

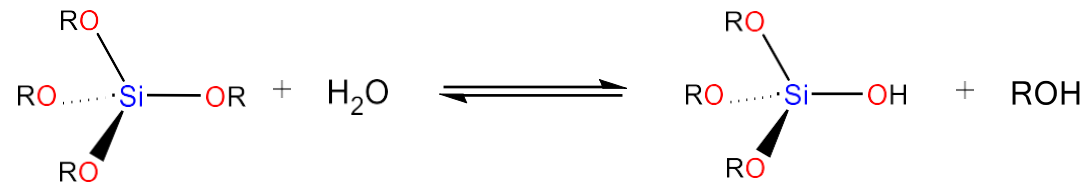
Ceramics: Silica and Polysilsesquioxane Sol-Gels

- Please print references or bring your laptop for access to all listed references during lab
- Reference information is provided at the end of this manual and on the course website

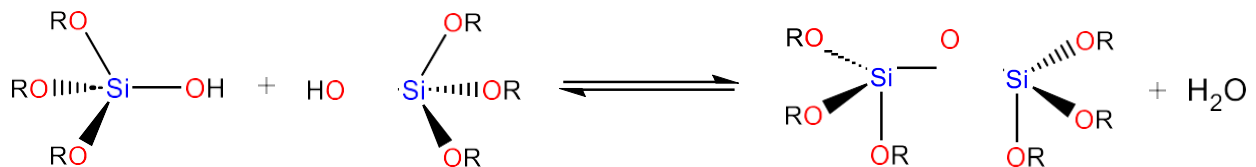
Introduction

Sol-gels are special **solutions** that have the potential to turn into **gels** via polymerization. The transition is marked by a dramatic increase in viscosity. The sol-gel reaction can be catalyzed under acidic or basic conditions that initiate the sequential reactions depicted in Figure 1 of hydrolysis and condensation polymerization. The most popular sol-gel is made up of silicon dioxide (SiO_2) in which a silicon atom is covalently bound to four oxygen atoms. The main goal during polymerization is to form the siloxane (Si-O-Si) bond over and over again. As the reaction persists, the number of siloxane bonds will increase and the network will grow into a particle during nucleation and growth processes, Figure 2. Once polymerized, the network may resemble a disordered or cage structure on a molecular level and this is known as an amorphous polysilsesquioxane, Figure 2. The continued polymerization results in solid particles that can range in size from nanometers to microns. The particles are initially free-floating in solution and this is known as colloidal formation. When the particles are numerous enough or become large enough, they may run into each other and bond, eventually forming a larger network, which we observe as a gel. The conditions of the polymerization and stability of particles in solution will determine if a gel is obtained.

Hydrolysis - silicon reaction with water



Condensation - reaction of two -OH groups to form siloxane bond and water as a by-product



Net Reaction - water reacts with silicon based monomer unit to form a siloxane network (polymer) that grows into what we observe as particles and potentially gels

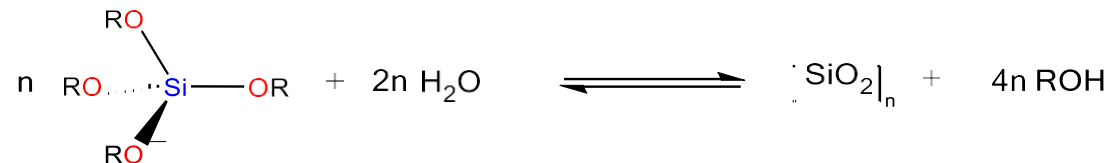


Figure 1. Chemical Reactions of Silica Sol-Gel. May be acid or base catalyzed.

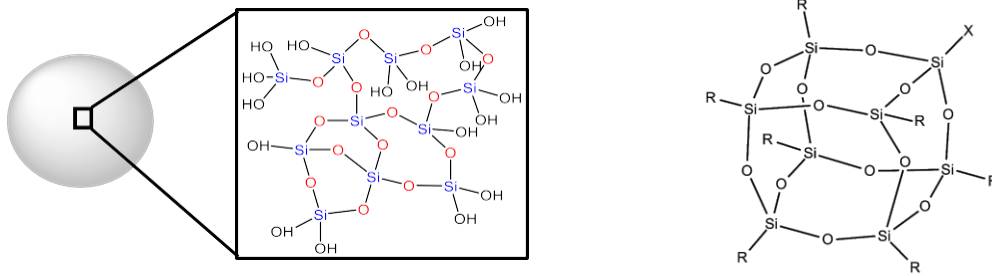


Figure 2. Silica nanoparticle and amorphous molecular structure of silica network and polysilsesquioxane 3D cage

Sol-gels can be thought of as precursors to ceramics but are useful substances in their own right because many of their properties can be tuned for a variety of applications. Other metals such as aluminum, iron and titanium may also be used in place of silicon, each having their own unique properties and applications. Some applications for silica particles are for purification of a chemical during column chromatography, chemical sensing, surface coating, or to host other molecules for catalysis or catch-and-release mechanisms. In this lab, you will be synthesizing your very own silica sol-gels. You will see gelation occur and then modify synthetic variables to make large or small silica particles, which could result in colloidal solutions, aggregated particles or even uniquely designed hard or glassy xerogels!

Going beyond the basic sol-gel, silica particles can be tailored for a particular application through chemical modification with a specific group of atoms bonded to each other (known as a functional group). This heavily applies to the area of organic chemistry. Modifying the silica with organic functional groups is known as making an ORMOSIL, organically-modified-silica. Researchers, including those at UCI, use this method of functionalization in their experiments and it could be useful for future research that you might conduct too!

In this lab, you will also synthesize different types of ormosils shown below in Figure 3 and compare their properties. Notice that each group contains different organic groups with some functional groups actually acting as bridges between two different silicon atoms. These groups are known as bridged polysilsesquioxanes (BPS). BPS materials are monomers that can be polymerized similarly to silica, but their added organic group provides additional properties, which you will investigate.

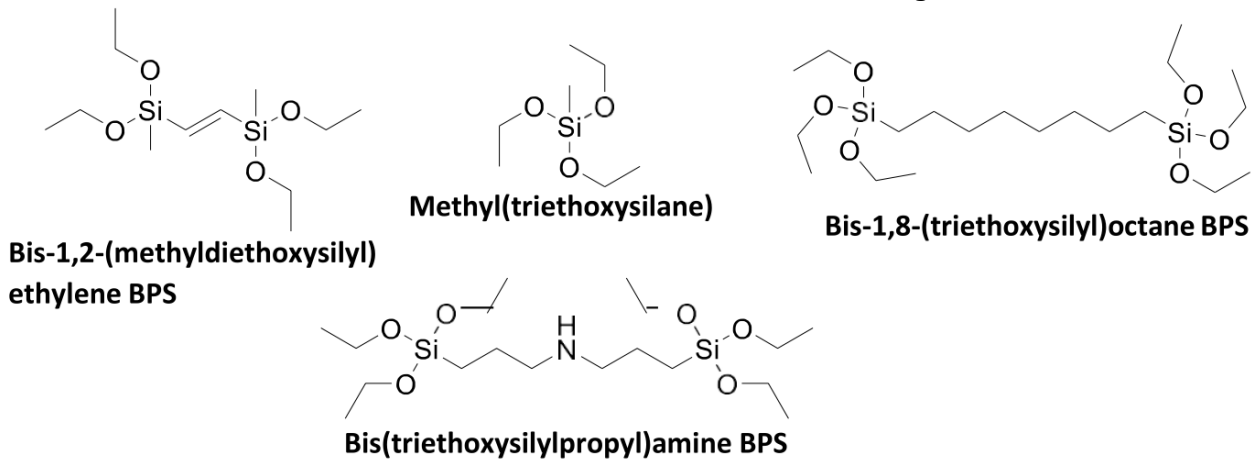


Figure 3. Ormosil polysilsesquioxane and bridged polysilsesquioxane monomers

Objective

In this lab, you will receive an introduction to the synthesis of silica particles, the Stöber synthesis method, tuning particle size and observing a change in particle functionality with the polymerization and processing of an ormosil.

It is the goal of this lab for you to be able to observe and characterize the materials you make during the sol-gel process and determine how they can be manipulated to give different properties with a variety of potential applications.

Equipment & Materials for Synthesis

Part One

- 4 10 mL plastic vials
- 4 stir bars
- Stir plate
- Sample rack
- Micropipette
- Tetraethylorthosilicate (TEOS)
- Ethanol (EtOH)
- Ammonium Hydroxide (NH₄OH)
- Parafilm
- DI water

Part Two

- 2 10 mL plastic vials
- Stir bar
- Stir plate and sample holder
- 0.12 M Hydrochloric Acid
- Micropipette

Methods

Part One - Silica Nanoparticle Synthesis

This component will consist of synthesis of silica nanoparticles and control of particle size by varying synthesis conditions. You will be making systematic changes to the procedure below to arrive at samples with different and distinct/uniform particle sizes. The size of particles will determine their opacity, surface area, overall applications and how they can be processed. Having a uniform particle size throughout the sample, monodispersity, is essential to having exact, reproducible and reliable particle properties. A general Stöber synthesis procedure is given below to make **660** nm monodisperse silica particles.

Procedure

1. *To a polypropylene tube, add ethanol (1.34 mL, 22.4 mmols) and TEOS (250 μ L, 1.1 mmols). Add a small stir bar and start stirring this solution with visible vortex on a stir plate, situated in a sample rack. Then add the 7 M ammonium hydroxide catalyst (aq) (2.4 mL, 16.7 mmols). Allow this solution to react at room temperature (RT) for 48 hrs. Make observations when appropriate.*
2. *Centrifuge particles at 4000 rpm for 1 minute to separate the solution from the nanoparticles. Wash the particles three times with ethanol to remove residual reaction mixture and unreacted components. Dry under vacuum at room temperature overnight or under heat and vacuum to reduce drying time.*

Your job is to synthesize **four samples of differently sized particles** using the general Stöber method. You must be systematic in your approach as you must experimentally determine and **explain at least two trends you observe for controlling particle size**. Reference materials come in handy here for ideas!

You are allowed to:

- vary the molar ratio of the reagents: TEOS, ethanol, water which are pure substances, not solutions
- vary the molarity of the catalyst (upper limit is 14.5 M)
- determine how you would like to process your sample (ex. heat in oven at 60°C, leave at RT)
- determine how fast or how long you would like to mix your sample
- determine when you would like to add the reagents. Which component should you add last? (Make sure you know this answer before you start your synthesis)

You are limited by:

- You must use the general Stöber chemical reaction above (all reagents must be used)
- You must make a total of 4 samples and cannot go above this number. It is possible to collaborate with another group in order to increase your sample size to observe the two trends, but you are responsible for reporting all synthesis completed, predictions and data obtained for those samples.
- The total volume is capped at 5 mL
- The reaction may take place at RT or 60°C
- Unless it gels or you choose to stop stirring, your solution will be mixing for 24 hrs and then ageing for 24 hours
- You must react your sample for at least 1 hr before any processing may begin

Record your expectations in terms of appearance and relative particle size during experimentation to compare with actual results in your report. We will be analyzing the particles via SEM (Scanning Electron Microscopy) next week, so you have some time to figure out what you would like to do and make changes.

*It would be a good idea to make a group plan and discuss how you expect certain variables to change the particle size beforehand. This discussion and group decision-making as well as calculations should be where you focus your time as the actual synthesis is quite simple in most cases.

**You will not be graded on the accuracy of your predictions of particle size, but your logic in terms of comparing the relative size of your samples and the trends you observe versus those predicted.

Analytical Methods for Part 1

Dynamic Light Scattering (DLS)

X-Ray Diffraction (XRD)

Scanning Electron Microscopy (SEM)

Part Two - ORMOSIL – Organically-Modified-Silica Xerogels

Group 1 - Methyl(triethoxysilane) (MW: 178.30 g/mol, d: 0.895 g/mL)

Add 0.925 mL of 0.12 M HCl to each of two 5 mL vials with stir bar, followed by 0.555 mL of propanol to each as well. Add your monomer (0.0046 moles, 0.925 mLs) to the stirring solutions and allow the reaction to persist for 60 minutes at room temperature.

Group 2 - 1,8-bis(triethoxysilyl)octane (MW: 438.75 g/mol, d: 0.926 g/mL)

Add 0.925 mL of 0.12 M HCl to each of two to 5 ml vials with stir bar, followed by 0.555 mL of propanol to each as well. Add your monomer (0.0046 moles, 2.2 mLs) to the stirring solutions and allow the reaction to persist for 30 minutes at room temperature.

Group 3 - 1,2-bis(methyldiethoxysilyl)ethylene (MW: 292.52 g/mol, d: 0.918 g/mL)

Add 0.925 mL of 0.12 M HCl to each of two 5 ml vials with stir bar, followed by 0.555 mL of propanol to each as well. Add your monomer (0.0046 moles, 1.48 mLs) to the stirring solution. Allow the reaction to persist for 60 minutes at room temperature.

Group 4 - Bis-(3-triethoxysilylpropyl)amine (MW: 425.71 g/mol, d: 0.97 g/mL)

Add 0.925 mL of 0.12 M HCl to each of two 5 ml vials with stir bar, followed by 0.555 mL of propanol to each as well. Add your monomer (0.0046 moles, 2.02 mLs) to the stirring solution. Allow the reaction to persist for 30 minutes at room temperature.

All Groups

1.1 M NH₄OH is added to the vials in 1 mL aliquots. These vials are tightly capped and mixed via vortex for one minute. The vials are secured in housing and allowed to age at room temperature for one day. Your instructor will remove the lids after 24 hrs to allow samples to dry until the next lab period. Observe any changes in samples throughout the lab period and upon arrival of the next lab period.

Next week - All Groups

Remove samples from vials and place into glass dishes. Observe their appearance. Your instructor will cut your samples into sections for characterization and testing of contact angle, swelling behavior, and chemical composition.

Sinter: Samples will be placed in sintering boats and heated to 450 C at 5 C/min and held for 3 hours. Your instructor will assist with the oven. Make observations before and after.

FTIR: Using your solid samples, you will determine the functional groups present in your samples before and after sintering. The samples should be in gel or powder form for this test. Make use of the online reference for analysis.

Contact angle: After sintering, if your sample is mechanically robust, grind it to flatness and measure contact angle. If this is unfeasible, grind up 50 mg of sample with a mortar and pestle, disperse in ethanol, and drop cast onto glass slides. Take contact angle measurements once the ethanol evaporates.

Swelling Density Test: This test will help determine if there is any change in sample density based on exposure to certain liquids (aqueous or organic) after sintering experiments. You will have a vial for water and a vial for Sec-butanol in the chemical fume hood. You will also have vials containing each of your samples for the swelling test.

Determine the weight and volume of your sample before the swelling test via caliper measurement and calculation of density (mass/volume). Place the sample in the testing solvent for 10 minutes. Make observations. Place the sample back into its original vial, tapping off any residual solvent into the solvent vial, and reweigh the sample vial. Carefully measure the volume of the sample.

Sample	aqueous	organic
Initial sample radius		
Initial sample height		
Initial sample volume		
Initial sample density		
Initial sample weight		
Initial solvent weight		
Final solvent weight		
Final sample weight		
Final sample radius		
Final sample height		
Final sample volume		
Final sample density		
Percent density change		
Observations		

Data Exchange: After your analysis, exchange swelling test and contact angle data between groups. You will use this data to compare properties attributed to chemical composition of the materials tested.

Analytical Methods for Part 2

Contact angle/hydrophobicity testing

FTIR

Swelling Density test

Analytical Methods Briefly Defined

SEM - Scanning Electron Microscopy - Different than SAXS, SEM can be used to study the local characteristics of a surface. You will need to pay attention to particle size and any observable porosity/surface characteristics of your samples with this technique. You will need to download ImageJ

software in order to analyze the images for your report. The instructor will go over this with you in class.

DLS - This technique will be used to determine the size of your particles

FTIR - This technique is a quick way to determine the organic functional groups present in your sample or lack thereof. It does not show how these groups are bonded, which you can use Nuclear Magnetic Resonance Spectroscopy for, but is a great confirmation test for seeing groups of organic species. This will be our primary means of observing the effects of sintering on chemical species in your samples.

Swelling Density Test - This is an easy test for the observation of the behavior of your samples before and after sintering in terms of how they respond to organic versus aqueous environments and why. It is also important to understand the implications of their behavior.

Contact Angle/hydrophobicity - We will look at the xerogels and determine if the surface chemistry of the material has changed at the solid-liquid interface due to sintering and what significance this bears.

References

1. *Sol-Gel Preparation of Silica*. J. of Chem. Ed. **1994**, 71, 7.
2. *Preparation of Spherical Silica Nanoparticles: Stober Silica*. J. Am Sci. **2010**, 6, 11, 985-989.
3. *The Sol-Gel Process Review*. Chem. Rev. **1990**, 90, 33-72.
4. *Organo-silica hybrid functional nanomaterials: how do organic bridging groups and silsesquioxane moieties work hand-in-hand?* Chem. Soc. Rev., **2011**, 40, 688-695.
5. *Intrinsically Superhydrophobic Organosilica Sol-Gel Foams*. Langmuir **2003**, 19, 5626-5631.

Links to Chemical MSDS - Read them, as safety information may show up on a quiz!

- [Tetraethyl Orthosilicate \(TEOS\)](#)
- [Ethanol \(EtOH\)](#)
- [Ammonium Hydroxide \(NH₄OH\)](#)
- [Hydrochloric Acid \(HCl\)](#)
- [1-Propanol](#)

- [Methyltriethoxysilane](#)
- [1,8-Bis\(triethoxysilyl\)octane](#)
- [Bis\(3-triethoxysilylpropyl\)amine](#)
- [1,2-Bis\(methyldiethoxysilyl\)ethylene](#)
- [2-Butanol](#)