**Supplemental Information: Engineering Mesoporous Silica for Superior Optical and Thermal Properties**

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**Ambient drying**

Ambient drying of silica gels is one method for obtaining mesoporous silica materials with small pore size and narrow pore size distribution.1 In contrast to aerogels, which require supercritical (typically CO2) drying techniques, and xerogels, which are dried in polar solvents, ambigel synthesis makes use of high vapor pressure and nonpolar drying solvents that can minimize the surface tension on the silica network. Limiting capillary forces and pore collapse in ambigels leads to a smaller pore size than in aerogels and a larger fraction of porosity than in xerogels.2–4 The reason that the reduced surface tension produces higher porosity can be understood by evaluating the Young-Laplace equation expressing the capillary pressure *Pc* exerted by a solvent on the walls of a pore with diameter *d* as

 , (Eqn. S1)

where *γLV*is the surface tension of the solvent/air interface and *θ* is the contact angle between the solvent and the pore wall.5 Thus, an organic solvent with low surface tension results in reduced capillary forces and minimal pore collapse during drying.6,7 Another consideration in creating a high porosity, monolithic, ambiently dried gel is careful regard of the sol components such as alkoxide precursors, solvent ratios, catalysts, and additives.8 The use of chemical additives to the sol, such as formamide, has been shown to produce a relatively uniform pore size distribution and to enable ambient drying without cracking.1,9–11

**Thermogravimetric analysis and Fourier transform infrared spectroscopy**

TGA data for pre-calcined ambigel samples TEOS1 and TEOS1:MTES as well as non-calcined TEOS1:MTES:0.5TMCS are shown in **Figure S1**. The methyl content measured by TGA is summarized in **Table 2**. Although TEOS1:MTES was pre-calcined to remove organics, some methyl groups remain on the surface and are only removed by calcination above 500°C, as indicated by TGA and FTIR. Analysis of the FTIR spectra is summarized in **Table S1.**

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**Figure S1.** TGA of TEOS1, TEOS1:MTES pre-calcined ambigel samples and non-calcined TEOS1:MTES:0.5TMCS ambigel sample at a ramp rate of 10 °C min-1 to 700 °C for TEOS1 and 1000°C for TEOS1:MTES and TEOS1:MTES:0.5TMCS. The ~ 5 % weight loss below 150 °C in TEOS1 is due to the evaporation of physiosorbed water and highlights the hydrophilicity of the non-surface modified gels compared to the TEOS1:MTES and TEOS1:MTES:0.5TMCS gels with surface methyl groups. The weight loss above 300 °C in TEOS1:MTES and TEOS1:MTES:0.5TMCS is attributed to the removal of remaining surface methyl groups in TEOS1:MTES and TEOS1:MTES:0.5TMCS. The weight loss above 200 °C in TEOS1 can be attributed to induced crosslinking and subsequent dehydration.

**Table S1.** Summary of observed FTIR peaks in cm-1 and attributed structural unit vibrations for TEOS1, TEOS1:MTES and TEOS1:MTES:0.5TMCS silica ambigel samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **TEOS1** | **TEOS1:MTES** | **TEOS1:MTES: 0.5TMCS** | **Structural unit and type of vibration** | **Ref.** |
| 460 | 450 | 450 | O-Si-O deformation | 12,13 |
| 562 | 575 | 572 | Si-O stretching | 13 |
| 800 | 795 | 776 | Si-O symmetric stretching | 13 |
|  |  | 845 | Si-C stretching | 14 |
|  | 955 | 945 | Si-O in-plane stretching | 12,14 |
| 1088 | 1079 | 1070 | Si-O-Si antisymmetric stretching | 12,13 |
| 1188 | 1160 | 1151 | Si-O-Si antisymmetric stretching | 5,12,14  |
|  | 1277 | 1275 | C-H symmetric bending | 13 |
|  |  | 1384 | C-H symmetric bending | 12,14 |
| 1636 | 1634 | 1633 | H-O-H deformation | 12 |
|  |  | 2857 | C-H symmetric stretching vibration | 12 |
|  |  | 2928 | C-H antisymmetric stretching vibration | 12 |
|  |  | 2971 | C-H symmetric stretching vibration | 12,14 |
| 3450 |  | 3450 | SiO-H and H-O-H deformation | 13 |

**Color Rendering Index**

The color rendering index (CRI) was used to evaluate the quality of color appearances when viewed through the silica ambigel and aerogel slabs.15,16 A value close to 100 indicates that the material can accurately depict a variety of colors that are close to those seen under daylight and can relay a constant spectral transmittance. The CRI for good quality window glass is higher than 80 while an excellent quality window has a CRI > 90. The color rendering index of the TEOS1, TEOS1:MTES, and TEOS1:MTES:0.5TMCS were systematically above 99%, respectively, confirming that color images viewed through the 0.5–0.7 mm thick ambigels were excellent. Increasing the thickness of TEOS1:MTES and TEOS2:MTES gels to 2.02 mm and 2.5 mm, respectively, gives transmittance values greater than 91% and haze values less than 4.5% across the entire visible spectrum (denoted TEOS1:MTES:THK ambigel samples in Table 1). Additionally, the TEOS1:MTES:THK ambigel sample had measured CRI of > 99% confirming the excellent color rendering of images seen through gels with small pores even when the thickness is substantially increased. The excellent optical clarity of gels can be seen qualitatively in the photographs of Figure 1.

**U-Value reduction of a single pane window with ambigel coating**

In order to gain perspective on the practical effects of ambigels in window applications, the U-values of a single pane window with a low-emissivity (low-*e*) coating and a single pane retrofitted with a 3 mm thick ambigel slab sandwiched between a 3 mm thick glass pane and the low-*e*coating were predicted (**Figure S2**).17 The U-value of a multilayer system is the inverse of its thermal resistance and a lower U-value indicates better insulation properties.17 Using the Window 7 software provided by LBNL18 and assuming NFRC100-2010 environmental conditions19, a 6 mm thick single pane window (κpane  = 1 W m-1K-1) has a center-of-glass U-value of 0.608 Btu h-1f-2°F-1 as shown in Figure S2. Replacing 3.0 mm of the single pane window with a 3.0 mm thick silica ambigel thermal barrier (κTB = 0.04 W m-1K-1) reduces the center-of-glass U-value by over 20% to 0.472 Btu h-1f-2°F-1.

(a)

(b)

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**Figure S2**. Schematic of windows used for calculating the U-value of (a) a classic single-pane window and (b) a single-pane window with 3.0 mm thick ambigel and low-*e* coating.

**Supplemental Experimental Procedure**

*Structural Characterization:* Nitrogen adsorption–desorption isotherms were measured at –196 °C on an accelerated surface area and porosity analyzers ASAP2020 Plus and ASAP2010 manufactured by Micromeritics Instruments Corp. [Norcross, GA]. Specific surface area was calculated using the Brunauer–Emmett–Teller method (BET) based on nitrogen adsorption data in the relative pressure range 0.05–0.2 and assuming the cross-section area of a nitrogen molecule to be 0.162 nm2.20,21 Total pore volume was calculated by converting the amount of nitrogen adsorbed at a relative pressure ≈0.98 to the volume of liquid nitrogen assuming the density conversion factor of 0.0015468. Pore width was estimated from the position of a peak maximum in the pore size distribution determined using the Kruk–Jaroniec–Sayari (KJS) methodusing (i) the adsorption branch of nitrogen isotherm, (ii) the modified Kelvin equation 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. 22–24 We define *α*s as the ratio of the amount of nitrogen adsorbed on a reference material surface at a given relative pressure to the amount of nitrogen adsorbed at a reference material surface at the relative pressure p/p0 = 0.4. . Micropore volume was calculated using the αs methodin the reduced adsorption range (a) *α*s = 0.4–0.8 for TEOS1, TEOS2, TEOS5, and TEOS2:MTES,samples, (b) *α*s = 0.6–1.0 for TEOS3 and TEOS4 samples, or (c) *α*s = 0.2–0.5 for the TEOS1:MTES sample) and using macroporous silica LiChrospher Si-1000 as the reference.21 Mesopore volume was calculated as a difference between the total pore volume and the micropore volume. Transmission electron microscopy (TEM) images were obtained on a FEI Technai G2 T20 [Thermo Fisher Scientific]. Ambigel fractal dimensions *D* were calculated from the adsorption isotherms using the Frenkel-Halsey-Hill method as 25

(Eqn. S2)

where *n* is the quantity of N2 gas adsorbed in cm3 STP g-1, and *P* is the pressure and *Po* is the saturation vapor pressure.

*Optical Measurements:* The normal-hemispherical transmittance and the diffuse transmittance were measured with a double-beam UV-Vis spectrometer (3101-PC Shimadzu, Kyoto, Japan) and an integrating sphere with an internal diameter of 60 mm (ISR 3100 Shimadzu, Kyoto, Japan). The normal-hemispherical transmitted signal was measured and corrected for the reference signal and the dark signal according to

 (Eqn. S3)

The dark signal was collected when no light entered the integrating sphere while the reference signal was measured in the same configuration as for but without a sample present.

The diffuse transmitted signal represents the fraction of light that is scattered and transmitted by the sample. It was measured by removing the highly reflecting plate facing the sample in the integrating sphere so that the unscattered light left the integrating sphere. Finally, the visible transmittance is defined as the spectral transmittance of the total fenestration system weighted by the photopic response of the eye according to26

 (Eqn. S4)

where is the photopic spectral luminous efficiency function of the human eye, i.e., the function representing the wavelength-dependent sensitivity of the eye during daytime.27

The spectral haze in the visible was computed according to ASTM D1003-11 as

 (Eqn. S5)

where is the signal measured in the same configuration as for but without a sample present. Here also, one can define the visible haze

 (Eqn. S6)

The color rendering index measures the color difference before and after transmission through the sample for eight different colors. The source of transmitted light is the illuminant , which is a CIE (International Commission on Illumination) standard illuminant reproducing average midday light. The color rendering index was expressed as28

 (Eqn. S7)

where is the special color rendering index of the ith test color. For each test color, the special color rendering index was expressed as28

 (Eqn. S8)

where is the geometrical distance in the CIE 1964 uniform chromaticity space between the color perceived without the glass and with the glass. It was expressed according to the trichromatic coordinates in the CIE 1964 space domain namely , , and , as28

 (Eqn. S9)

The trichromatic coordinates , , and of each test color were calculated from the normal-hemispherical transmittance of the glass in the visible range taken from EN 410:2011 for the reference illuminant without transmission through the sample.28

 *Thermal Measurements:* The time-domain thermoreflectance (TDTR) method is a reliable method that has been used to accurately measure thermal conductivity of a wide range of materials, including amorphous materials, porous structures, and aerogels. 29,30 In the present study, the samples were first coated with a thin layer of Al (80 nm) to convert the photon energy of the pump laser pulse into thermal energy. Prior to TDTR measurements, the samples were heated to 160 ºC for 1 hour at a pressure < 1 Pa and cooled to room temperature in a cryostat to fully dry the sample. The pump beam consisted of laser pulses at wavelength 400 nm and of width of 100 fs delivered onto the Al coating for generating heat. The probe beam consisted of laser pulses at 800 nm with variable pulse width to determine the temperature changes. After the instantaneous temperature rise caused by the pump beam, the temperature decay was recorded by the probe beam by controlling the delay time between the pump and probe beams from 0 ps to 6000 ps and utilizing the linear relationship between reflectivity and temperature of the Al film. The full transient decay curve was fitted with a multilayer heat conduction model to obtain the thermal conductivity of the sample.21 More details about the working principles, experimental setup and successful applications for various materials including silica aerogel can be found in previous studies.31 To avoid biased characterization which could be due to inhomogeneity due to the nanoscale porous structure of the ambigel monoliths, a laser spot size of 20 μm in diameter was used to cover a surface area encompassing a large number of nanoscale pores. For each sample, the thermal conductivity was averaged from ten different measurements on different spots for each sample. The reported thermal conductivity was the average for 3 samples for the TEOS1—TEOS5 ambigel monoliths and for 2 samples for the TEOS1:MTES and TEOS2:MTES ambigel monoliths. The error bars accounted for uncertainties in individual measurements as well as from inter-sample variability. The effective specific heat Cp was measured directly through differential scanning calorimetry (DSC) of ambigel samples at room temperature and after heating to 150 ºC and cooling back to room temperature to remove water, as described in previous work.32

 The effective thermal conductivity *keff* at room temperature of the ambigel monoliths was also measured using a guarded hot plate apparatus based on ASTM C177-13 standard in a single-sided mode. The apparatus in double-sided mode was described in detail in Ref.33 and need not be repeated. In brief, an ambigel monolith with thickness *t* was sandwiched between a hot plate and a cold plate. The whole stack was placed between two thermally insulating blocks and wrapped in multiple layers of fiberglass insulation to minimize heat losses. The cold plate was maintained at constant temperature by a liquid coolant provided by a chiller. It also featured an embedded thermocouple measuring the plate temperature *Tc*. The hot plate was composed of two concentric sections: an inner metered section with area *Ah,m* and an outer guard section with area *Ah,g*. The metered heater was used for thermal conductivity measurement while the guard heater was used to minimize lateral heat losses that could decrease the accuracy of the measurements. Both metered and guard heaters had embedded (i) thermocouples that measured their respective temperatures *Th,m* and *Th,g* and (ii) resistive wires with resistance *Rh,m* and *Rh,g*, respectively. The resistive wires were connected to two separate digital power supplies to independently control their temperatures *Th,m* and *Th,g* by Joule heating using currents *Ih,m* and *Ih,g* supplied to the metered and guarded sections, respectively. The current flowing through the resistive wires heated the hot plate due to Joule heating. The generated heat imposed a heat transfer rate between the hot and cold plates such that, under steady state, it equaled the heat generation rate, i.e., and . The temperatures *Tc* and *Th,m* were adjusted to maintain the average temperature of the measurement at room temperature. The effective thermal conductivity was calculated using Fourier's law expressed as . The setup was described in detail in previous work, but used in double-sided mode instead of the single-sided mode used in the present study.33

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