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Abstract. As the world's focus is turned even stronger toward miscellaneous energy efficiency and saving aspects, the development of new high-performance thermal insulation materials for building applications will play an important role in this regard. The aim of the presented study is to develop an understanding for the governing thermal transport mechanisms and utilize the Knudsen effect in nanoporous insulation materials through theoretical concepts and experimental laboratory explorations, thus being able to synthesize nano insulation materials (NIM) with very low thermal conductivity values as a major goal. NIMs based on hollow silica nanospheres (HSNS) have been synthesized by a sacrificial template method, where the idea is that the heat transport by gas conductance and gas/solid state interactions decreases with decreasing pore diameters in the nano range as predicted by the Knudsen effect. HSNS with reduced thermal conductivity compared to their solid counterparts have been prepared where the hollow sphere cavities and voids between the spheres are filled with air at atmospheric pressure, i.e. eliminating the need for various measures like e.g. protective metallized foils to maintain a vacuum or expensive low-conducting gases in the cavities and voids. Hence, HSNS represent a promising stepping-stone toward the future high-performance thermal insulation materials.

1. Introduction

In the years ahead there will probably be a continued increased attention and focus on energy efficiency and saving aspects alongside utilization of renewable and non-polluting energy sources. Miscellaneous energy sources and harvesting opportunities are being explored like e.g. solar cells and building integrated photovoltaics (BIPV) [1-10]. However, the energy you are not using you do not have to produce. In this respect, the development of new high-performance thermal insulation materials for building applications will be important [11-13]. A crucial property of these materials is the thermal conductivity, where it is an expressed goal to reach as low thermal conductivity as possible.

Traditional thermal insulation materials have thermal conductivity values typically in the range 20 to 50 mW/(mK) with cellulose and cork being in the higher end having values between 40 to 50 mW/(mK), mineral wool like glass wool and rock wool being in the middle range with values between 30 to 40 mW/(mK), polystyrene products like expanded polystyrene (EPS) and extruded polystyrene (XPS) also having values in the middle range between 30 to 40 mW/(mK), and polyurethane (PUR) being in the lower end having values between 20 to 30 mW/(mK) [12]. In this respect, one should note that the thermal conductivity may increase to considerably higher values if the moisture content is increased in most of these materials. It should also be noted that even if PUR is safe in its intended use, it represents a potential serious health concern and hazard in case of a fire as PUR will when burning release poisonous gases of hydrogen cyanide (HCN) and isocyanates, where the HCN toxicity arises from the cyanide anion (CN^-) which prevents cellular respiration. These traditional thermal insulation materials may be cut and adjusted at the building site without any loss of thermal resistance, however, due to their relatively high thermal conductivities, walls, floors and roofs may become rather thick in order to achieve the desired thermal resistance of today's and the coming energy-efficient and zero emission buildings of the future.

Hence, there is a quest to make thermal insulation materials with substantially reduced thermal conductivity values.

State-of-the-art thermal insulation materials like vacuum insulation panels (VIP) [14-21], gas-filled panels (GFP) [22,23] and aerogels [24-29] have the potential of reaching substantially lower thermal conductivity values than the traditional thermal insulation materials. In addition, phase change materials (PCM) [30-32] may also become part of the thermal building envelope by absorbing and releasing energy when needed.

VIPs consist of an open-porous core surrounded by a laminate foil, where the laminate foil should have as low air and water vapour diffusion as possible in order to maintain a close-to-zero gas pressure, i.e. vacuum, inside the VIP core. Typically, VIPs with fumed silica cores have pristine (non-aged) thermal conductivity values between 3 to 4 mW/(mK), which with time will increase due to diffusion of air and moisture through the laminate foil and into the core (design values are often reported as 7 to 8 mW/(mK) taking into account diffusion/ageing effects and often also heat bridge effects caused by the enveloping laminate foil), and when perforated the thermal conductivity increases to about 20 mW/(mK). GFPs are in principle similar to VIPs, but with thermally low-conducting gases in their cores, where the pores in the GFPs are macroscopic pores and thus much larger than the VIP core pores which are in the micro and nano range. Although the potential of GFPs may seem high, they still have not come into relatively widespread use as e.g. VIPs, where currently VIPs may seem the better choice of these two. Note that both VIPs and GFPs can not be cut or adapted at the building site as that would cause a loss of vacuum and low-conducting gases, which none the less will also take place by diffusion in both VIPs and GFPs. Commercial aerogels as thermal insulation materials have thermal conductivity values typically in the range 12 to 20 mW/(mK), i.e. considerably higher values than for VIPs in their pristine condition and even than for typical VIP design values. Aerogels have an air content of 95 to 99 vol% and are thus mostly consisting of air by volume fraction, hence the aerogels are also very brittle. In addition, the aerogel products of today are very expensive. An advantage of aerogels is that they may be produced either as opaque, translucent or transparent materials, and they may also be cut and adjusted at the building site without any loss of thermal resistance.

Thus, there is a quest to make new thermal insulation materials as robust and flexible as the traditional thermal insulation materials and with as low thermal conductivity values as the state-of-the-art thermal insulation materials, more specifically as low as the VIPs in their pristine condition but with no increase of thermal conductivity during time.

The quest for making better thermal insulation materials is often concentrating the efforts around producing porous materials either filled with air, low-conducting gases (e.g. argon, krypton and xenon) or near-vacuum. A very interesting aspect in this regard is what happens when the pore diameters of the porous material are lowered into the nano range, i.e. that the thermal conductivity is substantially lowered due to the Knudsen effect, which basically is occurring when the pore diameter is reduced to a value smaller than the mean free path of the molecules in the pores [11-13]. For further details and elaborations around the Knudsen effect including the governing equations it is referred to the available literature within this research field.

In such a case and of immense significance is that very low values of the thermal conductivity can be reached even with air-filled pores at atmospheric pressure. Hence, by exploiting the Knudsen effect, there is a large potential for being able to manufacture high-performance thermal insulation materials in form of nano insulation materials (NIM) [11-13] which will be robust towards any perforations and may be cut as desired at the building site without loss of performance due to the air-filled nanopores. The term super insulation materials (SIM) has also come into common usage within this field, with thermal conductivity values below 26 mW/(mK) (stagnant air value), 20 mW/(mK) or 10 mW/(mK) as examples of common borders for SIMs.

The objective of the work presented herein is to investigate the pathway of creating nano insulation materials by making hollow silica nanospheres (HSNS) by a sacrificial template method. In this method, templates of polystyrene (PS) are first fabricated, thereafter the PS templates are coated with a silica layer, and finally the PS templates are removed by burning them away by a diffusion process through the silica layer.

2. Experimental

Hollow silica nanospheres (HSNS) have been made by a sacrificial template method. Polystyrene (PS) template spheres were first fabricated and then coated with a silica layer. The silica precursor was either tetraethyl orthosilicate (TEOS) or water glass (Na_2SiO_3). The samples were placed in a heat incubator and the PS template spheres were burnt away by a diffusion through the enveloping silica layer. The final result was then the HSNS. Basically, the HSNS synthesis follows the schematic procedure as illustrated in figure 1. Further details and elaborations concerning the experimental conditions may be found in our earlier studies and a forthcoming one [13,33-38].

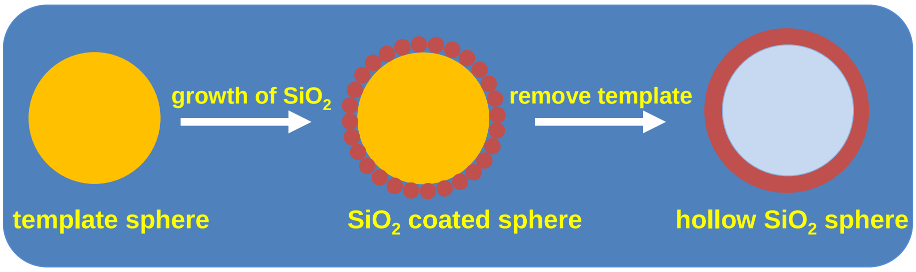

Figure 1. Illustration of the synthesis process when fabricating hollow silica nanospheres (HSNS) by the sacrificial template method.

The visual appearance of HSNS at nano level with their dimensional attributes were characterized by scanning electron microscopes (SEM) and transmission electron microscopes (TEM). Furthermore, the thermal conductivity λ of the HSNS was determined by calculation of the product $\lambda=\alpha\rho c_p$ 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 calometry (DSC). The details of these measurements and the corresponding HSNS syntheses will be published in a forthcoming and more extensive article [33]. In the following, a few excerpts and highlights will be given.

3. Results and discussion

The overall objective of this work is to gain insight into thermal transport mechanisms in nanoporous materials, thus enabling the opportunity of tailor-making materials with as low thermal conductivity as possible. That is, to fabricate nano insulation materials with the lowest possible thermal conductivity by utilizing the Knudsen effect.

The results presented herein are based on various syntheses of hollow silica nanospheres (HSNS) by the sacrificial template method [34-38], where polystyrene (PS) spheres have acted as sacrificial templates for these investigations. In general, the preparation of PS spheres with small dimensions and inner pore diameters well below 100 nm, which is needed in order to get the full effect of the Knudsen effect, has proven to be rather challenging in our experimental laboratory studies. Nevertheless, the further below 100 nm in inner sphere diameter one may reach, the lower thermal conductivity values are expected, although other parameters like e.g. sphere shell thickness, sphere packing density and mesoporosity, may also influence this. However, the actually obtained and henceforth measured values may sometimes be quite different from the anticipated ones.

Examples of synthesized PS spheres are shown in the SEM images given in figure 2, depicting several spheres together and measurement of the diameter of a single sphere. In this particular case, these PS template spheres have diameters of 85 nm (figure 2).

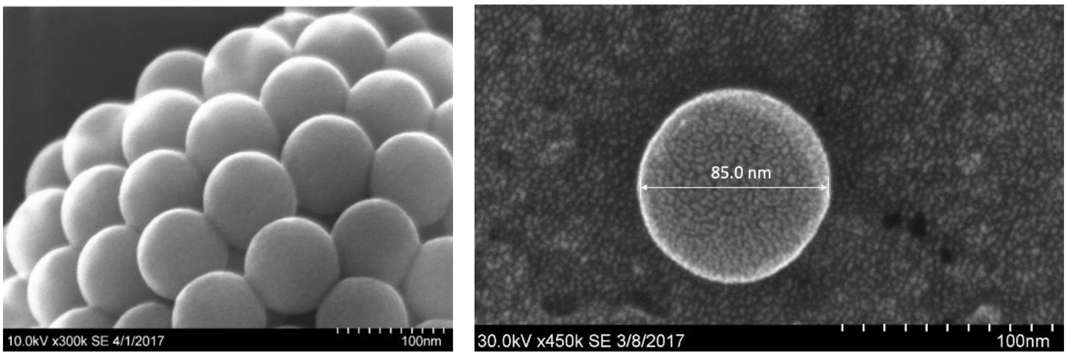

Figure 2. SEM images of PS template spheres with diameters of 85 nm.

After having prepared the PS template spheres, these templates were coated with a silica layer often consisting of small silica nanoparticles which give a relatively rough surface, whereas in some other cases the silica layer may look like a large, wrinkled silica sheet (not shown here), the wrinkled silica sheet surface being substantially smoother than the rough silica particle surface. These surface differences may greatly influence the interfacial interaction between the spheres when packed together, and hence also influence the thermal transport properties and the overall thermal conductivity.

Then, after the silica coating process, the PS template spheres were removed by heating the powder sample so that the PS could escape by diffusion through the silica shell, thereby leaving hollow silica nanospheres (HSNS) as the final result.

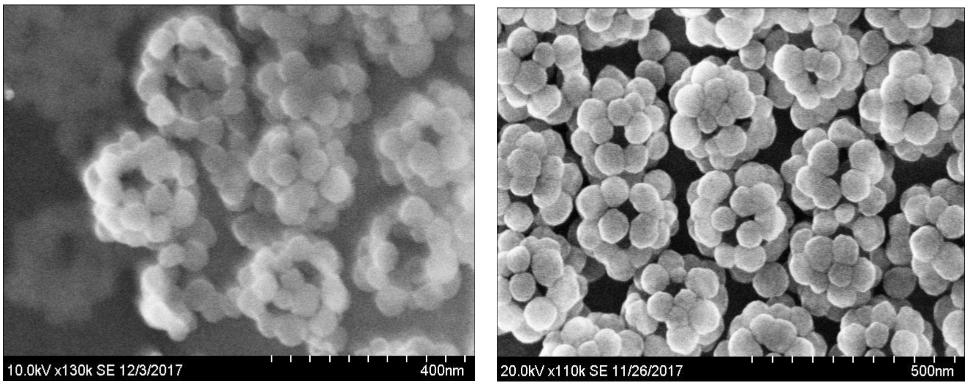

Figure 3. SEM images of HSNS with inner diameter 85 nm and two different shell thicknesses of 34 nm (left) and 67 nm (right).

Examples of the resulting HSNS are depicted in figures 3 and 4, the latter one also depicting the measurements of the silica nanoparticle diameters (shell thicknesses), where SEM images are given of HSNS with inner diameter 85 nm and two different shell thicknesses of 34 nm and 67 nm. As can be observed from the SEM images, the HSNS surfaces of these specific samples are rather rough and porous due to the relatively large silica particles constituting the HSNS shell.

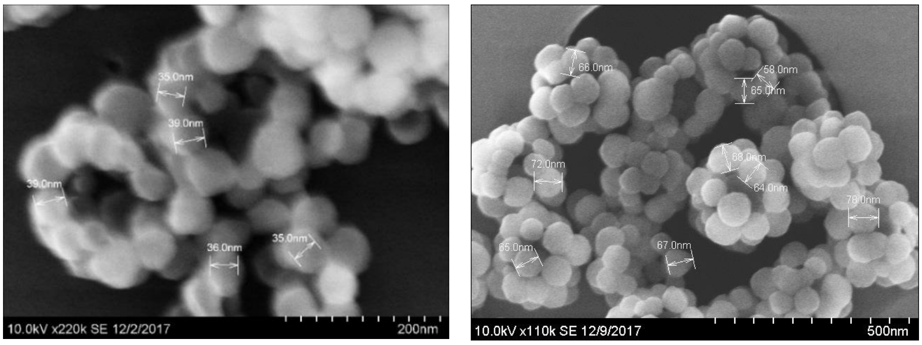

Figure 4. SEM images of HSNS with inner diameter 85 nm and two different shell thicknesses of 34 nm (left) and 67 nm (right), also depicting the measurements of the silica particle diameters.

In the study reported herein several different synthesis parameters have been varied in order to study their influence on the HSNS appearance (e.g. morphology) and their thermal conductivity. A detailed study of these aspects will be published in a more comprehensive and in-depth article [33]. As a main result and as anticipated, the thermal conductivity of HSNS was found to decrease with decreasing PS template sphere diameter and thus the resulting HSNS inner diameter. Here, the inner diameters of the synthesized HSNS were ranging between 85 to 213 nm. Correspondingly, the thermal conductivities of these HSNS have been measured (calculated based on measured values) between 14.3 to 29.7 mW/(mK). That is, the lowest measured thermal conductivity was found for the HSNS with the smallest inner diameters.

Thus, although a rather challenging task, one should attempt to make PS spheres as small as possible, i.e. with diameters well below 100 nm, e.g. down to 40 nm or even below. Success with the PS template preparation will probably lead to success with synthesizing HSNS with much lower thermal conductivities. The goal of manufacturing super insulation materials (SIM) would in such a case have been achieved, except from the commercial aspects in these matters. However, there are a lot of issues to be addressed and investigated much more in-depth in the field of making SIMs. In addition to specific synthesis aspects, general viewpoint issues like robustness assessment [39], durability and accelerated climate ageing [40], as well as life cycle analysis [41], should also be considered.

Nevertheless, to have reached as low value as 14.3 mW/(mK) in thermal conductivity, without having utilized very small inner sphere diameters and hence without having fully exploited the Knudsen effect (i.e. far below 100 nm), is promising with respect to forthcoming and future optimization attempts in the quest for SIMs.

4. Conclusions

Nano insulation materials (NIM) have been made as hollow silica nanospheres (HSNS) by utilizing the Knudsen effect with pore sizes, i.e. inner diameters of the HSNS, in the nano range.

The HSNS have been manufactured by employing a sacrificial template method, where the polystyrene (PS) templates have been removed from the silica spheres by heating and thus a subsequent diffusion process through the silica shell, hence leaving hollow silica spheres with inner diameters in the nano range as the result from the synthesis.

In the specific syntheses and experiments reported within this study, HSNS with inner diameters ranging between 85 to 213 nm have been made, with corresponding thermal conductivity values calculated to be between 14.3 to 29.7 mW/(mK), respectively, based on measured values of diffusivity, specific heat capacity, mass and volume, the two latter ones giving the mass density.

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