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(54) **HYDROPHOBIC AEROGELS**

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(57) **ABSTRACT**

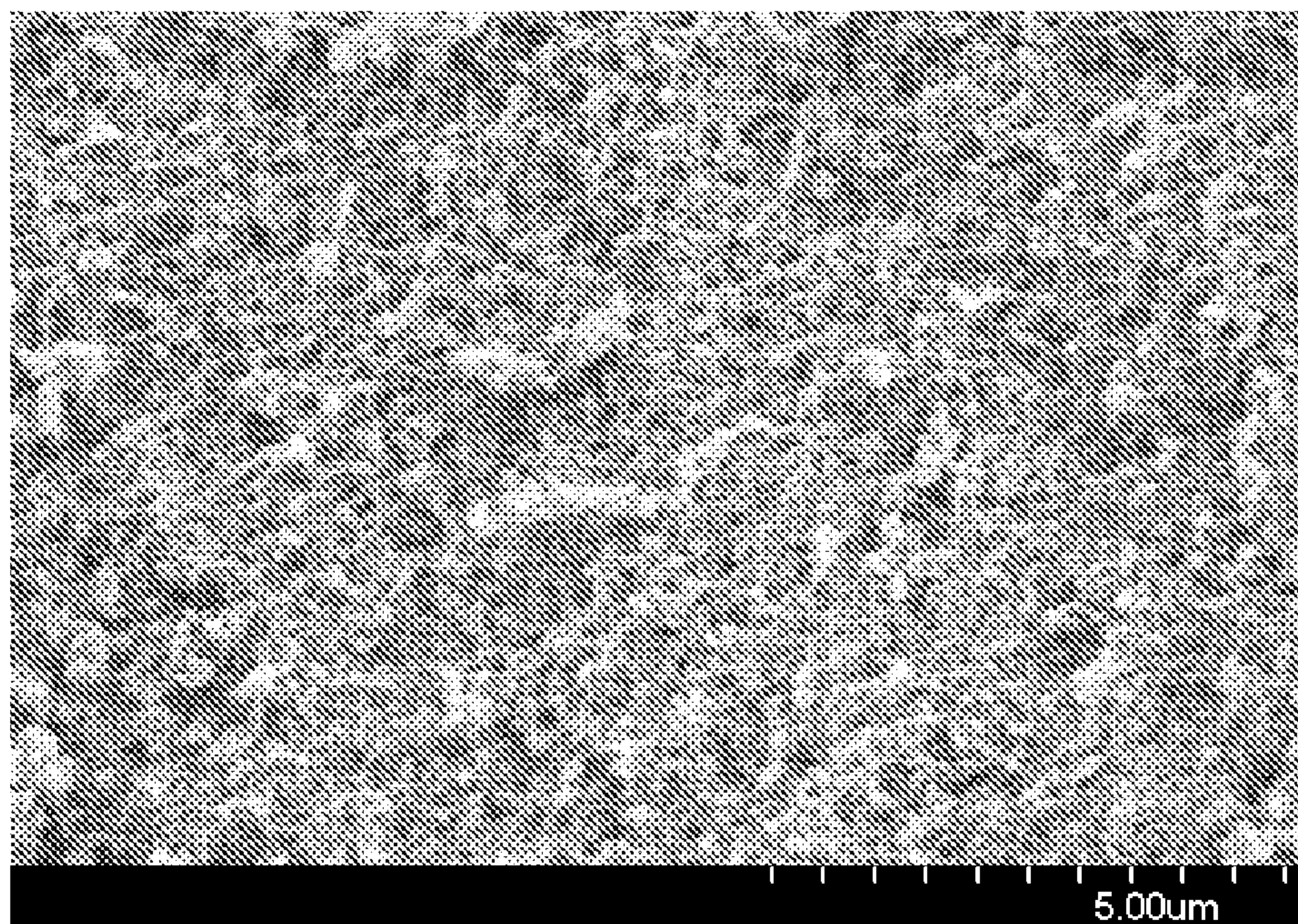
Methods of making hydrophobic aerogels are described. Disclosed methods include forming a surface-modified metal oxide aerogel precursor from a sol comprising a solvent, a metal oxide precursor, and a hydrophobic surface modifying agent. The resulting modified precursor can be dried to form hydrophobic aerogels. Methods of forming the surface-modified metal oxide aerogel precursor include hydrolyzing the metal oxide precursor and co-condensing the hydrolyzed metal oxide precursor and the hydrophobic surface modifying agent. Hydrophobic aerogels and hydrophobic aerogel articles are also disclosed.

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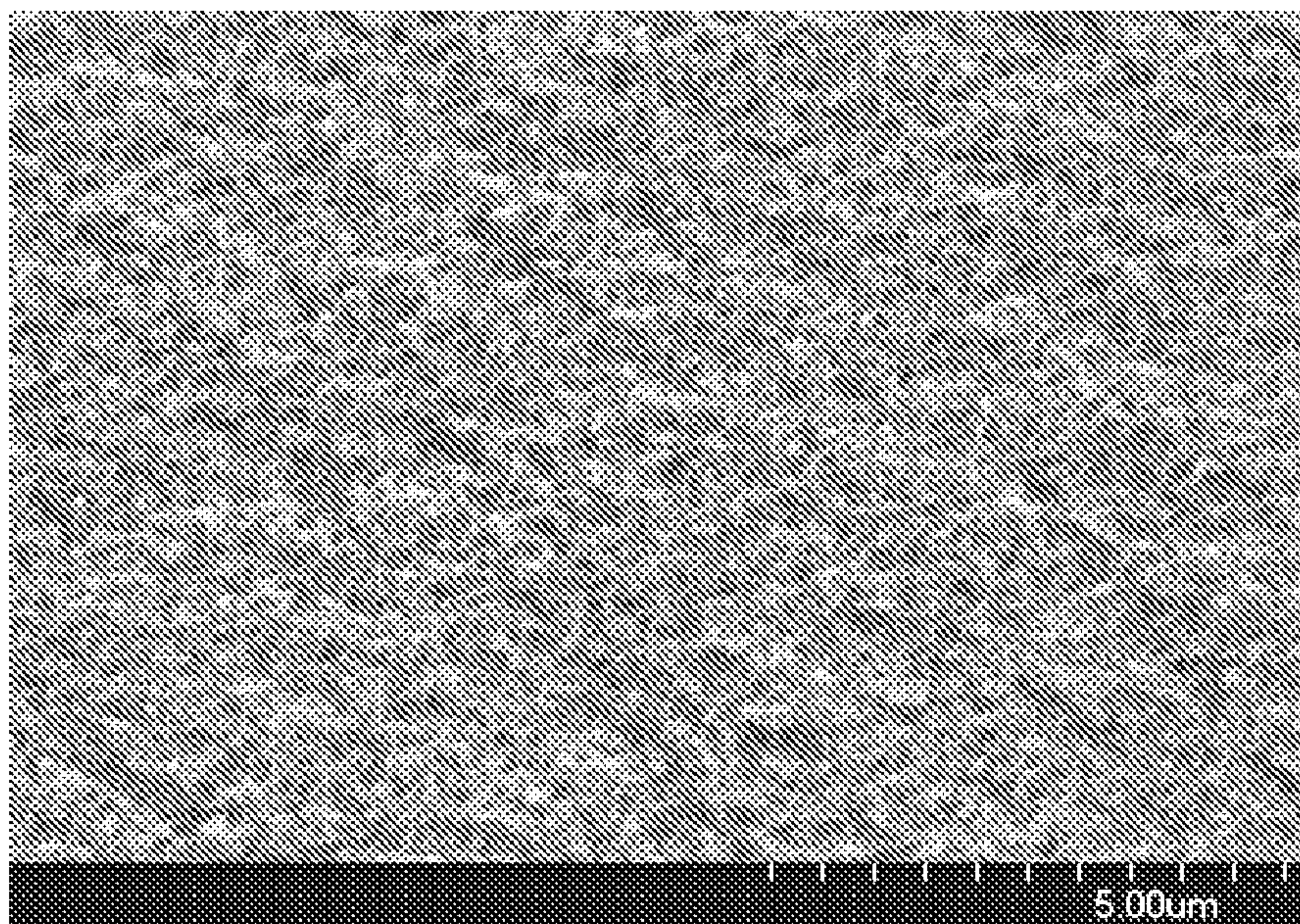


Fig. 1

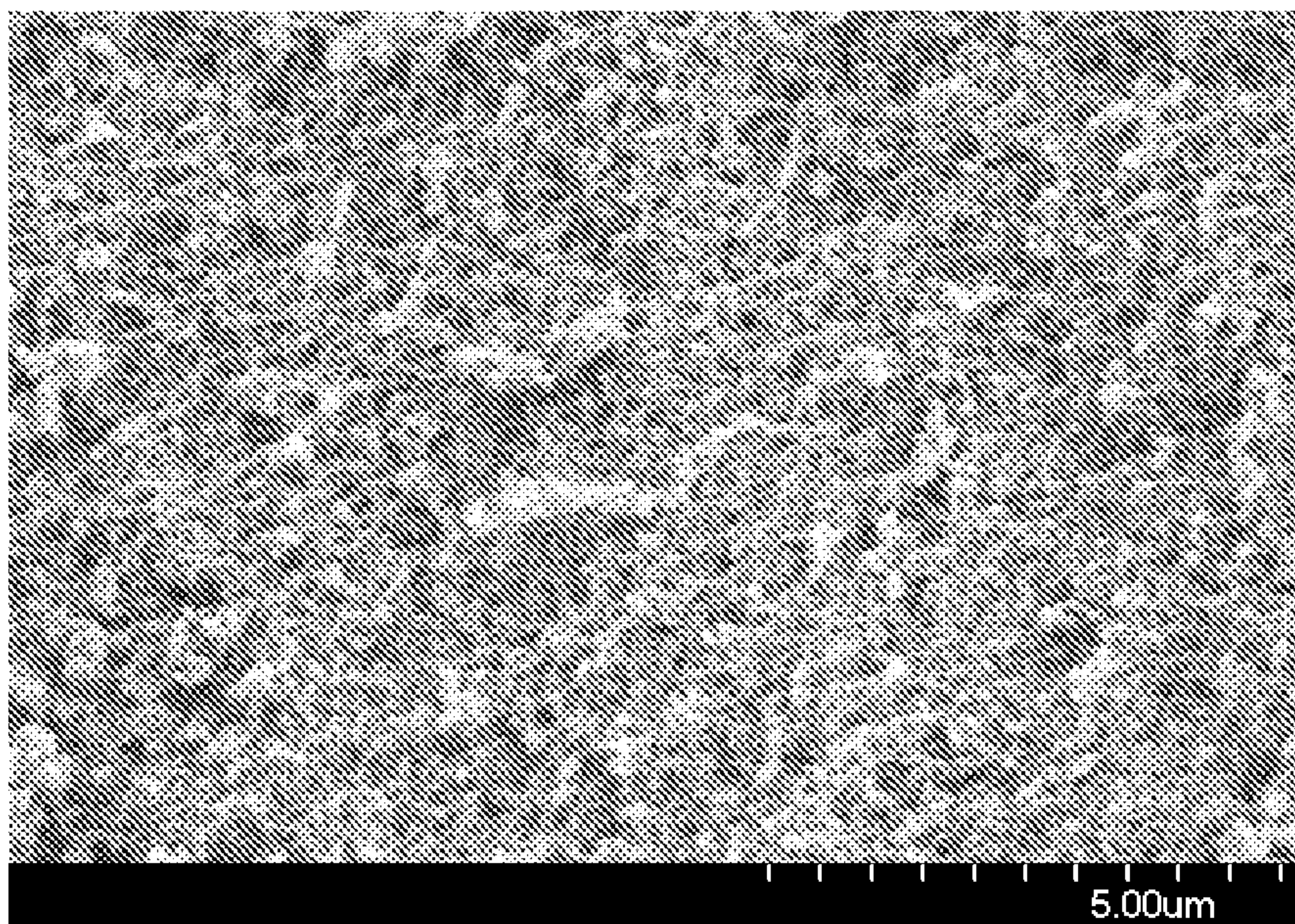


Fig. 2

HYDROPHOBIC AEROGELS

FIELD

[0001] The present disclosure relates to hydrophobic aerogels and methods of making hydrophobic aerogels. In particular, the methods of the present disclosure include combining a hydrophobizing agent with an aerogel precursor prior to gelation rather than adding a hydrophobizing agent to an existing gel.

BACKGROUND

[0002] Aerogels are a unique class of ultra-low-density, highly porous materials. The high porosity, intrinsic pore structure, and low density make aerogels extremely valuable materials for a variety of applications including insulation. Low density aerogels based upon silica are excellent insulators as the very small convoluted pores minimize conduction and convection. In addition, infrared radiation (IR) suppressing dopants may easily be dispersed throughout the aerogel matrix to reduce radiative heat transfer.

[0003] Escalating energy costs and urbanization have lead to increased efforts in exploring more effective thermal and acoustic insulation materials for pipelines, automobiles, aerospace, military, apparel, windows, houses as well as other appliances and equipment. Silica aerogels also have high visible light transmittance so they are also applicable for heat insulators for solar collector panels.

[0004] Aerogels tend to be very hygroscopic due to the presence of hydroxyl groups on the surface. Unmodified aerogels absorb water and other organic solvents adversely affecting desired properties (e.g., surface area, porosity, and density) thereby degrading performance (e.g., thermal insulation). However, many applications of aerogels require exposure to water or atmospheric moisture. Therefore, methods are needed to prepare aerogels having hydrophobicity at ambient conditions as well as over a range of temperature and pressure conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is an SEM image of the aerogel of Example 25.

[0006] FIG. 2 is an SEM image of the hydrophobic aerogel of Example 27.

SUMMARY

[0007] In one aspect, the present disclosure provides methods of preparing a hydrophobic aerogel. Such methods comprise forming a surface-modified metal oxide gel from a sol comprising a solvent, a metal oxide precursor, and a hydrophobic surface modifying agent; and drying the gel to form the hydrophobic aerogel.

[0008] In some embodiments, the methods further comprise solvent-exchanging the hydrophobic, aerogel precursor with an alkyl alcohol to form a hydrophobic alcogel. In some embodiments, the methods further comprise supercritically drying the alcogel to form the hydrophobic aerogel.

[0009] In some embodiments, the solvent comprises water. In some embodiments, the solvent comprises an alkyl alcohol.

[0010] In some embodiments, the metal oxide precursor comprises an organosilane. In some embodiments, the organosilane comprises a tetraalkoxysilane, optionally wherein the tetraalkoxysilane is selected from the group consisting of

tetraethoxysilane, tetramethoxysilane, and combinations thereof. In some embodiments, the organosilane comprises an alkyl-substituted alkoxysilane, optionally wherein the alkyl-substituted alkoxysilane comprises methyltrimethoxysilane. In some embodiments, the organosilane comprises a pre-polymerized silicon alkoxide, optionally wherein the pre-polymerized silicon alkoxide comprises a polysilicate.

[0011] In some embodiments, the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is no greater than 1. In some embodiments, the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is at least 0.2.

[0012] In some embodiments, the sol comprises at least two moles of water per mole of metal oxide precursor. In some embodiments, the sol further comprises an acid, optionally wherein the acid is hydrochloric acid.

[0013] In some embodiments, the methods further comprise applying the mixture to a substrate prior to forming surface-modified metal oxide gel. In some embodiments, the substrate is non-woven substrate. In some embodiments, the substrate is a bonded web.

[0014] In another aspect, the present disclosure provides aerogel articles made according to the methods of the present disclosure.

[0015] In yet another embodiment, the present disclosure provides hydrophobic aerogels made by the methods of the present disclosure.

[0016] The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

DETAILED DESCRIPTION

[0017] There are two main processes for making aerogels. The first process involves the hydrolysis and condensation of a metal oxide precursor (e.g., alkoxysilane precursors) followed by supercritical drying. This process typically yields monolithic aerogels. The second process is a waterglass-based synthesis route that typically yields powders, beads, or granules.

[0018] A typical method for making aerogels hydrophobic involves first making a gel. Subsequently, this preformed gel is soaked in a bath containing a mixture of solvent and the desired hydrophobizing agent in a process often referred to as surface derivatization. For example, U.S. Pat. No. 5,830,387 (Yokogawa et al.) describes a process whereby a gel having the skeleton structure of $(\text{SiO}_2)_n$ was obtained by hydrolyzing and condensing an alkoxysilane. This gel was subsequently hydrophobized by soaking it in a solution of a hydrophobizing agent dissolved in solvent. Similarly, U.S. Pat. No. 6,197,270 (Sonada et al.) describes a process of preparing a gel having the skeleton structure of $(\text{SiO}_2)_m$ from a water glass solution, and subsequently reacting the gel with a hydrophobizing agent in a dispersion medium (e.g., a solvent or a supercritical fluid).

[0019] Due in part to the very fine pore structure of the gel, mass transfer occurs by diffusion alone, and the rate of penetration of the hydrophobizing agent into the gel is slow. Therefore, it often takes many hours for the hydrophobizing agent to penetrate throughout the skeletal structure of the gel. In addition, large amounts of solvent may be required to complete the process.

[0020] Commonly used hydrophobizing agents typically cannot be added prior to gelation because such agents inhibit, alter, or completely prevent gelation. However, the methods of the present disclosure allow for the hydrophobizing agent to be included prior to gelation without significantly affecting gel times. In some embodiments, the hydrophobizing agent provides a catalyst for gelation.

[0021] Generally, the methods of the present disclosure begin with a sol comprising a solvent, a metal oxide precursor, and a hydrophobic surface modifying agent. In some embodiments, the solvent comprises water. In some embodiments, one or more organic solvents such as an alkyl alcohol may be used. In some embodiments, the sol may include both water and one or more organic solvents, e.g., a water/alkyl alcohol blend.

[0022] The methods of the present invention are not particularly limited to specific metal oxide precursors. In some embodiments, the metal oxide precursor comprises an organosilane, e.g., a tetraalkoxysilane. Exemplary tetraalkoxysilanes include tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). In some embodiments, the organosilane comprises an alkyl-substituted alkoxysilane, e.g., methyltrimethoxysilane (MTMOS). In some embodiments, the organosilane comprises a pre-polymerized silicon alkoxide, e.g., a polysilicate such as ethyl polysilicate.

[0023] Generally, during the gel formation process, the hydrophobic surface modifying agent combines with the skeletal structure formed by the metal oxide precursor to provide a hydrophobic surface. In some embodiments, the hydrophobic surface modifying agent is covalently bonded to the metal oxide skeleton. In some embodiments, the hydrophobic surface modifying agent may be ionically bonded to the metal oxide skeleton. In some embodiments, the hydrophobic surface modifying agent may be physically adsorbed to the metal oxide skeleton.

[0024] Generally, the hydrophobic surface modifying agent comprises two functional elements. The first element reacts with (e.g., covalently or ionically) or absorbs on to the metal oxide skeleton. The second element is hydrophobic. Exemplary hydrophobic surface modifying agents include organosilane, organotin, and organophosphorus compounds. One exemplary organosilane is 1,1,1,3,3,3-hexamethyldisilazane (HMDZ).

[0025] Following gel formation, the solvent is removed, drying the gel to form a hydrophobic aerogel. Generally, any known gel drying technique may be used. In some embodiments, the gel may be supercritically dried using, e.g., supercritical carbon dioxide. After solvent removal, the resulting material is typically referred to as an aerogel.

[0026] In some embodiments, a solvent exchange step may precede the drying step. For example, it may be desirable to replace water present in the initial sol with other organic solvents. Generally, any known method of solvent exchange may be used with the methods of the present disclosure. Generally, it may be desirable to replace as much water as possible with the alternate organic solvent. However, as is commonly understood, it may be difficult, impractical, or even impossible to remove all water from the gel. In some embodiments, the exchange solvent may be an alkyl alcohol, e.g., ethyl alcohol. After solvent exchange with an organic solvent, the resulting gel is often referred to as an organogel as opposed to a hydrogel, which refers to gel wherein the solvent is primarily water. When the exchange solvent is an alkyl alcohol, the resulting gel is often referred to as an alcogel.

[0027] In some embodiments, the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is no greater than 1, e.g., no greater than 0.8, or even no greater than 0.6. In some embodiments, the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is at least 0.2, e.g., at least 0.3.

[0028] In some embodiments, the sol comprises at least two moles of water per mole of metal oxide precursor. In some embodiments, the sol comprises 2 to 5, e.g., 3 to 4, moles of water per mole of metal oxide precursor.

[0029] In some embodiments, the sol further comprises an acid. In some embodiments, the acid is an inorganic acid, e.g., hydrochloric acid. In some embodiments, the sol comprises between 0.0005 and 0.0010 moles of acid per mole of metal oxide precursor. In some embodiments, comprises between 0.0006 and 0.0008 moles of acid per mole of metal oxide precursor.

[0030] In addition to forming hydrophobic aerogels, the methods of the present disclosure may be used to form aerogel articles, e.g., flexible aerogel articles. For example, in some embodiments, the sol may be applied to a substrate prior to forming a gel. Gelation, solvent exchange (if used), and drying may then occur on the substrate.

[0031] In some embodiments, the substrate may be porous, e.g., a woven or nonwoven fabric. Exemplary substrates also include bonded web such as those described in U.S. patent application Ser. No. 11/781,635, filed Jul. 23, 2007.

EXAMPLES

Test Methods

[0032] Brunauer, Emmett, and Teller (BET). Surface area was measured via BET analysis, conducted using an AUTOSORB-1 model AS1 MP-LP instrument and associated software (AS1Win version 1.53) available from Quantachrome Instruments (Boynton Beach, Fla.). Sample material was placed in a 9 mm sample tube with a uniform initial weight of approximately 0.0475 grams. The samples were degassed for at least 24 hours at 80° C. prior to analysis. Nitrogen was used as the analyte gas. The BJH method was applied to desorption data to determine pore volume and diameter.

[0033] Hydrophobicity. A small sample was placed in a 4.5 ounce jar containing deionized water at room temperature (about 22° C.). If the samples remained floating after 30 minutes, it was judged to be hydrophobic. If the sample was not floating after 30 minutes, it was judged to be non-hydrophobic.

[0034] Bulk Density. To enable measurement of bulk density, aerogel cylinders were synthesized within plastic syringes with one end cut off. Once gelled, the aerogel cylinder was extracted from the syringe using the syringe plunger and dried. The diameter and length of the dried cylinders were measured and the volume calculated. The weights of the samples were measured on an analytical balance. The bulk density was then calculated from the ratio of weight to volume.

[0035] Skeletal Density. The skeletal density was determined using a Micromeritics ACCUPYC 1330 helium gas pycnometer. The instrument uses Boyle's law of partial pressures in its operation. The instrument contains a calibrated volume cell internal to the instrument. The sample was placed in a sample cup, weighed and inserted into the instrument. The sample was pressurized in the instrument to a known

initial pressure. The pressure was bypassed into the calibrated cell of the instrument and a second pressure recorded. Using the initial pressure, the second pressure, and the volume of the calibrated cell, the skeletal volume of the sample was determined. The skeletal density was then determined from the skeletal volume and the sample weight.

[0036] Porosity. The percent porosity was calculated from the measured bulk density (ρ_{bulk}) and the skeletal density ($\rho_{skeletal}$) using the following formula:

$$\text{porosity}(\%) = \left(1 - \left(\frac{\rho_{bulk}}{\rho_{skeletal}} \right) \right) \times 100$$

[0037] Thermal Conductivity. Thermal conductivity was measured at a mean temperature of 12.5° C. using a LASER-COMP “Fox200” instrument.

[0038] Supercritical Fluid Drying. The sample was weighed and placed in a permeable cloth bag sealed with a draw string. The bag containing the sample was placed inside a stainless steel chamber. The bottom and top of this chamber were fitted with metal frits and O-rings. This chamber was inserted into a vessel rated to handle high pressure (40 MPa (6000 psig)). The outside of this vessel was heated by a jacket.

[0039] Carbon dioxide was chilled to less than minus 10 degrees Celsius and pumped with a piston pump at a nominal flow rate of one liter per minute through the bottom of the unit. After ten minutes, the temperature of the unit was raised to 40° C. at a pressure of 10.3 MPa (1500 psig). The carbon dioxide is supercritical at these conditions. The drying period was conducted for a minimum of seven hours. After the drying period, the carbon dioxide flow was ceased and the pressure was slowly decreased by venting the carbon dioxide. When the pressure was at 370 kPa (40 psig) or lower, the now dry samples were removed and weighed.

Examples 1-6

TEOS-Based Aerogels with Pre-Hydrolyzation and Surface Treatment Prior to Gelation

[0040] A stock solution was prepared by mixing 209.39 grams of tetraethoxysilane (TEOS, 99+%) (Alfa Aesar) with 234.95 grams of ethanol (EtOH, 200 proof) (Aaper Alcohol), 54.09 grams of deionized water (H₂O) and 0.701 grams of 1 Molar hydrochloric acid (1M HCl) (J. T. Baker) in a round bottom flask fitted with water cooled reflux condenser. The mixture was heated to 70° C. for 1 hour under constant stirring.

[0041] 1,1,1,3,3,3-hexamethyldisilazane (HMDZ) was used as a silylating/surface modifying agent to render the silica gel hydrophobic. In principle, other silylating agents can also be used for this purpose. The silylating agent here performs the dual role of modifying the surface and providing ammonia upon reaction with water, which acts as a catalyst for the hydrolysis and condensation of the silica precursor.

[0042] For each synthesis, 49.57 grams of the stock solution was transferred to a glass jar. Under vigorous stirring using a stir bar, 1,1,1,3,3,3-hexamethyldisilazane (HMDZ, 99+%) (Alfa Aesar) was added to the mixture. Gel time was defined as the required after mixing all reactants for the sol to substantially cease moving even when the glass jar is moved or inverted. In some cases, a stop watch was used to measure the gel time. The start time was the point at which all the reactants were mixed. The point at which the stir bar stopped

moving was taken as the end time. If the gel continues to move slowly then the gel quality is weak, otherwise the gel was considered strong. Those examples which resulted in gels were solvent exchanged three times with 75 ml of EtOH. After the final solvent exchange, the samples were supercritically dried.

[0043] The molar ratios of the various reactants and the resulting gel times and gel characteristics are shown in Table 1. Example 1 gelled but was not hydrophobic indicating insufficient surface treatment. Examples 2-4 gelled in less than one minute and were hydrophobic. In the case of Example 5, even though gelation occurred in less than one minute, the gel quality was poor and hence the sample could not be supercritically dried. Example 6 did not gel.

TABLE 1

Formulations, gel times, and gel characteristics for Examples 1-6							
Ex.	TEOS	Ratio of moles per mole TEOS				Gel time	gel characteristic
	(moles)	H ₂ O	EtOH	HCl	HMDZ		
1	1	3	5	0.0007	0.033	47 sec. (a)	strong
2	1	3	5	0.0007	0.2	14 sec.	strong
3	1	3	5	0.0007	0.33	12 sec.	strong
4	1	3	5	0.0007	0.5	10 sec.	strong
5	1	3	5	0.0007	1	11 sec.	weak
6	1	3	5	0.0007	2	did not gel	did not gel

(a) Seconds (“sec.”).

[0044] The characteristics of Examples 1-5 are shown in Table 2. The surface areas and densities of Examples 2-4 are typical of aerogels. These examples clearly demonstrate a process by which silica aerogels can be prepared in the presence of surface modifying agents in a time efficient manner when an appropriate amount of HMDZ is used for surface modification.

TABLE 2

Characteristics of the aerogels of Examples 1-5.						
Ex.	surface area (m ² /g)	pore volume (cc/g)	bulk density (g/cc)	skeletal density (g/cc)	porosity (%)	hydrophobic
1	N/A	N/A	N/A	N/A	N/A	No
2	684	3.0	0.36	1.51	76	Yes
3	569	2.1	0.27	1.59	83	Yes
4	554	1.8	0.35	1.73	80	Yes
5	N/A	N/A	N/A	N/A	N/A	Yes

Examples 7-14

TEOS-Based Aerogels with Pre-Hydrolyzation and Surface Treatment Prior to Gelation

[0045] Examples 7-14 were prepared in a manner similar to Examples 1-6 except that the H₂O/TEOS and EtOH/TEOS molar ratios were varied. Table 3 shows that the gel time trends for Examples 7-14 are similar to those for Examples 1-6. Examples 8 and 12 did not gel. Example 9 was not hydrophobic due to insufficient surface treatment, while Examples 7, 10, 11, 13, and 14 were hydrophobic. As summarized in Table 4, Examples 11 and 13 exhibited characteristic aerogel surface areas and densities.

TABLE 3

Formulations and gel times for Examples 7-14.						
Ex.	TEOS (moles)	Moles per mole of TEOS				gel time
		H ₂ O	EtOH	HCl	HMDZ	
7	1	3.5	5	0.0007	0.5	>15 min. (b)
8	1	3.5	5	0.0007	2	did not gel
9	1	4	5	0.0007	0.033	25 sec.
10	1	4	5	0.0007	0.5	4 sec.
11	1	4	5	0.0007	0.33	3 sec.
12	1	4	5	0.0007	2	did not gel
13	1	3	6	0.0007	0.33	14 sec.
14	1	3	7	0.0007	0.33	21 sec.

(b) Minutes ("Min.").

TABLE 4

Characterization results for Examples 11 and 13.					
Ex.	surface area (m ² /g)	Pore volume (cc/g)	bulk density (g/cc)	skeletal density (g/cc)	porosity (%)
11	612	2.5	0.22	1.50	86
13	596	2.4	0.32	1.44	77

Examples 15-20

TEOS-Based Aerogels without Pre-Hydrolyzation
but with Surface Treatment Prior to Gelation

[0046] Tetraethoxysilane (TEOS, 99+%) (Alfa Aesar) was mixed with 1,1,1,3,3,3-hexamethyldisilazane (HMDZ, 99+%) (Alfa Aesar) in a glass beaker to prepare solution A. In another beaker, ethanol (EtOH, 200 proof) (Aaper Alcohol), deionized water (H₂O) and 1 molar hydrochloric acid (1M HCl) (J. T. Baker) were mixed to form solution B. Solution B was added instantaneously to Solution A under vigorous stirring, such that the vortex formed by stirring approached the bottom of the container. The molar ratios of the various reactants and the gelation times for these mixtures are listed in the Table 5. For Examples 15-20, the molar ratio of H₂O/TEOS and EtOH/TEOS was kept constant at 3 and 5, respectively. Those examples which resulted in gels were solvent exchanged three times with 75 ml of EtOH. After the final solvent exchange the samples were supercritically dried.

[0047] Examples 15-17 did not gel within 15 minutes; however, gelation did occur after several days. Examples 18-20 did not gel even after several days (samples were observed for a period of two weeks). Higher HMDZ/TEOS ratios (>0.5) resulted in no gelation or very long gel times.

TABLE 5

Formulations, gel times, and gel characteristics for Examples 15-20							
Ex.	TEOS (moles)	Moles per mole of TEOS				gel time	gel charac- teristics
		H ₂ O	EtOH	HCl	HMDZ		
15	1	3	5	0.0007	0.033	days	strong, opaque
16	1	3	5	0.0007	0.2	days	strong, translucent
17	1	3	5	0.0007	0.33	days	strong, opaque

TABLE 5-continued

Formulations, gel times, and gel characteristics for Examples 15-20							
Ex.	TEOS (moles)	Moles per mole of TEOS				gel time	gel charac- teristics
		H ₂ O	EtOH	HCl	HMDZ		
18	1	3	5	0.0007	0.5	did not gel	clear
19	1	3	5	0.0007	1	did not gel	clear
20	1	3	5	0.0007	1.3	did not gel	clear

[0048] Example 16 was hydrophobic and had a surface area of 453 m²/g, a pore volume of 2.5 cc/g, a bulk density of 0.26 g/cc, a skeletal density of 1.48 g/cc, and a porosity of 83%.

Examples 21-24

TEOS-Based Aerogels without Pre-Hydrolyzation,
but with Surface Treatment Prior to Gelation

[0049] Solutions A and B were prepared and mixed as described for Examples 15-20. The molar ratios of the various reactants and the gelation times for these mixtures are listed in the Table 6. For Examples 21-24, the molar ratios of H₂O/TEOS and EtOH/TEOS were varied while the molar ratio of HMDZ/TEOS was held constant at 0.33. Those examples which resulted in gels were solvent exchanged three times with 75 ml of EtOH. After the final solvent exchange the samples were supercritically dried.

[0050] No gelation was observed within 15 minutes for Examples 21-24; however, gelation occurred several days later. The resulting gels were hydrophobic.

TABLE 6

Formulations, gel times, and gel characteristics for Examples 21-24							
Ex.	TEOS (mol)	Moles per mole of TEOS				gel time	gel charac- teristics
		H ₂ O	EtOH	HCl	HMDZ		
21	1	4	5	0.0007	0.33	>15 min.	opaque
22	1	7	5	0.0007	0.33	>15 min.	opaque
23	1	3	6	0.0007	0.33	>15 min.	opaque
24	1	3	7	0.0007	0.33	>15 min.	opaque

Examples 25-29

TMOS-Based Aerogels without Pre-Hydrolyzation,
but with Surface Treatment Prior to Gelation

[0051] Tetramethoxysilane (TMOS, 98+%) (Alfa Aesar) was mixed with 1,1,1,3,3,3-hexamethyldisilazane (HMDZ, 99+%) (Alfa Aesar) in a glass beaker to prepare solution C. In another beaker Methanol (MeOH, 99.8%) (J. T. Baker), deionized water (H₂O) and 1 Molar Hydrochloric acid (1M HCl) (J. T. Baker) were mixed to form solution D. These solutions were cooled in a dry ice bath. Solution D was added instantaneously to Solution C under vigorous stirring, such that the vortex formed by stirring approached the bottom of the container. The molar ratios of the various reactants and the gelation times for these mixtures are listed in the Table 7. Those examples which resulted in gels were solvent exchanged three times with 75 ml of MeOH. After the final solvent exchange the samples were supercritically dried.

[0052] Except for Example 29, all examples gelled in 1 minute or less. Example 29 shows longer gelation time and had a higher HMDZ/TMOS molar ratio. This is consistent with examples shown above for TEOS-based gels where higher HMDZ/TEOS ratios also resulted in longer gel times and, in some cases, no gelation was observed.

TABLE 7

Formulations, gel times, and gel characteristics for Examples 25-29.							
Ex.	TMOS (moles)	moles per mole TMOS				gel time	gel charac- teristics
		H ₂ O	EtOH	HCl	HMDZ		
25	1	3	5	0.0007	0.033	1 min.	clear, strong
26	1	3	5	0.0007	0.2	15 sec.	clear, strong
27	1	3	5	0.0007	0.33	15 sec.	trans- lucent, strong
28	1	3	5	0.0007	0.5	15 sec.	trans- lucent, strong
29	1	3	5	0.0007	1	>15 min.	opaque, weak

[0053] Characteristics of the aerogels of Examples 25-29 are summarized in Table 8. The surface areas and densities are characteristic of TMOS-based aerogels. Example 25 was not hydrophobic and had a low HMDZ/TMOS molar ratio, which is consistent with results for TEOS-based aerogels. Examples 26-29 were all hydrophobic.

TABLE 8

Characteristics of the aerogels of Examples 25-29.						
Ex.	surface area (m ² /g)	pore volume (cc/g)	bulk density (g/cc)	skeletal density (g/cc)	porosity (%)	hydro- phobic
25	N/A	N/A	0.22	1.88	89	No
26	N/A	N/A	0.20	1.64	88	Yes
27	503	2.6	0.17	1.64	90	Yes
28	N/A	N/A	0.14	1.78	92	Yes
29	N/A	N/A	N/A	N/A	N/A	Yes

[0054] A scanning electron microscope was used to obtain images of the aerogels. FIG. 1 is an image of the aerogel of Example 25. FIG. 2 is an image of the hydrophobic aerogel of Example 27.

Examples 30-41

TEOS-Based Aerogels Derived from a Commercially-Available Pre-Hydrolyzed Sol, Surface Treated Prior to Gelation

[0055] Ethyl polysilicate containing 45-47 wt % SiO₂ (SIL-BOND 50 from Silbond Corporation) was mixed with 1,1,1,3,3,3-hexamethyldisilazane (HMDZ, 99+%) (Alfa Aesar) in a glass beaker to prepare solution E. In another beaker ethanol (EtOH, 200 proof) (Aaper Alcohol), deionized water (H₂O) and 1 molar hydrochloric acid (1M HCl) (J. T. Baker) were mixed to form solution F. Solution F was added instantaneously to Solution E under vigorous stirring, such that the vortex formed by stirring approached the bottom of the con-

tainer. Those examples which resulted in gels were solvent exchanged three times with 75 ml of EtOH. After the final solvent exchange the samples were supercritically dried.

[0056] All the compositions in Table 9 are listed in weight (grams). Generally, very low concentrations of HMDZ led to long gel times (e.g., Examples 30 and 34). In contrast, samples with very high concentrations of HMDZ (e.g., Example 33) showed no gelation. For higher concentrations of water (e.g., Example 35), the gel time is the shortest (2 minutes). A trend similar to Examples 30-37 was observed in the case of Examples 38-41 where no hydrochloric acid was used in the syntheses.

TABLE 9

Formulations (in grams), gel times, and gel characteristics for Examples 30-41							
Ex.	ethyl poly- silicate	H ₂ O	EtOH	HCl	HMDZ	gel time	gel charac- teristics
30	20	3.8	16.4	0.073	0.35	15 min.	clear, strong
31	20	3.8	16.4	0.068	3.54	3 min.	clear, strong
32	20	3.8	16.4	0.067	5.64	5 min.	clear, strong
33	20	3.8	16.4	0.071	11.1	did not gel	N/A
34	20	3.8	16.4	0.072	0.36	20 min.	translucent strong
35	20	3.8	16.4	0.069	3.55	2 min.	clear, strong
36	20	3.8	23.4	0.073	0.36	25 min.	clear, weak
37	20	3.8	23.4	0.067	3.55	4 min.	clear, strong
38	20	3.8	16.4	0	3.59	3 min.	clear, strong
39	20	3.8	23.4	0	3.55	5 min.	clear, strong
40	20	3.8	16.4	0	0.36	18 min.	clear, strong
41	20	3.8	16.4	0	5.63	5 min.	clear, strong

[0057] Generally, the aerogels were hydrophobic and had surface area and densities characteristic of aerogels. For example, the aerogel of Example 31 was hydrophobic and had surface area of 690 m²/g, a pore volume of 1.9 cc/g, a bulk density of 0.14 g/cc, a skeletal density of 1.48 g/cc, and a porosity of 71%.

Examples 42-49

TEOS-based aerogels prepared from a pre-hydrolyzed sol subject to further pre-hydrolysis and surface treatment prior to gelation.

[0058] Ethyl polysilicate containing 45-47 wt % SiO₂ (SIL-BOND 50 from Silbond Corporation) was mixed with ethanol (EtOH, 200 proof) (Aaper Alcohol), deionized water (H₂O) and 1 molar hydrochloric acid (1M HCl) (J. T. Baker) in a glass jar. The mixture was heated at 50° C. for 15 minutes under constant stirring. While vigorously stirring, different amounts of 1,1,1,3,3,3-hexamethyldisilazane (HMDZ, 99+%) (Alfa Aesar) were added to the mixture. Those samples which resulted in gels were solvent exchanged three times with 75 ml of EtOH. After solvent exchange the samples were supercritically dried.

[0059] All the compositions in Table 10 are listed in weight (grams). Comparing Examples 30-41 with Examples 42-49 shows that further pre-hydrolysis (Examples 42-49) resulted in shorter gel times. Examples 43, 44, 45, 47 and 49 were hydrophobic. Examples 42, 46, and 48 were not.

TABLE 10

Formulations (grams), gel times, and gel characteristics for Examples 42-49.							
Ex.	Ethyl poly-silicate	H ₂ O	EtOH	HCl	HMDZ	gel time	gel characteristics
42	20.024	3.77	16.4	0.072	0.364	7 min.	translucent
43	19.994	3.77	16.4	0.069	3.545	1 min.	translucent
44	19.995	3.77	16.4	0.069	5.639	10 sec.	opaque strong
45	19.993	3.77	16.4	0.068	11.104	days	opaque slurry
46	19.993	7.2	16.4	0.069	0.357	10 min.	translucent
47	20.01	7.2	16.4	0.074	3.554	30 sec.	opaque
48	20.012	3.77	23.4	0.073	0.364	12 min.	clear
49	20.033	3.77	23.4	0.074	3.576	3 min.	translucent

Examples 50-60

TEOS/MTMOS-Based Aerogels with Pre-Hydrolyzation and Surface Treatment Prior to Gelation

[0060] Tetraethoxysilane (TEOS, 99+%) (Alfa Aesar) and methyltrimethoxysilane (MTMOS, 95%) (Aldrich) were mixed with ethanol (EtOH, 200 proof) (Aaper Alcohol), deionized water (H₂O) and hydrochloric acid (HCl) (J. T. Baker) in a glass jar. For Examples 50-55, 0.005M HCl was used and for Examples 56-60 μ M HCl was used. The glass jar containing the mixture was heated at 50° C. for 45 minutes under constant stirring. While vigorously stirring, HMDZ was added to the mixture. The molar ratios of the various reactants in the final mixture are listed in Table 11. The resulting gels were solvent exchanged three times with 75 ml of EtOH. After the final solvent exchange the samples were supercritically dried.

TABLE 11

Formulations, gel times, and gel characteristics for Examples 50-60.								
Ex.	Relative Mole %		Moles per total moles TEOS and MTMOS				gel time	gel characteristics
	TEOS	MTMOS	H ₂ O	EtOH	HCl	HMDZ		
50	50	50	9	3	0.0007	0.33	5 min.	clear
51	50	50	9	3	0.0007	0.2	N/A	clear
52	50	50	9	3	0.0007	0.033	N/A	clear
53	50	50	9	3	0.0007	0.5	N/A	clear
54	90	10	9	3	0.0007	0.33	7 min.	translucent
55	80	20	9	3	0.0007	0.33	6 min.	clear
56	90	10	2.5	5	0.0007	0.33	8 min.	clear
57	90	10	2.5	5	0.0007	0.2	N/A	clear
58	90	10	2.5	5	0.0007	0.033	N/A	clear
59	80	20	3	5	0.0007	0.33	1 min.	clear
60	70	30	3	5	0.0007	0.33	3 min.	clear

[0061] Examples 50-60 were all hydrophobic. Generally, the inclusion of MTMOS increased the gel time compared to the pure pre-hydrolyzed TEOS samples (e.g., Examples 59 and 60 showed an increase in gel time with increasing MTMOS content relative to Example 3, which did not contain MTMOS). Examples 50-60 also showed that surface modification prior to gelation can be used with other organosilanes (containing Si—C groups) and not just pure silica precursors like tetraalkoxysilanes (e.g., TEOS and TMOS), pre-hydrolyzed TEOS, and pre-polymerized silicon alkoxides (e.g., SILBOND 50).

Examples 61 and 62

Flexible Aerogels with Surface Treatment Prior to Gelation on a Nonwoven Substrate

[0062] The gel precursor of Example 3 was prepared. The pre-hydrolyzed TEOS and HMDZ were cooled using dry ice prior to mixing in order to slow gelation. The mixture was coated onto a bonded fibrous flexible substrate. (A 75-25 blend of 3d WELLMAN PET fibers and 6d KOSA PET fibers at 30 gsm was carded, corrugated, and bonded to 30 gsm of PP 7C05N strands wherein the corrugating pattern had 10 bonds per 2.54 cm (i.e., 10 bonds per inch). The sample gelled in about 5 minutes. The substrate containing the gel was solvent exchanged using EtOH three times to remove residual water. The substrate containing the gel was then supercritically dried. The thermal conductivity of the Example 61, measured at a mean temperature of 12.5° C., was 29.4 mW/m-K. Example 62 was prepared in the same manner as Example 61, except that the gel precursor of Example 54 was used. The thermal conductivity of the Example 62, measured at a mean temperature of 12.5° C., was 25.9 mW/m-K.

[0063] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

1. A method of preparing a hydrophobic aerogel comprising forming a surface-modified metal oxide aerogel precursor from a sol comprising a solvent, a metal oxide precursor, and a hydrophobic surface modifying agent; and drying the surface-modified metal oxide aerogel precursor to form the hydrophobic aerogel.

2. The method of claim 1, wherein forming the surface-modified metal oxide aerogel precursor comprises hydrolyz-

ing the metal oxide precursor and co-condensing the hydrolyzed metal oxide precursor and the hydrophobic surface modifying agent.

3. The method of claim 1, further comprising solvent-exchanging the surface-modified metal oxide aerogel precursor with an alkyl alcohol to form an alcogel.

4. The method of claim 1, further comprising supercritically drying the aerogel precursor or the alcogel to form the hydrophobic aerogel.

5. The method of claim 1, wherein the solvent comprises water.

6. The method of claim 1, wherein the solvent comprises an alkyl alcohol.

7. The method of claim 1, wherein the metal oxide precursor comprises an organosilane.

8. The method of claim 7, wherein the organosilane comprises a tetraalkoxysilane selected from the group consisting of tetraethoxysilane, tetramethoxysilane, and combinations thereof.

9. The method according to claim 7, wherein the organosilane comprises methyltrimethoxysilane.

10. The method according to claim 6, wherein the organosilane comprises a polysilicate.

11. The method of claim 1, wherein the hydrophobic surface modifying agent comprises 1,1,1,3,3,3-hexamethyldisilazane.

12. The method of claim 1, wherein the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is no greater than 1.

13. The method of claim 1, wherein the molar ratio of the hydrophobic surface modifying agent to the metal oxide precursor is at least 0.2.

14. The method of claim 1, wherein the sol further comprises at least one of hydrochloric acid and oxalic acid.

15. The method of claim 1, further comprising applying the sol to a substrate prior to forming surface-modified metal oxide gel.

16. The method of claim 15, wherein the sol is applied to the substrate prior to forming the surface-modified metal oxide aerogel precursor.

17. The method of claim 15, wherein the substrate is non-woven substrate.

18. The method of claim 15, wherein the substrate is a bonded web.

19. An aerogel article made according to the method of claim 15.

20. A hydrophobic aerogel made by the method of claim 1, wherein a sample of the hybrid aerogel placed in a jar containing deionized water at 22° C. remains floating after 30 minutes.

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