Hydrophobic silica aerogels by silylation

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ABSTRACT

In this work, silica gel networks were modified with a silylating agent dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF_3) to obtain hydrophobic aerogels of various surface energy values. The baseline aerogels were synthesized from tetraethoxy silane (TEOS) using a two-step sol–gel process followed by supercritical drying in liquid carbon dioxide. The resultant aerogels were characterized using scanning electron microscopy, Instron tensile tester, contact angle goniometry, and nitrogen adsorption–desorption isotherms. Three modification methods were studied. In method 1, TEOS and SiF_3 were combined before gelation; in method 2, SiF_3 was added after TEOS was hydrolyzed and before its condensation, and in method 3, SiF_3 was added after the gels were produced from TEOS. It was found that method 3 produced the best results in terms of achieving high values of hydrophobicity and compressive properties. The data on solid state ^{13}C and ^{29}Si NMR spectra revealed chemical reactions between the silylating agents and the silanol groups on silica surface. The bulk density and the fractal dimensions of silica networks gleaned from small angle X-ray scattering (SAXS) data showed weak dependence on the degree of silylation. The silylation process rendered the aerogels strongly hydrophobic and also doubled its compressive modulus.

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1. Introduction

Aerogels are highly porous solid materials derived from gels by replacing the liquid inside the pores by air [1]. The solid particle networks and associated pores in the gels survive the capillary stress if the liquid is removed under supercritical conditions. Silica aerogels are a unique class of highly porous materials (porosity > 95%) and offer the following properties: low density (3–350 mg/cm³) [2,3], large surface area (500–1200 m²/g), low thermal conductivity (ranging from 0.004 to 0.03 W/m·K), low dielectric constant (1.1–2.2) [4,5], low index of refraction (~1.05) [6], and an array of optical appearances such as transparency [7,8], opacity, or translucence [9]. These interesting properties make silica aerogels suitable for applications in high-energy particle physics (Cherenkov emitters) [10]. Monolithic silica aerogels are well suited to deal with the energy savings coupled with alleviating some of the environmental concerns [11], e.g., transparent and super-insulating double windows [12], or promising space science application [13]. Additionally, silica aerogels can be used as adsorbents, e.g. for oils and organic liquids, or used as sensors [14], catalysts [15], storage media, and templates [16]. A number of applications of silica aerogels in life sciences are emerging, such as in biocatalysis [17] with a lipase enzyme or in a process to detect a viral particle by immobilized bacteria [18].

Despite these applications, fragility at low mechanical stress and hygroscopic nature are two deterrents to more widespread applications.

It is believed that a few Si–O–Si bonds in the "neck" regions hold the neighbouring spherical secondary silica particles together [19]. Consequently, much focus is given to the neck regions for reinforcement of silica based aerogels [20–22]. Various approaches have been exploited by building extra covalent bonds in the "neck" regions using small molecules, polymers, and hybrid nanoparticles. Leventis et al. [19,23,24] reported mechanically reinforced silica aerogels through the reaction of isocyanates with the residual hydroxyl groups on the secondary silica particles. Duan et al. reported significant improvements in compressive modulus and hydrophobicity by reacting silica particles with 1–3 nm size polyhedral oligomeric silsesquioxane (POSS) molecules [25] and by using silane-terminated polyurethanes [26] as a co-precursor with small changes in bulk density.

To alter the hygroscopic nature of silica aerogels and to make them suitable for more widespread applications, surface modification of silica particles with silane-containing organic groups was considered in this work. Previous work showed that moderately hydrophobic [27] and even super-hydrophobic [28] silica aerogels can be obtained by aging the alcogels in solution of halogen-containing silanes; alkyl–alkoxy silanes with chlorine atoms are the most commonly used [27,28]. Water contact angle values were measured by placing water droplets directly on the aerogel surfaces and, therefore, reflected the influence of trapped air inside the mesoporous structures. However, surface modification alleviates the concerns related to the collapse of silica networks during

Table 1

Composition and contact angle data of TEOS-based aerogels as function of different modification steps. The contact angle data was obtained by placing liquid drops on compressed discs of aerogels.

Sample no.	Modification process	Weight of SiF_3 added (g)	Contact angle with H_2O	Contact angle with CH_2I_2
1	TEOS w/o SiF_3	None	$27.5 \pm 0.3°$	$25.7 \pm 0.4°$
2	Method 1	4.0	$106.0 \pm 0.6°$	$51.5 \pm 1.0°$
3	Method 1	5.0	$134.0 \pm 1.0°$	$85.9 \pm 0.6°$
4	Method 2	4.0	$70.6 \pm 0.9°$	$38.6 \pm 0.6°$
5	Method 3	5.0	$142.2 \pm 0.8°$	$106.1 \pm 0.8°$

drying and particle network coarsening due to reactions between adjacent silica particles. Therefore, it is critical to understand the impact of silylating agent and incorporation process on the final morphology and properties of aerogels. A more thorough review on synthesis of hydrophobic silica aerogels is presented elsewhere [29].

In this work, a silane molecule with trifluoropropyl substitution — dimethoxy-methyl (3,3,3-trifluoropropyl) silane, denoted as SiF_3, was used to modify the silica alcogels. It was expected that this silylating agent would diffuse into the small pores of silica alcogels and eliminate the residual Si–OH groups by silylating reactions. As a consequence, the process would render the surfaces of the silica particles hydrophobic and, in addition, might produce mechanical reinforcement. It was anticipated at the outset that such treatment would not exert significant effects on morphology and density. The study answered several questions: What should be an appropriate scheme for introduction of SiF_3 molecules into silica networks? How much SiF_3 can enter into silica network? Can SiF_3 molecules produce mechanical reinforcement, much the same way as coarsening of silica networks? Silica networks are known to have fractal structures. Do SiF_3 molecules alter the fractal nature of silica particles or the pore structures or the density? What are the effects of silylation on surface energy of silica particles? Prior work [28]

reported super hydrophobic aerogels by treating silica particles with TMCS and HMDZ, although the changes of polarity of silica particles due to such treatment were not reported. Moreover, it is evident that measurement of water contact angle on aerogel surface would be strongly influenced by air trapped inside the mesoporous structures. Such measurements would not yield surface energy data as function of chemical treatment of silica particles.

2. Experimental

2.1. Materials

The silica particles network was derived from tetraethoxy silane (TEOS) [27,28]. Dimethoxy-methyl (3,3,3-trifluoropropyl) silane (denoted as SiF_3) was selected due to its high fluorine content and higher surface energy compared to chlorine atoms. All solvents and reagents were used as received from the manufacturers. TEOS, nitric acid (70%), and ammonium hydroxide solution (28.0–30.0% NH_3 basis) were purchased from Sigma Aldrich. Reagent grade ethanol was purchased from Fisher Scientific. Dimethoxy-methyl (3,3,3-trifluoropropyl) silane (97.0% GC grade) was purchased from Gelest Inc. (Morrisville, PA).

2.2. Preparation of silica aerogels modified with SiF_3 silane

The synthesis of aerogels involved two steps: (1) preparation of the alcogel and (2) removal of the solvent from the alcogels via supercritical drying. The alcogels were prepared by a two-step acid–base catalyzed sol–gel process. Solution A, containing 22.30 mL TEOS, 7.20 mL of water (7.20 g) and 30.50 mL ethanol, was hydrolyzed under acidic conditions using nitric acid (pH ~ 2). The mixture was sealed and stirred by a stir bar for 1 h and then cooled in a dry ice–acetone bath. Solution B, which contained 5.40 mL water, 34.60 mL ethanol, and a base catalyst ammonium hydroxide solution (pH ~ 9), was cooled in dry ice–acetone
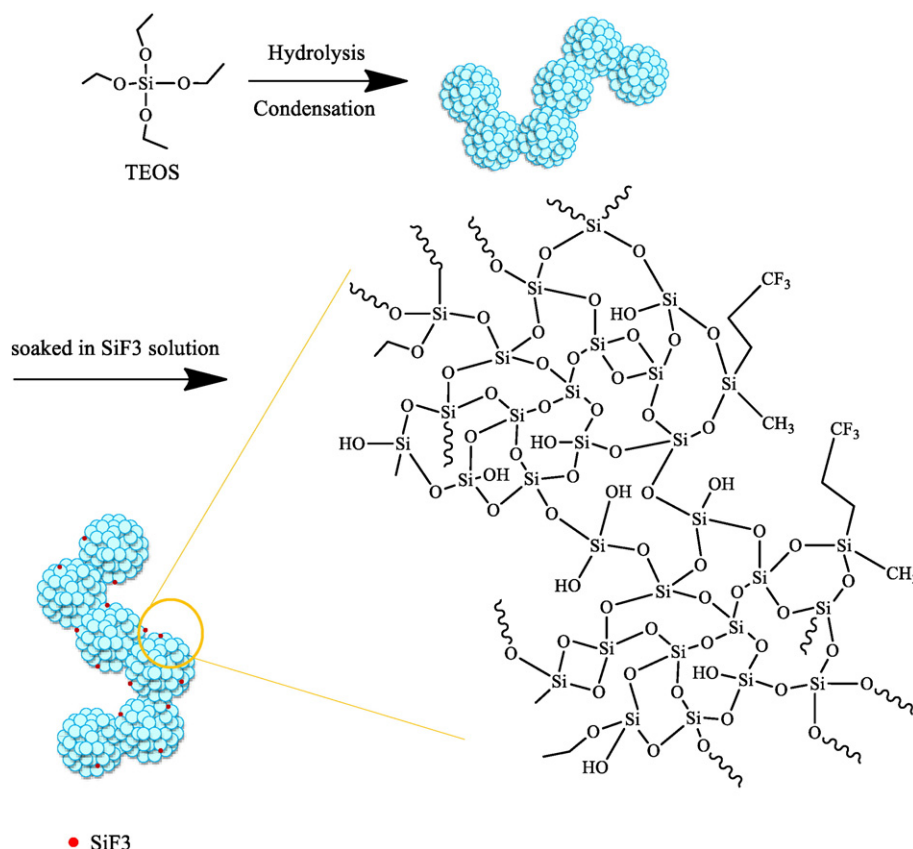

Fig. 1. Structure of silica networks modified with SiF_3 by method 3.