Experimental Pathways for Achieving Superinsulation through Nano Insulation Materials

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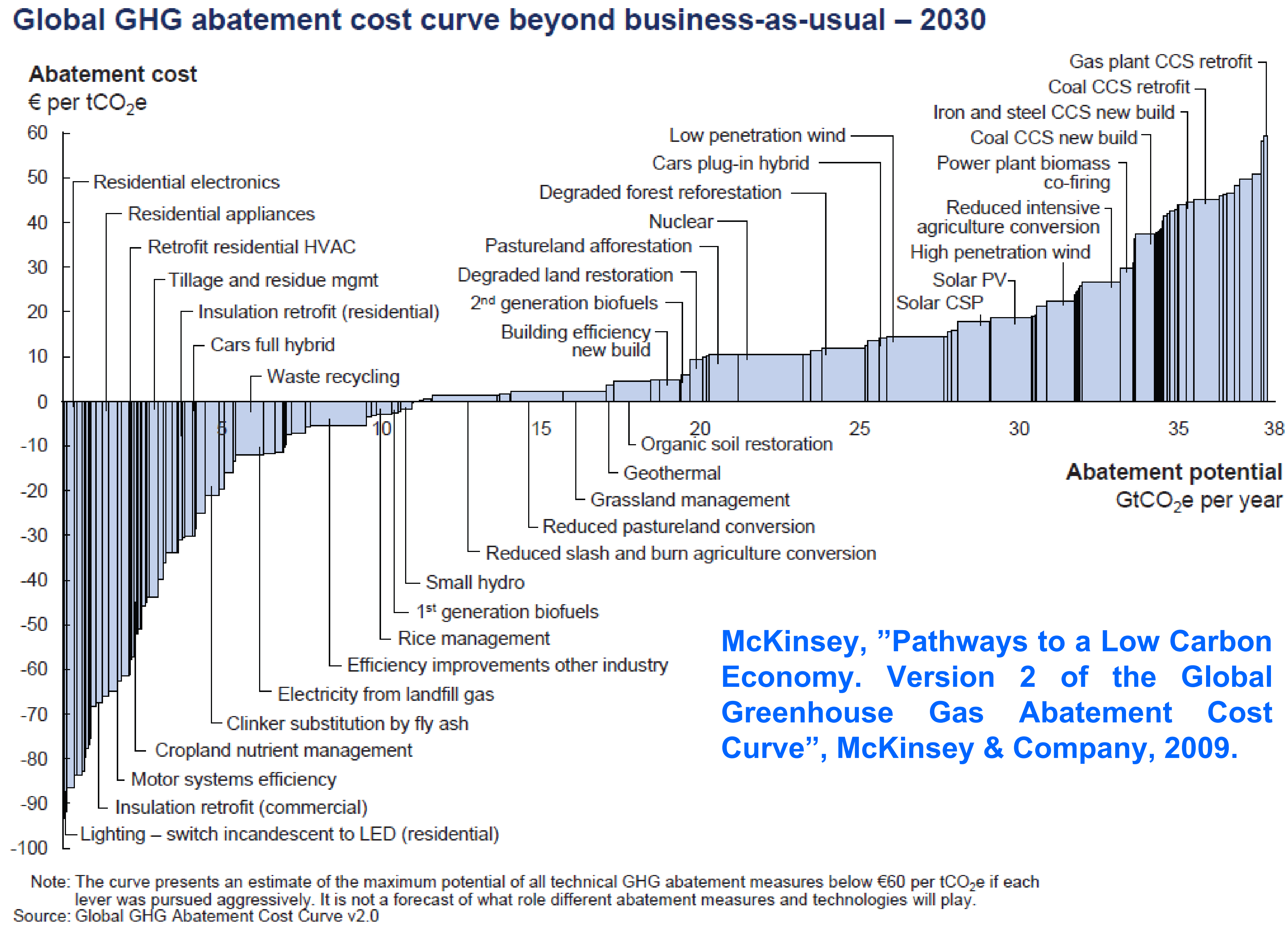
Why is Thermal Insulation Important ?
- What Measures Amounts the Most ?



McKinsey, "Pathways to a Low Carbon Economy. Version 2 of the Global Greenhouse Gas Abatement Cost Curve", McKinsey & Company, 2009.

Thermal Background

- Thermal Conductivity Contributions

$$\lambda_{\mathbf{tot}} = \lambda_{\mathbf{solid}} + \lambda_{\mathbf{gas}} + \lambda_{\mathbf{rad}} + \lambda_{\mathbf{conv}} + \lambda_{\mathbf{coupling}} + \lambda_{\mathbf{leak}}$$

λ_{tot} = total overall thermal conductivity

λ_{solid} = solid state thermal conductivity

λ_{gas} = gas thermal conductivity

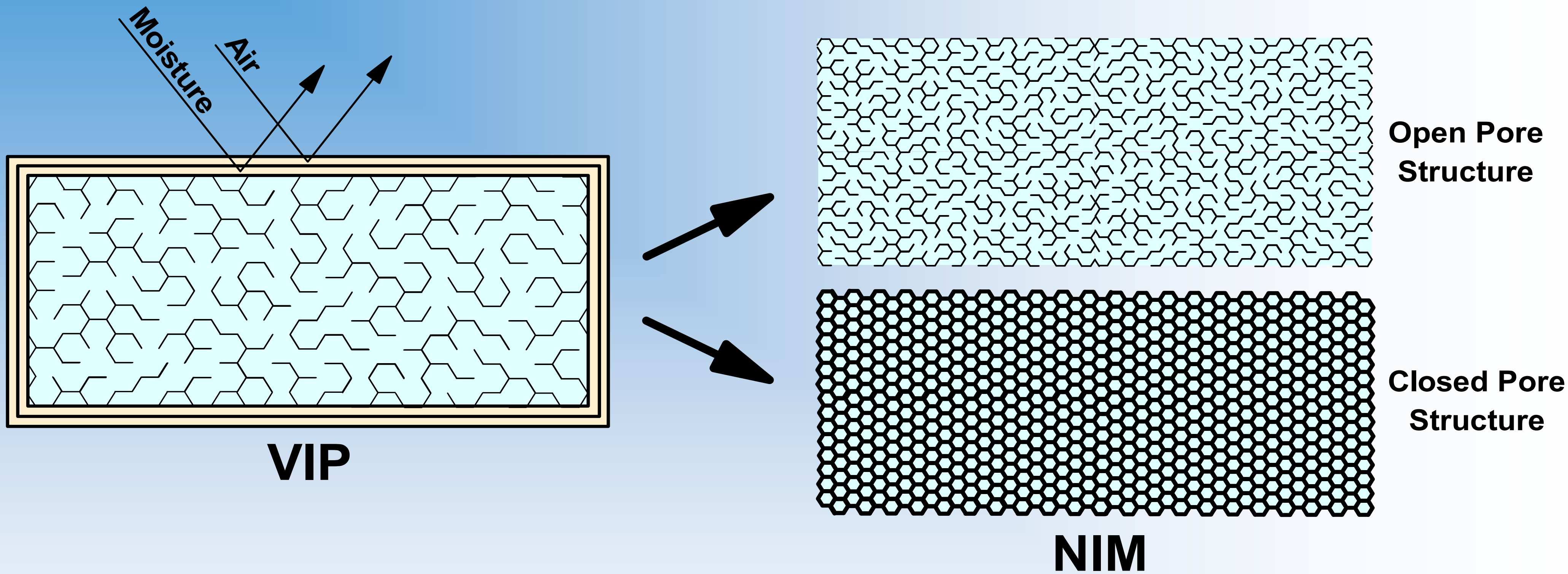
λ_{rad} = radiation thermal conductivity

λ_{conv} = convection thermal conductivity

$\lambda_{coupling}$ = thermal conductivity term accounting for second order effects between the various thermal conductivities

λ_{leak} = leakage thermal conductivity

Nano Insulation Material (NIM)



NIM - A basically homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition

The Knudsen Effect – Nano Pores

Gas Thermal Conductivity λ_{gas}

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1+2\beta Kn} = \frac{\lambda_{gas,0}}{1+\frac{\sqrt{2}\beta k_B T}{\pi d^2 p\delta}}$$

$\sigma_{mean} > \delta$

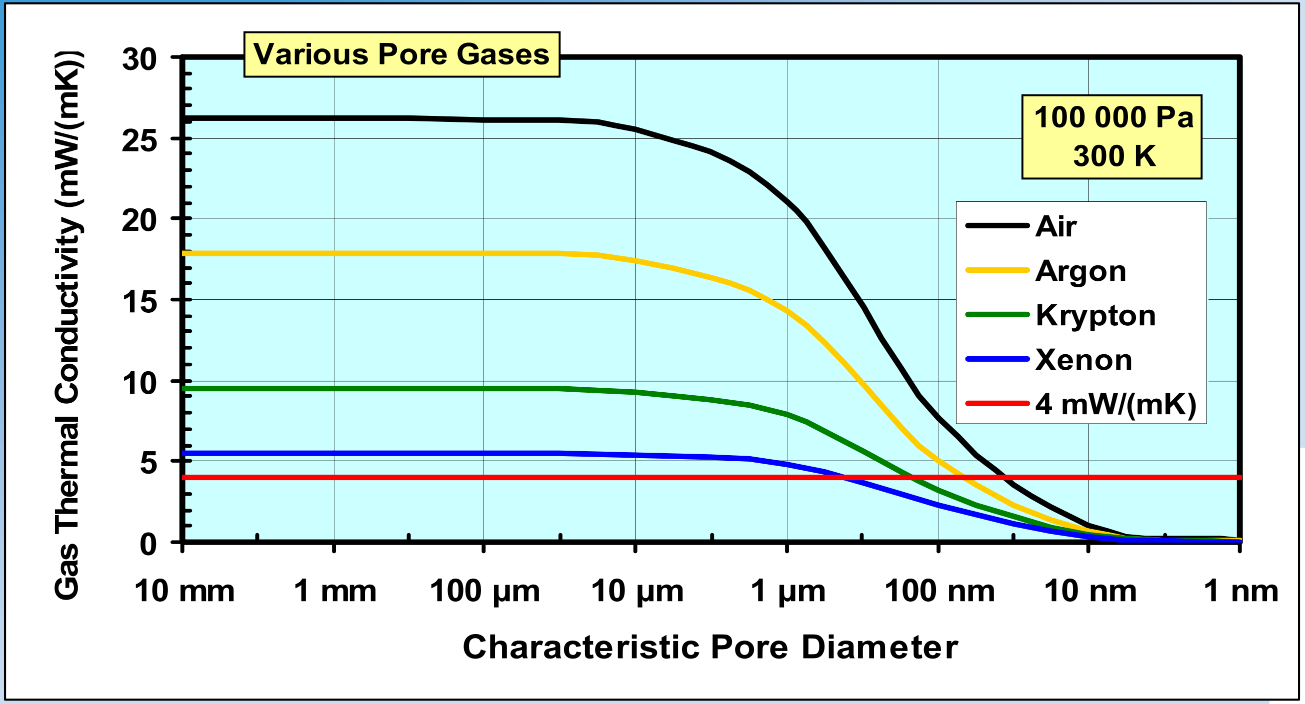
$\Rightarrow$ low λ_{gas}

where

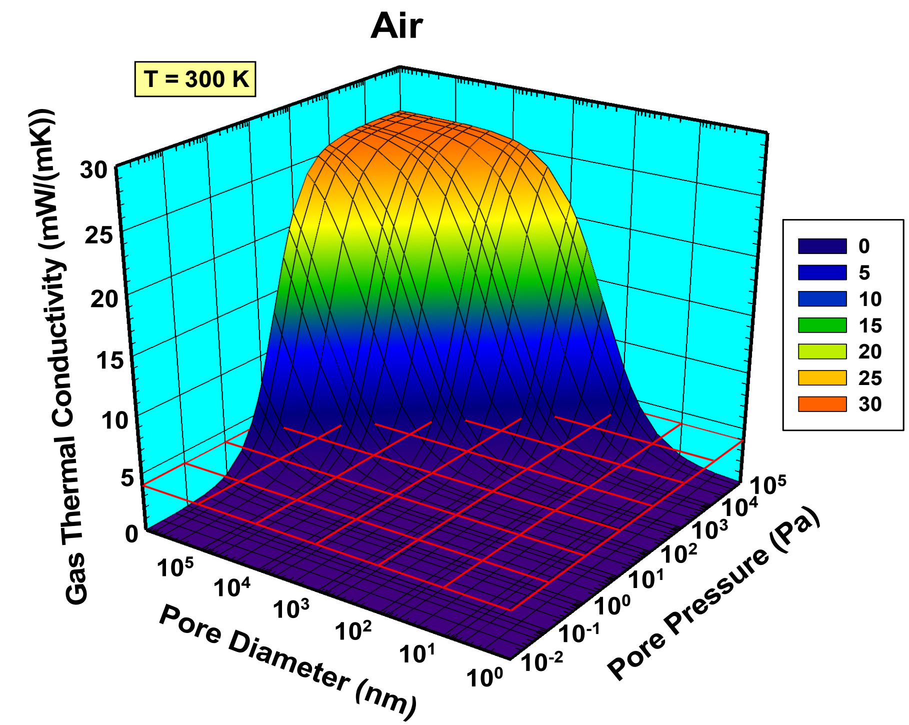
$$Kn = \frac{\sigma_{mean}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 p\delta}$$

λ_{gas} = gas thermal conductivity in the pores (W/(mK))
$\lambda_{gas,0}$ = gas thermal conductivity in the pores at STP (standard temperature and pressure) (W/(mK))
β = coefficient characterizing the molecule - wall collision energy transfer efficiency (between 1.5 - 2.0)
Kn = $\sigma_{mean}/\delta = k_B T/(2^{1/2}\pi d^2 p\delta)$ = the Knudsen number
k_B = Boltzmann's constant $\approx 1.38 \cdot 10^{-23}$ J/K
T = temperature (K)
d = gas molecule collision diameter (m)
p = gas pressure in pores (Pa)
δ = characteristic pore diameter (m)
σ_{mean} = mean free path of gas molecules (m)

Gas Thermal Conductivity



Conductivity vs. Pore Diameter and Pore Pressure



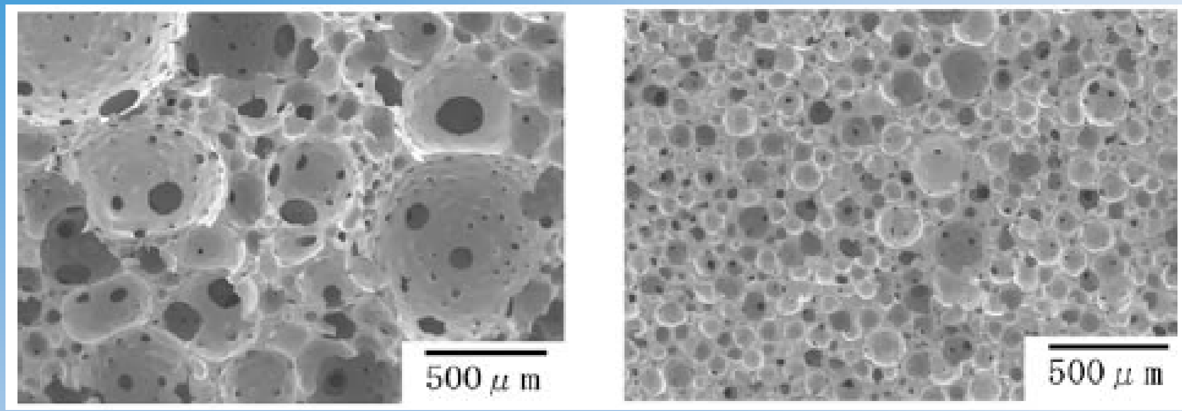
Our First Experimental Attempts towards NIMs as *Hollow Silica Nanospheres* did follow Three Main Preparation Methods:

1. **Membrane Foaming:** Use a membrane to prepare foam with nanoscale bubbles, followed by hydrolysis and condensation of a precursor within bubble walls to make a solid structure.

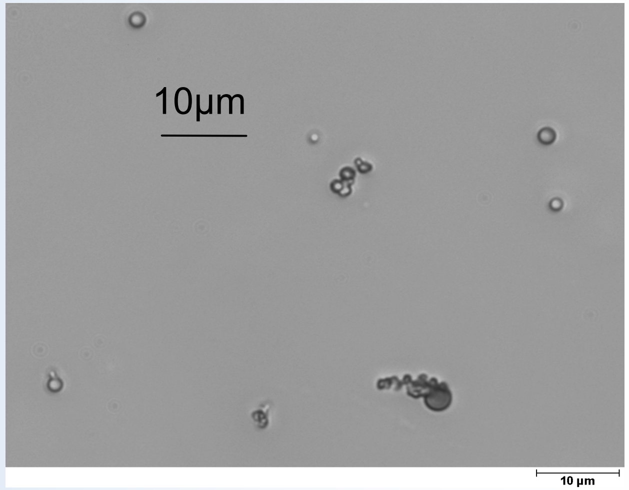
2. **Internal Gas Release:** Controlled decomposition or evaporation of a component to form nanobubbles in a liquid system, followed by formation of a solid shell at the bubble perimeter.

3. **Templating:** Formation of a nanoscale liquid or solid structure, followed by reactions to form a solid shell at the perimeter. Finally, the core is removed to make a hollow sphere.

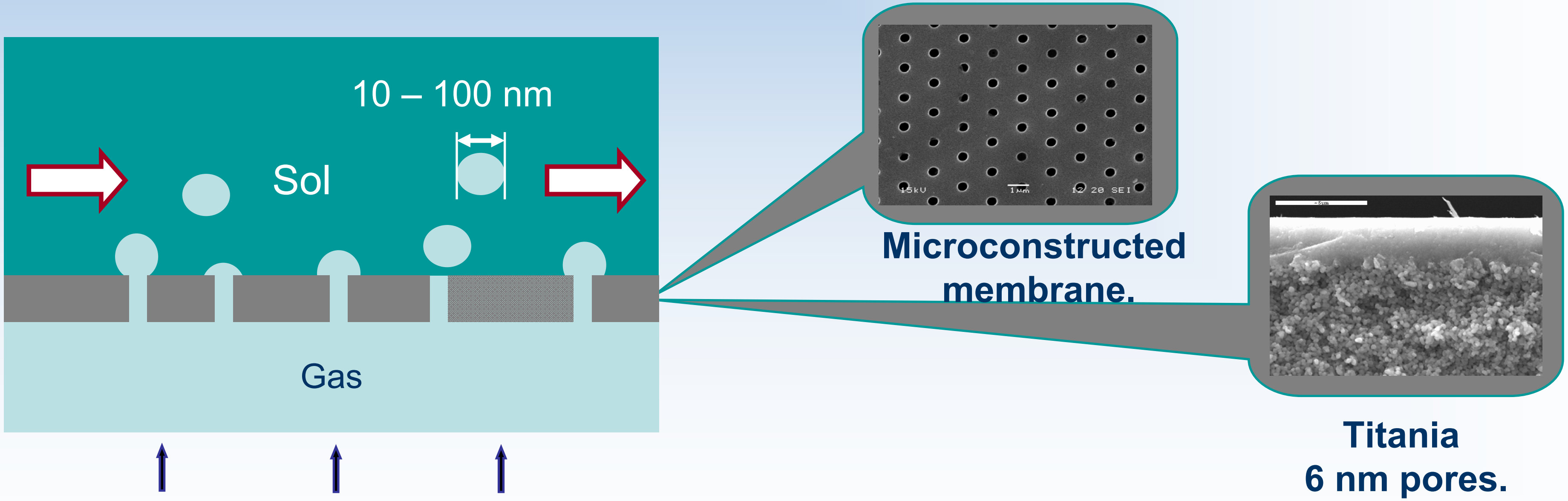
Membrane Foaming



Silica sol stir foamed at 1000 (left) and 2500 (right) mPas
T. Tomita et al. *J. Porous Mater.* **12** (2005) 123.



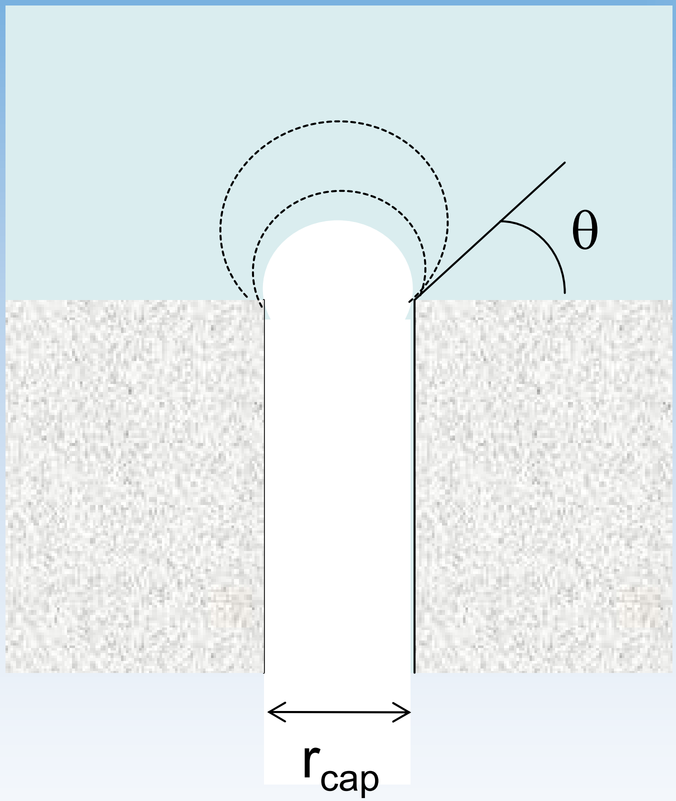
Gas capsules by membrane emulsification. J. Yang et al. SINTEF.



Microconstructed membrane.

Titania 6 nm pores.

Foam Formation



Requirement for nanosized bubbles:

Controlled pressure to avoid continuous gas stream.

$\Delta\rho$: Density difference between gas and liquid, should be large.

r_{cap}: Pore radius, should be small.

σ_l : Surface tension of liquid, should be small.

θ : Contact angle, should be large.

Foam walls should be thin and stable:

η : Liquid viscosity, should be low.

σ_l : Surface tension of liquid, should be small.

Stability: Requires surfactant bialayers.

Membrane Foaming Attempts not Successful:

- Reaction too slow; bubbles broke (with smoke).
- No suitable surfactant systems found to stabilize alcohol-based foams.

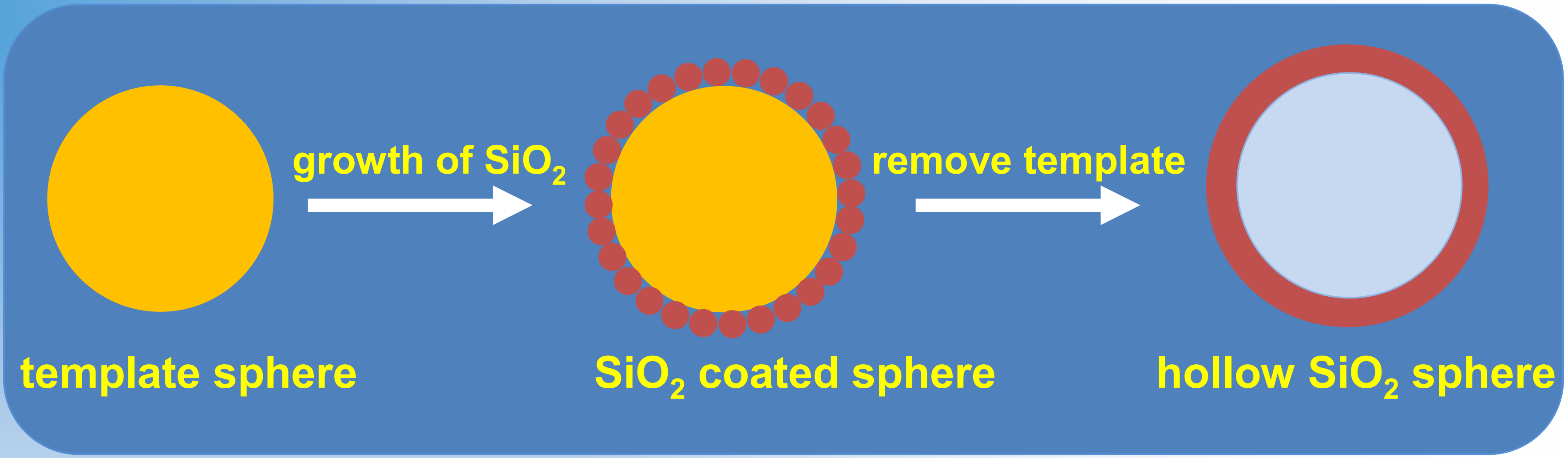
Internal Gas Release Attempts Terminated:

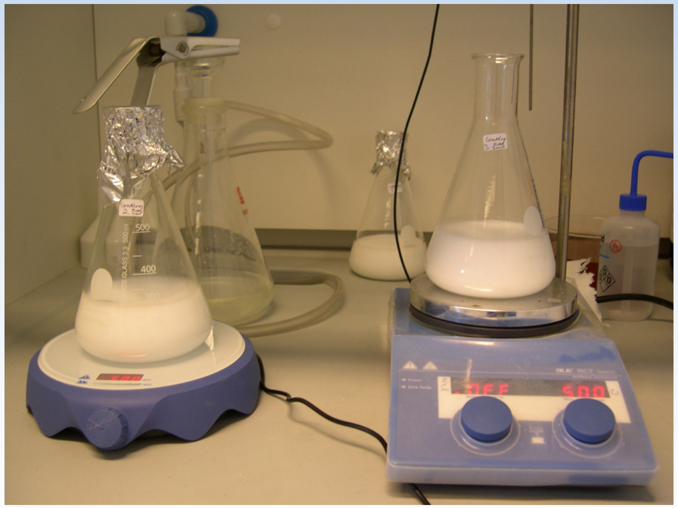
- Very demanding experimental conditions, work terminated.

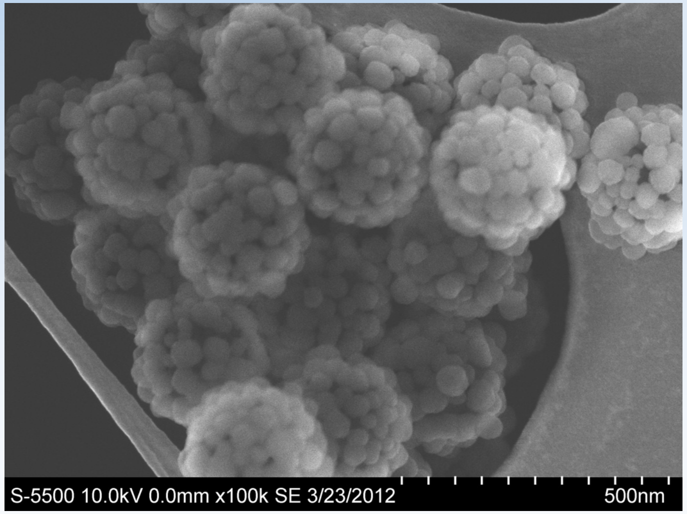
Future experiments may prove different, though.

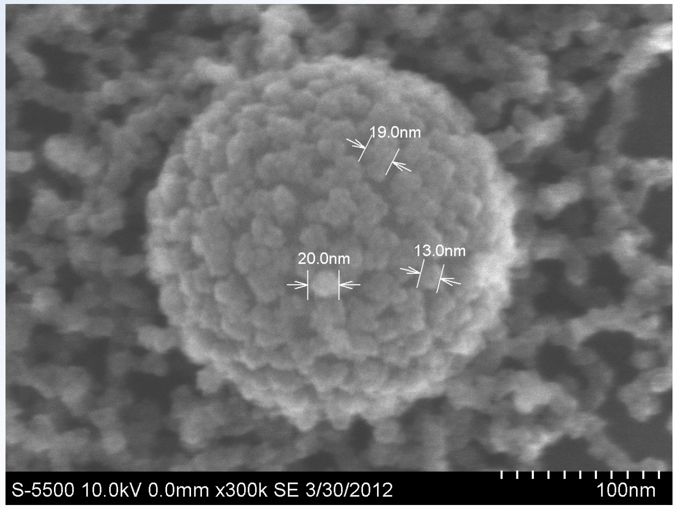
Templating Process: Hollow Silica Nanospheres

Hollow silica nanospheres by making and applying equal-sized templates

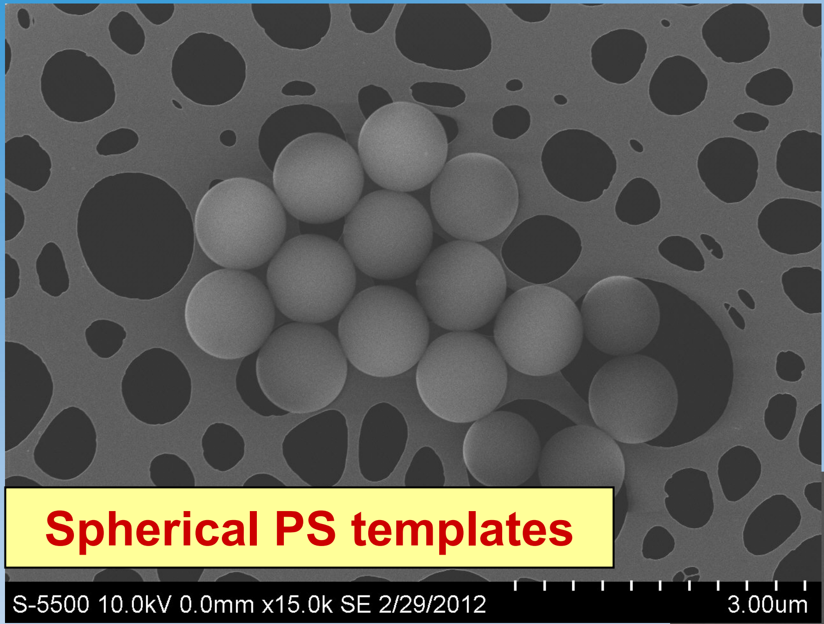






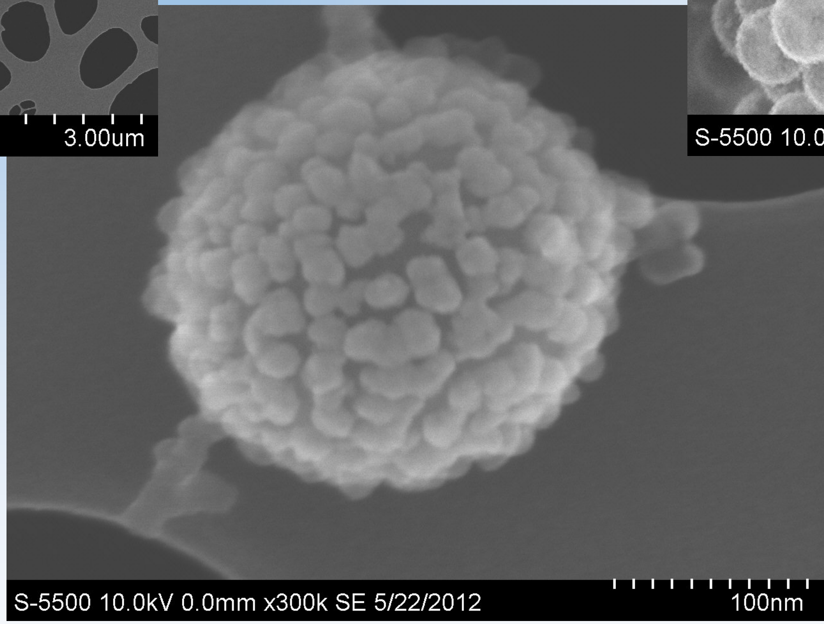


SEM Photos



Spherical PS templates

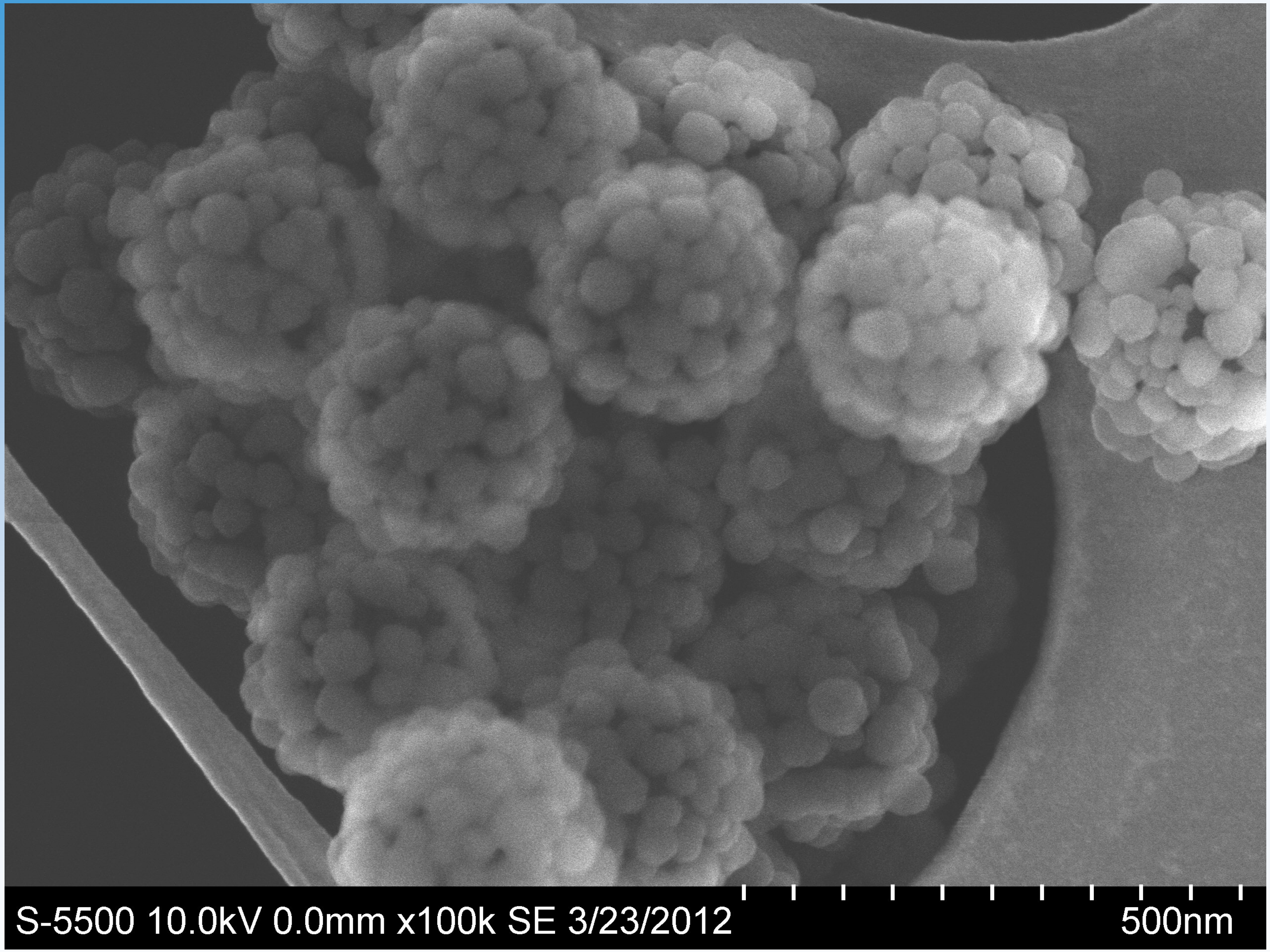
HSNS after removal of PS



Small silica particles coated around a spherical PS template

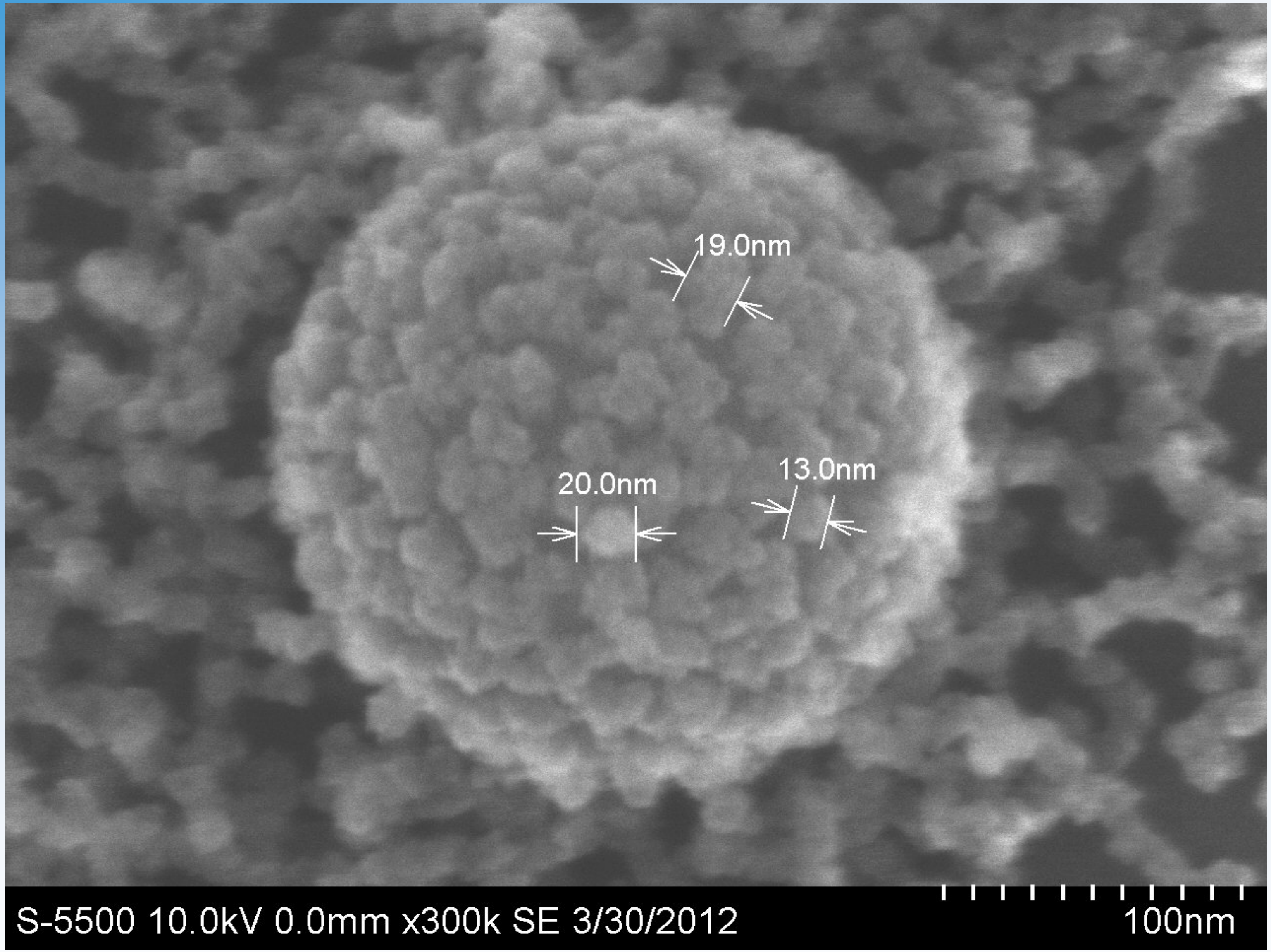
PS = Polystyrene
HSNS = Hollow Silica Nanospheres

SEM Photos



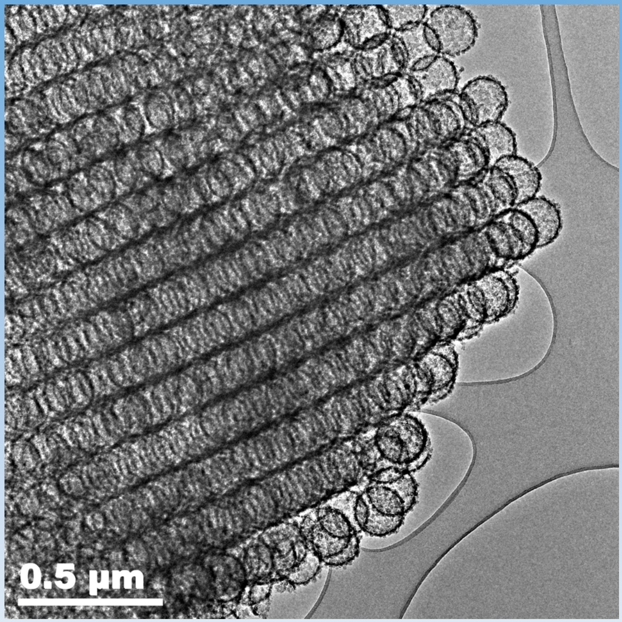
Hollow silica nanospheres by making and applying equal-sized templates

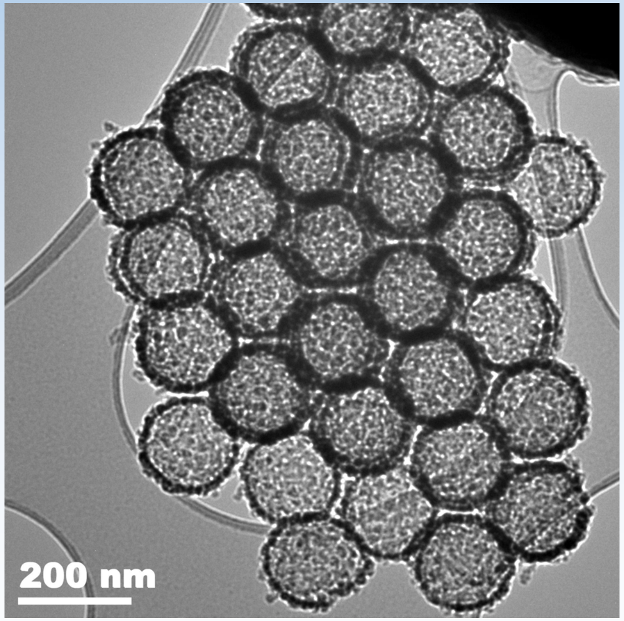
SEM Photos

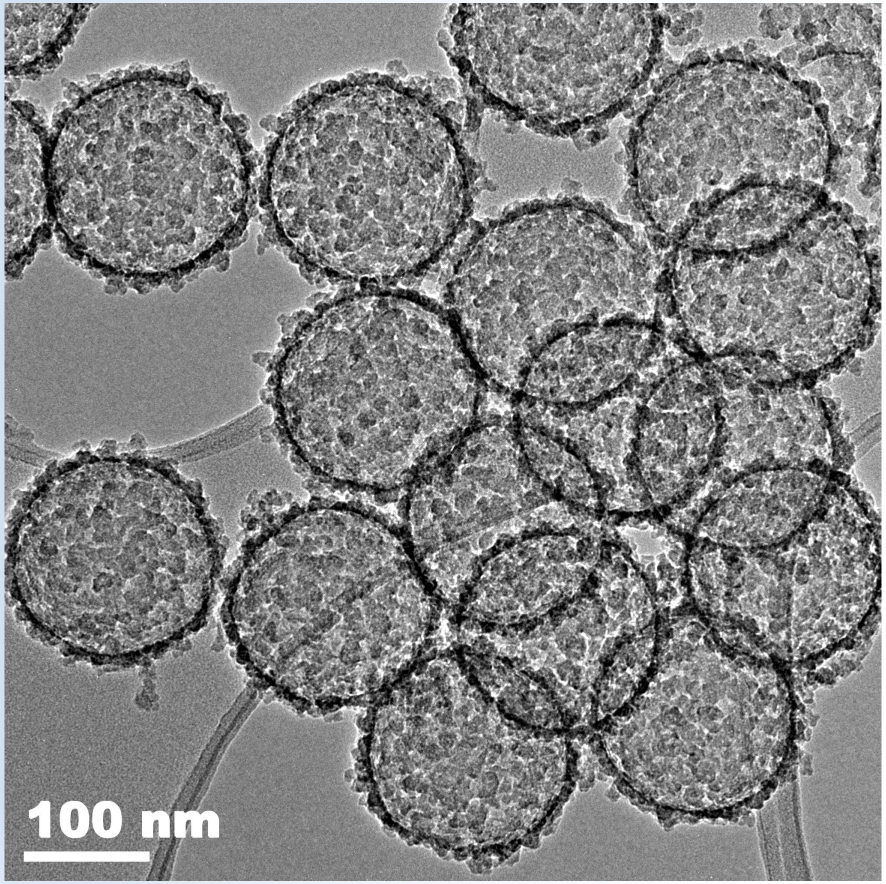


Hollow silica nanospheres by making and applying equal-sized templates

TEM Photos



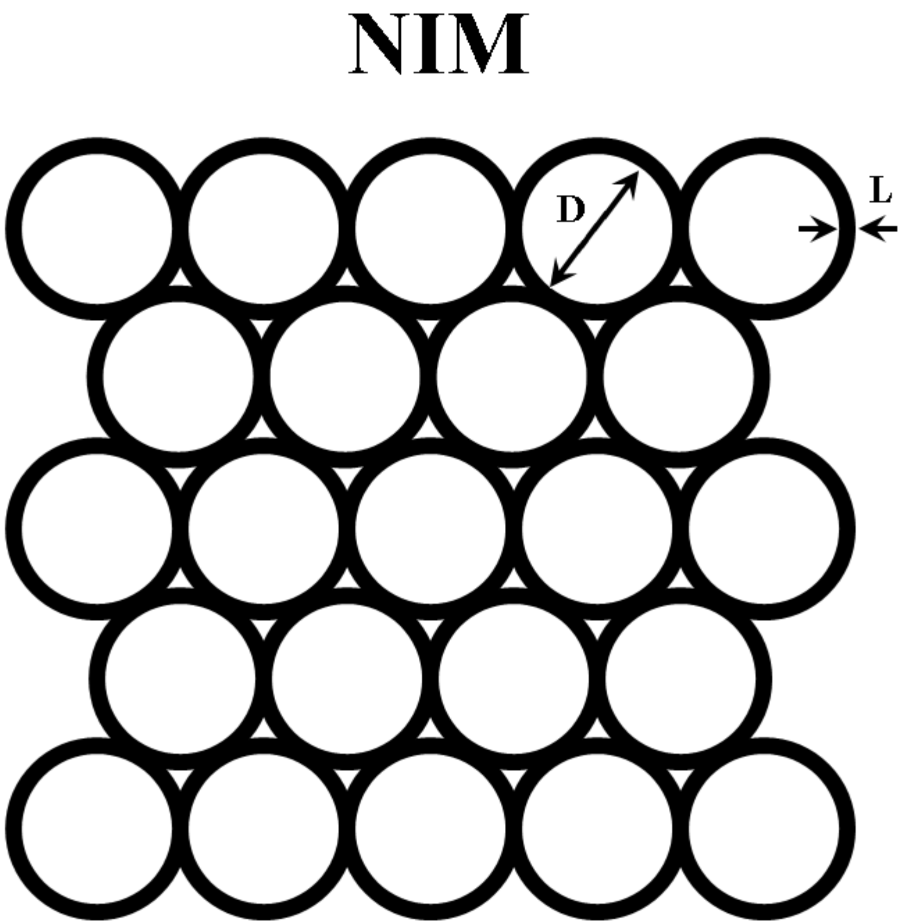


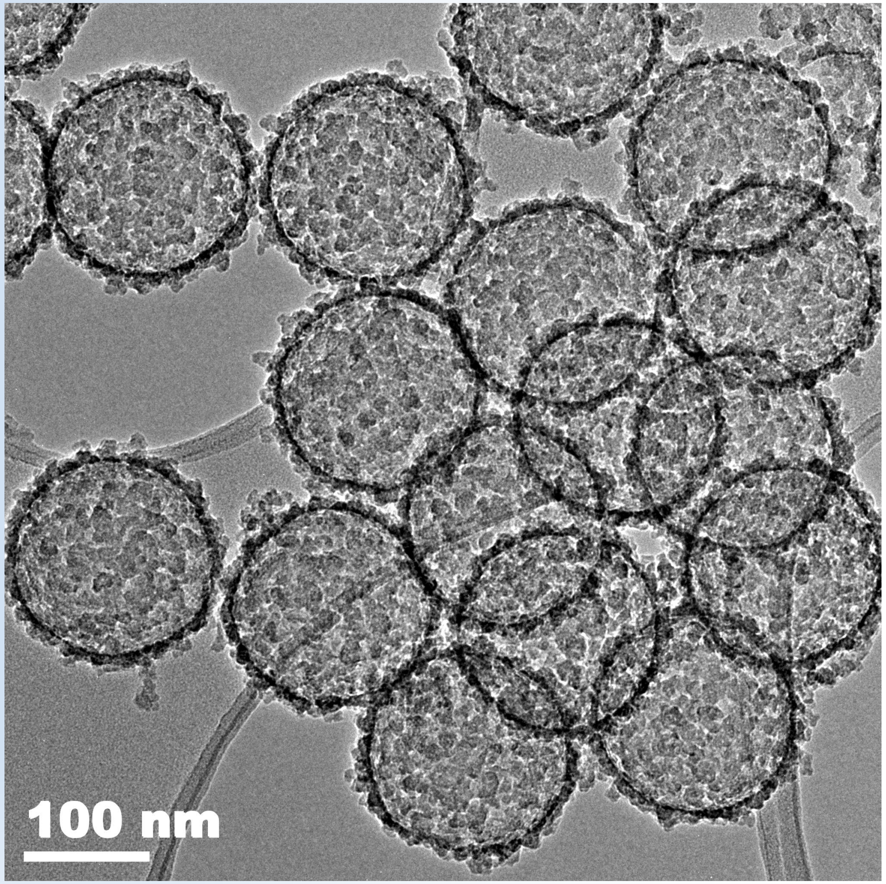


Hollow silica nanospheres by making and applying equal-sized templates

Hollow Silica Nanospheres

Hollow silica nanospheres by making and applying equal-sized templates

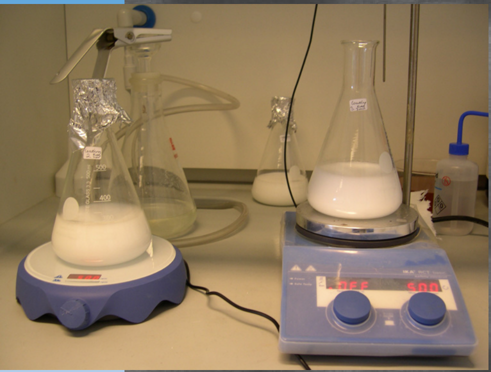


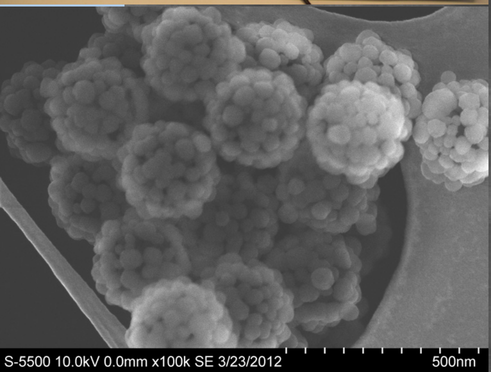


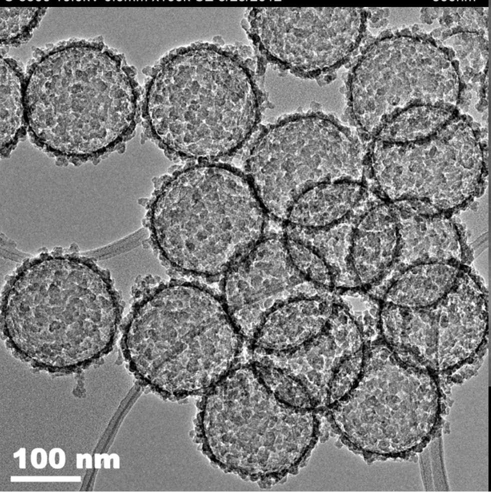
- Controlling:
- Sphere inner diameter
- Sphere wall thickness

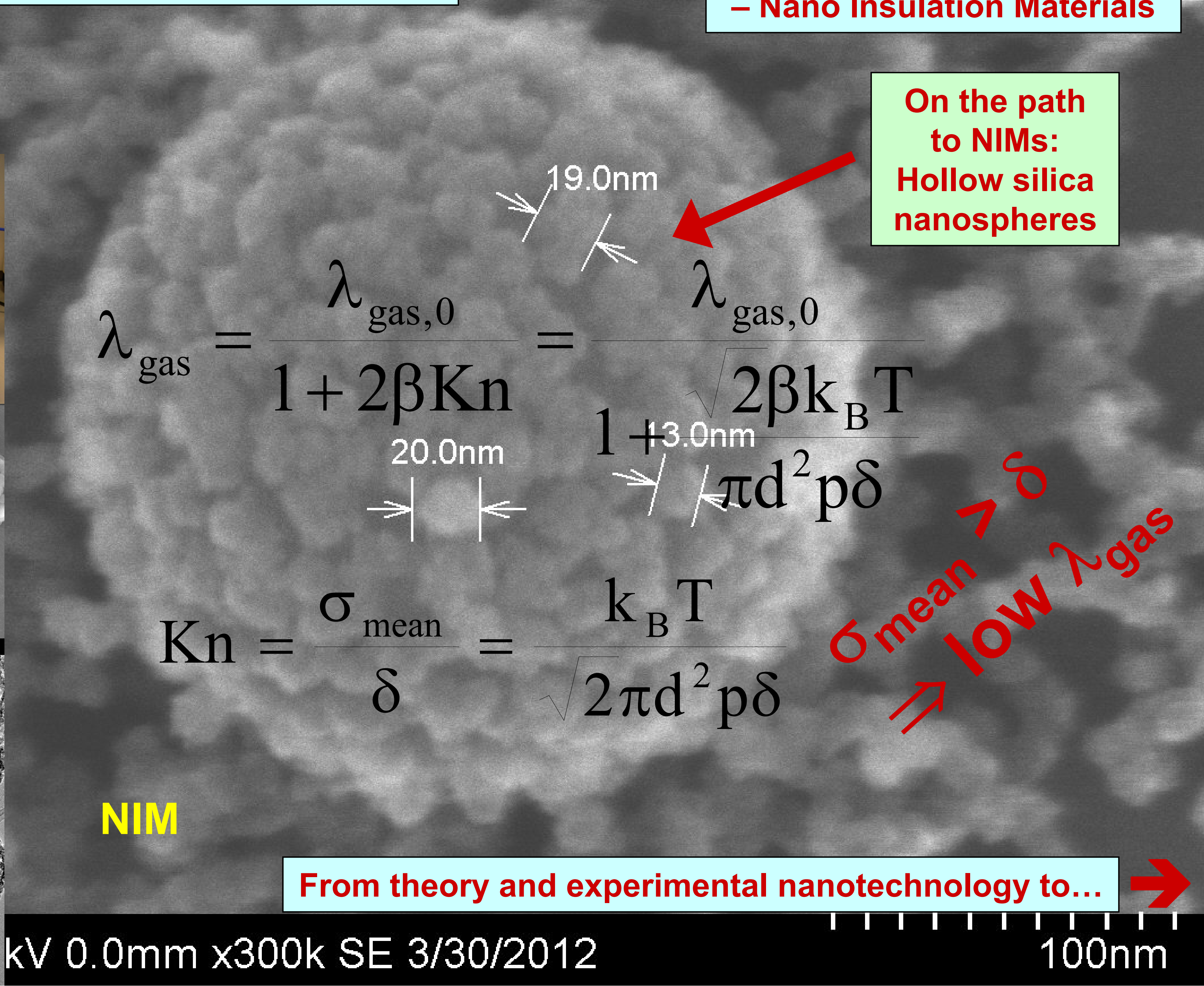
Looking into the Crystal Ball and Seeing ... the Building Envelopes of Tomorrow...

Devloping NIMs – Nano Insulation Materials









On the path to NIMs: Hollow silica nanospheres

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1 + 2\beta Kn} = \frac{\lambda_{gas,0}}{1 + \frac{\sqrt{2}\beta k_B T}{\pi d^2 p \delta}}$$

$$Kn = \frac{\sigma_{mean}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 p \delta}$$

$\sigma_{mean} > \delta \Rightarrow$ **low** λ_{gas}

From theory and experimental nanotechnology to…

Conclusions and The Path Ahead

- Various paths to make nano insulation materials (NIM) as hollow silica nanospheres (HSNS).
- Future NIMs may not necessarily be based on HSNS.
- Investigations on HSNS represent a possible stepping-stone towards achieving high performance thermal insulation materials.
- Powder samples of HSNS have measured thermal conductivity values ~ 20-90 mW/(mK), though some uncertainties in the Hot Disk apparatus measurement method have to be further clarified.
- Further optimization.
- Then to piece HSNS together to form a bulk material.
- Other paths…?