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Low-cost and fast synthesis of nanoporous silica cryogels for thermal insulation applications

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Abstract
Nanoporous silica cryogels with a high specific surface area of 1095 m\(^2\) g\(^{-1}\) were fabricated using tert-butyl alcohol as a reaction solvent, via a cost-effective sol–gel process followed by vacuum freeze drying. The total time of cryogel production was reduced markedly to one day. The molar ratio of solvent/precursor, which was varied from 5 to 13, significantly affected the porous structure and thermal insulating properties of the cryogels. The silica cryogels with low densities in the range of 0.08–0.18 g cm\(^{-3}\) and thermal conductivities as low as 6.7 mW (m \(\cdot\) K\(^{-1}\)) at 100 Pa and 28.3 mW (m \(\cdot\) K\(^{-1}\)) at 10\(^5\) Pa were obtained using this new technique.

Keywords: tert-butyl alcohol, vacuum freeze drying, silica cryogels, thermal insulating

1. Introduction
Porous materials have numerous applications owing to their unique properties such as low density, large surface area and high permeability [1]–[3]. Silica (SiO\textsubscript{2}) aerogels are one of the most popular porous materials and possess excellent properties such as high optical transparency (~98%) [4], porosity (98%) and surface area (~1500 m\(^2\) g\(^{-1}\)) [5, 6], as well as extremely low thermal conductivity (~0.02 W (m \(\cdot\) K\(^{-1}\)) [7] and density (0.03 g cm\(^{-3}\)) [8]. Therefore, these aerogels can be used in thermal insulators [9]. Cerenkov radiation detectors, catalytic supports, filters, radio luminescent power sources and inertial confinement fusion (ICF) targets [10]–[13]. In particular, owing to their superior thermal insulation properties [14], silica aerogels have been widely used in solar energy systems, windows, piping and cooling or heating systems [9].

Traditionally, silica aerogels with excellent properties have been obtained by drying wet gels under supercritical conditions to avoid the formation of meniscus [15]. However, this process is expensive and hazardous [16], which limits large-scale production. Many attempts have been made to develop another technique for large-scale production, which is known as ‘ambient pressure drying’ [17, 18]. By this method, the capillary forces are reduced by forming new siloxane bonds [15] on the surface of the wet gel, so that the shrinkage of the networks is very low owing to a spring-back effect [19]. The materials produced by this method are defined as ‘xerogels’. The properties of xerogels are similar to those of aerogels, but unfortunately, the drying process involves the use of hazardous solvents for tedious solvent exchange and surface modification, which is harmful to humans and the environment. Another promising technique is vacuum freeze drying. It is based on sublimation, i.e. direct conversion from the solid to gaseous state, and thus avoids the formation of liquid–vapor meniscus [20, 21]. The freeze-dried gels are called ‘cryogels’ [22]. More recently, Mukai et al [23] have reported ice-templated silica gels with various shapes prepared through the unidirectional freezing of silica hydrogels and hydrosols. The process involved the
liquid nitrogen (77 K) immersion and water exchange steps with tert-butyl alcohol (TBA) repeated three times, which resulted in porous structures with different shapes.

The synthesis of the wet gel before drying affects the properties of the resulting porous aerogels except for the drying technique. The sol–gel method has been widely used to prepare the silica wet gels in many excellent research and review papers [15, 24, 25]. A series of factors including precursors, catalysts, molar ratios of initial materials and reaction temperature have been studied. However, research on reaction solvents has been very limited, despite the fact that the solvent impregnating the wet gel can determine the overall process time. Wet gels are usually prepared using ethanol, methanol and isopropanol as solvents, and the sequence of solvent exchange and drying steps results in a long process time.

Here, we report a novel technique to prepare porous silica using TBA as a reaction solvent to synthesize silica wet gels in combination with vacuum freeze drying. TBA was rarely used as a reaction solvent to prepare silica wet gels because its high viscosity led to poor dispersion properties at room temperature (~25 °C). Besides, owing to their strong surface tension, the TBA-based wet gels are not suitable for drying under direct supercritical or ambient pressure. Fortunately, a combination of vacuum freeze drying with an improved synthesis route can overcome these disadvantages. The wet gels were prepared using TBA as a reaction solvent at an elevated temperature of 50 °C, which significantly decreases the viscosity of TBA. The high freezing point of TBA (25 °C), as compared with those of ethanol (~97.8 °C) and methanol (~117.3 °C), facilitates the vacuum freeze drying process. TBA excellently disperses the precursor in the solution at 50 °C, as well as ethanol at room temperature. Moreover, TBA in this technique not only serves as the reaction solvent to prepare silica wet gels, but also acts as the drying medium without the need for exchange with any other solvent, which shortens the process time and significantly reduces the cost. The effects of solvent content on the properties of cryogels were studied by varying the molar ratio of TBA/precursor, which was set at X = 5, 7, 9, 11 and 13. After freeze drying, semi-translucent silica cryogel powders with high specific surface area and low thermal conductivity were obtained.

2. Experimental details

2.1. Materials

The chemicals used for the preparation of alcogels were tetraethoxysilane (TEOS, SiO₂ ≥ 28.5%), TBA (99%), hydrochloric acid (HCl, 36.5%) and ammonia (NH₄OH, 28%), which were purchased from Aladdin Reagent Database Inc. (China). The double-distilled water (H₂O) was prepared in the authors’ laboratory.

2.2. Preparation of cryogels

In a typical experiment, TEOS and TBA were used as precursor and solvent, respectively. Hydrochloric acid (HCl) was added to induce the hydrolysis of the precursor, and then the irreversible polycondensation reaction took place in the presence of a base catalyst (NH₄OH). Firstly, TBA/TEOS mixtures were prepared with the molar ratios X = 5, 7, 9, 11 and 13. Then, a diluted HCl (0.12 mol⁻¹) was added into the mixture under continuous stirring for 30 min at 50 °C. Secondly, diluted NH₄OH (1.44 mol⁻¹) was added drop wise to the acid-catalyzed sols under rapid stirring for 5 min, until the PH became about 8. The alcosols were transferred to a culture dish (inner diameter 100 mm, height 15 mm) at room temperature and gelled for 10–50 min. The molar ratio of TEOS : H₂O : HCl : NH₄OH was 1 : 3.7 : 1.08 × 10⁻⁴ : 1.24 × 10⁻³. Thirdly, the transparent gels were aged at 50 °C for 3 h to strengthen the gel networks. Finally, the wet gels were dried in a vacuum freeze dryer (Christ Alpha 2-4 LSC, Germany) using a special program (see Appendix A). The total production time of the cryogel powders was about 17 h.

2.3. Characterization methods

The porosity of the cryogels was characterized by nitrogen absorption/desorption measurements (Autosorb-iQ, Quantachrome, USA). The specific surface area and pore size distribution were analyzed by the Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods, respectively. The morphology was observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). The thermal conductivity of the cryogel powders was measured with a thermal constant analyzer (GHP456/3/1 Titan, NETZSCH, Germany), using the guarded hot plate (GHP) method and varying the pressure from 1 to 10⁵ Pa (details in Appendix B). The packing density of the cryogel powders was measured on the basis of the mass to volume ratio without compacting, as reported in [26]–[30].

3. Results and discussion

3.1. Novel technique to prepare silica cryogel powders

Figure 1 shows a schematic of the preparation of silica cryogel powders using TBA as a reaction solvent. At the beginning, silanol groups (Si–OH) derived from the hydrolysis of precursor were dispersed in the solvent. Then gelation occurred after the addition of a base catalyst owing to the condensation of silanol groups. Stiff silica networks were formed after aging, whose space was filled up by TBA and residual hydrolyzed liquid, which could be easily frozen and sublimed because of the high freezing point of TBA. Loose silica networks with empty pores were left after vacuum freeze drying and formed cryogel powders as shown in figure 1. The merits of our chosen solvent, TBA, are as follows. Firstly, it is an excellent solvent at elevated temperatures, having the similar chemical components similar to those of solvents traditionally used in the preparation of wet gels; thus TBA can homogenize the precursor for dissolution. Secondly, the high freezing point of TBA allows the elimination of the solvent exchange steps thereby shortening the production time. Thirdly, TBA is cheaper than many other solvents such as ethanol and isopropanol.
Combining with the virtues of vacuum freeze drying, this synthesis technique can markedly improve the production technology and reduce its costs.

3.2. Microstructure

The porosity of silica cryogels prepared using TBA as a reaction solvent was investigated by the N\textsubscript{2} absorption/desorption, and the derived pore size distribution is shown in figure 2. The physisorption isotherm is of type IV, which is typical of mesoporous materials [28]. The SiO\textsubscript{2} cryogels with X = 11 exhibit an extremely high specific surface area of 1095 m\textsuperscript{2} g\textsuperscript{−1}, and the pore size is distributed in the range of 0.3–35 nm with a high density of micro- and mesopores (0.35–4 nm) as shown in figure 2(b). Such high surface area and small homogeneous pores can be attributed to not only the excellent dispersive function but also to the intrinsic small molecular volume of the solvent used in this technique, which easily impregnated the wet gels and then vacated the pores. The SEM images of gels with X = 7 and 11 in figure 3 also confirm the porous structures with relatively uniform particle sizes and well-tailored silica networks. The pores of the SiO\textsubscript{2} cryogels are smaller than the mean free path of air (∼70 nm) under ambient conditions, indicating that the cryogels can hinder the gaseous heat conduction. These properties are valuable for applications such as catalyst support [11] and thermal insulator [8].

3.3. Thermal conductivity

Thermal conductivity is crucial for insulation applications. However, there are only a few reports on the thermal conductivity of aerogels/xerogels [8, 31–34]. Figure 4 compares the thermal conductivities of typical silica cryogel powders (K\textsubscript{C}, X = 11) with those of pure nitrogen and a standard reference material (SRM, Glass fiberboard, NIST-certified 1450c, 300 × 300 × 25 mm) at 25°C and different pressures. The K\textsubscript{C} is very low (6.7 mW (m·K)\textsuperscript{−1}) at 100 Pa, and then slightly increases with pressure. Between 20 and 2 × 10\textsuperscript{4} Pa, the thermal conductivity of silica cryogels is much lower than those of nitrogen (K\textsubscript{N}) and SRM (K\textsubscript{S})

The above-described phenomena can be explained as follows. Firstly, the solid conductivity (λ\textsubscript{s}) strongly depends on the density (ρ), which can be expressed as λ\textsubscript{s} < ρ\textsuperscript{α} for ρ = 70–300 kg m\textsuperscript{−3} [31]. The loose silica cryogel networks obtained using TBA as a solvent have low densities in the range of 0.08–0.18 g cm\textsuperscript{−3} (table 1), which can effectively reduce the heat transfer from the contacted silica particles [32]. However, K\textsubscript{N} is much higher than K\textsubscript{C} and K\textsubscript{S} at pressures below 100 Pa, at which the heat conduction takes place directly via the nitrogen molecular vibrations. Secondly, the radiative conduction was prevented partially via the multiple absorption, re-emission and scattering processes [35] owing to the nanoporous structures of the silica cryogels at low temperature (<100°C), whereas infrared opacifiers must be doped to resist the radiative heat conduction for the high-temperature application due to the absorption of silica
Table 1. Effects of the molar ratio of TBA/TEOS (X) on the physical properties of silica cryogel powders; λ is thermal conductivity at 25°C and 10^5 Pa.

<table>
<thead>
<tr>
<th>X</th>
<th>Density ±0.01 (g cm⁻¹)</th>
<th>BET surface area ±5 (m² g⁻¹)</th>
<th>Average pore size ±0.2 (nm)</th>
<th>λ ± 0.3 (mW (m·K)⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.18</td>
<td>761</td>
<td>4.6</td>
<td>33.4</td>
</tr>
<tr>
<td>7</td>
<td>0.14</td>
<td>910</td>
<td>4.4</td>
<td>31.8</td>
</tr>
<tr>
<td>9</td>
<td>0.10</td>
<td>989</td>
<td>4.0</td>
<td>30.4</td>
</tr>
<tr>
<td>11</td>
<td>0.08</td>
<td>1095</td>
<td>3.8</td>
<td>28.3</td>
</tr>
<tr>
<td>13</td>
<td>0.09</td>
<td>1072</td>
<td>3.9</td>
<td>29.6</td>
</tr>
</tbody>
</table>

at 3–8 µm [8, 31]. Thirdly, the gaseous conduction in the porous structure relating to the pressure of the system is more complicated. The porous structure of silica cryogels with small homogeneous pores as shown in figure 2(b) can significantly hinder the gaseous conduction according to Knudsen’s equation [31].

At low pressures, the mean free path (λ) is larger than the average pore size (l) of the samples according to the Maxwell average molecular free path equation (1)

$$\lambda = \frac{kT}{\sqrt{2\pi d^2}P}$$  \hspace{1cm} (1)

where $k$ is the Boltzmann constant, $T$ is the temperature, $d$ is the effective particle diameter and $P$ is the pressure of the system.

The gaseous heat conduction depends on the collisions between the gas molecules and the pore walls, whose frequency is proportional to the pressure of the system. Therefore, the gaseous heat conduction is negligible at low pressures and can be ignored for porous materials, and the intrinsic heat conduction dominates the thermal conductivity of our samples. Increasing the pressure facilitates the gas transport because the mean free path of the gas decreases according to (1), resulting in an increase in the total thermal conduction. The $K_S$ begins to increase at a lower pressure of 10 Pa while $K_C$ increases at a higher pressure of 100 Pa; both thresholds are determined by the onset of gas conduction within the pores of the pellets [24], implying that the average pore size of the silica cryogels is smaller than that of SRM. At higher pressures, the gaseous heat conduction becomes steady and mainly depends on the solid conductivity. This is consistent with the results for nitrogen at 50–10⁵ Pa and SRM at 10⁴–10⁵ Pa.

Although the thermal conductivity is higher for our cryogel powders than for aerogels prepared by supercritical drying in reports [24, 36], our technique is simple and inexpensive, and can be used in large-scale thermal insulating applications at low pressures, such as vacuum insulating plates [37] and silica granulate insulating materials [38, 39].
3.4. Physical properties

The physical properties including density, porosity and thermal conductivity of the cryogel powders as functions of the solvent/precursor molar ratio are presented in Table 1. The densities of the cryogel powders decrease while the BET surface areas increase with an increase in the volume of the reaction solvent. These tendencies can be explained by the fact that an increase of the solvent content results in a better separation of the reacting species [40] and a lower precursor concentration in the hydrolyzed products and final gels. Moreover, the volume shrinkage of the wet gels is small when using TBA as a reaction solvent followed by vacuum freeze drying, resulting in loose silica networks with low density and high specific area. However, there is a limit to the increase of the reaction solvent molar ratio. This is because the silica networks break into fractal aggregates [41] at high solvent/precursor ratios \( X \) owing to Oswald ripening [42], leading to a severe shrinkage during the drying process. In this work, the best ratio was determined as \( X = 11 \) in terms of low density and high surface area with small average pore sizes. This ratio provides sufficient space for the growth of strong networks to withstand the shrinkage during freeze drying according to the formation mechanism of silica gels [8, 15]. The thermal conductivity depending on the density and porous structure was also affected by the \( X \) value. Obviously, the cryogels with lower density and higher specific surface area are better thermal insulators. Besides, their small average pore sizes (<5 nm) also reduce the thermal conductivity. In summary, the properties of silica cryogels prepared using our technique are much better than those of the cryogels prepared using ethanol as a reaction solvent [43]. Moreover, our approach has eliminated several preparation steps, thereby significantly shortening the production time.

4. Conclusions

We have presented a new cost-effective technique for the production of silica cryogels using vacuum freeze drying and TBA as a solvent. The use of TBA eliminates several solvent exchange and surface modification steps, thereby reducing the costs and duration of the synthesis. This technique has overcome some limitations of aerogels/xerogels and holds promise for a large-scale cryogel production. It can be extended beyond nanoporous silica to other porous materials such as ceramics, catalysts and biomaterials. The silica cryogels obtained by this technique possess excellent porous structure and low thermal conductivity, which are comparable to those of aerogels. This technology is promising for commercial applications such as thermal insulators, catalyst supports and storage media.

Acknowledgments

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Appendix A

Wet gels were dried in a vacuum freeze dryer (Christ Alpha 2–4 LSC, Germany) in two steps. Firstly, the wet gels were cooled to \(-30^\circ C\) in the ice condenser chamber and kept there for 4 h. Secondly, the vacuum pump was switched on and the drying procedure has started. The temperature was increased from \(-30^\circ C\) to \(10^\circ C\) at \(10^\circ C\) steps and a fixed pressure of 0.12 mbar and was kept for 1.5 h at every step. Then, it was increased from 10 to \(5^\circ C\) at \(5^\circ C\) steps and was kept for 15 min at a pressure of 0.63 mbar at every step. The temperature was raised at a rate of 0.67 °C min⁻¹ controlled using the microprocessor. During this process, the frozen liquid was sublimed from solid to gas and removed using the vacuum pump. The obtained cryogels were very fragile, semi translucent powders.

Appendix B

The thermal conductivity of the cryogel powders was measured with a thermal constant analyzer (GHP 456/3/1 Titan, NETZSCH, Germany) using the guarded hot plate (GHP) method and the following equation.

\[
k = \frac{-0.5 \times \phi \times d}{A \times \Delta T}.
\]  

Here, \( k \) is the thermal conductivity, \( \phi \) is the electric power provided by the hot plate, \( d \) is the thickness of the cryogel, \( A \) is the area of heat transfer and \( \Delta T \) is the temperature difference between the top and bottom samples.

The GHP 456 system yields the absolute thermal conductivity without the need for system calibration or reference material. The thermal conductivity is characterized by the quantity of heat passing per unit time per unit area as a result of a temperature drop of 1 °C per unit length.

Figure B.1 shows a schematic of the GHP 456 Titan setup used for testing cryogel powders, which is similar to the previous ones such as the vacuum hotplate setups reported in [44, 45]. The measurement of thermal conductivity consisted of the following steps: firstly, a glass-fiber board (NIST-certified standard reference material 1450c) was measured over the certified temperature range (0–60 °C). The

![Figure B.1. Schematic of the GHP 456 Titan setup.](image-url)
results agreed with the literature values (taken from the NIST certificate) within a deviation of 1% indicating the outstanding accuracy of the analyzer. The sensitivity of the GHP 456 analyzer is 0.1 mW (m·K)^{-1}. Secondly, pure dry nitrogen was gently filled in the high-vacuum system, and the pressure dependence of thermal conductivity was measured between 0.1 and 10^5 Pa at 25 °C. Thirdly, the crushed cryogel powders with relatively uniform sizes were enclosed in two powder test vessels made of calcium silicate and sealed with non-woven fabrics. The hot plate and guard heater were sandwiched between the two cryogel samples with the same size of 260 × 260 × 15 mm. The measurement was carried out by decompression, using a turbo pump from 1 × 10^5 to 1 Pa, in the vacuum-tight housing of the analyzer at 25 °C. Finally, the thermal conductivity of the SRM 1450c (300 × 300 × 25 mm) sample was measured for comparison.

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