Transparent silica aerogel slabs synthesized from nanoparticle colloidal suspensions at near ambient conditions on omniphobic liquid substrates

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Highlights
- Silica aerogels were synthesized on liquid substrates from silica nanoparticles.
- Novel method produced large and thick monoliths at ambient conditions.
- Combination of aging, solvent exchange, and ambient drying ensured large porosity.
- Aerogel monoliths featured high visible transmittance and low thermal conductivity.

Abstract
This paper presents a novel sol-gel method to synthesize large and thick silica aerogel monoliths at near ambient conditions using a commercial aqueous solution of colloidal silica nanoparticles as building blocks. To achieve slabs with high visible transmittance and low thermal conductivity, the method combines the strategies of (i) synthesizing gels on an omniphobic perfluorocarbon liquid substrate, (ii) aging at temperatures above room temperature, and (iii) performing solvent exchange with a low-surface-tension organic solvent prior to ambient drying. The omniphobic liquid substrates were used to prevent cracking and ensure an optically-smooth surface, while nanoparticle building blocks were small (<10 nm) to limit volumetric light scattering. Gels were aged at temperatures between 25 and 80 °C for up to 21 days to make them stronger and stiffer and to reduce shrinkage and cracking during ambient drying. Ambient drying was achieved by first exchanging water in the gel pores for octane, followed by drying in an octane-rich atmosphere to decrease capillary forces. The synthesized nanoparticle-based silica aerogel monoliths had thicknesses up to 5 mm, diameters up to 10 cm, porosities exceeding 80%, and thermal conductivities as low as 0.08 W m⁻¹ K⁻¹. Notably, the slabs featured visible transmittance exceeding 75% even for slabs as thick as 5 mm. The as-synthesized aerogel monoliths were exposed to TMCS vapor to induce hydrophobic properties resulting in a water contact angle of 140° that prevented water infiltration into the pores and protected the aerogels from water damage. This simple synthesis route conducted at near ambient conditions produces hydrophobic aerogel monoliths with promising optically transparent thermal insulation.
transient and thermally insulating properties that can be adhered to glass panes for window insulation and solar-thermal energy conversion applications.© 2021 Elsevier Inc. All rights reserved.
methods [2]. In this work, we use the terms “aerogels” and “xerogels” to refer to mesoporous silica with porosity above and below 70%, respectively.

A successful synthesis of silica aerogels at ambient conditions, sometimes referred to as “ambigels”, was achieved by modifying the gels with organic groups to exploit the “spring back” effect [15]. In this method, hydroxyl groups on the internal surface area of the gels are replaced with organic groups by reaction with chlorosilanes such as trimethylchlorosilane (TMCS) [15]. The modified gels initially shrink when the pore liquid evaporates but expand back to almost its original volume once completely dried, i.e., in the absence of capillary forces [15]. The latter expansion, i.e., the “spring back,” is possible because, in the absence of surface hydroxyl groups, no new bonds are formed that can prevent the expansion after the shrinkage. By contrast, plain silica gels retain the size imposed by the shrinkage process as previously separated surface hydroxyl groups come in close proximity and form new bonds, making the gels stiffer and preventing expansion [13]. Unfortunately, while aerogels synthesized using the “spring back” effect can retain large porosity, they are often hazy or opaque due to the presence of large pores (>50 nm) that scatter visible light and render the monoliths hazy [16–22].

Recently, Butts et al. [23] developed a new synthesis method producing mesoporous organo-silica ambigel slabs with large visible transmittance, small haze, and low thermal conductivity. These slabs were synthesized by co-condensation of TEOS and MTES precursors or edge lengths up to 4.5 cm, depending on the shape and size of the molds used [27]. However, the slabs were dried from water resulting in relatively low porosity (46–56%) and moderately low effective thermal conductivity (0.10–0.16 W m⁻¹ K⁻¹) compared with much more porous albeit more hazy aerogels [27].

This paper presents a new method using colloidal silica nanoparticles as building blocks to synthesize silica aerogel slabs with high visible transmittance and low effective thermal conductivity at near ambient conditions. The use of nanoparticles as building blocks avoids the need for molecular precursors and prevents incorporation of easily degradable organic groups. It also offers a synthesis route that can be generalized to other material compositions. The study also aims to investigate the effects of the different synthesis parameters on the silica aerogels’ microstructure as well as on their optical and thermal performance. The nanostructure of the synthesized aerogels was characterized by transmission electron microscopy (TEM), nitrogen porosimetry, and small-angle X-ray scattering (SAXS). Optical properties were characterized in terms of visible transmittance and haze while the thermal conductivity was measured using the guarded hot plate method. Hydrophobic aerogels were also prepared by a post-synthesis modification with an organochlorosilane and characterized by droplet contact angle measurements.

2. Experiments

2.1. Chemicals

Colloidal solutions of silica nanoparticles NaCl 2326 (15 wt% in water, NH₄Cl stabilized, lot number BP71239A1) were purchased from NaCl Chemical Company (Naperville, IL, USA). Hydrochloric acid (34–37% in water, TraceSELECT) was acquired from Sigma-Aldrich, Co. (St. Louis, MO, USA). Perfluoropolyether oils Krytox GPL 100, GPL 104, and GPL 106 with general formula [CF(CF₂)₂CF₂O]ₙ where n = 10–60 were procured from Miller-Stephenson Chemical Company Inc. (Danbury, CT, USA). Fluorinert FC-70 and perfluorotetradecahydrophenanthrene (PFTDH, 80%) were purchased from SynQuest Laboratories, Inc. (Alachua, FL, USA). Ethanol (200 proof), acetone (HPLC grade, 99.5%), and n-octane (97%) were acquired from Decon Labs, Inc. (King of Prussia, PA, USA). Perfluoropolyether oils were acquired from Alfa Aesar (Haverhill, MA, USA). All chemicals were used as received without further purification.

2.2. Materials synthesis

Scheme 1 shows the synthesis method used to produce transparent nanoparticle-based silica aerogel monoliths with gelling and aging on omniphobic PFC liquid substrates followed by solvent exchange and drying under ambient conditions.

Optionally, the nanoparticle-based silica aerogel slabs can be made hydrophobic by post-synthesis reaction with TMCS vapor. Specifically, the as-synthesized slabs were placed in a sealed container holding TMCS vapor and left to react overnight. The transparent slabs became hazy after reacting with TMCS. However, the hazy appearance disappeared once the slabs were degassed at 160 °C prior to the reaction with TMCS. This indicates that the haze was likely due to the reaction of TMCS with residual water physically adsorbed on the internal surface of the aerogels.

Hydrophobic aerogels prepared in this manner are discussed...
exclusively in Section 3.5 while the rest of the manuscript discusses properties of the as-synthesized aerogel slabs. Finally, this study used commercial colloidal silica nanoparticles, but any colloidal silica nanoparticles can be used in the proposed synthesis. Moreover, the same synthesis (Scheme 1) could potentially be used to synthesize aerogel slabs made of other nanoparticles such as titania and zirconia. Also, most PFC liquids were recovered after the synthesis and were reused in subsequent experiments. This was made possible by the omniphobic properties of the PFC liquids ensuring that they did not mix with the aqueous colloidal solution and could be easily recovered once the gels had formed. Indeed, the colloidal solution and the gels had adsorbed at relative pressure \( p/p_0 = 0.98 \) and assuming that the nitrogen in the pores was in the liquid state with molar density of 34.38 cm\(^3\) mol\(^{-1}\) [34]. Then, the porosity \( \phi \) of the nanoparticle-based silica aerogels was calculated as [35]

\[
\phi = \frac{V_T \rho_s}{1 + V_\text{p} \rho_s}
\]

where \( \rho_s = 2.2 \text{ g cm}^{-3} \) is the density of bulk silica [14].

The pore size distribution \( dV_p/dw \) was calculated using the Kruk–Jaroniec–Sayari method [36] based on the Barrett–Joyner–Halenda (BJH) method [37] and using (i) the adsorption branch of nitrogen isotherm, (ii) the modified Kelvin equation [36] calibrated for cylindrical pores up to 19 nm in diameter, and (iii) the statistical film thickness curve derived from the nitrogen adsorption isotherm measured for macroporous silica LiChrospher Si-1000 [38]. The peak pore width \( w_p \) (in nm) was estimated as the maximum of the pore size distribution, i.e., \( dV_p/dw \left( w = w_p \right) = 0 \).

The surface fractal dimension \( D_s \) was calculated based on nitrogen adsorption data according to [39]

\[
\ln n = (D_s - 3) \ln A + B \text{With } A = \frac{RT\ln p_0}{w_p}
\]

where \( n \) (in moles) is the measured amount of adsorbed nitrogen at relative pressure \( p/p_0 \), \( B \) is a fitting constant, \( R = 8.314 \text{ K mol}^{-1} \text{ K}^{-1} \) is the universal gas constant [14], and \( T = 77.4 \text{ K} \) is the temperature during adsorption measurements.

Two-dimensional small-angle X-ray scattering (2D-SAXS) patterns were collected at the Stanford Synchrotron Radiation Light-source using beam line 1–5, with a wavelength of 0.1033 nm operating at an X-ray energy of 12.002 keV. A sample-to-detector distance of 2.870 m was used in conjunction with a Rayonix-165 CCD detector. The 2D-SAXS data was calibrated using silver behenate, and then reduced using the Nika package from Igor Pro [40]. The reduced SAXS patterns were then fitted using the Unifit fit macro in the Irena package [41] by applying two Guinier-Porod levels [42–44] for magnitude of the scattering vector \( q \) in the range \( q = 0.03–0.1 \text{ Å}^{-1} \) (Level 1) and \( q = 0.01–0.03 \text{ Å}^{-1} \) (Level 2). The \( R_c \) cutoff parameter was applied for the second level to treat both levels as representing one population of scatterers. The fitting resulted in two sets of parameters describing each of the Guinier-Porod levels, namely a Porod exponent \( P_1 \) and radius of gyration \( R_{g1} \) for Level 1 and a Porod exponent \( P_2 \) and radius of gyration \( R_{g2} \) for Level 2 (see Table S1 in Supplementary material).

The diameters of the associated X-ray scatterers \( d_1 \) and \( d_2 \) were calculated assuming a dense-sphere shape according to

\[
d_1 = 2 \sqrt{\frac{2}{3}} R_{g1} \text{ and } d_2 = 2 \sqrt{\frac{2}{3}} R_{g2}
\]

Optical characterization. The spectral normal-hemispherical transmitted signal \( S_{\text{nmh}} \) and diffuse transmitted signal \( S_{\text{d}} \) through the nanoparticle-based silica aerogel monoliths were measured
with a double-beam UV-Vis spectrometer 3101-PC (Shimadzu, Kyoto, Japan) equipped with an integrating sphere ISR 3100 (Shimadzu, Kyoto, Japan) with internal diameter of 6 cm. Then, the spectral normal-hemispherical transmittance $T_{\text{nh,i}}$ was calculated as

$$T_{\text{nh,i}} = \frac{S_{\text{nh,i}} - D_{\text{nh,i}}}{B_{\text{nh,i}} - D_{\text{nh,i}}}$$

where $D_{\text{nh,i}}$ is the dark signal collected in the absence of light and $B_{\text{nh,i}}$ is the reference signal measured in the absence of a sample using the same procedure as that used to measure $S_{\text{nh,i}}$. In addition, the spectral haze $h_i$ was calculated according to ASTM D1003-13 standard as [45]

$$h_i = \frac{S_{\text{nh,i}} - M_{\text{nh,i}}}{B_{\text{nh,i}}}$$

where $M_{\text{nh,i}}$ was the signal measured in the absence of a sample using the same procedure as that used to measure $S_{\text{nh,i}}$. Then, the visible transmittance $T_{\text{vis}}$ and haze $h_{\text{vis}}$ of nanoparticle-based silica aerogel monoliths were calculated as [46,47]

$$T_{\text{vis}} = \frac{1}{8} \sum_{i=1}^{8} \left(100 - 4.6 \Delta E_i\right)$$

where $\Delta E_i$ is the geometrical distance between the perceived color with and without a sample for the $i^{th}$ test color. The geometrical distance $\Delta E_i$ was calculated for each of the eight test colors considered as [48]

$$\Delta E_i = \sqrt{\Delta W_i^2 + \Delta u_i^* + \Delta v_i^*}$$

with $i = 1, 2, \ldots, 8$

where $\Delta W_i$, $\Delta u_i^*$, and $\Delta v_i^*$ are distances in the CIE 1964 uniform color space domain, between the trichromatic coordinates perceived with and without a sample for the $i^{th}$ test color. The trichromatic coordinates $W_i$, $u_i^*$, and $v_i^*$ of each test color perceived with a sample were calculated from the spectral normal-hemispherical transmittance $T_{\text{nh,i}}$ while those perceived without a sample, i.e., of the reference illuminant $D_6$, were taken from BS EN 410:2011 standard [48]. A CRI above 95 and close to 100 represents good and excellent color reproduction, respectively [49]. As a reference, most glass and windows have CRI in the range 80–96 [50].

**FTIR characterization.** Pellets for the FTIR measurements were prepared by grinding 7 mg of the nanoparticle-based mesoporous slab with 150 mg of potassium bromide (KBr) using a mortar and pestle until a fine powder was obtained. Then, 15 mg of the powder mixture was pressed into a pellet using a pellet press (Mini-Pellet Press Kit – Asia, Specac, UK) under 1.5 ton load. The spectral normal-normal transmittance of the pellets was measured using a nitrogen-purged FTIR spectrometer (Nicolet™ iS50, Thermo Scientific, M. Marszewski, S.C. King, T. Galy et al. Journal of Colloid and Interface Science 606 (2022) 884–897) with a potassium bromide (KBr) beam splitter with a deuterated triglycine sulfate (DTGS) detector was used in the 2.5–20 μm spectral range.

**Thermal conductivity characterization.** The effective thermal conductivity $k_{\text{eff}}$ of the nanoparticle-based silica aerogel slabs was measured at room temperature using a guarded hot plate apparatus similar to that described in Ref. [51] following the C177-13 ASTM standard [52] and operated in a single-sided mode. Specifically, an aerogel monolith was placed between two 1 mm thick 3 M silicone thermal pads no. 5519 (3 M, Saint Paul, MN, USA) with thermocouples embedded in each pad. Then, the padded sample was sandwiched between a cold plate and a hot plate. Finally, the entire stack was placed between two blocks of expanded polystyrene and gently compressed to ensure good thermal contact. The ensemble was wrapped in multiple layers of insulation cloth to minimize heat loss. The temperature of the cold plate was controlled by a chiller circulating water at constant temperature $T_c$. The hot plate consisted of two concentric sections, each with a separate set of resistive wires that were connected to two separate power supplies to independently control currents and, thus, the heat generated in each section by Joule heating. The inner section was used for thermal conductivity measurement while the outer section was used to minimize lateral heat losses. The effective thermal conductivity was calculated under steady state conditions based on energy conservation principles and Fourier’s law according to

$$k_{\text{eff}} = \frac{Q_{\text{in}}L}{A_m(T_m - T_c)} = \frac{R_m \rho_{\text{eff}} L}{A_m(T_m - T_c)}$$

Here, $Q_{\text{in}}$ is the heat generation rate (in W) at steady state ($Q_{\text{in}} = R_m \rho_{\text{eff}}$) where $R_m$ is the resistance (in Ω) of the resistive wires embedded in the hot plate inner section, $T_m$ is the supplied current (in A), $A_m$ is the area of the inner section (in m²), and $T_c$ and $T_m$ are the temperatures (in °C) recorded by thermocouples embedded in silicon pads on the cold and hot sides of the sample, respectively. Note that $T_c$ and $T_m$ were controlled to ensure that the average temperature of the measurement was at room temperature and that $T_m - T_c$ was large enough (−10 °C) to achieve acceptable experimental uncertainties per ASTM standard.

**Contact angle measurements.** The water droplet contact angle $\theta$ on the hydrophobic nanoparticle-based silica aerogels was measured by the static sessile drop method using a FTA125 contact angle goniometer (First Ten Ångstroms Inc, Portsmouth, VA, USA). Before any measurement, the surface of the slabs was cleaned from any dust by flowing nitrogen gas. Then, a water droplet, with volume of 0.02 to 0.10 mL, was placed onto the slab’s surface. The contact angle was determined by non-spherical liquid-vapor curve fitting using the Fta32 Video 2.1 software (First Ten Ångstroms Inc). Measurements were performed multiple times on the top and bottom sides of the slab with droplets of different sizes and at various locations. The reported contact angle and the associated uncertainty were calculated as the mean and standard deviation of the mean value of all measurements, respectively.

3. Results and discussion

3.1. Synthesis

The synthesis method (Scheme 1) developed in this study combined several strategies to synthesize large and thick silica aerogel monoliths with large visible transmittance and low thermal conductivity. First, the synthesis employed omniphobic substrates such as PTFE and PFC liquids to limit adhesion between the gel and the substrate. Our previous study [27] showed that non-stick substrates such as smooth PTFE and PFC liquids enable gels to
shrink freely during aging and drying without cracking because they lessened the competing stresses created by compressive capillary forces and adhesive forces. Note that PFC liquids are excellent substrates here because (i) they do not mix with the colloidal solution of silica nanoparticles, (ii) they have high density, ensuring that the colloidal solution floats on top of the PFC liquid, and (iii) they feature large surface tension with water, resulting in a flat and stable liquid-liquid interface between the colloidal solution and the PFC liquid. The latter interface produces aerogel slabs with an optically-smooth bottom surfaces that achieve high transmittance and low haze by reducing surface light scattering [27].

The second key strategy used here is the fact that the aerogels were synthesized using small silica nanoparticles ($d_{\text{np}} = 6–12 \text{ nm}$) as building blocks, so as to reduce visible light scattering and to achieve high visible transmittance and low haze. Scattering was limited because the silica nanoparticles and the mesopores separating them were much smaller than the wavelength of light. The use of nanoparticles also helped avoid excessive shrinkage during aging, resulting in large porosity and reduced risks of cracking. The shrinkage was limited because almost all silica was bound in the silica nanoparticles and only a small amount of reactive silica was available in the solution; reactive silica can cause the gel to shrink through condensation reactions [13].

The third key processing step was to gel the colloidal solution of the nanoparticles by lowering the pH. This method produced gels with a large volume fraction of water, resulting in aerogels with larger porosity compared with our previous approach of gelation by evaporation [27]. It is also significantly faster than evaporative gelation, with gels forming in a few minutes to hours, as opposed to several days. Note that the stability of any colloidal solution depends on the size, concentration, and surface charge of the suspended nanoparticles [13]. Lowering the pH reduced the surface charge of the nanoparticles, destabilizing the colloidal solution and leading to gelation. The nanoparticle-based gels contained the same water volume fraction ($\phi_w \approx 93 \text{ vol\%}$) as the original colloidal solution since no water was removed during the process.

Fourth, to reduce shrinkage and prevent cracking, the gel slabs were aged at temperature above 25 °C to improve their mechanical strength before drying. During aging, Ostwald ripening results in dissolution of silica from regions of the gel with high curvature and precipitation in regions of low curvature resulting in silica transport (i) from small to large nanoparticles and (ii) from nanoparticles to the necks connecting them [13]. This process is slow at room temperature but is greatly accelerated at elevated temperatures due to the combined increase of (a) kinetics of dissolution and precipitation, (b) solubility, and (c) diffusion coefficient of silica in water [13].

Finally, in the fifth key processing strategy, the aged gel slabs were driedambiently by exchanging water contained in the pores of the gels with octane [53]. This exchange reduced the capillary forces during drying because the surface tension of the octane/air interface is three times smaller than that of the water/air interface (i.e., 21.17 vs. 72.06 mN m$^{-1}$) [14]. Here, octane was preferred over other solvents with similar surface tension such as cyclohexane and heptane [53] because it has a much lower vapor pressure of 1.86 kPa at 25 °C compared with 13.0 and 6.09 kPa for cyclohexane and heptane, respectively [14]. This greatly reduced the evaporation rate and the occurrence of cracking [14].

Table 1 summarizes the conditions and structural characterization of the nanoparticle-based silica aerogels synthesized in the present study. Note that results for the nanoparticle-based mesoporous silica slabs reported in Ref. [27] are also included as a reference.

### 3.2. Optical characterization

Fig. 1 shows photographs of transparent nanoparticle-based silica aerogel monoliths synthesized on omniphobic substrates (Scheme 1) and aged using different conditions, namely (a) Sample 3 synthesized on PTFE and aged at room temperature for 1 day, (b) Sample 7 synthesized on PTFE and aged at 40 °C for 3 days, and (c) Sample 21 synthesized on PFC liquid and aged at 50 °C for 14 days. Note that all the monoliths shown were dried from octane and calcined in oxygen at 450 °C for 4 h. Fig. 1 shows that the aerogel slabs were circular and optically transparent with a slight blue tint. Their porosity $\phi$ was between 73% and 80%, their diameter $D$ ranged from 2.5 to 10 cm, and their thickness $L$ was between 2.8 and 5 mm. The diameter $D$ was controlled by the diameter of the mold used, which ranged from 3.8 to 14.2 cm. Their thickness was determined by the initial volume of the colloidal solution. Note that it is also possible to use molds of different shapes, such as a square, as demonstrated previously [27].

Fig. 2(a) shows the spectral normal-hemispherical transmittance $T_{\text{nh}}$ for the three representative aerogel slabs shown in Fig. 1. It indicates that the transmittance $T_{\text{nh}}$ increased with increasing wavelength from 400 to 700 nm due to stronger scattering at wavelength $< 500$ nm resulting in the blue tint observed in Fig. 1. This was confirmed by the spectral haze $h$, (Fig. S1 in Supplementary material). Moreover, Fig. 2(a) compares the transmittance $T_{\text{nh}}$ of Samples 3, 7, and 11 with that of a precursor-based supercritically-dried silica aerogel slab of thickness $L = 5.5$ mm and porosity $\phi = 96\%$ reported by Zhao et al. [54]. Similarly, Fig. 2(b) compares the transmittance $T_{\text{nh,500}}$ at wavelength $\lambda = 500$ nm for Samples 3, 7, and 11 with that of the precursor-based silica aerogels reported in Ref. [54] as a function of thickness. Both figures indicate that the present aerogels with porosity of 70–80% had much higher normal-hemispherical transmittance than conventional aerogels. This was likely due to the presence of larger pores with larger porosity in supercritically dried aerogels resulting in stronger light scattering and, thus, smaller transmittance and larger haze. Thus, slightly less porous nanoparticle-based aerogels with considerably larger transmittance may be more appropriate than conventional aerogels for applications where optical transparency is essential, such as for window solutions and solar-thermal conversion systems.

Table 2 summarizes the optical characterization of Samples 3, 7, and 11 considered in Figs. 1 and 2. It shows that the visible transmittance $T_{\text{vis}}$ decreased with increasing thickness $L$ but still exceeded 75% even for slabs as thick as 5.0 mm. Table 2 also indicates that these aerogel slabs featured a color rendering index (CRI) exceeding 90 indicating relatively good color reproduction.

### 3.3. Structural characterization

#### 3.3.1. TEM characterization

Fig. 3 shows (a,c) TEM images and (b,d) particle size histogram (blue) and Gaussian distribution fit (red) of the nanoparticle-based silica aerogels synthesized on omniphobic substrates and aged using different conditions, namely (a,b) Sample 4 aged at room temperature for 1 day and (b,d) Sample 25 aged at 80 °C for 1 day. Note that both aerogels were synthesized on PTFE, dried from octane, and analyzed without calcination. Figs. 3(a) and 3(b) indicate that Sample 4 was made of loosely aggregated silica nanoparticles with diameter $d_{\text{np}} = 5.9–8.9$ nm and little to no necks between them. By contrast, Figs. 3(c) and 3(d) show that Sample 25 was made of silica nanoparticles of diameter $d_{\text{np}} = 7.1–11.9$ nm connected with thick necks such that the larger the nanoparticle diameter, the thicker the necks. In addition, the wide particle size...
Summary of the synthesis conditions and structural characterization of the nanoparticle-based silica aerogels synthesized in the present study. Results for nanoparticle-based mesoporous silica slabs reported in Ref. [27] are also included as a reference.

Temperatures that produce mechanical robustness should be used to improve optical clarity. Elevated temperature and suggest that the lowest possible aging temperatures that produce mechanical robustness should be used to improve optical clarity.

Overall, the TEM images provide direct evidence of colloid growth during aging at elevated temperature and suggest that the lowest possible aging temperatures that produce mechanical robustness should be used to improve optical clarity.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Aging temp./time</th>
<th>Drying solvent</th>
<th>Calcination</th>
<th>BET (m²/g)</th>
<th>V₁ (cm³ g⁻¹)</th>
<th>ϕ (%)</th>
<th>wₘ (nm)</th>
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<tbody>
<tr>
<td>SiO₂-PTFE-rt [27]</td>
<td>PTFE</td>
<td>25 °C/3 days</td>
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<td>Water</td>
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<td>Water</td>
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<td>1.57</td>
<td>78</td>
<td>22.6</td>
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<td>12</td>
<td>PTFE</td>
<td>50 °C/4 days</td>
<td>Octane</td>
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<td>1.67</td>
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<td>13</td>
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<td>Octane</td>
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<td>1.65</td>
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<td>1.68</td>
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<td>Octane</td>
<td>–</td>
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<td>1.36</td>
<td>75</td>
<td>19.0</td>
</tr>
<tr>
<td>25</td>
<td>PTFE</td>
<td>80 °C/1 day</td>
<td>Octane</td>
<td>–</td>
<td>360</td>
<td>1.91</td>
<td>81</td>
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3.3.2. Nitrogen porosimetry

Fig. 4 shows (a) nitrogen adsorption–desorption isotherms and (b) the corresponding adsorption pore size distributions (PSDs) dVp/dw of the nanoparticle-based silica aerogels synthesized in PTFE molds and aged for 1 day at temperatures T of 25 to 80 °C followed by solvent exchange. These four samples were selected to discuss the general features and structure of pores common to all aerogels considered in this study. Note that nitrogen adsorption–desorption isotherms and the corresponding pore size distributions of all other aerogels are included in the Supplementary material (Figs. S2 and S3). All isotherms were of type IV(a) with H2(h) hysteresis loops, according to the IUPAC classification [56,57], indicating that the aerogel pore structures consisted of interconnected mesopores with different sizes [56,57]. This observation is
consistent with the mesoporous structure observed in TEM images (Fig. 3). Fig. 4(b) shows that the aerogels had broad pore size distributions with pore width ranging from \( w = 5–7 \) nm up to \( w \approx 26–35 \) nm. Notably, Fig. 4 shows that increasing the aging temperature and dried from water (SiO\(_2\)-PTFE-rt, SiO\(_2\)-PFC-rt, SiO\(_2\)-PTFE-hc, SiO\(_2\)-PFC-hc) had a broadened pore size distribution, as explained later in the section “Effects of aging temperature and duration”.

We next consider how key parameters, including the specific surface area, the fractal dimension, and the average pores size, change with the overall porosity. Fig. 5 shows (a) the specific surface area \( S_{\text{BET}} \) and the surface fractal dimension \( D_s \) and (b) the peak pore width \( w_p \), as functions of porosity \( \phi \) for the synthesized nanoparticle-based silica aerogels (Table 1) and for the mesoporous slabs reported previously [27]. Fig. 5(a) indicates that their specific surface area \( S_{\text{BET}} \) did not significantly depend on either the porosity \( \phi \) or the aging conditions. In addition, comparing mesoporous slabs [27] aged at room temperature and dried from water (SiO\(_2\)-PTFE-rt, SiO\(_2\)-PFC-rt, SiO\(_2\)-PTFE-hc, SiO\(_2\)-PFC-hc) with aerogels also aged at room temperature but dried from octane (Samples 2–5) established that the specific surface area \( S_{\text{BET}} \) was also unaffected by the drying solvent. Fig. 5(b) further indicates that the surface fractal dimension \( D_s \) of the nanoparticle-based silica aerogels and mesoporous slabs [27] synthesized on omniphobic substrates exceeded 2.5 and increased almost linearly with increasing porosity \( \phi \).

Fig. 5(b) establishes that the peak pore width \( w_p \) increased sharply with increasing porosity \( \phi \) namely from \( 5 \) nm to \( 25 \) nm as porosity increased from 50% to 80%. This observation can be attributed to the fact that the solvent-exchanged gel slabs were subjected to less compression during drying thanks (i) to lower capillary forces from octane evaporation and/or (ii) to a stronger and stiffer structure obtained from aging above room temperature. Fig. 5 also shows the theoretical predictions of the peak pore width for non-intersecting monodisperse cylindrical or spherical pores denoted by \( w_{pc} \) or \( w_{ps} \), respectively, and expressed as [35]

\[
w_{pc} = \frac{4V_I}{S_{\text{BET}}} \frac{4\phi}{\rho_s (1 - \phi)} \quad \text{and} \quad w_{ps} = \frac{6V_I}{S_{\text{BET}}} \frac{6\phi}{\rho_s (1 - \phi)}
\]

where \( S_{\text{BET}} = 368 \text{ m}^2\text{ g}^{-1} \) is the specific surface area averaged over all samples listed in Table 1. Due to the complex shape of pores created between aggregated nanoparticles (Fig. 3), the peak pore width \( w_p \) fell between \( w_{pc} \) and \( w_{ps} \).

### 3.3.3. Effects of solvent exchange

Table 1 indicates that using octane for ambient drying substantially increased the porosity of the aerogel samples compared with water [27], even without aging at elevated temperature. Specifically, all aerogel samples aged at room temperature and dried from octane (Samples 2–5) featured porosity \( \phi = 71–73\% \) and peak pore width \( w_p = 16.8–18.3 \) nm compared with \( \phi = 46–49\% \) and \( w_p = 5.0–6.1 \) nm for those synthesized at room temperature and dried from water (SiO\(_2\)-PTFE-rt, SiO\(_2\)-PFC-rt, SiO\(_2\)-PTFE-hc, SiO\(_2\)-PFC-hc) [27]. The increase in porosity with octane was due to the reduction in the capillary forces and in the compression of the nanoparticle network during drying.

Finally, the IR transmittance spectra (Fig. S5 in the Supplementary material) of KBr pellets of nanoparticle-based mesoporous silica samples dried from water (Sample 1) and octane (Sample 8) featured only peaks corresponding to Si–O–Si, Si–OH, and H\(_2\)O vibrational modes and none corresponding to C–H modes. Thus, all samples were composed of silica with no trace of organic substance observed.

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**Table 2**

Optical characterization of selected transparent nanoparticle-based silica aerogel monoliths synthesized on omniphobic substrates and aged using different conditions (see Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity, ( \phi ) (%)</th>
<th>Peak pore width, ( w_p ) (nm)</th>
<th>Thickness, ( L ) (mm)</th>
<th>Visible transmittance, ( T_{nh} ) (%)</th>
<th>Visible haze, ( h_{vis} ) (%)</th>
<th>CRI</th>
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<tr>
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<td>74</td>
<td>17.7</td>
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<td>17</td>
<td>91</td>
</tr>
<tr>
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<td>80</td>
<td>25.0</td>
<td>5.0</td>
<td>75</td>
<td>31</td>
<td>91</td>
</tr>
</tbody>
</table>

**Fig. 2.** (a) Spectral normal-hemispherical transmittance \( T_{nh} \) of the transparent nanoparticle-based silica aerogel monoliths shows in Fig. 1 and of a precursor-based silica aerogel slab with thickness \( L = 5.5 \) mm and porosity \( \phi = 96\% \) reported in Ref. [54] and (b) normal-hemispherical transmittance \( T_{nh,100} \) of the same three nanoparticle-based aerogel slabs and of precursor-based silica aerogels reported in Ref. [54] as a function of thickness. Note that lines serve as eye guides only.
3.3.4. Effects of aging temperature and duration

Fig. 6 shows the porosity $\phi$ and peak pore width $w_p$ of the nanoparticle-based silica aerogels synthesized on omniphobic substrates and aged using different conditions namely (a,b) Sample 4 aged at room temperature for 1 day and (c,d) Sample 25 aged at 80 °C for 1 day. Note that both aerogels were synthesized on PTFE, dried from octane, and analyzed without calcination. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. (a) Nitrogen adsorption–desorption isotherms and (b) the corresponding adsorption pore size distributions of the nanoparticle-based silica aerogels synthesized on omniphobic substrates and aged at temperatures $T = 25–80$ °C.

3.3.4. Effects of aging temperature and duration

Fig. 6 shows the porosity $\phi$ and peak pore width $w_p$ of the nanoparticle-based silica aerogels synthesized on omniphobic substrates as functions of (a) aging temperature $T$ for aerogels aged for 1 day and (b) aging time $t$ for aerogels aged at 50 °C (see Table 1). Fig. 6(a) indicates that the porosity $\phi$ increased from 72% to 81% and the peak pore width $w_p$ increased from 17 nm to 26 nm as the aging temperature increased from 25 to 80 °C. The larger
porosity and pore width and the wider pore size distribution (Fig. 4) resulted from a combination of larger colloidal building blocks (see Fig. 3) and a stronger, less compressible silica network obtained upon aging at higher temperature. For the same reasons, Fig. 6(b) establishes that the porosity increased from $\frac{\rho}{\rho_s} = 74\%$ to $80\%$ and peak pore width from $w_p = 18.2$ to $25$ nm as the aging time $t$ increased from 1 to 14 days at an aging temperature of $50$ °C.

These results demonstrate that porosity can be increased by aging the gel at higher temperature and/or for a longer period of time. For example, Samples 21 and 25 both had porosity $\phi \approx 80\%$ with Sample 21 aged at $50$ °C for 14 days and Sample 25 aged at $80$ °C for only 1 day. Note, however, that the aging temperature seems to have a much stronger impact on porosity and peak pore width than the aging duration. It is also worth noting that aging at higher temperature offers the benefit of reducing the synthesis duration and increasing productivity.

3.3.5. No effect of different omniphobic substrates or calcination on porosity

Table 1 indicates that (i) using different omniphobic substrates or (ii) calcining the dried slabs at $450$ °C for 4 h had little to no effect on the porosity or peak pore width of the aerogels. For example, Samples 16–19 aged at $50$ °C for 6 days had similar porosity $\phi = 77$–80% and peak pore width $w_p = 24.0$–26.0 nm even though they were synthesized on different omniphobic substrates, namely PTFE, GPL PFC, FC–70 PFC, or PFTDHP PFC. Similarly, Samples 2 and 3 had similar porosity $\phi = 73$ and 72% and peak pore width $w_p = 17.2$ and 18.3 nm without and with calcination, respectively. This result is important, because the ability to change omniphobic substrate and to forgo energy intensive calcination provides opportunities to optimize materials and processing for a variety of applications.
3.3.6. Small-angle X-ray scattering

Fig. 7(a) shows small-angle X-ray scattering patterns obtained on Samples 3, 7 and 25. These samples were chosen to be representative of all nanoparticle-based silica aerogels synthesized in the present study. All SAXS patterns consisted of two separate Guinier-Porod levels (i = 1, 2), each characterized by its own Porod exponent $P_i$ and radius of gyration $R_{gi}$ (see Table S1). For all samples (Table S1), Level 1 featured a Porod exponent $P_1 = 4$, corresponding to non-fractal scatterers, i.e., dense particles with smooth surface. Similarly, for all samples, the Level 1 radius of gyration $R_{g1} = 3–4$ nm, corresponding to the radius of the silica nanoparticles, based on Eq.(3), and as observed in TEM images (Fig. 3). This indicates that Level 1 simply corresponded to silica nanoparticles used as building blocks of the mesoporous slabs. Level 2 featured a Porod exponent $P_2$ in the range 1.05–1.43 and radius of gyration $R_{g2}$ in the range 5.6–10.3 nm, across all samples (see Table S1). This indicates that Level 2 was associated with the fractal structure ($P_2 = D_m$) of the pores created by the aggregated silica nanoparticles. In fact, Fig. 7(b) shows the diameter $d_2$ of the Level 2 scatterers, calculated by approximating the pores as solid spheres [Eq.(3)], correlates with the peak pore width $w_p$ calculated from nitrogen porosimetry measurements. Fig. 7(b) indicates that the solid sphere approximation generally overestimated the pore size, on average by 10%. Finally, The size of the Level 2 scatterers $d_2$ increased with aging temperature $T$ and duration $t$ [Fig. 7(c, d)]. Interestingly, no correlation was observed between the Level 1 radius of gyration $R_{g1}$ or the mass fractal dimension $D_m$ (see Table 1) and the specific surface area, porosity, peak pore width, the substrate type, or the calcination conditions of the aerogels synthesized.

3.4. Thermal conductivity

Fig. 8 plots the effective thermal conductivity $k_{eff}$ as a function of porosity $\phi$ for the nanoparticle-based silica aerogel slabs synthesized in the present study. For comparison, Fig. 8 also shows the effective thermal conductivity of other mesoporous silica materials with a wide range of porosities and different synthesis methods including (i) nanoparticle-based mesoporous silica slabs [27], (ii) nanoparticle-based mesoporous silica thin films [58], (iii) hydrophobic TEOS-based silica aerogels dried at ambient pressure [23,59,60], (iv) hydrophobic sodium silicate-based silica aerogels dried at ambient pressure [61], and (v) hydrophobic and hydrophilic silica aerogels dried using supercritical CO2 [62]. The aerogel monoliths reported in the present study and the mesoporous silica slabs [27] and thin films [58] were all synthesized using the same colloidal silica nanoparticles and had similar structures based on the reported TEM images and nitrogen adsorption–desorption...
gels had mass fractal dimension $D$ connected structure. In fact, the present nanoparticle-based aerogels have lower thermal conductivities due to their branched and inter-connected structure. Indeed, for a given porosity, aerogels with larger fractal dimension as theoretically predicted $[64]$ and experimentally confirmed $[23]$. Due to differences in the fractal dimension of the different aerogels, reported in the literature $[25,26,63]$. These differences were likely due to variations in the synthesis method, such as (i) slow drying and achieve optically smooth surfaces, (ii) fast gelation and drying and achieve optically smooth surfaces, (iii) accelerated aging at elevated temperatures to reinforce the silica network, and (iv) exchange of water within the pores with a low surface tension solvent to reduce capillary forces during ambient drying and achieve large porosity (70–80%). The synthesized transparent nanoparticle-based silica aerogel monoliths had thicknesses up to 5 mm, diameters up to 10 cm, porosities exceeding 80%, and effective thermal conductivities as low as 0.081 W m$^{-1}$ K$^{-1}$. In addition, the slabs had visible transmittance exceeding 75% even for slabs as thick as 5 mm. They could be easily made hydrophobic and were sufficiently strong to be handled by hand and adhered to a glass substrate with UV-curing adhesive. The aging duration and temperature and number and amount of solvent exchange, need to be optimized to minimize the processing time and environmental impact of the synthesis method.

4. Conclusion

This paper presented a novel sol-gel method to synthesize thick, large, and highly porous yet transparent silica aerogel monoliths from suspensions of silica nanoparticles and dried under ambient conditions. The synthesis combined the following strategies (i) use of omniphobic substrates to reduce stress during gelation and drying and achieve optically smooth surfaces, (ii) fast gelation of a colloidal solution by adjusting its pH, (iii) accelerated aging at elevated temperatures to reinforce the silica network, and (iv) exchange of water within the pores with a low surface tension solvent to reduce capillary forces during ambient drying and achieve large porosity (70–80%). The synthesized transparent nanoparticle-based silica aerogel monoliths had thicknesses up to 5 mm, diameters up to 10 cm, porosities exceeding 80%, and effective thermal conductivities as low as 0.081 W m$^{-1}$ K$^{-1}$. In addition, the slabs had visible transmittance exceeding 75% even for slabs as thick as 5 mm. They could be easily made hydrophobic and were sufficiently strong to be handled by hand and adhered to a glass substrate with UV-curing adhesive. The aging duration and temperature and number and amount of solvent exchange, need to be optimized to minimize the processing time and environmental impact of the synthesis method.

**CRediT authorship contribution statement**

Michal Marszewski: Conceptualization, Methodology, Formal analysis, Data curation, Visualization, Writing – original draft.
Sophia C. King: Resources, Investigation, Formal analysis, Validation.
Tiphaine Gay: Investigation, Formal analysis, Data curation.
Glaresh N. Kashkanchi: Resources, Investigation, Formal analysis, Data curation, Validation.
Ali Dashti: Investigation, Formal analysis, Data curation.
Man Li: Investigation, Formal analysis, Data curation.
Danielle M. Butts: Resources, Investigation, Data curation.
Patricia E. McNeil: Resources, Investigation, Formal analysis, Data curation.
Esther Lan: Resources, Investigation.
Bruce Dunn: Methodology, Supervision, Funding acquisition.
Yongjie Hu: Methodology, Supervision, Funding acquisition.
Sarah H. Tolbert: Methodology, Supervision, Funding acquisition.
Laurent Pilon: Conceptualization, Methodology, Formal analysis, Project administration, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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References


