Hollow Silica Nanospheres as Superinsulating Material

Mathieu Grandcolas [a*], Georges Etienne [a], Bente Gilbu Tilset [a], Tao Gao [b], Linn Ingunn Christie Sandberg [c], Arild Gustavsen [b] and Bjørn Petter Jelle [cd]**

[a] SINTEF Materials and Chemistry,
Department of Energy Conversion and Materials, NO-0314 Oslo, Norway.

[b] Norwegian University of Science and Technology (NTNU),
Department of Architectural Design, History and Technology, NO-7491 Trondheim, Norway.

[c] Norwegian University of Science and Technology (NTNU),
Department of Civil and Transport Engineering, NO-7491 Trondheim, Norway.

[d] SINTEF Building and Infrastructure,
Department of Materials and Structures, NO-7465 Trondheim, Norway.

* Corresponding author, mathieu.grandcolas@sintef.no
** Presenting author, Phone +47 73593377, Fax +47 73593380, bjorn.petter.jelle@sintef.no

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NTNU ZEB The Research Centre on Zero Emission Buildings SINTEF

Why Superinsulation Materials?


www.glava.no

- **Increasing requirements → Thicker walls with traditional insulation**
- **When space is an issue:**
  - Vacuum insulation panels (VIP)
  - Areogels


www.nanopore.eu


www.glava.no

- **Drawbacks:**
  - High costs
  - High embodied energy
  - VIP: Degradation/ageing, puncture, loss of vacuum
  - Aerogels: Brittleness

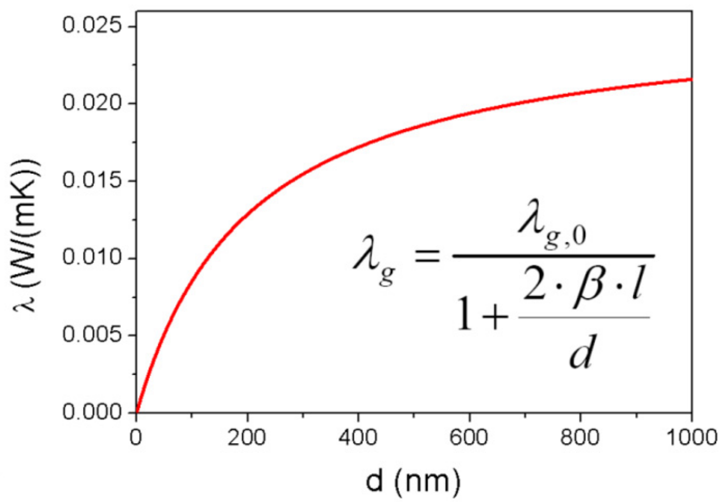

www.stardust.jpl.nasa.gov

Conceptual: Nano Insulation Materials (NIM)

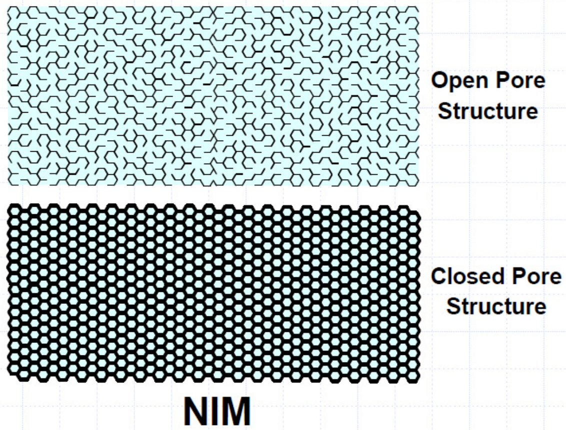
$$\lambda_{tot} = \lambda_{cond} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + (dx/dT)q_{coupling}$$

- λ_{gas} : limited by Knudsen diffusion in small pores
- λ_{cond} : small amount of low-conductive solid
  (λ = thermal conductivity)

Size-dependent thermal conduction in NIM – *gas*



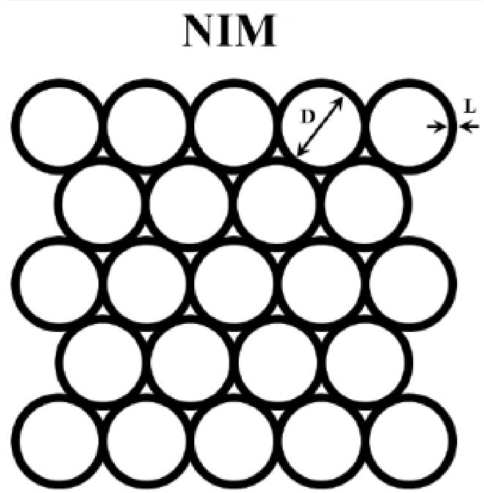
NIM – the dimension for gaseous transport need to be in nanometer range (typically < 100 nm)



NIM - A basically homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 0.004 W/mK in the pristine condition.

Theoretical Approach – Practical Solutions?

- **Spheres:**
  - Good mechanical stability with thin shell (L) and large core (D)
  - Minimizes solid fraction in shell (low surface-to-volume ratio)



- **Silica:**
  - Abundant, environmentally friendly
  - Extensive industrial and academic knowledge
  - Relatively low thermal conductivity

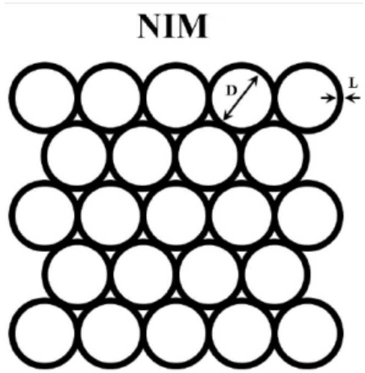
- **Gas:**
  - Air
  - Other gases would give lower λ, but difficult to make shell gas-tight

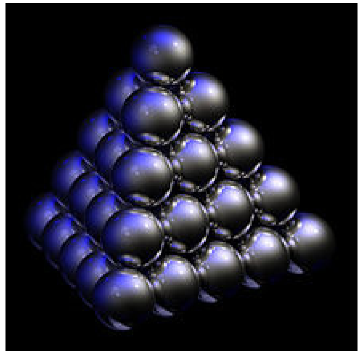
Packing is Important:

- Close packing of solid spheres: 74 % solid
- Close packing of hollow spheres:

D (nm)	L (nm)	% solid
15	15	71
50	10	47
100	15	40
70	10	39
Inner sphere diameter	**Wall thickness**	

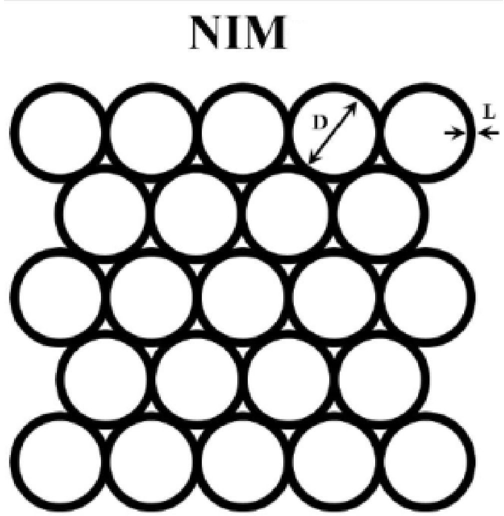
- 70 nm spheres:
  - Good size for Knudsen effect
  - Difficult to make shell < 10 nm
- Still too high solid contribution to λ
- Less dense packing is needed, even if spheres are hollow





http://en.wikipedia.org

Core (D) and Shell (L) Details



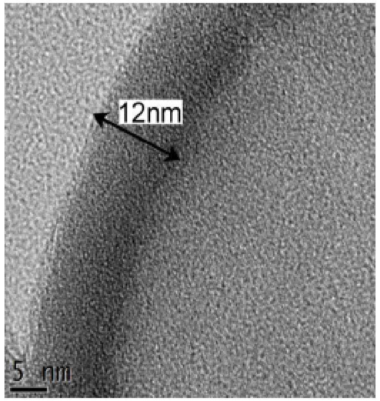
- **Core size by controlled template**
  - Small core: Polyacrylic acid (PAA) template
  - Larger core: Polystyrene (PS) template

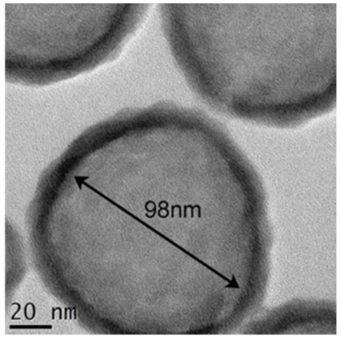
- **Shell thickness**
  - Adjusted by controlled reaction of tetraethoxysilane (TEOS)

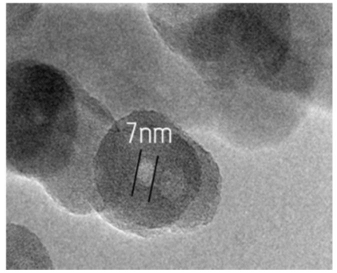
- **Shell morphology**
  - Dense or porous – depending on reaction conditions
  - Dense: Expected better mechanical stability, higher λ
  - Porous: Expected less mechanical stability, lower λ

Polyacrylic Acid (PAA) Template

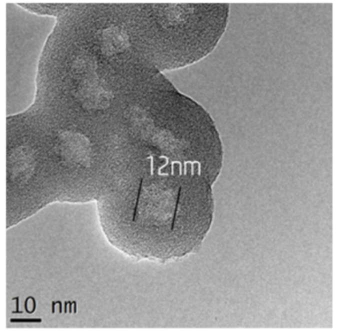
- Core size 7 nm – 100 nm
- PAA template: Mainly ammonia solution!
- Base-catalysed reaction at interface
- Template removed by washing
- Even shell structure

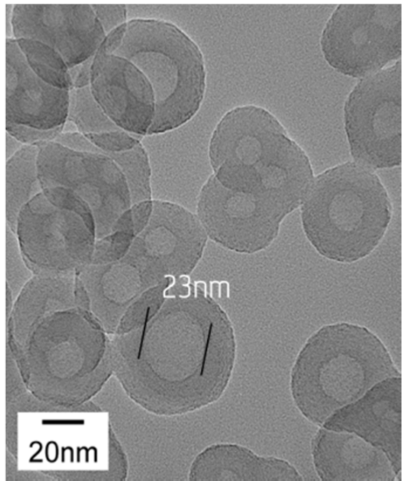


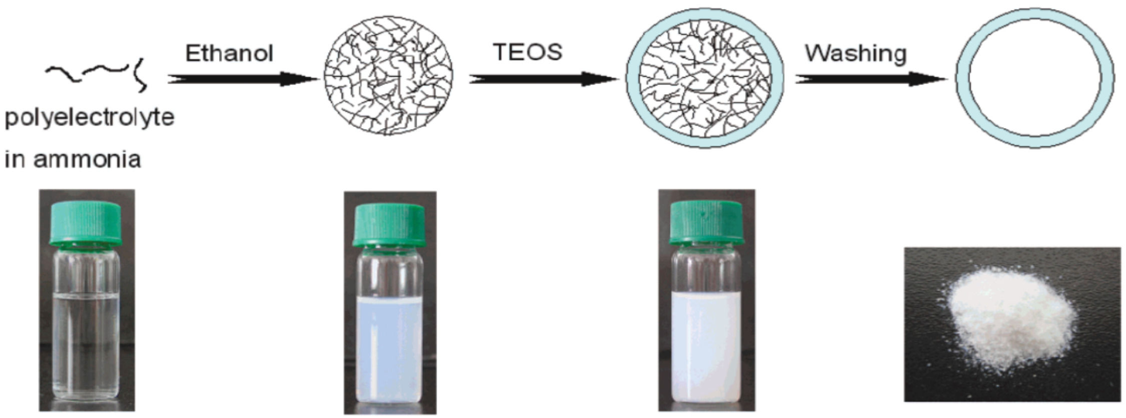




TEM photos





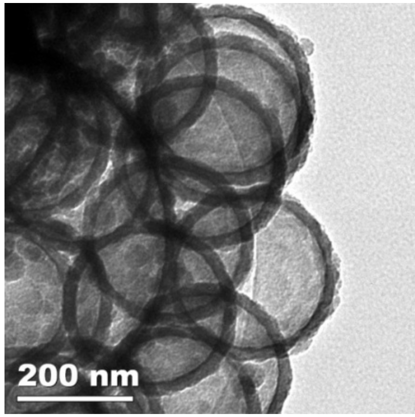


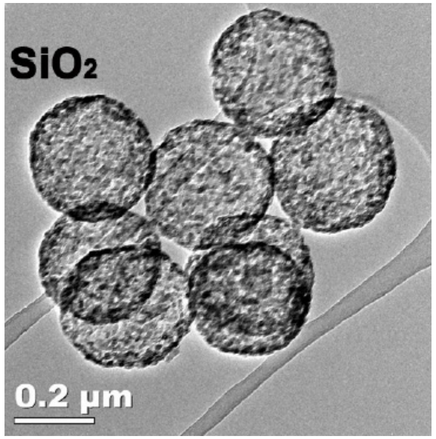
Wan and Yu, *J. Phys Chem. C* (2008)

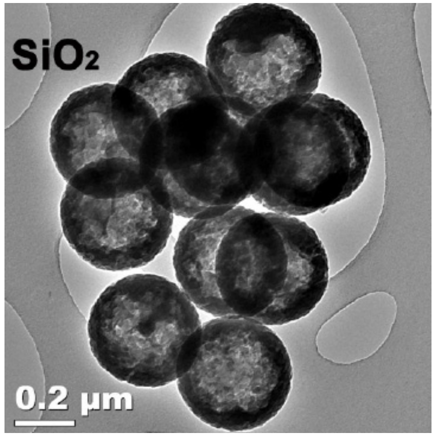
Polystyrene (PS) Template

TEM photos

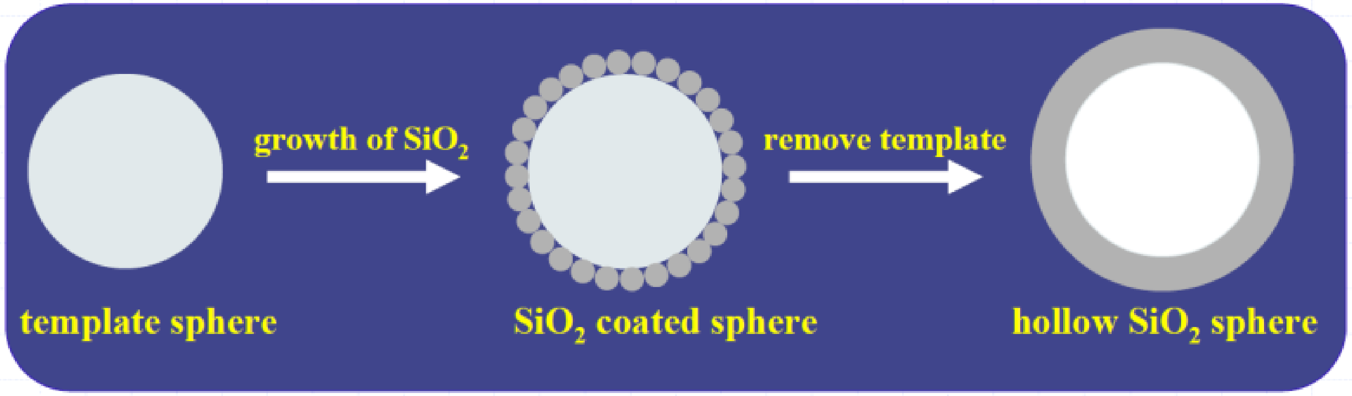
- Core size: 100 nm – 1 µm
- PS template: Polymer solid
- Base-catalysed reaction in solution
- Nanoparticles captured on PS surface
- Template removal by burning
- Rough/porous shell structure



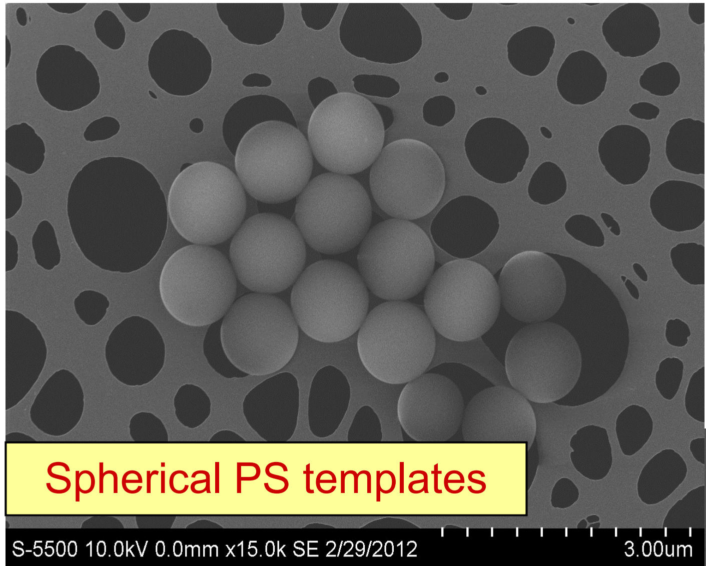




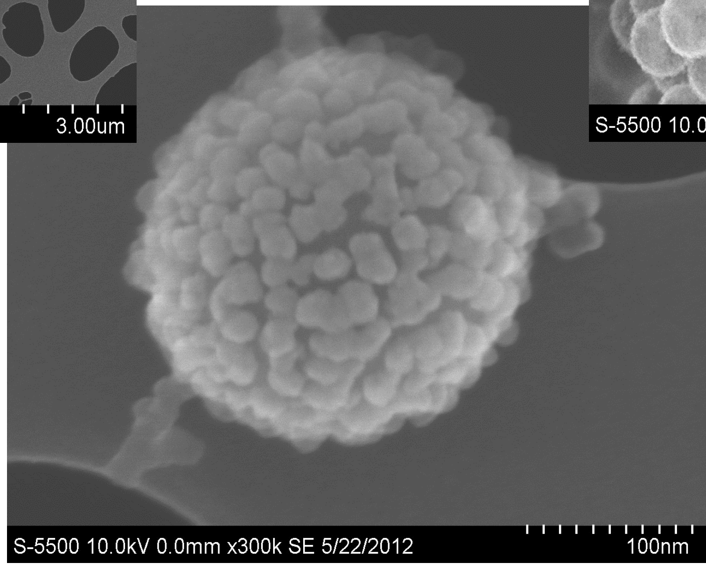
Sacrificial template process



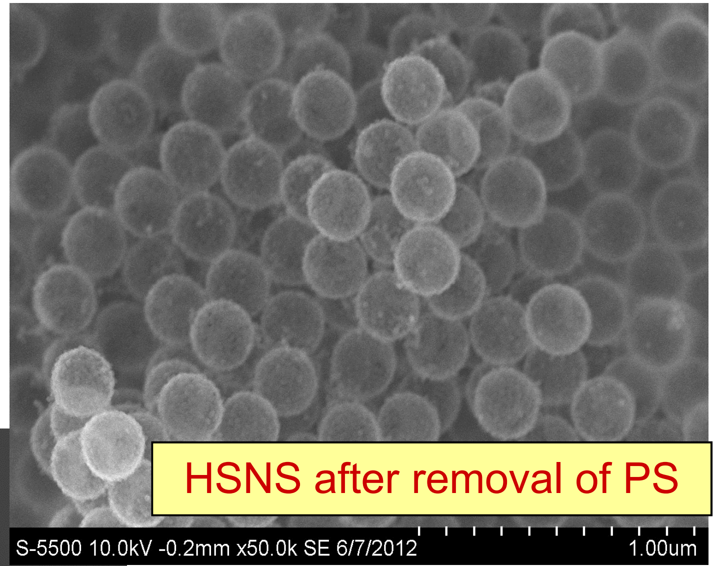
SEM Photos



Spherical PS templates



Small silica particles coated around a spherical PS template

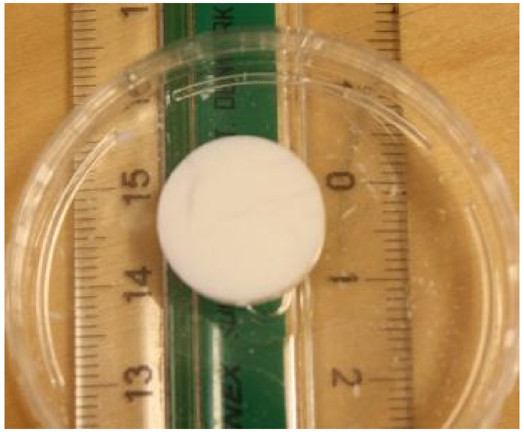


HSNS after removal of PS

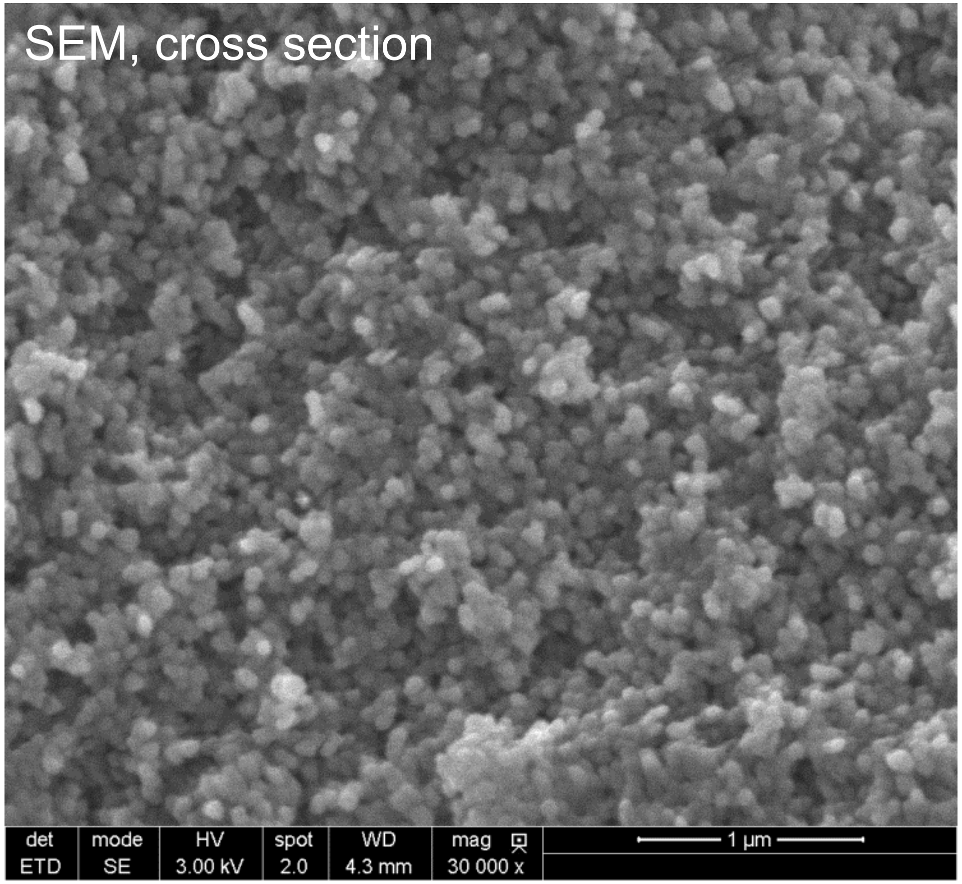
PS = Polystyrene
HSNS = Hollow Silica Nanospheres

Example: Packing of Particles – Initial Testing

- Aggregates crushed in a mortar
- Pellet made with pressure 2.5 T



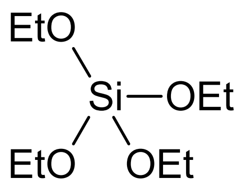
Pellet of nanoparticles, λ = 0.2 W/(mK) = λ powder

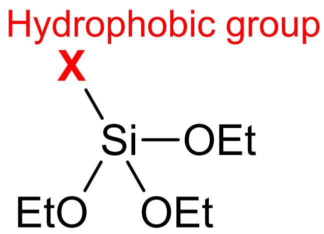


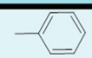
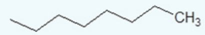
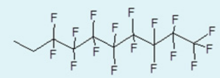
Hydrophobic Surface Needed to Avoid Capillary Condensation of Water

1. "Direct or in-situ" synthesis of hydrophobic hollow spheres

Co-hydrolysis and condensation principle

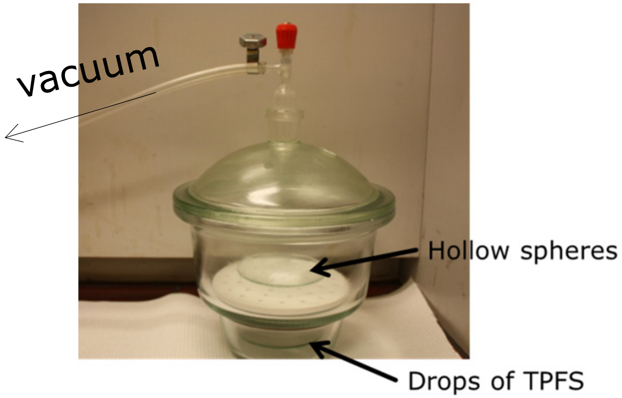


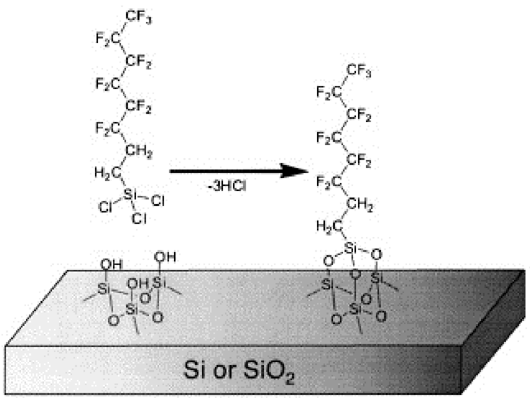


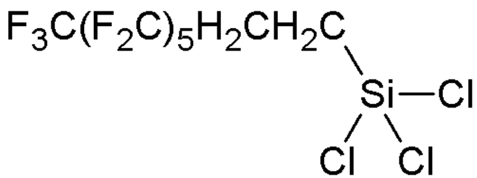
Chemical name	Organo-group
phenyltriethoxysilane	
n-Octyltrimethoxysilane	
(Heptadecafluoro...tetra hydrodecyl) triethoxysilane (FAS)	

More hydrophobic

2. Gas phase hydrophobization of prepared hollow spheres



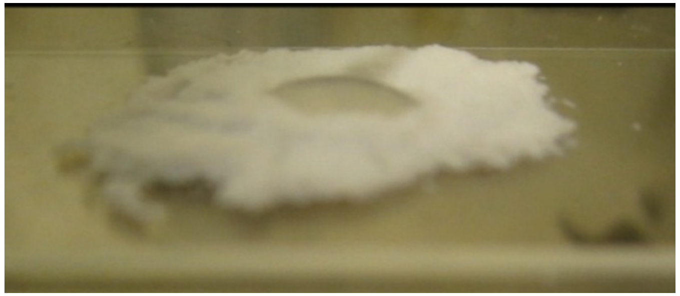




Hydrophobic Treatment

- Confirmed by IR spectra
- Confirmed by simple testing of water droplets on:

HYDROPHILIC silica nanospheres



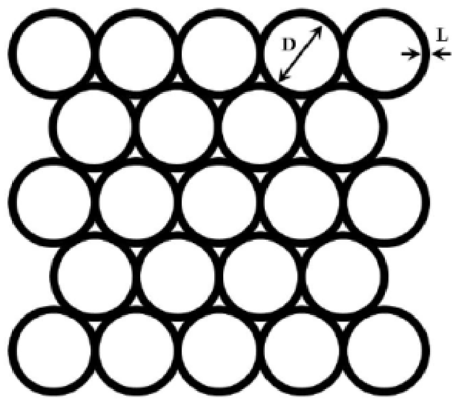
HYDROPHOBIC silica nanospheres

- Does not change the thermal conductivity of the sample

Thermal Conductivity of Powder Samples

Inner diameter D (nm)	Shell thickness L (nm)	Sample (powder) density (g/cm^3)	Theoretical close-packed density (g/cm^3)	Template	Measured effective thermal conductivity (W/(mK))
Bulk silica		2.6	2.6		1.2-1.4
Silica nanoparticles			1.9		0.090
PCAS aerogel					0.023
15	15	0.37	1.8	PAA	0.089
25	12	0.2	1.7	PAA	0.065
25	12	0.2	1.7	PAA, with hydrophobic post-treatment	0.062
100	12	0.33	0.9	PAA	0.076
150	15	0.27	1.0	PS	0.040

NIM



Trends?

- **All samples had thin shells, varying core size**

- **Core size and shell thickness – gas content vs. solid state content**

- **Sample powder density does not correlate to theoretical close-packed density**
    - Sphere packing is currently not controlled

- **Lowest λ for aerogel sample (higher than expected)**
- Second lowest for sample D = 150 nm, L = 15 nm, made from PS template
    - Could be due to high shell porosity and low sample density
    - Not so much Knudsen effect for such large spheres…

- **For samples from PAA template:**
    - Lowest λ for sample with lowest density
    - Hydrophobic treatment does not influence λ

Life Cycle Assessment (LCA)

- **Preliminary and rough LCA carried out**
- **Hollow silica nanospheres (HSNS) exhibit a relative high embodied energy, although comparable to that of silica aerogels**
- **Recycling of chemicals, up-scaling production, and use of environmentally friendly materials can affect greatly the process environmental footprints of HSNSs**

Table 3. Production Impact Associated with Making 1 g HSNSs

		embodied energy (MJ/kg)	amount (g)	production energy (MJ/g)
materials	PS	105[64]	0.5[a]	0.053
	ethanol	15.7[65]	162	2.54
	NH_4OH	43.15[66]	1.05[b]	0.045
	TEOS		4.76[c]	
electricity		10.5 MJ/kWh[66]	0.81 kWh[a,d]	0.009
total				2.65

[a]Assuming that 10 g of styrene converts totally into PS; only part of the PS suspension is used for the one synthesis of HSNSs. [b]The weight of NH_3. [c]The value correlates also with the purity of TEOS, 98%. [d]Part of the electricity from step 1 adds to those consumed in steps 2 and 3 (see Table 2).

Conclusions

- **Nanospheres show promise as building blocks for superinsulating materials**
  - Possible to control core size and shell thickness
  - Core size and shell thickness – gas content vs. solid state content
  - Hydrophobic treatment does not increase thermal conductivity
  - Optimum core size probably ≤ 100 nm
  - Optimum shell thickness 10-20 nm, depending on mechanical property needs

- **Continuation**
  - Alternative production routes to lower costs and environmental impact by carrying out life cycle analyses (LCA)
  - Optimize nanosphere dimensions (core size and shell thickness)
  - Develop packing techniques to obtain a low-density materials