Experimental Synthesis of Hollow Silica Nanospheres for Application as Superinsulation in the Buildings of Tomorrow

Bjørn Petter Jelle[1], Tao Gao[2], Linn Ingunn Christie Sandberg[3], Bente Gilbu Tilset[4], Mathieu Grandcolas[5] and Arild Gustavsen[6]

ABSTRACT

The path toward energy-efficient buildings with a low or zero carbon footprint, e.g. zero energy and zero emission buildings, involves the development of high-performance thermal insulation, aiming at reaching thermal conductivities far below 20 mW/(mK). Applying such superinsulation will allow the construction of relatively thin building envelopes yet maintaining a high thermal resistance, thus also increasing the architectural design possibilities. A vacuum insulation panel (VIP) represents a state-of-the-art thermal insulation solution with a thermal conductivity of typical 4 mW/(mK) in the pristine and non-aged condition. However, the VIPs have issues with fragility, perforation vulnerability, increasing thermal conductivity during time and lack of building site adaption by cutting as four cardinal weaknesses, in addition to heat bridge effects and relatively high costs. Therefore, the VIPs of today do not represent a robust solution. Hence, our aim is from theoretical principles, utilizing the Knudsen effect for reduced thermal gas conductance in nanopores, to develop experimentally a high-performance nano insulation material (NIM). This work presents the current status of the development of NIM as hollow silica nanospheres (HSNS) in our laboratories, from the experimental synthesis to the material characterization by e.g. thermal conductivity measurements. One attempted approach for tailor-making HSNS is the sacrificial template method and optimization of the sphere diameter and shell thickness with respect to low thermal conductivity. The results so far indicate that HSNS represent a promising candidate for achieving the high-performance thermal superinsulation for application in the buildings of tomorrow.

Keywords: *Silica, Nanosphere, HSNS, Superinsulation, Thermal conductivity, Building.*

INTRODUCTION

Energy-efficient buildings will increase in demand in the years to come. High performance thermal building insulation materials and solutions will play an important role in this regard, where one possible and promising way to tailor-make superinsulation is to exploit the Knudsen effect by decreasing the gas thermal conductivity by decreasing the pore diameter in a material below the mean free path of the gas molecules, i.e. in the nanometer range. The objective of the work reported

---

[1] Bjørn Petter Jelle, SINTEF Building and Infrastructure, Department of Materials and Structures, NO-7465 Trondheim, Norway, and, Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, NO-7491 Trondheim, Norway. E-mail: bjorn.petter.jelle@sintef.no

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

[3] Linn Ingunn Christie Sandberg, Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, NO-7491 Trondheim, Norway.

[4] Bente Gilbu Tilset, SINTEF Materials and Chemistry, Materials and Nanotechnology Sector, NO-0314 Oslo, Norway.

[5] Mathieu Grandcolas, SINTEF Materials and Chemistry, Materials and Nanotechnology Sector, NO-0314 Oslo, Norway.

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

herein is to summarize and explore the experimental pathway for achieving superinsulation through nano insulation materials (NIM) (Baetens et al. 2010; Jelle et al. 2009; Jelle et al. 2010; Jelle 2011; Jelle et al. 2012) as hollow silica nanospheres (HSNS) being manufactured by utilizing selected sacrificial template methods (Gao et al. 2012; Gao et al. 2013; Gao et al. 2014b; Grandcolas et al. 2013; Jelle et al. 2011; Jelle et al. 2013; Sandberg et al. 2013; Schlanbusch et al. 2014ab).

THE CONCEPT OF DECREASED THERMAL CONDUCTIVITY

A very low thermal conductivity is targeted in the development of thermal superinsulation, hence all the contributions to the conductivity have to be minimized. The total overall thermal conductivity λ_{tot}, i.e. the thickness of a material divided by its thermal resistance, is in principle made up from the following parts:

$$\lambda_{tot} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coupling} + \lambda_{leak} \quad (1)$$

where λ_{tot} is the total overall thermal conductivity, λ_{solid} is the solid state thermal conductivity, λ_{gas} is the gas thermal conductivity, λ_{rad} is the radiation thermal conductivity, λ_{conv} is the convection thermal conductivity, $\lambda_{coupling}$ is the thermal conductivity term accounting for second order effects between the various thermal conductivities in Equation 1, and λ_{leak} is the leakage thermal conductivity. The leakage thermal conductivity λ_{leak}, representing an air and moisture leakage driven by a pressure difference, is normally not considered as insulation materials and solutions are supposed to be without any holes enabling such a thermal leakage transport. The coupling term $\lambda_{coupling}$ may be included to account for second order effects between the various thermal conductivities in Equation 1, however, this coupling effect can be quite complex and will be neglected in the following. Besides, theoretical approaches to thermal performance of vacuum insulation panels (VIP) usually assume this coupling effect to be negligible (Heinemann 2008). Note that in general another coupling term may also be included in Equation 1, i.e. the interaction between the gas molecules and the solid state pore walls. However, as we will see in the following this last coupling term is included through a factor in the expression for the gas conductivity as given in Equation 2 for the Knudsen effect. For further information on thermal conductivity aspects it is referred to the studies by Jelle et al. (2010) and Jelle (2011).

A possible solution towards thermal superinsulation is the development of nano insulation materials (NIM). In a nano insulation material (NIM) the pore size within the material is decreased below a certain level, i.e. 40 nm or below for air, in order to achieve an overall thermal conductivity of less than 4 mW/(mK) in the pristine (non-aged) condition. That is, a NIM is defined as basically a 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 (Jelle et al. 2010). The low thermal conductivity in a NIM, without applying a vacuum in the pores, is achieved by utilizing the so-called Knudsen effect. The gas thermal conductivity λ_{gas} taking into account the Knudsen effect may be written in a simplified way as (Baetens et al. 2010; Jelle et al. 2010; Jelle 2011):

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

where

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

where λ_{gas} is the gas thermal conductivity in the pores (W/(mK)), $\lambda_{gas,0}$ is the gas thermal conductivity in the pores at standard temperature and pressure (STP) (W/(mK)), β is a coefficient characterizing the molecule-wall collision energy transfer (in)efficiency (between 1.5 - 2.0), k_B is 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), and σ_{mean} is the mean free path of gas molecules (m).

If the pore size within a material is decreased below a certain level, i.e. a pore diameter of the order of 40 nm or below for air, the gas thermal conductivity, and thereby also the overall thermal conductivity, becomes very low (< 4 mW/(mK) with an adequate low-conductivity grid structure) even with air-filled pores. This is explained by the Knudsen effect where the mean free path of the gas molecules is larger than the pore diameter. That is, a gas molecule located inside a pore will hit the pore wall and not another gas molecule, and where the solid state and gas interaction is taken care of by the β coefficient. Thus, the resulting gas thermal conductivity λ_{gas}, also including the gas and pore wall interaction, versus pore diameter and pore gas pressure, may be calculated in this simplified model and depicted as in Figure 1. Further details on NIM and the Knudsen effect, also including thermal radiation aspects, are given in the work by Jelle et al. (2010).

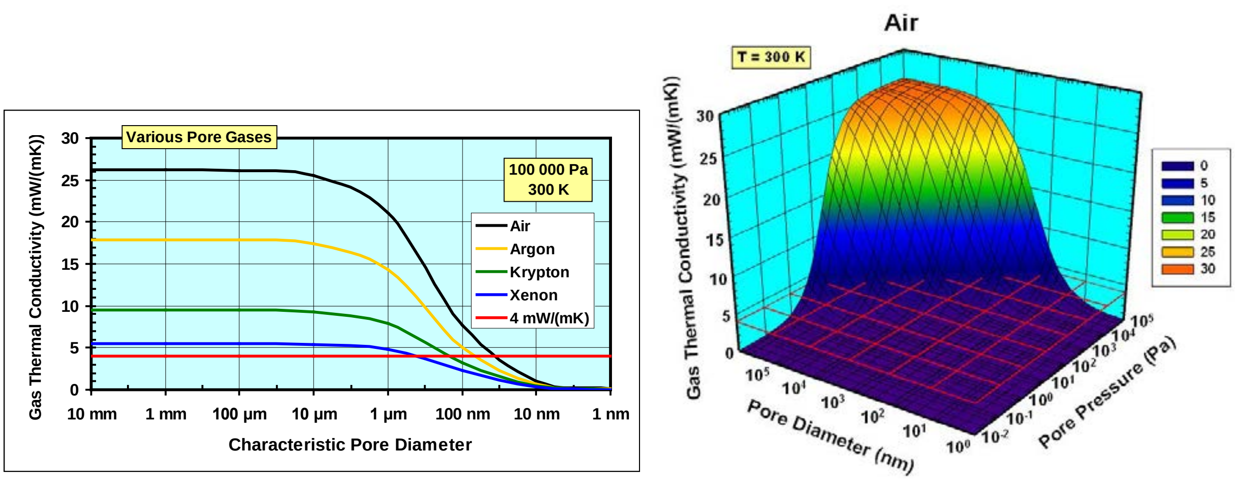

Figure 1: Gas thermal conductivity with (left) 2D-plot depicting the effect of pore diameter for air, argon, krypton and xenon and (right) 3D-plot depicting the effect of pore diameter and gas pressure in pores containing air (Jelle et al. 2010).

EXPERIMENTAL PATHWAYS

Our first experimental attempts for making nano insulation materials were carried out along three pathways, that is membrane foaming, gas release and templating. The principle of membrane foaming is to produce foams with nanoscale bubbles, followed by condensation and hydrolysis within the bubble walls to obtain a silica nanofoam, where a gas is pressed through a membrane to obtain bubbles with controlled size. As no surfactant was found that could stabilize nanofoams long enough, this experimental pathway has so far been abandoned. The gas release method requires simultaneous formation of nanosized gas bubbles throughout the reaction system, followed by hydrolysis and condensation to form a solid at the bubble perimeter, where the bubble formation could be achieved by either evaporation or decomposition of a component in the system. This method is similar to a process described by Grader et al. (1998), where crystals were heated to produce foams with closed cell structures. Due to various experimental difficulties the gas release approach has at the moment been terminated. Utilizing the templating process, a nanoscale structure in the form of a nanoemulsion or polymer gel is prepared, followed by hydrolysis and condensation to form a solid. Our starting point was based on the work by Du et al. (2010), who used the method to prepare antireflection coatings, and the work by Wan and Yu (2008). For further details it is referred to our initial experimental studies (Jelle et al. 2011). In the following, results from utilizing the template method forming hollow silica nanospheres (HSNS) will be presented.

HOLLOW SILICA NANOSPHERES

Miscellaneous detailed experimental information and procedures concerning the various fabrications of hollow silica nanospheres (HSNS) are found in our earlier studies (Gao et al. 2012; Gao et al. 2013; Gao et al. 2014b; Grandcolas et al. 2013; Jelle et al. 2011; Jelle et al. 2013; Sandberg et al. 2013). Basically, the HSNS manufacturing applies the template method as described earlier, with either polyacrylic acid (PAA) or polystyrene (PS) as sacrificial templates, where PAA and PS have been removed by a washing and a heating process, respectively (the template materials diffuse and evaporate through the silica shell). The principle of the sacrificial template method for HSNS fabrication is illustrated in Figure 2.

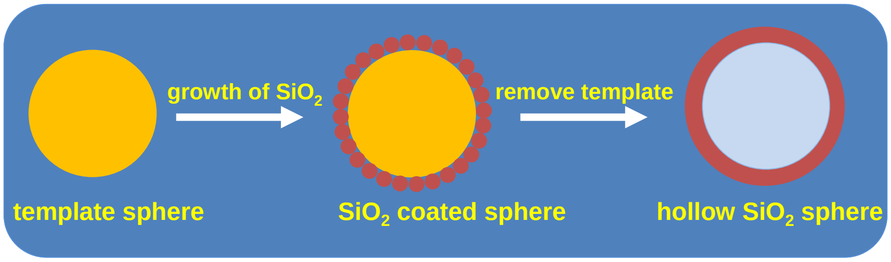

Figure 2. Illustration of the sacrificial template method for manufacturing of HSNS. Compare with actual experimental HSNS fabrication in Figure 4.

Nano insulation materials (NIM) have been attempted manufactured in the laboratory as various hollow silica nanospheres (HSNS). A principle drawing of a NIM alongside a transmission electron microscope (TEM) image of actual manufactured HSNS are given in Figure 3, thus depicting the close resemblance from theoretical concepts to experimental fabrication attempts.

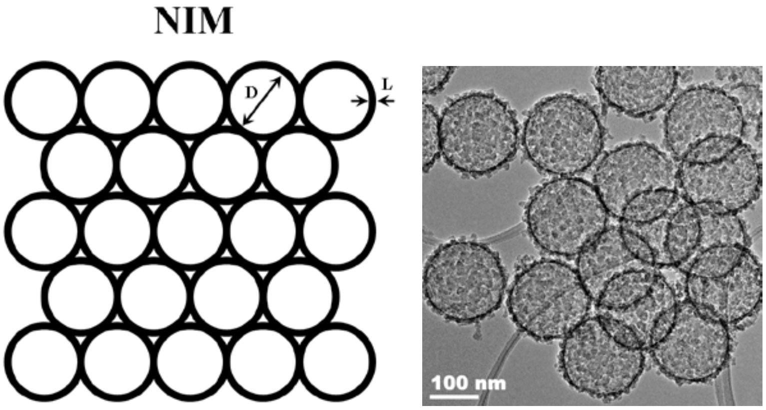

Figure 3. From theory to practice by experiments depicting a principle drawing of a NIM (left) alongside a TEM image of actual manufactured HSNS (right).

Scanning electron microscope (SEM) images of fabricated spherical PS templates are shown in Figure 4 (left). The PS templates were thereafter coated with small silica particles, where an example is depicted in Figure 4 (middle). By removal of the PS templates, HSNS are formed, depicted in Figure 4 (right). Furthermore, another SEM image example of HSNS with PS templates underneath is shown in Figure 5 (left), depicting a more coarse silica surface than the one given in Figure 4 (middle). Note that when attempting to make monodisperse PS nanospheres, the results are not always as planned or hoped for, although some rather intriguing patterns may be revealed in the SEM images, where an example is shown in Figure 5 (right).

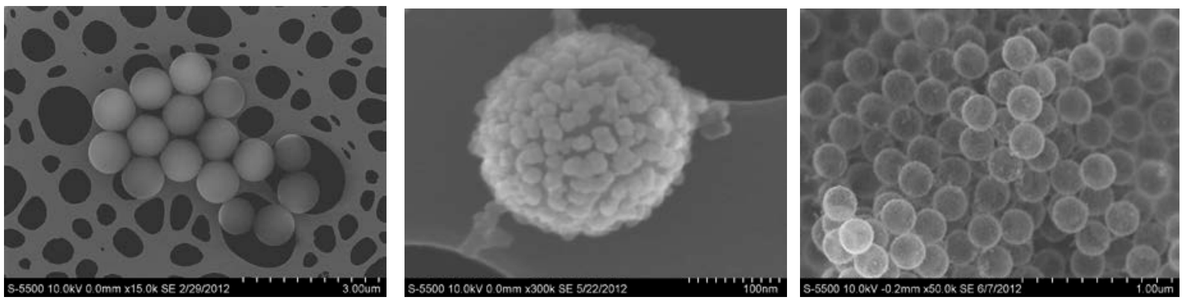

Figure 4. SEM image of (left) spherical PS templates, (middle) small silica particles coated around a spherical PS template, and (right) HSNS after removal of PS. Compare with illustration in Figure 2.

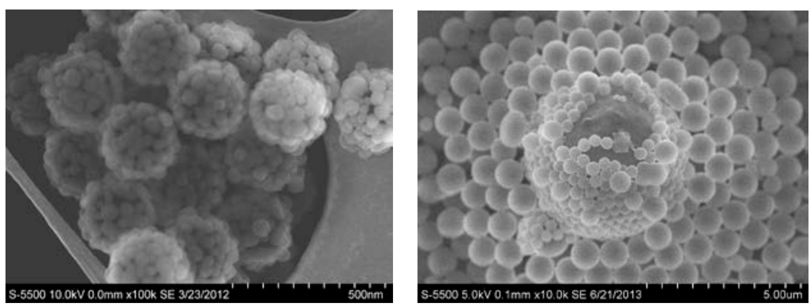

Figure 5. (left) SEM image of small silica particles coated around spherical PS templates, i.e. HSNS before removal of PS (with a more coarse silica surface than the one given in Figure 4 (middle)). (right) When attempting to make monodisperse PS nanospheres, the results are not always as planned, although some rather intriguing patterns may be revealed in the SEM images.

The thermal conductivity has been measured for various powder samples of HSNS, where the conductivity values are typically in the range 20 to 90 mW/(mK), though some uncertainties in the Hot Disk apparatus measurement method have to be further clarified (Grandcolas et al. 2013; Jelle et al. 2013). Regarding thermal conductivity measurements, the specific powder packing of the HSNS in the bulk condition is also an issue to be addressed. At the moment, the thermal conductivity is being attempted lowered by a parameter variation and optimization of the hollow silica sphere inner diameter and wall thickness. In addition, aspects like e.g. thermal radiation, mesoporosity, powder packing at bulk scale and nanosphere packing at nano scale should be addressed. In general, it is of major importance to investigate the durability of building materials and components, also newly developed ones, e.g. by carrying out accelerated climate ageing in the laboratory (Jelle 2012). Hence, performing a robustness assessment of these materials and components may also be found to be beneficial (Jelle et al. 2014). That is, a durability and robustness evaluation of the new superinsulation materials (when ready) should be carried out.

Life cycle analysis (LCA) of NIM as HSNS has been performed in the studies by Gao et al. (2013; 2014b) and Schlanbusch et al. (2014ab). Initial experiments attempting to improve the thermal resistance of concrete by incorporation of aerogel have also been performed (Gao et al. 2014a), and is still ongoing, where naturally any new development of NIM, HSNS and related materials will be interesting for further work. For additional information on the fabrication of monodisperse PS nanospheres it is referred to the work by Du and He (2008). More information on hollow silica nanospheres may be found in the studies by e.g. Liao et al. (2011), Wang et al. (2010), Han et al. (2011) and Yuan et al. (2010).

FORTHCOMING WORK

Our NIM research has currently a main focus on various attempts to tailor-make HSNS by manufacturing and applying different sacrificial templates, synthesis procedures, parameter variations, and inner diameters and shell thicknesses of the nanospheres. A crucial issue will be how to assemble the HSNS together into a practical, robust and sustainable bulk material. It is emphasized that the future NIM may not necessarily be based on HSNS, nevertheless the investigations on the HSNS represent a possible stepping-stone towards the ultimate goal of achieving thermal superinsulation materials.

It should be noted that although we for the time being are not pursuing fabricating NIM according to the membrane foaming and gas release methods, these methods should definitely not be forgotten as they may still represent a possible way of achieving NIM and thermal superinsulation materials. Finally, it should be emphasized that also methods and materials not included within this summary, even hitherto unknown methods and materials, may hold the solution for the thermal superinsulation materials of tomorrow.

CONCLUSIONS

Hollow silica nanospheres (HSNS) have been manufactured by a sacrificial template method. The experimental synthesis of the HSNS represent a possible stepping-stone and a promising candidate for the development of the future thermal superinsulation materials. Further studies are needed though, and along the path of these, they may also reveal hitherto unknown methods and materials for reaching the goal of a robust and sustainable superinsulation material.

ACKNOWLEDGEMENTS

This work has been supported by the Research Council of Norway and several partners through ”*The Research Centre on Zero Emission Buildings*” (ZEB).

REFERENCES

Baetens, R., Jelle, B.P., Thue, J.V., Tenpierik, M.J., Grynning, S., Uvsløkk, S., and Gustavsen, A., ”Vacuum insulation panels for building applications: A review and beyond”, *Energy and Buildings*, **42**, 147-172, 2010.

Du, X., and He, J., ”Facile size-controllable syntheses of highly monodisperse polystyrene nano- and microspheres by polyvinylpyrrolidone-mediated emulsifier-free emulsion polymerization”, *Journal of Applied Polymer Science*, **108**, 1755-1760, 2008.

Du, Y., Luna, L.E., Tan, W.S., Rubner, M.F., and Cohen, R.E., ”Hollow silica nanoparticles in UV-visible antireflection coatings for poly(methyl methacrylate) substrates”, *ACS Nano*, **4**, 4308-4316, 2010.

Gao, T., Sandberg, L.I.C., Jelle, B.P., and Gustavsen, A., ”Nano insulation materials for energy efficient buildings: A case study on hollow silica nanospheres”, in ”Fuelling the Future: Advances in Science and Technologies for Energy Generation, Transmission and Storage”, A. Mendez-Vilas (Ed.), BrownWalker Press, pp. 535-539, 2012.

Gao, T., Jelle, B.P., Sandberg, L.I.C., and Gustavsen, A., ”Monodisperse hollow silica nanospheres for nano insulation materials: Synthesis, characterization, and life cycle assessment”, *ACS Applied Materials and Interfaces*, **5**, 761-767, 2013.

Gao, T., Jelle, B.P., Gustavsen, A., and Jacobsen, S., ”Aerogel-incorporated concrete: An experimental study”, *Construction and Building Materials*, **52**, 130-136, 2014(a).

Gao, T., Sandberg, L.I.C., and Jelle, B.P., ”Nano insulation materials: Synthesis and life cycle assessment”, *Procedia CIRP*, **15**, 490-495, 2014(b).

Grader, G.S., Hazan, Y.de, and Shter, G.E., ”Ultra light ceramic foams”, *Sol-Gel Synthesis and Processing*, **95**, 161-172,1998.

Grandcolas, M., Etienne, G., Tilset, B.G., Gao, T., Sandberg, L.I.C., Gustavsen, A., and Jelle, B.P., ”Hollow silica nanospheres as a superinsulating material”, *Proceedings of the 11th International Vacuum Insulation Symposium (IVIS 2*013), pp. 43-44, Dübendorf, Zürich, Switzerland, 19-20 September, 2013.

Han, L., Gao, C., Wu, X., Chen, Q., Shu, P., Ding, Z., and Che, S., ”Anionic surfactants templating route for synthesizing silica hollow spheres with different shell porosity”, *Solid State Sciences*, **13**, 721-728, 2011.

Heinemann, U., ”Influence of water on the total heat transfer in ‘evacuated’ insulations”, *International Journal of Thermophysics*, **29**, 735-749, 2008.

Jelle, B.P., Gustavsen, A., and Baetens, R., ”Beyond vacuum insulation panels - How may it be achieved?”, *Proceedings of the 9th International Vacuum Insulation Symposium (IVIS 2009)*, London, England, 17-18 September, 2009.

Jelle, B.P., Gustavsen, A., and Baetens, R., ”The path to the high performance thermal building insulation materials and solutions of tomorrow”, *Journal of Building Physics*, **34**, 99-123, 2010.

Jelle, B.P., ”Traditional, state-of-the-art and future thermal building insulation materials and solutions - Properties, requirements and possibilities”, *Energy and Buildings*, **43**, 2549-2563, 2011.

Jelle, B.P., Tilset, B.G., Jahren, S., Gao, T., and Gustavsen, A., ”Vacuum and nanotechnologies for the thermal insulation materials of beyond tomorrow - From concept to experimental investigations”, *Proceedings of the 10th International Vacuum Insulation Symposium (IVIS-X)*, pp. 171-178, Ottawa, Canada, 15-16 September, 2011.

Jelle, B.P., ”Accelerated climate ageing of building materials, components and structures in the laboratory”, *Journal of Materials Science*, **47**, 6475-6496, 2012.

Jelle, B.P., Gustavsen, A., and Baetens, R., ”Innovative high performance thermal building insulation materials - Today's state-of-the-art and beyond tomorrow”, *Proceedings of the 3rd Building Enclosure Science & Technology (BEST 3 - 2012) Conference*, Atlanta, Georgia, U.S.A., 2-4 April, 2012.

Jelle, B.P., Gao, T., Tilset, B.G., Sandberg, L.I.C., Grandcolas, M., Simon, C., and Gustavsen, A., ”Experimental pathways for achieving superinsulation through nano insulation materials”, *Proceedings of the 11th International Vacuum Insulation Symposium (IVIS 2*013), pp. 99-100, Dübendorf, Zürich, Switzerland, 19-20 September, 2013.

Jelle, B.P., Sveipe, E., Wegger, E., Gustavsen, A., Grynning, S., Thue, J.V., Time, B., and Lisø, K.R., ”Robustness classification of materials, assemblies and buildings”, *Journal of Building Physics*, **37**, 213-245, 2014.

Liao, Y., Wu, X., Liu, H., and Chen, Y., ”Thermal conductivity of powder silica hollow spheres”, *Thermochimica Acta*, **526**, 178-184, 2011.

Sandberg, L.I.C., Gao, T., Jelle, B.P., and Gustavsen, A., ”Synthesis of hollow silica nanospheres by sacrificial polystyrene templates for thermal insulation applications”, *Advances in Materials Science and Engineering*, **2013**, 6 pages, Article ID 483651, 2013.

Schlanbusch, R.D., Jelle, B.P., Sandberg, L.I.C., Fufa, S.M., and Gao, T., ”Integration of life cycle assessment in the design of hollow silica nanospheres for thermal insulation applications”, *Building and Environment*, **80**, 115-124, 2014(a).

Schlanbusch, R.D., Jelle, B.P., Sandberg, L.I.C., Fufa, S.M., and Gao, T., ”Life cycle assessment integrated in the design of a new nano insulation material”, *Proceedings of the 20th Annual International Sustainable Development Research Conference (ISDRC 2014)*, Trondheim, Norway, 18-20 June, 2014(b).

Wan, Y., and Yu, S.-H., ”Polyelectrolyte controlled large-scale synthesis of hollow silica spheres with tunable sizes and wall thicknesses”, *Journal of Physical Chemistry C*, **112**, 3641-3647, 2008.

Wang, X., Miao, X., Li, Z., and Deng, W., ”Fabrication of mesoporous silica hollow spheres using triblock copolymer PEG–PPG–PEG as template”, *Journal of Non-Crystalline Solids*, **356**, 898-905, 2010.

Yuan, J., Zhou, T., and Pu, H., ”Nano-sized silica hollow spheres: Preparation, mechanism analysis and its water retention property”, *Journal of Physics and Chemistry of Solids*, **71**, 1013-1019, 2010.