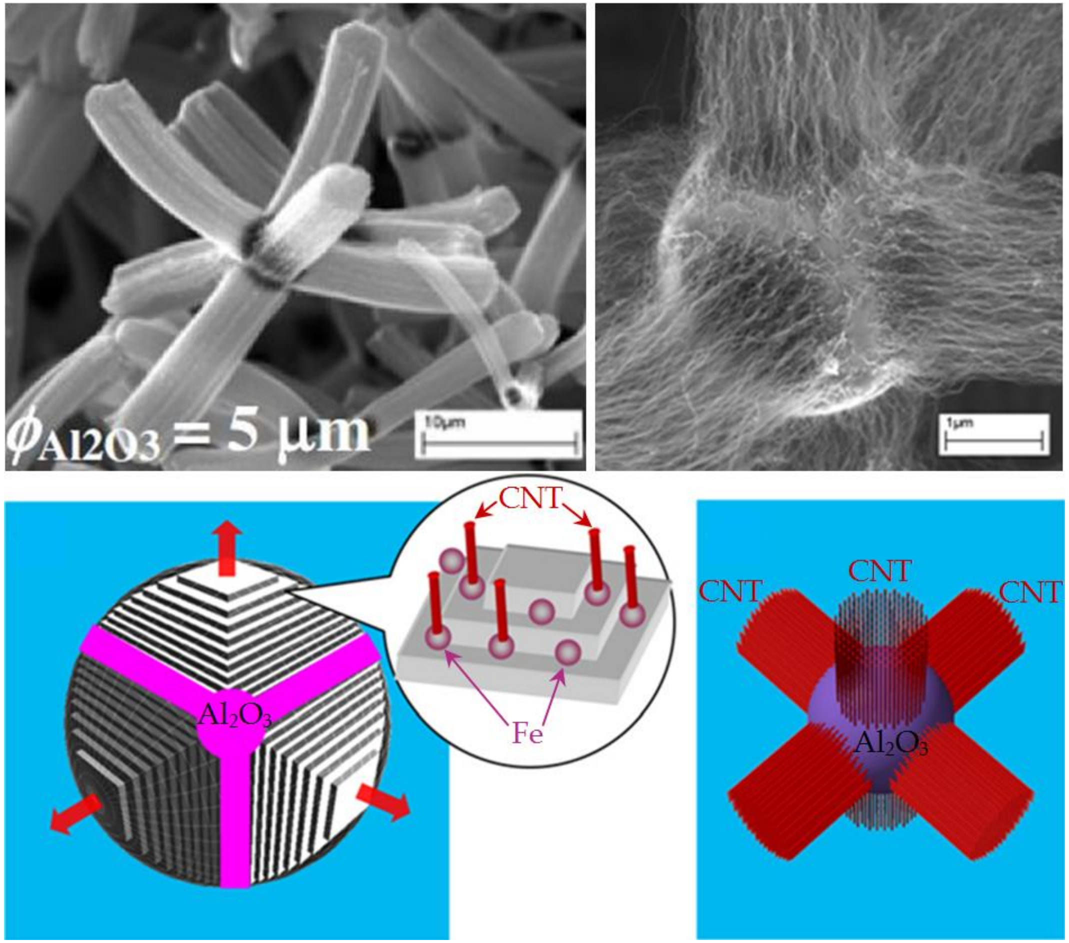
(A) and (B) are the TEM and SEM images of ZrO_2, respectively

(C) and (D) are the TEM and SEM images of $ZrO_2@SiO_2$ CSNs

1.1 Special Ceramic Powders

Introduction: Colloidal Particles design

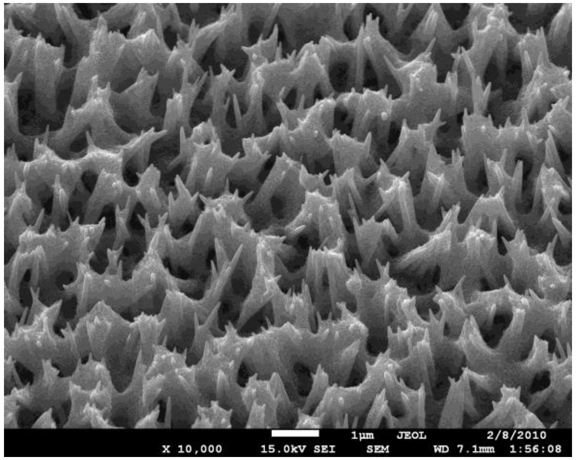
http://www.intechopen.com/books/carbon-nanotubes-synthesis-characterization-applications/carbon-nanotube-synthesis-and-growth-mechanism

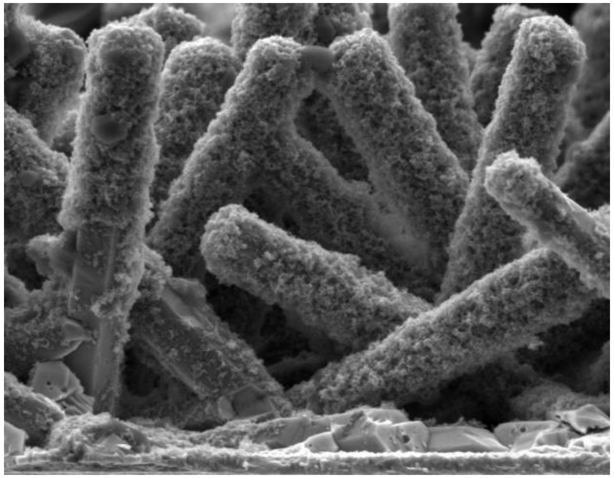


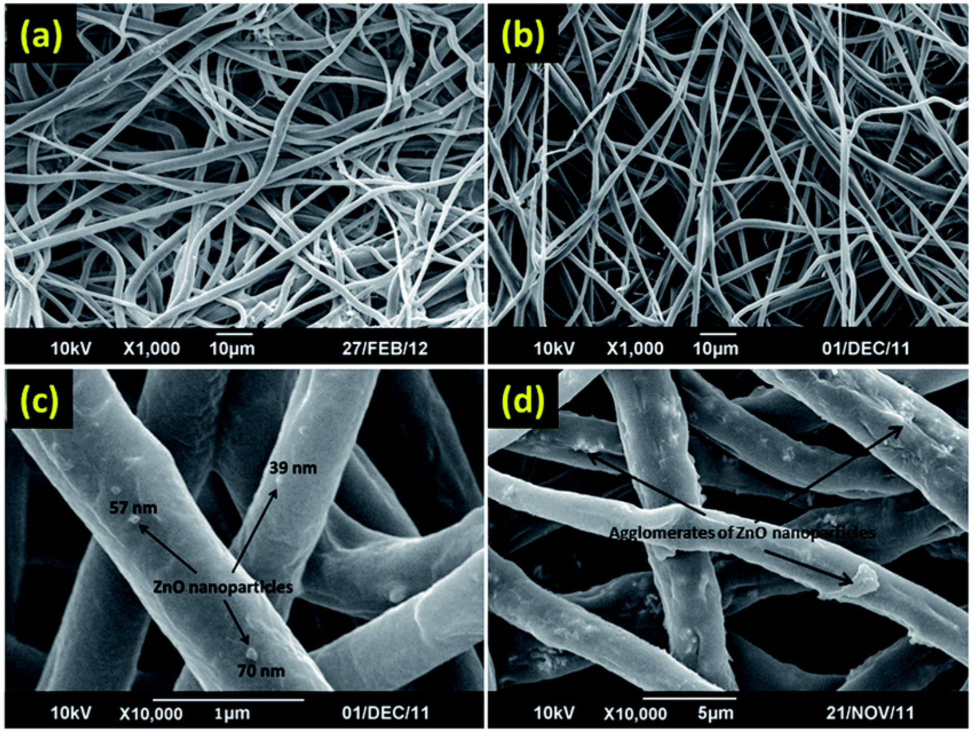
Orthogonal growth of **CNTs** from an **Al_2O_3** substrate.

1.1 Special Ceramic Powders

Introduction: Colloidal Particles design



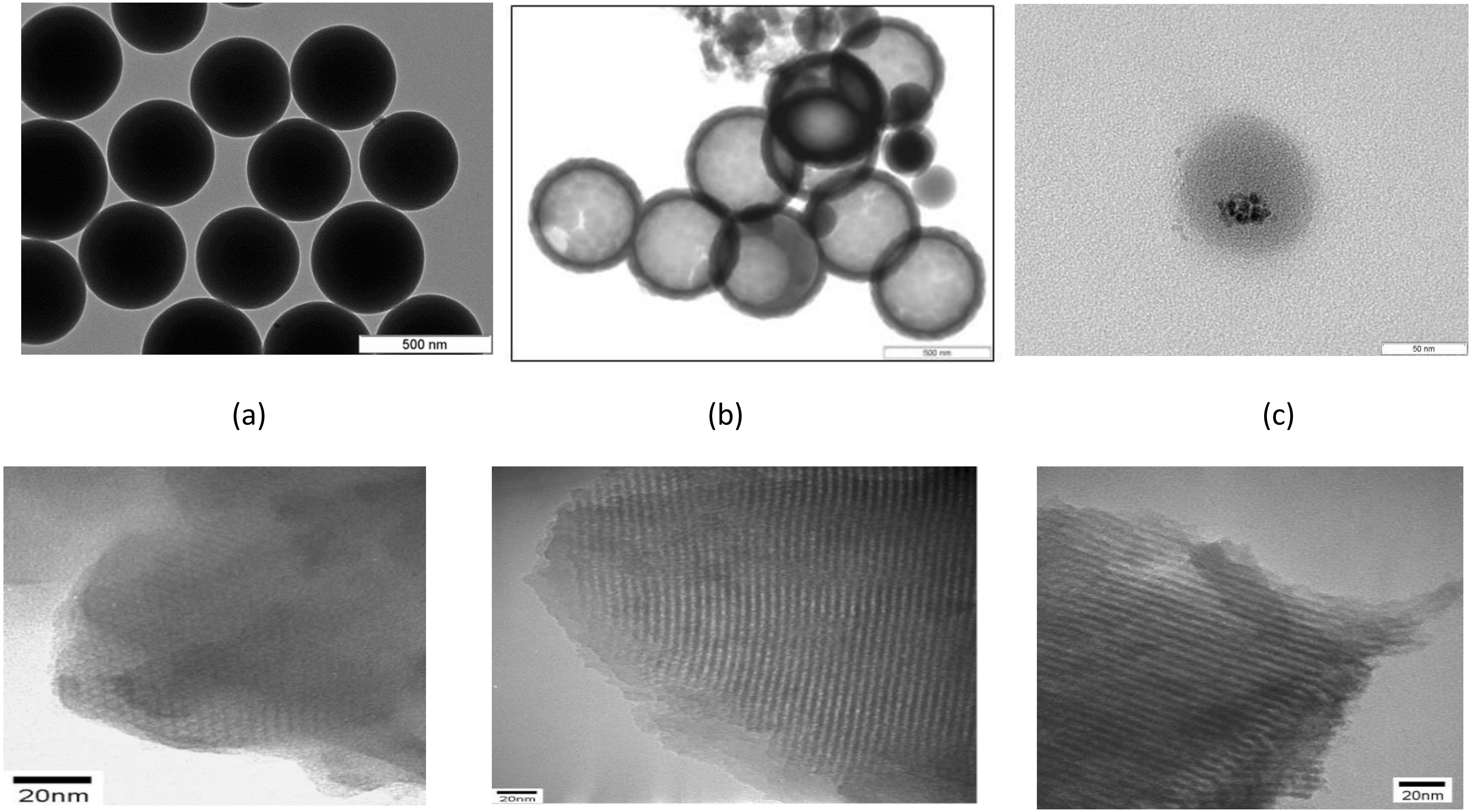




ZnO nanostructures with different morphologies

1.1 Special Ceramic Powders

Introduction: Colloidal Particles design



(a) (b) (c)

(d)

SiO_2 nanoparticles: dense (a), hollow, (b) core-shell nanostructured (c) and $Brij_{56}$ templated (d)

Top-down

- lithography
- wet ball milling

Bottom-up

- precipitation
- hydrothermal
- sol-gel

Special Ceramic Powders

Powders from chemical solution techniques

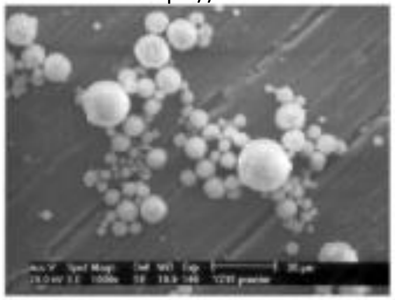
Precipitation, solvent evaporation and solvent extraction

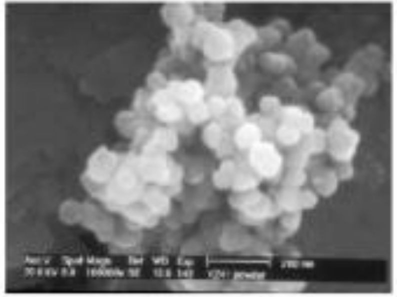
Chemical solutions techniques provide a relatively convenient means for achieving powders of high purity and fine size.

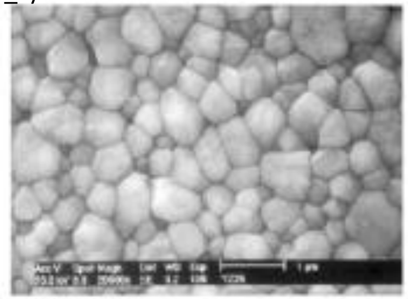
First a suitable liquid solution containing the cations of interest is prepared and analyzed. A solid particulate phase may be formed by **precipitation**, **solvent evaporation**, or **solvent extraction**.

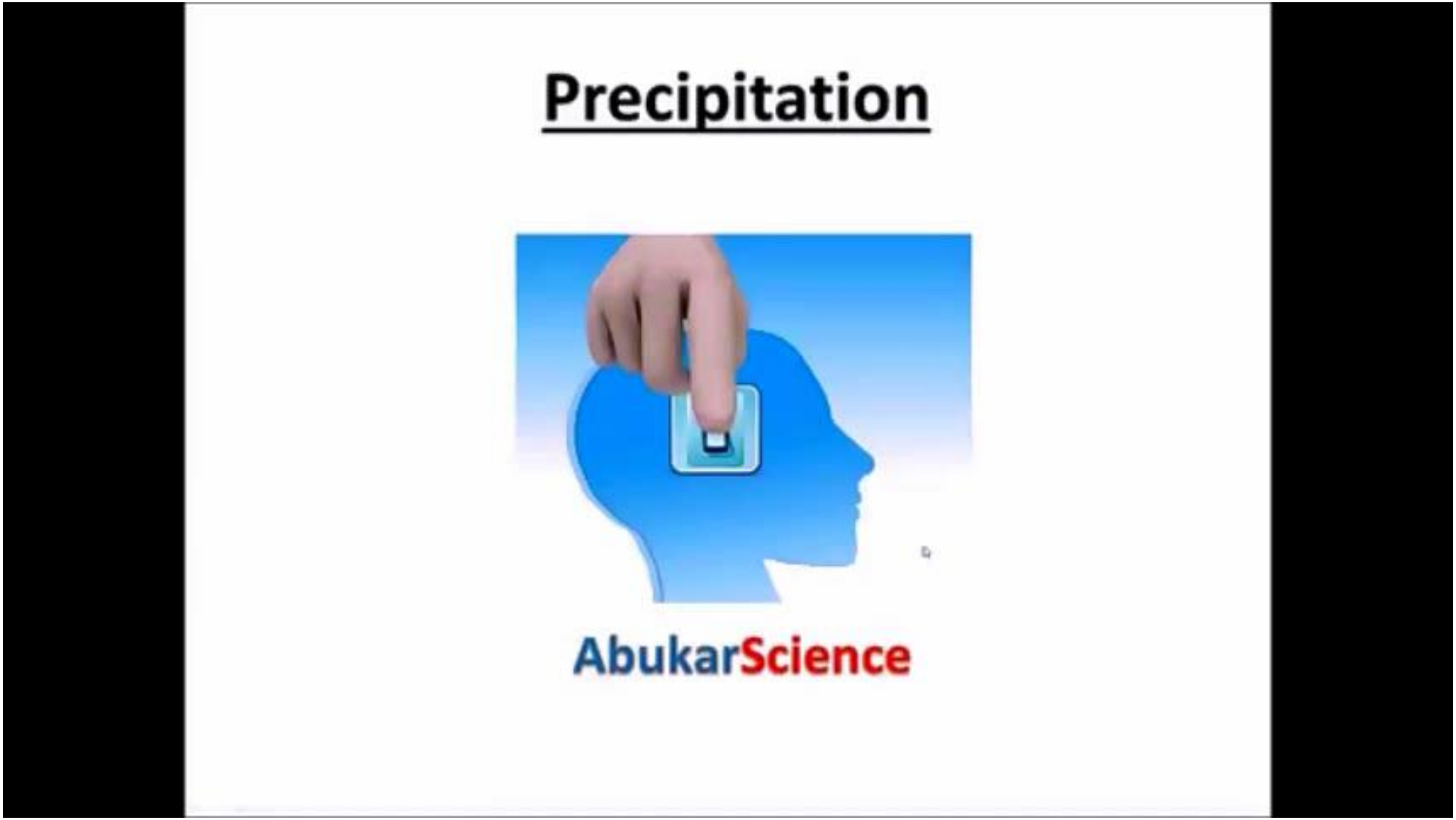
Segregation is minimized by combining the ions in a precipitate or gel phase or by extracting the solvent in a few miliseconds from a microscopic drop. The solid state phase is usually a salt that can be decomposed without melting by calcination at a relatively low temperature. Finally a porous calcine material is ground relatively easily to a submicron size.

https://www.mtm.kuleuven.be/Onderzoek/Ceramics/Powder_synthesis


Spray-dried ZrO_2-powder


Y_2O_3-coated ZrO_2-powder


Sintered Y-TZP ceramic



Precipitation

AbukarScience

https://www.youtube.com/watch?v=5VeCkEc47ck&t=52s

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

Chemical precipitation techniques can be used to prepare a wide variety of inorganic salts.

The addition of a chemical compound the solution or a change in temperature or pressure may decrease the solubility limit and cause **precipitation**.

Precipitation occurs by **nucleation and growth**. Impurity ions in solution that are adsorbed on particular surfaces of the particles may affect their growth rates.

Relatively slow growth rate along particular crystallographic direction will cause the precipitate particles to have na anisometric shape.

A higher degree of supersaturation may increase the nucleation rate and produce a **smaller particle size**, but if precipitation is extremely rapid, foreign ions tend to be ocluded in the particle.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

The mixing rate and temperature must be controlled to obtain a **controlled precipitate**.

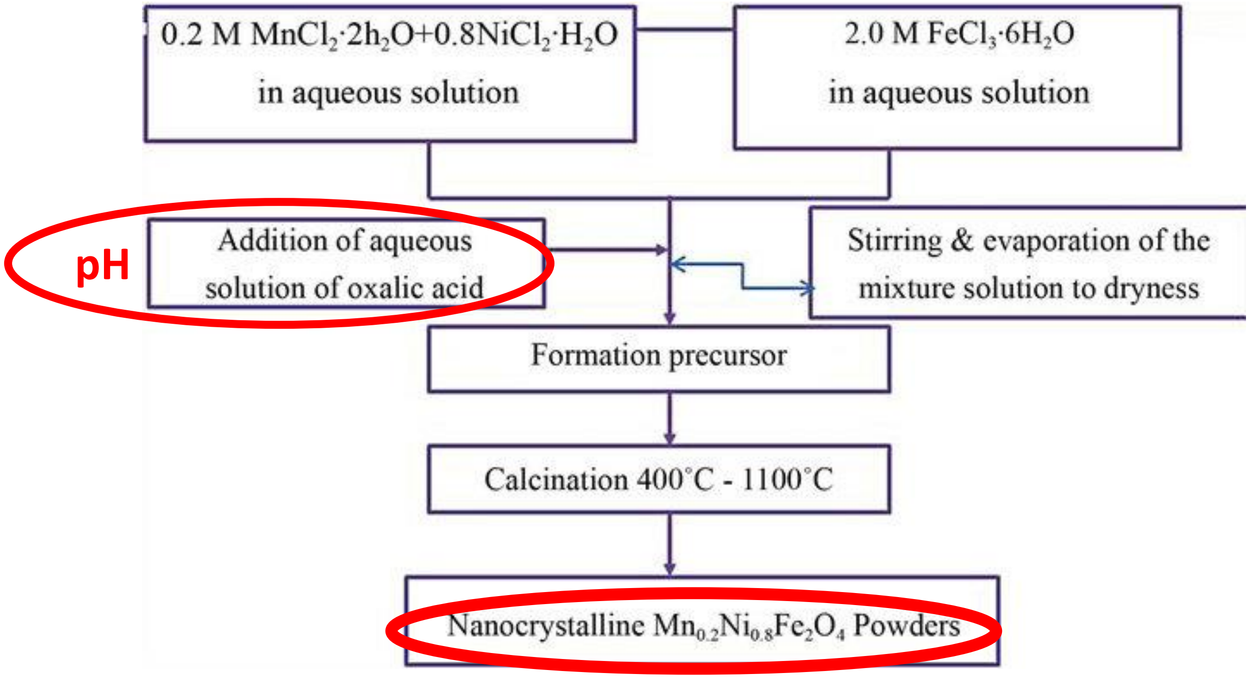
When the cations in solution are of about the same size and chemically similar of the designed precipitate, the precipitation of a salt containing the cations in **solid solution** may occur: this is called **co-precipitation**.

In **heterogeneous precipitation**, the concentration of an ion in the salt differs from that in the solution, and the composition of the coprecipitate may change as precipitation progresses. Less soluble isomorphs tend to concentrate in the salt.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques



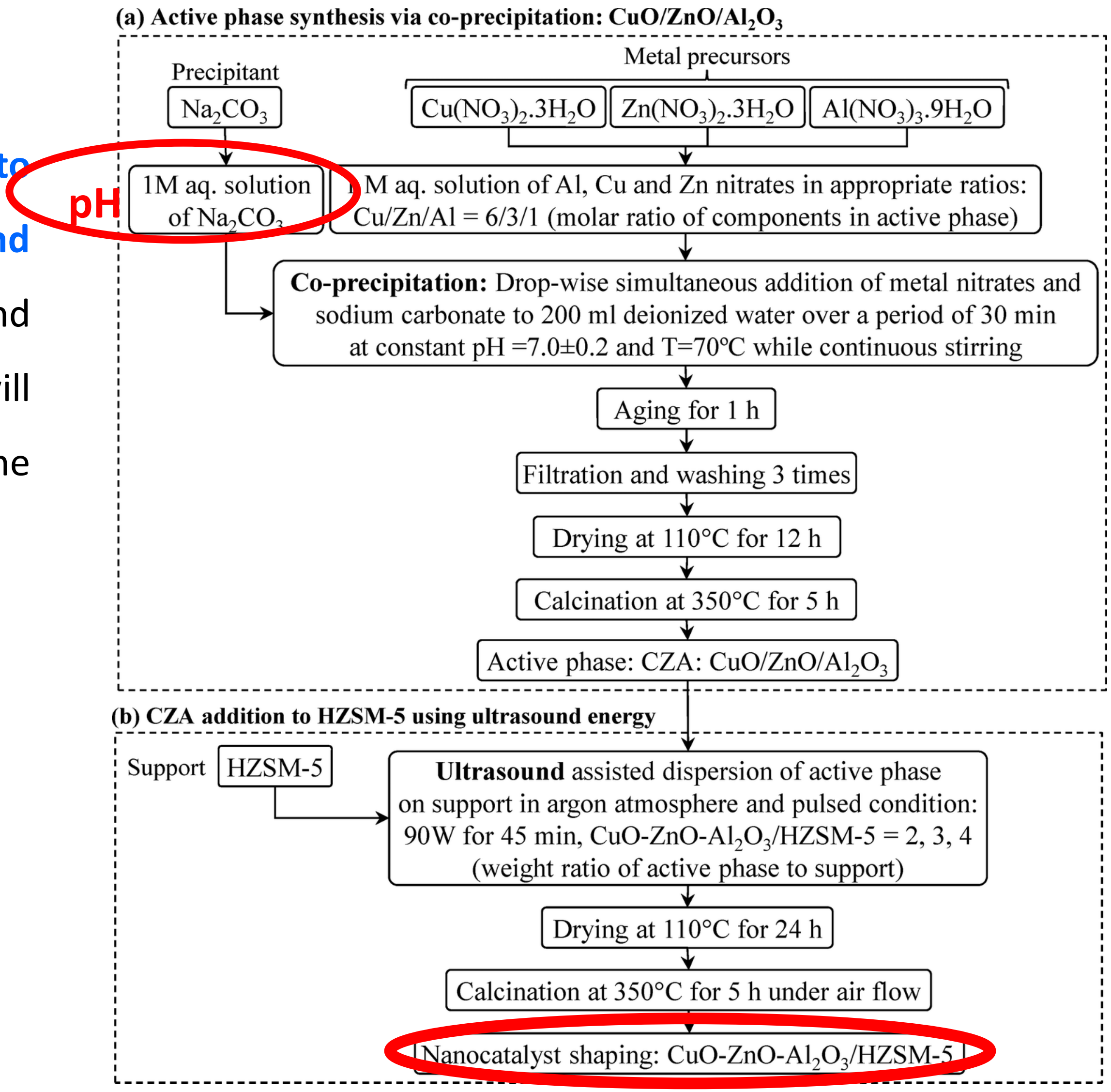
In some cases, it may be possible **to precipitate a specific compound containing more than one cation**, and the composition of the precipitate will be uniform regardless of the concentration of ions in solution.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

In some cases, it may be possible **to precipitate a specific compound containing more than one cation**, and the composition of the precipitate will be uniform regardless of the concentration of ions in solution.



(a) Active phase synthesis via co-precipitation: $CuO/ZnO/Al_2O_3$

Precipitant: Na_2CO_3 → 1M aq. solution of Na_2CO_3

pH

Metal precursors: $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.3H_2O$, $Al(NO_3)_3.9H_2O$ → 1M aq. solution of Al, Cu and Zn nitrates in appropriate ratios: Cu/Zn/Al = 6/3/1 (molar ratio of components in active phase)

Co-precipitation: Drop-wise simultaneous addition of metal nitrates and sodium carbonate to 200 ml deionized water over a period of 30 min at constant pH =7.0±0.2 and T=70°C while continuous stirring

Aging for 1 h

Filtration and washing 3 times

Drying at 110°C for 12 h

Calcination at 350°C for 5 h

Active phase: CZA: $CuO/ZnO/Al_2O_3$

(b) CZA addition to HZSM-5 using ultrasound energy

Support: HZSM-5

Ultrasound assisted dispersion of active phase on support in argon atmosphere and pulsed condition: 90W for 45 min, $CuO\text{-}ZnO\text{-}Al_2O_3/HZSM\text{-}5$ = 2, 3, 4 (weight ratio of active phase to support)

Drying at 110°C for 24 h

Calcination at 350°C for 5 h under air flow

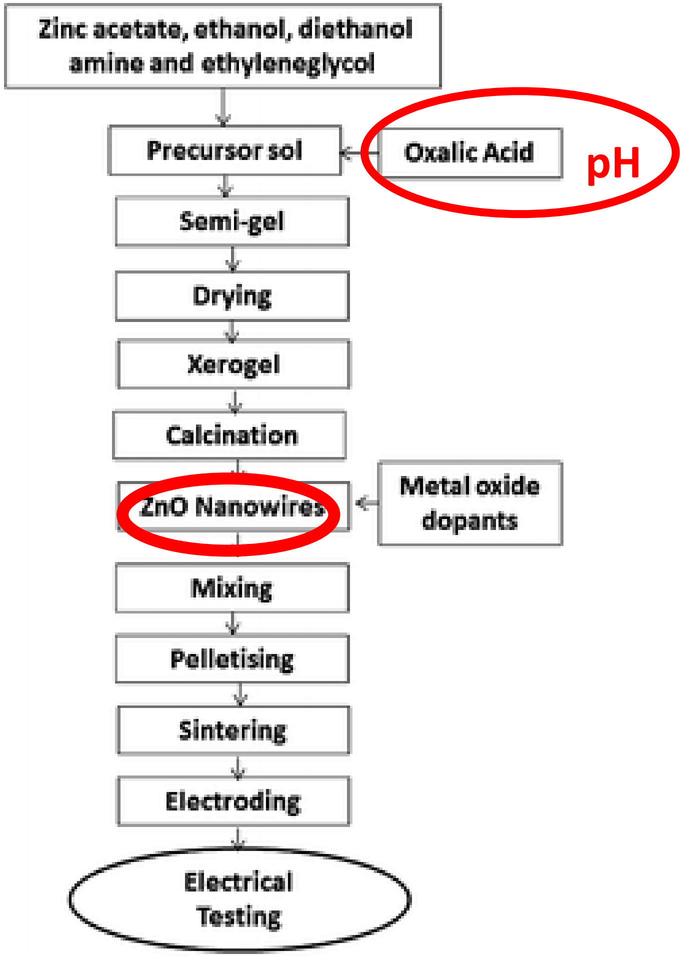
Nanocatalyst shaping: $CuO\text{-}ZnO\text{-}Al_2O_3/HZSM\text{-}5$

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

Thermal decomposition of the oxalate salt in air and at a temperature bellow 500ºC may be a chemical route to porduce ZnO powders.

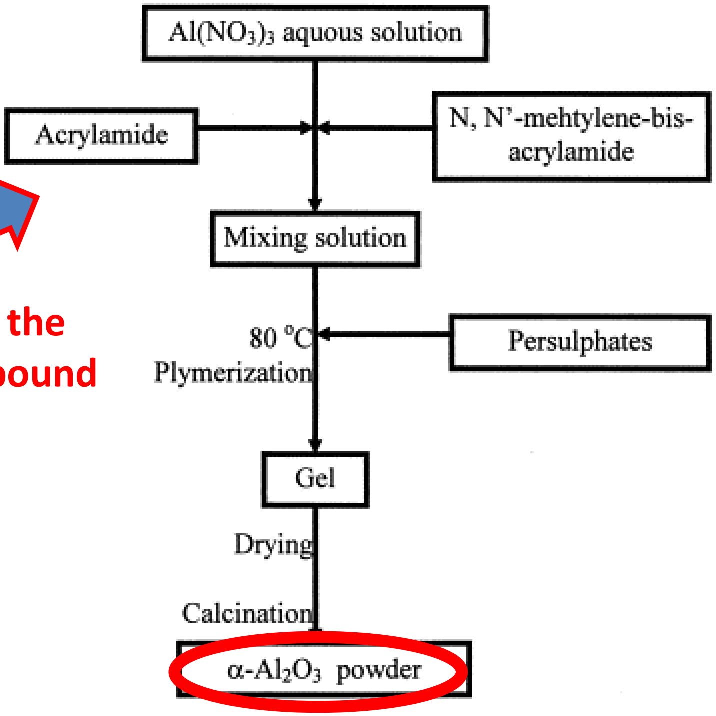


1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

Complex formation followed by precipitation at relatively low temperatures (80ºC in the present case) may be a chemical route to produce Al_2O_3 powders.



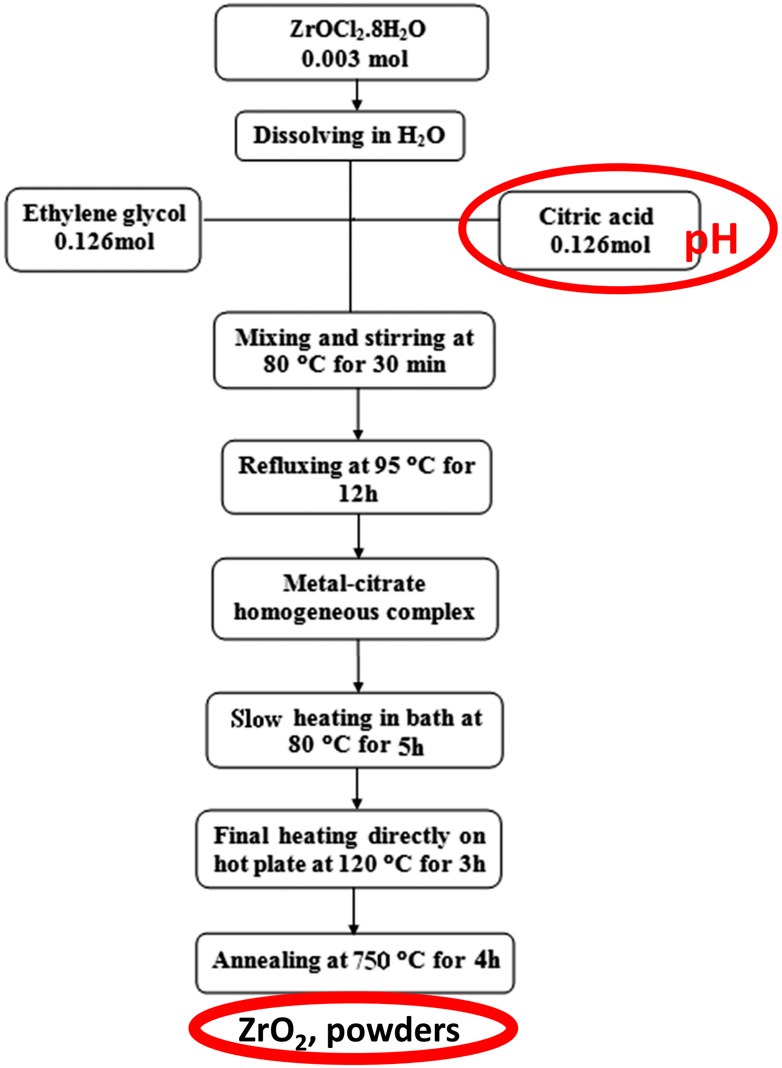
Solubility change due to the addition of a second compound

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

Complex formation followed by precipitation at relatively low temperatures (80ºC in the present case) may be a chemical route to produce ZrO_2 powders.



$ZrOCl_2.8H_2O$
0.003 mol

Dissolving in H_2O

Ethylene glycol
0.126mol

Citric acid
0.126mol

pH

Mixing and stirring at 80 °C for 30 min

Refluxing at 95 °C for 12h

Metal-citrate homogeneous complex

Slow heating in bath at 80 °C for 5h

Final heating directly on hot plate at 120 °C for 3h

Annealing at 750 °C for 4h

ZrO_2, powders

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Precipitation techniques

Precipitates may be purified by digestion (Ostwald ripening), washing, and, in some cases, re-precipitation prior to filtration.

Digestion (**Ostwald ripening**) is growth of the larger precipitate particles at the expense of the finer particles while the precipitate is in the solution; surface-adsorbed impurities decrease as the specific area decreases.

Washing will improve the purity if surface-adsorbed impurities are removed without precipitating other ions in solution films on particles.

Dissolving and **reprecipitation** in a fresh solution may reduce the concentration of minor impurities.

Particle sizes **as small as 2 nm** have been produced for some systems, and these have been used as commercial catalysts.

1.1 Special Ceramic Powders

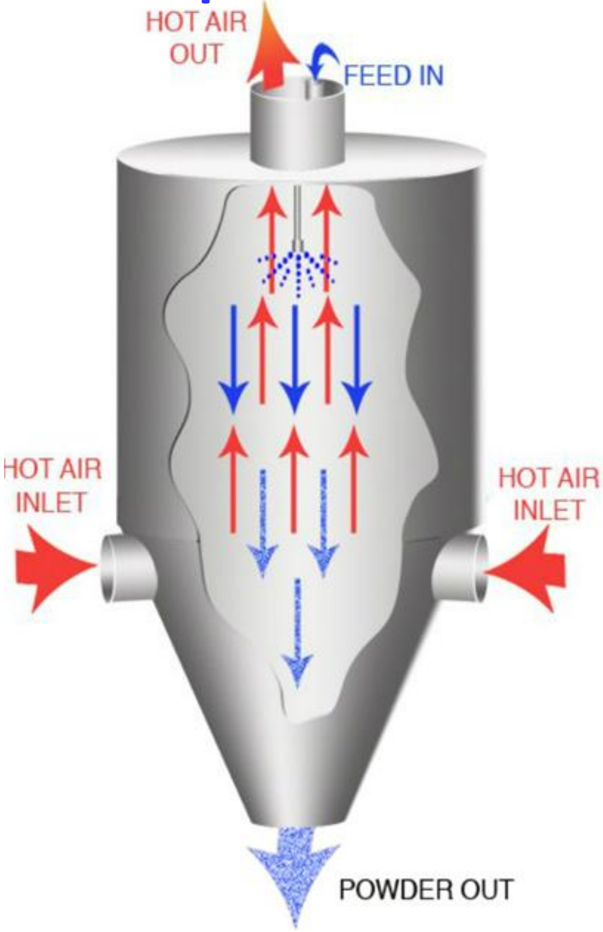
Powders from chemical solution techniques

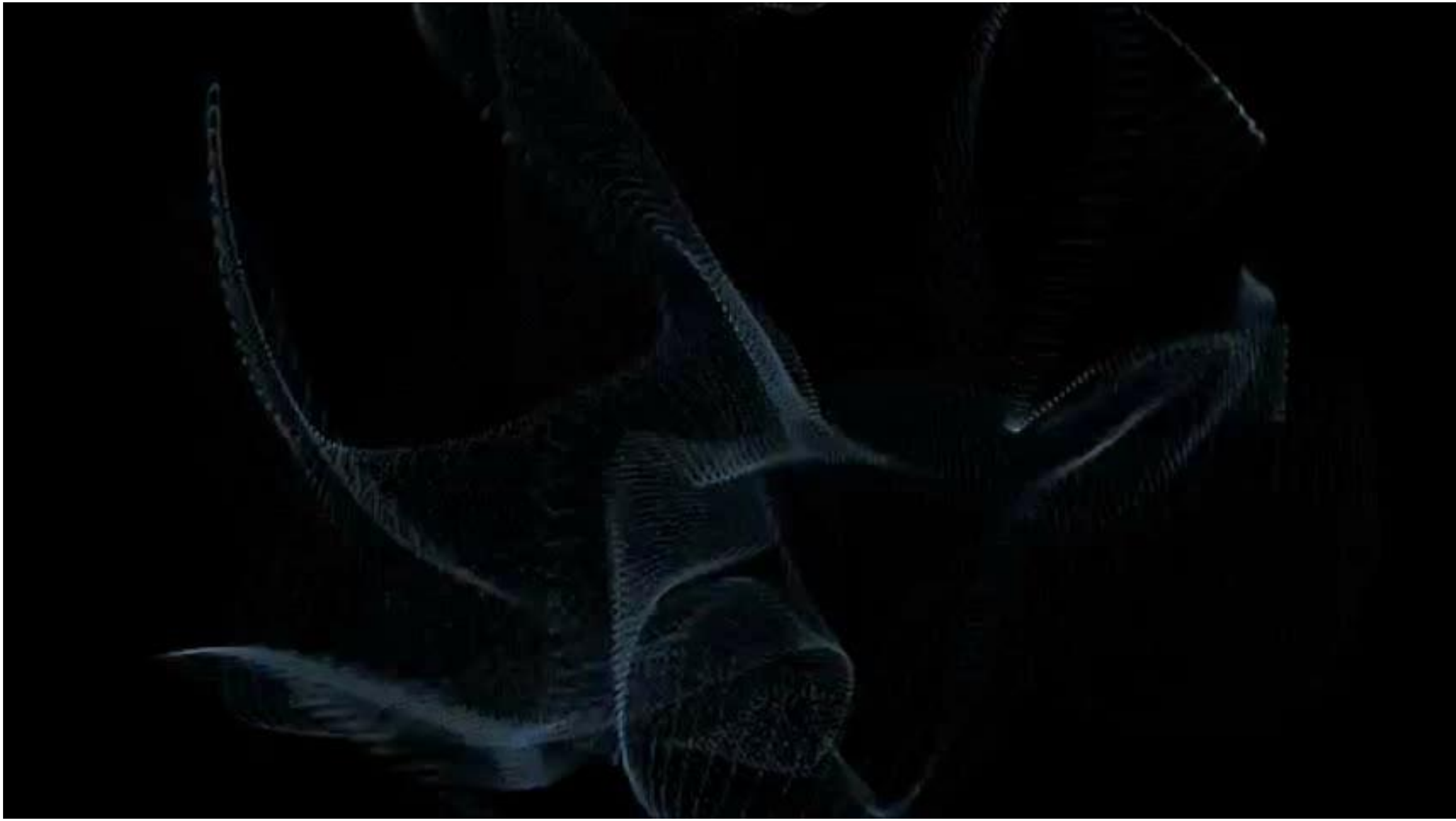
Solvent evaporation and extraction techniques techniques

An alternative way to prepare special powders is **to disperse the solution containing the ions** of interest into **microscopic volumes** and than **remove the solvent** as a **vapor,** forming a **salt**.

Maintenance of atomic-scale homogeneity will be possible for multicomponent systems only when the components are of about equal solubility or when the salts forms extremely rapidly.

Spray-drying has been used to porduce and dry salt particles **10-20 μm** in diameter (to be discussed in **Forming and Predensification).**



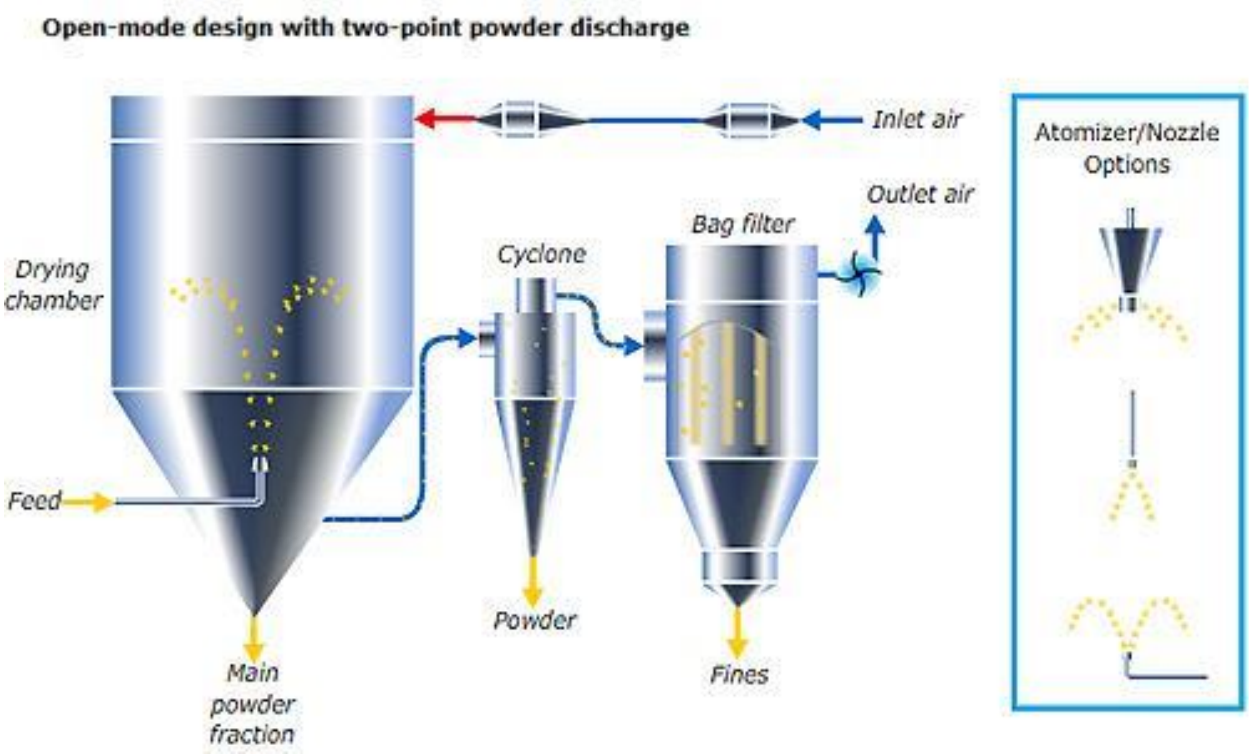


https://www.youtube.com/watch?v=0o4ZCjHnaRw&t=25s

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Solvent evaporation and extraction techniques techniques

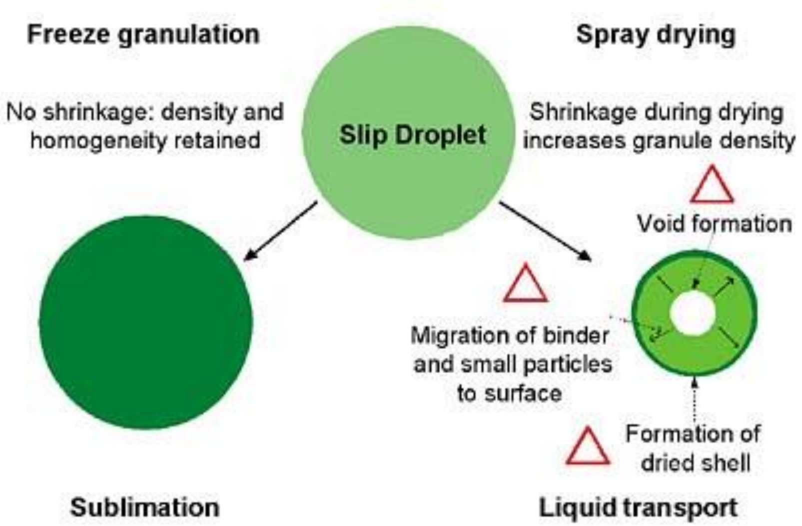


If a hot furnace is combined with the **spray-drying**, drying and calcination are operated in one single step; because the heating rate is several hundred degrees per second, complete decomposition occurs only if the salt decomposes at a relatively low temperature.

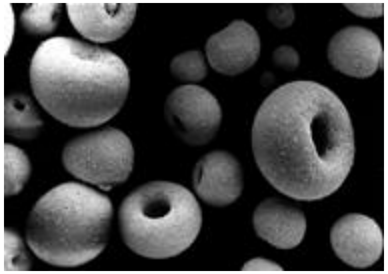
1.1 Special Ceramic Powders

Powders from chemical solution techniques

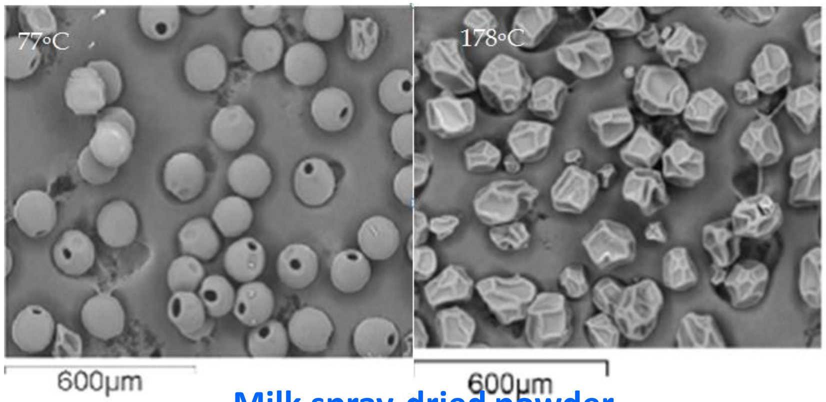
Solvent evaporation and extraction techniques techniques



http://coen.boisestate.edu/rickubic/teaching-research/mse-421/



http://cdn.intechopen.com/pdfs-wm/30919.pdf



Milk spray-dried powder

If a hot furnace is combined with the **spray-drying**, drying and calcination are operated in one single step; because the heating rate is several hundred degrees per second, complete decomposition occurs only if the salt decomposes at a relatively low temperature.

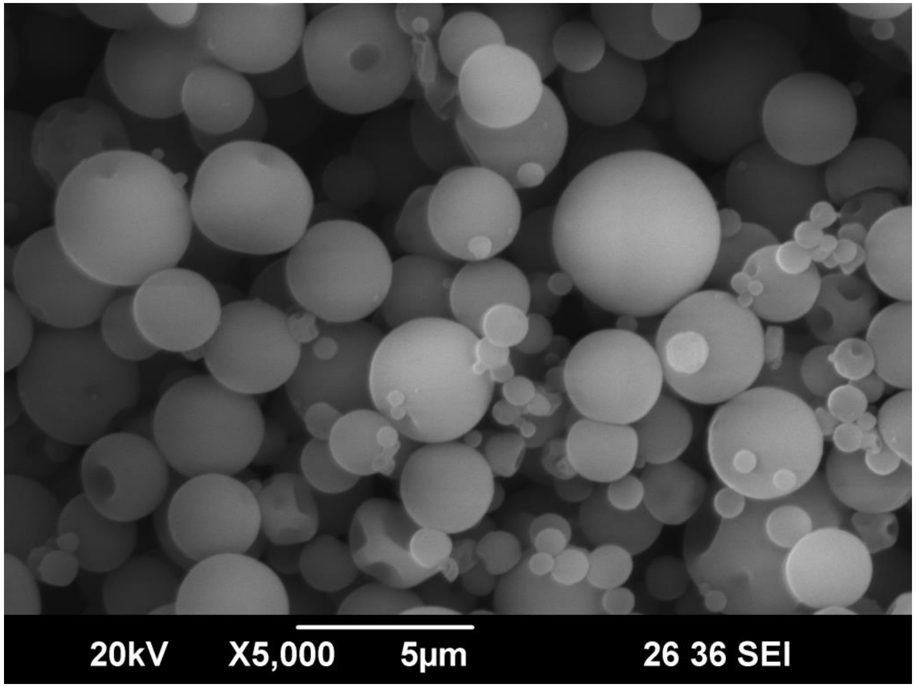
1.1 Special Ceramic Powders

Powders from chemical solution techniques

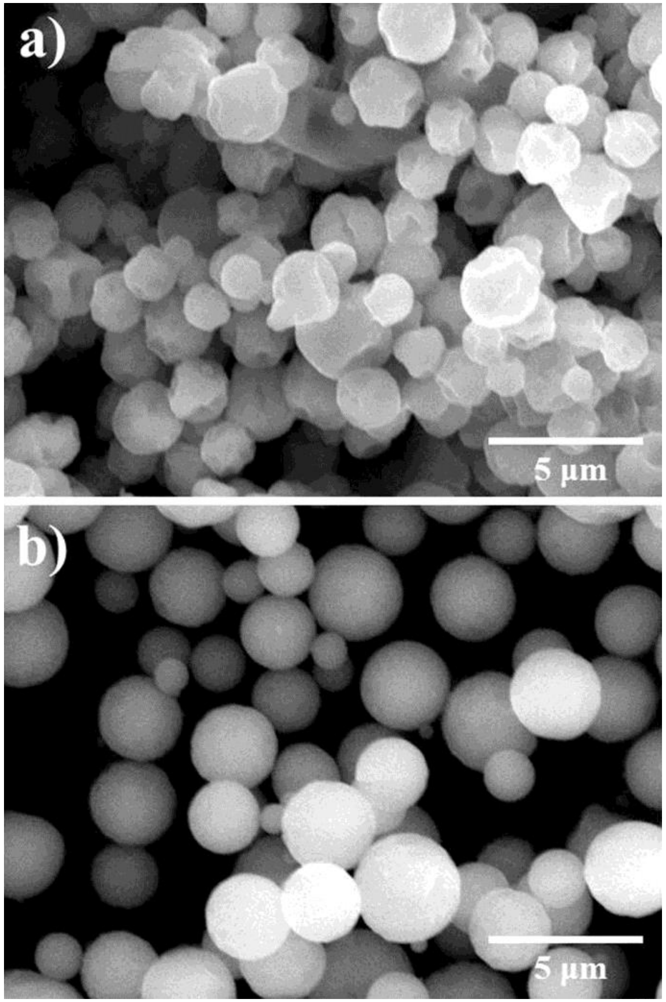
http://www.nature.com/articles/srep05857?message-global=remove

Solvent evaporation and extraction techniques techniques

http://chobotix.cz/research-2/encapsulation-technologies/spray-drying/

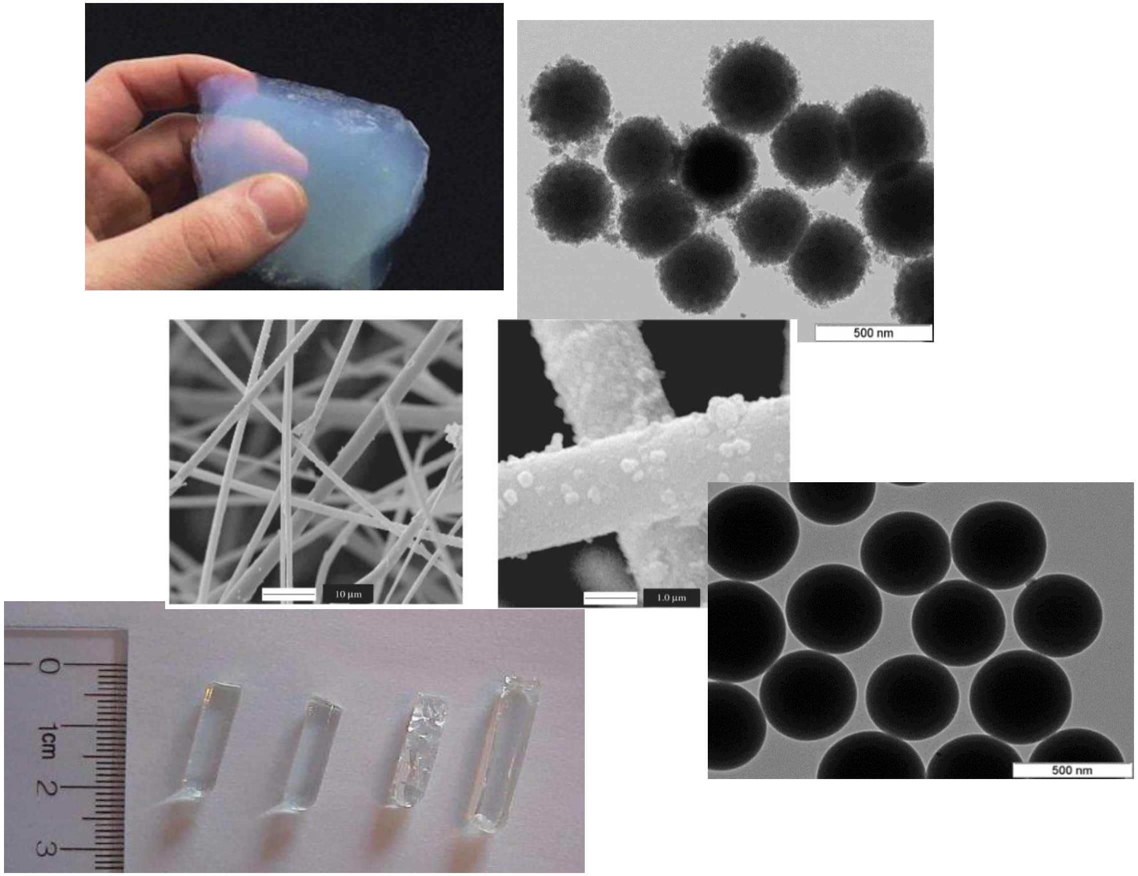


Chitosan spray-dried powders



$ZnFe_2O_4$ spray-dried powders

Sol-Gel Methodology



1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques

The SG chemistry consists of chemical reactions involving **i**) colloidal particles in a sol, or **ii**) between alkoxide-derived polymeric species and water in a solution, leading to a highly porous amorphous gel network, where a liquid phase (solvent, catalyst and eventually excess water and precursors) may be retained. During drying and sintering, the open network typically undergoes at least 50% linear shrinkage caused by removal of the liquid phase and drastic reduction of the porosity, ultimately forming a **dense sol-gel material** (inorganic glass or **ceramics**). Depending on several interrelated experimental parameters, a wide range of microstructured sol-gel products may be obtained.

These include ***i)*** inorganic or hybrid coatings on a substrate, for which the sol-gel process is a highly convenient technique which starts at ambient temperature and pressure, ***ii)*** hollow, dense, porous or structured nanoparticles, ***iii)*** high-purity powders from which dense ceramics can be obtained via sintering and ***iv)*** very low-density aerogels obtained by supercritical drying of wet gels and rather difficult to prepare by other techniques; ***v)*** fibers can also be fabricated, although sol-gel is not the best available technology in this case.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques

Conversion of a **solution** or a **sol** into a dense material requires the following steps:

SOLUTION or SOL
↓
GELATION
↓
COLLOIDAL GEL NETWORK
↓
FORMING
↓
DRYING
↓
HEAT TREATMENT
↓
FINAL PRODUCT
(**inorganic** or **hybrid**, **glass** or **ceramic**)

2.Sol-Gel methodology

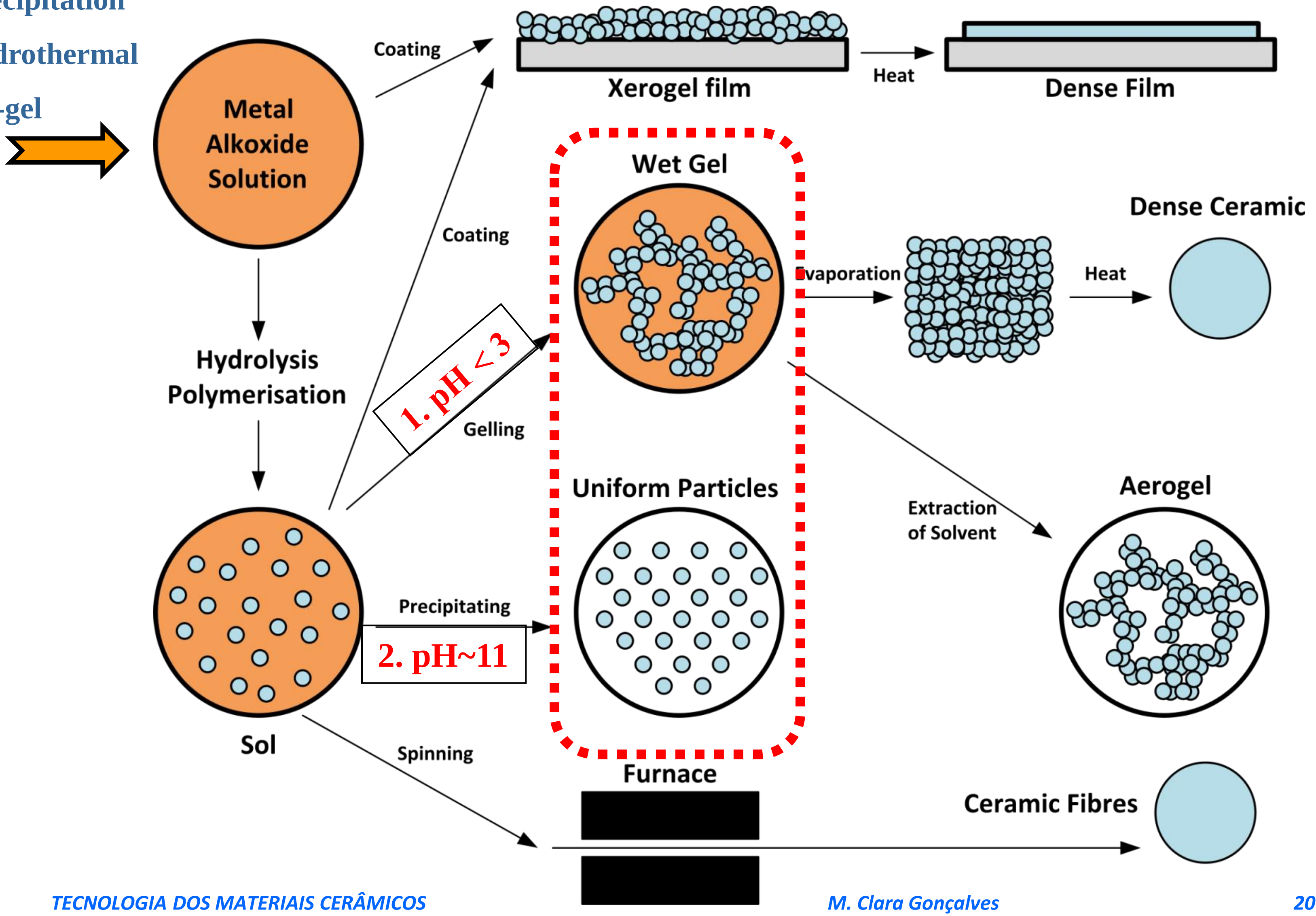
Top-down

- lithography
- wet ball milling

Bottom-up

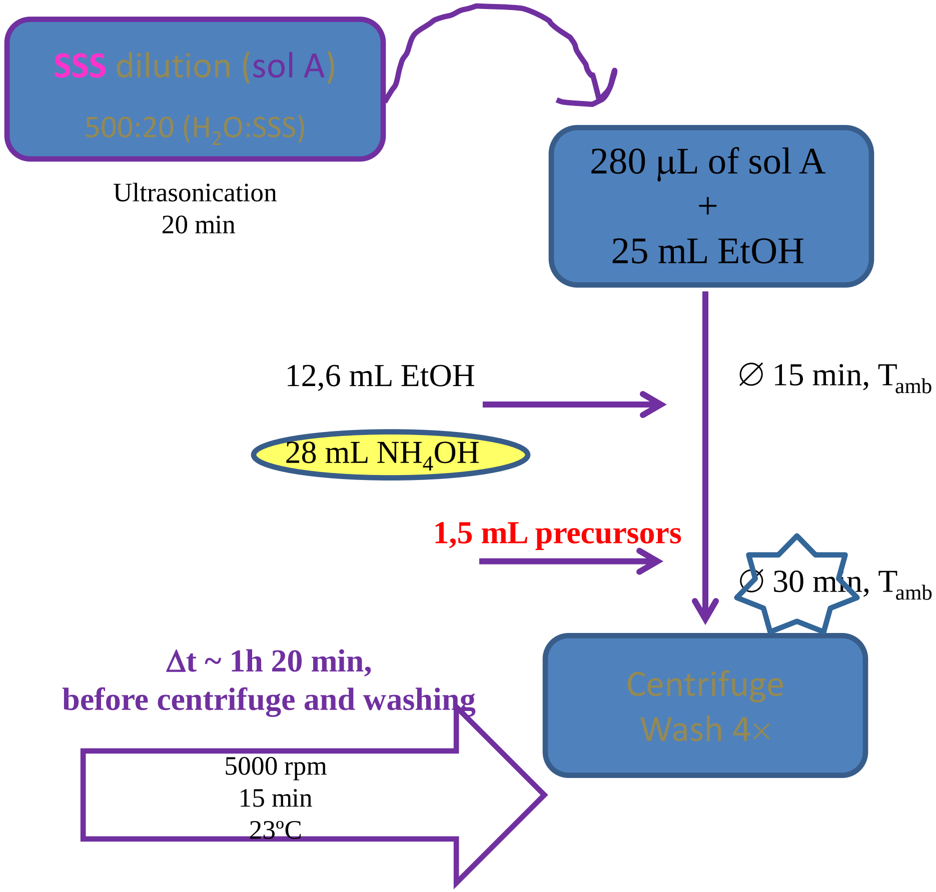
- precipitation
- hydrothermal
- sol-gel

Why sol-gel?



2.Sol-Gel methodology

Stober Method



SSS dilution (sol A)

500:20 (H_2O:SSS)

Ultrasonication
20 min

280 µL of sol A
+
25 mL EtOH

12,6 mL EtOH

∅ 15 min, T_{amb}

28 mL NH_4OH

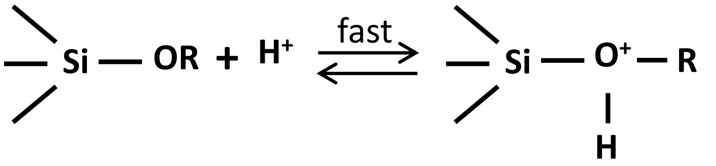
1,5 mL precursors

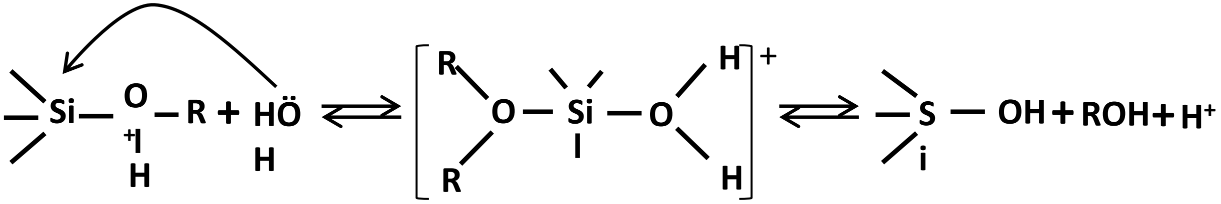
∅ 30 min, T_{amb}

Δt ~ 1h 20 min,
before centrifuge and washing

5000 rpm
15 min
23ºC

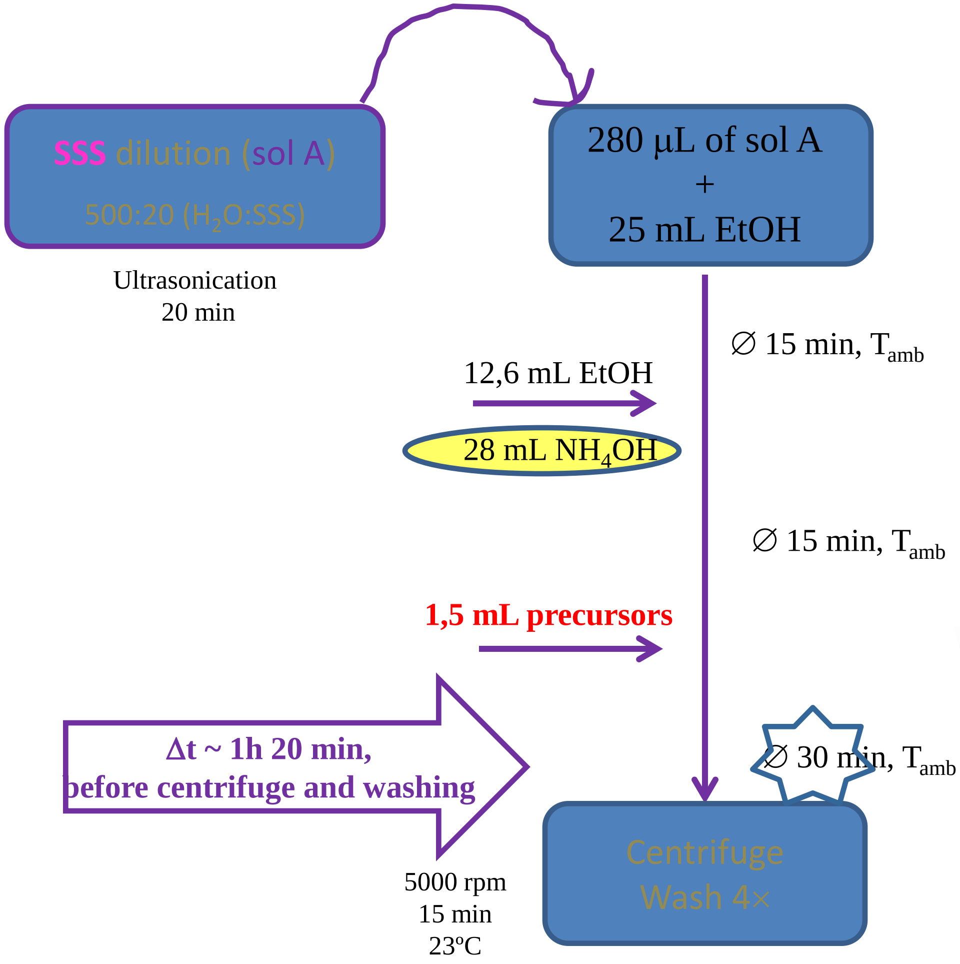
Centrifuge
Wash 4×





2.Sol-Gel methodology

Route 2, pH ~11



SSS dilution (sol A)

500:20 (H_2O:SSS)

Ultrasonication
20 min

280 µL of sol A
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∅ 15 min, T_{amb}

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1,5 mL precursors

∅ 30 min, T_{amb}

Δt ~ 1h 20 min,
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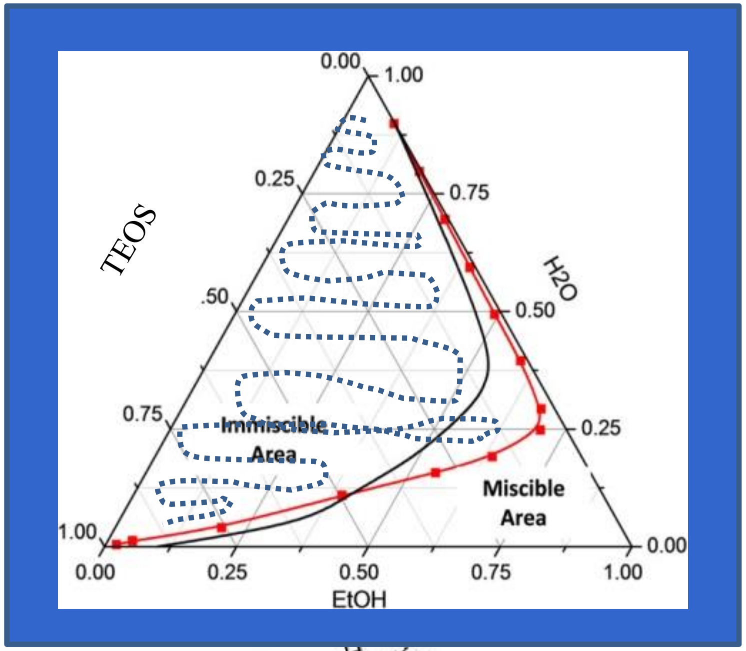
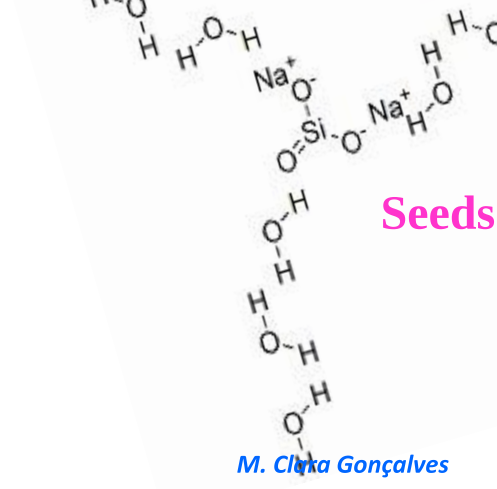
5000 rpm
15 min
23°C

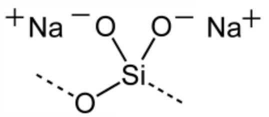
Centrifuge
Wash 4×

Stober Method



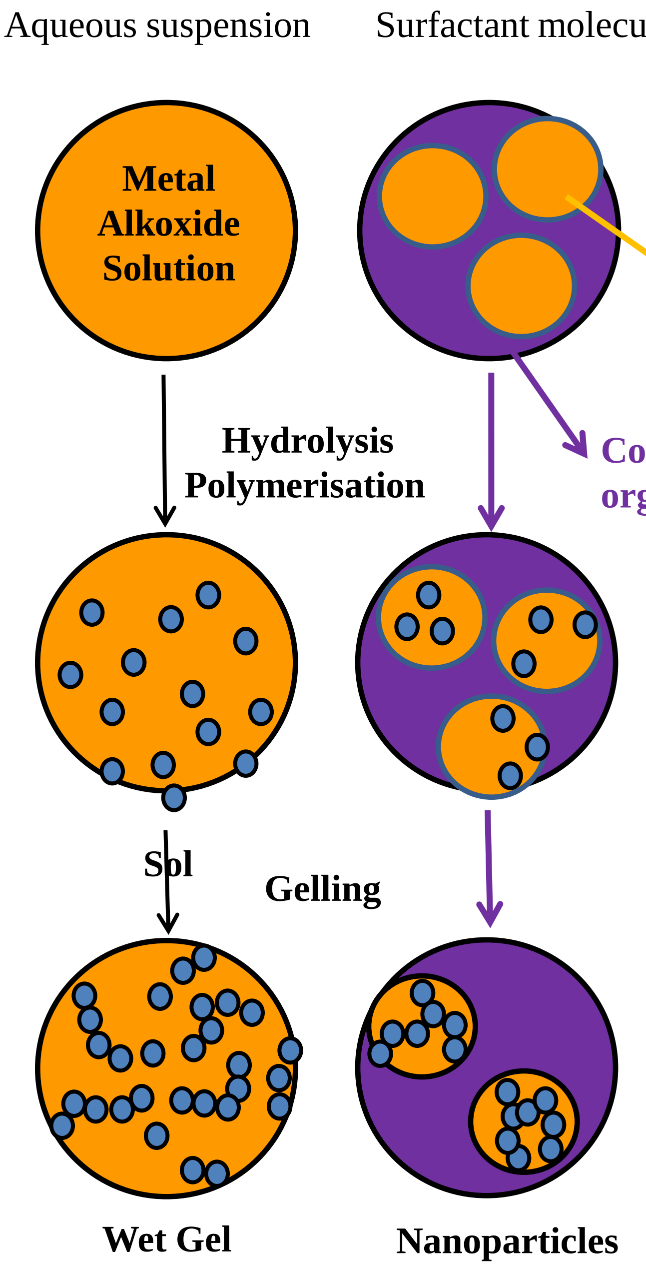


Seeds: water glass SSS

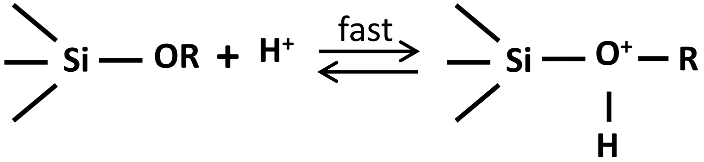


Route 1, pH 2-3

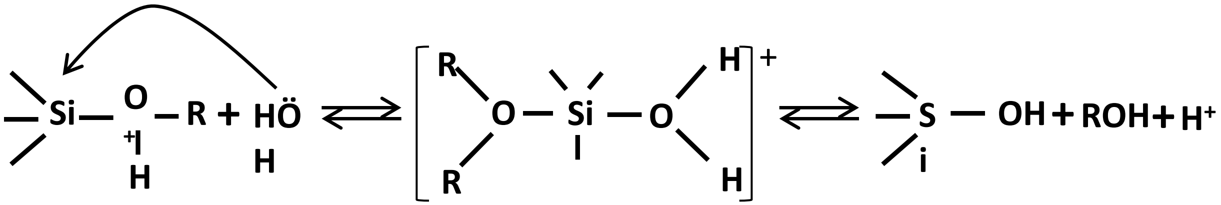
2.Sol-Gel methodology



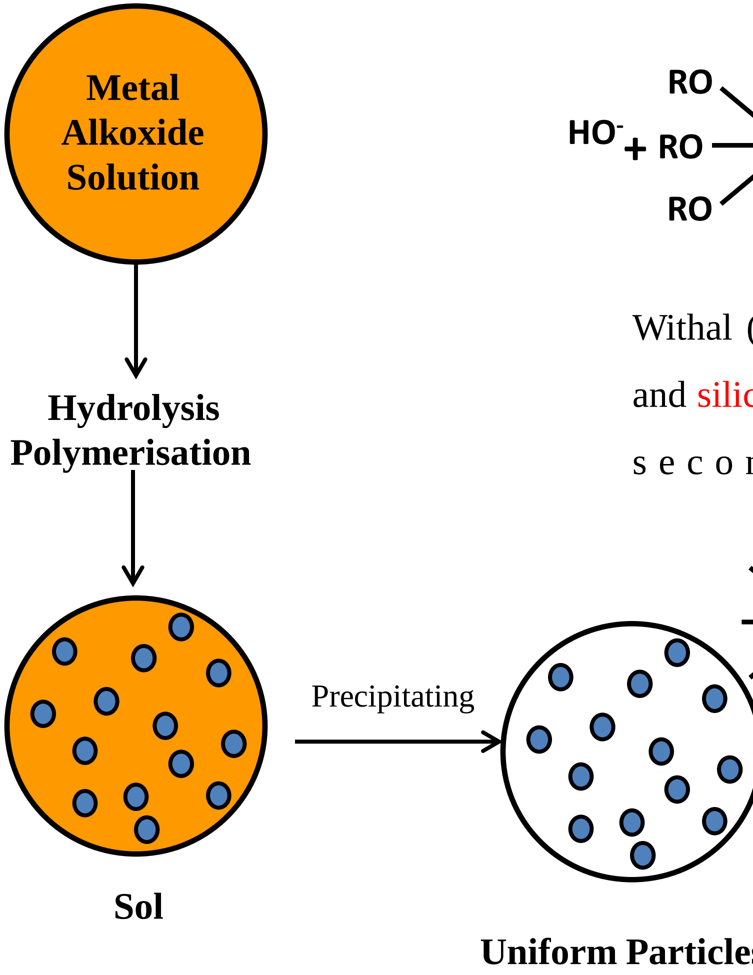
Under acid catalysis the hydrolysis is performed by electrophilic attack. At **pH** values as low as **2-3**, complete hydrolysis developed, producing linear or highly branched polymeric species, with **a 3D fractal structure**.



At low pH values (2-3), condensation starts only after hydrolysis completion, originating a **fractal 3D amorphous SiO_2 network** with **nanopore diameters** (< 2 nm).



Route 2, pH ~11



Metal Alkoxide Solution

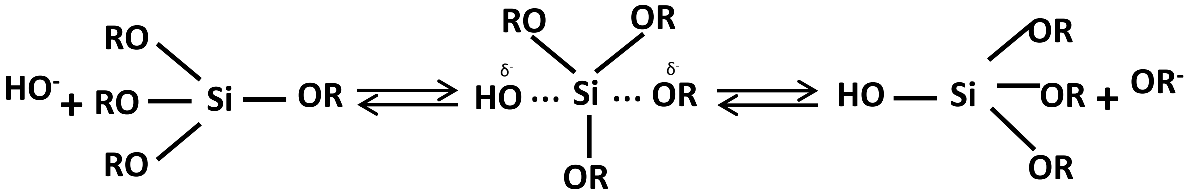
Hydrolysis Polymerisation

Sol

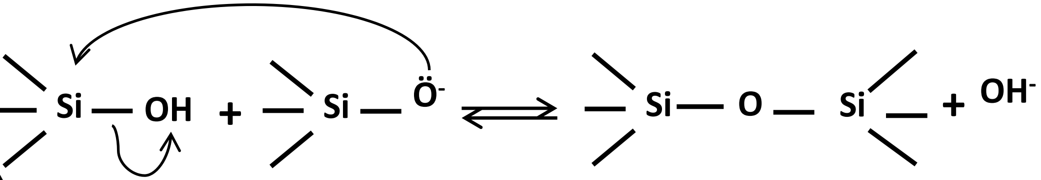
Precipitating

Uniform Particles

At **pH over 7**, **water dissociates immediately**, while a hydrolysis reaction progresses slowly, by nucleophilic attack, according to: :

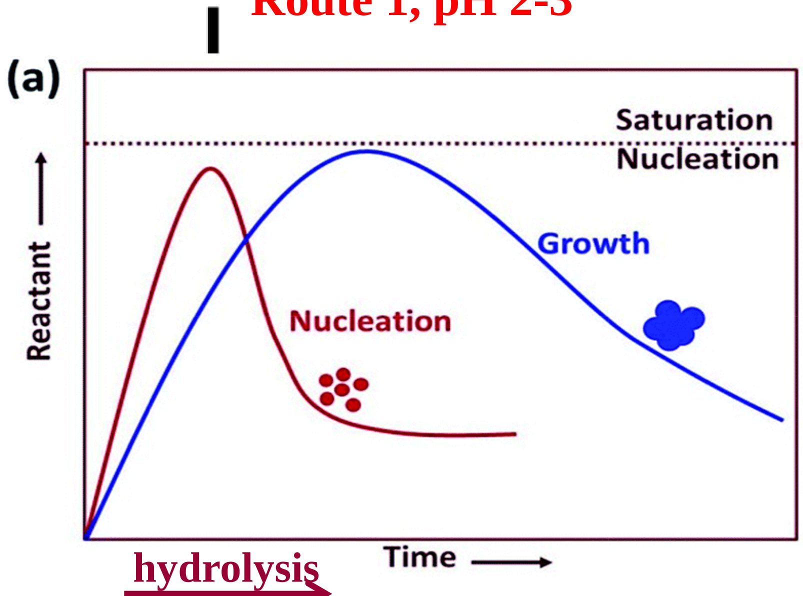


Withal (pH~7) **condensation** (and **dissolution**) reactions become relevant, and silicate monomers start **condensing** before being fully hydrolyzed, by a second nucleophilic attack, according to :



2.Sol-Gel methodology

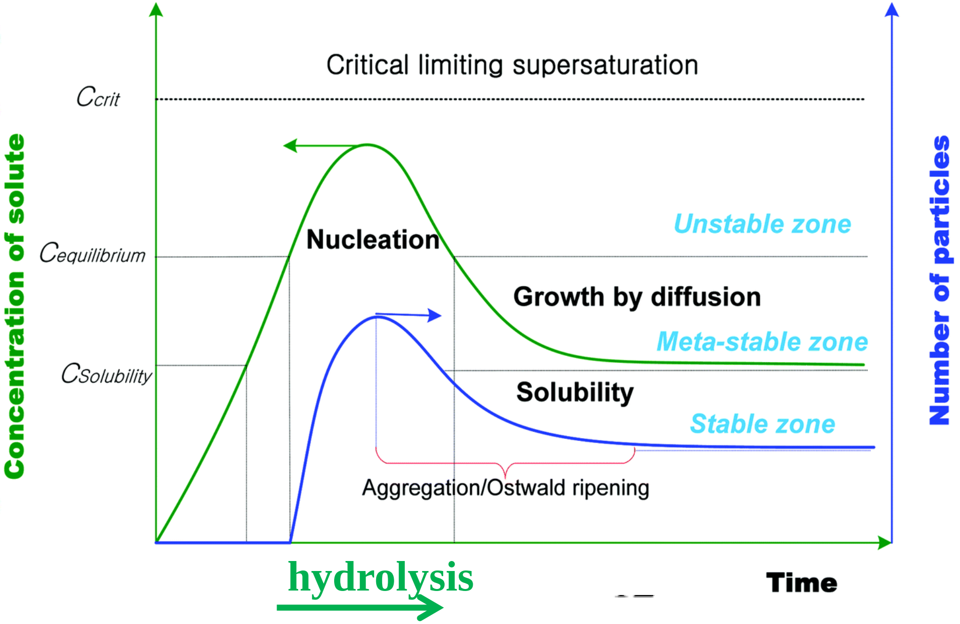
Route 1, pH 2-3



hydrolysis

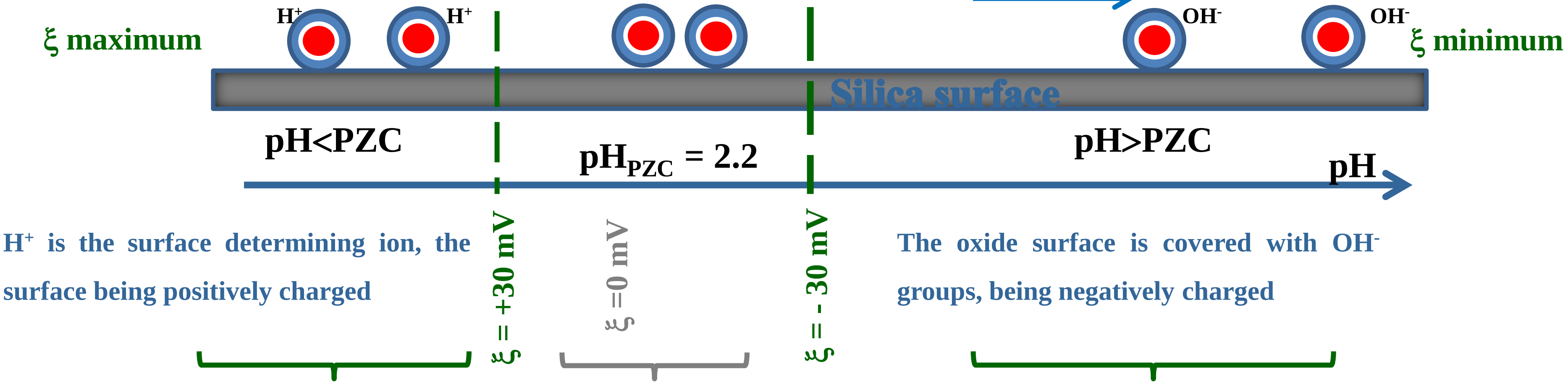
condensation

Route 2. pH ~11



hydrolysis

condensation



H^+ is the surface determining ion, the surface being positively charged

The oxide surface is covered with OH^- groups, being negatively charged

kinetically stable

ξ ≥ + 30 mV

not stable

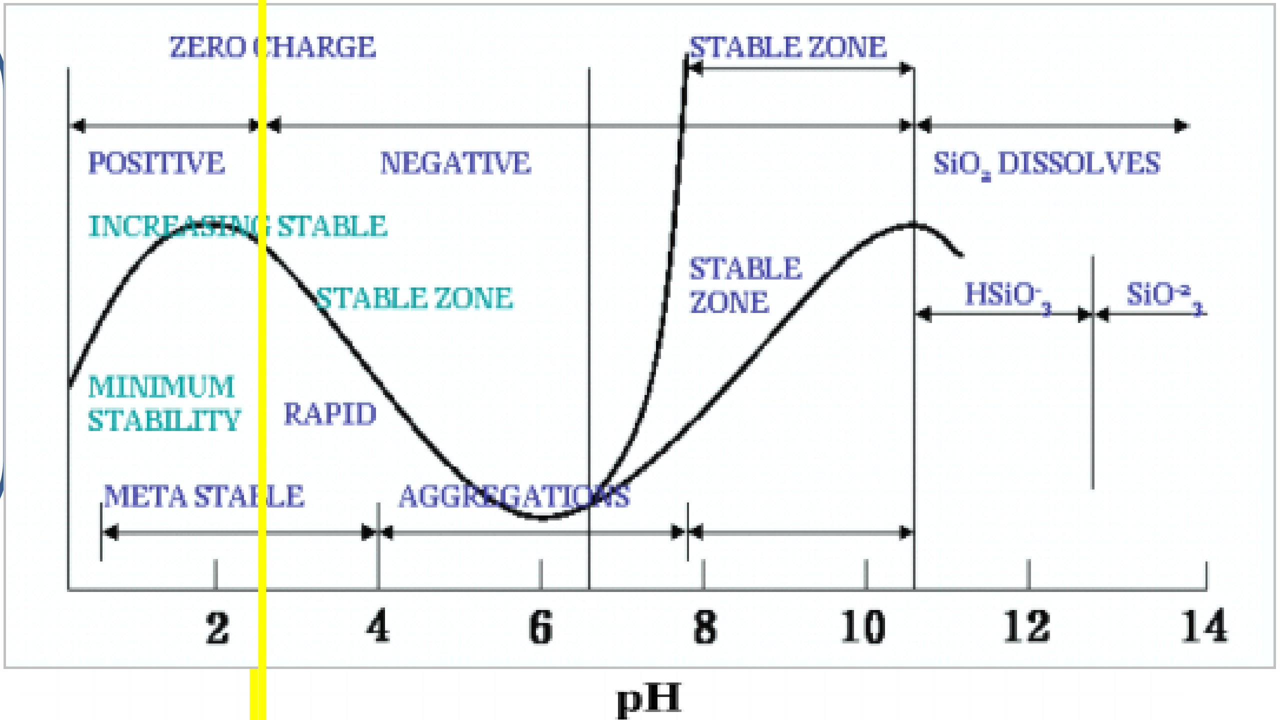
kinetically stable

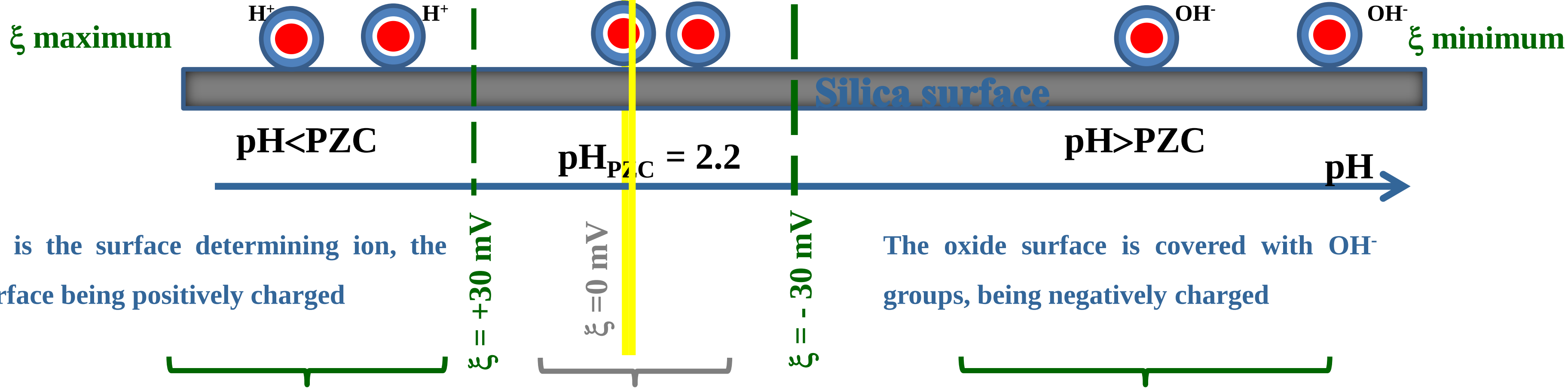
ξ ≤ -30 mV

2.Sol-Gel methodology

The surface hydrophilic Si-OH groups' will act as binding sites (H^+ bonds) for water.

The protonation and deprotonation of the Si-OH groups (which are pH dependent) will determine the surface charge of SiO_2 NPs





ξ maximum

ξ minimum

pH<PZC

pH_{PZC} = 2.2

pH>PZC

H^+ is the surface determining ion, the surface being positively charged

ξ = +30 mV

ξ =0 mV

ξ = - 30 mV

The oxide surface is covered with OH^- groups, being negatively charged

kinetically stable

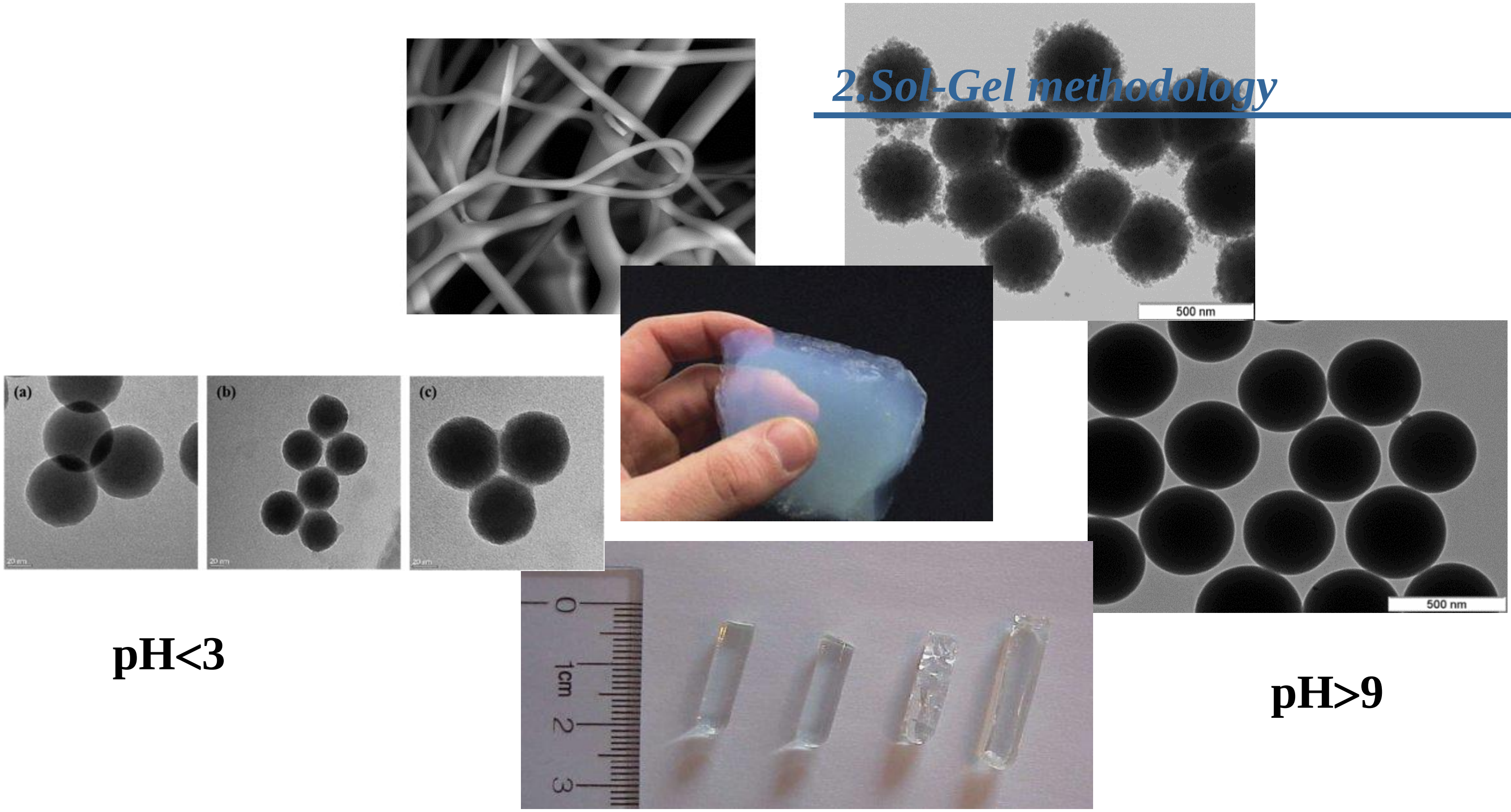
ξ ≥ + 30 mV

not stable

kinetically stable

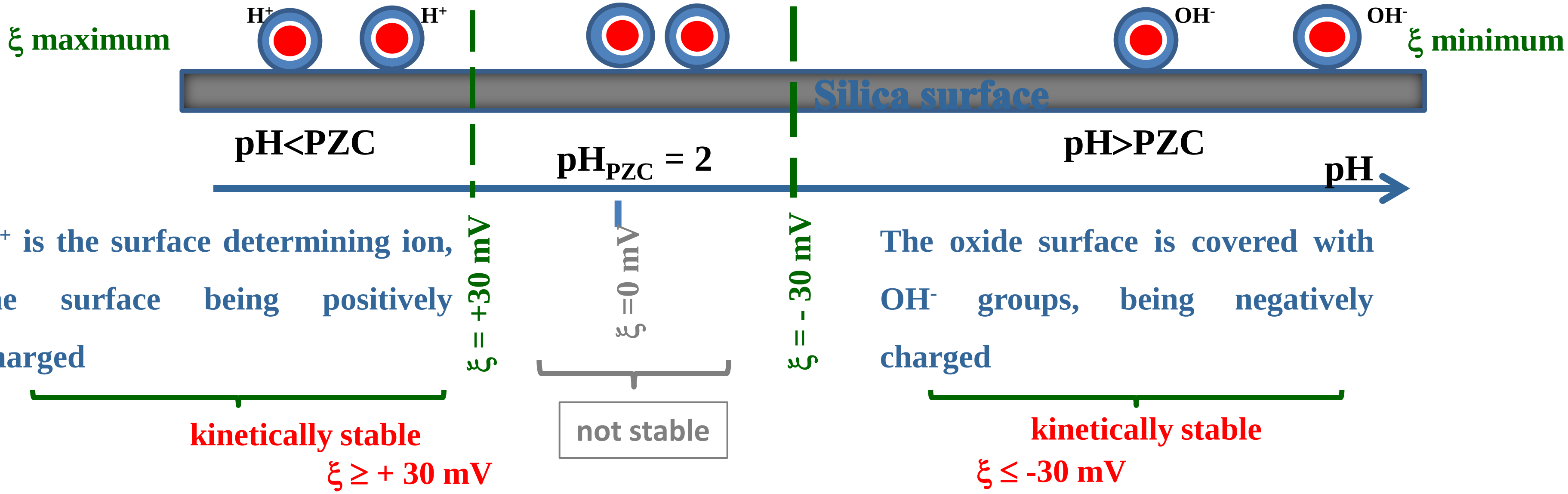
ξ ≤ -30 mV

2.Sol-Gel methodology



pH<3

pH>9



ξ maximum

H^+

H^+

OH^-

OH^-

ξ minimum

Silica surface

pH<PZC

$pH_{PZC} = 2$

pH>PZC

pH

$\xi = +30$ mV

$\xi = 0$ mV

$\xi = -30$ mV

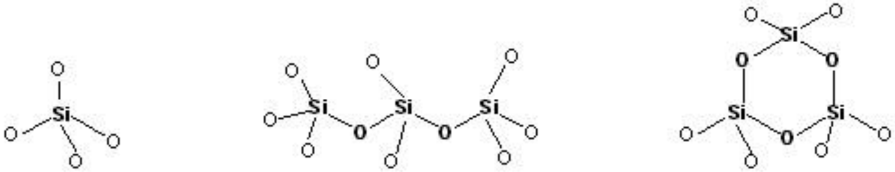
H^+ is the surface determining ion, the surface being positively charged

The oxide surface is covered with OH^- groups, being negatively charged

kinetically stable
$\xi \geq +30$ mV

not stable

kinetically stable
$\xi \leq -30$ mV



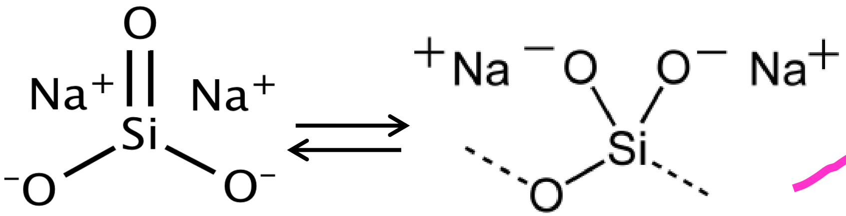
2.Sol-Gel methodology

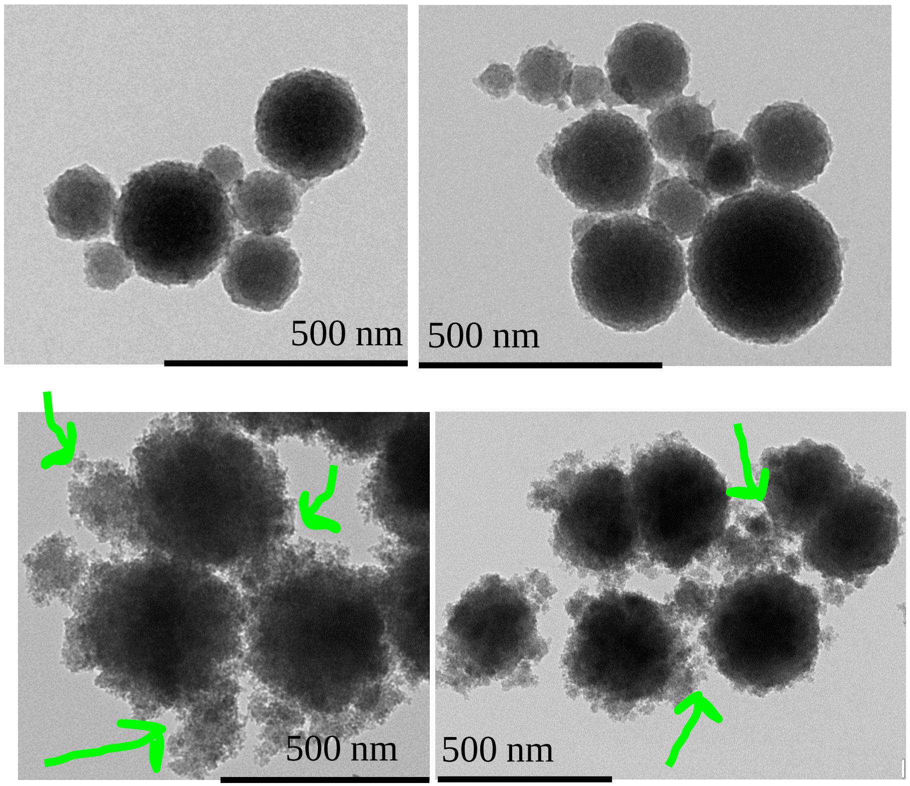
Route 2, pH ~11

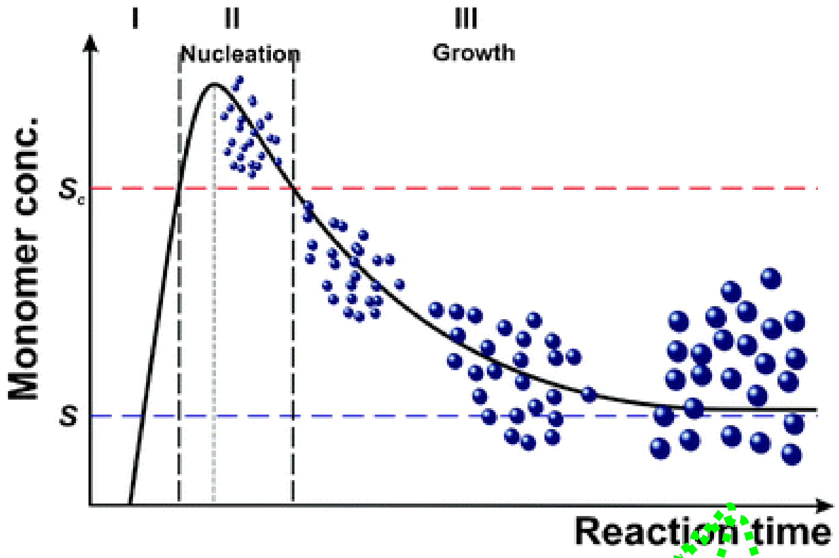
Stober Method

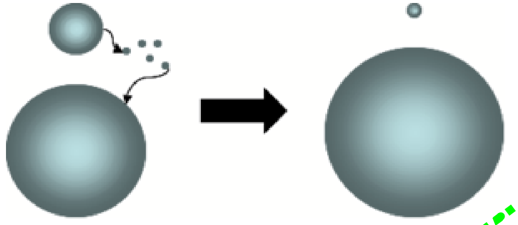
$SiO_2 : Na_2O$

Seeds: water glass SSS





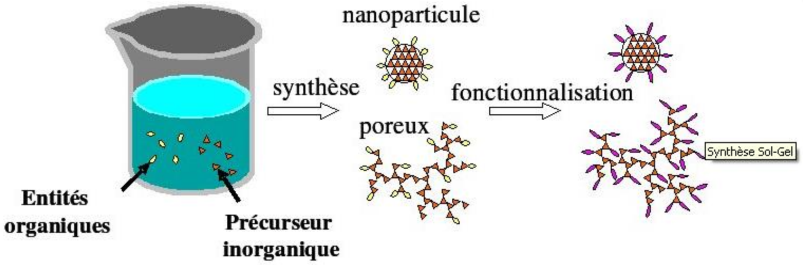


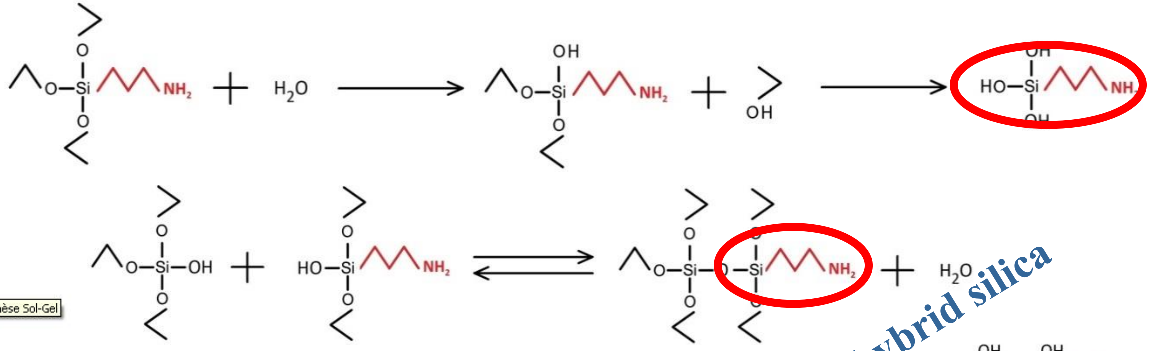


1. *in situ* functionalization

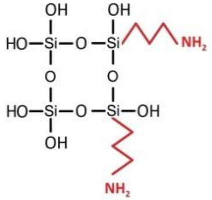
2.Sol-Gel methodology

i. *in situ* functionalization

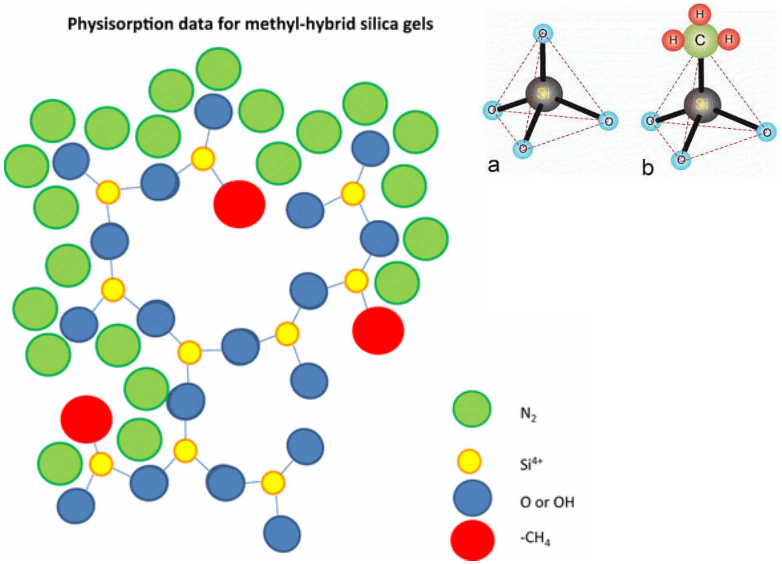


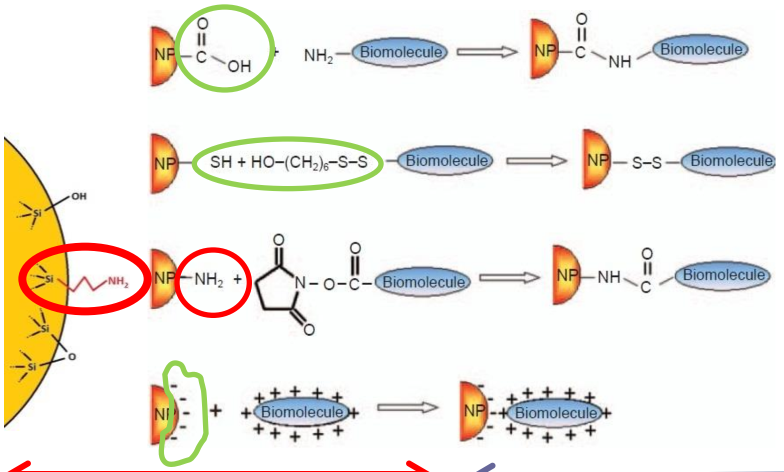


hybrid silica



ii. further bioconjugation/decoration/complexation


Physisorption data for methyl-hybrid silica gels

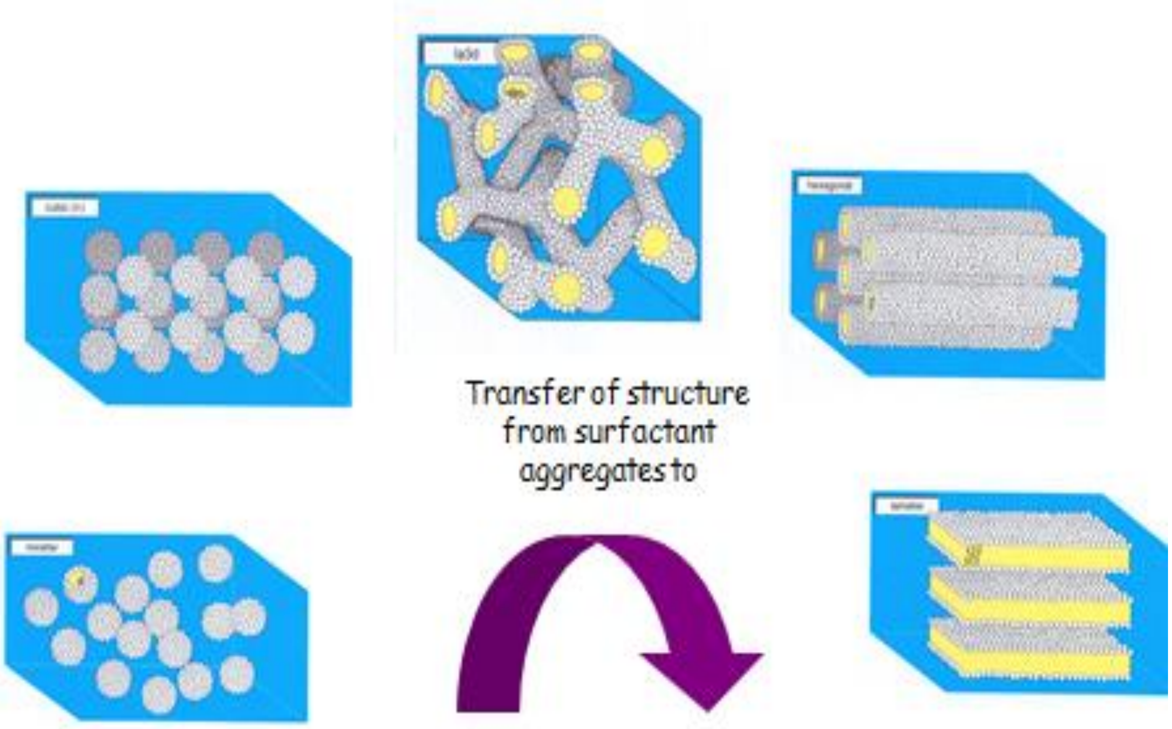


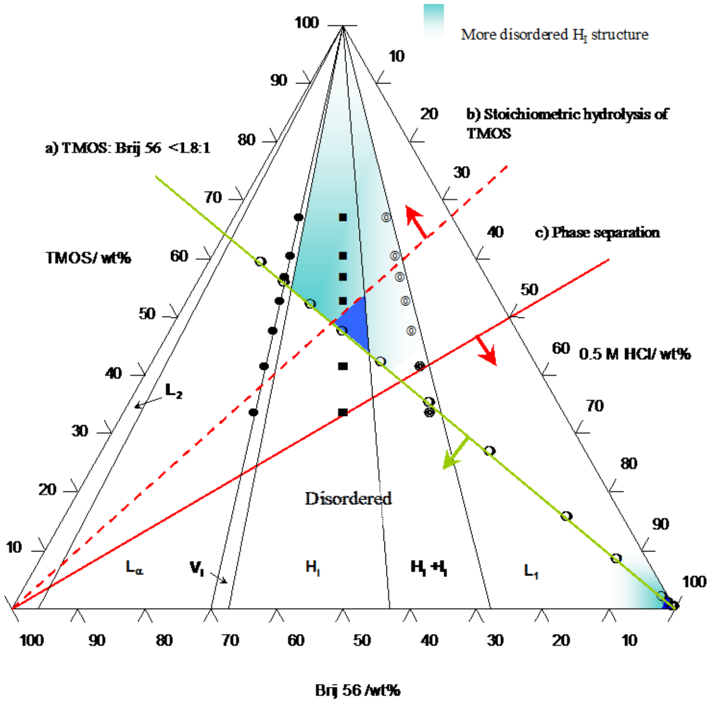
functionalization

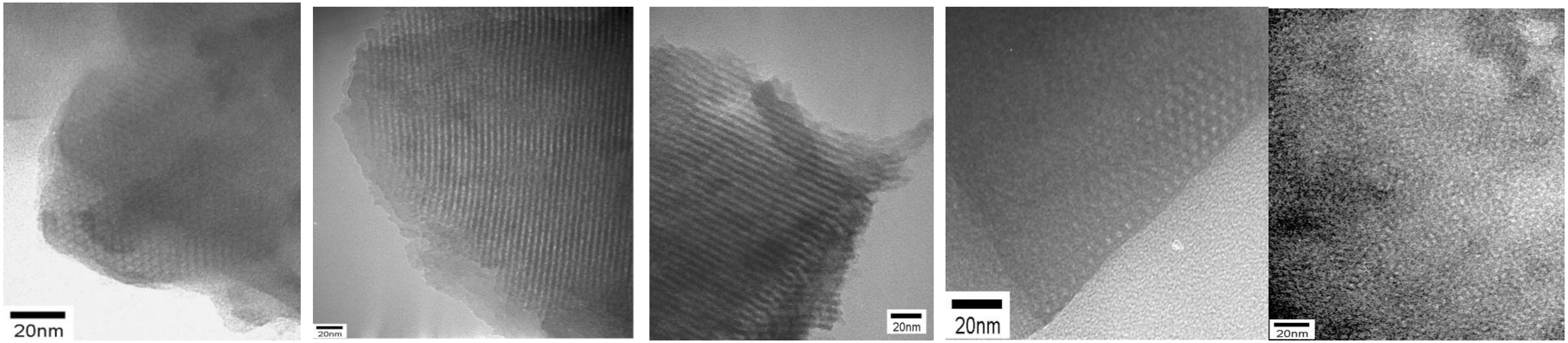
bioconjugation/decoration/complexation

2. *in situ* mesoporous templating

2.Sol-Gel methodology

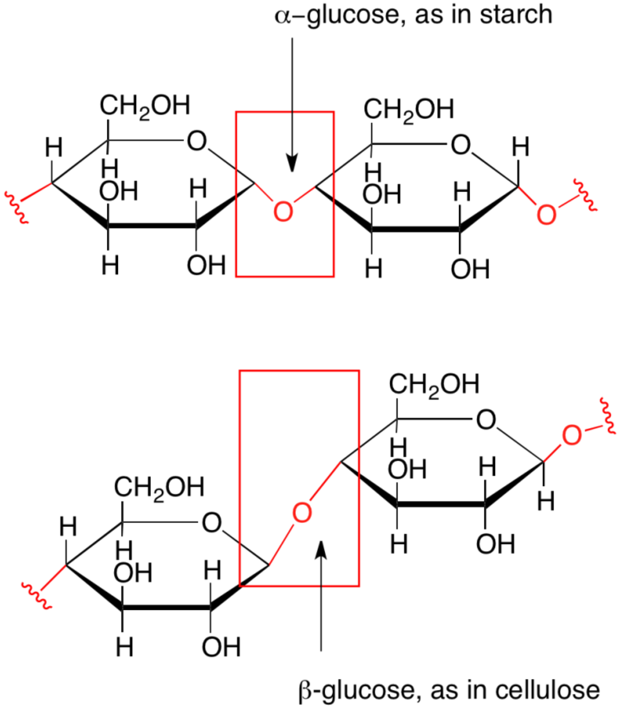

Transfer of structure from surfactant aggregates to $a\text{-}SiO_2$ inorganic films.

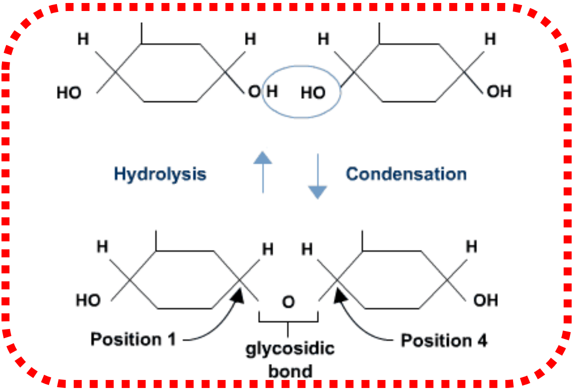


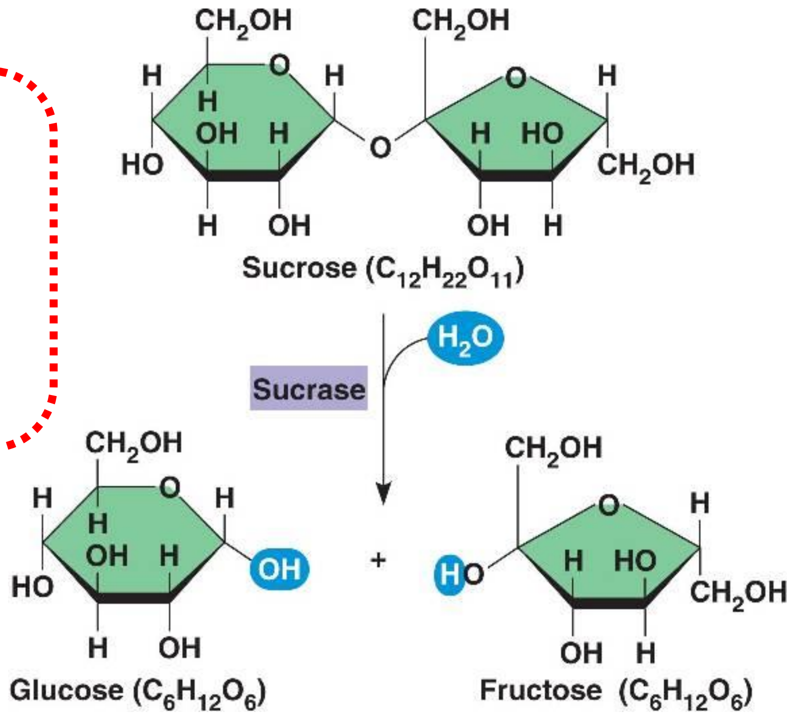


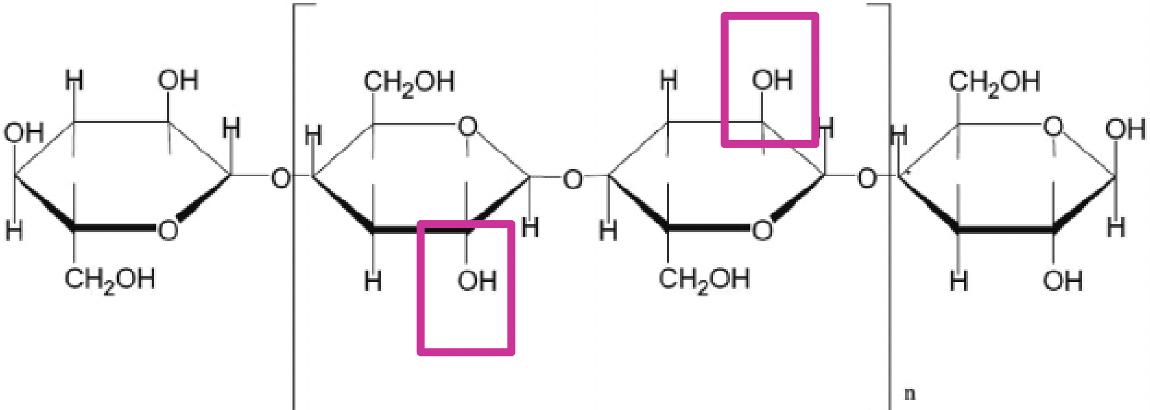
3. *in situ* mixed matrix

2.Sol-Gel methodology





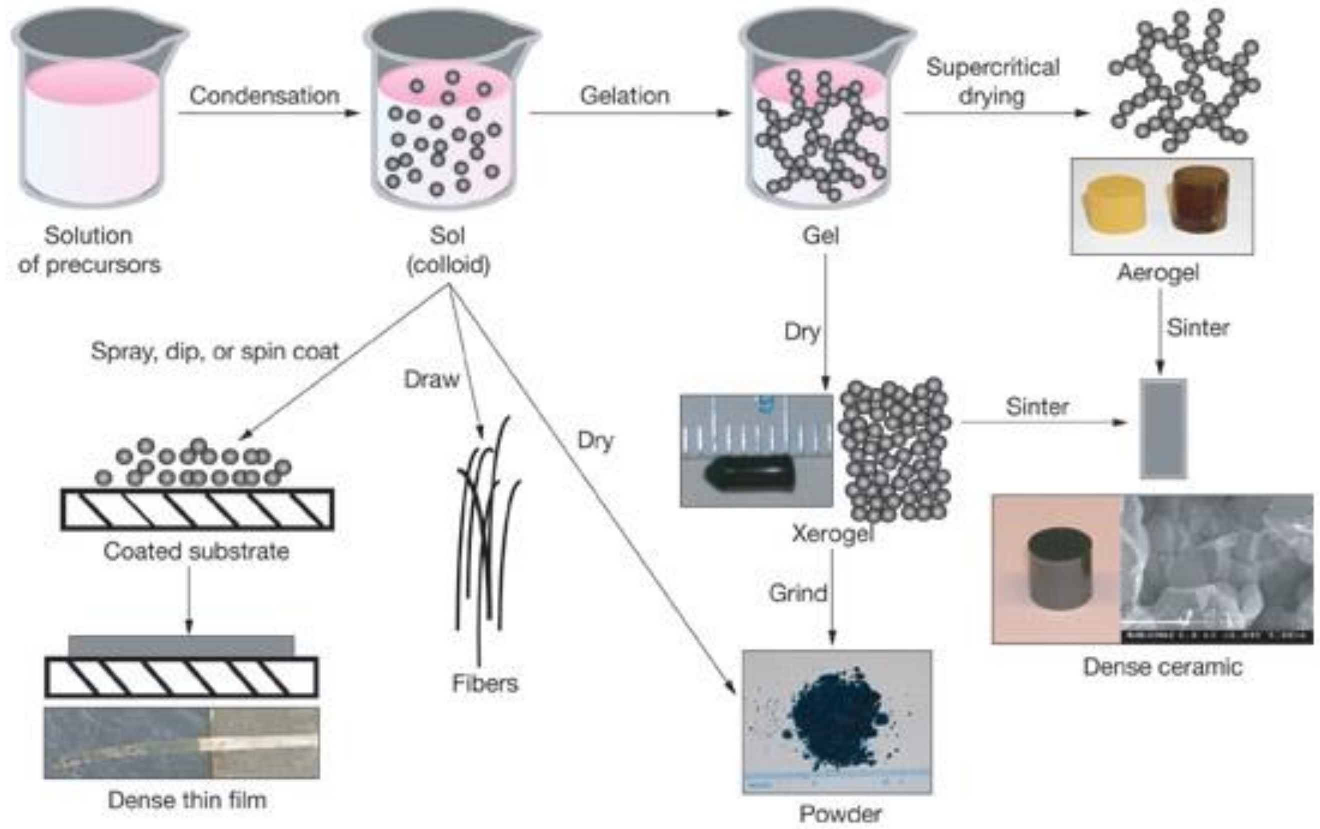




1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques

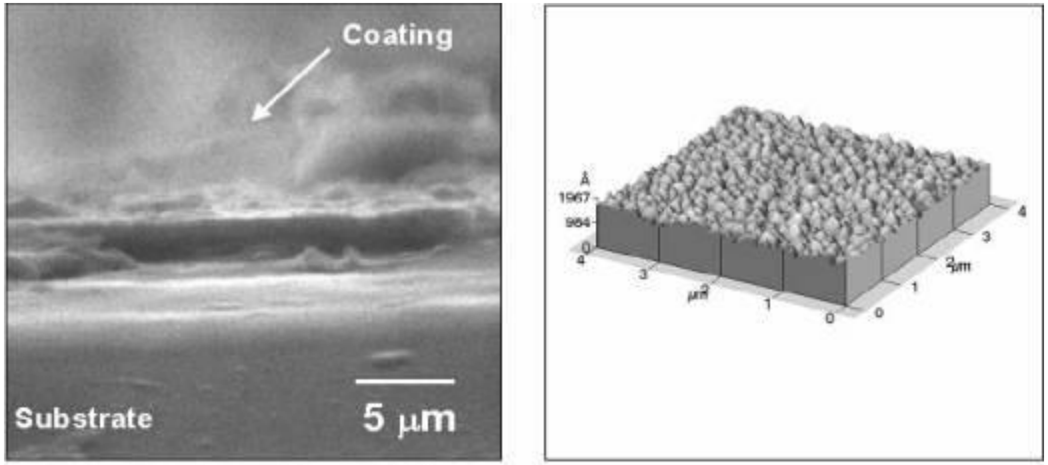


1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *i)* inorganic or hybrid coatings on a substrate

http://www.azom.com/article.aspx?ArticleID=2635



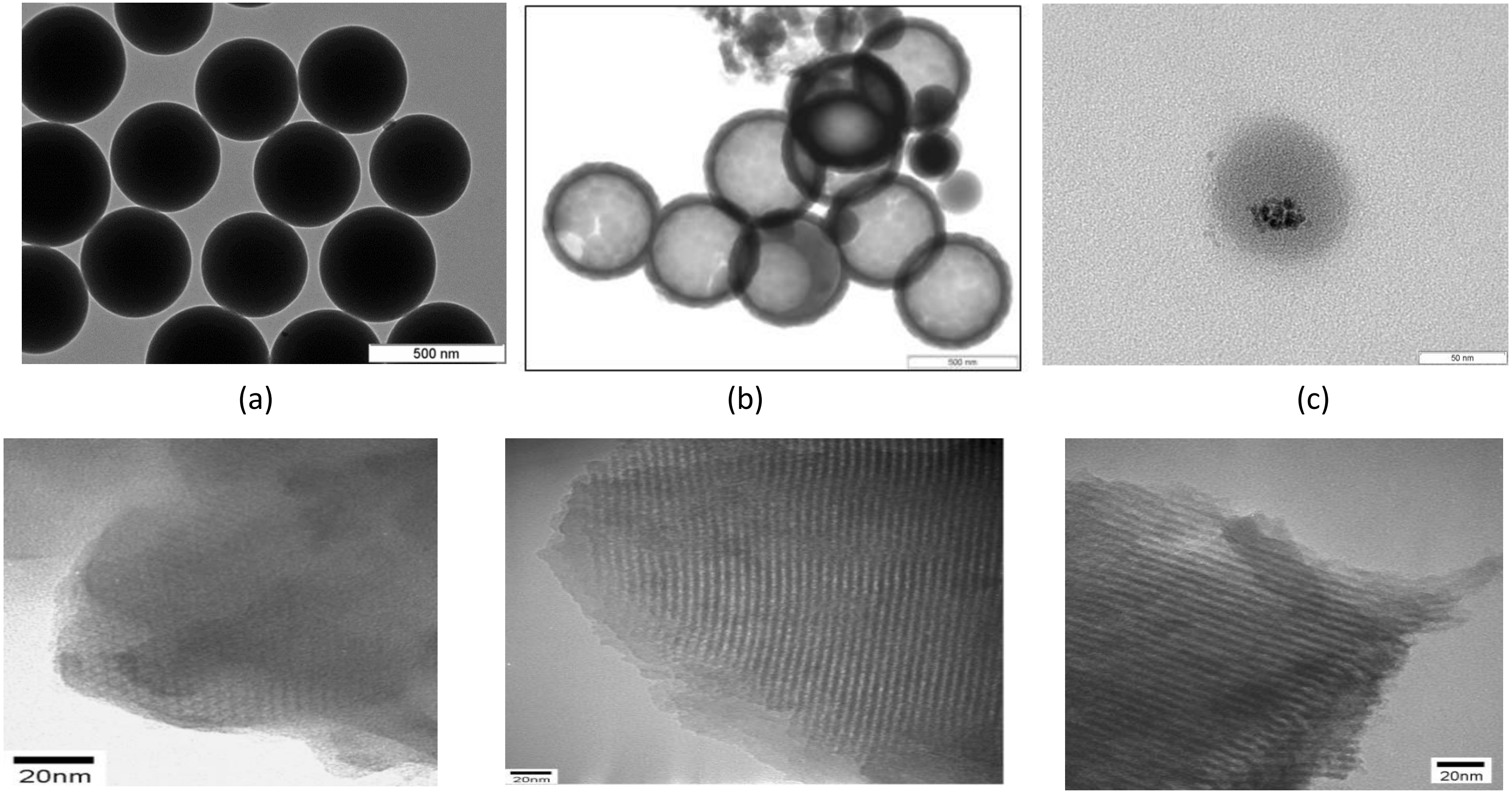
(a) (b)

(a) SEM and (b) AFM image of a sol-gel derived hydroxyapatite coating

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *ii)* hollow, dense, porous or structured nanoparticles



(a) (b) (c)

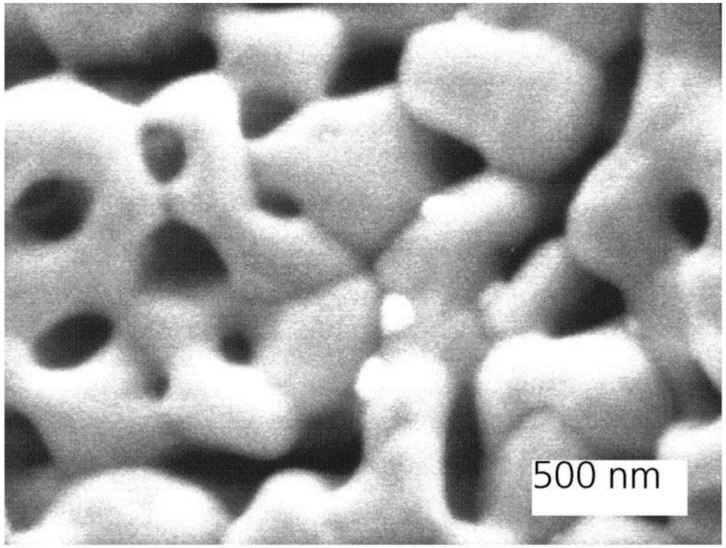
(d)

SiO_2 nanoparticles: dense (a), hollow, (b) core-shell nanostructured (c) and $Brij_{56}$ templated (d)

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *iii)* high-purity powders from which dense ceramics can be obtained via sintering



http://www.ikts.fraunhofer.de/en/research_fields/materials/porousceramics_filterceramics/proesekeramiken/Corundum_for_microfiltration.html

Sol-gel corundum (**α-Al_2O_3**) for microfiltration

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *iv)* very low-density aerogels

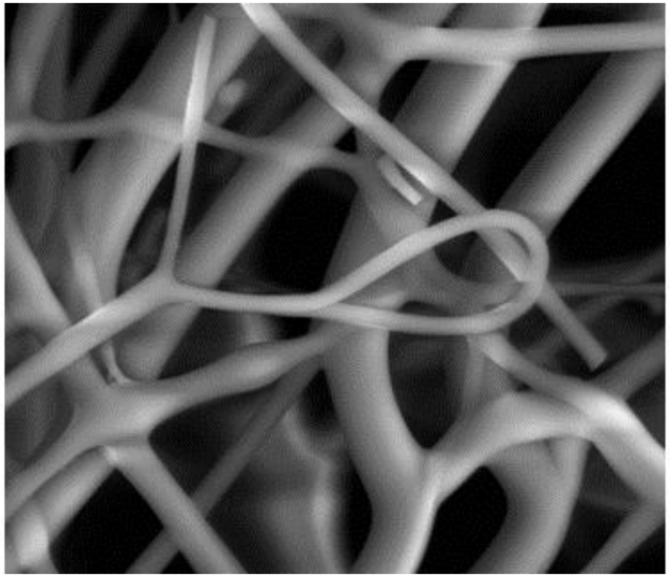
http://www.aerogel.org/?p=16

SiO_2 aerogel

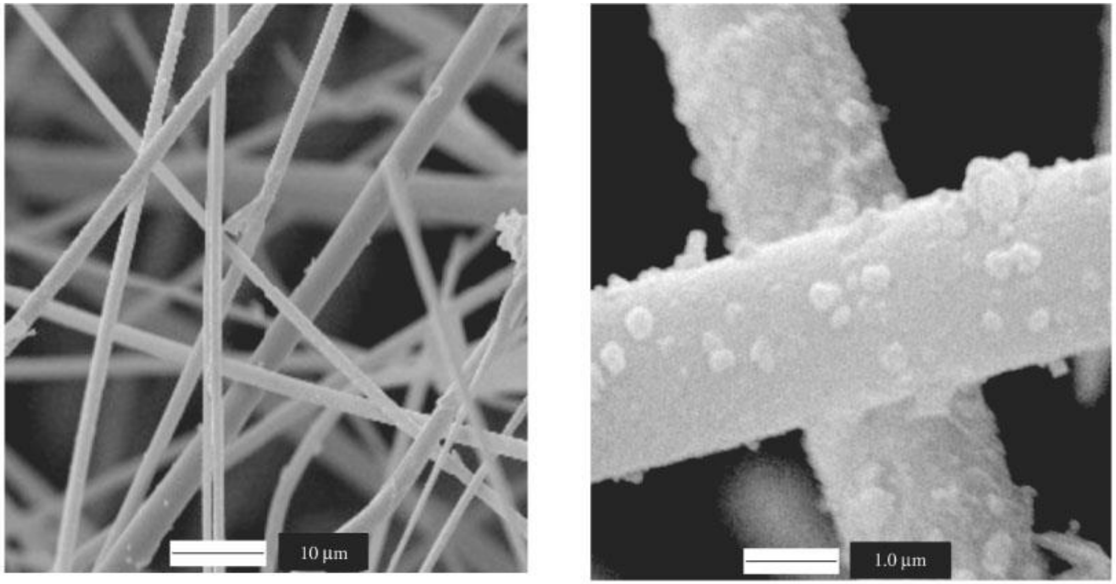
1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *v)* fibers



SEM image of **electrospun sol-gel fibers**



(a)

(b)

Commercial glass fiber FM® (Fiber Max) **coated** with **TEOS** by **sol-gel** to enhance their bioactivity.

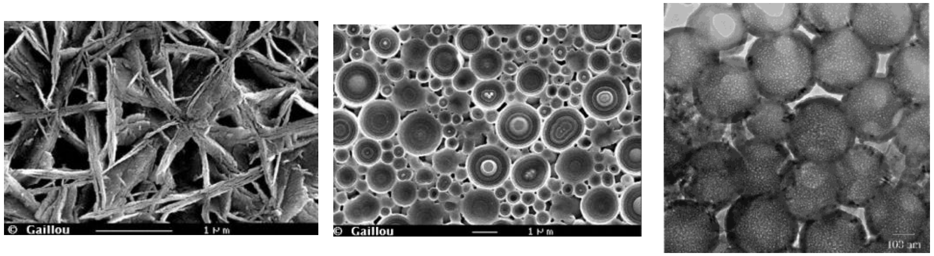
1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: colloidal route

In the ***colloidal route***, colloidal particles are formed in an aqueous medium from ionic species according to the principles of colloidal chemistry. In the case of silica, for example, the ~ 1 nm SiO_2 particles present in sols of dilute silicic acid undergo rapid growth to 2 - 4 nm at pH 2-3. As described below, the silica solubility increases so much above pH 7 that the particles grow up to 4-6 μm by coalescence and Ostwald ripening (digestion). Monomeric silicic acid then helps cementing the amorphous nanoparticles to form a bulk gel.

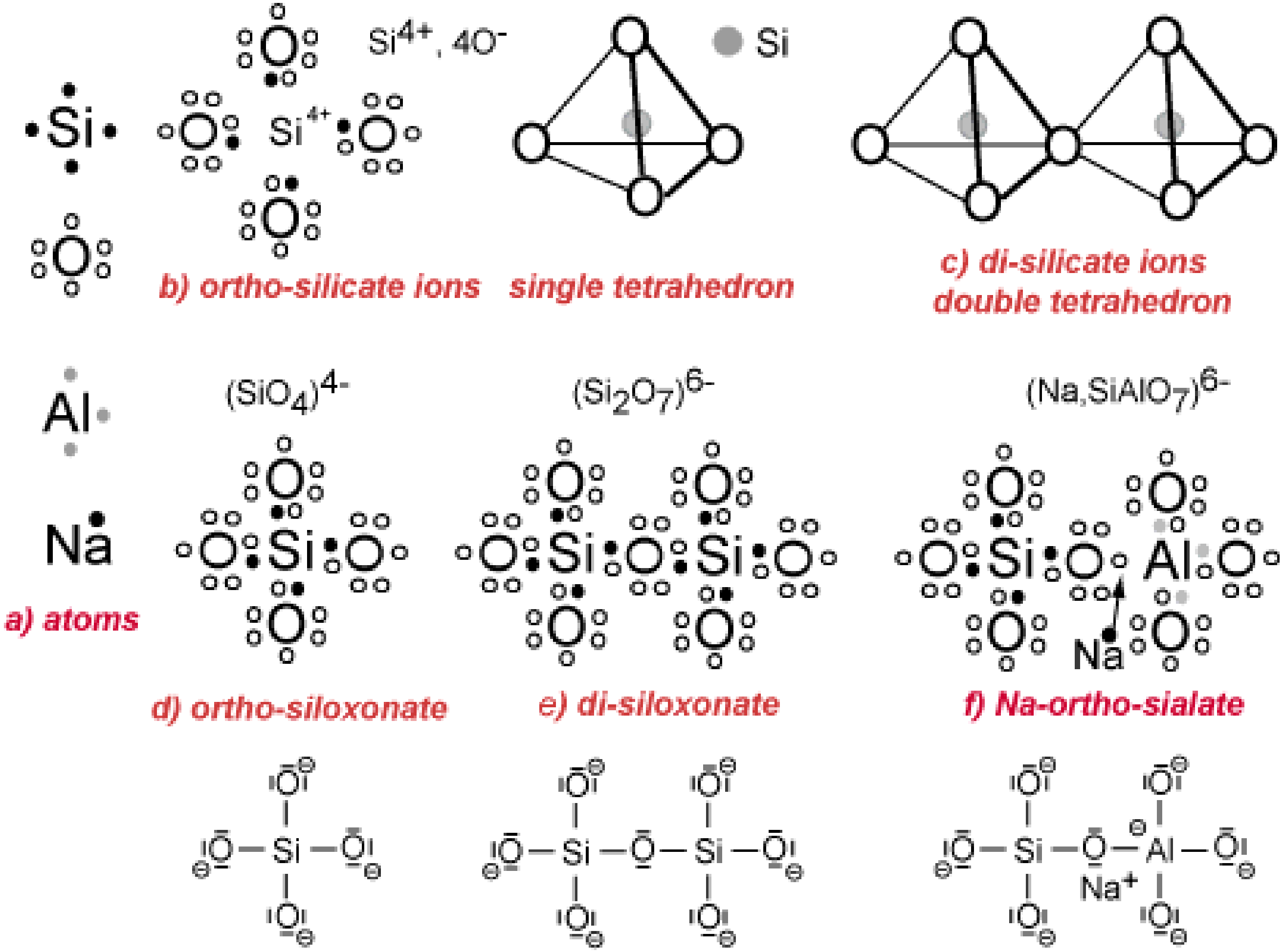
This is how nature produces opal mineral!



1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *silica-based ionic species in solution*



a) atoms

b) ortho-silicate ions

single tetrahedron

c) di-silicate ions
double tetrahedron

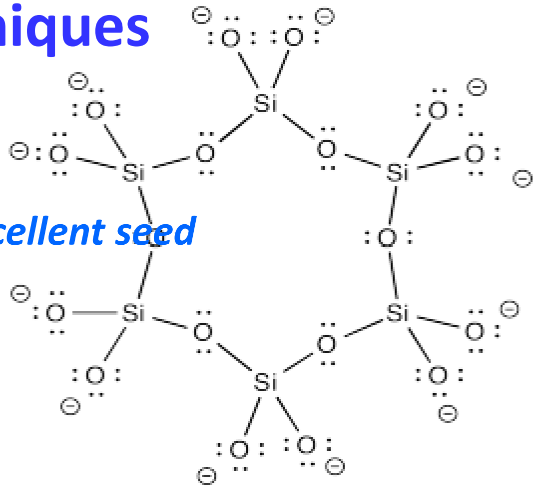
d) ortho-siloxonate

e) di-siloxonate

f) Na-ortho-sialate

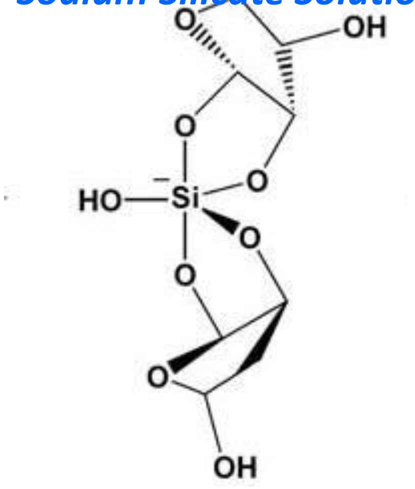
1.1 Special Ceramic Powders

Powders from chemical solution techniques

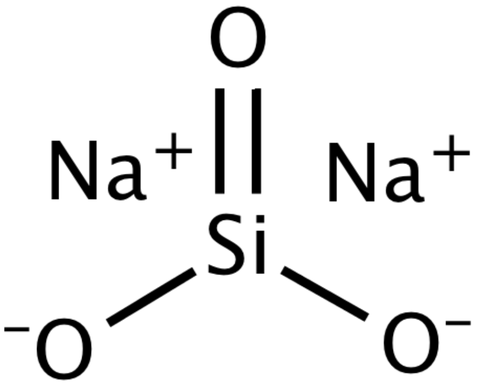


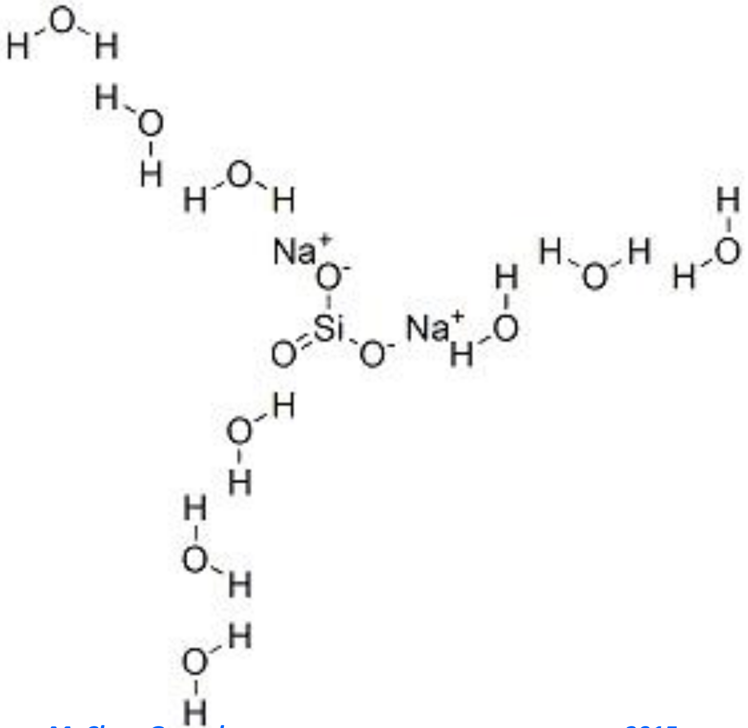
Sol-Gel techniques: ***silica-based ionic species in solution***

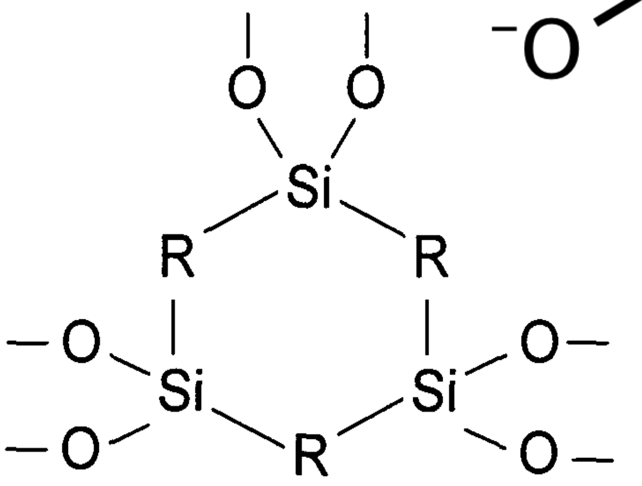
Sodium Silicate Solution (SSS) (is not a solution but a suspension!) ***is an excellent seed***



$(NaOH)_x\ (Na_2SiO_3)_y \bullet zH_2O$







1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: polymeric route

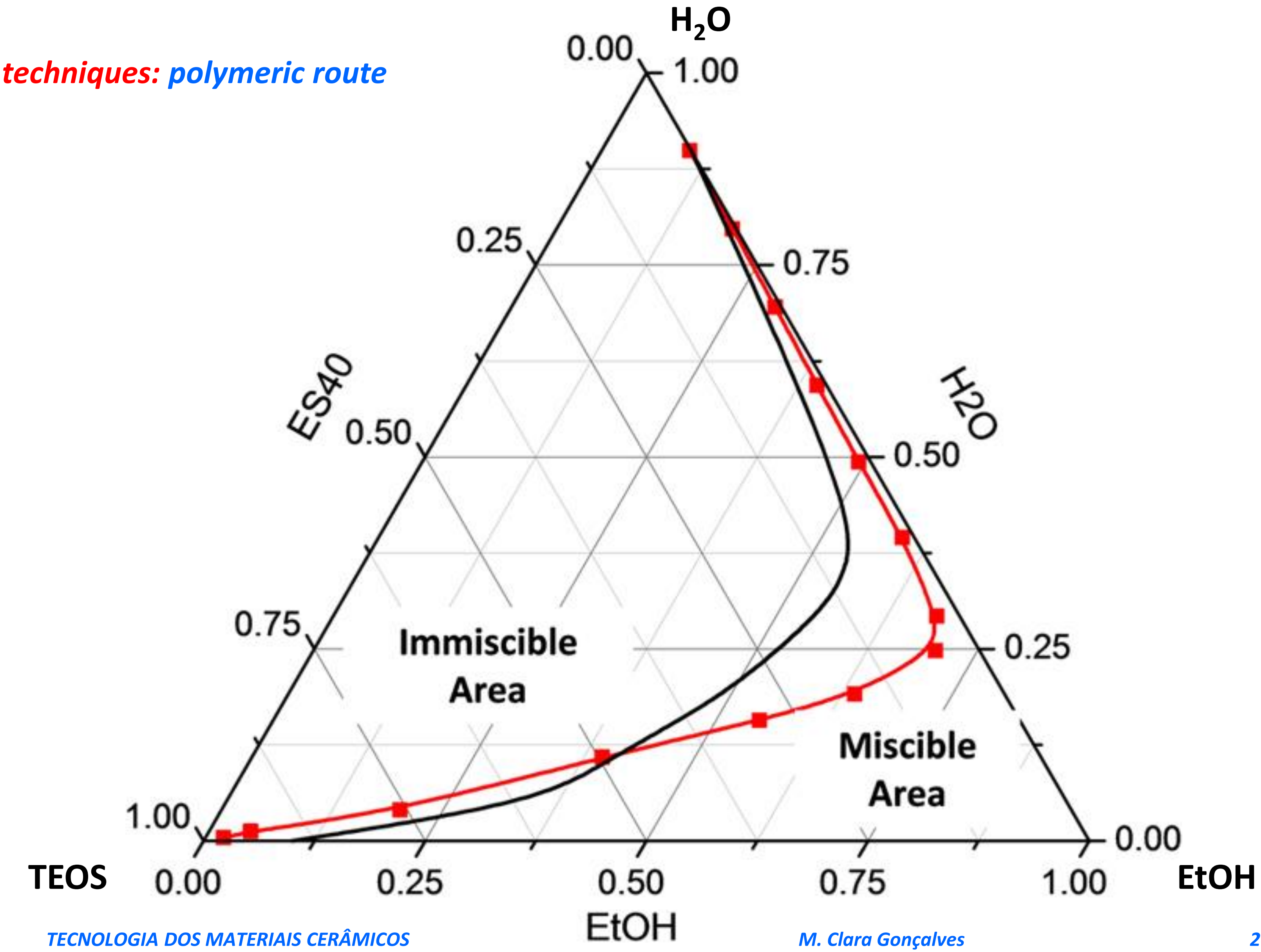
The most common synthesis process, however, involves the ***polymeric route***, which may also be exemplified with silica. Here, metallic salts, metal alkoxides, or other more complex organometallic precursors undergo **hydrolysis** and **polycondensation** to form the gel. Because of the **hydrophobic nature of the alkyl groups**, organometallic precursors and water are not miscible, so that addition of a common solvent (usually an alcohol) becomes mandatory to promote miscibility between the reactants.

In the most common case where an alkoxide is used as precursor, the alkoxide molecules in solution undergo hydrolysis, usually with the help of a catalyst, either an acid or a base.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: polymeric route



1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques

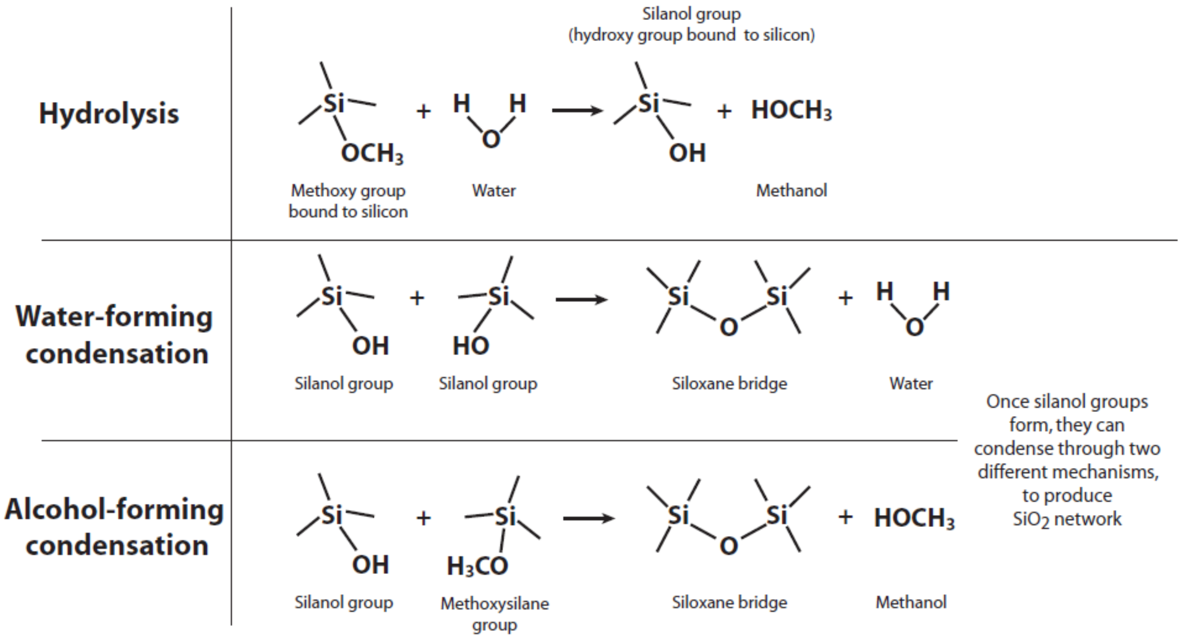
The **hydrolysis** is followed by **water** and/or **alcohol forming condensation reactions**. Hydrolysis and condensation **occur simultaneously rather than sequentially**; in fact, Si-O-Si (siloxane) bonds have been observed immediately after the addition of water and catalyst to the alkoxide solution, suggesting that condensation is initiated as soon as the first alkoxy group has been hydrolyzed. The initial condensation is quite fast, within minutes or less, although it slows down as polymerization progresses. For $Si(OC_2H_5)_4$, tetraethyl orthosilicate (TEOS), the most popular silica precursor, it has been experimentally found that the time for hydrolysis completion is less than 10% of the time for gelation under acid-catalyzed conditions.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques

THE THREE PRIMARY REACTIONS IN SILICA GEL FORMATION
VIA THE ALKOXIDE TECHNIQUE



Once silanol groups form, they can condense through two different mechanisms, to produce SiO_2 network

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: polymeric route

Acid catalysts — usually HCl, HNO_3 or CH_3COOH — are thought to promote hydrolysis by electrophilic attack. The rate of hydrolysis increases with the decrease in pH, starting from 7; meanwhile, the condensation reaction rate exhibits a local minimum at the **silica isoelectric point at pH 2**. Acid-catalyzed sols exhibit longer gelling times than basic-catalyzed ones, yielding gels with a large volume shrinkage.

When a **base**, such as ammonia, is selected instead as a catalyst, hydrolysis takes place by nucleophilic attack and progresses slowly, whilst silicate monomers start condensing before being fully hydrolyzed. Base-catalyzed products generally shrink less than those synthesized under acidic conditions, thus being **lower density products**.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: pH

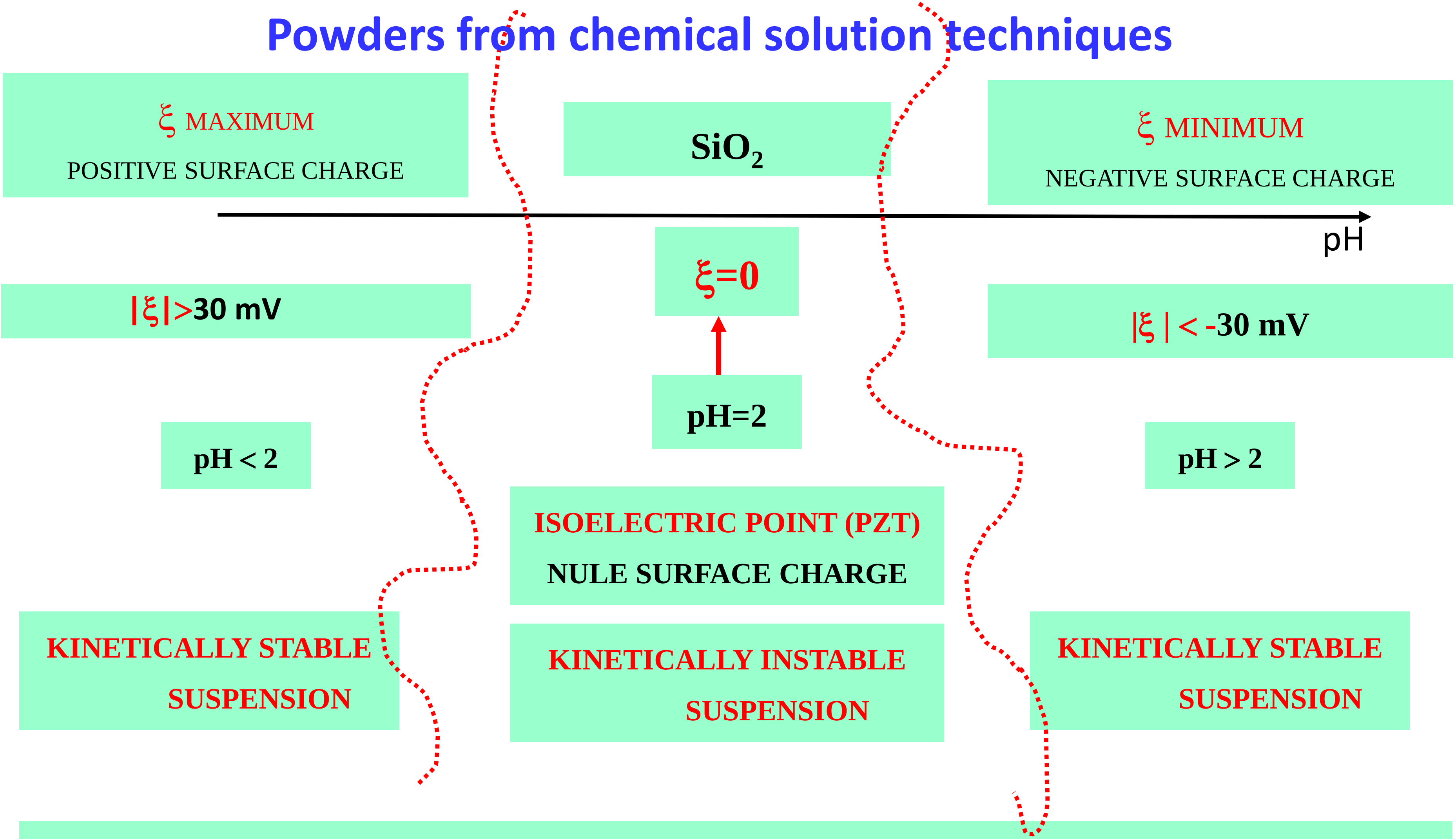
The **pH plays a critical role** in all SG processes. **At low pH**, particularly **below 3**, complete hydrolysis, whereby four moles of water are consumed per mole of TEOS, produces linear or highly branched polymeric species that have a fractal structure and nanopore diameters **lower than 2 nm**.

As the pH increases toward 7, dissolution and condensation reactions become relevant, promoting Ostwald ripening or coalescence and enhancing the coarsening of the structure.

Above pH 7, the **particle rate of growth is maximum** because an increasing silica solubility promotes depolymerization of siloxane bonds. In turn the monomeric silica produced helps the aging process through an Ostwald ripening-coarsening mechanism that yields mesopore diameters of well **above 2 nm**.

1.1 Special Ceramic Powders

Powders from chemical solution techniques



ξ MAXIMUM

POSITIVE SURFACE CHARGE

SiO_2

ξ MINIMUM

NEGATIVE SURFACE CHARGE

pH

$|\xi|>30$ mV

$\xi=0$

$|\xi| < -30$ mV

pH=2

pH < 2

pH > 2

ISOELECTRIC POINT (PZT)

NULE SURFACE CHARGE

KINETICALLY STABLE SUSPENSION

KINETICALLY INSTABLE SUSPENSION

KINETICALLY STABLE SUSPENSION

Floculation is maximum at PZT, point where electrophoretic velocity (and consequently **zeta potential**) **equals zero**.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: multicomponent gel

For **synthesis of multicomponent gels**, the polymeric solution route offers great possibilities. The miscibility of different alkoxide compounds allows in principle complete polymerization of all metal species to be achieved and, thus, **highly homogeneous products** to be synthesized.

This principle notwithstanding, the distinct rates of metal alkoxide hydrolysis may cause inhomogeneities and phase separation in the final gel.

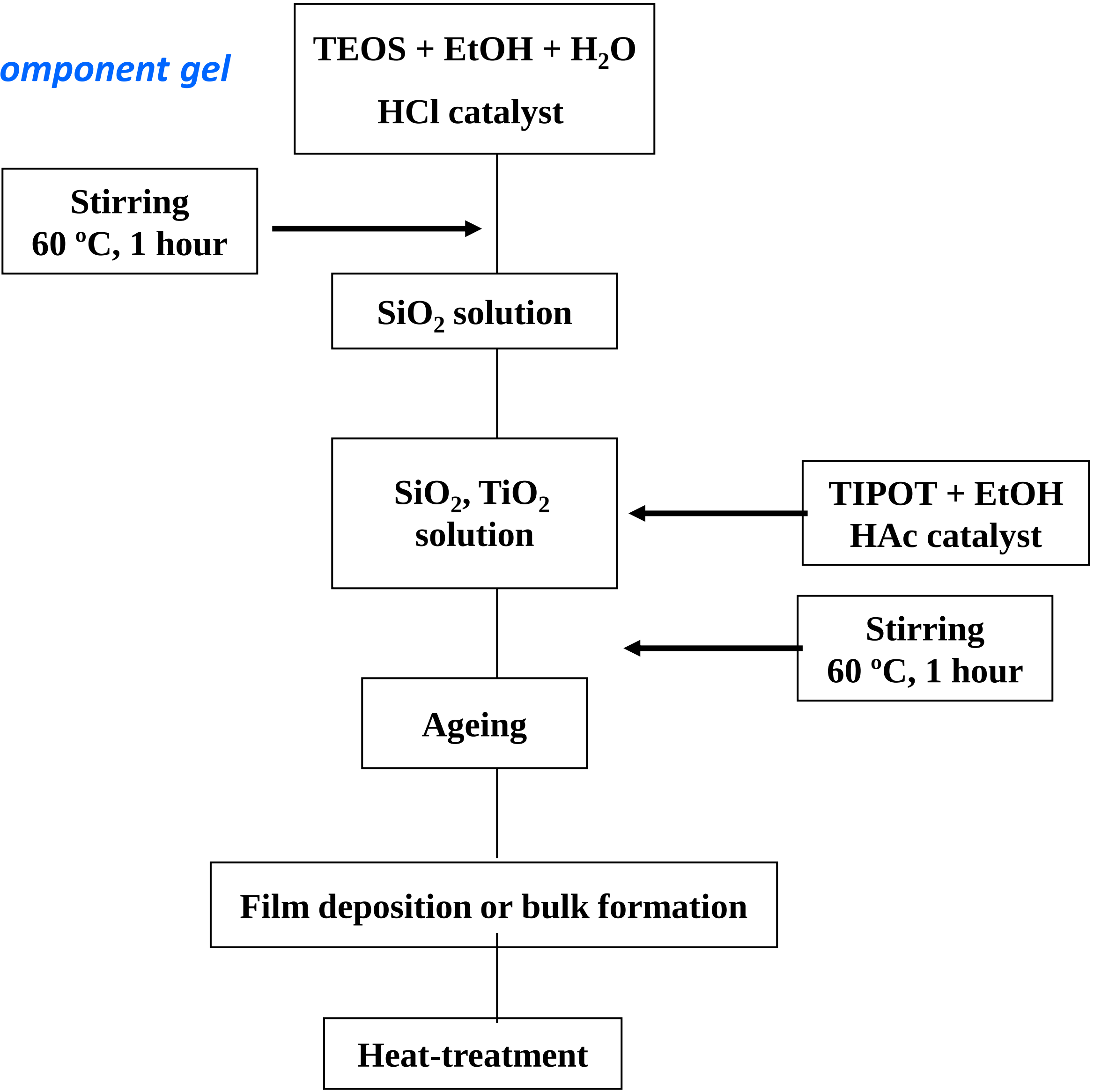
If two different metal alkoxide precursors are used, however, a sequential addition process in which the least-reactive alkoxide is pre-hydrolyzed to some extent before the more reactive is added tends to prevent inhomogeneities from appearing, allowing the two metal species to be placed randomly along the polymer chain.

As an example, the flowchart for the **SiO-TiO_2 sol-gel synthesis** is shown, where Ti isopropoxide (TIPOT) is the source of titania, the catalyst is acetic acid and ethanol (EtOH) the solvent; the composition of these products can vary all the way from pure silica to pure titania.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: ***multicomponent gel***



TEOS + EtOH + H_2O

HCl catalyst

Stirring
60 °C, 1 hour

SiO_2 solution

SiO_2, TiO_2
solution

TIPOT + EtOH
HAc catalyst

Stirring
60 °C, 1 hour

Ageing

Film deposition or bulk formation

Heat-treatment

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: hybrid material

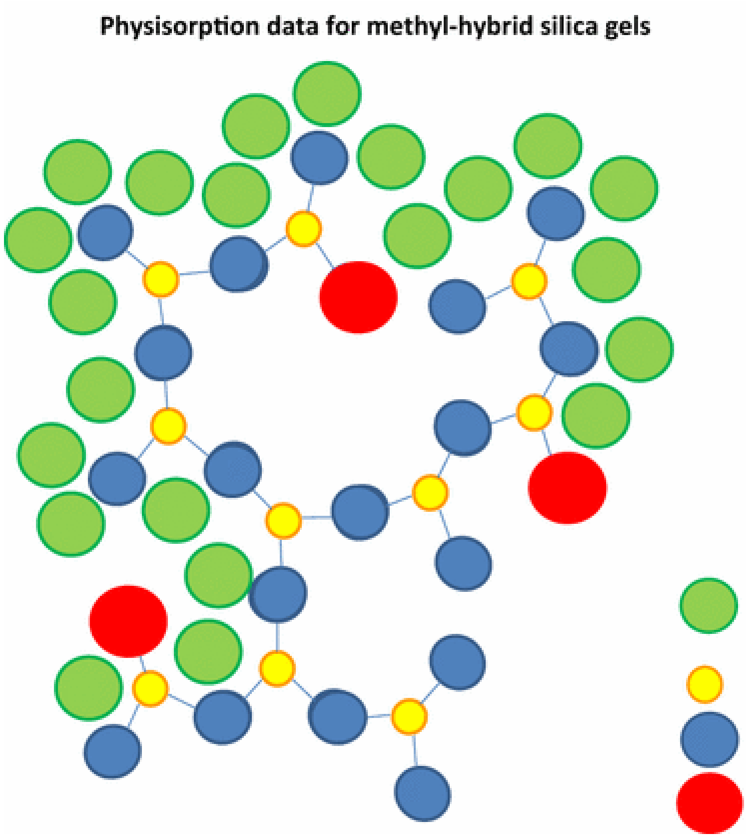
In the late 1970's, organic groups such as **$-CH_3$, $-C_2H_5$** and **$-C_{11}H_{24}O_4$** began to be incorporated into the gel network within which bonding was made possible by the **non-hydrolyzable Si-C bonds** of the precursors. This procedure gave rise to the so-called **ORganically MOdified SILica materials**, known as **ORMOSILS**, which belong to the general category of hybrid (organic/inorganic) materials. The presence of the more compliant organic groups, together with the eventual cross-linking between hybrid polymeric chains, allows mechanical properties to be tailored and stress to be dissipated by plastic deformation.

For example, ORMOSIL materials combine the mechanical strength, chemical resistance, thermal stability and optical transparency of glasses and ceramics with the toughness, flexibility and lightweightness of organic polymers. Further, network porosity and surface chemistry can be **tailored to** the designed performance. These materials have even a higher versatility than silica: the presence of organic groups not only makes them more flexible, but it also allows wettability to be **adjusted by a judicious choice of the ratio of hydrophilic (≡Si-OH, ≡Si-O-Si≡) to hydrophobic (≡Si-R) groups**.

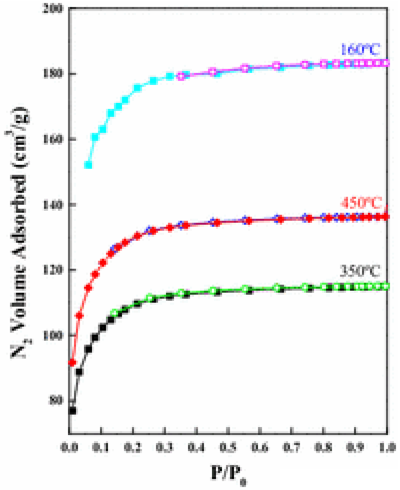
1.1 Special Ceramic Powders

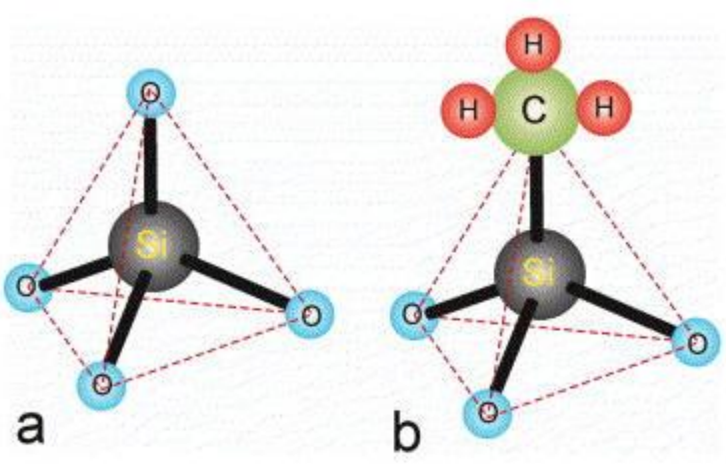
Powders from chemical solution techniques

Sol-Gel techniques: hybrid material



Physisorption data for methyl-hybrid silica gels





1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: aerogel

Supercritical drying is another possible method to avoid gel shrinkage. Here, the liquid is removed through drying above its critical point so that **no capillary stresses** develop since no liquid-vapor interface exists. The resulting gel, named ***aerogel***, has a volume similar to that of the dried wet gel, with a huge residual porosity. This causes the aerogel materials to be for example extremely good thermal and sound insulators.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: *iv)* very low-density aerogels

http://www.aerogel.org/?p=16

SiO_2 aerogel

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: templated gel

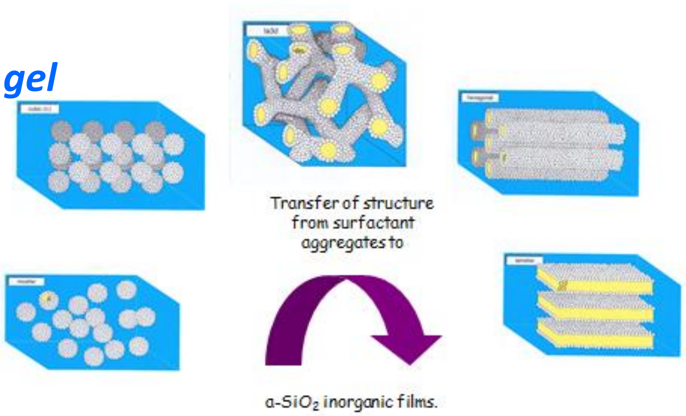
Sol-gel materials with a **tailored porosity** are another interesting products. After seminal work conducted in the early 1990's by researchers at the Mobil Oil Corporation, **surfactants** such as **Brij56™**, C16TAB or C12TAB (**lyotropic liquid crystalline phases**) have been used as templates for sol-gel materials.

One of the advantages of using homogenous phases as templates is that **the nano-architecture of the reaction mixture is retained throughout the condensation and gelation processes** so that the nanostructure of the material can be determined *a priori.* Thin films of nanostructured mesoporous silica, for example, are of interest for a range of applications, in particular for medicine and integrated sensors.

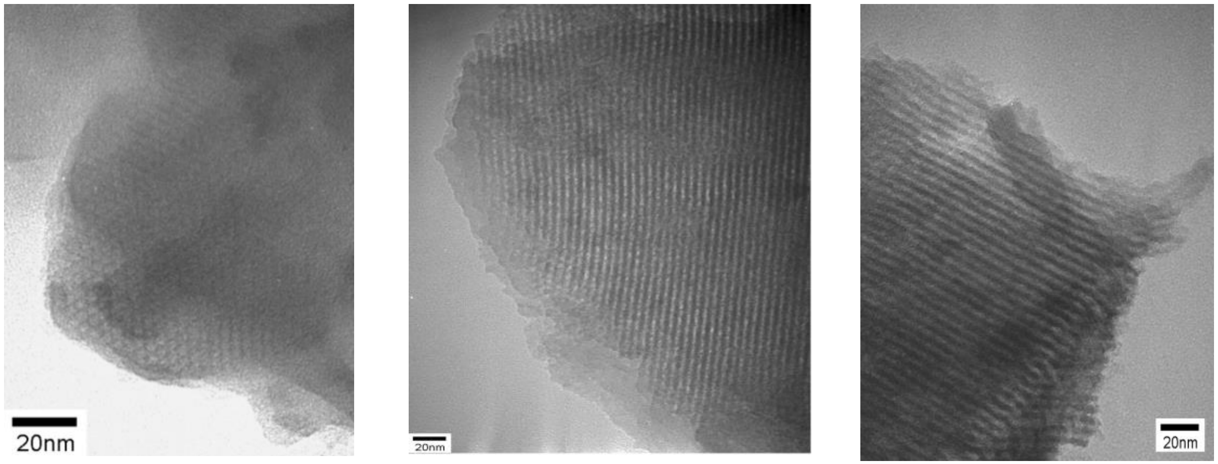
1.1 Special Ceramic Powders

Powders from chemical solution techniques

***Sol-Gel techniques:* templated gel**


Transfer of structure from surfactant aggregates to a-SiO_2 inorganic films.

Surfactant as template in nanostructured silica NPs.



(a) (b) (c)

TEM images of nanostructured silica NPs: (a) cubic domain, (b) biphasic I1+HI, (c) L_a

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: nanoparticles

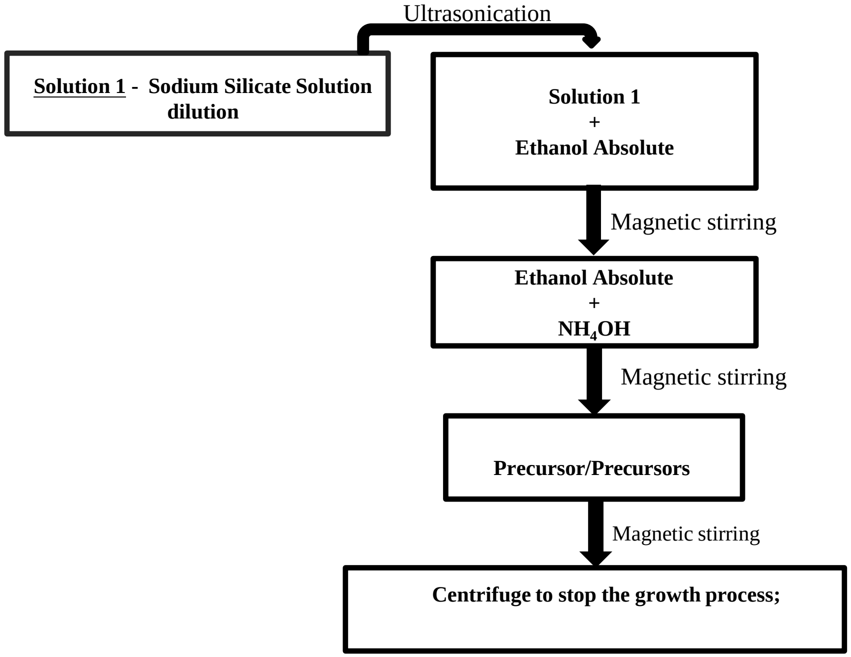
As exemplified by SiO_2 nanoparticles, the classical sol-gel aqueous route comprises two main alternatives: the **microemulsion process** (or reverse microemulsion) and **Stöber method**. In the first case, a reverse-micelle or water-in-oil microemulsion system is formed by mixing water, oil and surfactant. The sol-gel reactions take place in the dispersed aqueous phase, forming confined reaction vessels.

In the **Stöber procedure**, SiO_2 nanoparticles are produced by hydrolysis of an alkoxide precursor such as TEOS in an ethanolic solution, under basic catalysis. This hydrolysis starts producing silicic acid, which condenses to form highly porous amorphous nanoparticles. The Stöber method is a room temperature, surfactant-free route that ensures an eco-friendly synthesis of nano- or microparticles, with diameters comprised between 30 nm and 2 mm.

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: nanoparticles



Solution 1 - Sodium Silicate Solution dilution

Ultrasonication

Solution 1 + Ethanol Absolute

Magnetic stirring

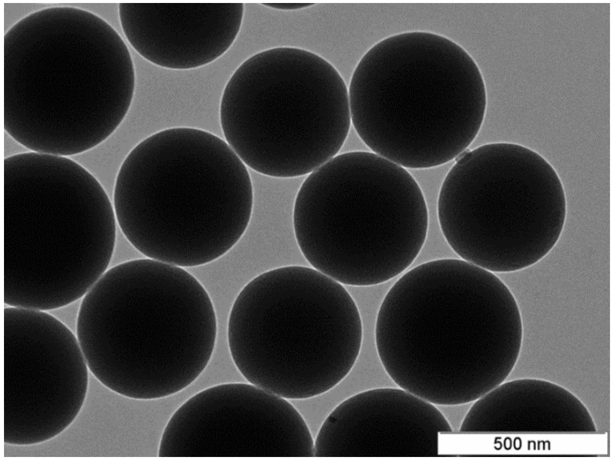
Ethanol Absolute + NH_4OH

Magnetic stirring

Precursor/Precursors

Magnetic stirring

Centrifuge to stop the growth process;

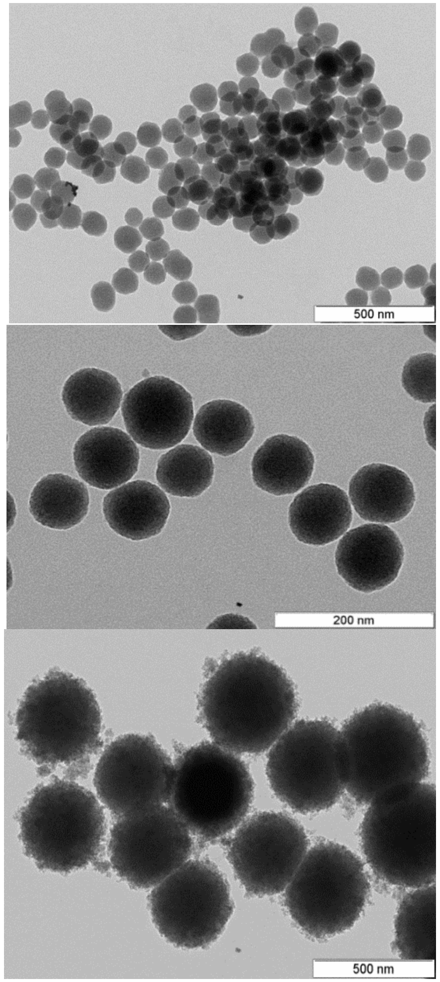


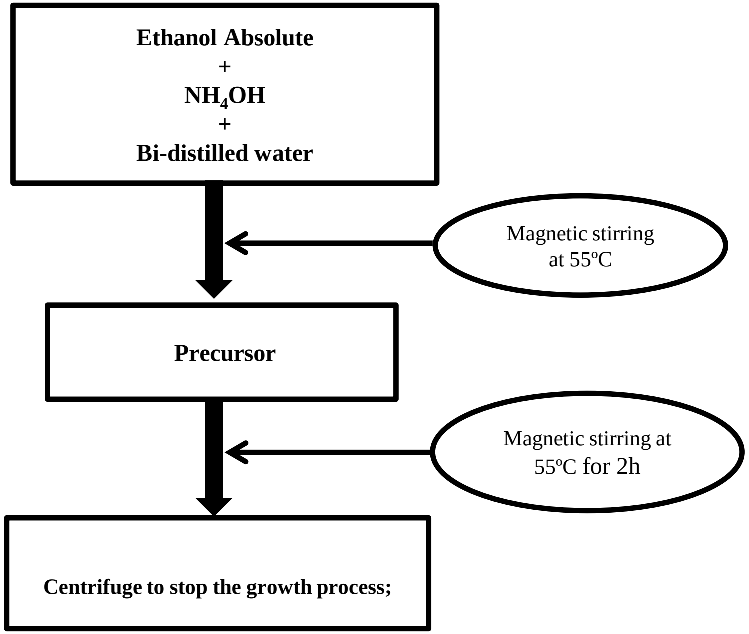
TEM images of SiO_2 NPs synthesized through the Stöber method

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: nanoparticles





Ethanol Absolute
+
NH_4OH
+
Bi-distilled water

Magnetic stirring at 55ºC

Precursor

Magnetic stirring at 55ºC for 2h

Centrifuge to stop the growth process;

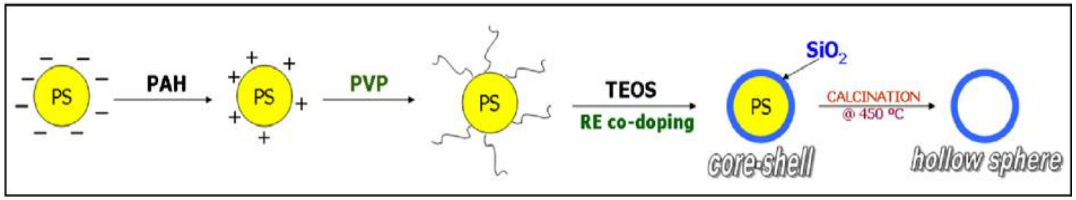
TEM images of silica nanoparticles synthesized by LaMer method:

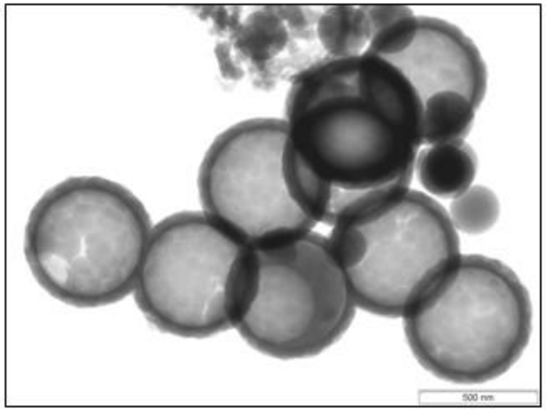
(a) inorganic SiO_2
(b) *in situ* amine-functionalized silica NPs
(c) *in situ* GPTMS-functionlized SiO_2 NPs.

1.1 Special Ceramic Powders

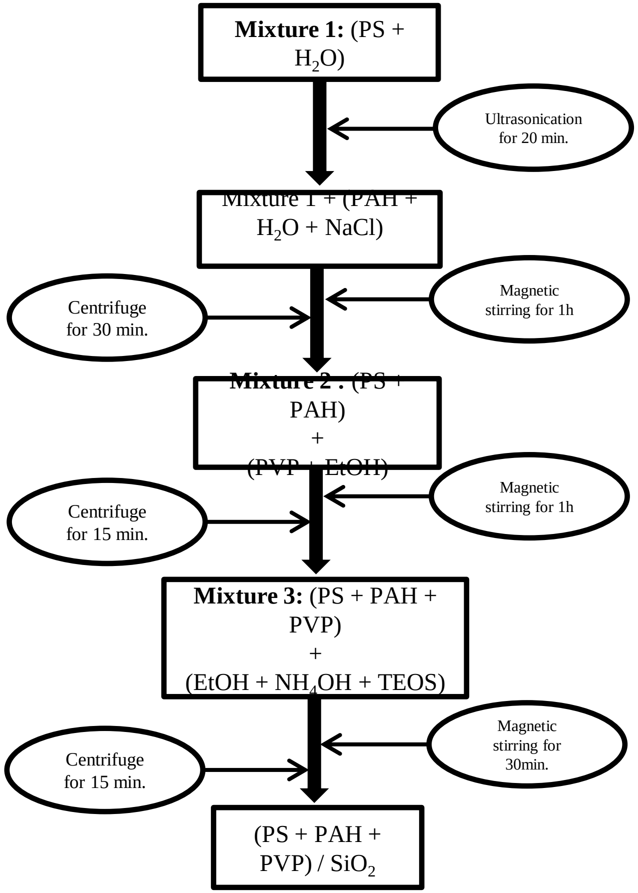
Powders from chemical solution techniques

Sol-Gel techniques: nanoparticles





TEM image of **Hollow SiO_2 NPs**



Mixture 1: (PS + H_2O)

Ultrasonication for 20 min.

Mixture 1 + (PAH + H_2O + NaCl)

Magnetic stirring for 1h

Centrifuge for 30 min.

Mixture 2 : (PS + PAH) + (PVP + EtOH)

Magnetic stirring for 1h

Centrifuge for 15 min.

Mixture 3: (PS + PAH + PVP) + (EtOH + NH_4OH + TEOS)

Magnetic stirring for 30min.

Centrifuge for 15 min.

(PS + PAH + PVP) / SiO_2

1.1 Special Ceramic Powders

Powders from chemical solution techniques

Sol-Gel techniques: non-aqueous process

Aqueous sol-gel chemistry may nonetheless be complex when it comes to nanoparticle synthesis. The difference in reactivity of the metal oxide precursors, the competition between hydrolysis and condensation reactions and possible aggregation or Ostwald ripening may prevent the control of nanoparticle size, size distribution and morphology. Additionally, the as-synthesized oxide nanoparticles are often amorphous and the final crystallization process may harm process reproducibility.

Although much less popular, another chemical route to produce oxide nanoparticles is a **nonaqueous approach**. Here no water is present, the oxygen being provided by solvents such as ethers, alcohols, ketones or aldehydes, or by the organic constituents of the alkoxide or acetylacetone precursors.

1.1 Special Ceramic Powders

Powders from vapor phase reactions

Two examples

Titania may be synthesized by reacting a titania chloride with water vapor at a high temperature:

$$TiCl_{4(g)} + 2H_2O_{(g)} \rightarrow TiO_{2(g)} + 4HCl_{(g)}$$

Silicon nitrade powder may be formed by reacting silicon tetrachloride and ammonia in plasma below 1000ºC:

$$3SiCl_{4(g)} + 4NH_{3(g)} \rightarrow Si3N_{4(g)} + 12HCl_{(g)}$$

Vapor phase techniques produce sub-micron, well dispersed particles entrained in large volumes of gas. Large, complex collection systems are required to remove the powder.

Additional Information

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth

According to the Classical Nucleation Theory, which applies for supersaturated solution (or vapor) and supercooled liquid (or gas), when a liquid (or vapor) matrix/crystal nucleus interface is formed, with interfacial energy γ, for spherical nuclei with a radius r, the decrease of volume energy, $\Delta\mu_V$, is described by:

$$\Delta\mu_V = \frac{4}{3}\pi r^3 \Delta G_V$$

where ΔG_v represents the volumetric Gibbs energy change. However, this energy reduction is counter balanced by an increase in the surface energy, given by:

$$\Delta\mu_S = 4\pi r^2 \gamma$$

being the overall change in Gibbs free energy of the system, ΔG:

$$\Delta G = \Delta\mu_V + \Delta\mu_S = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma \qquad [16]$$

where ΔG^* is the energy barrier that nucleation must overcome, and r^* represents the minimum size of a stable spherical nucleous.

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth

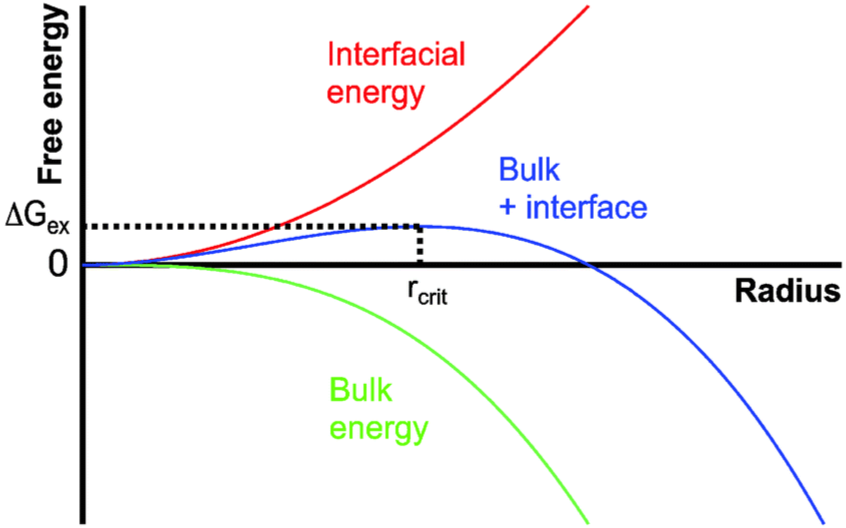
Assuming a spherical nucleus with a radius r:

$$\Delta G = \Delta\mu_v + \Delta\mu_s = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Gibbs free energy

volume energy

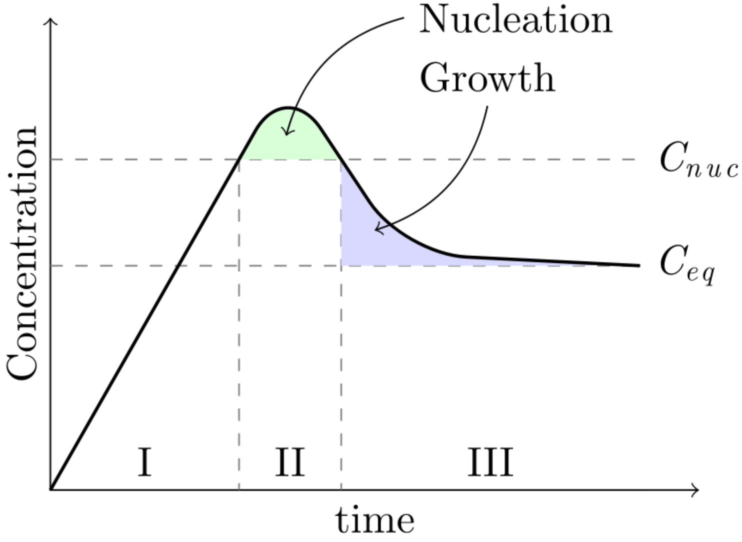
surface energy



- **REDUCTION OF GIBBS FREE ENERGY IS THE DRIVING FORCE FOR NUCLEATION AND GROWTH**

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth



→ **Nucleation** occurs when the concentration reaches the minimum saturation required to overcome the critical energy barrier

→ **Nucleation rate increases** very rapidly as the conc. increases further

→ **Growth rate** is above zero for a conc. above its equilibrium solubility

→ **One nuclei are formed**, **growth occurs simultaneously**

→ Above the minimum conc., nucleation and growth are inseparable processes

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth

(cont.)

→ The newly formed nucleus is stable and continues to grow bigger only if its radius equals or exceeds a critical size, r*. When the nucleus is smaller than r*, it will dissolve into the solution to reduce the overall free energy.

→ In the synthesis of nanoparticles by nucleation from supersaturated solution (or vapor), **this critical size represents the limit on how small nanoparticles can be synthesized**. To reduce the critical size (and free energy), one needs to increase the change of Gibbs free energy, ΔG_V, and reduce the surface energy of the new phase, γ. For the synthesis of monosized nanoparticles, it is desirable that all nuclei form at the same time, i.e., **nucleation should occur in a very short period of time**.

Introduction: nucleation and crystal growth (revisited)

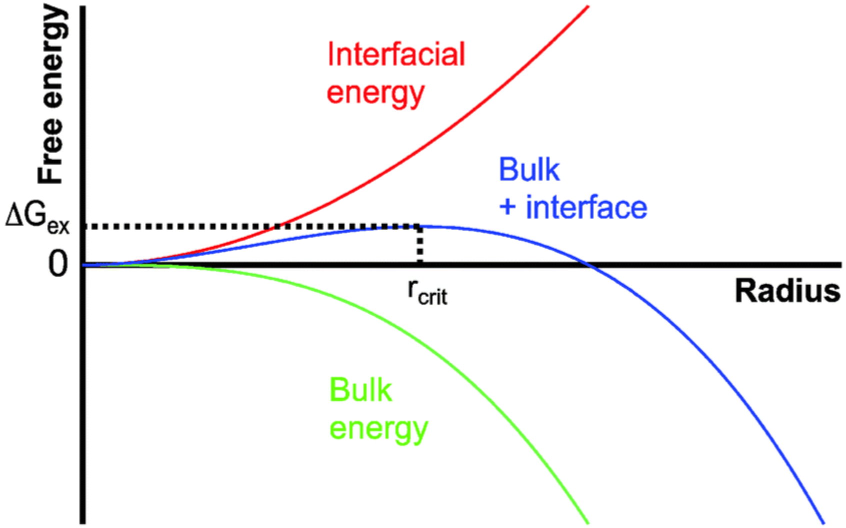
Homogeneous nucleation and growth

radius critical size ←

$$r^* = -2\frac{\gamma}{\Delta G_v}$$

critical Gibbs energy ←

$$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2}$$



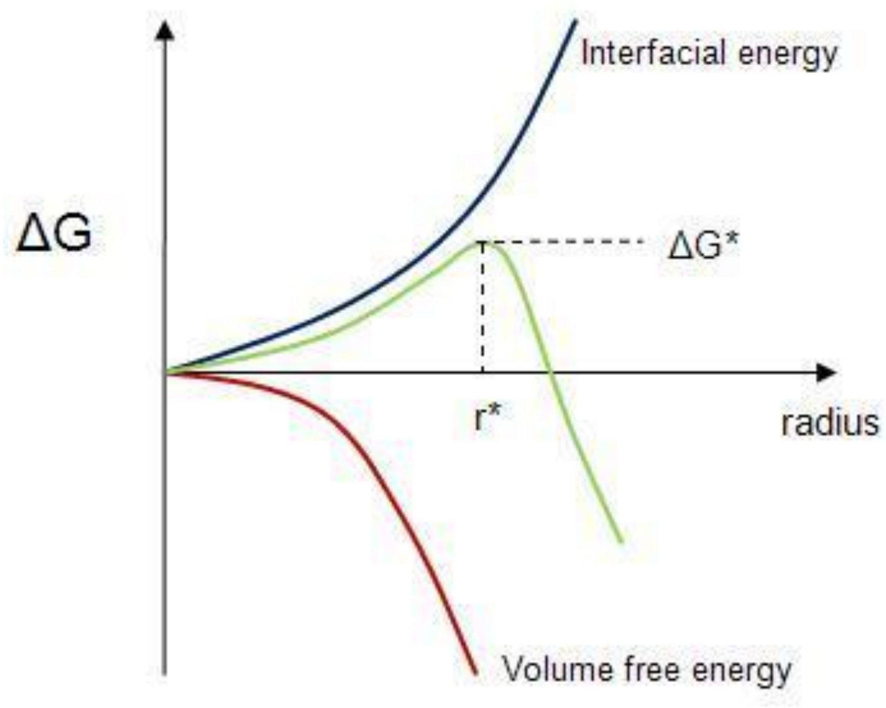
r > r* - newly formed nucleous is **stable** only when its radius exceeds a critical size **r***

r < r* - nucleous dissolves into the solution to reduce the overall free energy of the system

r = r* - **$d\Delta G / dr = 0$**

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth



Schematic change of **volume free energy**, $\Delta\mu_V$, **surface free energy**, $\Delta\mu_S$, and **total free energy**, ΔG, as function of nucleus' radius

Introduction: nucleation and crystal growth (revisited)

Homogeneous nucleation and growth

In the synthesis of **colloidal particles** by **homogeneous nucleation** from supersaturated solution or vapor, the **radius critical size** represents the **limit** on **how small particles** can be synthesized.

radius critical size ← $r^* = -2\dfrac{\gamma}{\Delta G_v}$

critical Gibbs energy ← $\Delta G^* = \dfrac{16\pi\gamma}{(3\Delta G_v)^2}$

↓ r*, ↓ΔG* ⟷ **↑ ΔGv , ↓ γ**

↑ ΔGv ⟷ **↑σ (supersaturation)**

Introduction: motivation to growth

Motivation to growth

One of the great challenges in fabrication and processing of nanomaterials is **to overcome the surface energy**, and to **prevent** the nanostructures and nanoparticles from **agglomeration** or **growth in size**, driven by the reduction of overall surface energy.

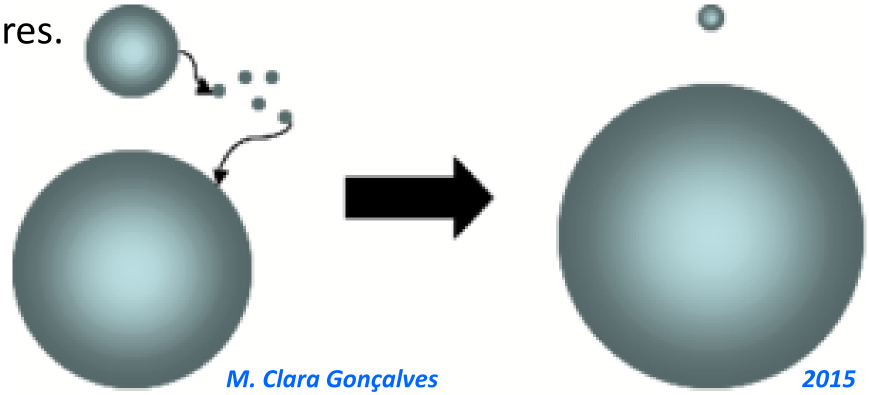
The **reduction of surface energy** is the **driving force** behind **surface relaxation** or **restructuring**, **oxidation** or **passivation**, **physical** or **chemical absorption**, **compositional segregation**, **the formation of faceted** (rather than nanospherical) **nanocrystals**, **sintering** (when around ambient temperature), **Ostwald ripening** or **agglomeration**. All these mechanisms allow the surface energy of nanoparticles, nanostructure or nanosystems to be reduced.

Introduction: motivation to growth

Ostwald ripening

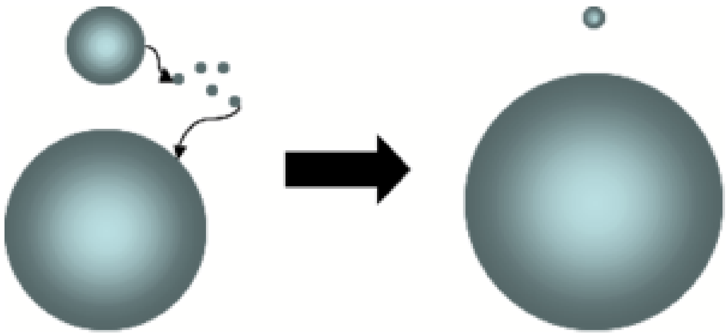
When two particles with different radii ($R_1 >> R_2$) are dissolved or suspended in a liquid, each particle will develop equilibrium with the liquid. According to **Kelvin equation**, the smaller particle will have a higher solubility. Consequently, the solute will diffuse from the environment closer the smaller particle to the environment closer to the larger particle. To keep the thermodynamic equilibrium, solute will deposit onto the surface of the larger particle. To compensate the solute diffused away the smaller particle will continue dissolving. As a result, the **small particle gets smaller**, whereas the **large particle gets larger**.

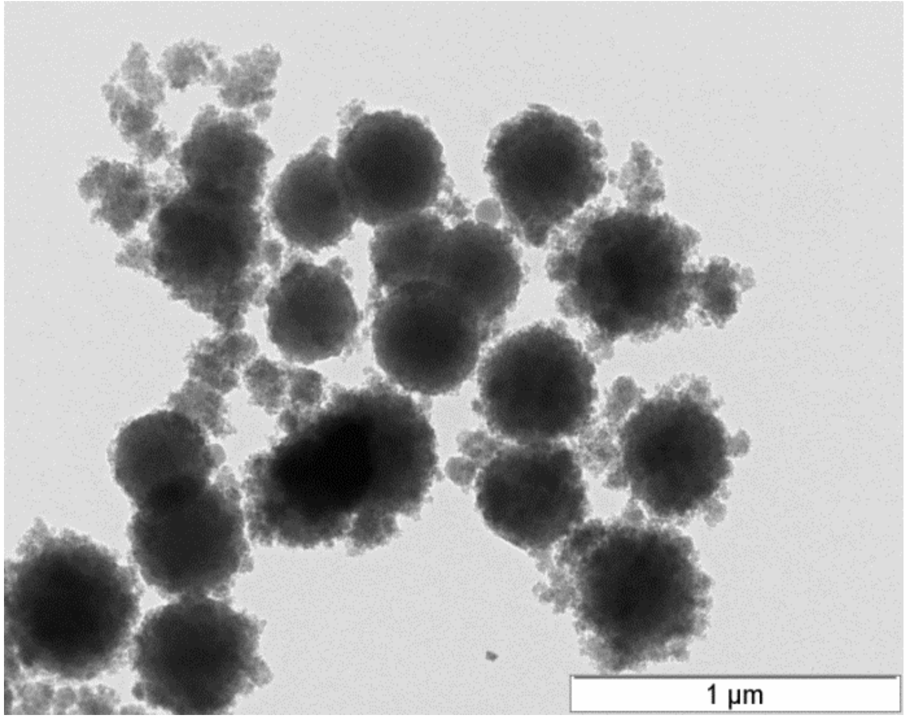
Ostwald ripening is an expontaneous process, quite useful in narrowing nanoparticles size distribution, and can be promoted by varying process temperatures.



Introduction: motivation to growth

Ostwald ripening

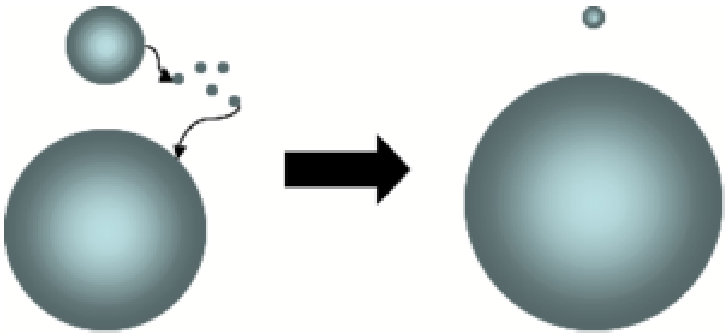


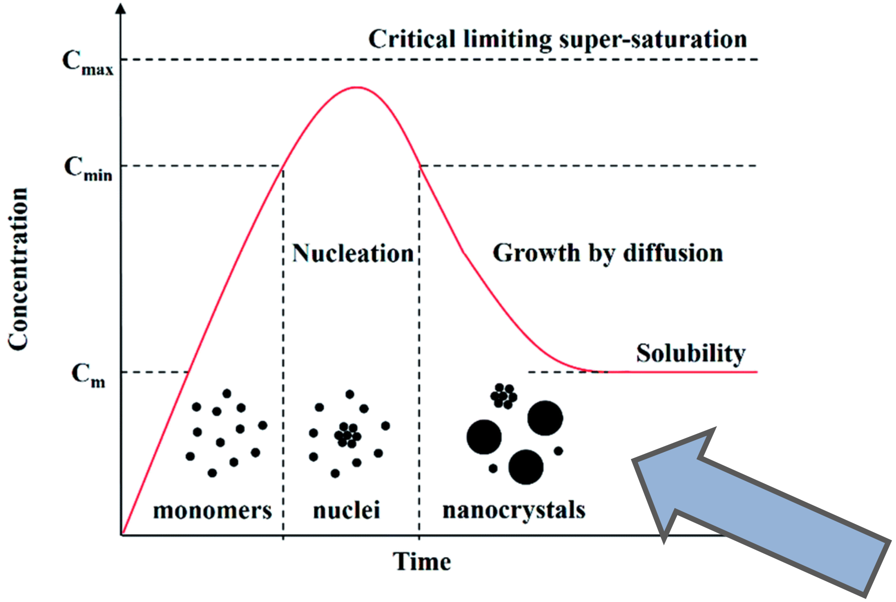


TEM images evidencing **Ostwald ripening** in **SiO_2** functionalized NPs

Introduction: motivation to growth

Ostwald ripening



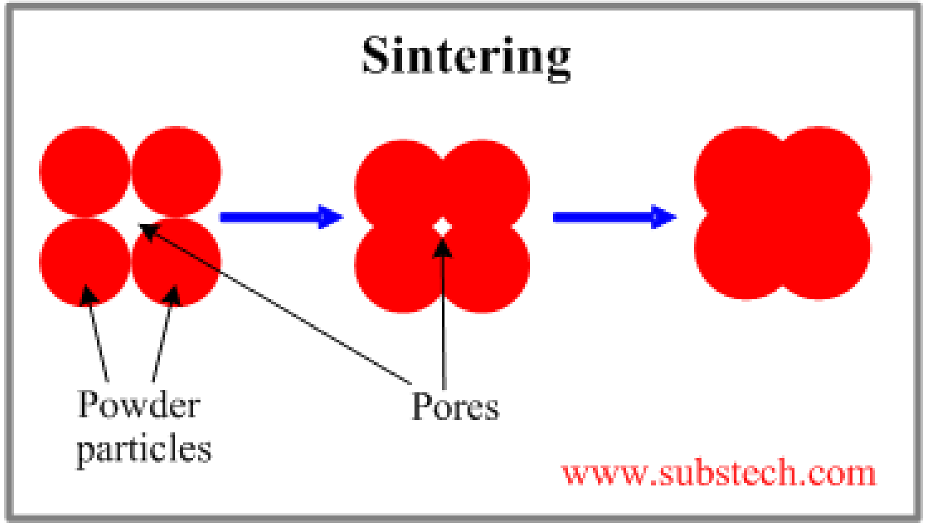


Ostwald ripening

Introduction: motivation to growth

Sintering

To preserve nanoparticles (after synthesis) sintering must be avoid. **Sintering** is a complex process that involves **solid-state diffusion**, **evaporation-condensation** or **dissolution-precipitation**, **viscous flow** and **dislocation creep** and can occur at quite low temperatures when nanoparticles are present. Sintering promotes the replacement of solid-vapor by a solid-solid interface through **reshaping of nanoparticles**, promoting higher efficient packing of the nanocrystals.



Introduction: motivation to growth

Surface relaxation and restructuring

One of the mechanisms responsible for surface energy reduction is **surface relaxation**, where the surface atoms shift inwardly. **Surface relaxation** is more common in liquids than in solids due to its rigid structure.

Surface restructuring occurs through the combination of surface dangling bonds into stained new chemical bonds.

Oxidation and passivation

Surface adsorption takes place through chemical or physical adsorption of chemical species onto the surface by forming chemical or physical bonds.

Oxidation and **passivation** are special surface adsorption cases, where the surface atoms bound to oxygen, forming a surface (protective) film.

Introduction: Colloidal Particles design

→ New and potential uses of ceramics in what are called **high-performance** or **high technology** applications have stimulated much interest in **novel techniques** for preparing **special ceramic powders with special characteristics**.

→ Characteristics sought include a **purity in excess of 99.9%**, a precisely **controlled**, **reproducible chemical composition** including **dopants**, **chemical homogeneity on na atomic scale**, and a precisely **controlled** and **consistent submicron particle size**. In some applications, a special particle **shape** may be a goal. The variety of components prepared in the laboratory is extensive.

→ Although ceramics have been produced for years from these special powders on a laboratory scale, relatively few of these special powders have been used in industrial processing. However, the successful commercial applications of special materials for products such as optical fibers, and thick film electronic ceramics and large potential markets for more advanced ceramics have increased the interest in and the evaluation of these techniques for industrial fabrication.

Introduction: Colloidal Particles design

→ In addition to their outstanding surface-to-volume ratio, NPs possess unique thermal, mechanic, electrochemical, catalytic, optical, electronic and magnetic properties, depending on their size, shape and composition. Thus, instead of changing the NPs composition, one may play with the size and/or shape, **to fine tune the desired property or set of properties**.

→ NPs may exhibit a wide range of geometries – from spherical to tubular, through centric, eccentric and star like – may be plain or nanostructured – core-shell or porous structure - exhibit different sizes and shell thicknesses, may be hollow, may differ in crystallinity and surface morphology, and finally may be fine-tuned relative to one or more properties.

→ Further, NPs can be functionalized and eventually bioconjugated with a wide range of small ligands and/or large biomolecules. Additionally, NPs enable the encapsulation and controlled release of various substances (e.g., drugs, biomolecules, cosmetics, and dyes), and may play singular performance in certain biomedical devices.

Introduction: Colloidal Particles design

→ And finally, NPs can be multifunctional, i.e., capable of accomplishing multiple objectives such as imaging and therapy (*theranostics*), or performing a single advanced function through incorporation of multiple functional units. For biomedical applications, an appropriate size range (~ 10 - 200 nm) and a monosized distribution are normally required for effective operation.

→ Due to the nanoscale associated to these materials, classical physics are often unable to explain their properties, which are easier to understand in the domain of quantum mechanics. While the use of quantum mechanics enables many interesting hypothesis, it also increases the degree of difficulty in the complete understanding of materials.

Introduction: Colloidal Particles design

→ The properties of nanomaterials are determined mainly by the **properties of their surfaces** (opposed to bulk properties), due to their extraordinary high surface area to volume ratio. As a result, irregular shapes with higher surface area to volume ratio play a larger role in dictating those properties. Further, non-spherical NPs do have energetically different surface sites (**surface/edge/corner**) which may differently act in chemical processes. Besides, shape may be characteristic of a crystalline structure, and that is an additional reason to avoid shape distribution.

→ **Surface roughness/smoothness** may affect the contact area between a NPs and its environment (biological or other), thus reducing/increasing the number of accessible active surface sites. Chemical and structural identical NPs not surprisingly may exhibit different behavior depending on surface roughness/smoothness.

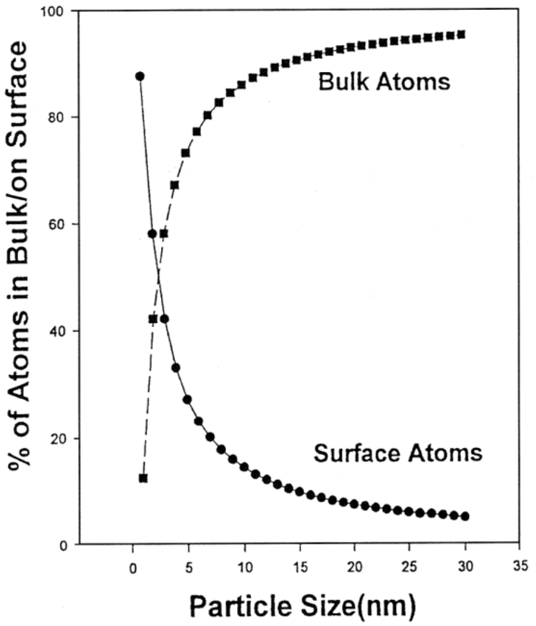
→ **Surface hydrophobicity/hydrophilicity**, which may be tuned during the synthesis processes, controls the wettability of a NP in respect to a specific environment, determining the number of accessible active surface sites.

Introduction: Colloidal Particles design

Size matters

Nanostructures and nanomaterials possess a large fraction of surface atoms *per* unit volume. If one successively divides a macroscopic object into nanoscale, the ratio of surface atoms to interior atoms increases exponentially. Let's consider a spherical microparticle with 10 mm in diameter. If we now break it into several *nano*particles measuring 10 nm (in diameter) each, we will obtained 10^9 *nano*particles. The ratio of the *radii* is 10^3 while the ratio of the surface areas is 10^6, and the specific surface area is increased by a factor of 10^3!

(The value of this estimate does not take into account the contraction caused by the reduction of surface tension).



Bulk/surface atoms function of particle size diameter

Introduction: Colloidal Particles design

Shape matters

When considering nanomaterials, shape must also be taken into account, since it contributes to the value of the specific surface area. It is the fact that nanomaterials' properties depend on *size* and *shape* (keeping constant the composition and the number of atoms/molecules) that gives them such great potential.

One of the main concepts in surface science and nanotechnology is the **surface energy** or **surface tension**, γ. In any material, bonds are affected by the formation of **new surfaces**, where **some bonds are broken or modified**. As a result, the **average energy of the surface atoms will increase with the surface area**.

Superficial energy is defined as **the energy supplied to make a unit surface area**, A, at temperature **T**, volume **V** and chemical potential μ, **constants**:

$$\gamma = \left(\partial H / \partial A\right)_{T,V,\mu}$$

where H is the Helmholtz's free energy.

Introduction: Colloidal Particles design

Shape matters

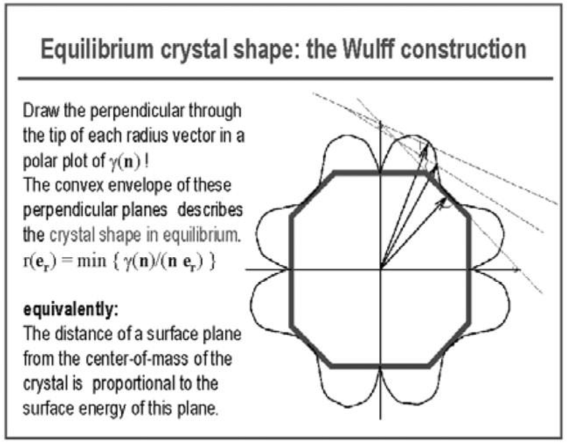
Superficial energy is proportional to the number of interatomic bonds broken down at the surface, times the atomic planar density. In the case of crystalline solids, atomic planar density depends on the crystallographic plan, so thus the surface energy.

In polycrystalline materials (or nanocrystals) the anisotropy is such that the equilibrium form of a crystal is determined by the superficial energy values of the different surfaces. The anisotropy of a crystal can be studied through the superficial energy γ's diagram.

If γ is isotropic, the equilibrium form is obviously a sphere. When γ is anisotropic, the equilibrium form is not a sphere, but a polyhedron. The precise polyhedron shape can be obtained through the Wulff diagram.

Introduction: Colloidal Particles design

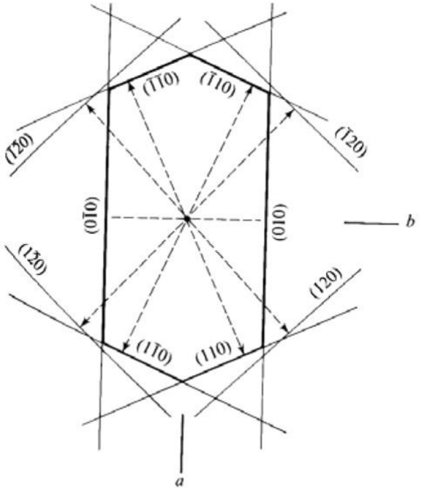
Shape matters

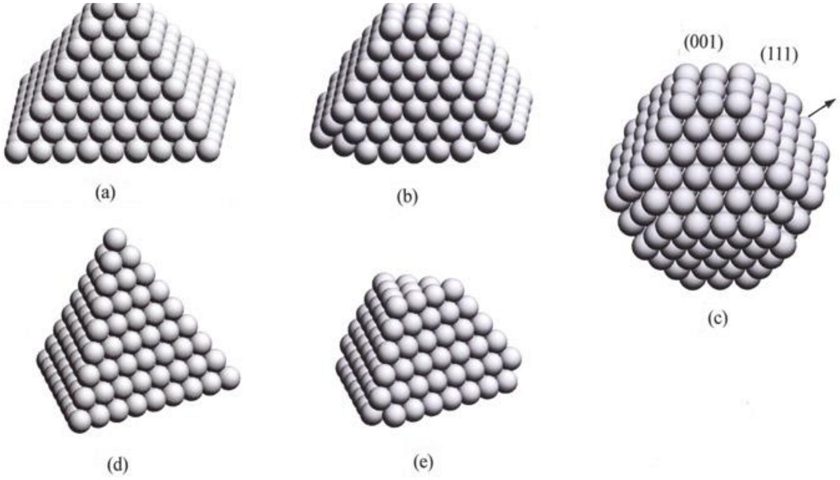


Equilibrium crystal shape: the Wulff construction

Draw the perpendicular through the tip of each radius vector in a polar plot of $\gamma(\mathbf{n})$!
The convex envelope of these perpendicular planes describes the crystal shape in equilibrium.
$r(\mathbf{e}_r) = \min \{ \gamma(\mathbf{n})/(\mathbf{n}\ \mathbf{e}_r) \}$

equivalently:
The distance of a surface plane from the center-of-mass of the crystal is proportional to the surface energy of this plane.





(a) (b) (c) (d) (e)

Wulff diagram construction (I) and external shape of epitaxial particles(II):

(a) (001) epitaxial particle with pyramid shape

(b) truncated (001) epitaxial particle

(c) Wulff polyhedron,

(d) (111) epitaxial particle with regular tetrahedron shape

(e) truncated (111) epitaxial particle

http://www.k5.dion.ne.jp/~inos1936/shozoHP2E.html

Introduction: Colloidal Particles design

Shape matters

Polyhedral nanoparticles

The outer planes of a crystal (and, therefore, its polyhedral shape) can be determined theoretically (**Wulff's theorem** provides a quick method for showing how they are determined, minimizing the crystal's Gibbs energy). For an fcc structure of pure metals, the crystal shape, in thermodynamic equilibrium, is cubo-octahedral with 14 sides. It has 12 surface atoms and 1 inside atom. It is important to stress that the shape of a crystal which grew in thermodynamic equilibrium cannot always be predicted theoretically.

Sometimes, **above a certain temperature**, the energy difference between the different planes is gradually lost, and the crystal becomes spherical rather than polyhedral. This temperature is known as the ***roughening temperature***. If a particular crystal rises above the *roughening temperature*, it will produce a sphere rather than a polyhedron. Kinetic properties can also condition crystal shape.

Introduction: Colloidal Particles design

Shape matters

Spherical nanoparticles

One common shape of nanoparticles is spherical (the shape adopted by liquids and isotropic solid materials), since this is the shape which minimises the surface area to volume ratio.

For a sphere with a radius of *r*, the surface area is given by,

$$A = 4\pi r^2$$

and the volume by;

$$V = \frac{4\pi r^3}{3}$$

Therefore the surface area to volume ratio is given by;

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r}$$

as the nanoparticle radius decreases, we get closer and closer to a critical value, after which the increase in surface area is extremely fast.

Knowing that many reaction phenomena take place on the interface, the increase in surface area will lead to a significant increase in the nanoparticle's reactivity.

Introduction: Colloidal Particles design

Shape matters

Polyhedral nanoparticles

For anisotropic crystalline solids, the shape taken on by the nanoparticles is not spherical but polyhedral. This can be observed in the initial phases of crystal growth. **In polyhedral nanoparticles (or nanocrystals) surfaces, edges and vertices exhibited different surface energy values**.

Let us consider a certain crystalline material. From a thermodynamic point of view, the equilibrium shape of a crystal is determined by:

$$\sum A_i \gamma_i = mínimo$$

in which γ_i is the surface energy of each face *i,* and A_i, the respective area.

Introduction: Colloidal Particles design

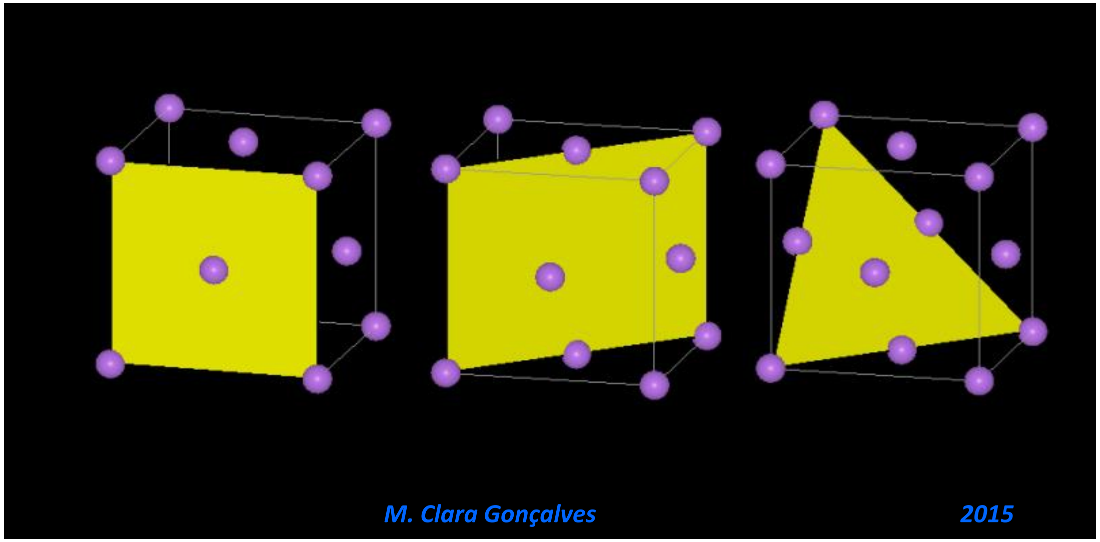
Shape matters

Polyhedral nanoparticles

Different crystallographic planes with different planar atomic densities will have different Gibbs free energy values. In the case of the *fcc* structure, the surface energy of highly symmetrical planes, {100}, {110} and {111}, is given, respectively, by:

$$\gamma_{\{100\}} = \frac{4\varepsilon}{a^2} \qquad \gamma_{\{110\}} = \frac{5}{\sqrt{2}}\frac{\varepsilon}{a^2} \qquad \gamma_{\{111\}} = 2\sqrt{3}\frac{\varepsilon}{a^2}$$

and it is ordered in a monoatomic ***fcc*** crystal in the following way, **γ{111} < γ{110}< γ{100},** unlike planar density, **pa{111}>pa{110}>pa{100}.**



Introduction: Colloidal Particles design

Shape matters

Magic numbers

N	6	7	8	9	10	11	12	13
	2	4	8	18	57	145	366	988

A set of chemically bonded atoms form a molecule. After a certain dimension threshold, instead of molecules they can be designated ***nanoparticles***. Let us consider the formation of nanoparticles (with a single type of atoms), where the interatomic interactions are depicted by the Lennard-Jones potential:

$$V_{LJ}(r) = -2/r^{6} + 1/r^{12}$$

where r is the interatomic distance.

As the number of atoms N increases, the geometric array varies. The atoms self-assemble in *clusters*, with defined geometries. When N is high enough, it is possible to have several geometric arrangements for the same N. For example, if N=6, we witness two local minimums of Gibbs local energy – octahedral structure (stable) and tripyramide (metastable); if N=7, the number of local minimums is 4. The number of local minimums grows rapidly with N.

Introduction: Colloidal Particles design

Shape matters

Magic numbers

For each N, the Gibbs energy of the several local minimums (metastable) is close to each other, as well as to the absolute minimum of the system. The presence of different metastable states with energy values very close to each other, suggests that the excess energy can be spread through different states; hence at fusion and solidification temperatures, different nanoparticles' forms may be present. During heating, the melting temperature is unique and defined thermodynamically. During cooling, solidification temperature differs from melting temperature.

In *clusters* (and nanoparticles) the fusion temperature is inferior to the one observed in bulks. For big *clusters*, we witness another phenomenon. Not only does the fusion temperature (and the heat of the fusion) vary with nanoparticles size, it also varies according to their forms.

Introduction: Colloidal Particles design

Shape matters

Magic numbers

The ***magical numbers*** were first observed in 1980. *Magical numbers* correspond to predominant *clusters* (with a determined number of N atoms) in the production of pure metal nanoparticles, such as Na (monovalent), Cd, Zn (bivalents), Al (trivalent) and also in the transition metals (Cu, Ag, Au).

Let us consider gold (Au), silver (Ag), nickel (Ni), aluminium (Al), copper (Cu) or platinum (Pt), all face-centred cubic system (*fcc)*. For a *cfc* nanocrystal with the size of a single cell, all (14) atoms are surface atoms.

When we add a layer of atoms to the *fcc* unit cell, the number of surface atoms becomes:

$$N_{Total}^{S} = 12n^2 + 2$$

and the number of atoms inside becomes:

$$N_{Total}^{I} = 4n^3 - 6n^2 + 3n - 1$$

Introduction: Colloidal Particles design

Magic numbers for *cfc* structure

n	N^S Surface atoms	N^I Interior atoms	N^S / N^I	N^S (%)
1	14	0	-	100
2	50	13	3,85	79,3
3	110	62	1,78	63,9
4	194	171	1,13	53,1
5	302	364	0,83	45,3
6	434	665	0,665	39,4
7	590	1098	0,535	34,9
8	770	1687	0,455	31,3
9	974	2456	0,395	28,3
10	1202	3429	0,350	25,9
100	120 002	3 940 299	0,0304	2,9

Magic numbers for *cube-octahedral* structure

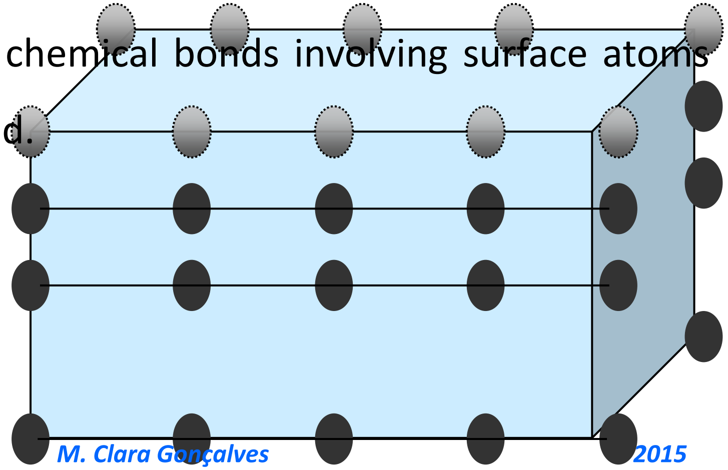
n	N^S Surface atoms	N^I Interior atoms	N^S / N^I	N^S (%)
2	12	1	12	92,3
3	42	13	3,2	76,4
4	92	55	1,6	62,6
5	162	147	1,1	52,4
6	252	309	0,8	44,9
7	362	561	0,6	39,2
8	492	923	0,5	34,8
9	642	1415	0,4	31,2
10	812	2057	0,39	28,3
100	98 000	3 280 000	0,029	3,0

Introduction: Colloidal Particles design

Shape matters

Lattice parameter

Real solids are finite. This is why the chemical environment around surface atoms is different from that around inside atoms. Inside, the attractive forces which act on each atom are isotropic, when observed over time. At the surface, atoms have some of their bonds broken, so their coordination number, CN (the number of closest neighbours), is lower than the CN of inside atoms. The chemical environment around each surface atom is asymmetrical. This asymmetry submits surface particles to a force which works from the outside in; surface atoms are *pulled* towards the inside of the crystal. The length of chemical bonds involving surface atoms is smaller than chemical bonds inside the solid. The high surface/volume ratio of nanoparticles makes the number of chemical bonds involving surface atoms higher, meaning that the lattice constant is appreciably reduced.



Further reading

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- **Sol-Gel Materials. Chemistry and Applications**. J. D. Wright, N. A. J. M. Sommerdijk, Gordon and Breach Science Publishers (2001)
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1.1 Special Ceramic Powders

And now let's see how industry prepare ceramic raw materials!