Production of Micro- and Nanoporous, Superhydrophobic layers from Sol-Gels

Neil J. Shirtcliffe, Paul Roach, Glen McHale, Michael Newton, Carole C. Perry

Silicate Sol Gels

Sol-Gel= preparation of oxide materials from solution

Usually organosilicon compounds hydrolysed to form intermediates

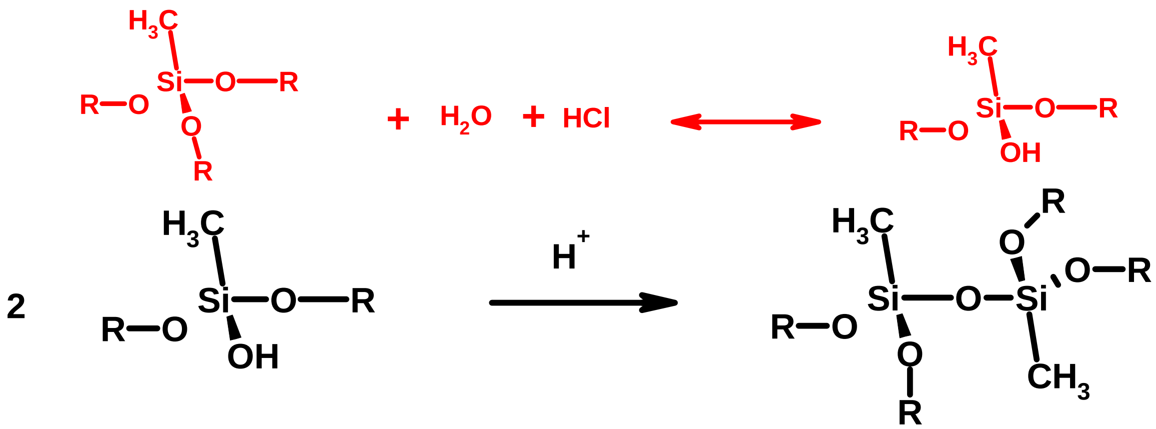
Partially & fully hydrolysed silicates can link together

Solvent creates porous structure unless complete separation occurs

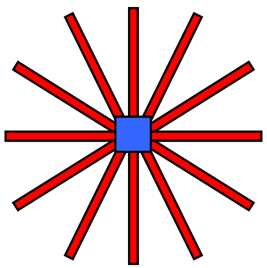
Hydroxide and organic groups usually present until thermally treated

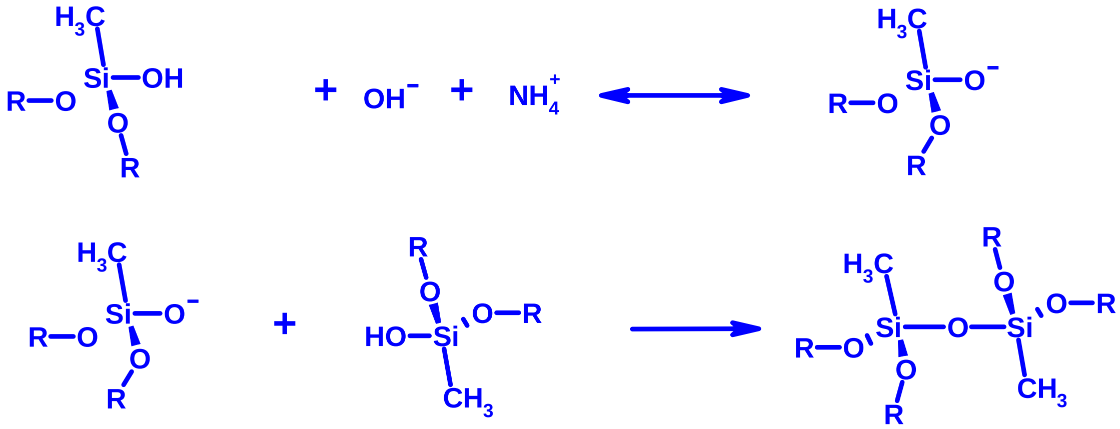
Mechanism

Acid Hydrolysis

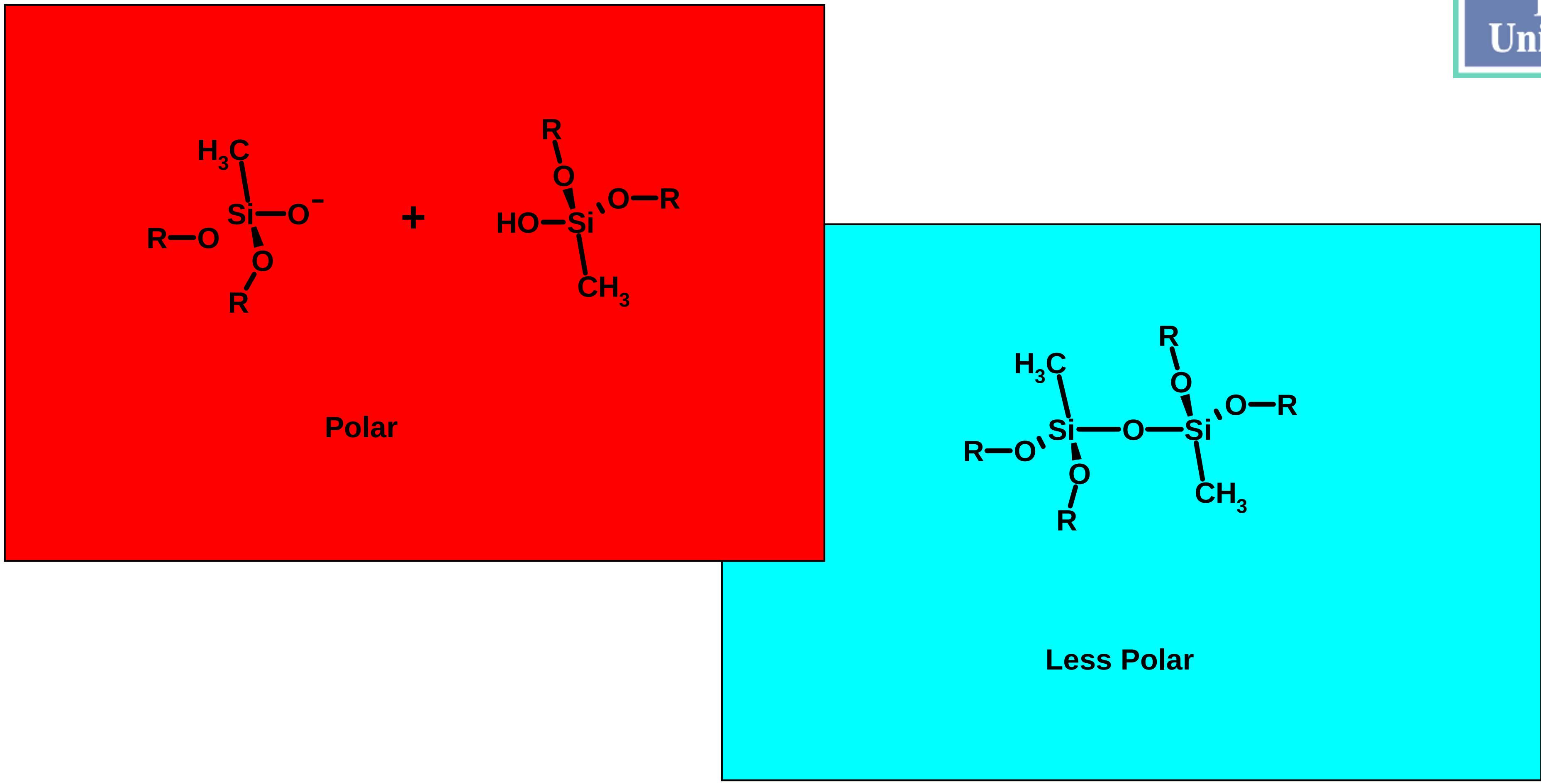


Base Catalysed Gelation



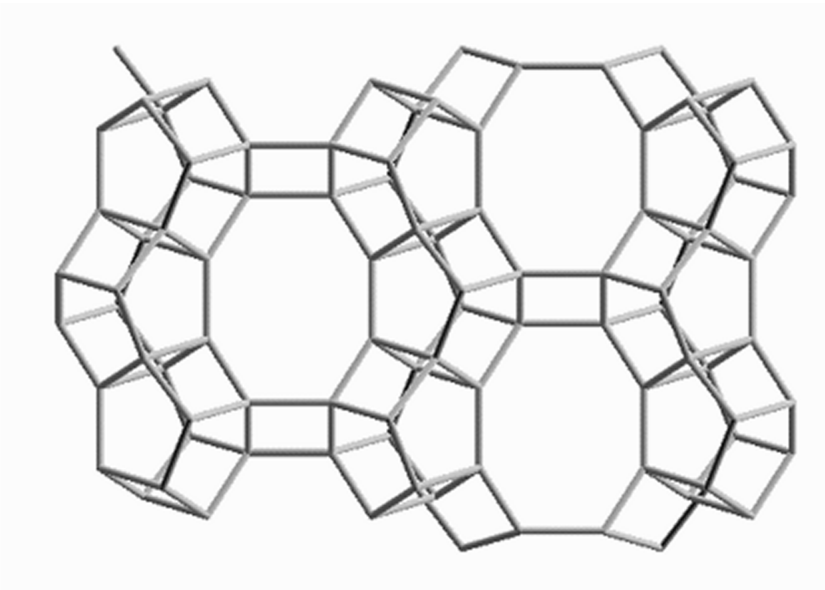


Sol-Gel Phase Separation

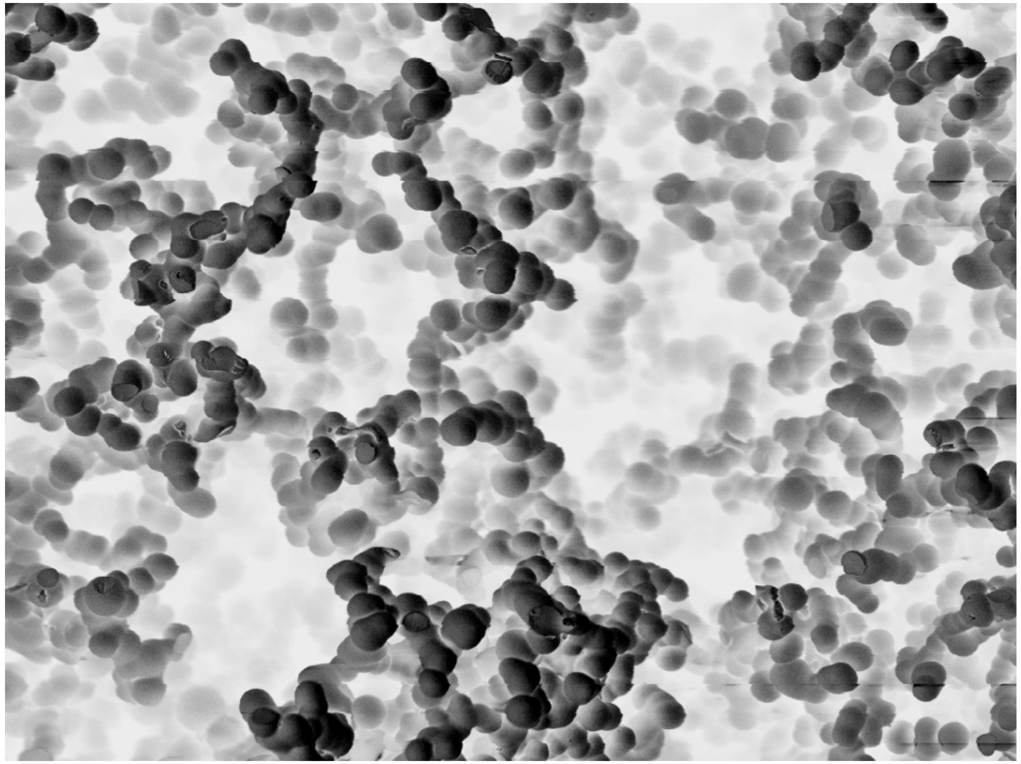


As the chains grow they become more hydrophobic and eventually phase separate to form a bicontinuous structure

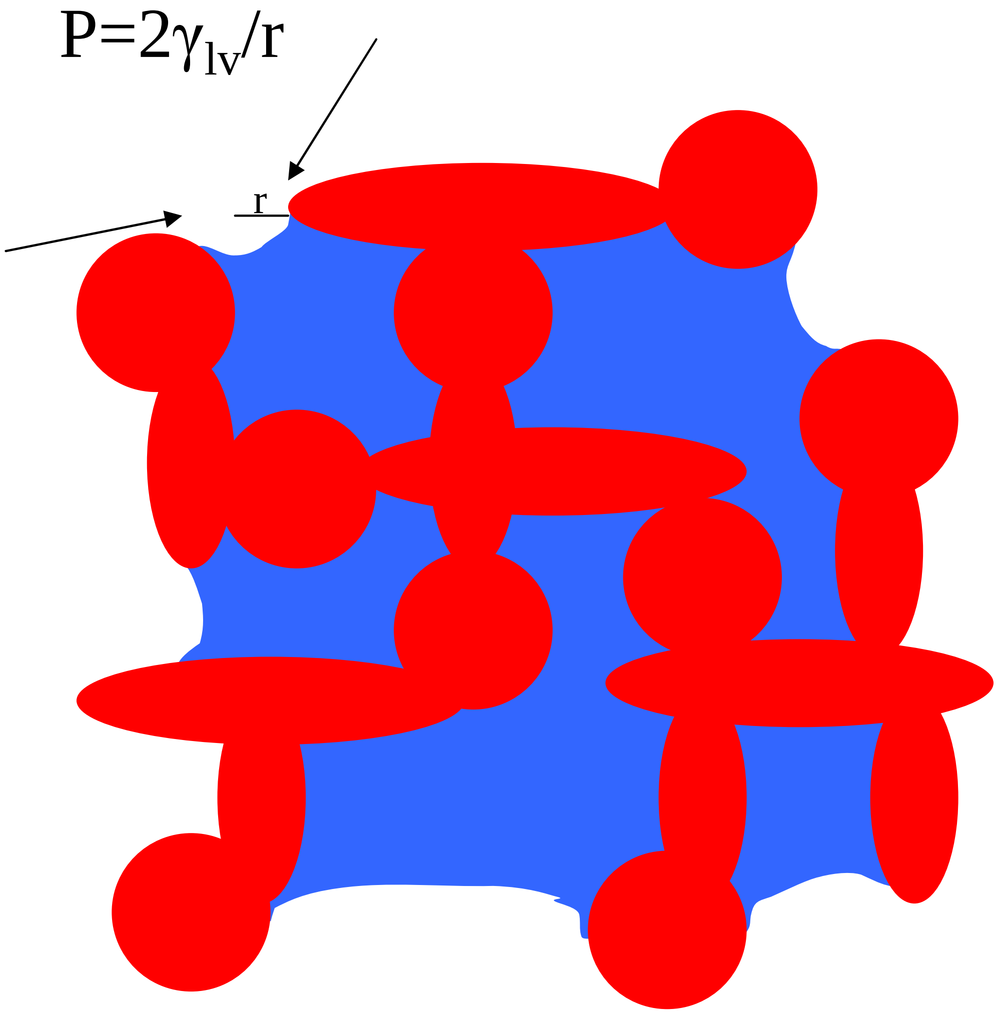
Bi-continuous Structure



M. Stockenhueber



Shrinkage



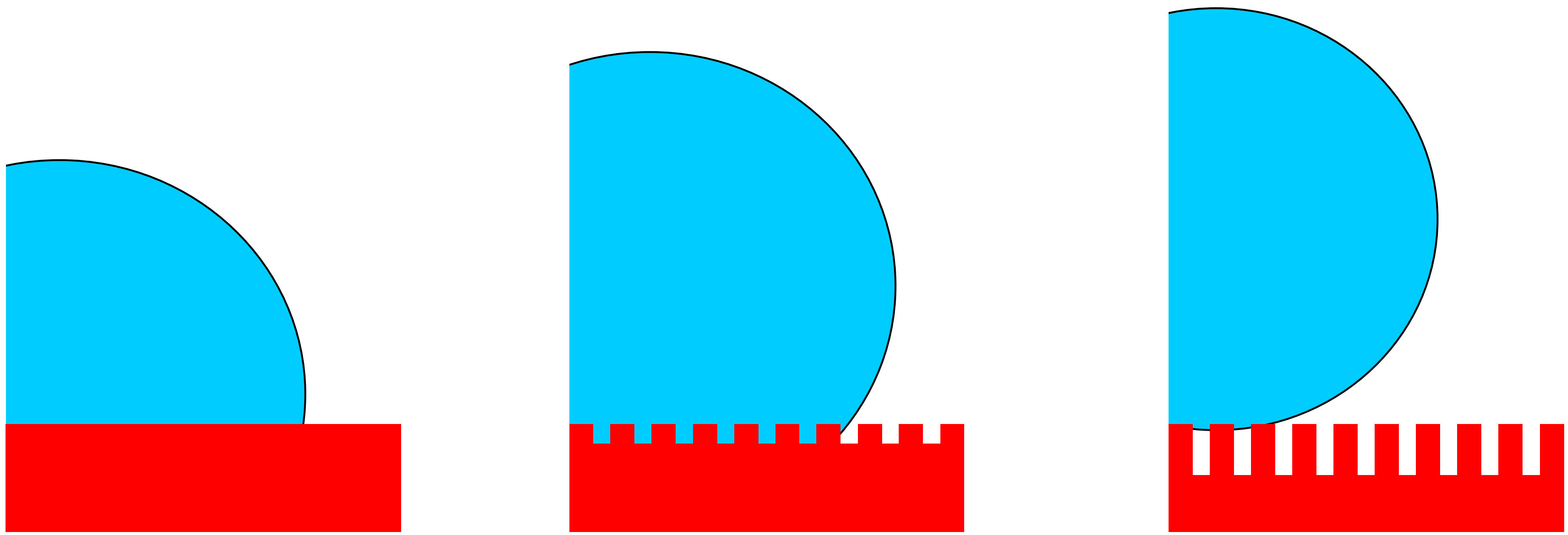
Shrinkage caused by surface tension of drying solvent, varies with pore size. Means that total pore volume decreases with pore size.

Can be overcome by supercritical drying, this is technically easy but takes time=money

Size Of Domains

- Rate of phase separation
    - Polarity of solvent
    - Starting material
    - Temperature
- Rate of hardening
    - Starting material
    - Time in acid
    - Temperature
- Shrinkage
    - Surface tension
    - Contact angle of solvent “r”
    - Pore Size “r”
    - Strength
    - (Temperature/pH=coarsening)

Super-hydrophobicity

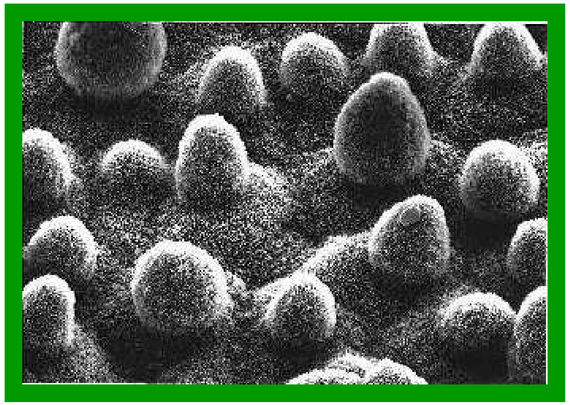


Max. Angle 120°

Super-hydrophobicity

Flat Teflon

Lotus Leaf
Barthlott&
Neinhuis

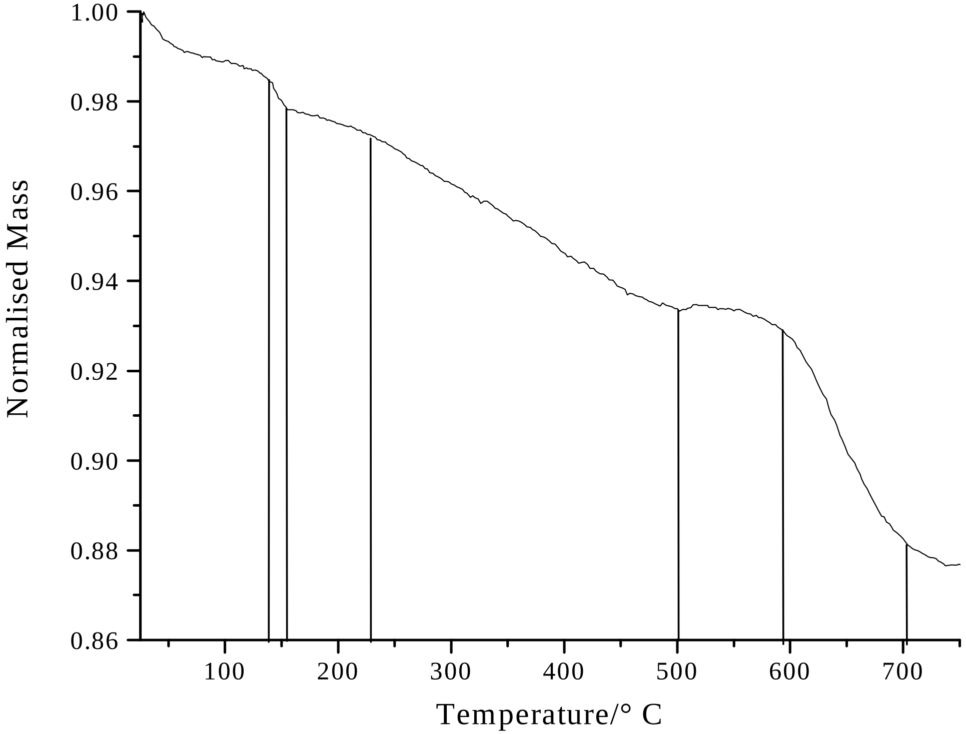


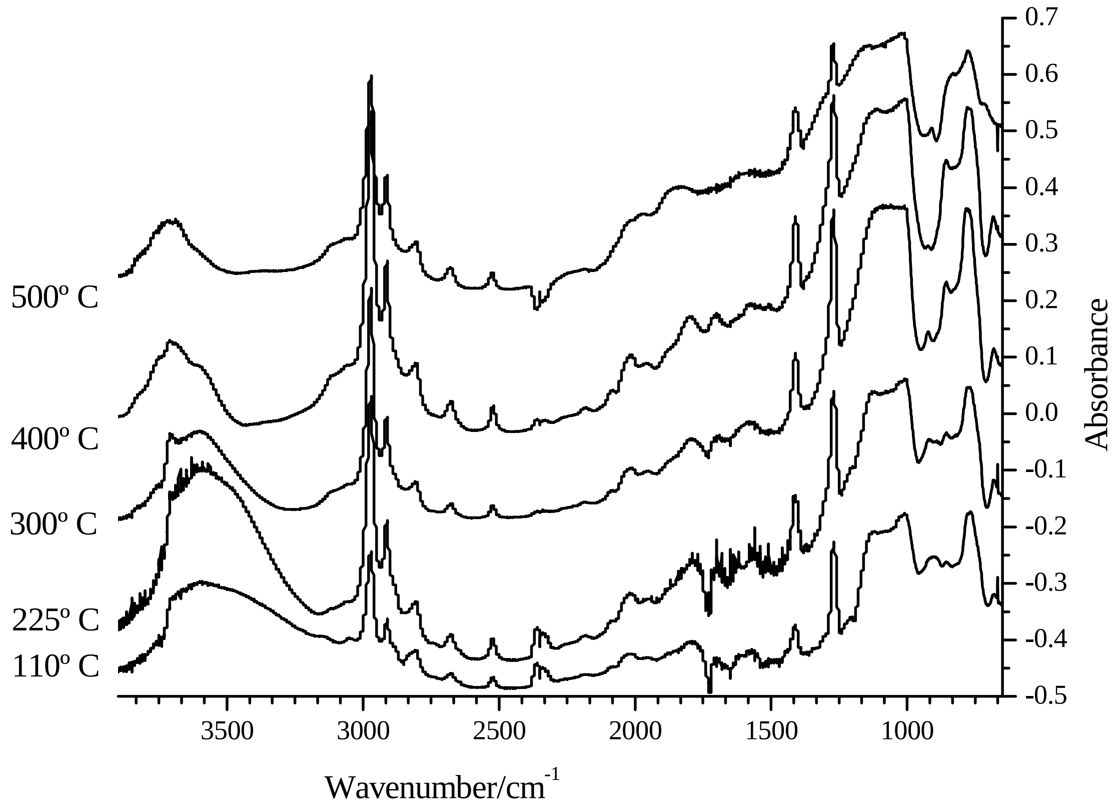
Sol-Gel Foams

Advancing and receding contact angles of drops of water on organo-silica flat surfaces and foams. Foam 1- MTEOS sol-gel produced using 1.1 M ammonia: Foam 2- sol-gel produced using MTEOS and 2.2 M ammonia.

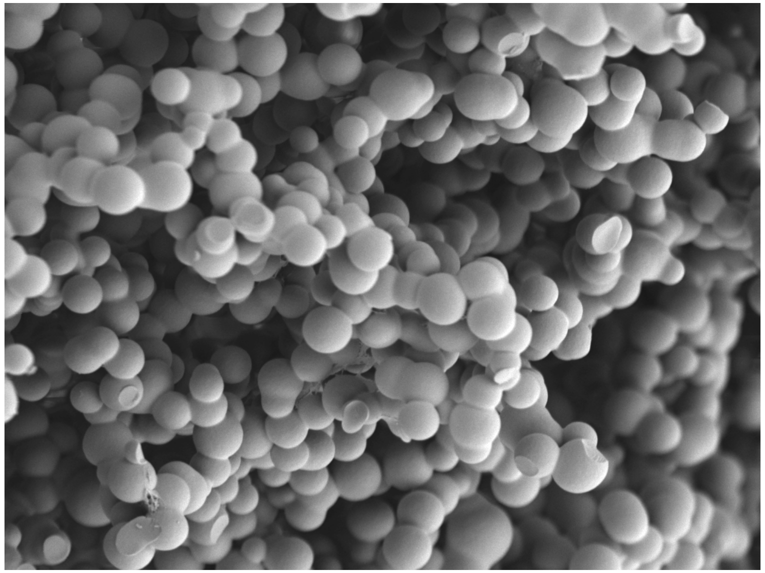
Materials			Advancing Angle Θ/°	Receding Angle Θ/°	Hysteresis ΔΘ/°
Sample	**Temp./° C**	**Post treatment**			
Flat	300	None	107	87	20
Flat	400	None	90	69	21
Flat	500	None	81	67	14
Flat	550	None	54	31	12
Foam1	300	None	153	137	16
Foam1	300	Abraded	156	152	4
Foam2	300	None	155	149	6
Foam1	400	None	Absorbed	Absorbed	-

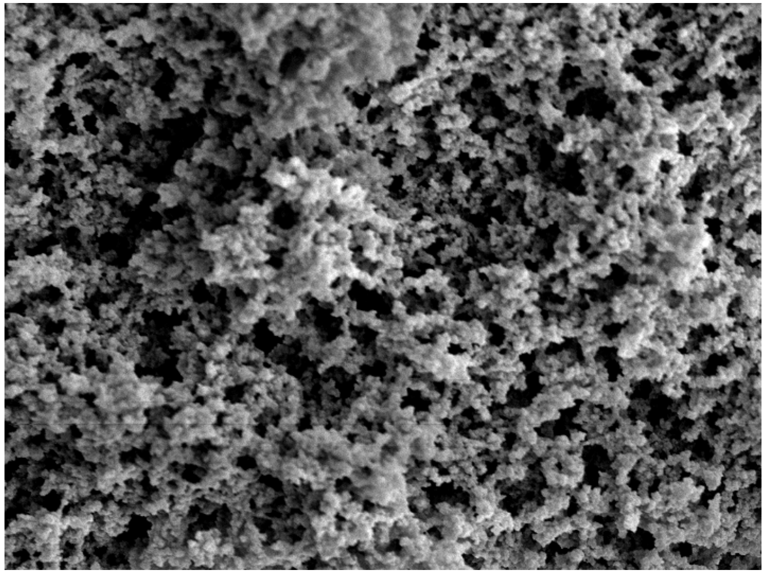
Effect of Heating





Pore Size/ Ammonia



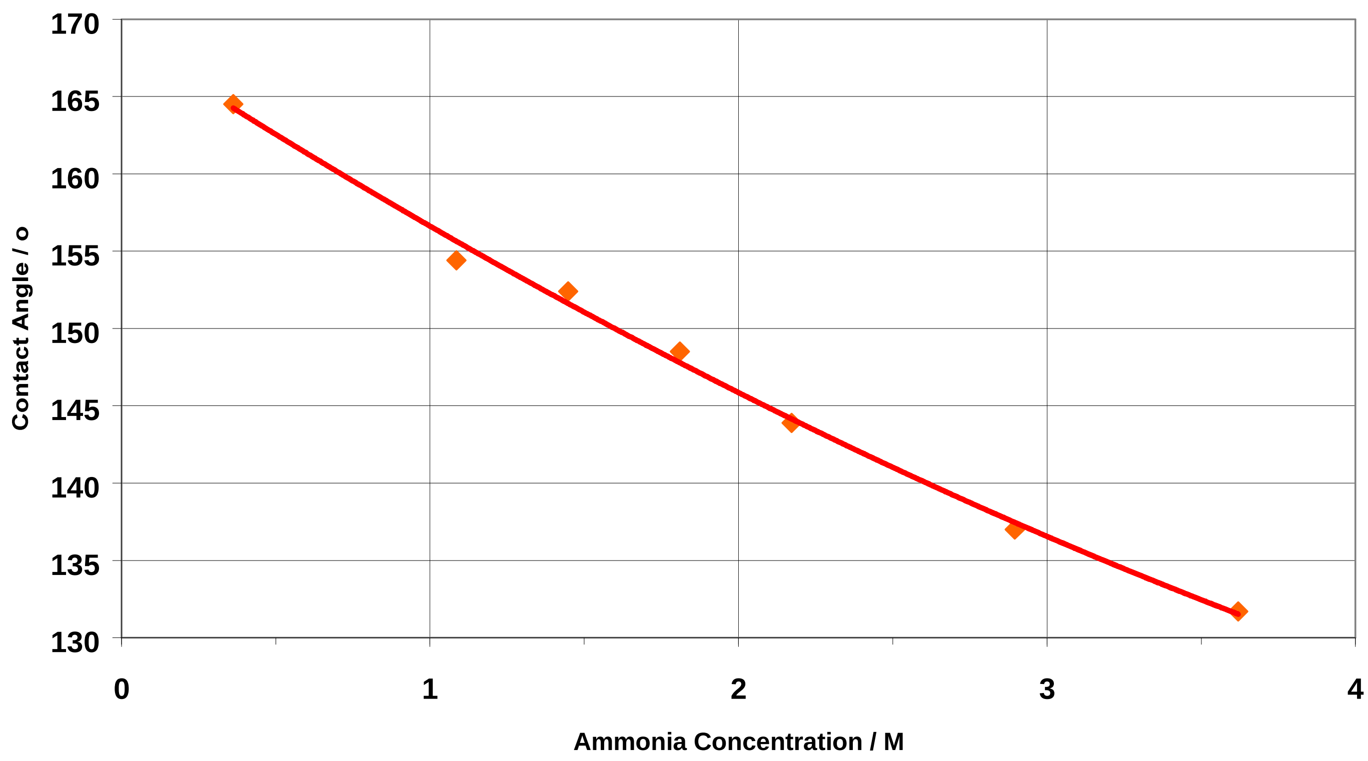


10 μm

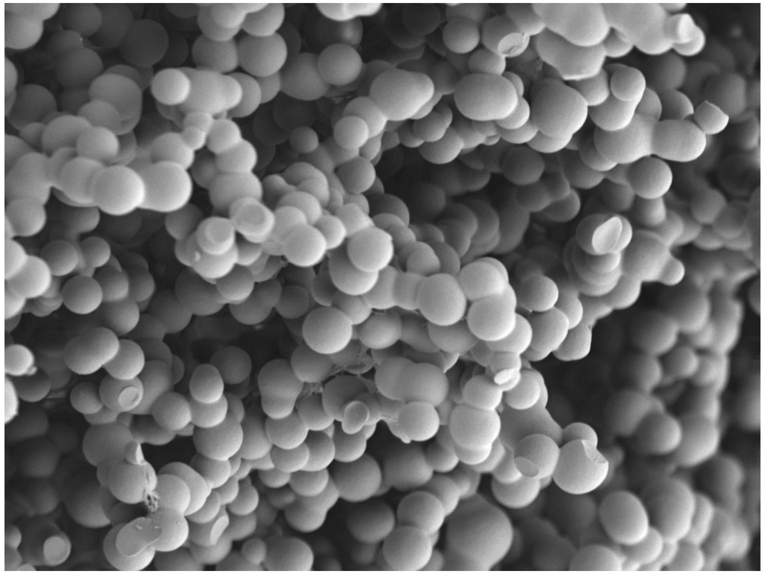
MTEOS with 1.1 M ammonia, heated to 300° C

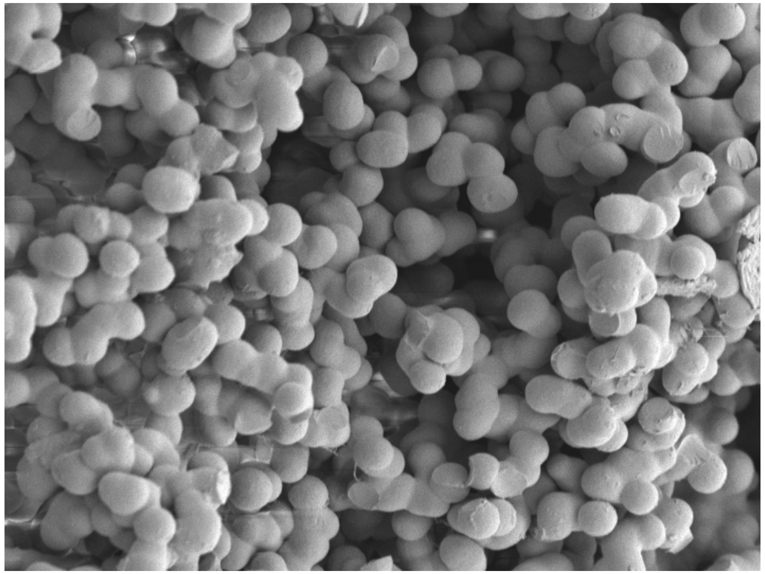
MTEOS with 2.2 M ammonia, heated to 300° C

Contact Angle/Ammonia



Pore Size/End Group

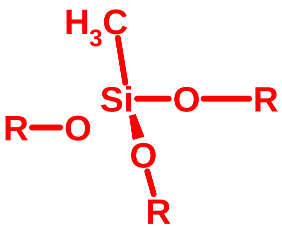


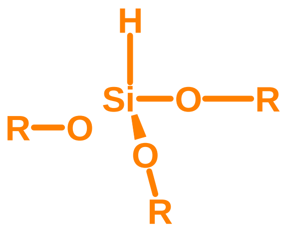


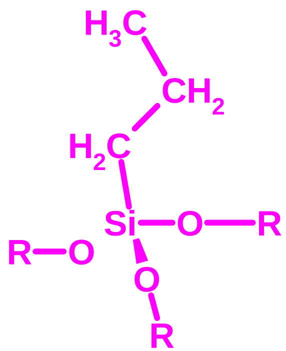
MTEOS with 1.1 M ammonia, heated to 300° C

10 µm

PTEOS with 22 M ammonia, heated to 300° C



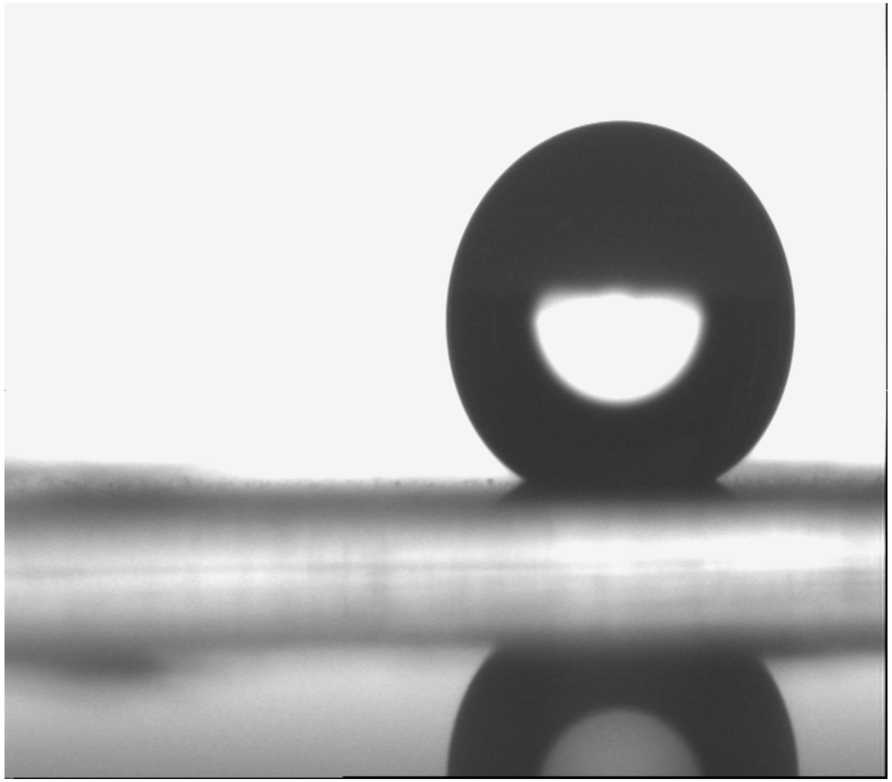




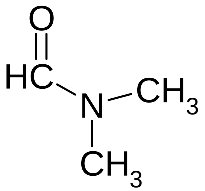
Sol-Gel Films

Properties

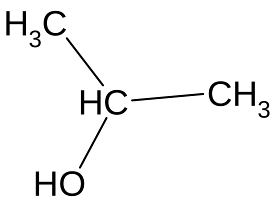
Thermally insulating
Waterproof or water absorbing
Gas permeable
Useful thickness depends on pore size



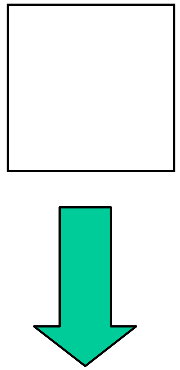
Recipe

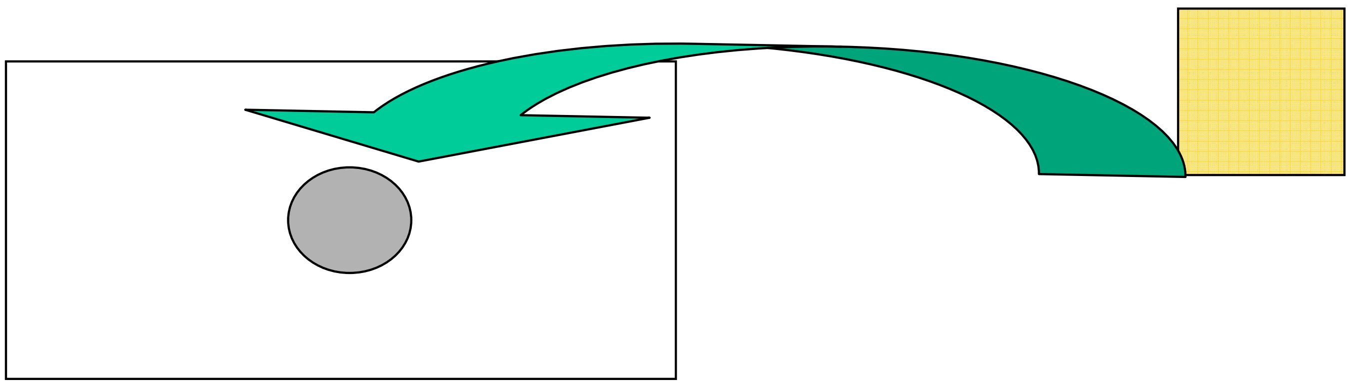


DMF

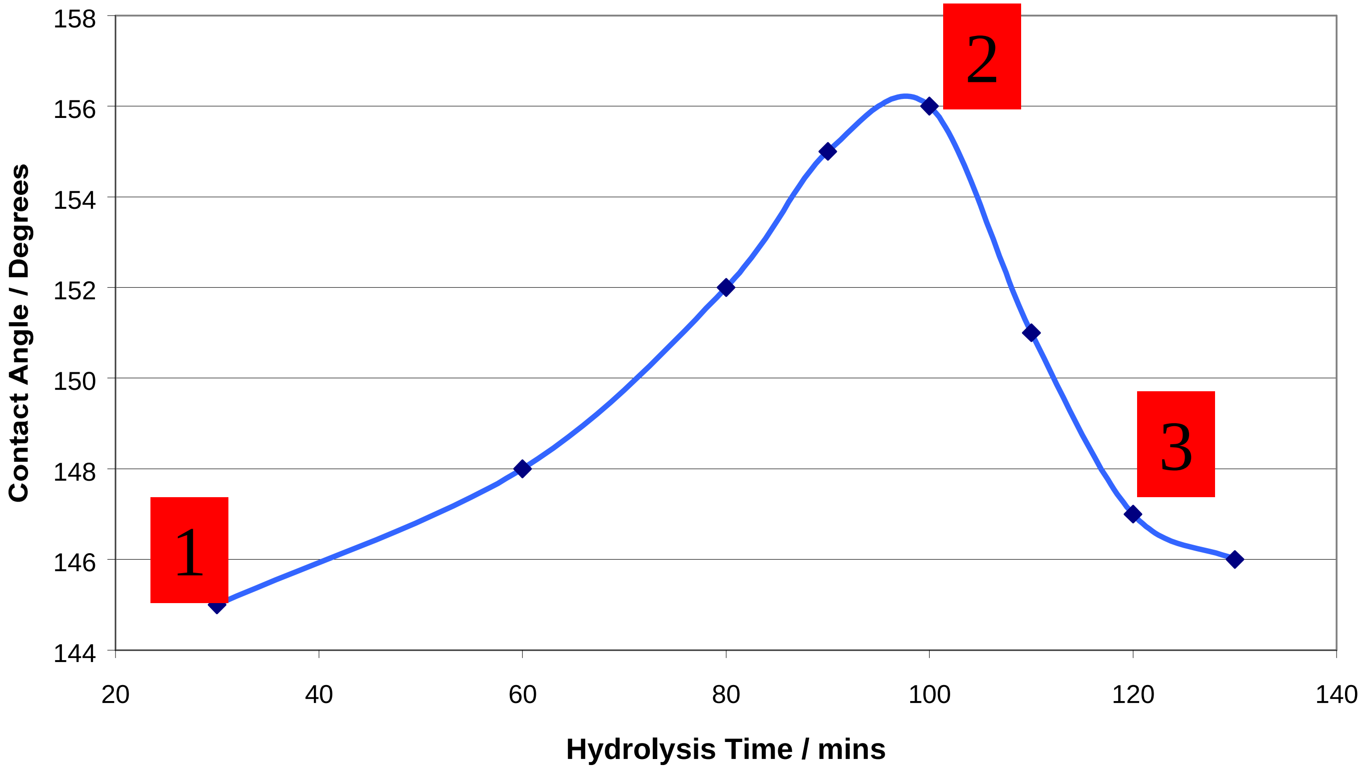


IPA

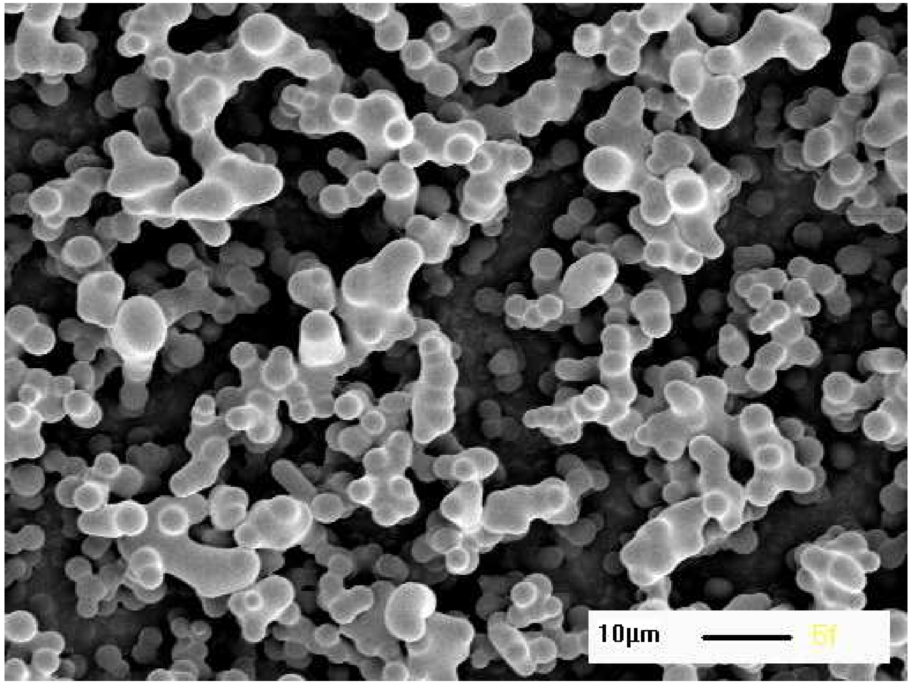


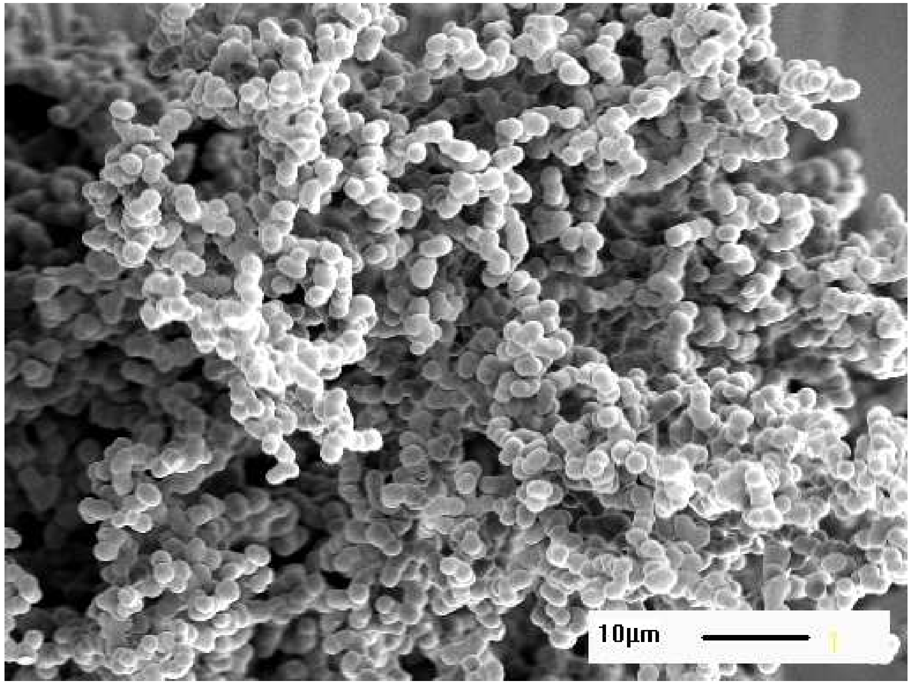


Water Contact Angle/Hydrolysis Time



Thin Films Look Like Trees





and have lower contact angles

Conclusion

- Can produce layers of sol-gel that are very hydrophobic and porous.
- Can vary pore size using hydrolysis time, solvent polarity and monomer
- Can vary hydrophobicity by thermal treatment
- With supercritical drying, will be attempting to decouple pore size and pore fraction
- With suitable coupling agents have coated glass and gold