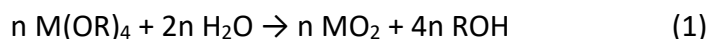


## Laboratory

### Preparation of silica nanoparticles by the sol-gel method

#### The sol-gel method

Sol-gel methods use metal alkoxide precursors to produce a metal oxide according to the overall reaction



For silica, R is usually an alkyl group and the M is Si. In this case the precursors are tetraalkoxysilanes (such as tetramethoxysilane, TMOS, or tetraethoxysilane, TEOS).

The precursors are hydrolyzed and polymerizes by a condensation mechanism, to form a colloidal solution (a sol), that evolves to a network (or gel) of amorphous material (silica, in this case). The hydrolysis can occur under acid catalysis (at  $\text{pH} < 2$ , Figure 1) or base catalysis (at  $\text{pH} > 2$ , Figure 2). The crossover at  $\text{pH} = 2$  corresponds to the isoelectric point of silica, where silica has no electric charge and the reaction rates are extremely low.

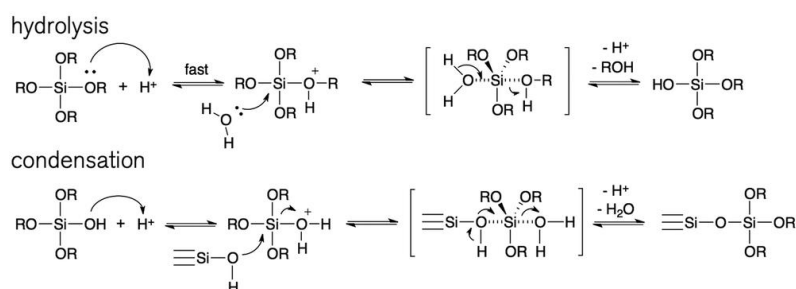


Figure 1. Mechanism of silica formation by acid catalyzed hydrolysis and condensation of alkoxysilane precursors.

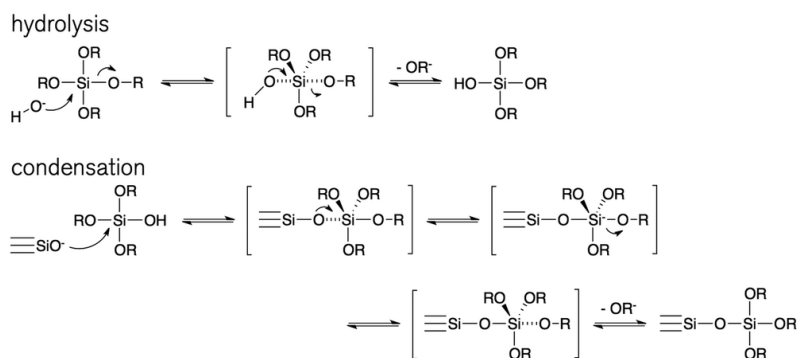


Figure 2. Mechanism of silica formation by base catalyzed hydrolysis and condensation of alkoxysilane precursors.

Although the overall reaction (1) suggests that two equivalents of water produce one equivalent of silica ( $\text{SiO}_2$ ), in practice this is usually not the case. Depending on the reaction conditions, a significant amount of incompletely condensed  $\text{SiOH}$  and/or  $\text{SiOR}$  species can be present in the

structure. This is related to the porosity of the final material. The degree of condensation can be partially controlled by the synthetic conditions (temperature, solvent used, amount of water, etc.) or by post-synthetic modifications to increase condensation.

### Experimental procedure

Silica nanoparticles will be synthesized by a sol-gel method first described by Stöber, under base catalyzed reaction conditions.

1. Add the appropriate amount of water, ethanol and ammonia solution in a polypropylene flask as described in Table 1.
2. Put the bottle with a magnetic stirrer in an oil bath at a desired temperature (Table 1), under gentle stirring.
3. When the temperature of the oil bath is stable, add the TEOS (Table 1).
4. Let the reaction proceed for 1 hour.

**Table 1**

Group	T (°C)	H <sub>2</sub> O	Ethanol (absolute)	NH <sub>4</sub> OH 28%	TEOS
		m (g)	m (g)	V (mL)	V (mL)
1	30	11,028	53,179	2,386	4,460
2	30	11,028	53,179	1,350	4,460
3	40	11,028	53,179	2,386	4,460
4	40	11,028	53,179	1,350	4,460
5	50	11,028	53,179	1,350	4,460
6	50	11,028	53,179	2,386	4,460
7	60	11,028	53,179	2,386	2,230
8	60	11,028	53,179	2,386	4,460
9	70	11,028	53,179	2,386	2,230
10	70	11,028	53,179	2,386	4,460

### Characterization of the nanoparticles

The particle size and size distribution will be determined using three complementary techniques. Dynamic Light Scattering (DLS) and Nanoparticle Tracking Analysis (NTA) are scattering techniques that measure the diffusion coefficient of the nanoparticles in a liquid. From this, it is possible to obtain the size of the particles using Stokes-Einstein equation. While DLS retrieves the diffusion coefficient distribution from the overall correlation curve for the particle ensemble, in NTA one measures the diffusion coefficient of the particles individually, and constructs the size distribution curve from these.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) will also be used, not only to image the nanoparticles, but also to measure their size distribution using image analysis software (suggested software: <http://fiji.sc/Fiji>).

## **References**

J. W. Kim, L. U. Kim, and C. K. Kim, *Biomacromolecules* **2007**, 8, 215-222.

W. Stöber and A. Fink, *J. Colloid Interface Sci.* **1968**, 26, 62-69.