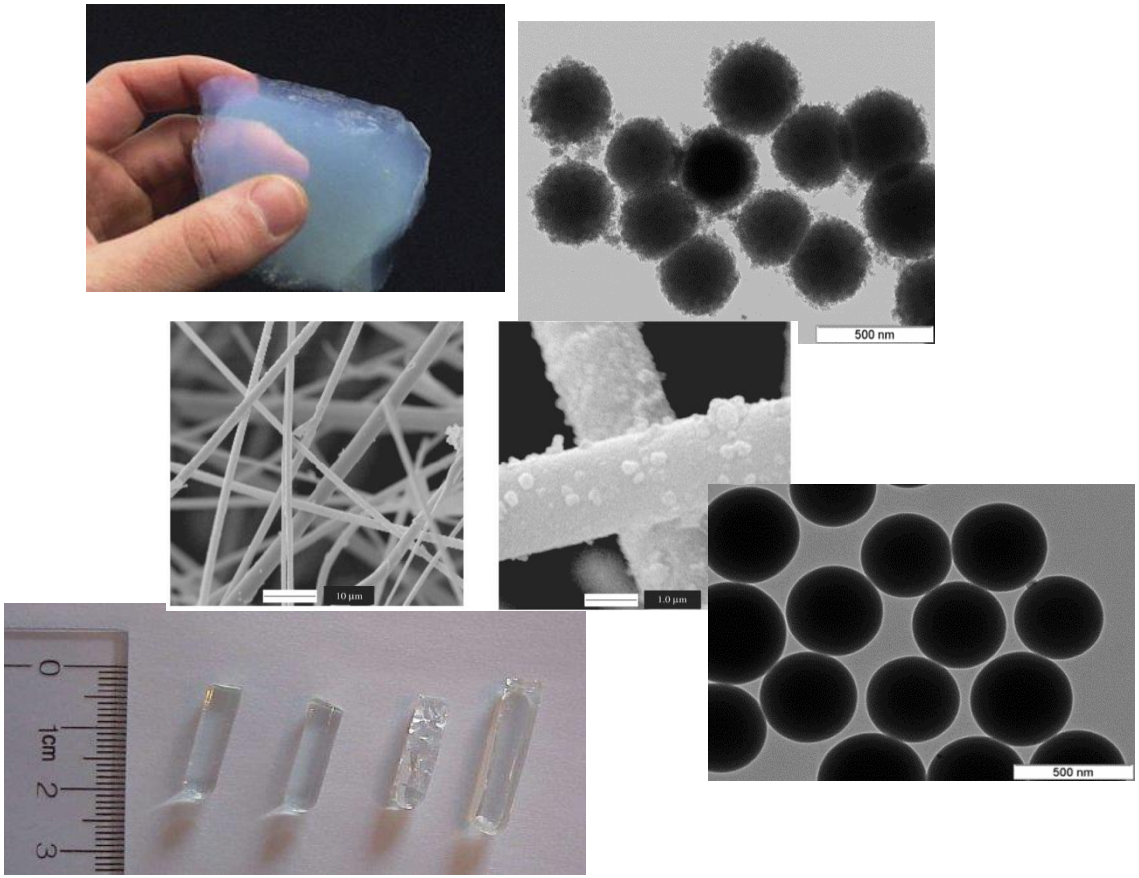
Sol-Gel Process

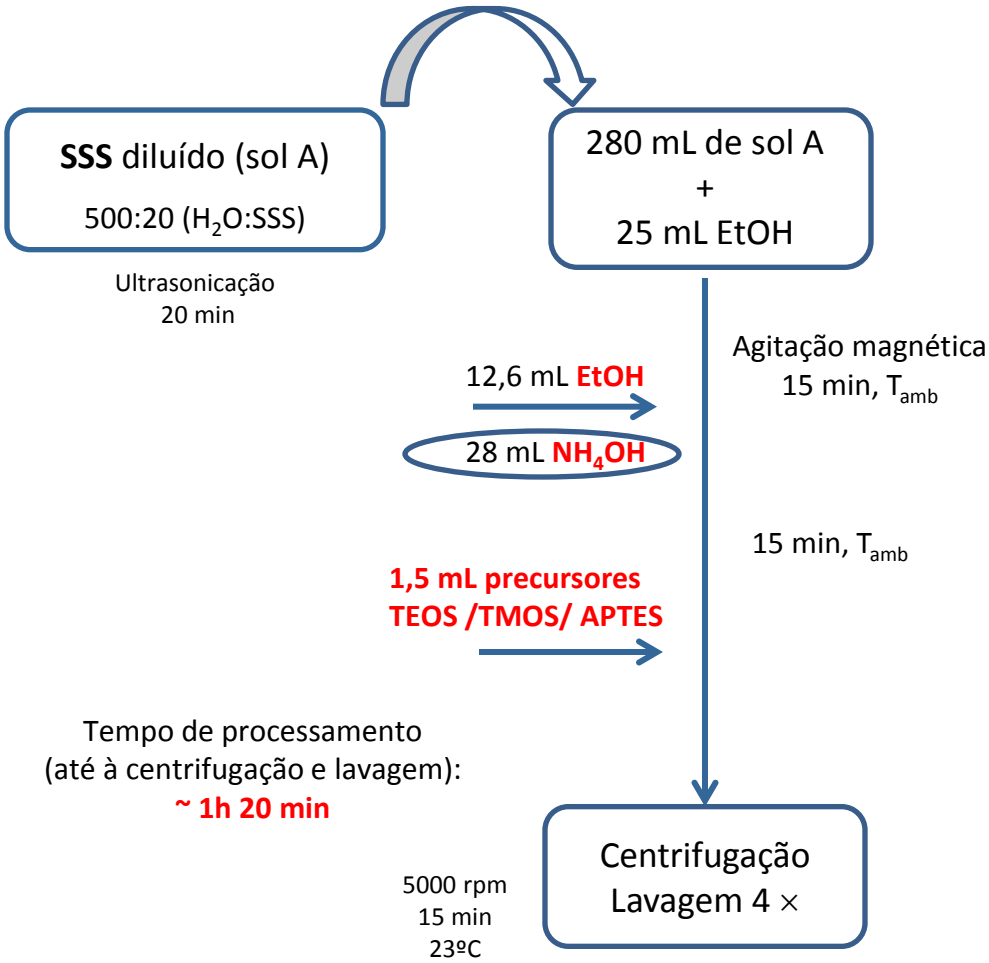


Sol-Gel Process

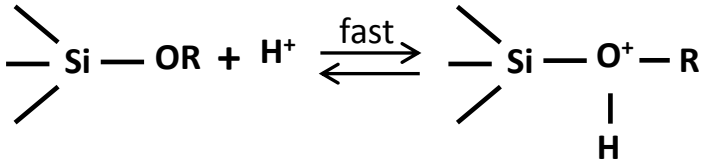
Sol-Gel Process

Via 2, pH ~11

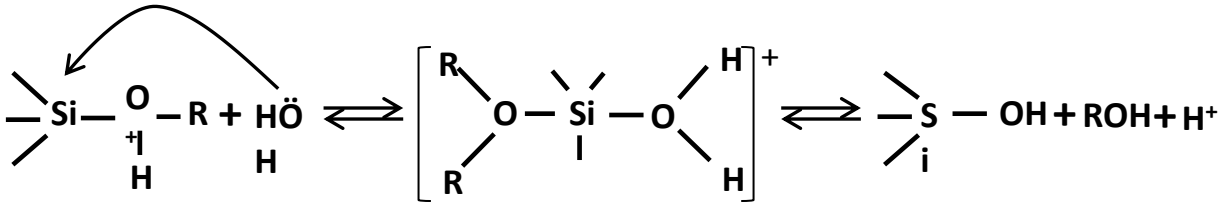
Método de Stöber



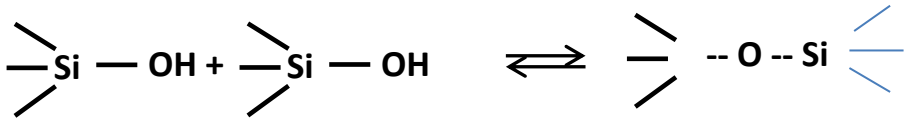
Stöber, Werner; Fink, Arthur; Bohn, Ernst (January 1968). "Controlled growth of monodisperse silica spheres in the micron size range". *Journal of Colloid and Interface Science*. **26** (1): 62–69. doi:10.1016/0021-9797(68)90272-5



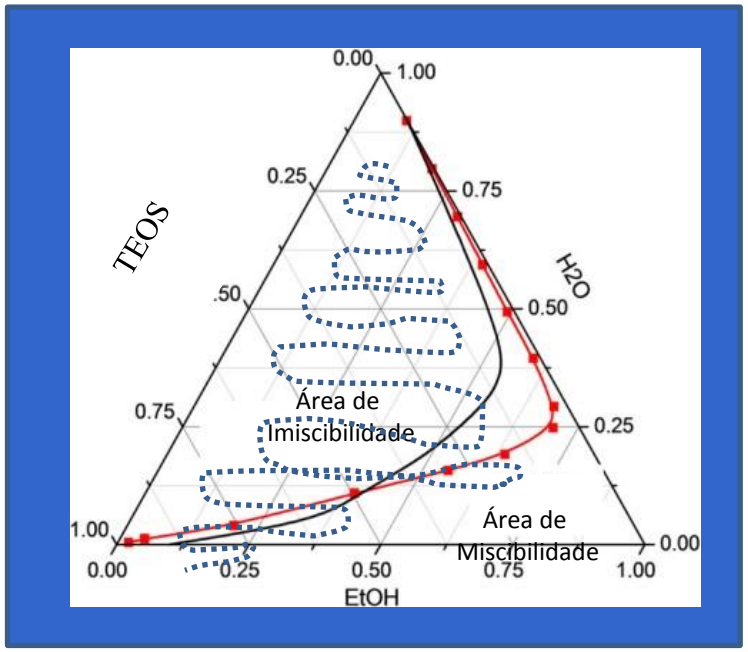
Hydrolysis



Condensation



Si



Sol-Gel Process

Via 2, pH ~11

SSS diluído (sol A)

500:20 (H_2O:SSS)

Ultrasonicação
20 min

280 mL de sol A
+
25 mL EtOH

Agitação magnética
15 min, T_{amb}

12,6 mL EtOH

28 mL NH_4OH

15 min, T_{amb}

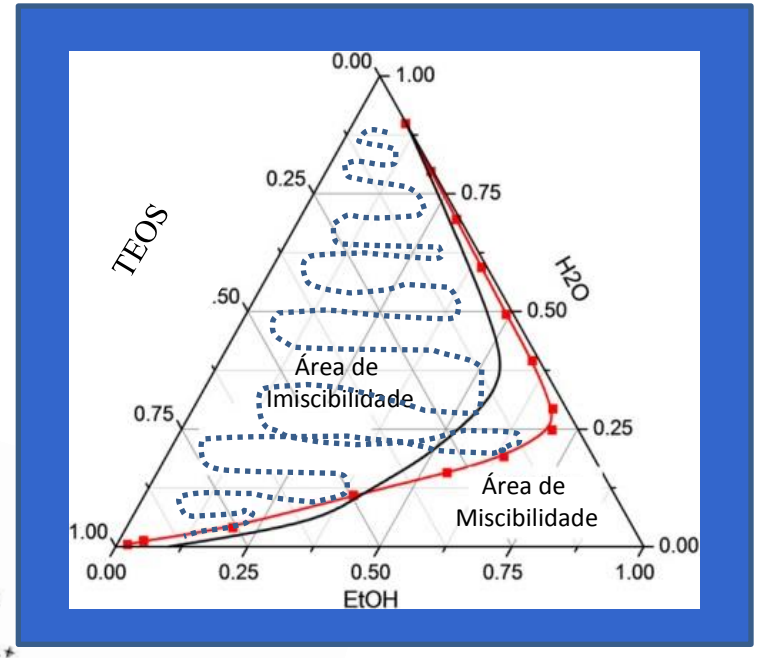
1,5 mL precursores
TEOS /TMOS/ APTES

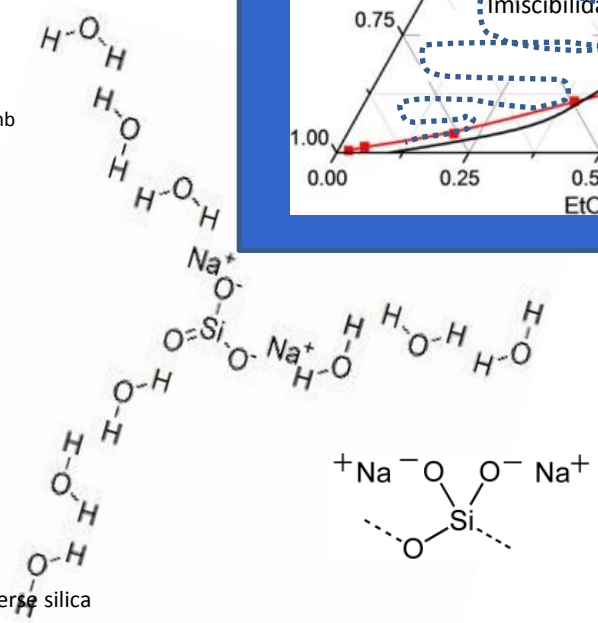
Tempo de processamento
(até à centrifugação e lavagem):
~ 1h 20 min

5000 rpm
15 min
23ºC

Centrifugação
Lavagem 4 ×

Método de Stöber

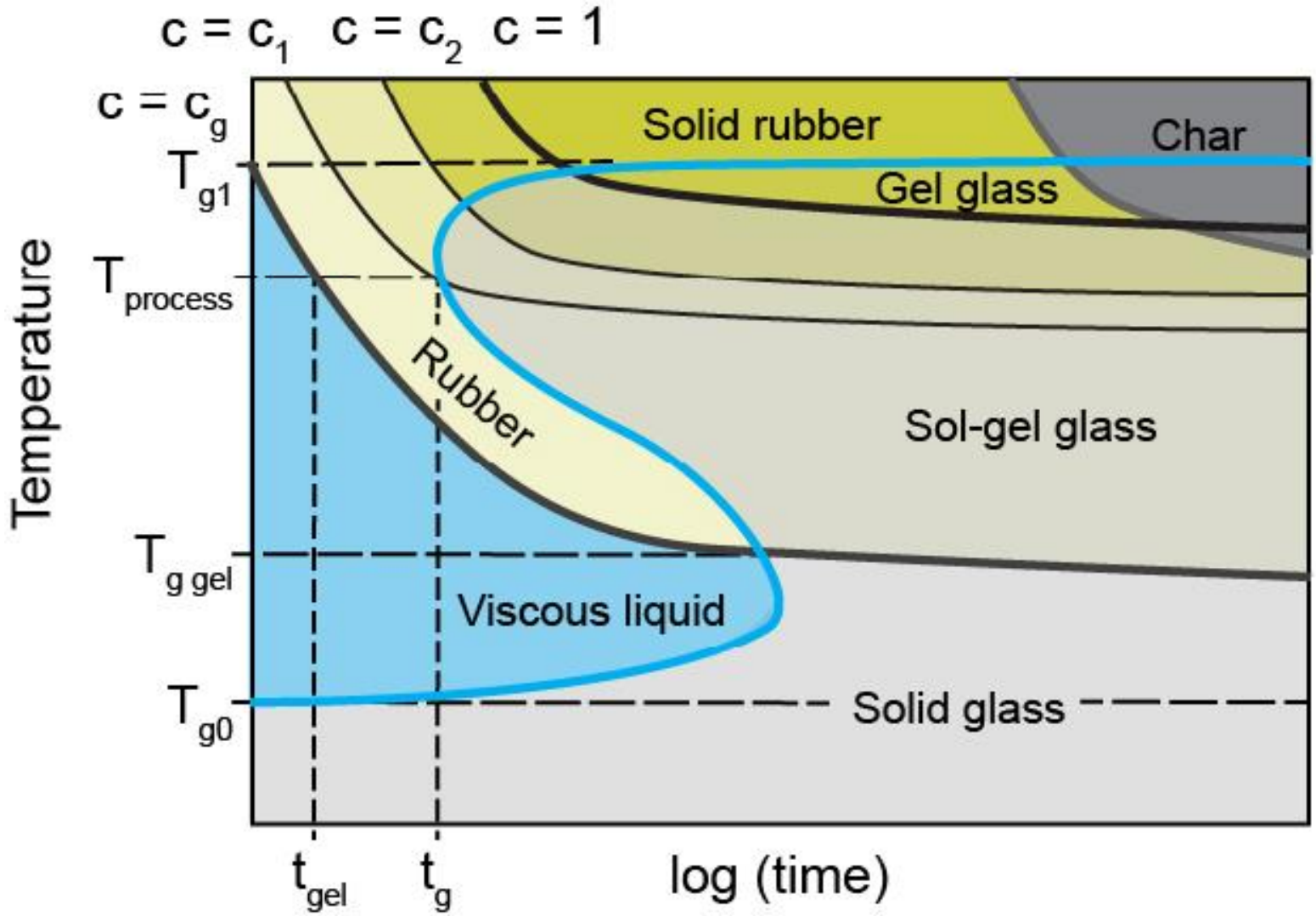


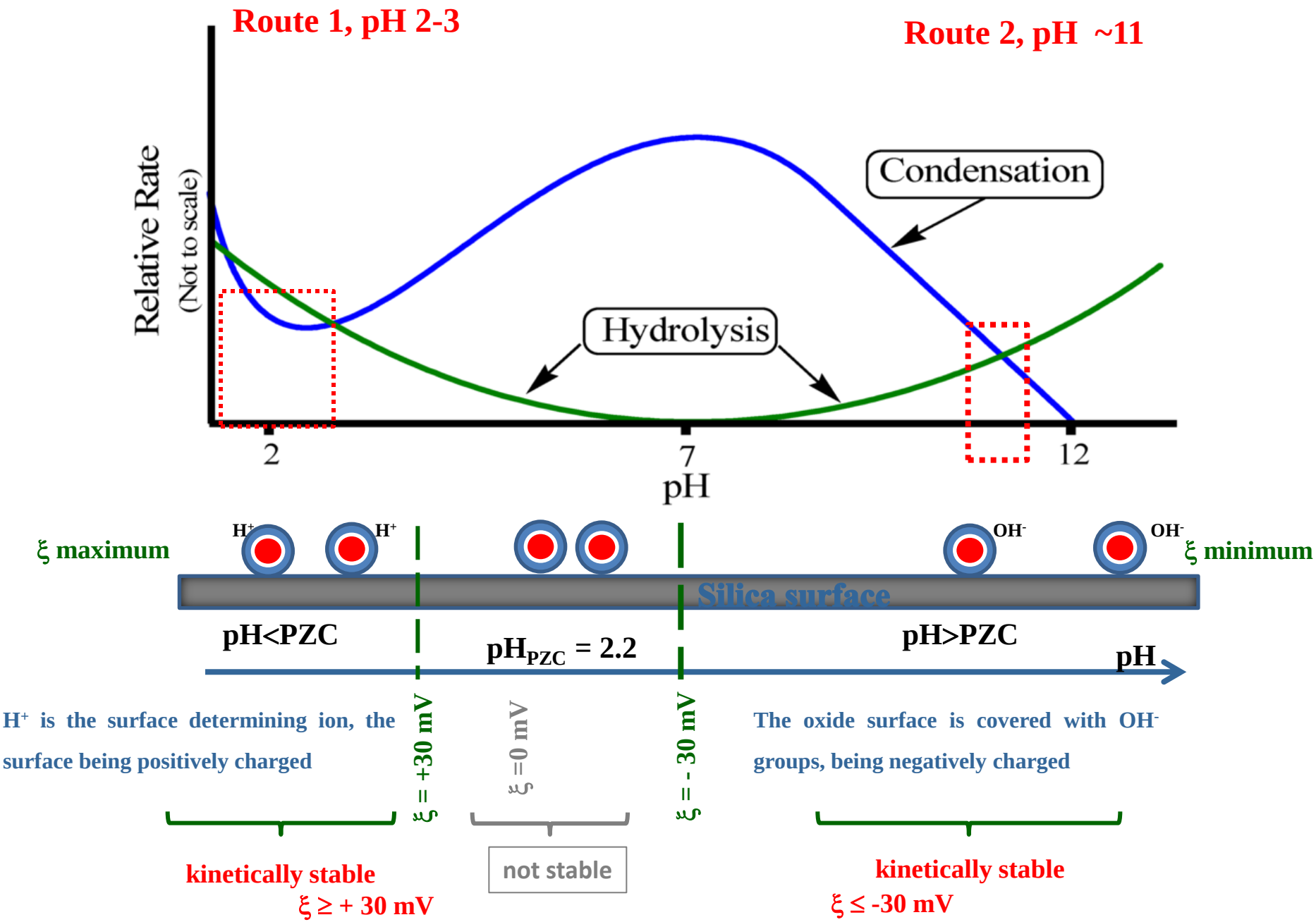


Agente nucleante: solução de silicato de sódio

Stöber, Werner; Fink, Arthur; Bohn, Ernst (January 1968). "Controlled growth of monodisperse silica spheres in the micron size range". *Journal of Colloid and Interface Science*. **26** (1): 62–69. doi:10.1016/0021-9797(68)90272-5

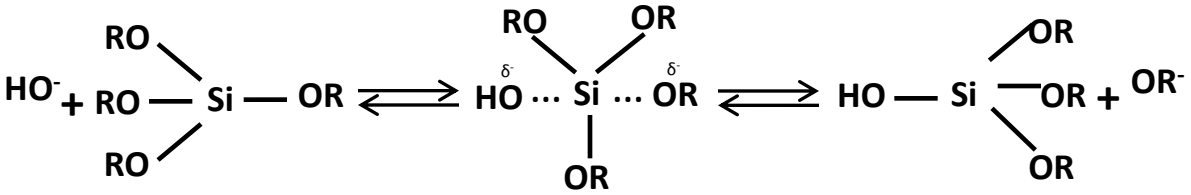
Sol-Gel Process



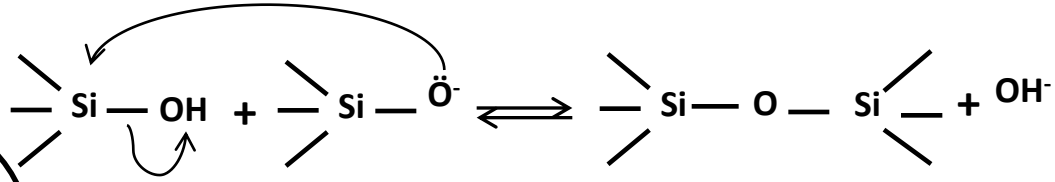

Route 1, pH 2-3
Route 2, pH ~11
Relative Rate
(Not to scale)
Condensation
Hydrolysis
2
7
12
pH
ξ maximum
H+
H+
OH-
OH-
ξ minimum
Silica surface
pH<PZC
pH_PZC = 2.2
pH>PZC
pH
H+ is the surface determining ion, the surface being positively charged
ξ = +30 mV
ξ =0 mV
ξ = - 30 mV
The oxide surface is covered with OH- groups, being negatively charged
kinetically stable
ξ ≥ + 30 mV
not stable
kinetically stable
ξ ≤ -30 mV

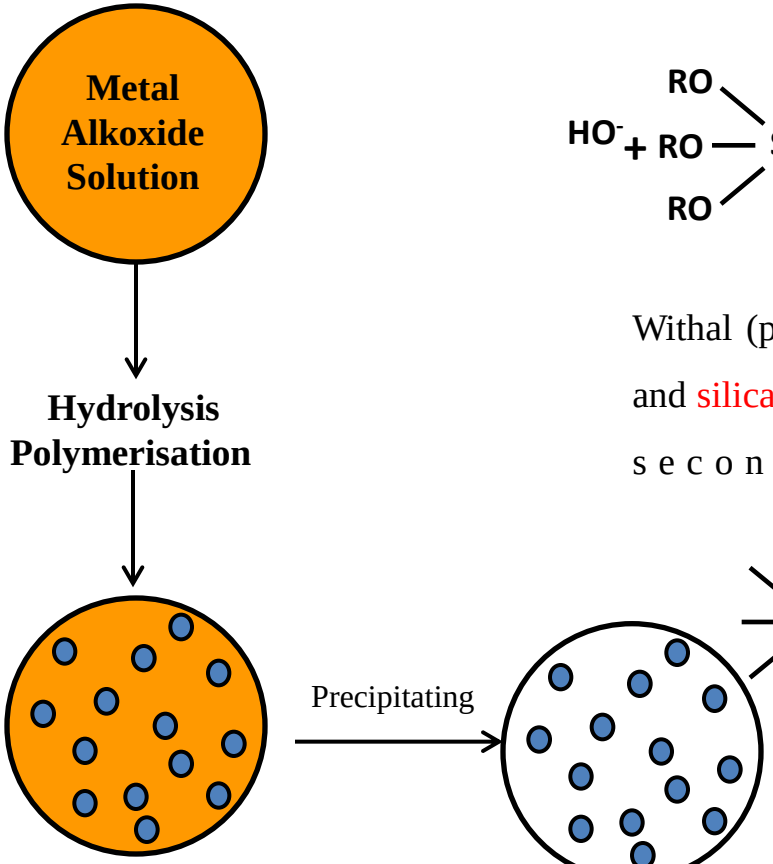
Route 2, pH ~11

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



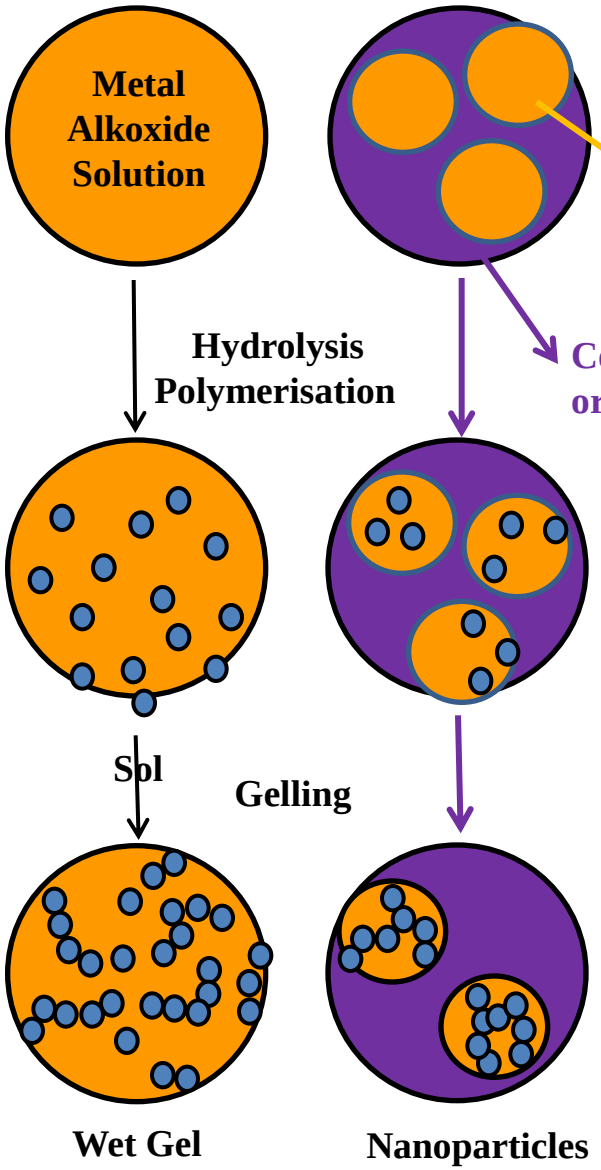
Withal (pH~7) **condensation** (and **dissolution**) reactions become relevant, and silicate monomers start **condensing** before being fully hydrolyzed, by a second nucleophilic attack, according to :





Route 1, pH 2-3

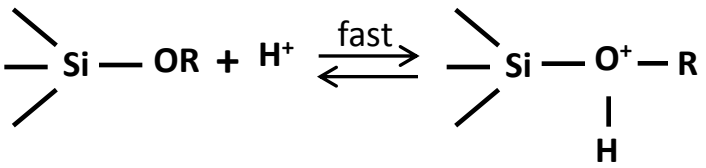
Aqueous suspension Surfactant molecules



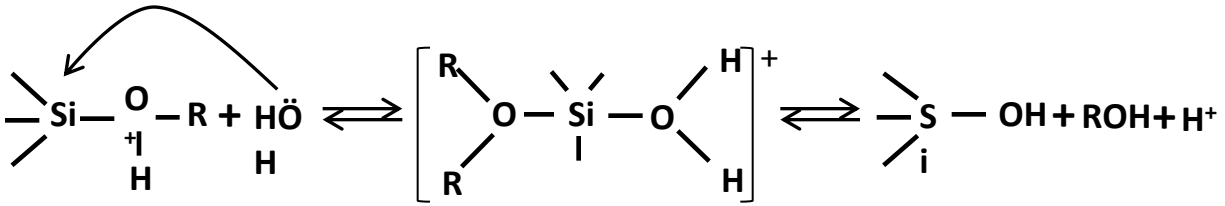
Under acid catalysis the hydrolysis is performed by electrophilic attack. At **pH** values as low as **2-3**, complete hydrolysis developed, producing linear or highly branched polymeric species, with **a 3D fractal structure**.

Water-in-oil microemulsion
(reverse micelle nanoreactor)

Continuous organic phase



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).



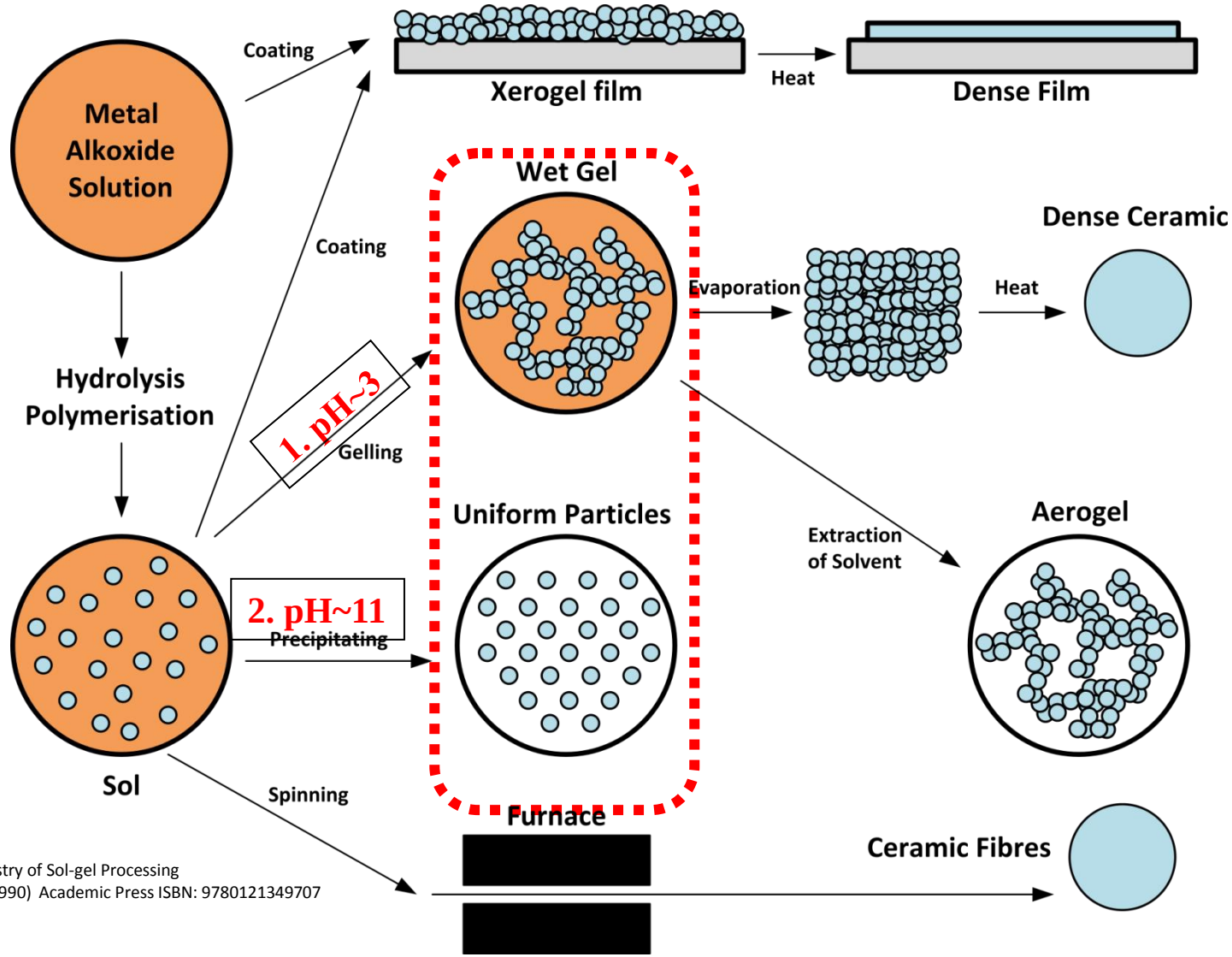
Top-down

- lithography
- wet ball milling

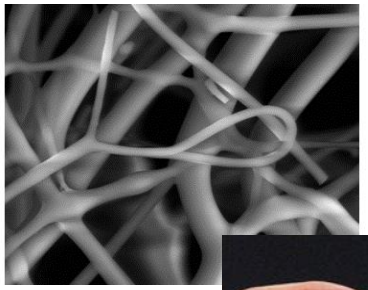
Bottom-up

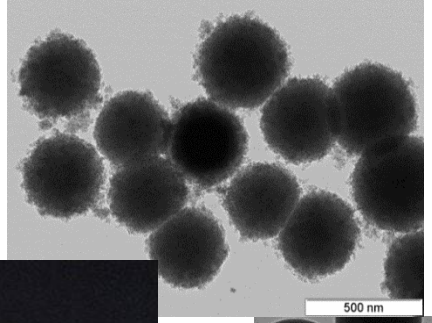
- precipitation
- hydrothermal
- sol-gel

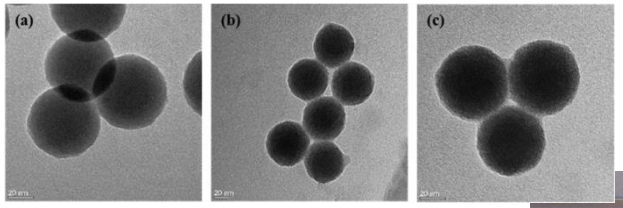
Why sol-gel?

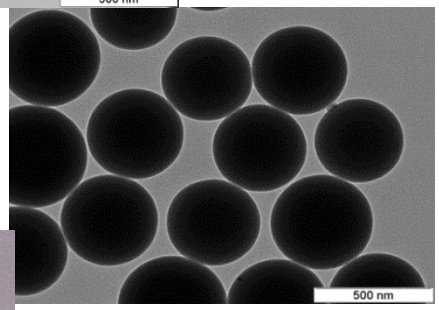


Sol-Gel Science: The Physics and Chemistry of Sol-gel Processing
C. Jeffrey Brinker, George W. Scherer (1990) Academic Press ISBN: 9780121349707



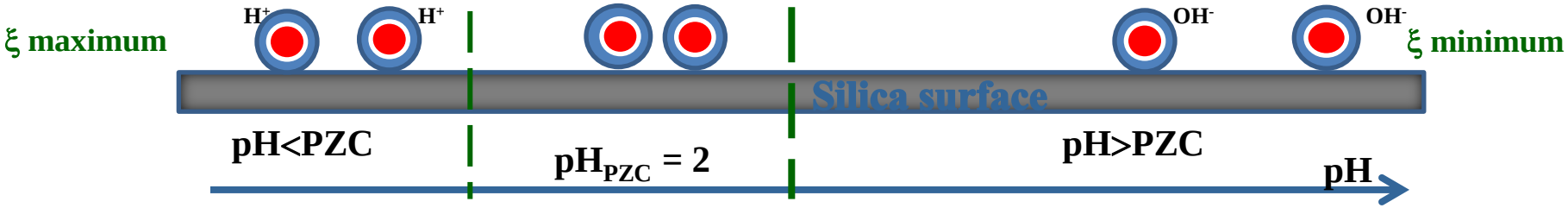






pH<3

pH>9



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

$\xi \geq +30$ mV

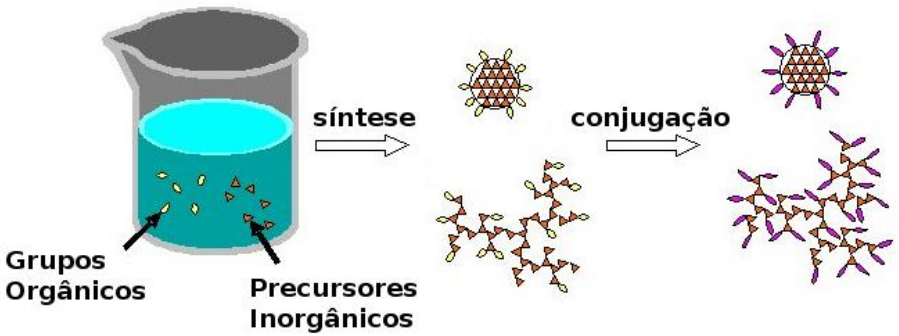
not stable

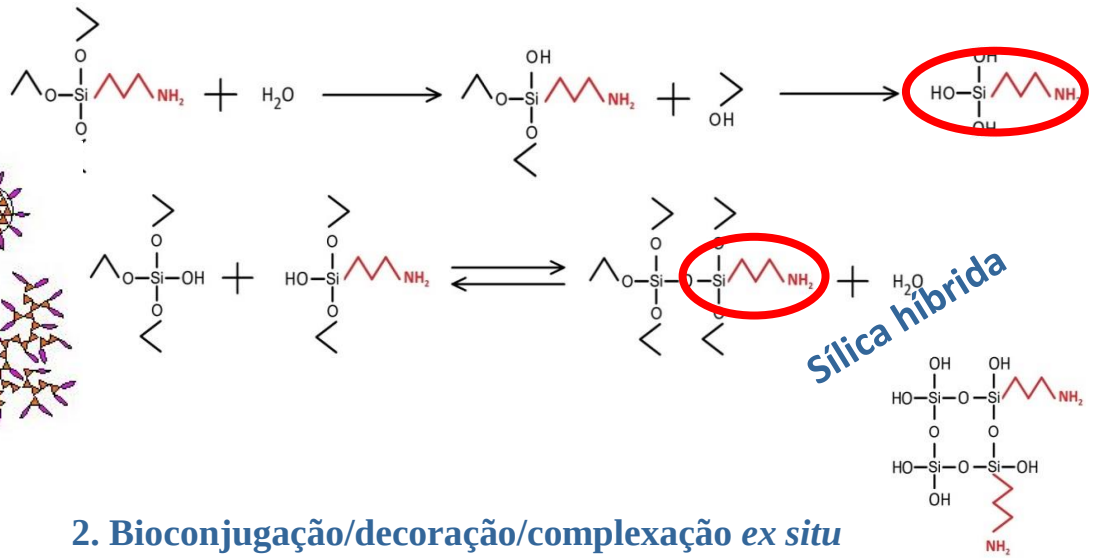
kinetically stable

$\xi \leq -30$ mV

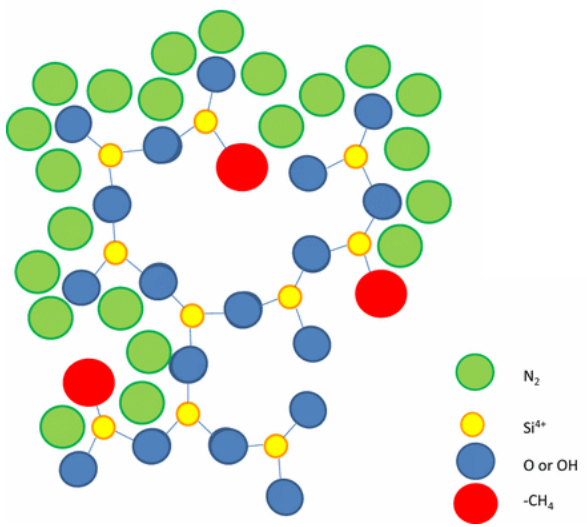
Sol-Gel Process

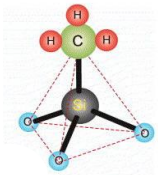
1. Funcionalização *in situ*

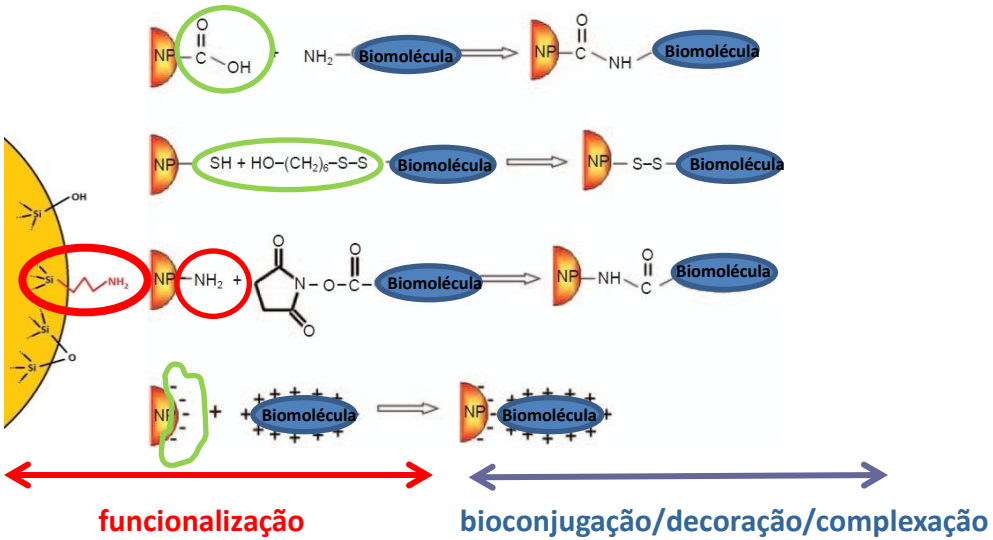




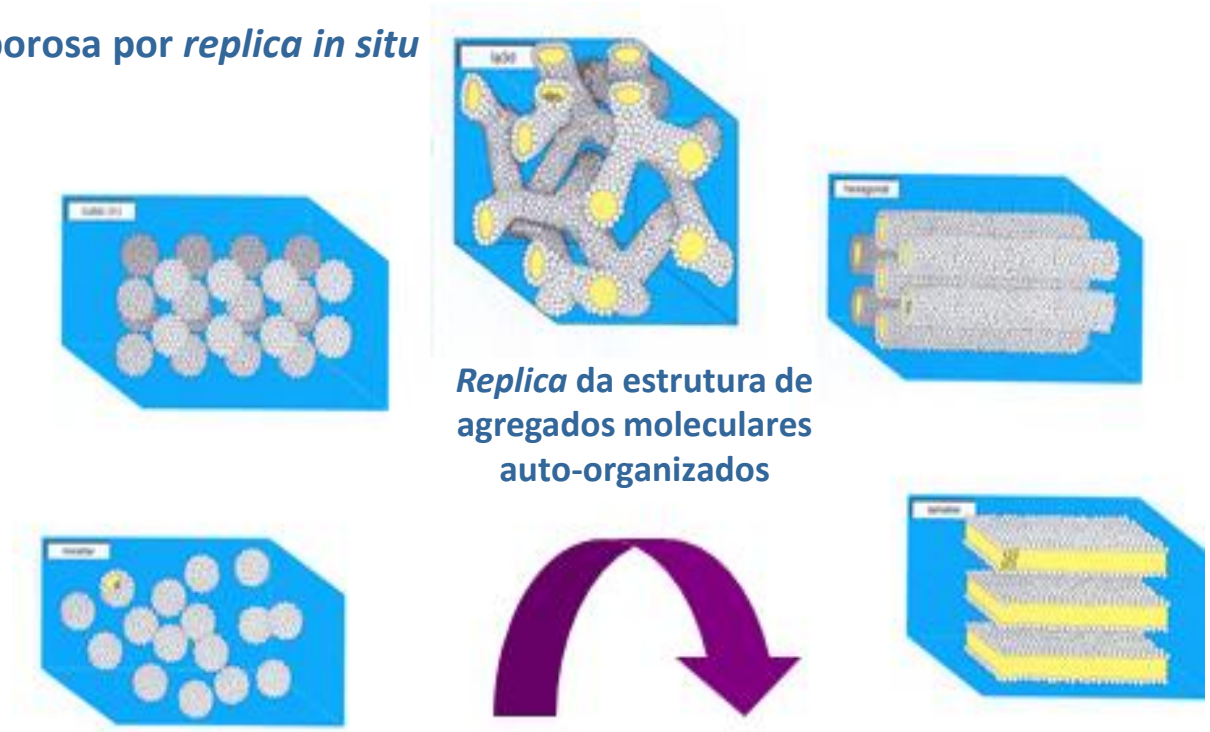
2. Bioconjugação/decoração/complexação *ex situ*





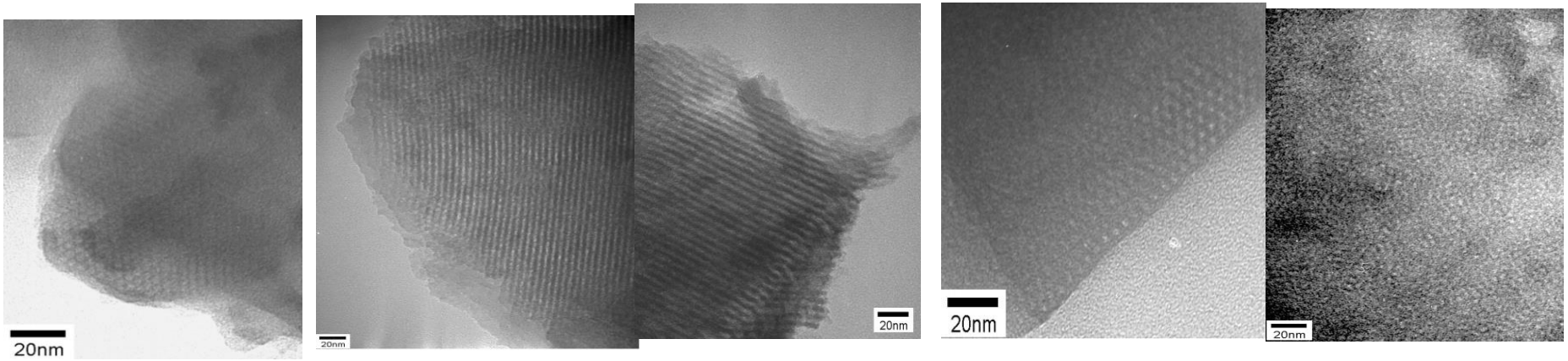


3. Sílica mesoporosa por *replica in situ*

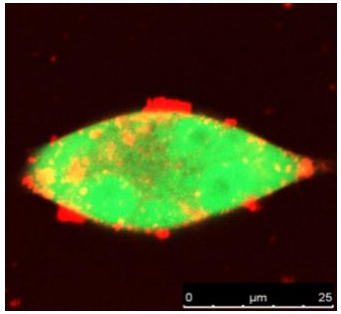


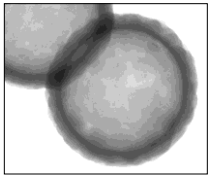
Replica **da estrutura de agregados moleculares auto-organizados**

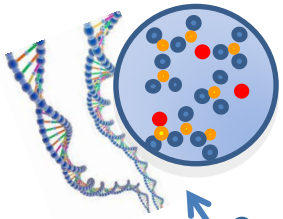
a-SiO_2 inorgânicos

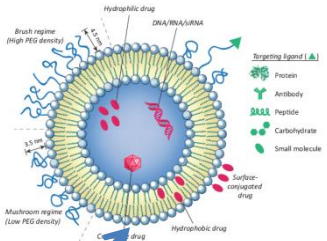


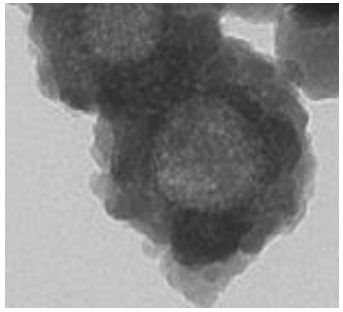
Cases studies







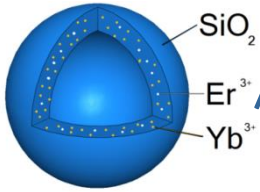




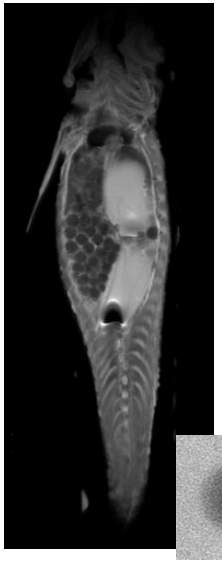
Gene

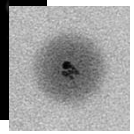
Anfifílic

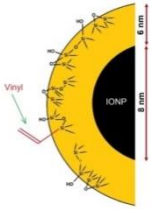
Drug delivery



Fluorescence

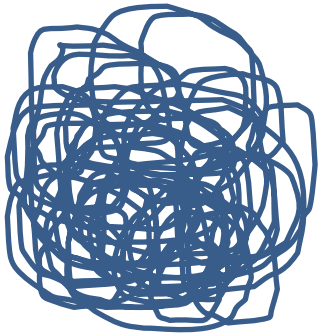






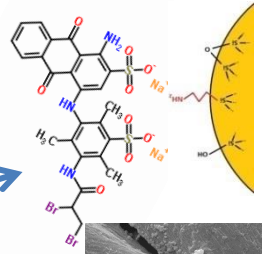
IRM

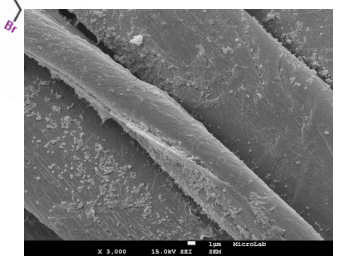
Bioimagiolo

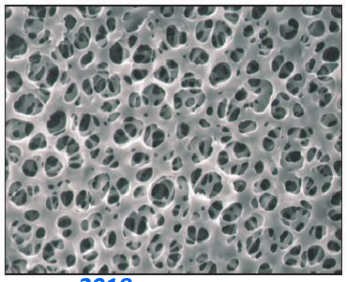


Silica NPs formulation

Transdermal







Further reading

- **The Coloidal Domain. Where Physics, Chemistry, Biology, and Technology.** Meet. D. F. Evans, H. Wennerstrom, Wiley-VCH (1999)
- **Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing**. C. Brinker George Scherer, Academic Press (2013)
- **Sol-Gel Materials. Chemistry and Applications**. J. D. Wright, N. A. J. M. Sommerdijk, Gordon and Breach Science Publishers (2001)
- **Sol-Gel Silica Nanoparticles in Medicine: A Natural Choice. Design, Synthesis and Products.** M.C. Gonçalves *Molecules* 2018, *23*(8), 2021; https://doi.org/10.3390/molecules23082021
- **Photonic Band Gap and Bactericide Performance of Amorphous Sol-Gel Titania: An Alternative to Crystalline TiO_2.** M. C. Gonçalves, J. C. Pereira, J. C. Matos, H. C. Vasconcelos *Molecules* 2018, *23*(7), 1677; https://doi.org/10.3390/molecules23071677