Ultralight Silica Foams with a Hierarchical Pore Structure via a Surfactant-Free High Internal Phase Emulsion Process

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ABSTRACT: An ultralight silica aerogel is among the most versatile materials available for technical applications; however, it remains a huge challenge to reduce its manufacturing cost. Here, we report on a simple approach for the preparation of silica foam monoliths with ultrahigh porosity up to 99.5% and specific surface area as high as 755 m² g⁻¹, which are similar to those of an aerogel. Our strategy is based on the effective stabilization of water-in-oil high internal phase emulsions by a hydrophobic silica precursor polymer, hyperbranched polyethoxysiloxane because of its hydrolysis-induced amphiphilicity. After conversion of this precursor polymer to silica, the emulsions are solidified without significant volume shrinkage. Thus, mechanically strong macroporous silica monoliths are obtained after removal of its liquid components. According to nitrogen sorption data, the resulting silica foams exhibit a high specific surface area and a foam skeleton consisting of both micropores (<2 nm) and mesopores (2–50 nm). The pore size, porosity, and surface area can be regulated by varying pH as well as the concentration of the silica precursor in the oil phase. In addition, the pore size can be adjusted by controlling shear force during emulsification. This work opens a new avenue for producing ultralight porous materials amenable to numerous applications.

INTRODUCTION

Porous solid materials that are often referred to as cellular solids or solid foams appear widely in nature, forming, for example, the most-abundant load-bearing structures such as wood, bone, and coral. This has inspired and driven remarkable development of synthetic porous structures. Controlled introduction of porosity into a solid can significantly reduce the density, meanwhile maintaining material properties or even imparting additional functionalities. Foams can be formed by a large variety of materials, and organic polymer foams are probably the best-known examples, and they penetrate into all aspects of our daily life for insulation, cushion, absorption, packaging, and so forth.7–9 Techniques now exist not only for foaming polymers but also for metals and ceramics.8 In the foam manufacturing process, blowing agents are mostly used. They include gases that expand during the pressure release, liquids that develop to cells while evaporated, and chemical agents that react to generate a gas. A sol–gel method is a process to generate oxide materials from molecular precursors at low temperature, and meso- and microporosities are an inherent feature of the resulting amorphous gels.9 Any kind of structure-directing agents can be added during solidification as a porogen to induce the formation of extra pores.10 Examples are molecular species,11 surfactant assemblies,12 emulsion droplets,13,14 or solid particles.15 Sol–gel technology can be combined with foaming processes to obtain ceramic foams with big pores.16,17 Among the various porous materials, aerogel is probably the most exciting one derived by means of a sol–gel process.18–21 Aerogel designates a gel, in which the liquid dispersed phase has been replaced with a gas.22 It is a solid with a very high relative pore volume, extremely low density, and large surface area. Aerogel can be made from different materials, and the first reported one was silica aerogel,23 which is now the most versatile materials available for technical applications.24 The straightforward and most promising application of silica aerogel is thermal insulation because of its extremely low thermal conductivity.25 In addition, it can be used in catalysis, sensors, nuclear particle detection, waste management, optics, electronic devices, and so forth.21,24 The production of silica aerogel often involves the solvent exchange, hydrophobization of silica skeletons, and supercritical drying in order to maintain the porous texture of the wet state, thus leading to its high price that limits the application field.

High internal phase emulsion (HIPE) templating is another route toward well-defined porous materials.27–33 HIPEs are an...
interesting class of emulsions characterized by an internal phase volume fraction exceeding 74%, the volume ratio of uniform, undistorted spherical droplets in the most compact arrangement.\textsuperscript{34} The conventional method for manufacturing HIPEs consists of dissolving a suitable emulsifier (a surfactant\textsuperscript{34−36} or solid particles\textsuperscript{37−42}) in the component constituting the continuous phase followed by stepwise addition of the dispersed phase under continuous moderate stirring. Macroporous materials with embedded emulsion droplets are then obtained by solidification of the continuous phase. By polymerization of water-in-monomer HIPEs, polymer foams with a very low density of significantly less than 0.1 g cm\textsuperscript{-3} can be formed. Inorganic porous materials may also be synthesized by means of HIPE templating. For instance, monodisperse macroporous materials of silica, titania, and zirconia were prepared by first mixing a monodisperse oil-in-formamide HIPE with a metal oxide sol in formamide, followed by gelling the continuous sol phase and subsequent heat treatment.\textsuperscript{43} This procedure was modified for silicone oil-in-water (O/W) HIPEs, and macroporous silica with a nonuniform pore size distribution was obtained.\textsuperscript{44} The combination of HIPE at the macroscale and micellar templates at the mesoscale can lead to materials with dual meso-/macroporous structures. In a two-step method, an organic macroporous foam was first prepared and it imbibed a sol−gel solution containing inorganic oxide precursor and surfactant molecules, which co-assembled to form an ordered mesostructure.\textsuperscript{45} The resulting composite material was then dried and calcined in air to obtain the meso-/macroporous inorganic material. A single-step method that makes use of the common structure of HIPEs containing micellar aggregates located in the continuous phase has been developed as well.\textsuperscript{46} By this means, silica with a specific surface area as high as 800 m\textsuperscript{2} g\textsuperscript{-1} associated with a very low bulk density of 80 mg cm\textsuperscript{-3} was obtained. However, the O/W procedure needs a large amount of organic solvent as the dispersed phase and leads to powder rather than monoliths at volume fractions of the internal phase above 80%. A simple way for preparing porous silica materials is to evaporate liquid components of emulsions stabilized by silica particles alone, that is, Pickering emulsions.\textsuperscript{47} The resulting macroporous silica reported so far has a pretty high density.

Recently, we reported on the stabilization of both O/W\textsuperscript{48−51} and water-in-oil (W/O)\textsuperscript{51} miniemulsions using a silica precursor polymer, hyperbranched polyethoxysiloxane (PEOS). PEOS is a highly hydrophobic liquid, which becomes amphiphilic upon hydrolysis at the oil/water interface. The interfacial tension between an organic solution containing PEOS and water is significantly lower than that arising from the pure solvent/water interface. In this study, we attempt to utilize PEOS as the sole stabilizer to form HIPEs, which can in turn be converted to porous silica after condensation of PEOS and evaporation of liquid components. In order to achieve very low density coupled with mechanical integrity, the PEOS-containing oil component should compose the minor continuous phase to form W/O HIPEs. It was investigated that under which conditions such kind of emulsions can be formed. Another key question is whether the conversion of PEOS leads to phase inversion and eventually collapse of HIPEs. Finally, the influence of preparation conditions on the morphology of resulting silica materials was studied.

### RESULTS AND DISCUSSION

When the internal phase volume in an emulsion exceeds a critical limit, phase inversion tends to take place, that is, an O/W type emulsion becomes a W/O emulsion and vice versa. This can in principle be avoided by proper choice of a surfactant which is completely insoluble in the dispersed phase of the emulsion.\textsuperscript{52} PEOS can be a perfect candidate to stabilize W/O HIPEs because it is soluble in most organic solvents but insoluble in water even after its hydrolysis at the oil/water interface.\textsuperscript{52} Nevertheless, W/O HIPEs can only be formed by adding water into a PEOS solution in toluene, and the resulting mixture should be shaken for at least 2 min before emulsification using a high-speed rotor-stator homogenizer. Addition of the PEOS solution into water or high-speed homogenization without prior shaking results only in O/W emulsions. Water droplets are formed while adding water into the oil phase (Figure 1a). However, it takes a certain time for

![Figure 1.](image)

PEOS molecules to hydrolyze at the interface to form a stabilizing layer around the water droplets. High-speed homogenization then reduces the size of the water droplets; meanwhile, the phase inversion from W/O to O/W is prevented by the tough PEOS layer at the interface. Figure 1b shows a photo of a water-in-toluene/PEOS HIPE, which is stable and remains liquid for at least 1 h at room temperature before it is converted to a solid material. Optical fluorescent microscopy of the HIPE confirms the formation of water droplets with a mean diameter of 18.6 ± 5.4 μm in the oil phase, although water composes the major phase (Figure 1c).

Even at room temperature, hydrolysis and condensation of PEOS can still take place as indicated by continuous increase
of the emulsion viscosity and the PEOS-stabilized HIPEs are eventually solidified. This process can be accelerated by raising the reaction temperature. In this work, a HIPE is placed into a cylindrical Teflon mold, which is then sealed in a metallic container. After heating in an oven at 60 °C for 12 h, the HIPE is converted to a piece of solid, which is then rinsed with acetone to remove both water and toluene. Subsequent drying in a vacuum oven at 80 °C results in a porous silica monolith, that is, a silica foam. In Figure 2, the Fourier transform infrared (FT-IR) spectra of PEOS, silica foams, and silica foams calcined at 800 °C are compared. The characteristic peaks for alkyl groups at 2800 cm⁻¹ disappeared after the conversion of PEOS to silica. The spectra of silica foams before and after calcination are similar, and all absorption bands are characteristic for pure silica, indicating a complete conversion of PEOS even at a low reaction temperature. The reduction of the intensity of the absorbance band at 3500 cm⁻¹ after calcination can be accounted for by loss of absorbed water and further condensation of silanol groups. Any shape change, volume shrinkage, and variation of pore structure are not observed during the calcination, indicating an outstanding thermal stability. Remarkably, the silica foams are extremely light and highly porous. Their density is clearly below the typical density range of silica aerogels and can reach values as low as 10 mg cm⁻³ (cf. Table 1).

It is well known that the hydrolysis and condensation kinetics of silica precursors such as PEOS as well as the resulting silica structure are strongly affected by pH. HIPEs can be formed in a wide pH range of the aqueous media from 1 to 11, and the structure and properties of the resulting silica foams are pH-dependent. On the one hand, the foam density decreases and the corresponding porosity increases with the increase of pH, when the PEOS concentration in toluene and the volume fraction of water are kept constant (Table 1). The dried silica foam prepared at pH 7 has a density of 24 mg cm⁻³ and a porosity of 98.9% that are very close to the theoretical values calculated by assuming that the silica foam occupies the same volume as the initial HIPE. A bit higher density and lower porosity at lower pH therefore imply a slight shrinkage of the sample volume during the PEOS conversion. On the other hand, the mechanical integrity improves with the decrease of pH. At pH 11, instead of intact silica foam monoliths, small pieces of silica fragments are formed after complete solidification. At such a high pH, PEOS molecules lose their interfacial activity very fast because of the high rate of hydrolysis and condensation. Therefore, the initially formed HIPEs quickly break down before a continuous silica layer can form around the water droplets. At pH 9, the resulting foam products exhibit a clear macroporous structure derived from the water droplet templating, indicating a high stability of the HIPEs throughout the whole sol–gel reaction, although they are quite brittle and fall into big pieces when removed from the Teflon mold. This mechanical integrity of the silica foams is greatly improved when the aqueous pH is lower than 7.

Although the foams are very light (Figure 3a), they possess pretty good mechanical strength. For instance, a cylindrical foam sample (density 24 mg cm⁻³ and mass 228 mg) with a diameter of 2.2 cm and a height of 2.5 cm can support a weight of 500 g (Figure 3b). The mechanical properties under

![Figure 2. FT-IR spectra of (a) PEOS and (b) silica foams (entry 3 in Table 1) before and (c) after calcination at 800 °C.](image)

### Table 1. Recipes for the Preparation of HIPEs with 16 g of Water

<table>
<thead>
<tr>
<th>entry</th>
<th>PEOS (g)</th>
<th>toluene (g)</th>
<th>aqueous pH</th>
<th>speed a (rpm)</th>
<th>mean water droplet size b (µm)</th>
<th>density c (mg cm⁻³)</th>
<th>porosity d (%)</th>
<th>mean macropore size e (µm)</th>
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<tbody>
<tr>
<td>1</td>
<td>2.00</td>
<td>1.96</td>
<td>11</td>
<td>15 000</td>
<td>21.5 ± 7.3</td>
<td>24</td>
<td>98.9</td>
<td>9.2 ± 3.2</td>
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<tr>
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<td>2.00</td>
<td>1.96</td>
<td>9</td>
<td>15 000</td>
<td>18.6 ± 5.4</td>
<td>26</td>
<td>98.8</td>
<td>4.9 ± 1.9</td>
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<td>2.00</td>
<td>1.96</td>
<td>7</td>
<td>15 000</td>
<td>15.5 ± 4.3</td>
<td>30</td>
<td>98.6</td>
<td>3.8 ± 1.8</td>
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<tr>
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<td>2.00</td>
<td>1.96</td>
<td>5</td>
<td>15 000</td>
<td>10.4 ± 3.9</td>
<td>33</td>
<td>98.5</td>
<td>2.9 ± 1.4</td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
<td>1.96</td>
<td>3</td>
<td>15 000</td>
<td>4.9 ± 2.6</td>
<td>10</td>
<td>99.5</td>
<td>11.2 ± 1.5</td>
</tr>
<tr>
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<td>2.00</td>
<td>1.96</td>
<td>1</td>
<td>15 000</td>
<td>22.1 ± 4.6</td>
<td>20</td>
<td>99.1</td>
<td>7.3 ± 1.2</td>
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<td>2.87</td>
<td>7</td>
<td>15 000</td>
<td>19.7 ± 3.8</td>
<td>30</td>
<td>98.6</td>
<td>2.4 ± 0.9</td>
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<td>15 000</td>
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<td>24</td>
<td>98.9</td>
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<tr>
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<td>1.96</td>
<td>7</td>
<td>18 000</td>
<td>15.1 ± 4.3</td>
<td>24</td>
<td>98.9</td>
<td>4.8 ± 1.7</td>
</tr>
</tbody>
</table>

aCircumferential speed of the rotor-stator homogenizer. bMean size of water droplets was estimated by an averaging diameter of 1000 water droplets in fluorescent microscope images. cDensity of silica foams (ρ) was determined by measuring volume and mass of monoliths obtained in a cylindrical form. dPorosity was calculated using the following equation: porosity = (1 − ρ/ρs) × 100%. Where ρ is the density of silica foam and ρs is the density of amorphous silica that equals 2.2 g cm⁻³. eMean size of macropores was estimated by an averaging diameter of 1000 pores in field emission scanning electron micrographs.
compression were measured for silica foams prepared with aqueous media of different pH values. In contrast to traditional silica aerogels with densities lower than 100 mg cm\(^{-3}\), which are ductile and can be easily deformed under load,\(^{55,56}\) the silica foams prepared in this work appear to be hard (Figure S1). The compression modulus of the silica foam obtained at pH 7 is measured as 0.5 MPa (Figure 4a). When decreasing pH from 7 to 1 (entries 3–6 in Table 1), the compression modulus continuously increases and reaches a maximum of 1.75 MPa at pH 1, whereas the density of the foams keeps almost unchanged. In the meantime, the compressive strength of silica foams also increases significantly from 37 to 80 kPa with decreasing pH values from 7 to 1. In general, these silica foams are mechanically stronger than traditional silica aerogels.

Figure 3. (a) Silica foam (diameter ≈ 2.2 cm, height ≈ 2.5 cm) on a leaf. (b) Silica foam (228 mg; diameter ≈ 2.2 cm, height ≈ 2.5 cm) supports a weight of 500 g.

Figure 4. (a) Compressive modulus and (b) strength of silica foams prepared at different pHs (entries 3–6 in Table 1). The error bars represent the standard deviation.

pH from 7 to 1 (entries 3–6 in Table 1), the compression modulus continuously increases and reaches a maximum of 1.75 MPa at pH 1, whereas the density of the foams keeps almost unchanged. In the meantime, the compressive strength of silica foams also increases significantly from 37 to 80 kPa with decreasing pH values from 7 to 1. In general, these silica foams are mechanically stronger than traditional silica aerogels. For instance, it was reported that a series of silica aerogels with an average density of 80 mg cm\(^{-3}\) possessed compressive modulus from 0.5 to 0.8 MPa,\(^{57}\) and even lower modulus and strength were observed for another series of silica aerogel samples.\(^{58}\) Besides the high specific mechanical strength, the silica foams prepared in this work also have a low thermal conductivity. The thermal conductivity of a foam sample with a porosity of 98.9% is measured as 48 mW m\(^{-1}\) K\(^{-1}\) under ambient conditions, very close to the values of macroporous polymer foams with similar porosity (normally in the range of 20–50 mW m\(^{-1}\) K\(^{-1}\)),\(^{1}\) which are employed extensively as thermal insulation materials. A more detailed investigation on thermal conductivity of silica foams will be performed in our future work.

Field emission scanning electron microscopy (FE-SEM) images of silica foams prepared at different pHs of the aqueous phase are shown in Figure 5. It can be seen that macroporous silica foams with a closed-cell structure are formed in a wide range of pH from 1 to 9. In comparison to the size of the water droplets in the HIPE, the pore size of the corresponding silica foams. FE-SEM images of silica foams prepared with different PEOS concentrations in toluene: (a) 21.8% and (f) 59.0% (entries 7 and 9 in Table 1).

Figure 5. FE-SEM images of silica foams prepared at different aqueous pHs: (a) 9, (b) 7, (c) 5, and (d) 1 (entries 2–4 and 6 in Table 1). The insets show the enlarged view of the skeletons of corresponding silica foams. FE-SEM images of silica foams prepared with different PEOS concentrations in toluene: (e) 21.8% and (f) 59.0% (entries 7 and 9 in Table 1).
resulting pore size increase when the pH arises. With further growth of pH to 11, no macroporous structure is observed according to FE-SEM data (Figure S2) because of the breakdown of the HIPE during the sol–gel reaction. Smaller pore size and higher density are clearly responsible for better mechanical strength of the silica foams formed at lower pH.

There can be two main reasons for the pore size to be smaller than the size of the water droplets. First, in contrast to hydrophobic PEOS, the product silica is hydrophilic and can adsorb a pretty large amount of water. Second, the oil phase consists of a W/O miniemulsion at higher pH,51 and water is consumed to convert PEOS stabilizing the W/O miniemulsion in the oil phase. At lower pH, the W/O miniemulsion is not stable because of too fast hydrolysis of PEOS.51 The formation of a W/O microemulsion in the oil phase of a HIPE was previously reported by several research groups.59−61 In our case, a W/O miniemulsion with small nanosized water droplets rather than a microemulsion is formed because a high-energy emulsification process is required. Furthermore, ethanol, which is released upon the PEOS conversion, destabilizes the (mini)emulsions, creating water channels between the water droplets.62 It becomes clear that the formation of a W/O miniemulsion in the oil phase at higher pH accounts not only for the more significant pH dependence of the water droplet size but also for the different fine structures in the pore wall. The difference in the HIPE structure at different pHs of aqueous media might also be responsible for the observed volume change during the sol–gel reaction. At high pH, the solidification of the PEOS-stabilized W/O miniemulsion in the oil phase results in an additional silica network that seems to prevent shrinkage of the whole system.

Besides the pH of the aqueous media, the pore size can also be reduced by more intensive homogenization. By changing the circumferential speed of the rotor-stator homogenizer from 12 000 to 18 000 rpm, the mean pore size is reduced from 7.2 to 4.8 μm (entries 10 and 11 in Table 1). It can therefore be expected that the pore size can be further reduced by using high-energy homogenizers such as ultrasonic device and microfluidizer.

In this work, PEOS acts as not only the HIPE stabilizer but also the silica precursor. Its concentration in the oil phase can influence both the HIPE formation and the density of the resulting silica foams. The density of the silica foams decreases linearly with the decrease of the PEOS concentration in toluene under the same reaction conditions (Table 1). Meanwhile, the dilution of the PEOS solution causes an increase in pore size (Figures 5 and S4) because of the reduction of the concentration of the effective emulsifier (partially hydrolyzed PEOS) as well as interfacial dilational modulus ε.

FE-SEM images in Figure 5 show clearly that the pore walls of the silica foams are porous. It is well known that silica obtained from a sol–gel process without high-temperature densification is mesoporous with a large specific surface area.63 To prove the mesoporous nature of the silica foams, nitrogen sorption measurements were performed. The size of macropores templated by HIPEs generally ranges from 3 to 11 μm, so they contribute barely to the specific surface area. All silica foams prepared at different pHs exhibit type IV nitrogen adsorption and desorption isotherms with H3 or H4 hysteresis loops (Figure 7a), which are characteristic for mesoporous materials.64 The pore size distribution determined from the

![Figure 6](image_url)

*Figure 6. (a) Water droplet size in HIPEs and (b) pore size of silica foams prepared at different pHs of the aqueous media (entries 2−6 in Table 1). The error bars represent the standard deviation.*

![Figure 7](image_url)

*Figure 7. (a) Nitrogen adsorption–desorption isotherms and pore size distribution curves calculated with the BJH method (inset) for silica foams prepared at different pHs (Table 1, entries 2−6). (b) Surface area of silica foams vs pH.*
Conclusions

Silica macro-/mesoporous foams with ultrahigh porosity (99.5%) and high specific surface area (755 m² g⁻¹) have been prepared via W/O HIPE templating. The obtained HIPEs are formed by emulsifying water in a toluene solution containing a silica precursor polymer PEOS, which becomes amphiphilic by hydrolysis at the oil/water interface, under high-speed homogenization. After the conversion of PEOS to silica, the emulsions solidify and silica foam monoliths with macropore sizes in the range of 1–20 μm are obtained after removing the solvent. These foams are mechanically stronger than traditional silica aerogels because of their closed-cell structure. According to nitrogen sorption data, the resulting silica foams exhibit a high specific surface area and the foam skeletons are micro- and mesoporous. pH has a strong influence on the structure of the foams because of the pH dependence of hydrolysis and condensation of PEOS. The increase of pH results in an increase of porosity and pore size as well as a decrease of surface area. The pore size can further be controlled by PEOS concentration and homogenization intensity. Thermal insulating and mechanical properties are expected to be improved by further reducing the pore size to submicron range. This work opens a new avenue for manufacture of formable ultralight porous inorganic materials, and such kind of ultralight silica foams may replace expensive aerogels in a number of application fields.

Methods

Materials. Tetraethoxysilane (reagent grade, 98%, Sigma-Aldrich), acetic anhydride (ACS reagent, ≥98.0%, Sigma-Aldrich), toluene (≥99.5%, Sinopharm Chemical Reagent Co., Ltd), hydrochloric acid (36.0–38.0%, Sinopharm Chemical Reagent Co., Ltd), ammonium hydroxide (25.0%, Jiangsu Tongsheng Chemical Reagent Co., Ltd), and titanium trimethylsiloxyde (ABCR) were used as received. Deionized water was used throughout the experiments. Hyper-branched PEOS was synthesized according to the method published elsewhere.65 The resulting PEOS had the following characteristics: degree of branching 0.54, SiO₂ content 49.2%, SiO₂ content 49.2% (measured by gel permeation chromatography), and M₀/Mₙ 1.9 (measured by gel permeation chromatography in chloroform with an evaporative light scattering detector calibrated using polystyrene standards).

Preparation of HIPEs. The resulting mixture was gently shaken for 2 min and then emulsified for 3 min with a rotor-stator homogenizer (T18 digital Ultra-Turrax, IKA). The compositions of the emulsions are summarized in Table 1. The volume fraction of internal aqueous phase was kept to be 80%.

Preparation of Silica Foams. The obtained HIPE was transferred to a Teflon form, which was then sealed in a metallic container. The whole system was placed in an oven and heated at 60 °C for 12 h. The content of the form was then washed in a Soxhlet extractor with acetone. Finally, the product was dried in an oven at 100 °C for 2 h.

Characterization. Optical microscopic observation of emulsions was conducted on a Fluorescence microscope (Axiovert 200, Zeiss, Germany) mounted with a charge-coupled device (AxioCam HRC, Zeiss, Germany). For these measurements, a small amount of sodium fluorescein was dissolved in the aqueous phase.

The pore structure of silica foams was investigated using a Zeiss Ultra 55 FE-SEM. All samples were placed onto lacy carbon-coated substrates and sputtered with gold before observation. The mean pore size of silica foams was obtained by averaging the size of at least 1000 pores from FE-SEM images.

FT-IR spectra were recorded on a Thermofisher Nicolet 6700 FT-IR spectrometer using a KBr pellet technique.

Nitrogen adsorption–desorption isotherms were recorded on a Quadrasorb evo surface area and porosity analyzer (Quantachrome Instruments, USA) by static adsorption procedures at 77 K. The specific surface areas of the samples were calculated by applying the BET equation. The pore size and volume were determined from the adsorption branch of the isotherm using the BJH model.

The mechanical properties of silica foams were studied on a SANS CMT-6503 table-top universal testing machine (MTS Systems Co., Ltd, China) equipped with a 100 N load cell. For the compression tests, the cylindrical samples were placed between the self-leveling plates and compressed at a rate of 1 mm/min. The environmental temperature was 25 °C, and relative humidity (RH) was 50%.

Thermal conductivity λ of a monolith sample was measured on a thermal constant analyzer (TPS 3500, Hot Disk Sweden) equipped with a 5465 Kapton-insulated heat flow sensor using a transient plane heat source method (hot disc) method. The environmental temperature was 25 °C, and RH was 50%.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b02094.

Additional experimental procedure and data, including strain–stress curve and FE-SEM images (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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