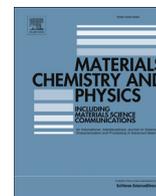




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# Ambient pressure dried shape-controllable sodium silicate based composite silica aerogel monoliths

Zaidong Shao<sup>a,1</sup>, Xiaoyong He<sup>a</sup>, Ziwei Niu<sup>a</sup>, Teng Huang<sup>a</sup>, Xuan Cheng<sup>a,b,\*</sup>, Ying Zhang<sup>a,b</sup>

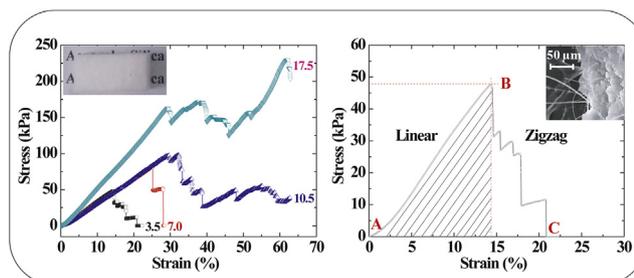
<sup>a</sup> Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, Fujian 361005, China

<sup>b</sup> Fujian Key Laboratory of Advanced Materials, Xiamen University, Xiamen, Fujian 361005, China

## HIGHLIGHTS

- Fiber reinforced silica aerogel monoliths with shape controllable.
- Possess excellent integrity, low thermal conductivity and good mechanical property.
- Discuss the effects of fiber on structures and properties of silica aerogels.
- Conclude the complete surface modifications achieved by a two-step reaction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The shape-controllable sodium silicate based fiber reinforced silica aerogel monoliths with excellent integrity and thermal insulating property were prepared by ambient pressure drying. The non-woven silica fiber up to 17.5 wt% could be uniformly distributed and well incorporated into the three-dimensional silica network since the fiber introduced and silica precursor could simultaneously react with methyltriethoxysilane (MTES) and trimethylchlorosilane (TMCS) during the two-step surface modification. The densities and porosities of the composite silica aerogel monoliths were 0.104–0.146 g/cm<sup>3</sup> and 93%–95%, respectively, with the thermal conductivities of 21–31 m W/(m K) and the average modulus of 323–535 kPa. The characteristic linear and zigzag responses were observed from the compression stress–strain curves. Incomplete modification due to a large amount of fiber incorporation led to severe volume shrinkage during ambient pressure drying.

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## 1. Introduction

Silica aerogel has been considered as the best thermal insulating material and the lightest solid material owing to its extremely low

thermal conductivity (12–20 m W/(m K)) and density (0.03 g/cm<sup>3</sup>) [1]. The apparent fragility and poor integrity have limited its application as a monolithic material. Fiber reinforcement can significantly improve the integrity and strength of composite silica aerogel [2]. Diversified fibers including cellulose fiber [3], non-woven polypropylene fiber [4], silica fiber or glass fiber [5–7], ceramic fiber [8], polymer fiber [9,10], and carbon fiber [11] have been used to reinforce silica aerogel matrix. The integrity and flexibility with the enhanced mechanical property could be

\* Corresponding author. Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, Fujian 361005, China.

E-mail address: [xcheng@xmu.edu.cn](mailto:xcheng@xmu.edu.cn) (X. Cheng).

<sup>1</sup> Present address: Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, China.

achieved, but the density and thermal conductivity of composite silica aerogel were adversely affected. For example, the composite silica aerogel prepared by crosslinked cellulose fiber exhibited high density ( $>0.3 \text{ g/cm}^3$ ) and large thermal conductivity ( $30\text{--}50 \text{ mW/m}\cdot\text{k}$ ) with low silica content ( $\sim 60\%$ ) [3], while the ceramic fiber reinforced silica aerogel showed the density of  $0.29 \text{ g/cm}^3$  with the compression stress of  $\sim 1 \text{ MPa}$  at 30% strain [8]. However, the current predominant preparation process to obtain highly integrated fiber reinforced silica aerogel requires relatively matured but rather dangerous supercritical drying. Furthermore, fibers have to be pretreated to form woven fiber blanket or crosslinked fiber structure.

In recent years, much effort has been made to synthesize silica aerogel monolith with an alternative safer and less expensive drying. By simply introducing surface modification and solvent exchange after sol–gel processes, ambient pressure drying can be substituted for supercritical drying. Tetraethylorthosilicate (TEOS) has been most widely used as a silica precursor, and preparations of TEOS based silica aerogel monoliths via ambient pressure drying have been extensively investigated [12,13]. Sodium silicate (water glass) has been considered as an idea inexpensive silica precursor to prepare silica aerogels. Compared with TEOS, more than 90% (by volume) of pore water generated from sodium silicate seriously inhibit the hydrogel to react with modifying agents. Therefore, the synthetic routes of ambient pressure dried sodium silicate based silica aerogels are also very complicated with huge consumptions of expensive modifying agents, which leads to poor physical properties [14,15]. By using a mixed silica precursor made of sodium silicate and TEOS with fractions varying from 0 to 50 vol% TEOS, the density of  $0.104 \text{ g/cm}^3$  with the porosity of 95.0% could be obtained with 25 vol% TEOS–75 vol% sodium silicate to be immersed into silica blankets which were prepared by woven glass wool and modified by alumina sol [16]. The more portions the sodium silicate presented, the poorer were the physical properties. The density and BJH pore volume of glass fiber (silica fiber) reinforced silica aerogel were  $0.127 \text{ g/cm}^3$  and  $2.66 \text{ cm}^3/\text{g}$ , respectively with TEOS based, while  $0.195 \text{ g/cm}^3$  and  $1.52 \text{ cm}^3/\text{g}$ , respectively, with sodium silicate based [7]. However, because of poor integrity and poor physical properties associated with fiber reinforced silica aerogels prepared at ambient pressure drying, little information about thermal insulating and mechanical properties is available. Furthermore, the major drawbacks in preparation of ambient pressure dried fiber reinforced silica aerogels are the requirements of expensive TEOS as a main silica precursor, a complex surface modification and solvent exchange step which consumes a large amount of solvents and expensive modifying agents. The superhydrophobic and transparent ambient pressure dried sodium silicate based silica aerogel with the density as low as  $0.12 \text{ g/cm}^3$  could be prepared by a simple two-step surface modification route involving methyltriethoxysilane (MTES) modification and trimethylchlorosilane (TMCS) modification [17]. However, the monolithic silica aerogel exhibited visible cracks and poor integrity.

In order to overcome the fragility and to achieve good mechanical and thermal insulating properties of ambient pressure dried sodium silicate based silica aerogel prepared by the MTES–TMCS modification, the non-woven silica fiber was introduced to reinforce silica aerogel using the same preparation route. The amount of fiber added, the way through which fiber incorporated into aerogel matrix, and their effects in control structure and property were investigated. Possible formation mechanism of ambient pressure dried sodium silicate based fiber reinforced silica aerogel monoliths synthesized by the two-step MTES–TMCS modification is discussed.

## 2. Experimental

### 2.1. Materials and chemicals

Sodium silicate of industrial grade was provided by Fujian Sanming Tongsheng Chemical Co., Ltd., China. The sodium silicate was composed of 6.2 wt% sodium oxide ( $\text{Na}_2\text{O}$ ) with the molar ratio of silica ( $\text{SiO}_2$ ) to  $\text{Na}_2\text{O}$  being 3.13. Silica fiber was supplied by Xiamen Goot New Material Co., Ltd., China. The 732 cation exchange resin, trimethylchlorosilane (TMCS) ( $\geq 98.0\%$ ), ethanol ( $\geq 99.7\%$ ), ammonia (25.0–28.0%), and n-hexane ( $\geq 97.0\%$ ) were obtained from Sinpharm Chemical Reagent Company, China, while methyltriethoxysilane (MTES) ( $\geq 98.0\%$ ) was purchased from Shanghai Silicon Mountain Chemical Macromolecular Materials Company, China.

### 2.2. Preparation of silica aerogels

The sodium silicate based silica fiber reinforced silica aerogels (composite silica aerogels) were obtained based on the two-step surface modification and ambient pressure drying route of sodium silicate based silica aerogel (pure silica aerogel) as described previously [8]. Briefly, the hydrolysis of MTES was performed by dissolving MTES with distilled water in a beaker, followed by continuous agitation for 12 h. The solution containing the mixture of sodium silicate and hydrolyzed MTES passed through the 732 cation exchange resin and the collected silica sol had a pH range of 2.5–3.0. The weighed amount of silica fiber was added to the silica sol followed by stirred for 1 h in order to be dispersed in silica sol, then the ammonia was added to the silica sol to form hydrogel. After gelation, the silica hydrogel was immersed into ethanol at  $55 \text{ }^\circ\text{C}$  for 24 h to allow the strengthening of gel network and the alcoholization of silica hydrogel. The alcoholized silica aerogel was carried out by immersing in TMCS/ethanol/n-hexane solutions at  $35 \text{ }^\circ\text{C}$  for 48 h. Finally, the surface modified wetgel was washed by n-hexane in order to remove the remaining TMCS and dried at atmospheric pressure in an oven at  $55 \text{ }^\circ\text{C}$ ,  $80 \text{ }^\circ\text{C}$  and  $130 \text{ }^\circ\text{C}$  for 2 h, 3 h and 4 h, respectively. The volume ratio of hydrogel over ethanol was 1:1.2 during the alcoholization process. The molar ratio of MTES to sodium silicate was 0.3. The optimized volume ratio of TMCS/ethanol/hexane was determined to be 2:1:8. The amounts of silica fiber added into reinforced silica aerogels were selected to be 3.5, 7.0, 10.5 and 17.5 wt%. For comparison the pure silica aerogel was also prepared using the same synthesis procedure as that of the composite silica aerogel without adding silica fiber.

### 2.3. Characterizations of silica aerogels

The bulk density of either pure or composite silica aerogel was measured from weight to volume ratio, and the percentage of volume shrinkage was determined based the relative change in the volumes of wetgel and aerogel via ambient pressure drying. The surface area, pore volume and pore size were estimated by nitrogen adsorption–desorption isotherm (Tristar 3020). The surface and cross-sectional morphologies were examined by scanning electron microscope (LEO 1530, Germany). The thermal conductivity was measured by the transient plane heat source method (Hot-Disk, TPS 2500, Sweden). The compressive test was performed with the aerogel specimen having a dimension of  $10 \text{ mm} \times 10 \text{ mm} \times 15 \text{ mm}$  by universal testing machine (KaiQiangLi, KD-II 100N, China). The  $^{29}\text{Si}$  and  $^1\text{H}$  MAS NMR spectra were collected on a Bruker Avance III spectrometer at 400 MHz.

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