Tailor-Making Nano Insulation Materials with Lowered Thermal Conductivity by Utilizing the Knudsen Effect

Bjørn Petter Jelle [a]*, Sohrab Alex Mofid [a] and Mathieu Grandcolas [b]

[a] Norwegian University of Science and Technology (NTNU),
Department of Civil and Environmental Engineering, NO-7491 Trondheim, Norway.
[b] SINTEF Industry,
Group of Nano and Hybrid Materials, NO-0314 Oslo, Norway.

* Corresponding author: bjorn.petter.jelle@ntnu.no (e-mail).

ABSTRACT

A possible and promising pathway to fabricate thermal super insulation materials (SIM) is to utilize the Knudsen effect where the pore diameters of these materials are attempted lowered below the mean free path of the air molecules, i.e. in the nanorange, thus creating a nano insulation material (NIM) with a nanoporous structure. A particular pathway to manufacture a NIM is to make hollow silica nanospheres (HSNS) by a sacrificial template method, where one may tailor-make the HSNS by controlling their inner sphere diameter and shell thickness. Hence, one may then in principle also be able to tailor-make HSNS with the desired thermal conductivity, normally with as low thermal conductivity as possible. This study presents our latest experimental results with these NIMs made through HSNS, demonstrating a decreasing thermal conductivity with a decreasing inner sphere diameter. These experimental results are also compared with theoretical predictions by the Knudsen effect.

Keywords: nano insulation material, hollow silica nanosphere, super insulation material, thermal conductivity.

1 INTRODUCTION

The world of today is turning its focus even more towards aspects like energy efficiency and renewable and non-polluting energy harvesting, including the building sector with e.g. new thermal insulation materials [1-13], phase change materials [14,15], electrochromic windows [16-29] and building integrated photovoltaics (BIPV) [30-40]. Currently, a huge amount of the energy usage in buildings is tied to heating and cooling and hence it is crucial to minimize the thermal transport connected to heat loss or warming up of buildings. Thus, the quest has been set for developing high-performance thermal insulation materials with very low thermal conductivities.

Traditional thermal insulation materials [2] are still in widespread use, e.g. including mineral wool, expanded polystyrene (EPS), extruded polystyrene (XPS), cellulose, cork, polyurethane (PUR) and similar products, and will still be for many years into the future. Nevertheless, new state-of-the-art thermal insulation materials with considerably lowered thermal conductivities such as vacuum insulation panels (VIP) and aerogels [2,41-45] are experiencing an increased interest and utilization in various building projects, especially when space restrictions are prevailing or space savings are of large importance for both new and existing buildings. Noteworthy, aerogels exhibit the unique feature of being able to be produced as either an opaque, translucent or transparent material, thereby enabling a large application range. However, the state-of-the-art thermal insulation materials have several disadvantages, e.g. loss of vacuum and correspondingly increased thermal conductivity for VIPs and very low mechanical strength for aerogels, also including high production costs for both VIPs and aerogels.

Thus, there is an increased attention to develop new and innovative thermal insulation materials with as low thermal conductivities as VIPs and aerogels, but without their drawbacks. A promising pathway in this respect is to exploit the Knudsen effect where the thermal conductivity is substantially lowered when the pore size of the porous thermal insulation material is decreased into the nanometer range, hence the term nano insulation materials (NIM).

Naturally, in the development of new building materials and components, it is important to carry out durability investigations, e.g. by conducting accelerated climate ageing in the laboratory [46]. In addition, it may also be beneficial to perform a robustness assessment [47].

A possible way of making NIMs are by a sacrificial template method where hollow silica nanospheres (HSNS) in principle may be tailor-made with specific inner sphere diameters and shell thicknesses and thereby also with the desired lowered thermal conductivities. In this study our latest experimental findings on NIMs as HSNS are presented alongside comparisons with theoretical predictions by the Knudsen effect.

2 EXPERIMENTAL

Miscellaneous pathways are possible when attempting to make nano insulation materials (NIM). Herein, we are reporting the results from applying the sacrificial template method for fabricating hollow silica nanospheres (HSNS).

The sacrificial template spheres have so far in our experimental investigations mainly been made as either polyacrylic acid (PAA) or polystyrene (PS) template spheres.

The silica source has in general been the silica precursors tetraethyl orthosilicate (TEOS) and water glass (Na_2SiO_3), and in particular TEOS for the main results reported within this study.

After the PAA or PS templates have been coated with a layer of silica, either in the form as small silica particles or as a large, wrinkled silica sheet (e.g. depending on the silica precursor), the PAA or PS templates have been removed. In this process the PAA templates have been removed by chemical treatment/washing and the PS templates have been removed by heat treatment, where the template materials have been diffusing and evaporating through the silica shells.

The final manufactured result is then a potential NIM in the form of HSNS. In principle, the HSNS synthesis process by the sacrificial template method is depicted in the cross-section illustration given in Fig.1, alongside an actual example of HSNS synthesis as shown in Fig.2 with scanning electron microscope (SEM) images of synthesized spherical PS templates, a PS template coated with small silica particles, and HSNS after removal of the PS templates, hence demonstrating an captivating and enchanting example of the scientific step from theoretical concept to actual experimental results.

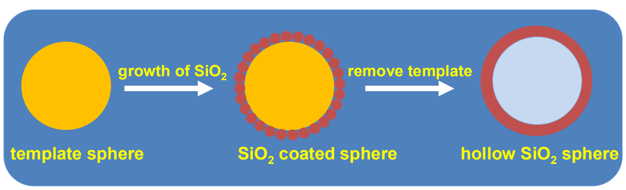

Figure 1. Illustrated cross-section of the hollow silica nanospheres (HSNS) synthesis process by the sacrificial template method.

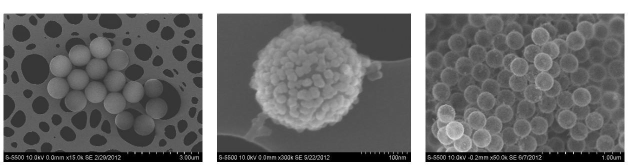

Figure 2. SEM images of an actual HSNS synthesis process with (left) spherical PS templates, (middle) small silica particles coated around a spherical PS template, and (right) HSNS after removal of PS templates.

Scanning electron microscopes (SEM) and transmission electron microscopes (TEM) have been applied in order to characterize the visual appearance and dimensional attributes at nano level for the synthesized HSNS and their corresponding PS sacrificial template spheres.

A Hot Disk apparatus has been employed for measuring the thermal conductivity values for miscellaneous HSNS powder samples in our earlier presented HSNS studies.

For the HSNS results presented in this study, the thermal conductivity λ of the HSNS was determined by calculation according to

$$\lambda = \alpha \rho c_p \qquad (1)$$

where the diffusivity α was measured by a laser flash apparatus, the mass density ρ was calculated as $\rho = m/V$ from mass m and volume V measurements, and the specific heat capacity c_p was measured by differential scanning calorimetry (DSC).

3 RESULTS AND DISCUSSION

In our first attempts to make nano insulation materials (NIM) as hollow silica nanospheres (HSNS), many different HSNS have been manufactured. Large variations have been observed concerning the HSNS size distributions, inner diameters, shell/wall thicknesses, silica particle dimensions, and surface roughness/smoothness and morphologies.

Examples of HSNS with different surface roughnesses and morphologies are shown in the SEM images in Fig.3, which are dependent on several synthesis parameters including the choice of silica precursor (e.g. TEOS or water glass in our experiments).

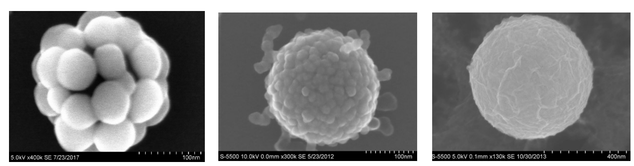

Figure 3. SEM images of HSNS with different surface roughnesses and morphologies, (left) TEOS as silica precursor giving silica shell as silica nanoparticles (magnification 400 000 x, scale-bar 100 nm), (middle) TEOS as silica precursor giving silica shell as silica nanoparticles (magnification 300 000 x, scale-bar 100 nm), and (right) water glass as silica precursor giving silica shell as large, wrinkled silica sheet (magnification 130 000 x, scale-bar 400 nm).

In a recent experimental study [13] we fabricated various HSNS with different inner sphere diameters, shell thicknesses and silica particle dimensions with a goal of observing and correlating the measured total thermal conductivity with the inner sphere diameters. That is, an attempt to tailor-make NIMs as HSNS with lowered thermal conductivity by utilizing the Knudsen effect.

The SEM images in Fig.4 depict an example of HSNS with the same inner diameter of 85 nm and two different shell thicknesses of 34 nm and 67 nm, where the shell thicknesses are approximately the dimensions of the diameters of the silica particles constituting the shells surrounding their inner voids.

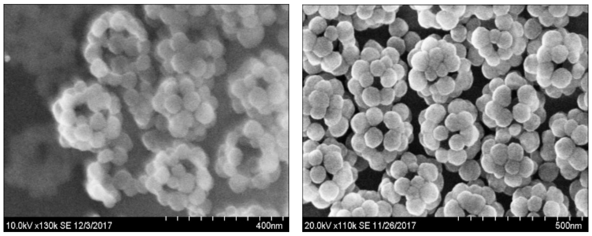

Figure 4. SEM images of HSNS with inner diameter 85 nm and a shell thickness of (left) 34 nm and (right) 67 nm.

The thermal conductivity of these HSNS samples have been measured with a laser flash apparatus as described in the above, with the results summarized as given in Table 1 and graphically plotted in Fig.5. Furthermore, the results are compared with the Knudsen calculated thermal conductivity in both Table 1 and Fig.5.

In short, the Knudsen calculated thermal conductivity λ_{Kn}, i.e. the gas thermal conductivity also including the gas and solid state interaction, is calculated according to the Knudsen effect in a simplified way as

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

where

$$Kn = \frac{\sigma_{mean}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 p \delta} \quad (3)$$

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

Table 1. HSNS samples with different inner diameters and measured total thermal conductivities calculated according to Eq.1. The sphere shell thickness is around 34 nm for all four samples. The calculated gas plus gas-solid interaction thermal conductivity λ_{Kn} according to the Knudsen effect is given, representing a lower limit for the thermal conductivity as the measured total one also includes solid state, convective and radiative thermal transport.

HSNS sample	Inner diameter (nm)	Thermal diffusivity α (mm^2/s)	Mass density ρ (kg/dm^3)	Specific heat capacity c_p (J/(kgK))	Measured total thermal conductivity λ (mW/(mK))	Knudsen calculated thermal conductivity λ_{Kn} (mW/(mK))
1	85	0.102	0.190	740	14.3	6.78
2	100	0.144	0.180	740	19.2	7.63
3	150	0.195	0.175	740	25.3	9.99
4	213	0.236	0.170	740	29.7	12.2

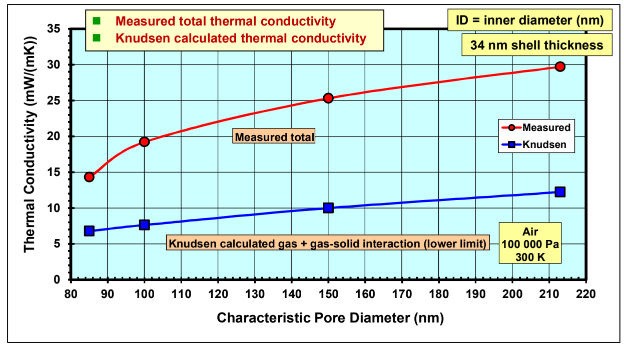

Figure 5. Measured total thermal conductivity for HSNS samples with different inner diameters. The sphere shell thickness is around 34 nm for all four samples. The calculated gas plus gas-solid interaction thermal conductivity according to the Knudsen effect is depicted, representing a lower limit for the thermal conductivity.

The measured thermal conductivity decreases with decreasing HSNS inner diameter as seen from Table 1 and Fig.5, which is also predicted by the Knudsen effect (Eq.2 and Eq.3). Furthermore, it is observed that for an inner sphere diameter reduction of HSNS from 213 nm to 85 nm, the measured thermal conductivity is reduced from 29.7 mW/(mK) to 14.3 mW/(mK), respectively.

Thus, for forthcoming HSNS development, PS spheres with diameters further below 85 nm should be attempted synthesized, even though so far it has been a challenging task to fabricate PS spheres with such small diameters. Nevertheless, if successful, HSNS with smaller inner diameters could be synthesized and thereby also even lower thermal conductivities. However, this is valid as long as one is able to keep the solid state (in general also the radiative) thermal conductivity sufficiently low, as the solid part (e.g. sphere shell thickness) and hence the mass density may increase with decreasing HSNS inner diameter.

4 CONCLUSIONS

In the quest to make nano insulation materials (NIM), a sacrificial template method has been applied to synthesize hollow silica nanospheres (HSNS). The HSNS may through the synthesis parameters be tailor-made with the desired inner sphere diameters and shell thicknesses.

It is observed that the measured thermal conductivity of the HSNS is decreasing with decreasing inner sphere diameters as anticipated in accordance with the Knudsen effect. HSNS samples with inner sphere diameters of 85 nm and shell thicknesses of 34 nm gave a measured total thermal conductivity of 14.3 mW/(mK).

ACKNOWLEDGEMENTS

This work has been supported by the Research Council of Norway through "High-Performance Nano Insulation Materials", and by Husbanken through "Multi-Functional Building Envelopes - Visions for the Future".

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