Design and Characterization of Interconnected, Microporous Hybrid Thin Films by a Sol−Gel Process

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Interconnected, microporous thin films have been prepared by formation of organic−inorganic hybrid materials via a sol−gel process. The spin-coating solution was obtained by hydrolyzing tetramethoxysilane (TMOS) with different portions of methyltrimethoxysilane (MTMS) under acidic catalyst. The organo−silicon groups incorporated into the structure reduced the extent of cross-linking of the silicate network during the curing process, and promoted the formation of a porous structure. The type I sorption isotherms and diffusion-controlled adsorption kinetic studies on the films indicated that the hybrid materials were microporous and that the interconnected pores had an effective pore size close to the diameter of nitrogen. The microporosity and microstructures of the hybrid materials were also qualitatively supported by using TEM, ^{29}Si MAS/NMR, and FTIR spectroscopy.

Introduction

Organic−inorganic hybrid materials have been synthesized as composites with a large variety of structures and compositions. The composite may have its organic phase act as a polymeric matrix and inorganic phase as a filler, and its particle size can be varied from nano- to micrometers. The composite can be prepared with less phase separation or the organic−inorganic phases can also be chemically bonded at the molecular scale.[1−3] These hybrid materials have shown many interesting mechanical, optical and thermal properties and have found commercial application. Systematic study of organically modified silicate materials, synthesized using the sol−gel process, started in the mid-1980s.[4,5] However, occasional studies of methyl-modified silicate (MMS) materials, one of the simplest systems in the hybrid materials, can be found decades before that. One of the first commercial products developed in the mid-1960s by Schott Glass, Germany, was silica core−MMS clad UV-fiber optics.[6] A recently introduced product is MMS-coated steel tapes by Nisshin Steel.[7] Also very recently, Nippon Sheet Glass reported the viability of fine-patterning of MMS films with precise grooves on glass substrates for optical memory disks.[8] Here we report that organic−inorganic hybrid MMS materials can also be used to design interconnected, microporous thin films by a sol−gel process.

Porous thin films, especially those with interconnected micropores, have been of great interest in preparation of selective chemical sensors,[9−12] membranes,[13,14] and other thin-film-based devices.[14,15] Different methods for the synthesis of powder or bulk porous materials have been developed during the past several decades. These techniques, however, cannot be used to prepare continuous, pinhole-free and crack-free thin-film counterparts. Xerogels prepared by the sol−gel process and dried by subcritical drying, for example, show a peak pore radius of 1.1 nm catalyzed by hydrochloric acid or larger than 10.5 nm catalyzed by hydrofluoric acid.[16] Their surface areas can be larger than 1000 m^2/g. Although a microporous xerogel can be easily obtained, thin films derived from the same sol−gel precursor solutions are nonporous.[17] Such a phenomenon is attributed to the overlap of solvent evaporation with condensation during film deposition. The fast evaporation may cause the pore to collapse and form a fully cross-linked, dense film upon thermal treatment.

Considerable literature has reported the formation of hybrid inorganic−organic structures to modify materials at the molecular scale.[18] One strategy to design porous thin films based on sol−gel coating is to reduce the extent of cross-linking by introducing organic terminal groups into the inorganic network. One possible approach is to replace some of the alkoxide groups by unhydrolyzable organic groups. The organic groups attached to the silicon through a Si−C bonding not only

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(1) Choi, K. M.; Shea, K. J. *J. Am. Chem. Soc.* **1994**, *116,* 9052.
(2) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95,* 1431.
(3) Mackenzie, J. D.; Chung, Y. J.; Hu, Y. J. *Non-Cryst. Solids* **1992**, *147,* 271.
(4) Schimdt, H. *Mater. Res. Soc. Symp. Proc.* **1984**, *32,* 327.
(5) Wilkes, G. L.; Orler, B.; Huang, H. H. *Polym. Prepr.* **1985**, *26,* 300.
(6) Dislisch, H.; Jacobsen, A. FRG-Patent 14 94 872, 1965.
(7) Uchida, Y. *New Glass* **1992**, *7,* 129.
(8) Matsuda, A.; Morio, K.; Kishimoto, T.; Mitsubishi, Y.; Tohge, N.; Minami, T. *Glass Surface, Sol−Gel Glasses: Proceedings of XVII international Congress on Glass*; Gong, F., Eds.; Academic Publishers: Beijing, 1995; Vol. 4, p 349.
(9) Yan, Y.; Bein, T. *Chem. Mater.* **1992**, *4,* 975; **1993**, *5,* 907.
(10) Yan, Y.; Bein, T. *J. Am. Chem. Soc.* **1995**, *117,* 9990.
(11) Feng, S.; Bein, T. *Nature* **1994**, *368,* 834; *Science* **1994**, *265,* 1839.
(12) Hoekstra, K. J.; Bein, T. *Chem. Mater.* **1996**, *8,* 1865.
(13) Lin, Y. S.; Burggraaf, A. J. *J. Am. Ceram. Soc.* **1991**, *74,* 219.
(14) Yan, Y.; Ray Chaudhuri, S.; Sarkar, A. *J. Am. Ceram. Soc.* **1996**, *79,* 1061.
(15) Yan, Y.; Ray Chaudhuri, S.; Sarkar, A. *Chem. Mater.* **1996**, *7,* 2007.
(16) Murata, H.; Kirkbir, F.; Meyers, D.; Ray Chaudhuri, S.; Sarkar, A. *SPIE, Sol−Gel Optics III* **1994**, *2288,* 709.
(17) Frye, G. C.; Ricco, A. J.; Martin, S. J.; Brinker, C. J. In *Better Ceramic Through Chemistry III*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Mater. Res. Soc. Proc. 121; Pittsburgh, PA, 1988; p 349.
(18) For recent reviews: Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater* **1995**, *7,* 2010.

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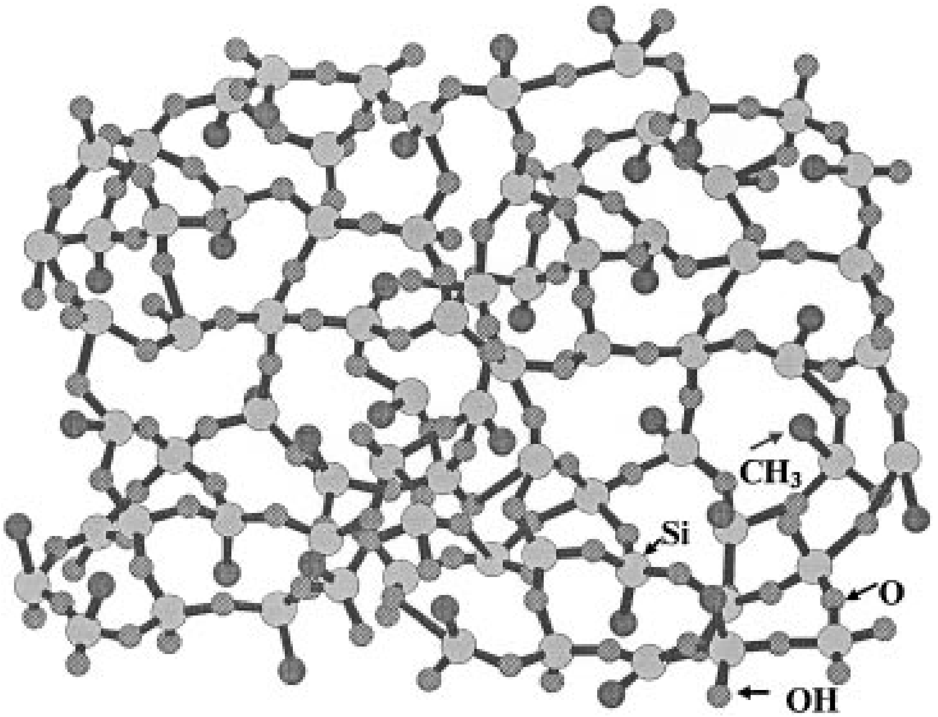

Figure 1. Spacer organic groups reduce the extent of cross-linking in the network and create a interconnected microporous nanophase in the hybrid thin film at molecular scale, regardless of the processing conditions.

reduce the number of Si−O−Si linkages but also act as a spacer in the inorganic network by forming an interconnected organic nanophase and hence a porous phase around the organic groups (Figure 1). In this paper we demonstrate that a crack-free, well-defined, and characterized microporous thin films can be obtained from the hybrid materials by using a simple dip-coating or spin-coating process.

Experimental Section

The coating solutions were prepared by using a similar process as we reported earlier.[19] Tetramethoxysilane (TMOS) was mixed with different portions of methyltrimethoxysilane (MTMS, Aldrich) in ethanol (EtOH). Under stirring, the solution was hydrolyzed with water containing hydrochloric acid (pH = 2). The typical concentration of the as prepared solution had a molecular ratio of xTMOS:yMTMS:2($x + y$)-EtOH:($4x + 3y$)H$_2$O, and the ratio of HCl to the CH$_3$O− group of (TMOS + MTMS) is equivalent to 0.0002. After reaction for 24 h at room temperature the solution was further diluted with 8($x + y$)EtOH. Thin films were spin-coated at 2000 rpm for 60 s on different substrates. The coatings had a typical thickness of 200 nm after being cured at 200 °C for 24 h. The thickness of the coating was also dependent on the ratio of MTMS/(TMOS + MTMS) in the solutions.

Infrared spectra of the thin films coated on KBr substrates were obtained on a Nicolet 740 FTIR spectrometer. Measurements were performed on the samples thermally treated at different temperatures (100−500 °C) in air for 4 h, during which the spectrometer was constantly purged with nitrogen. The morphology and microstructure of the films were characterized by transmission electron microscopy (TEM) performed on a Philips CM30 with an acceleration voltage of 300 kV. The hybrid films for the TEM analysis were directly deposited on a silicon wafer. The ^{29}Si solid-state magic angle spinning (MAS) NMR spectra were taken with a Chemagnetics CMX-200 spectrometer at 39.7 MHz using standard cross-polarization techniques. Cross-polarization contact times of 3 ms were used for the data acquisition. Sorptions of nitrogen were performed in a modified BET apparatus at the boiling point of nitrogen, in which the hybrid film were directly deposited on the surface of AT-cut piezoelectric crystals (6 MHz). The piezoelectric crystal vibrates in the thickness shear mode, and its oscillation frequency is sensitive to the change of spatial variation as a result of mass change over the face of the crystal. The mass changes on the thin-film matrix (<300 nm) caused by adsorption or desorption of the sorbates were in situ monitored by an auto-data-acquisition system. The system is sensitive to a change of sorption of 0.04 monolayer nitrogen on nonporous surfaces at constant partial vapor pressure. The thickness and refractive index of the coatings were measured by a spectroscopic ellipsometer (incident angles of 65° and 70°, MOSS, ES4G, Sopra) at ambient conditions.

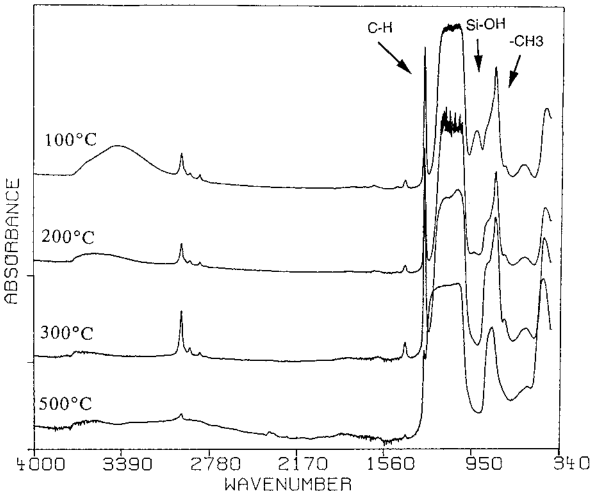

Figure 2. FTIR spectra of the 75% MTMS/(TMOS + MTMS) hybrid film thermal treated in air at different temperatures for 4 h.

Results and Discussion

Figure 2 shows the FTIR spectra of a hybrid film prepared from a coating solution derived from a 75% MTMS/(TMOS + MTMS) composition. One of the noticeable features is the Si−OH stretching vibration

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[19] Sarkar, A.; Yan, Y.; Fuqua, P. D.; Jahn, W. In *Glass Surface, Sol−Gel Glasses: Proceedings of XVII international Congress on Glass;* Gong, F., Ed.; Academic Publishers: Beijing, 1995; Vol. 4, p 228.

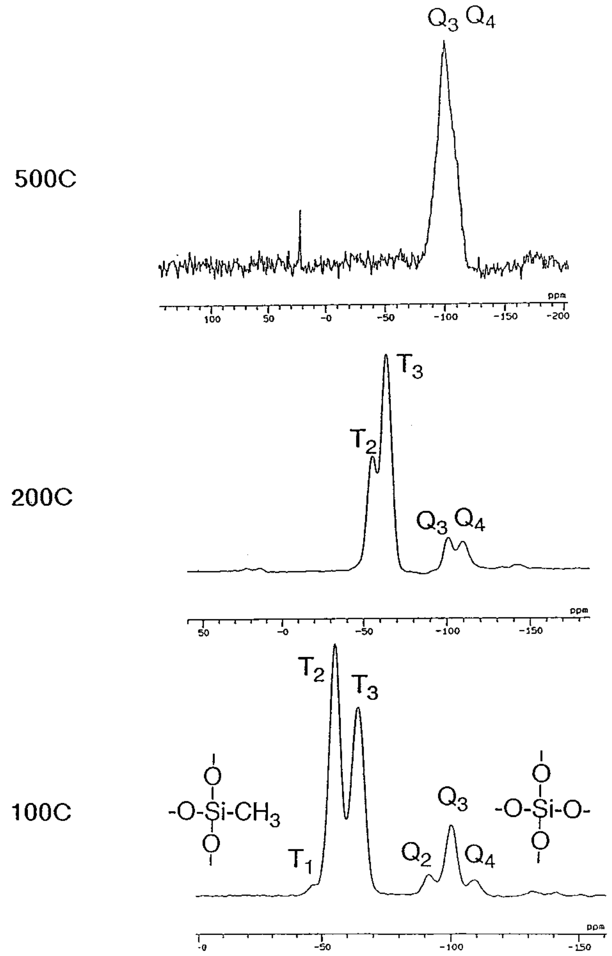

Figure 3. ^{29}Si CP/MAS solid-state NMR spectrum of 75% MTMOS/(TMOS +MTMS) hybrid materials thermally treated at different temperatures in air for 4 h.

Table 1. Comparison of the Properties of the 75% MTMS/(TMOS + MTMS) Hybrid Film with Inorganic Silica Film Prepared from Identical Alkoxides to Solvent, Water, and Acid Ratios and Cured at 200 °C

	thickness (nm)	refractive index	sorption of H_2O by wt at room temp ($P/P_0 = 50\%$)	sorption of N_2 by wt at LN_2 ($P/P_0 = 50\%$)
silica film	201.9	1.44	3.01%	0.677%
hybrid film	184.4	1.41	1.51%	8.40%

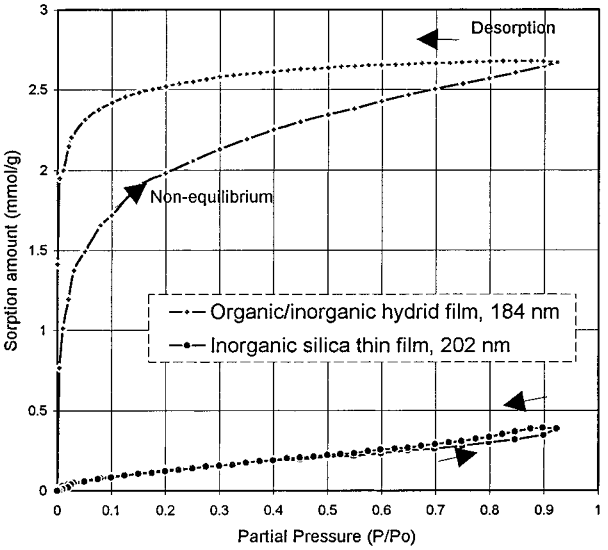

Figure 4. Adsorption–desorption isotherms of nitrogen at nitrogen boiling temperature on the inorganic silica and 75% MTMS/(TMOS + MTMS) hybrid methylsilica thin film (thickness <210 nm) cured at 200 °C.

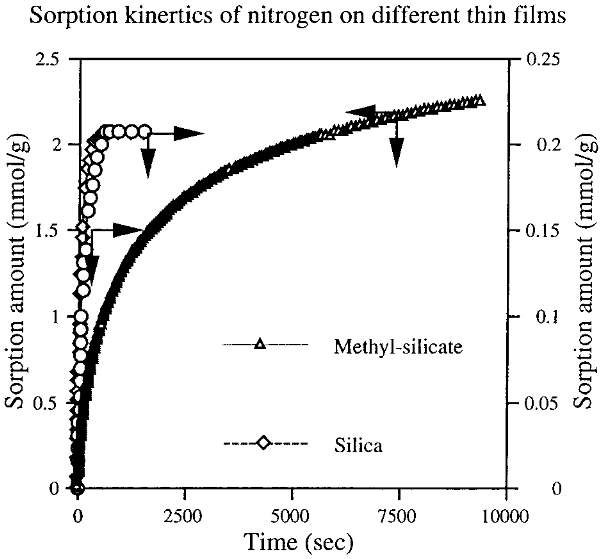

Figure 5. Adsorption kinetics of nitrogen at nitrogen boiling temperature on the inorganic silica and 75% MTMS/(TMOS + MTMS) hybrid methylsilica thin film (thickness <210 nm) cured at 200 °C.

at 930 cm^{-1} shown after 100 and 200 °C thermal treatments. The presence of a larger amount of the Si–OH groups at low temperature possibly provides sufficient ligands to bond the coating to the substrate. Indeed, this coating solution can form uniform, continuous thin-film coatings on the inorganic, metallic, and polymeric surfaces by using dip- or spin-coating techniques. The intensity of this peak is decreased with increasing temperature, which indicates the formation of more Si–O–Si linkages in the hybrid network. The presence of the organic terminal groups is reflected by the presence of the symmetric C–H bending vibration at 1277 cm^{-1} and the CH_3 rocking modes at 775 cm^{-1}. The intensity of the organic groups begin to decrease after thermal treatment in air between 280 and 300 °C, and the vibrations of those peaks can still be observed up to 420 °C. Thermal analyses of the bulk sample treated at different temperatures were consistent with the above observation.[20]

The hybrid materials cured at 100 °C are mainly cross-linked by T_2, T_3 and Q_2, Q_3 according to ^{29}Si CP/MAS NMR data (Figure 3), where $T_{2,3}$ and $Q_{2,3}$ denote the proportion of cross-linking silicon site in the network derived respectively from the MTMS and TMOS precursors. With increased temperature, cross-linking of the silicon increases, T_3, and Q_3 and Q_4 become dominant and most of Q_2 is converted to Q_3 and Q_4. At high temperature (500 °C), only Q_3 and Q_4 could be observed due to the decomposition and oxidation of Si–CH_3 bonds in agreement with IR results. ^{13}C CP/MAS solid-state NMR spectra (not shown) suggesting the presence of two kinds of C groups after 100 °C thermal treatment: the dominant peak located at −2.46 ppm is attributed to the Si–CH_3 carbon resonance, and a small peak at 51.7 ppm is associated with the SiO–CH_3 carbon resonance.

Table 1 lists some of the properties of the methyl–silicate hybrid thin film compared with those of a silica film. The silica film was prepared from a TMOS derived

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(20) Sarkar, A.; Yan, Y.; Duan, Z.; Hoshino, Y.; Ray Chaudhuri, S. *Mater. Res. Symp. Proc.* **1996**, *435*, 351, 307.

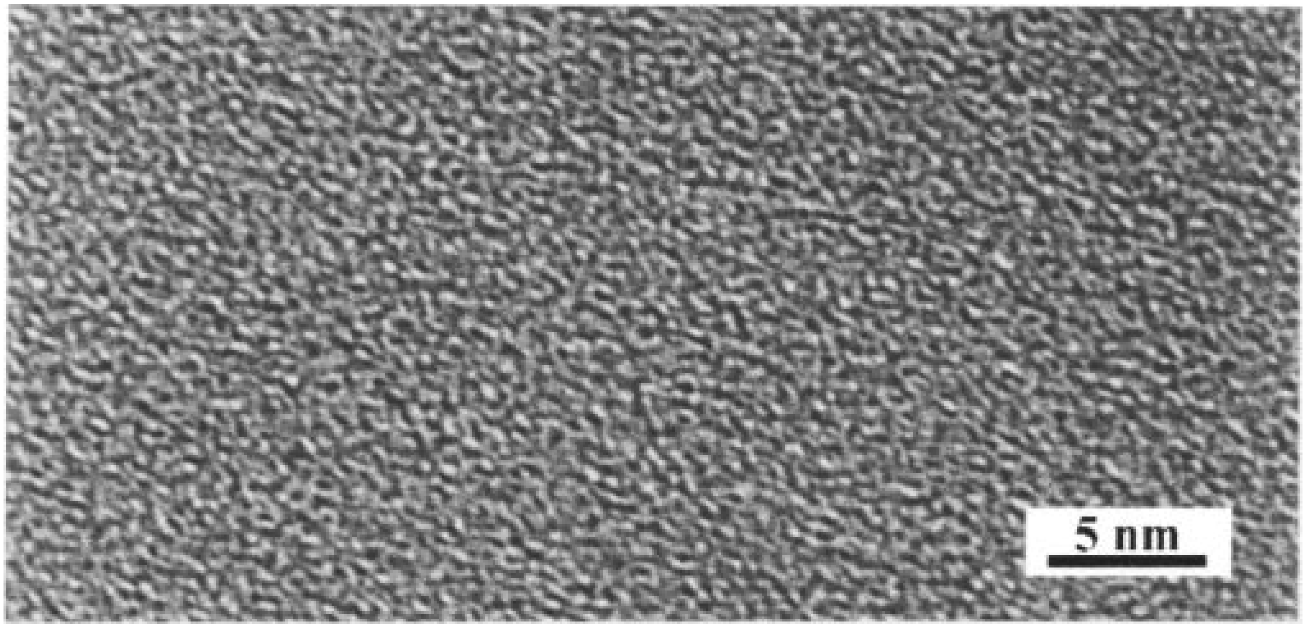

Figure 6. TEM micrograph of 75% MTMS/(TMOS + MTMS) hybrid thin film deposited on silicon wafer cured at 200 °C.

sol−gel coating solution. Both kinds of coating solutions were prepared from an identical alkoxides to solvent, water, and acid ratios. The prepared films have a comparable thickness, and the refractive indexes have values of 1.44 and 1.41 at the wavelength of 550 nm, respectively, for the silica and hybrid films cured at 200 °C. Those values are consistent with those reported by others.[21] One distinct difference between the films is the sorption capacity of water and nitrogen at 50% partial pressure. It was observed that only 1.50 wt % of water adsorbed on the hybrid film, while more than 3% adsorbed on the inorganic silica film dehydrated at 200 °C. In contrast the hybrid film has a nitrogen sorption capacity of more than 8%, which is 12 times higher than that adsorbed on the inorganic film. Figure 4 shows the sorption−desorption isotherm of nitrogen on the hybrid film deposited on a piezoelectric crystal. The adsorption isotherm, as indicated in the sorption kinetics (Figure 5), is a nonequilibrium process since each point was taken at 3 h intervals after changing the partial pressure. The desorption curve of the isotherm for the hybrid film shows a type I BET isotherm at liquid nitrogen temperature, which indicates the presence of microporosity in the film,[22−24] whereas the sorption and desorption curve of silica-based film shows a type II BET isotherm corresponding to a nonporous surface. These results suggest that the hybrid film is microporous and hydrophobic, whereas the inorganic film is nonporous and hydrophilic. The lower refractive index of the hybrid film obtained at ambient conditions can be partially attributed to the presence of porosity and the hydrophobic surface property in comparison with the inorganic film.

The sorption kinetics of nitrogen on the two films also behaved completely different (Figure 5). Sorption equilibrium is reached in a couple of minutes on the silica film (0.21 mmol/g). In contrast, no equilibrium is reached on the hybrid film (<200 nm) after 3 h of sorption (2.4 mmol/g). The activated diffusion sorption kinetics also suggests that the pore size of the amorphous hybrid thin film is close to that of the kinetic diameter of nitrogen at nitrogen boiling temperature. If the sorption of nitrogen on the bulk hybrid gel occurs at the same rate as that on the thin film, it might take more than 20 years for the sorption to reach equilibrium on a 8 cm^3 cubic bulk gel. Such an assumption also possibly explains why the bulk hybrid gels have been commonly reported as nonporous materials.

It should be also noted that the hybrid materials have a similar structure and composition compared to silicone based materials, such as poly(dimethylsiloxane). Siloxane polymers based on urethane block siloxanes, fluorinated side-chain siloxanes, and siloxanes macromers have been recently reported.[25] Polysiloxanes are known to be porous and have much higher permeability to gases.[26] Because of this, polysiloxane-based elastomers have long been considered as viable contact lens materials and membranes for extended wear.[27,28] The hybrid films of this study are about 100−1000 times thinner than the conventional polysiloxane membrane. The former materials have a relatively higher extent of crossing linkage and tend to be rigid, the latter ones have a 2-dimensional chain linkage attached with more organic groups to terminate the Si−O−Si linkage and tend to be elastomeric. The sorption study also suggests that the hybrid materials have a much smaller pore size compared to the silicone-based materials.

The presence of micropores in the hybrid film is also quantitatively supported by TEM studies. Figure 6 is the TEM image of the surface morphology of the film.

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[21] Dislich H. In *Sol−Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes*; Klein, L. C., Ed.; Noyes Publications: Park Ridge, NJ, 1988; p 50.

[22] Gregg, S. J.; King, K. S. *Adsorption Area and Porosity*, 2nd ed.; Academic Press: New York, 1982.

[23] Lowell, S.; Shields, J. E. *Powder Surface Area Porosity*; Chapman and Hall: New York, 1991.

[24] The micropore sizes in principle can be obtained from the Horvath−Kawazoe method by analyzing the sorption isotherm obtained in the region of 10^{-7}−10^{-2} partial pressure. Since the minimum partial pressure of the experiment was 5×10^{-4}, the effective pore size of the hybrid film was derived only from the characteristics of BET classification and its diffusion adsorption kinetics.

[25] Kunzler, J. F.; McGee, J. M. *Chem. Ind.* **1995**, *16*, 651.

[26] Mark, J. E. In *Silicon-based Polymer Science*: *A Comprehensive Resource*; Zeigler, J., Fearon, F. W. G., Eds.; Adv. Chem. Series 224; ACS: Washington, DC, 1990; p 47.

[27] Burdick, D. F.; Mishler, J. L.; Polmanteer, K. E. U.S. Patent 2,341, 490, 1967.

[28] Lai, Y. C. *Polym. Mater. Sci. Eng.* **1992**, *66*, 376.

[29] Seddon, A. B.; Capozzi, C. A.; Lana, S. L.; King, T. A.; Li, X.; Gall, G. J. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 181.

The observation of about 0.3–0.5 nm micropores is consistent with the nitrogen sorption kinetic data. A similar feature of TEM micrographs on the bulk hybrid materials and AFM micrographs of thin-film coatings with similar composition has also been reported.[20,29] In a comparative study, the nanofeatures of the hybrid film are absent from the dense, inorganic silica film (not shown). The amorphous, hybrid film possibly consists of interconnected porous channels around the organic phase. In contrast to the crystalline zeolitic systems, the narrow and tortured hybrid pores may account for the activated diffusion sorption of nitrogen on the film. It is possible to control the size of the micropore by tuning the molecular size and concentration of the organic groups, hence the extent of the network cross-linkage in the hybrid materials. The hybrid microporous thin films reported here may be interesting materials as the top layer coating for design separation membranes, such as separation of nitrogen (kinetic diameter is 3.64 Å, quadrupole 0.31 Å^3, and polarizability 1.74 Å^3) and oxygen (3.46 Å, 0.10 Å^3, and 1.58 Å^3) from air.

Conclusions

Porous hybrid thin films have been prepared by incorporation of stable, terminal methyl groups into the inorganic silica network via a sol–gel process followed by a curing step. The hybrid film has a micropore size close to the kinetic diameter of nitrogen while maintaining a hydrophobic surface. Formation of the organic–inorganic molecular composite can provide a general route to design microporous thin films.

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