Thick Transparent Nanoparticle-Based Mesoporous Silica Monolithic Slabs for Thermally Insulating Window Materials

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Supporting Information

ABSTRACT: This paper presents a novel template-free water-based sol–gel method to synthesize thick transparent and thermally insulating mesoporous silica monolithic slabs by gelation and drying of a colloidal suspension of silica nanoparticles under ambient conditions. For the first time, mesoporous silica slabs were synthesized on perfluorocarbon liquid substrates to reduce adhesion and enable the gels to shrink freely during aging and drying without incurring significant stress that could cause fracture. The free-standing nanoparticle-based mesoporous silica slabs were disks or squares, with thickness between 1 and 6 mm and porosity around 50%. The slabs had high transmittance and low haze in the visible spectrum due to small nanoparticles (<10 nm). The slabs’ effective thermal conductivity of 104–160 mW m⁻¹ K⁻¹ at room temperature was smaller than that of other mesoporous silicas with similar or even larger porosity reported in the literature. This was attributed to the slabs’ fractal structure and high mass fractal dimension. The mechanical properties were similar to those of common polymers. The simple synthesis is readily scalable and offers promising materials for window solutions and solar–thermal energy conversion, for example.

KEYWORDS: mesoporous silica, silica nanoparticles, optically transparent thermal insulators, transparent slabs, liquid substrates

1. INTRODUCTION

Mesoporous silica monoliths can take various shapes (e.g., slabs, discs, and rods) and feature large specific surface area and porosity, small pore size (2–50 nm), low effective thermal conductivity, and low dielectric constant. They have been commonly used in adsorption, catalysis, and chromatography for their large surface area and porosity. Recently, transparent mesoporous silica monoliths have found applications as optically transparent supports in photocatalysis, optics, and laser amplification. They have also been used as ultralow refractive index substrates for waveguides and as optically transparent thermal insulation in window solutions and in solar–thermal energy conversion.

Mesoporous silica films or powders are often prepared by using sol–gel methods. The synthesis typically uses organic templates (e.g., surfactants or block copolymers) that form mesopores with controlled shape and diameter between 1.5 and 30 nm and porosity up to 80%. However, mesoporous silica monoliths are much more difficult to synthesize by a sol–gel method because the silica network is subjected to significant capillary forces during evaporation of the solvent present in the mesopores. These forces impose enormous stress on the silica network, causing it to shrink during aging and drying. If the stress exceeds the compressive strength of the gel, the monolith cracks and may crumble into powder.

Synthesis of thick mesoporous silica monolithic slabs that are both transparent and thermally insulating is even more challenging. First, achieving low thermal conductivity requires large porosity. Second, transparency requires that the slab’s pores and surface roughness be much smaller than the wavelength of the incident visible light (400–700 nm) so as to minimize volumetric and surface scattering responsible for haze. However, mesoporous silica slabs with large porosity also tend to have larger pores that scatter light. For example, aerogels with porosity exceeding 80% have low thermal conductivity but are typically hazy because of their wide pore size distribution with some pores exceeding 40 nm in...
diameter.\textsuperscript{31} Third, in addition to capillary forces and stress caused by evaporation, mesoporous silica slabs synthesized by using sol–gel method may crack due to adhesion forces pinning the gel to the substrate.\textsuperscript{25} All mesoporous silica gels undergo significant shrinkage during aging and drying.\textsuperscript{25} Because gels are soft and fragile, opposing adhesion and compressive forces due to shrinkage almost inevitably result in cracking.\textsuperscript{25} In fact, adhesion forces are proportional to the footprint surface area of the gel, making it especially challenging to synthesize large slabs.

Several solutions to the cracking of mesoporous silica monoliths have been proposed. The two most common strategies include (i) supercritical drying\textsuperscript{25} and (ii) ambient drying by solvent exchange\textsuperscript{32}−\textsuperscript{35} of aged gels. Both strategies consist of exchanging water contained in the pores for a liquid with lower surface tension to minimize capillary forces. Both processes lead to mesoporous silica monoliths, but their scale-up is rendered difficult by the facts that (i) supercritical drying requires expensive high-pressure equipment and (ii) ambient drying may be time-consuming and requires large volumes of organic solvents used in solvent exchange.

Synthesis of mesoporous silica monoliths can also be achieved by (1) scaffolding silica network with a secondary material\textsuperscript{36−42} or by (2) inducing flexibility in the silica network.\textsuperscript{43−46} In the first method, a composite monolith is prepared that contains silica and a secondary material (e.g., carbon,\textsuperscript{36} polymers,\textsuperscript{37−40} nanofibril cellulose,\textsuperscript{41} or silica nanowires\textsuperscript{42}) that serves as a scaffold supporting the silica network and preventing cracking upon drying.\textsuperscript{42} In the second method, flexible mesoporous silica monoliths are fabricated by incorporating organic groups\textsuperscript{45,44} and carbon nanotubes\textsuperscript{45} or by double cross-linking of silica and organic networks.\textsuperscript{46} Such flexible monoliths shrink without cracking due to their mechanically compliant network, and once completely dry, they spring back to the original size.\textsuperscript{47} Although successful, both strategies are complicated to implement and most monoliths prepared by using these methods are opaque.\textsuperscript{36−45}

Few studies have reported synthesis of transparent (not translucent) mesoporous silica slabs with high transmittance and low haze. Rozière et al.\textsuperscript{48} synthesized transparent mesoporous silica slabs by a soft-templating sol–gel synthesis using tetraethylyorthosilicate (TEOS) as the silica precursor and the nonionic surfactant Brij 30 as the template. The resulting gels were calcined at 560 °C to remove the polymer template. Interestingly, other authors have reported cracking of similar soft-templated monoliths after calcination.\textsuperscript{49,50} However, Rozière et al.\textsuperscript{48} synthesized monoliths that did not crack and were 15 mm in diameter and 3 mm in thickness with porosity around 50% and average pore width of 2.3 nm. Unfortunately, neither the monoliths’ thermal conductivity nor their optical properties were reported, even though they appear optically clear.

This paper aims to develop a novel template-free method to synthesize thick transparent and thermally insulating mesoporous silica monolithic slabs made of silica nanoparticles. The nanoscale architecture of the mesoporous slabs was characterized by transmission electron microscopy (TEM), nitrogen porosimetry, small-angle X-ray scattering (SAXS), and surface profilometry. Their transmittance and haze were measured across the visible part of the spectrum while their effective thermal conductivity and effective Young’s modulus and hardness were measured at room temperature.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. Figure 1 shows the general scheme of the synthesis process for nanoparticle-based mesoporous silica slabs on a PFC liquid substrate. The method consists of (1) pouring the nanoparticle suspension into a mold whose bottom is covered with PFC liquid, (2) partly evaporating the water to drive gelation of the suspension, (3) aging of the gel, accompanied by shrinkage, (4) drying of the aged gel until all the water has evaporated, and (5) calcining the slabs in oxygen at 400 °C for 2 h using a 5 °C min\textsuperscript{-1} temperature ramp to remove NH\textsubscript{3} from the pores and any potential PFC residues from the bottom surface. Here, a commercially available colloidal solution of silica nanoparticles Nalco 2326 (15 wt % in water, NH\textsubscript{3} stabilized, lot number BP7J1239A1, Nalco Chemical Company, Naperville, IL) was used, but in general, the synthesis can be performed using any colloidal silica solution. The PFC liquids used as the liquid substrates were perfluoropolyether oils Krytox GPL 100, GPL 104, and GPL 106 (Miller-Stephenson Chemical Company Inc., Danbury, CT) with general formula \[\text{[CF(CF}_3\text{)CF}_2O}\], where \(n = 10−60\). Although these PFC liquids have slightly different molecular weights, they have the same chemical properties and thus were used interchangeably in the experiments. Changing the PFC liquids had no noticeable effect on the synthesized slabs. It is worth mentioning that the PFC liquids were recovered after the synthesis and reused in subsequent experiments since they did not mix with the colloidal solution and could be easily recovered once the solution had gelled. Note that the colloidal solution or gel of silica nanoparticles had an effective density ranging between 1.0 and 1.6 g cm\textsuperscript{-3} and thus floated on the PFC liquid substrate, whose density is 1.9 g cm\textsuperscript{-3}.\textsuperscript{51}

For comparison, mesoporous silica slabs were synthesized on a solid PTFE substrate by using the same procedure (Figure 1) except that the colloidal solution of silica nanoparticles was placed in an empty PTFE mold without PFC liquid. The mesoporous slabs prepared on PTFE were analyzed as synthesized, i.e., without calcination.

Nanoparticle-based mesoporous silica slabs synthesized on PFC liquid substrates were labeled as SiO\textsubscript{2}-PFC-rt, SiO\textsubscript{2}-PFC-40C, and SiO\textsubscript{2}-PFC-hc while those synthesized on PTFE substrates were labeled as SiO\textsubscript{2}-PTFE-rt, SiO\textsubscript{2}-PTFE-40C, and SiO\textsubscript{2}-PTFE-hc for slabs dried at room temperature or in an oven at 25 °C, in an oven at 40 °C, and in a humidity chamber at room temperature, respectively.

Details of the chemicals, quantities, and synthesis procedure are available in the Supporting Information.

2.2. Characterization Methods. The synthesized nanoparticle-based mesoporous silica slabs were characterized structurally by TEM. Low-temperature nitrogen porosimetry provided specific surface area, total specific pore volume, porosity, micro pore volume, pore size distribution, and peak pore width of the mesoporous slabs. Small-
angle X-ray scattering (SAXS) was used to analyze the fractal structure of the materials and to determine the mass fractal dimension. Profilometry gave the average and root-mean-squared surface roughness of the slab surfaces. The spectral normal-hemispherical and diffuse transmittances, haze, and color rendering index of the slabs in the visible spectrum were measured by using a UV–vis spectrometer equipped with an integrating sphere. Time-domain thermoreflectance was used to measure the effective thermal conductivity at room temperature under vacuum or in air. Nanoindentation was performed to retrieve the effective Young’s modulus and hardness of the mesoporous slabs. Details of the instrumentation and data analysis are also provided in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Synthesis Design. The present synthesis method (Figure 1) resulting in mesoporous silica monolithic slabs that are both transparent and thermally insulating combines several strategies aiming to address challenges in making crack-free highly porous slabs with small pores and optically smooth surfaces. For the first time, synthesis of mesoporous silica monolithic slabs used a PFC liquid substrate to minimize adhesion between the gel and the substrates and to obtain optically smooth surfaces. PFC liquids were selected as substrates because of (i) their omniphobic properties, ensuring immiscibility with the aqueous colloidal solution of silica nanoparticles, (ii) their high density, ensuring that the colloidal solution floated on the liquid substrate, and (iii) large surface tension with water, ensuring flatness of the liquid–liquid interface. The latter enabled the gels to shrink during aging and drying without incurring significant stress that would otherwise lead to fractures. Similar effects were achieved by using the PTFE substrate due to its nonstick properties, but the surface roughness of the PTFE was much greater. Moreover, despite its high chemical inertness, gels still slightly adhered to the PTFE substrate, resulting in lower yield of crack-free slabs. Note that this effect was negligible for slabs with small footprint surface area (<3 cm in diameter). However, larger slabs cracked noticeably more often during aging. By contrast, slabs prepared on PFC liquids did not crack during aging regardless of their size.

In addition, the present synthesis used small silica nanoparticles (6–12 nm in diameter) as the building blocks (i) to avoid large shrinkage during aging and drying and (ii) to ensure that the mesopores created between the nanoparticles were much smaller than the wavelength of visible light so as to minimize light scattering. Nanoparticle-based gels experienced smaller shrinkage than typical gels synthesized from molecular precursors (e.g., TEOS) because (a) virtually all silica is bound in the building blocks rather than dissolved in the solution and (b) there was little room for structural rearrangement and evolution once the network had formed. Most importantly, reactions of residual precursor and unreacted groups that drive shrinkage of typical gels are mostly absent in our nanoparticle-based gels. Conveniently, the reduced shrinkage of nanoparticle-based gels also enabled us to achieve large porosity.

Figure 2 shows optical images of representative thick transparent nanoparticle-based mesoporous silica monolithic slabs: (a) a circular slab with diameter of 3.6 cm and average thickness of 3 mm synthesized on PFC liquid at room temperature (SiO$_2$-PFC-rt) and (b) a square slab with round corners with size of 2.4 cm and average thickness of 5 mm synthesized on PTFE at room temperature (SiO$_2$-PTFE-rt). The difference in slabs’ size and shape was due to the different molds used in the slab preparation. Here, both cylindrical molds with diameter ranging from 3.8 to 6.2 cm and square molds with a size of 3.4 cm were used (see Figure S1 in the Supporting Information for circular slabs prepared on PTFE). While the final size and shape of the slabs were determined by those of the mold, the average thickness was determined by the initial volume of the colloidal solution of silica nanoparticles. Overall, mesoporous silica monolithic slabs with sizes between 2 and 4.5 cm and thickness between 1 and 6 mm were synthesized. Notably, the SiO$_2$-PFC-rt slabs had higher transparency than the SiO$_2$-PTFE-rt slabs. This difference will be discussed in the following sections.

3.2. Structural Characterization. Figure 3 shows representative TEM images and particle diameter histograms (insets) of transparent nanoparticle-based mesoporous silica monolithic slabs prepared (a) on PFC liquid and (b) on PTFE. Both types of slabs had similar structures with a network made of aggregated silica nanoparticles. The average diameters of silica nanoparticles were 8 ± 3 and 9 ± 3 nm for slabs synthesized on PFC and on PTFE, respectively, showing that the particle size in the final slabs was the same. However, the average nanoparticle diameters observed from TEM were larger than the manufacturer-specified nanoparticle diameter of 5 nm. This observation is likely due to the growth of silica nanoparticles in solution caused by Ostwald ripening. The latter is enhanced by the high pH around 9–10 used to stabilize the colloidal solution. Figure 3 also shows that the size of the mesopores between the silica nanoparticles was comparable to the size of nanoparticles; i.e., no large pores were observed, and the slab’s mesostructure and appearance were fairly uniform across the image.

Figure 4 shows (a) representative nitrogen adsorption–desorption isotherms and (b) the corresponding pore size distributions for nanoparticle-based mesoporous silica monolithic slabs prepared on PFC liquid and on PTFE. Both isotherms were of type IV with an H2(b) hysteresis loop according to the IUPAC classification. Figure 4a indicates that all slabs were mesoporous and had complex pore structures made of interconnected pores with different pore sizes that may have resulted in pore blockage. In addition, Figure 4b indicates that the slabs had both homogeneous and fairly small mesopores, with widths between 2 and 10 nm. Note also that the porosity in both samples was nearly identical despite the fact that the SiO$_2$-PFC-rt slab was calcined.
Table 1 summarizes the structural properties of the mesoporous silica monolithic slabs synthesized on PFC liquid and on PTFE and dried by using different conditions. All slabs dried under the same conditions had similar specific surface area, porosity, and pore width, regardless of the substrate used. Notably, the slabs dried at 40°C had larger porosity and pore width compared with those dried at room temperature. These differences were attributed to the fact that slabs dried at 40°C benefited from additional aging, compared with those dried at room temperature, due to the increased solubility and rates of dissolution and reprecipitation of silica at higher temperature. Drying at 40°C thus produced stronger silica network that could sustain the capillary forces caused by solvent evaporation during drying. This stronger network did not shrink as much as others, resulting in the largest porosity.

Figure 3. Representative transmission electron microscopy images and measured particle diameter histograms (insets) of nanoparticle-based mesoporous silica monolithic slabs: (a) SiO2-PFC-rt and (b) SiO2-PTFE-rt.

Figure 4. (a) Representative nitrogen adsorption–desorption isotherms and (b) the corresponding adsorption pore size distributions of nanoparticle-based mesoporous silica monolithic slabs synthesized on PFC liquid (SiO2-PFC-rt) and PTFE (SiO2-PTFE-rt) and dried at room temperature. Note that only SiO2-PFC-rt slab was calcined at 400°C for 2 h.

Table 1. Structural and Optical Characteristics of Nanoparticle-Based Mesoporous Silica Slabs Synthesized on PFC Liquid and on PTFE

<table>
<thead>
<tr>
<th>sample</th>
<th>average thickness, t (mm)</th>
<th>specific surface area, ( S_{\text{BT}} ) (m² g⁻¹)</th>
<th>porosity, ( \phi )</th>
<th>total pore volume, ( V_t ) (cm³ g⁻¹)</th>
<th>micropore volume, ( V_{\text{mi}} ) (cm³ g⁻¹)</th>
<th>peak pore width, ( w_p ) (nm)</th>
<th>transmittance, ( T_{\lambda,500} ) (%)</th>
<th>haze, ( h_{500} ) (%)</th>
<th>color rendering index (CRI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2-PFC-rt</td>
<td>3.5³</td>
<td>400⁶</td>
<td>0.46⁶</td>
<td>0.38⁶</td>
<td>0.00⁶</td>
<td>5.0⁶</td>
<td>92³</td>
<td>3.8³</td>
<td>97³</td>
</tr>
<tr>
<td>SiO2-PFC-hc</td>
<td>1.4³</td>
<td>360⁶</td>
<td>0.49⁶</td>
<td>0.44⁶</td>
<td>0.00⁶</td>
<td>5.8⁶</td>
<td>97³</td>
<td>0.8³</td>
<td>98³</td>
</tr>
<tr>
<td>SiO2-PFC-40C</td>
<td>1.7</td>
<td>370</td>
<td>0.54</td>
<td>0.53</td>
<td>0.00</td>
<td>7.2</td>
<td>92</td>
<td>2.6</td>
<td>99</td>
</tr>
<tr>
<td>SiO2-PTFE-rt</td>
<td>2.3</td>
<td>390</td>
<td>0.48</td>
<td>0.42</td>
<td>0.01</td>
<td>6.1</td>
<td>93</td>
<td>3.1</td>
<td>98</td>
</tr>
<tr>
<td>SiO2-PTFE-hc</td>
<td>2.7</td>
<td>390</td>
<td>0.47</td>
<td>0.41</td>
<td>0.00</td>
<td>5.5</td>
<td>91</td>
<td>6.6</td>
<td>98</td>
</tr>
<tr>
<td>SiO2-PTFE-40C</td>
<td>1.9</td>
<td>380</td>
<td>0.56</td>
<td>0.57</td>
<td>0.00</td>
<td>7.6</td>
<td>91</td>
<td>10.5</td>
<td>98</td>
</tr>
</tbody>
</table>

³Measurements done on two different samples. ⁶Measurements done on two different samples.
desorption isotherms presented in Figure 4.52,53 hysteresis loop observed in both nitrogen adsorption structure is consistent with the type IV isotherm with a H2(b) dimension 4 indicates a surface fractal structure with a surface fractal structures, but with different mass fractal dimensions. For SiO2-PFC-rt Dm = 2.6 while SiO2-PTFE-rt has a lower value of Dm = 2.3.

Mesoporous silica prepared through the sol–gel process are typically mass fractal structures due to their kinetically controlled growth.25 The latter proceeds either by monomer–cluster aggregation or cluster–cluster aggregation.25 In monomer–cluster aggregation, the fractal structure grows by gradual addition of nanoparticles to existing clusters of aggregated nanoparticles, while in cluster–cluster aggregation, all nanoparticles aggregate randomly at roughly the same time, forming clusters that grow by colliding with other clusters.25 Notably, monomer–cluster aggregation produces mass fractal structures with higher mass fractal dimension than cluster–cluster aggregation.25 We speculate that the higher mass fractal dimension of the SiO2-PFC-rt slabs was due to slight solubility of PFC liquid in the colloidal solution of silica nanoparticles.56 Any dissolved hydrophobic PFC molecules interacted with or adsorbed onto the silica nanoparticles, thus destabilizing the nanoparticle suspension. As a result, some silica nanoparticles started aggregating early in the drying process, resulting in the formation of a small number of clusters that then gradually grew by addition of nanoparticles from the solution. Thus, SiO2-PFC slabs may grow more through monomer–cluster aggregation than SiO2-PTFE, resulting in a higher mass fractal dimension.

3.3. Surface Roughness. For any optical applications, clarity is a key concern, and surface roughness can be a major source of scattering. Table 2 summarizes the average and root-mean-squared (rms) surface roughness of the two faces of nanoparticle-based mesoporous SiO2-PFC and SiO2-PTFE slabs along with that of commercial float glass obtained from Nippon Sheet Glass (Japan), used as a reference. While the top surface of the SiO2-PTFE slabs was optically smooth (R9 = 4.5 ± 0.2 nm), the bottom surface, which was in contact with the PTFE mold, had a much higher roughness R9 = 140 ± 9 nm, comparable to the wavelength of visible light. This roughness was caused by the roughness of the PTFE substrate imprinting onto the slab’s bottom surface during gel formation (Figure S2b). By contrast, both the top and bottom surfaces of the SiO2-PFC slabs were optically smooth with surface roughness between 13.4 and 15.5 nm (Figure S2a). In fact, the surface in contact with the PFC liquid substrate was as smooth as the top surface. Note that the SiO2-PFC slabs had rougher top surface

Table 2. Average and Root-Mean-Squared Surface Roughness of Thick Transparent Nanoparticle-Based Mesoporous Silica Slabs Synthesized on PFC Liquid and on PTFE along with Float Soda Lime Glass

<table>
<thead>
<tr>
<th></th>
<th>SiO2-PFC</th>
<th>SiO2-PTFE</th>
<th>float glass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>top</td>
<td>bottom</td>
<td>top</td>
</tr>
<tr>
<td>R RMS (nm)</td>
<td>15.5 ± 1.0</td>
<td>13 ± 9</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>R RMS (nm)</td>
<td>20.3 ± 0.9</td>
<td>18.6 ± 1.3</td>
<td>8 ± 2</td>
</tr>
</tbody>
</table>

Figure 5. (a) Representative small-angle X-ray scattering patterns of nanoparticle-based mesoporous silica monolithic slabs synthesized on PFC liquid (SiO2-PFC-rt) and on PTFE (SiO2-PTFE-rt) and (b) corresponding Porod plots obtained after subtracting contributions from disordered worm-like mesopores. The black dashed line with a slope of −4 corresponds to the behavior of nonfractal materials obeying the Porod’s law.54 Intensity scales in both panels are in arbitrary units.
than the SiO$_2$-PTFE slabs possibly due to the different aggregation mechanisms of silica nanoparticles during gelation of both slabs as discussed in section 3.2. As a reference, soda lime sheet glass had a surface roughness 10 times smaller than that of the mesoporous SiO$_2$-PFC slabs ($R_g = 1.6 \pm 0.1$ nm) resulting from the float glass process on liquid tin.\textsuperscript{59,60}

Another challenge for the SiO$_2$-PTFE slabs is that scratches and defects in the PTFE substrate resulted in the formation of air bubbles at the bottom surface of some SiO$_2$-PTFE slabs (Figure 3a). The scratches and defects acted as nucleation sites for bubbles formation from gases dissolved in the colloidal solution (Figure 3b). These bubbles strongly scattered light due to their large diameter, ranging between 0.1 and 1 mm. Both surface roughness and bubble nucleation were minimized either when PTFE molds with extremely smooth surfaces were used (Figure S3) or for all slabs synthesized on PFC liquid substrates (Figure 2a and Figure S1).

3.4. Optical Characterization. We used transmittance and haze measurements in the visible range and color rendering index to characterize the optical transparency of our mesoporous silica slabs. Figure 6 shows the spectral normal-hemispherical transmittance and haze $h_i$ of thick transparent nanoparticle-based mesoporous silica slabs synthesized on PFC liquid and on PTFE. The average thickness of the slabs is indicated in parentheses.

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Spectral normal-hemispherical transmittance $T_{nh,i}$ and haze $h_i$ of thick transparent nanoparticle-based mesoporous silica slabs synthesized on PFC liquid and on PTFE. The average thickness of the slabs is indicated in parentheses.

The differences in transmittance and haze between samples synthesized on PFC liquid and PTFE substrates with similar porosity and pore size distribution can mainly be attributed to differences in the slab surface roughness, which was responsible for stronger scattering and haze in SiO$_2$-PTFE slabs. Finally, all slabs listed in Table 1 had color rendering index exceeding 98, indicating excellent reproduction of colors.

3.5. Thermal Characterization. The goal of this work is to achieve mesoporous silica monolithic slabs with high optical transparency and low thermal conductivity. Here, we used time-domain thermoreflectance to measure the effective thermal conductivity of the slabs. The mesoporous SiO$_2$-PFC-hc slab had an effective thermal conductivity of $104 \pm 15$ mW m$^{-1}$ K$^{-1}$ at room temperature in air at atmospheric pressure while that of mesoporous SiO$_2$-PTFE-rt slab was $160 \pm 20$ mW m$^{-1}$ K$^{-1}$ at room temperature in a vacuum for similar porosity around 49%. While these two samples have slightly different drying conditions, they were both dried at room temperature, and they were selected for comparison because they had the most similar porosity among all the slabs. Other SiO$_2$-PFC and SiO$_2$-PTFE slabs had more variation in porosity, which is known to strongly affect the effective thermal conductivity.\textsuperscript{29} The difference in effective thermal conductivity despite similar porosity and pore size distribution (Figure 4) is likely due to the difference in mass fractal dimension between SiO$_2$-PFC and SiO$_2$-PTFE slabs, as determined by SAXS (Figure 5). Indeed, Emmerling and Frick\textsuperscript{61} showed that the effective thermal conductivity of nanoparticle-based mesoporous silica with a mass fractal structure can be expressed as:

$$\frac{k_{\text{eff}}}{k_{\text{SiO}_2}} \sim \left(\frac{\rho_{\text{eff}}}{\rho_{\text{SiO}_2}}\right)^{\frac{1}{D}}$$

where $k_{\text{eff}}$ and $\rho_{\text{eff}}$ are the effective thermal conductivity and effective density of the fractal nanoparticle-based mesoporous silica, and $k_{\text{SiO}_2}$ and $\rho_{\text{SiO}_2}$ are the thermal conductivity and density of the solid silica backbone. Here, $\nu = \frac{1}{2} \left(\frac{5 - D}{3 - D}\right)$ is a scaling factor, expressed as a function of the mass fractal dimension $D_{\text{mf}}$. Note that $\nu \geq 1$, since $1 < D_{\text{nf}} < 3$, and that $\nu$ increases monotonically with increasing $D_{\text{mf}}$. Therefore, based on eq 3, the effective thermal conductivity of a nanoparticle-based mesoporous silica with a mass fractal structure should decrease with increasing mass fractal dimension. Thus, the SiO$_2$-PFC slabs should have a lower effective thermal conductivity than the SiO$_2$-PTFE slabs due to their higher mass fractal dimension of $D_{\text{mf}} = 2.6$ compared to 2.3 for the SiO$_2$-PTFE slabs.

Importantly, both types of nanoparticle-based mesoporous silica slabs synthesized in this study had effective thermal conductivity somewhat smaller than those reported in the literature for other silica-based materials with similar porosity.\textsuperscript{29} For example, Coquil et al.\textsuperscript{29} synthesized mesoporous silica thin films on Si substrates with hexagonally ordered cylindrical pores using TEOS as the silica precursor and Pluronic P123 block copolymer as the template. The films featured porosity of 40–48% and effective cross-plane thermal conductivities of 220–180 mW m$^{-1}$ K$^{-1}$. Note that those films did not have a mass fractal structure because they lacked the required structural self-similarity\textsuperscript{29} due to their hexagonally ordered and uniform mesoporous structure. Thus, the fractal
structure of our slabs, regardless of the substrate used during synthesis, appears to lead to a lower effective thermal conductivity across all samples. For further comparison, Günay et al. synthesized hydrophobic silica aerogel slabs for solar–thermal energy conversion with very high porosity (≈93%) and an effective thermal conductivity of 130 ± 30 mW m⁻¹ K⁻¹. For comparison, our nanoparticle-based mesoporous SiO₂-PFC slabs had a lower effective thermal conductivity of only 104 ± 15 mW m⁻¹ K⁻¹, despite significantly lower porosity around 50%. This result indicates that the present nanoparticle-based mesoporous silica slabs are also promising candidates for solar–thermal energy conversion.

### 3.6. Mechanical Characterization

Table 3 summarizes the Young’s modulus and hardness of thick transparent nanoparticle-based mesoporous silica slabs synthesized on PFC liquid and on PTFE.

<table>
<thead>
<tr>
<th>sample</th>
<th>porosity, φ</th>
<th>Young’s modulus, $E_{\text{eff}}$ (GPa)</th>
<th>hardness, $H_{\text{eff}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂-PFC-rt</td>
<td>0.46</td>
<td>5.4</td>
<td>0.42</td>
</tr>
<tr>
<td>SiO₂-PFC-rt</td>
<td>0.47</td>
<td>5.7</td>
<td>0.47</td>
</tr>
<tr>
<td>SiO₂-PTFE-rt</td>
<td>0.46</td>
<td>6.2</td>
<td>0.51</td>
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<td>SiO₂-PTFE-rt</td>
<td>0.47</td>
<td>6.9</td>
<td>0.69</td>
</tr>
<tr>
<td>SiO₂-PTFE-rt</td>
<td>0.49</td>
<td>6.0</td>
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</tbody>
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nanoparticle-based mesoporous silica slabs synthesized on PFC liquid and on PTFE at room temperature. It is interesting to note that the SiO₂-PFC-rt slabs had Young’s moduli and hardness values slightly smaller than those of SiO₂-PTFE-rt slabs, despite the fact that all slabs had similar porosity around 0.47. The difference in mechanical properties was likely again due to the difference in mass fractal dimension between the SiO₂-PFC and SiO₂-PTFE slabs. Indeed, Emmerling and Fricke showed that the effective Young modulus of nanoparticle-based mesoporous silica with a mass fractal structure can be expressed as

$$\frac{E_{\text{eff}}}{E_{\text{SiO}_2}} \sim \left( \frac{\rho_{\text{eff}}}{\rho_{\text{SiO}_2}} \right)^{2\nu}$$

where $E_{\text{eff}}$ is the effective Young’s modulus of the fractal nanoparticle-based mesoporous silica and $E_{\text{SiO}_2}$ is the Young’s modulus of the bulk solid silica backbone. Following the argument outlined in section 3.5, eq 4 shows that the effective Young’s modulus of nanoparticle-based mesoporous silica with a mass fractal structure decreases with increasing mass fractal dimension $D_w$. Thus, it is expected that the SiO₂-PFC slabs should have a lower effective Young’s modulus than the SiO₂-PTFE slabs due to their higher mass fractal dimension. We speculate that the same reasoning and behavior is valid for hardness.

Overall, the measured effective Young’s moduli $E_{\text{eff}}$ of 5.4–6.9 GPa and hardness values $H_{\text{eff}}$ of 0.42–0.69 GPa are consistent with those reported for other mesoporous silica with similar porosity. Moreover, the Young’s moduli and hardness values of the synthesized slabs are superior to those reported for common polymers such as poly(vinyl chloride) (PVC) ($E = 2.64 \pm 0.10$ GPa, $H = 0.138–0.347$ GPa) and poly(methyl methacrylate) (PMMA) ($E = 2.34 \pm 0.15$ GPa, $H = 0.222–0.278$ GPa).

### 4. CONCLUSION

This paper presented a novel template-free water-based sol–gel method to synthesize thick, optically transparent, and thermally insulating mesoporous silica monolithic slabs under ambient conditions. For the first time, mesoporous silica slabs were synthesized on PFC liquid substrates (1) to reduce adhesion between gel and substrate, enabling the gels to shrink freely during aging and drying without incurring significant stress that would otherwise lead to fractures, and (2) to provide a smooth interface that results in slabs with optically smooth surfaces. The free-standing nanoparticle-based mesoporous silica slabs were made as disks or squares, with thickness between 1 and 6 mm and porosity of 45–55%. The slabs had high normal-hemispherical transmittance (>85%) and low haze (<5%) in the visible region of the spectrum due to small nanoparticle size, small pore size, narrow pore size distribution, and optically smooth surfaces, all of which resulted in limited volumetric and surface light scattering.

The lowest effective thermal conductivity achieved was 104 ± 15 mW m⁻¹ K⁻¹, and the mechanical properties are superior to common polymers such as PVC and PMMA. Most notable, however, is the fact that the slabs synthesized in this study had effective thermal conductivity smaller than those reported in the literature for other mesoporous silica materials with similar or larger porosity. This was attributed to the fractal structure and the high mass fractal dimension of the slabs synthesized in this study as established by small-angle X-ray scattering. Overall, the present nanoparticle-based mesoporous silica slabs are promising candidates for optically transparent and thermally insulating materials in window solutions and solar–thermal energy conversion, for example.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.9b00903.

#### EXPERIMENTAL DETAILS AND ADDITIONAL OPTICAL IMAGES (PDF)

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**Notes**

The authors declare no competing financial interest.

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**NOMENCLATURE**

- $a$ amount adsorbed (cm$^3$ STP g$^{-1}$)
- CRI color rendering index
- $d$ interplanar spacing (nm)
- $D$ Porod exponent
- $D_m$ mass fractal dimension
- $D_s$ surface fractal dimension
- $E$ Young’s modulus (GPa)
- $h$ haze (%)
- $H$ hardness (GPa)
- $I$ intensity (au)
- $k$ thermal conductivity (W m$^{-1}$ K$^{-1}$)
- $m$ mass (kg)
- $p$ pressure (Pa)
- $p_0$ saturation pressure (Pa)
- $Q$ scattering vector (nm$^{-1}$)
- $r$ radius (m)
- $R_a$ average surface roughness (nm)
- $R_{rms}$ root-mean-squared surface roughness (nm)
- $S_{SET}$ specific surface area ($m^2$ g$^{-1}$)
- $t$ average thickness (nm)
- $T_{nh}$ normal-hemispherical transmittance (%)
- $V_{mi}$ micropore volume (cm$^3$ g$^{-1}$)
- $V_p$ cumulative pore volume (cm$^3$ g$^{-1}$)
- $V_t$ total pore volume (cm$^3$ g$^{-1}$)
- $w_p$ pore width (nm)

**Greek Symbols**

- $\lambda$ wavelength (nm)
- $\nu$ scaling factor
- $\rho$ density (g cm$^{-3}$)
- $\phi$ porosity

**Subscripts and Superscripts**

- eff refers to effective
- $SiO_2$ refers to silica

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