

1 **Hollow Silica Nanospheres as Thermal Insulation Materials for**
2 **Construction: Impact of their Morphologies as a Function of**
3 **Synthesis Pathways and Starting Materials**

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12

13 Abstract

14 Hollow silica nanospheres (HSNS) show a promising potential to become good thermal insulators with
15 low thermal conductivity values for construction purposes. The thermal conductivity of HSNSs is
16 dependent on their structural features such as sizes (inner diameter and shell thickness) and shell
17 structures (porous or dense), which are affected by the synthetic methods and procedures including
18 reaction medium, polystyrene template, and silica precursor. . Formation of thermally insulating HSNS
19 was in general favoured by alkaline reaction, whereby highly porous silica shells were formed,
20 promoting less silica per volume of material, thus a lower solid state thermal conductivity. The Knudsen
21 effect is in general reducing the gas thermal conductivity including the gas and pore wall interaction for
22 materials with pore diameters in the nanometer range, which is also valid for our HSNS reported here.
23 Further decreasing the pore sizes would invoke a higher impact from the Knudsen effect. The additional
24 insulating effect of the inter-silica voids (median diameter $D_{50} \approx 15$ nm) within the shell coating
25 contributed also to the insulating properties of HSNS. The synthesis route with tetraethyl orthosilicate

26 (TEOS) was more robust and produced more porous silica shells than the one with water glass (Na_2SiO_3 ,
27 WG), although the latter might represent a greener synthetic method.

28

29 **Keywords:** Hollow silica nanosphere, HSNS, Nano insulation material, NIM, Thermal conductivity,
30 silica, Knudsen effect, porosity, green material.

31

32 **1. Introduction**

33 According to the EU commission, heating and hot water alone accounts for 79% of total final energy
34 use (192.5 Mtoe). While cooling is a fairly small share of total final energy use, demands from
35 households and businesses such as food industry rise during the summer months. Therefore, in order to
36 fulfil the EU's climate and energy goals of more than 20% energy savings by 2050, the heating and
37 cooling sector must sharply reduce its energy consumption.

38

39 High-performance thermal insulation materials for buildings is one of the most direct methods to meet
40 the demand of improved energy efficiency. Studies [1] have demonstrated that energy efficiency
41 measures such as thermal insulation retrofit are the most cost-effective with respect to CO_2 emissions,
42 whereas other measures e.g. solar photovoltaics and wind energy are far less cost-effective. Today,
43 efforts are being put into moving from the common thermal insulation materials [2] to develop new
44 materials with as low thermal conductivity as possible [3–9]. While this is the best solution for
45 construction purposes, the current state-of-the-art thermal insulation materials are still in their infancy.
46 Further work is needed before proper incorporation into the building industry could be achieved at an
47 affordable cost.

48

49 Both macro and micro scale developments have been conducted. The latest trend is to develop
50 nanostructured thermal insulation materials, which can function and thermally insulate from the nano
51 scale. A promising class of nanostructured thermal insulation materials are the nano-hybrid composite
52 consisting of organic/inorganic particles and inorganic hollow particles. These materials have been

53 investigated extensively in the context of chemistry and materials science. Principally, composite
54 organic/inorganic particles can be classified as organic core with an inorganic shell or vice versa. Both
55 polymer encapsulation of inorganic particles and coating of polymer particles with minerals can modify
56 the properties of the precursor particles and lead to nanocomposite particles with tailored structures and
57 morphologies [10,11]. Considerable research has been devoted to the preparation of mineral-coated
58 polymer particles, and there are three main approaches: sol-gel nano-coating [12–16], hetero-
59 coagulation [17] and layer-by-layer self-assembly [18]. By far, sol-gel synthesis is the most attractive
60 for forming core-shell particles due to its ease of operation. Hollow nanospheres can be produced from
61 hybrid nanoparticles, by extraction of the polymeric core through methods such as calcination, solvation,
62 etc.

63

64 Among the different elements, silica is the most abundant chemical compound in the earth crust, most
65 commonly found in nature as quartz and as the major constituent of sand. Its abundancy makes it a
66 logical starting point material on the path to create nano insulation materials (NIM) for the future [19–
67 21]. In parallel, our laboratory has been working on the development of new composite materials
68 involving silica aerogel-concrete hybrids for both structural and thermal insulation properties so as to
69 minimize the thickness of the material during construction [22–25]. Hollow silica nanospheres (HSNS)
70 could potentially be a replacement material for silica aerogels. HSNS could also potentially be a
71 replacement for thermal insulation materials such as expanded polystyrene (EPS) and extruded
72 polystyrene (XPS), materials that may suffer from challenges related to fire, apart from their relatively
73 large thermal conductivity values compared to silica aerogel [7].

74

75 This investigation thus aims to analyze the creation of thermally insulating hollow silica nanospheres
76 (HSNS) for construction purposes. The current investigation is a follow-up on our investigations on the
77 formation of HSNS based on a sacrificial polystyrene template and a silica precursor of tetraethyl
78 orthosilicate (TEOS) [19–21]. We have previously shown that through such synthesis methods, thermally
79 insulating materials with low thermal conductivity values of about 20 – 40 mW/(mK) can be produced [20,
80 26], although the overall carbon footprint may be relatively high due to the use of organic silica precursor. It

81 was then suggested that water glass (Na_2SiO_3 , WG) can be an alternative for lowering the carbon footprint.
82 The current investigation will thus explore the alternative synthesis route using water glass as the silica
83 precursor. The synthesis of spherical polystyrene templates and formation of HSNS with TEOS will first be
84 described to form the basis for a water glass based HSNS synthesis. Thereafter, a comparison of the
85 differences in morphological formation of the silica network by applying TEOS and water glass as precursors
86 will be discussed in relation to their thermal conductivity. The parameters affecting the formation, mode of
87 formation and final product will be highlighted.

88

89 **2. Materials and methods**

90 **2.1. Materials**

91 Reagent grade styrene (St), polyvinylpyrrolidone (PVP; $M_w \approx 40\text{k Da}$), potassium sulfate (KPS),
92 ammonium hydroxide (NH_4OH , 28~30 wt%), tetraethyl orthosilicate (TEOS), ethanol (96%), water
93 glass (sodium silicate solution, Na_2SiO_3 , WG) and 1 M hydrochloric acid (HCl) were supplied by Sigma
94 Aldrich.

95

96 **2.2. Synthesis of polystyrene templates**

97 Polystyrene (PS) templates based on varying PVP/St ratios were synthesized via emulsion
98 polymerisation. In a typical synthesis, 10 g of styrene and required amount of PVP were homogenized
99 in 90 g of distilled water at room temperature (RT) for 15 min in a 250 ml Erlenmeyer flask. The
100 following eleven PVP/St ratios were employed: 0.0050, 0.0075, 0.0100, 0.0500, 0.1000, 0.1500, 0.2000,
101 0.2500, 0.3000, 0.4000 and 0.5000. 0.10 g of KPS dissolved in 10 g of distilled water was then added
102 to the mixture maintained at a constant temperature of $70 \pm 1^\circ\text{C}$ in an oil bath under stirring conditions
103 of 300 rpm for 24 h before quenching by cooling in air at RT. The PS solutions are denoted as PS-ratio,
104 e.g. PS-0.0050.

105

106 **2.3. Coating PS templates with silica**

107 2.3.1 TEOS as silica precursor

108

109 6 g of PS-0.1000 was dispersed in 95 g of 96% ethanol at 500 rpm for 15 min. 1.5 mL of NH₄OH was
110 added (pH was about 13). The mixture was stirred for 15 min. 5 mL of TEOS in 5 mL of ethanol was
111 added to the reacting pot in three manners: (1) TEOS-1: all at once, (2) TEOS-2: 1/5 of the TEOS/ethanol
112 added at hourly interval over a period of 5 h and (3) TEOS-3: 1/100 of TEOS/ethanol added at 3 min
113 interval over 5 h. The final mix was stirred at 500 rpm overnight at RT.

114 2.3.2 WG as silica precursor

115

116 20 g of PS-0.1500 (or PS-0.3000) were mixed with 3 g of WG in 240 g of distilled water. When further
117 PS with lower PVP/St ratios were employed, no stable colloid could be formed at the original PS
118 concentration. For synthesis purposes, an optimized diluted system was employed. To PS-0.0050 and
119 PS-0.0075 samples, 5 g of PS was added to 1 g of WG in 50 g of distilled water. 1 M HCl was added to
120 all samples until a pH of 2.0 was reached. The solutions were left stirring at 400 rpm overnight at RT.

121

122 All coated PS-silica samples were subjected to centrifugation at 8000 rpm for 10 min, air dried overnight
123 and calcined at 500°C for 5 h (heating rate = 5°C/min) to remove the PS core.

124

125 **2.5. Characterization**

126 Microstructures of the obtained materials were analyzed by using a Hitachi S-5500 scanning
127 transmission electron microscope (STEM). Analysis with secondary electrons employed an acceleration
128 voltage of 10 kV and current of 7 μA while 30 kV was used in bright field transmission mode.

129

130 The thermal conductivity of unmodified PS-silica samples were determined by employing a Hotdisk
131 Thermal Constants Analyzer (TPS 2500S). A transient plane source technique was applied [27, 28] and
132 the PS-silica were measured using the Kapton sensor with radius of 3.189 mm. The sensor is sandwiched
133 between two well packed powder samples of PS-silica . The sensor acts both as a heat source, as well
134 as to register the temperature increase in the samples. The temperature increase over time is recorded
135 and used to calculate the thermal conductivity of the samples. The heating power and heating time can

136 be varied independently to obtain the most appropriate testing conditions for each sample. The
 137 conductivity measurements were performed with a heating power ranging from 100 to 700 mW and a
 138 heating time of 320 s. All unmodified PS-silica samples were measured only after cooling to ensure
 139 equilibrium of the thermal conductivity. Repacking of the samples for measurements were employed
 140 and the final reported data are given as the arithmetic mean of 3 to 5 individual results, depending on
 141 the repeatability of the measurements.

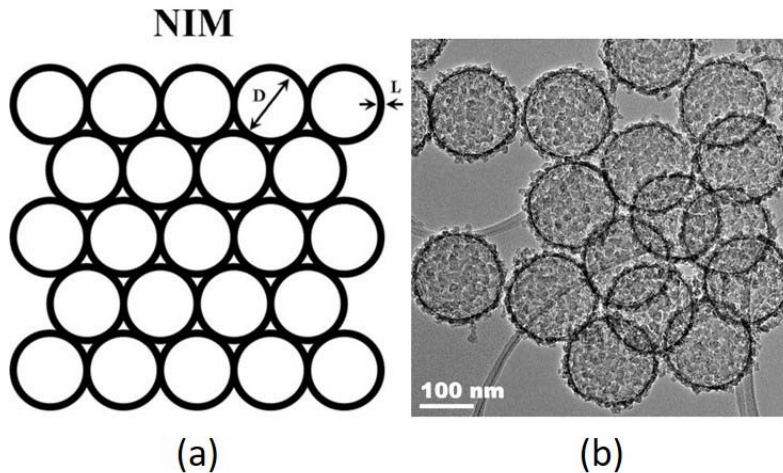
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143 3. Results and discussion

144 3.1. Size determination of PS templates

145 A nano insulation material (NIM) is a homogeneous, nanostructured material with closed or open nano-
 146 sized pores (**Figure 1**). The overall thermal conductivity (λ_{tot}) of NIM can be attributed in a simplified
 147 form to the proximity of gases to solid interfaces, molecular collisions and the inherent materials
 148 properties for heat transfer within a specific area or volume as governed by the following expression:

149



150

151 **Figure 1.** (a) Conceptual model of a hollow nanosphere NIM with the pore size D and shell thickness L
 152 as dimensional characteristics and (b) TEM image of actual hollow silica nanospheres.

$$153 \lambda_{tot} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coupling} \quad (1)$$

154

155 where λ_{tot} is the total overall thermal conductivity, λ_{solid} is the solid state thermal conductivity, λ_{gas} is the
 156 gas thermal conductivity, λ_{rad} is the radiation thermal conductivity, λ_{conv} is the convection thermal
 157 conductivity, commonly termed as part of the gas thermal conductivity and $\lambda_{\text{coupling}}$ is the thermal
 158 conductivity term accounting for second order effects between the various thermal conductivities in
 159 **Equation 1**. Generally, convection is not an issue in nanostructured thermal insulation materials. The
 160 three main determining factors are λ_{solid} and λ_{rad} , which are governed by the material bulk and surface
 161 properties, and λ_{gas} , which is exemplified by the Knudsen effect at nanometer levels [29]. In our
 162 investigations, the gas of concern is air at atmospheric pressure, since the air will be entrapped within
 163 the HSNS. λ_{gas} defined by the Knudsen equation is related to the mean free path of the gas or air
 164 molecules and the average diameter of the pores, which further includes the interaction between the gas
 165 molecules and the pore walls. It may be written as:

166

$$167 \quad \lambda_{\text{gas}} = \frac{\lambda_{\text{gas},0}}{1+2\beta Kn} \quad (2)$$

$$168 \quad Kn = \frac{\sigma_{\text{mean}}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 \rho \delta} \quad (3)$$

169

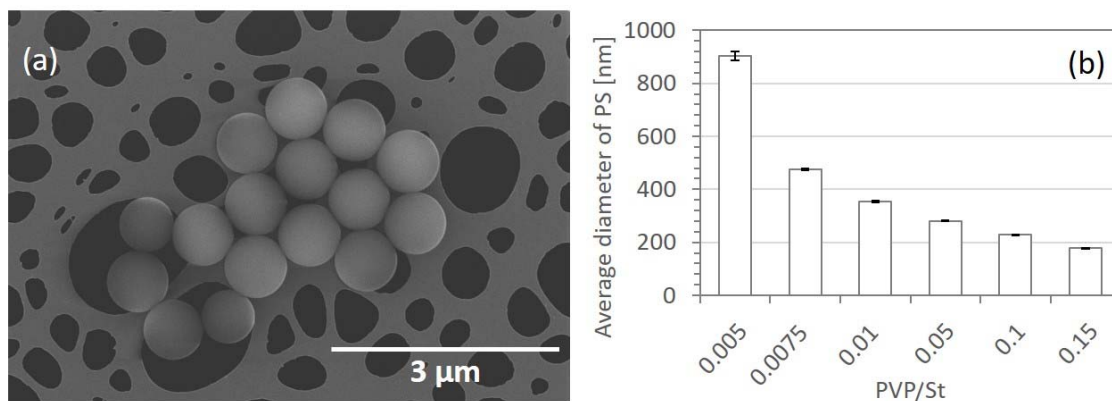
170 where λ_{gas} is the thermal conductivity of the gas inside the nano-sized pores (also including gas and pore
 171 wall interaction); $\lambda_{\text{gas},0}$ is the thermal conductivity of the gas at standard temperature and pressure (STP);
 172 β is the energy transfer (in)efficiency of the molecule-wall collisions (a unitless number between 1.5
 173 and 2.0); Kn is the Knudsen number; σ_{mean} is the mean free path of the gas molecules; δ is the
 174 characteristic pore size of the material; d is the collision diameter of the gas molecules; p is the gas
 175 pressure inside the pores; k_B is the Boltzmann's constant; and T is the temperature. It should be noted
 176 that when the pores in a material are reduced to matter of nanometers, the Knudsen number becomes
 177 very large, which will result in a gas thermal conductivity that approaches zero. As the distance between
 178 the pore walls becomes small relative to the mean free path of the gas molecules, it becomes increasingly
 179 likely for the molecules to not hit other molecules before colliding with the pore walls, thus reducing
 180 the gas thermal conductivity, also including gas and pore wall interaction, within the pores substantially.
 181 Therefore, to ensure an effective Knudsen effect and very low thermal conductivity, controlling the size

182 of PS templates (which influences the eventual length of flow space for air molecules in the insulator)
183 would be a main criteria in determining the thermal conductivity values of HSNS. It has been calculated
184 that the mean free path of ambient air is 68 nm [30], thus the Knudsen effect will be very large when
185 the pore diameter is less than that. As a result, a pore size smaller than or in the range of 68 nm as
186 determined by the smaller diameter of the PS template particles in the nanometer range, is desired in
187 order to achieve a theoretically low thermal conductivity, assuming all other factors are constant.

188

189 Similar to other investigations [31], PVP was found to be the most important factor in determining the
190 size of the PS particles, and in affecting the successful synthesis of PS/SiO₂ core-shell particles. The
191 stabilizing and surfactant effect of PVP allow size control of the growing PS, resulting in uniformly
192 distributed PS to be synthesized as a function of the PVP/St ratio. In the absence of PVP, PS particles
193 of varying sizes (spherical to oblong) with high polydispersity and diameters up to micro-meters were
194 formed, showing susceptibility to slight variations in KPS and temperature during polymerisation. Upon
195 the addition of PVP, the reaction stabilized and monodispersed PS particles with size dependency on
196 PVP content was attained (**Figure 2a**). The mean particle size distributions of the PS particles were
197 calculated from the SEM images by averaging over hundreds of particles. It was found that the median
198 particle diameter (D_{50}) of the PS particles decreased with increasing PVP amounts from 904 ± 17 nm at
199 a PVP/St ratio of 0.0050 till an optimal PVP/St ratio of 0.1500 with a D_{50} of 180 ± 1 nm (**Figure 2b**).
200 The growth profile of the PS particles can be attributed to the stabilizing effect of the surfactant PVP on
201 styrene, whereby incorporation of PVP on the surfaces of the PS particles mask the negative charges of
202 the pi bonds of St, hence preventing propagation of polymerisation.

203



204

205 **Figure 2.** (a) SEM images displaying monodisperse PS particles prepared with a PVP/St ratio of 0.0050,

206 (b) D_{50} of PS particles as a function of PVP/St.

207

208 Further increase in PVP/St up to a ratio of 0.3000 resulted in the formation of bimodal PS particles

209 (**Figure 3**). The samples prepared at a PVP/St ratio of 0.3000 displayed a bimodal particle size

210 distribution, with respective D_{50} of PS particles in the samples at approximately 450 μm and 120 μm.

211 At PVP/St ratios of 0.4000 and 0.5000, no PS particles were detected, potentially due to the over-

212 dispersing effectiveness of PVP on St, which increased the surface tension of PS particles and prevented

213 the formation of spherical particles. For subsequent studies, PS-0.1500 and PS-0.1000 with an average

214 diameter of ~200 nm, were mainly chosen for templating due to their sizes and stability in their

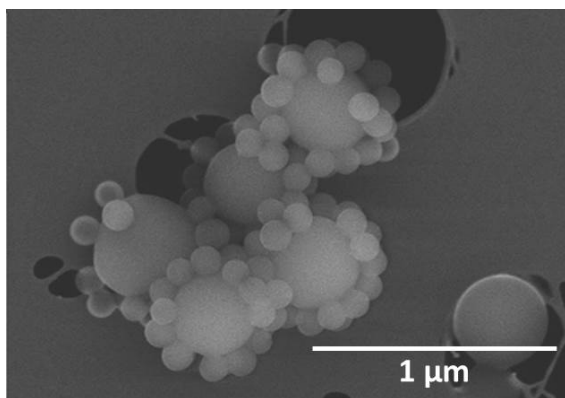
215 respective mediums.

216

217 The D_{50} of PS templates for subsequent employment signified a diminishing Knudsen effect in the HSNS

218 in our investigations.

219



220

221 **Figure 3.** SEM image displaying PS particles prepared at a PVP/St ratio of 0.3000.

222

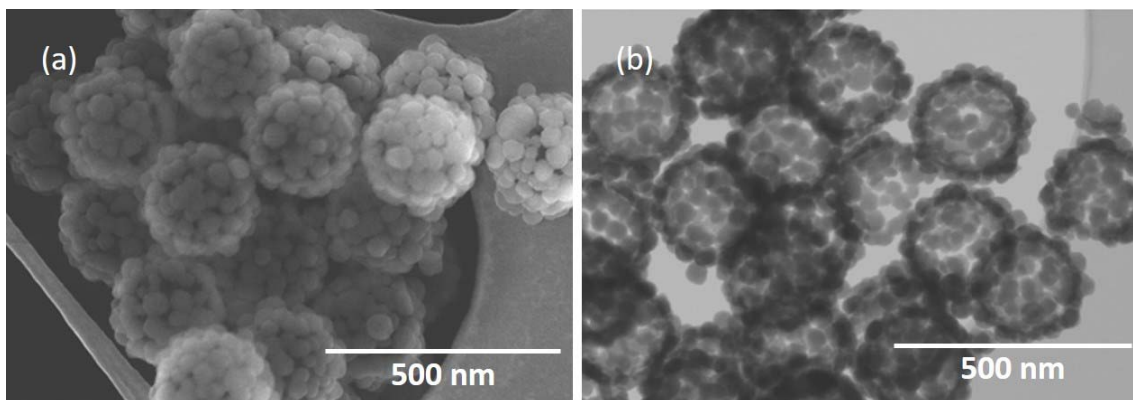
223 The amphiphilic characteristic of PVP arising from the presence of the highly polar amide group within
224 the pyrrolidone ring, polar methylene and methine groups in the ring [32, 33] and along the backbone,
225 allow modification of the PS surfaces to increase interfacial coupling with silica monomers or oligomers.
226 Therefore, PS particles were subjected to direct coating with silica precursors through a modified Stöber
227 process. A total of three different TEOS systems and one with WG were employed. The choice of WG
228 can be boiled down mainly to the environmental friendliness of this material, where the medium was
229 water. In the case of TEOS, ethanol was employed.

230

231 **3.2. TEOS as silica precursor**

232 Coating of PS-0.1000 under alkaline conditions by using TEOS as silica precursor was successful in all
233 cases, and showed high repeatability and robustness in their formations. Nanospheres of ~270 nm were
234 formed, showing a raspberry-like morphology. After calcination, all samples maintained the raspberry-
235 like appearance with an average particle size of ~250 nm and appeared as monodispersed globules of
236 consolidated silica nanoparticles. Under TEM imaging, these nanospheres/nanoclusters were hollow,
237 confirming that the PS template had been successfully removed during calcination (**Figure 4**, right).

238



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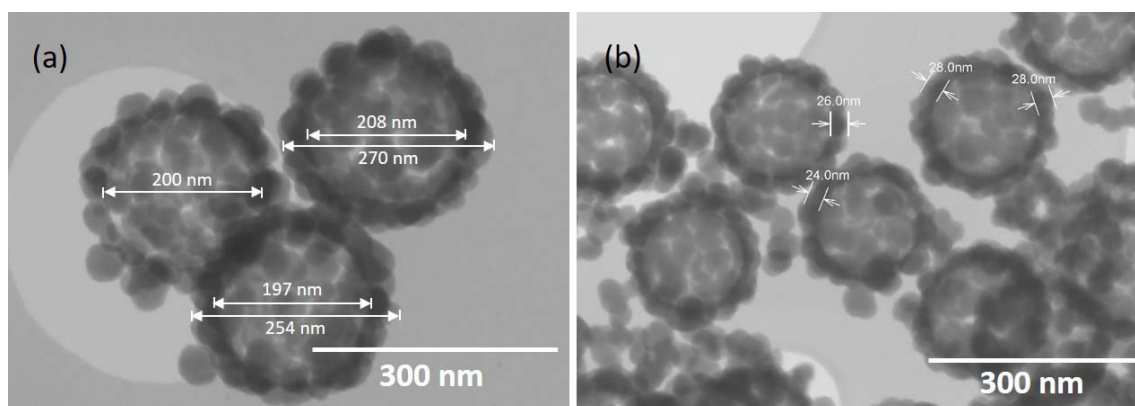
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241 **Figure 4.** HSNS prepared from PS-0.1000 and TEOS-1 after calcination (a) SEM image (b) TEM image.

242

243 The inner diameter of the globular particle was ~ 200 nm, 10% smaller than the original PS template
244 indicating a coalescing effect of the silica nanoparticles upon calcination. This causes the loosely bound
245 silica nanoparticles to be knitted more closely together. From the TEM image (**Figure 4b**), it can be
246 observed that gaps can still be observed between individual silica nanoparticles within each coating,
247 indicating a highly porous shell structure. The thickness of the silica shell was approximately 50 nm in
248 width (**Figure 5a**). Each individual silica nanoparticle was dense and had a D_{50} of ~ 30 nm, independent
249 of rate at which TEOS was added (**Figure 5b**). This signified that a mono- to bilayer of silica
250 nanoparticles was formed around the PS template during the coating process. The formation of
251 individual silica nanoparticles may be attributed to the formation of highly branched discrete silicate
252 oligomer species under alkaline conditions. The shapes and sizes of final products (solid core and hollow
253 silica nanospheres) were independent of the mode of TEOS/ethanol addition, implying that the synthesis
254 route of the silica monomers is more dependent on the size of the PS templates, surface tension of the
255 forming silica nanoparticles and their interaction with the medium, than on kinetic parameters or
256 conditions, indicating a robust formation pathway.

257



258

259 **Figure 5.** Measured nanosilica globules prepared from PS-0.1000 and TEOS-1, demonstrating by
 260 measurement bars the (a) inner and outer circumferences and (b) size of individual silica particles.

261

262 For determining the robustness of the synthesis route, a further experiment was performed to deduce the
 263 effect of the medium, i.e. addition of water on the hydrolysis rate of TEOS in forming the hollow
 264 nanospheres. It is known from literature that up to a threshold limit, increase in water content will favour
 265 hydrolysis of TEOS and gelation of silica [34]. In our investigations, when the purity of ethanol was
 266 altered from 96% to 100%, smaller silica nanoparticles of ~5% reduction in size were observed in the
 267 latter, indicating that despite the apparent effect of the hydrolytic consequence of water on the system,
 268 the overall medium dominated by the pH remains as the main determining factor in the formation of
 269 silica particles.

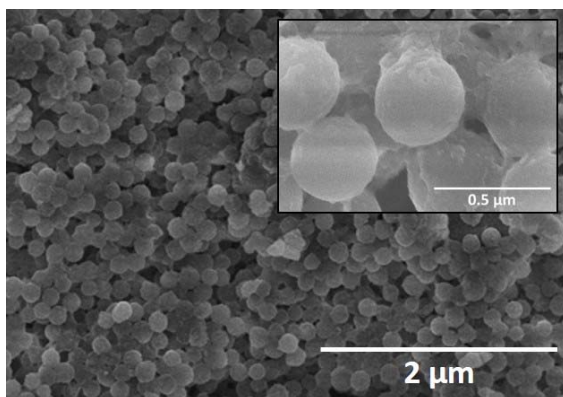
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271 3.3. WG as silica precursor

272 Due to the low reactivity of water glass (WG), it was employed as a silica precursor at a low pH of about
 273 2. This specific acidic condition was employed to promote electrostatic deposition onto PS as silica
 274 nanoparticles are positively charged below this isoelectric point [35]. Successfully coating of PS-0.1500
 275 with WG depicts a rough, continuous layer of amorphous silica deposit after synthesis and initial air
 276 cooling (**Figure 6**). This process of air drying was necessary to stabilize and retain the morphology of
 277 the silica structure. However, unlike its counter TEOS based formulation, by-products were often
 278 exhibited, such as silica rods (**Figure 7**). The occurrence of these by-products increases proportionally
 279 as the amount of added HCl decreases, suggesting the electrostatic buffering effect of the PVP on the

280 surfaces of PS particles, which suppressed the overall negative charge of the surfaces of PS particles.
281 Further research efforts are obviously required to optimize the synthetic conditions to achieve better
282 silica coatings from the WG system.

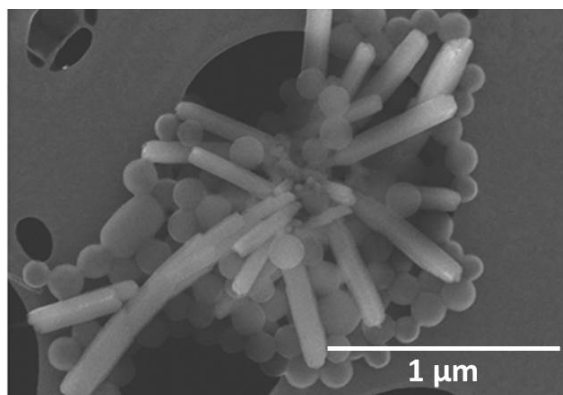
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284

285 **Figure 6.** Silica coated PS-0.1500 samples from water glass at pH =2.0.

286



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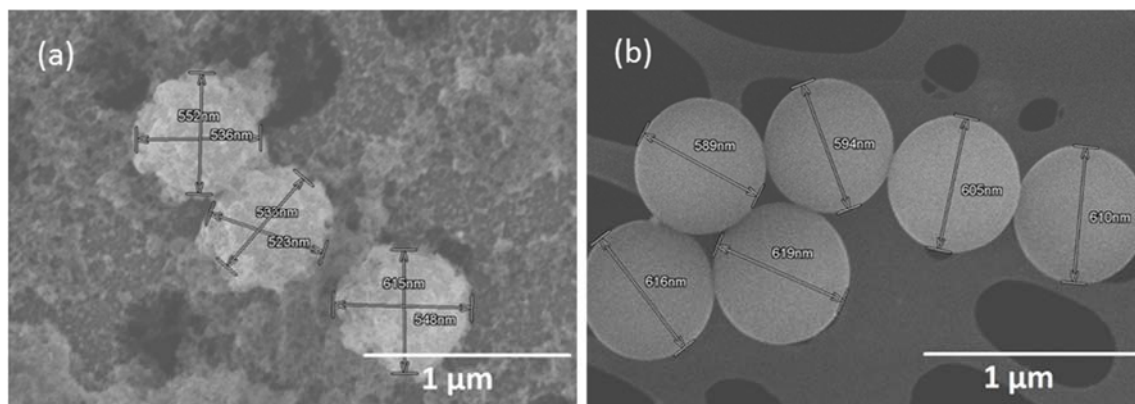
288 **Figure 7.** By-products from WG-PS-0.1500 silica rods and non-reacted PS particles.

289

290 To verify the viability of WG as a silica precursor without the negative impact from PVP, further
291 experiments were conducted with PS-0.0050 and PS-0.0075. According to extrapolation of values from
292 Zou et al. [31], the amount of PVP exposed on the surfaces of PS particles would be less than 1% and
293 3% for PS-0.0050 and PS-0.0075, respectively (versus 25% for PS-0.1500). This renders the buffering
294 effect of the PVP molecules to be insufficient to mask the negative charges on the PS particles arising
295 from the sulphate groups. In this way, electrostatic attraction between PS and silica under acidic

296 conditions can be promoted [36]. Samples containing WG and PS-0.0075 showed a blend of coated and
297 non-coated (PS templates that are not successfully coated by silica during reaction) samples. The
298 average diameter of the coated samples was between 500 nm to 600 nm (**Figure 8**).

299



300

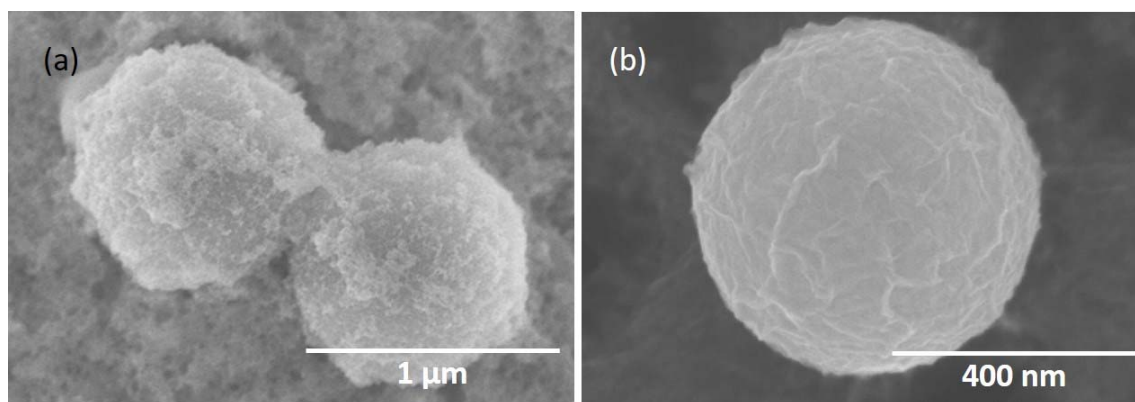
301 **Figure 8.** PS-0.0075 (a) coated and (b) non-coated with silica from water glass, pH =2.0.

302

303 On the other hand, successful full coating of PS-0.0050 was observed. Particles with average diameters
304 of between 600 to 1000 nm were produced (**Figure 9a**), implying the instability of the synthesis route,
305 particularly when using these PS templates. The larger particles could potentially be formed due to
306 coalescing of smaller PS particles together due to low amount of PVP stabilizer. On the other hand,
307 smaller WG-PS particles are created in the same manner as the previous PS-WG hybrid, with shrinkage
308 as a result of calcination. At higher magnifications, the surfaces of the resulting particles were unlike
309 the silica shells of the TEOS based nanospheres, but resembled a large, continuous wrinkled sheet
310 (**Figure 9b**). This may be explained by the tendency of polymerization to undergo slow hydrolysis at
311 low pH, whereby the silica tends to form linear molecules that are occasionally cross-linked. These
312 molecular chains can in turn entangle and form additional branches resulting in gelation and formation
313 of a continuous layer, as amplified by **Figure 9**.

314

315



316

317 **Figure 9.** (a) PS-0.0050 coated with silica from water glass pH= 2.0. (b) Appearance of the
318 silica shell when coated by WG PS-0.005

319

320 On the other extreme, PS-0.3000 samples were coated with WG in a similar fashion as the
321 former three samples and by-products of silica rods were found in higher amounts than that in
322 PS-0.15000 scattered in the sample. While not all PS templates were coated, similar forms of
323 continuous layers of silica coatings on the PS particles were observed. In such cases, the average
324 particle sizes of coated samples were smaller than when PS-0.1500 was employed, standing at
325 a value of ~150 nm. The larger PS on the other hand, were mostly non-coated (**Figure 10**).

326

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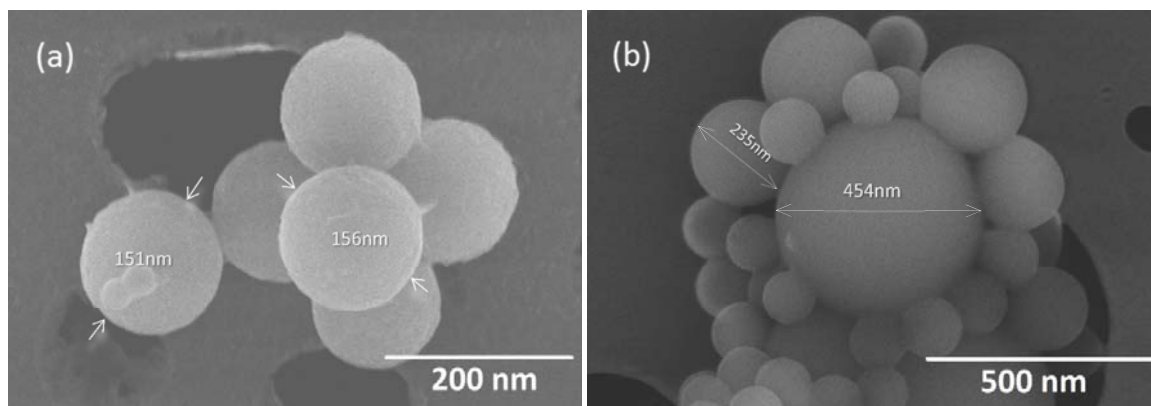
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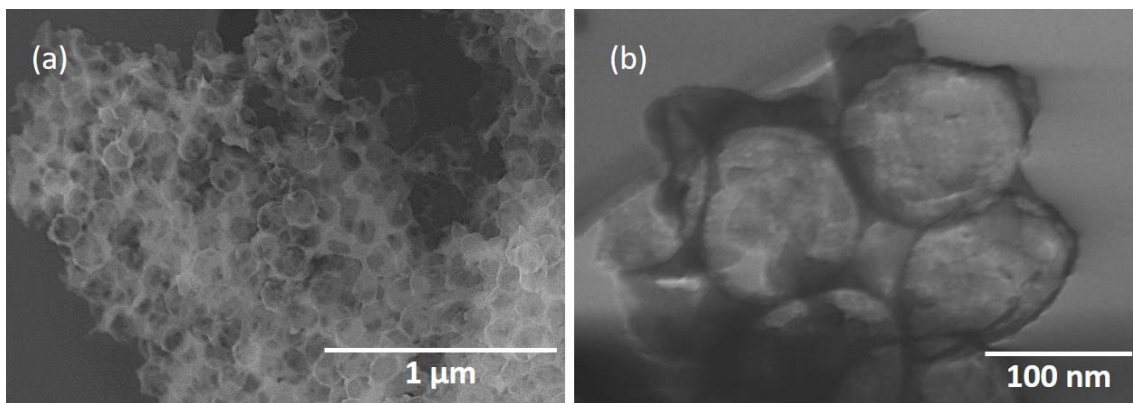


333 **Figure 10** (a) Coated PS-0.3000 particles and (b) non-coated PS-0.3000 particles in the
334 presence of WG.

335

336 Upon calcination, compact mass clusters of nanospheres were detected. For samples prepared with
337 PS-0.1500, the average D_{50} was ~ 120 nm (**Figure 11**). Two points could be observed here. Firstly, not
338 all PS from coated particles were successfully removed through calcination, potentially due to the
339 impermeable continuous layer of silica deposit on the PS particles (**Figure 9**). However, non-coated PS
340 appeared to be removed during calcination. Secondly, the WG-PS particles were much smaller than the
341 PS-0.1500 precursor (120 nm versus 180 nm, respectively), signifying a reduction of up to 35% in inner
342 core space of the HSNS during calcination. A similar trend was observed for the other WG-PS samples.
343 Higher magnification view of the silica layer displayed that no separation between single silica particles
344 could be detected. Instead, a single continuous layer of between 10 to 20nm of silica network could be
345 detected (**Figure 12**), approximately half to one-third the width of that from the TEOS systems.

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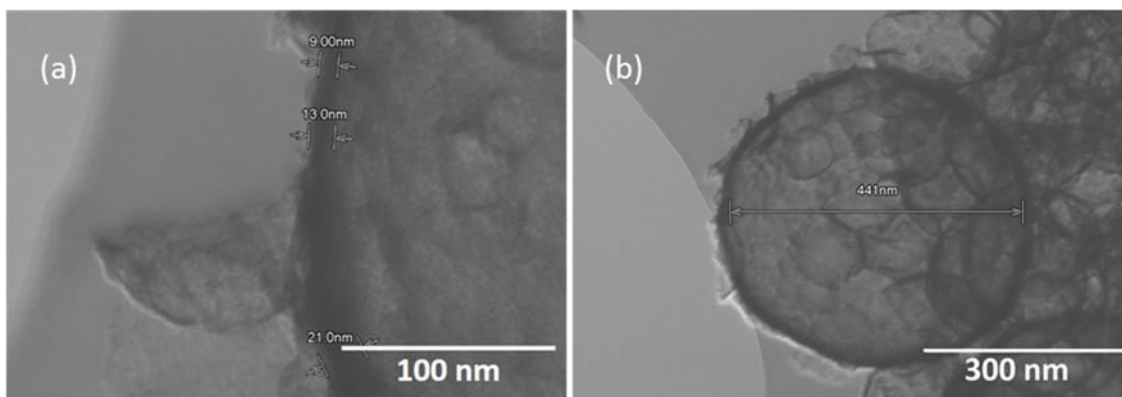


347

348 **Figure 11.** Hollow WG based PS-0.1500 samples after calcination, pH=2.0.

349

350



351

352 **Figure 12.** (a) Shell thickness of silica layer (between 10 to 20 nm) and measured inner diameter of
 353 HSNS prepared with WG and PS-0.1500 (b) lower magnification of same sample.

354

355 **3.4. Thermal conductivity of HSNS**

356 **Table 1** presents the thermal conductivities of the samples prepared from the TEOS and WG reaction
 357 systems. All samples were measured directly after calcination without further processing. Compared to
 358 the parent material of silica that possessed a thermal conductivity of ~ 1400 mW/(mK), the prepared
 359 HSNS were much lower in thermal conductivity.

360

361

362 **Table 1.** Thermal conductivities of HSNS and their corresponding median particle diameter (D_{50}) values
 363 (before and after coating).

364

No.	Sample name	Thermal conductivity [mW/(mK)]	D_{50} avg [nm]		
			PS only	Coated	Inner D [^]
1	TEOS-1PS-0.1000 (96% EtOH)	46	220	250	200
2	TEOS-2PS-0.1000 (96% EtOH)	45	220	250	200
3	TEOS-3PS-0.1000 (96% EtOH)	45	220	250	200
4	TEOS-1PS-0.1000 (100% EtOH)	48	220	245	195
5	WG-PS-0.3000*	72	160**	150**	135
6	WG-PS-0.1500*	102	180	120	105
7	WG-PS-0.0075	56	500	Varied***	-
8	WG-PS-0.0050	44	900	Varied***	-

365 *Presence of non-reacted silica rods dispersed within sample: WG-PS-0.3000 > WG-PS-0.1500.

366 **Only the smaller PS particles were taken into account here and measurements for coated samples are
 367 taken before calcination. Most of the large PS particles remained non-coated and were burnt off during
 368 calcination.

369 ***Particle sizes varied between 400 to 1000 nm.

370 [^]Estimated inner diameter based on silica layer thickness and final coated HSNS D_{50} values

371

372 All samples prepared with TEOS displayed thermal conductivity values of between 45 to 48 mW/(mK),
 373 which are much higher than the previously reported values [37]. This variation can be attributed to
 374 experimental uncertainties like e.g. variation in sample packing density during measurement, which can
 375 cause disturbances in the measured thermal conductivity. The consistent thermal conductivity values of
 376 TEOS prepared HSNS signified that slight variations in particle size and mode of formation did not
 377 affect the thermal conductivity of the final product.

378

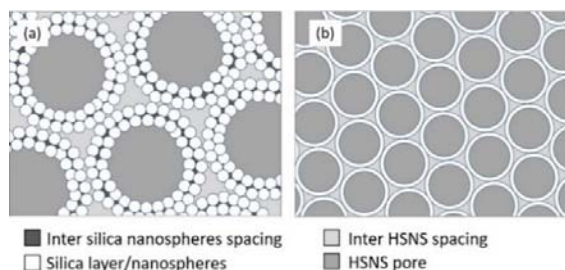
379 Comparing the TEOS and WG formed HSNS, the reaction medium played a crucial role in determining
380 the nature of the silica particles formed. When WG was employed, the thermal conductivity of the
381 resulting products varied as a function of the PVP/St ratio of the PS templates, whereby the lowest
382 thermal conductivity was registered for samples prepared with PS-0.0050 before attaining a maximum
383 of 102 mW/(mK) with PS-0.1500, and finally stabilizing at 72 mW/(mK) for PS-0.3000. At first glance,
384 it appeared that the variation in thermal conductivity was reversely proportional to the size of particles,
385 which would act against the Knudsen effect, or in a broader sense the overall gas thermal conductivity.
386 However, as observed in Equation 1, the overall thermal conductivity is a function of many different
387 parameters. The inverse trend may be explained by the amount of WG added at the onset of reaction.
388 About 33% more WG was added to PS-0.1500 and PS-0.3000 as compared to PS-0.0075 and PS-0.0050.
389 Therefore, a plausible explanation could be that the higher thermal conductivities were a result of the
390 higher solid state conductivity. Additionally, the variation in packing sizes and densities for WG-PS-
391 0.1500, WG-PS-0.0075 and WG-PS-0.3000 would cause slight variations among the samples.

392

393 The main discrepancy however, arose from the difference in thermal conductivity values between WG-
394 PS-0.15000 and TEOS-PS samples. While TEOS based HSNS were twice as large in dimensions as the
395 WG-PS based samples, the thermal conductivity was, however halved. This apparent discrepancy to the
396 theory based on the gas thermal conductivity may be explained by the presence of inter-particle spaces
397 between the silica nanospheres present in TEOS based HSNS (**Figure 13a**), which were absent in the
398 WG based samples (**Figure 13b**). By assuming a close packing network of identically sized silica
399 nanospheres, the average mass density of the silica nanoparticle layer made from the alkaline reaction
400 with TEOS was ideally at a maximum fraction of 0.74 relative to total volume of the sample, regardless
401 of the size of the particles. This implied that in reality, due to the porous nature of the silica layer from
402 the TEOS synthesis, more than 25% of the TEOS based silica coating was made up of nanopores filled
403 with air, bearing average lengths (pitch z) of ~ 15 nm. In this way, the coagulation of silica nanospheres
404 to form the walls of the TEOS based HSNS resulted in an effective reduction of silica mass per volume
405 of material and at the same time, increased the porosity (amount of air voids) within the sample. These
406 two variations would cause a lower λ_{solid} and λ_{gas} for the TEOS based samples as compared to the WG

407 based ones. The large number of nanopores with diameter less than the average mean free path of
 408 ambient air molecules (i.e. 68 nm) favored Knudsen effect and can effectively act as buffers for heat
 409 transfer, which further compensated for the difference in sizes between TEOS and WG based HSNS
 410 (HSNS core diameters: TEOS based 200 nm versus WG based 100 nm). In addition, a continuous
 411 connectivity existed between silica particles in the WG based HSNS, which was greatly minimized in
 412 the disconnected individually formed silica particles of the TEOS based HSNS. Due to the difference in
 413 morphological connectivity, the transmission of heat through the silica solid phase of WG based HSNS
 414 was more prevalent than that for TEOS based HSNS.

415



416

417 **Figure 13.** Illustration of existing interspacing for the different HSNS samples based on (a) TEOS and
 418 (b) WG precursors. Close packing lattices for both systems are assumed (down to scale).

419

420 In this way, the overall thermal conductivity of the HSNS was a balance between the λ_{solid} of the amount
 421 of silica particles, the λ_{solid} of the heat transfer based on solid state connectivity and the overall gas
 422 conductivity λ_{gas} , which was governed by the λ_{gas} in the HSNS pores, the λ_{gas} in the intra-silica layer
 423 (HSNS shell) and the λ_{gas} in the inter-HSNS. Thus, the net thermal conductivity of WG based HSNS
 424 was as a result, higher than that of TEOS based HSNS. In the case of WG-PS-0.0075 and WG-PS-
 425 0.0050, no predictable explanations could be given due to the irregularity in the HSNS formed.

426

427 In general, the importance of the gas conductivity and the solid state and gas interaction as given by the
 428 Knudsen effect should not be downplayed as it plays a major role in the attempts to make the new
 429 superinsulation materials of tomorrow. Also note as stated by Kalnæs and Jelle [35] regarding vacuum
 430 insulation panels (VIP): "In the case of panel perforation, fumed silica will still have a rather low thermal

431 conductivity of around 0.020 W/(mK) at atmospheric pressure. Note then that the difference between
432 0.004 W/(mK) (pristine condition) and 0.020 W/(mK) (punctured) of 0.016 W/(mK) is due entirely to
433 gas thermal conductivity (not taking into account any changes to the solid core due to the loss of vacuum).
434 That is, the combined solid state and radiation thermal conductivity of fumed silica is as low as
435 0.004 W/(mK) or in principle somewhat lower (as there is still a very small concentration of air inside
436 a VIP a small part of the 0.004 W/(mK) value is due to gas conduction). Hence, as it is possible to make
437 materials with such a very low solid state and radiation conductivity, there are rather good opportunities
438 to make a high performance thermal insulation material functioning at atmospheric pressure by lowering
439 the gas thermal conductivity."

440

441

442 **4. Conclusions**

443 A series of hollow silica nanospheres (HSNS) were synthesized with tetraethyl orthosilicate (TEOS)
444 and water glass (Na_2SiO_3 , WG) as silica precursors, in alkaline and acidic media, respectively. It was
445 found that the production with TEOS was more robust and provided a lower thermal conductivity than
446 samples prepared by WG due to increased porosity of the samples, which reduced the effective silica
447 amount per volume of sample (and thus solid state thermal conductivity) and gas thermal conductivity.
448 The lowest thermal conductivity of 44 mW/(mK) of the HSNS samples reported within this study falls
449 in the upper range of traditional thermal insulation materials. Further enhancement of the HSNS
450 properties may be achieved by decreasing the size of the sacrificial templates to decrease the gas thermal
451 conductivity as given by the Knudsen effect, thus making the HSNS a possible stepping-stone toward a
452 viable, new thermal insulation material.

453

454 It may be inferred from this investigation that the choice of reaction medium is very important for
455 effective production of thermally insulating HSNS. Therefore, for optimal production, deriving a new
456 synthesis route by using WG as silica precursor may be a possible way to achieve a greener and more
457 sustainable cost-effective method to produce HSNS.

458

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466

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