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# Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings

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**Abstract**

Sacrificial polystyrene (PS) templates have been used for synthesis of silica-based nano insulation materials (NIM). The PS was synthesized by a simple procedure where parameters as polyvinylpyrrolidone/styrene ratio and potassium persulfate amount were adjusted. Thereafter the PS templates were coated with silica by using tetraethyl orthosilicate (TEOS). The time used for adding TEOS was varied to investigate the effect on how the silica particles attached to the PS surface and the resulting silica spheres. By modifying the process, different PS templates were obtained. The thermal conductivity was measured for hollow silica spheres originating from the coating process of 198 nm PS templates, and the results showed thermal conductivities around 38 mW/(mK) for long-time measurements (160-640 s). Controlled synthesis of this silica-based NIM might be a stepping-stone on the path to a new generation of high-performance thermal insulation materials with low thermal conductivity, which can be used in the building envelope of low-energy or zero emission buildings in the future.


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*Keywords:* Nano insulation material; NIM; Knudsen effect; Zero emission building; ZEB

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## 1. Introduction

Increased global attention is given to environment in general, and especially sustainable development and energy use in buildings. This is regarded, in order to reach the goal set by the Intergovernmental Panel on Climate Change of limiting the global warming to 2 °C compared to pre-industrial level [1], as an important focus.

The building sector is often called the 40 % sector since it uses approximately 40 % of the materials and energy world-wide, and in addition accounts for 40 % of the annual global emissions of greenhouse gases (GHG) [2]. An important factor of the total energy use in a building is determined by the needs for heating and cooling, that has a varying share between 20 % and 80 %. This energy use is dependent on the building envelope. Thus, thermal insulation with significantly lower thermal conductivity than what is commonly used today may contribute to an overall reduced energy consumption in the building sector.

Today's commonly used solutions such as mineral wool and high-performance products as aerogel and vacuum insulation panels (VIP) all have their drawbacks. Mineral wool has a relatively high thermal conductivity, while aerogels are brittle and expensive and a VIP has the risk of puncture and in any case the inevitable vacuum loss over time due to diffusion of air and moisture into the VIP core, which can increase the thermal conductivity up to ten times the initial value. These disadvantages make it interesting to work with developing a new generation of thermal insulation materials.

A promising path to follow is to create nano insulation materials (NIM), where the goal is to utilize the Knudsen effect to reduce the thermal conductivity substantially [3]. NIM is proposed to be a homogenous structure with an overall conductivity of less than 4 mW/(mK). The structure can be both open or closed nanoporous [4]. For a VIP, the difference in thermal conductivity from pristine condition (4 mW/(mK)) to punctured (20 mW/(mK)) is entirely due to loss of vacuum, and therefore related to gaseous thermal conductivity. The heat transport within an insulation material is complex, but as VIPs illustrate may the gaseous thermal conductivity be of considerable importance. Reducing the pore diameter to nanoscale in a material may significantly reduce the thermal conductivity. An insulation material with considerable lower thermal conductivity than most commonly used materials today may not only save energy, but also money and space in every step from production and transport to installation, due to less material used.

The objective of this work is to attempt to have a controlled production of silica-based nanospheres using sacrificial polystyrene templates. Silica is used for many applications such as in medicine, electronics and water treatment on nano scale, and is shown to be a controllable and robust material [5–8]. Investigations for use in building envelopes, especially as core materials in VIPs, have also been conducted [9,10]. During the synthesis, several parameters are investigated in order to state their importance for the final product. Both the inner diameter of the spheres and the shell thickness may affect the thermal conductivity, and these are dependent on the size of the polystyrene spheres and the coating procedure, respectively. For the coating process may the time used for adding tetraethyl orthosilicate (TEOS) be important for the shell thickness.

## 2. Synthesis of silica-based nano insulation materials

The synthesis is carried out principally as described by Sandberg et al. [11], but with some modifications. The experimental work is explained in the following. The results from the different steps in the synthesis is showed in Figure 1.


Figure 1: Results of the steps in the synthesis. The first and left photo shows the polystyrene templates produced (1), in the second photo the polystyrene spheres coated with silica particles are showed both before (left) and after (right) centrifuging (2), the third photo shows the dried silica spheres (3), and the fourth photo depicts the powder in the Hot Disk for measurement of thermal conductivity (4).

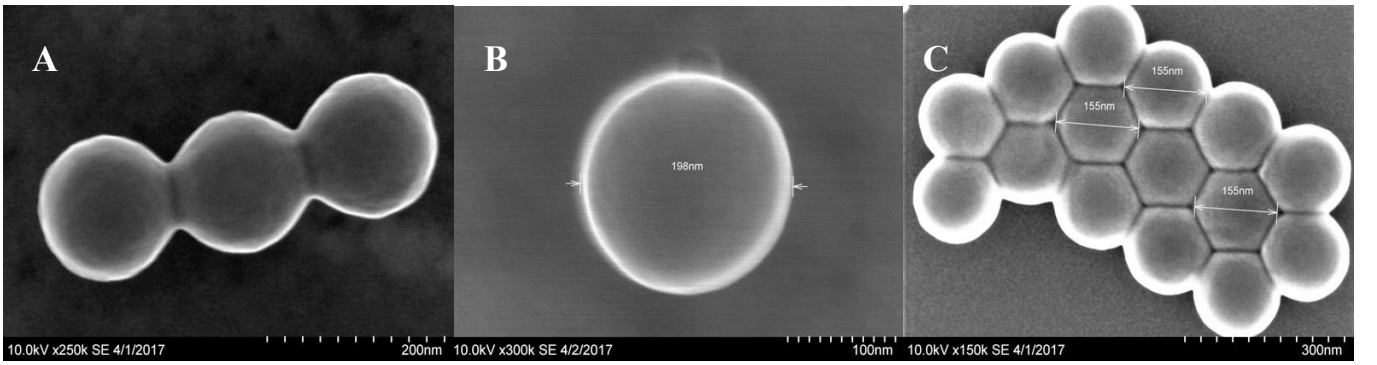


Figure 2: Scanning electron microscope (SEM) images of polystyrene templates A (160 nm), B (198 nm) and C (155 nm), dimensions referring to sphere diameter.

### *2.1. Materials*

Polyvinylpyrrolidone (PVP), reagent grade styrene, potassium persulfate (KPS), tetraethyl orthosilicate (TEOS) as source for silica, ammonium hydroxide solution ($NH_4OH$, 28-30 wt%) and 96 % ethanol. Throughout the synthesis of the PS templates was distilled water used as a reaction medium.

### *2.2. Preparation of polystyrene templates*

For the preparation of polystyrene (PS) templates, 10 g of styrene, 90 g of distilled water and a given amount of polyvinylpyrrolidone (PVP), were added in a single-neck round-bottom flask. The flask was immersed in an oil bath at 70 °C and magnetically stirred for 15 minutes before a KPS-water mixture (given amount of KPS in 10 g of distilled water) was added dropwise using a plastic pipette. The mixture was kept in the oil bath for approximately 24 hours, while magnetically stirred and heated at 70 °C. After this were the PS templates cooled down and stored at room temperature.

By varying the amount of KPS added, and the PVP/styrene-ratio, were different PS diameters achieved, see Table 1 and the scanning electron microscope (SEM) images in Figure 2.

Table 1: Average diameter of the polystyrene (PS) templates by varying the PVP/styrene-ratio and the amount of KPS.

| Polystyrene sample | PVP/styrene-ratio | Amount of KPS (g) | Measured diameter (nm) |
|---|---|---|---|
| A | 0.18 | 0.15 | 160 |
| B | 0.20 | 0.20 | 198 |
| C | 0.20 | 0.15 | 155 |

### *2.3. Coating of polystyrene templates*

For coating of the PS spheres, 6 g of PS were added to 115 g of 96 % ethanol in a 500 ml round-bottom flask with extra horizontal opening for a syringe. The mixture was magnetically stirred at 500 rpm before 5 ml of $NH_4OH$ was added. The flask was then closed with a ground glass stopper and vacuum grease to prevent evaporation. Then a 10 ml TEOS solution (5 ml TEOS and 5 ml 96 % ethanol) was added dropwise with the use of a syringe pump. The time used was adjusted to investigate possible changes. See Figure 3 for a photo of the setup. After the TEOS solution was added, the mixture was left over night while stirred. The solution was then centrifuged at 4500 rpm for 20 minutes to extract the silica coated PS templates. To remove the PS, was the sample dried at 475 °C for 12 hours.

Figure 3: TEOS solution added dropwise to the round bottom flask with the use of a syringe pump, a 10 ml syringe and a horizontal opening in the flask.

### *2.4. Characterization*

Size and morphology were characterized using a Hitachi S-5500 scanning electron microscope (SEM), which also has a transmission electron microscope (TEM) mode. A small sample of the synthesized material was solved in ethanol and dripped onto a TEM grid. The ethanol was evaporated in air before the grid was inserted in the SEM.

Thermal conductivity of the NIM was measured by the use of Hot Disk TPS 2500 S Thermal Constant Analyser. The sensor used had a diameter of 6.403 mm.

## 3. Results and discussion

### *3.1. Polystyrene templates*

The importance of the PVP/styrene ratio has been reported in several earlier publications [11,12]. Both size and monodispersity of the PS are dependent on this relation, but the effect is higher for smaller ratios [11]. This is shown by comparing sample A and C from this work, where the ratio was increased from 0.18 to 0.20 (≈ 11.1 %) and the diameter was reduced from 160 nm to 155 nm (≈ 3.2 %). For higher PVP/styrene ratios were there no monodispersity in the PS sample, which is important for creating a homogenous insulation material.

In this work, the effect of KPS was also investigated. It was found that for a PVP/styrene ratio of 0.20 and an increase in KPS, had a negative effect on the result. When increasing the amount of KPS from 0.15 to 0.20 (≈ 33.3 %), the diameter of the PS increased from 155 nm to 198 nm (≈ 27.7 %).

### *3.2. Coating of polystyrene templates*

The time used for applying the TEOS solution for coating of the PS samples was adjusted in the range of 1–5 hours to investigate if the time had any effect, and the results showed that the time was not of significant importance.

More important is the surface characteristics of the PS sample. Since silica particles have a tendency of being in the negatively charged range will they not attach to the PS surface unless the PS surface is positively charged [13].

In Figure 4 one can see an SEM image of silica spheres produced by coating of PS sample B, which under investigation with SEM proved to be the most monodisperse material and was therefore used for measurement of thermal conductivity. For this image, the sacrificial polystyrene templates have been removed by drying the sample in the oven for 12 hours.

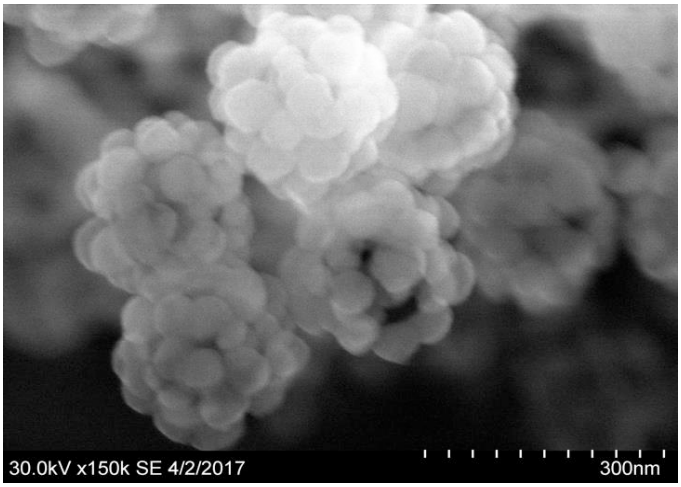


Figure 4: Scanning electron microscope (SEM) image of silica spheres produced by coating and drying of PS sample B.

### *3.3. Thermal conductivity measurements*

The thermal conductivity measurements were carried out on silica spheres produced using the PS sample B as a sacrificial template. A SEM image can be seen in Figure 4. Four measurements were performed on the same sample where only the measurement time was varied. As seen in Table 2 the thermal conductivity was measured lower for longer measurement time. Since the start temperature (23 °C) and output power (50 mW) were the same for all the measurements it is assumed that the initial heating phase of the material has a minor role for longer measurements, hence the thermal conductivity measurement stabilizes in the range of 38 mW/(mK) over time. Naturally, for applications in building envelopes will these long-time measurement values represent the relevant performance. The value of 38 mW/(mK) is approximately 10 % higher than the lowest values for mineral wool in dry conditions (32-34 mW/(mK)) [14]. It is assumed that with smaller silica spheres, the exploitation of the Knudsen effect may be improved, thus lower thermal conductivity values may be obtained.

Table 2: Thermal conductivity measurements of insulation materials produced by coating of 198 nm PS spheres. The measurements were carried out by using a Hot Disk TPS 2500 S apparatus.

| Measurement time (s) | Start temperature (K) | Output power (mW) | Thermal conductivity (mW/(mK)) |
|---|---|---|---|
| 80 | 296 | 50 | 42.1 |
| 160 | 296 | 50 | 38.9 |
| 320 | 296 | 50 | 38.0 |
| 640 | 296 | 50 | 37.9 |

An important notice for these measurements is that they are performed on the same sample, with the same packing density. The latter may affect the performance of the Hot Disk apparatus and alter the thermal conductivity measurements, and therefore also the obtained results. The influence of the packing density on the Hot Disk apparatus should be investigated in further studies.

## 4. Conclusions

The diameter of the polystyrene (PS) templates was adjusted by changes in the polyvinylpyrrolidone (PVP)/styrene ratio and potassium persulfate (KPS) amount used in the synthesis. A higher PVP/styrene ratio gave a smaller PS diameter, while an increase of KPS used gave an increase in the size of the PS templates.

For the coating process, it was discovered that the time used for adding the solution of tetraethyl orthosilicate (TEOS) and 96 % ethanol was not of significant importance and that the surface characteristics of the PS samples had a greater impact on the final results.

The thermal conductivity was measured to be in the range of 38 mW/(mK) when PS samples with sphere diameters of 198 nm were used. The thermal conductivity measurements were carried out over different time intervals, but on the same test sample with the same start temperature and the same output power for the Hot Disk TPS 2500 S apparatus. It is likely that the packing density of the silica powder can alter the thermal conductivity measurements in the Hot Disk apparatus. Hence, further studies should investigate the importance of this aspect.

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