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A novel silica nanowire-silica composite aerogels dried at ambient pressure

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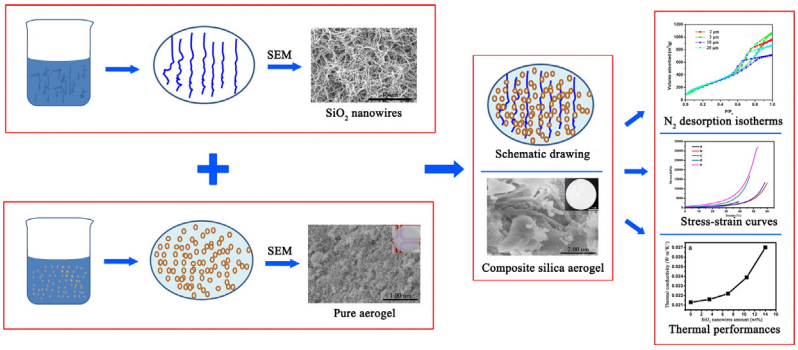
HIGHLIGHTS

- A novel silica nanowire-silica composite aerogels was prepared and dried at ambient pressure.
- The SiO_2 nanowire and silica aerogel matrix have excellent compatibility.
- The SiO_2 nanowires need not to be modified before being used to prepare composite silica aerogels.
- Silica nanowire-silica composite aerogels have outstanding mechanical and thermal insulation properties.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel silica nanowire-silica composite aerogels with excellent thermal insulation and mechanical properties was prepared by adding SiO_2 nanowires as a secondary phase into the silica matrix and drying at ambient pressure. The SiO_2 nanowires and silica aerogel matrix have outstanding compatibility and dispersibility because the components of nanowire and aerogel matrix all are silica, which contributes to the improvement of the mechanical property of the silica composite aerogels. The physical, mechanical and thermal properties of the SiO_2 nanowires based composite silica aerogel are investigated and discussed in detail. The results indicate that the monolithic aerogels with high specific surface area, porosity and large pore volume. The thermal conductivity of the composite silica aerogels only increases gently ($0.006\ W \cdot m^{-1}\ K^{-1}$) as the addition of SiO_2 nanowires rises from 0 wt% to 14 wt%, while their mechanical properties have been improved greatly. The SiO_2 nanowires based composite silica aerogel would be widely used in the thermal insulation application because of its outstanding thermal insulation property.

1. Introduction

In the past decades, silica aerogels have attracted great attention for their wide range of potential applications within the fields of thermal insulators, catalysis, drug release, drug delivery, waveguides and adsorption etc., because of their exceptional physical properties, such as high porosity and specific surface areas, low density and thermal conductivity [1–5]. However, the utilization of silica aerogels has been hampered by their poor mechanical properties. Silica aerogels are inherently fragile because of the weak pearl-necklace-like structure: the three-dimensional network consists of silica nanoparticles with diameters of

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3–10 nm connected by narrow inter-particle necks [1,2]. The reinforcement of silica aerogels by adding reinforced micro- or nanoscopic materials as a secondary phase into the silica matrix [6–11], such as nanoparticles [10,12,13], carbon nanotubes [14,15] or fibers has become one of the effective methods to improve the mechanical properties of the aerogels and without sacrificing other unique properties. With this strategy, the skeleton of the scaffold forms a continuous framework which mechanically supports the fragile mesoporous silica aerogel matrices.

The method about introducing various fibers into the matrix is simple, straightforward and easy adaptable to large-scale production. Many studies are made on this method of a secondary phase into the silica matrix, such as glass fiber [16–18], sepiolite fiber [19], mullite fiber [20,21], carbon fiber [22–24], ceramic fiber [11,25]and so on [26,27]. For example, Bo yuan et al. [16] introduced a kind of glass fiber based composite silica aerogel were prepared by press forming of silica aerogel powders and dispersed glass fibers. The mechanical property of the composite silica aerogel was improved but the heat insulation property was adversely affected. Also, glass fiber silica aerogel composites can be fabricated by immersing glass fibers into silica sol [17]. Kim et al. [18] synthesized glass fiber/silica aerogel composites by varying colloidal silica and tetraethylorthosilicate-based sol fractions. The aerogel composites synthesized from colloidal and TEOS-based mixed sols have bigger pore size and specific surface area than those of aerogel composites made of only colloidal silica. Li et al. [19] presented a sepiolite/silica aerogel composite prepared by supercritical drying, which has excellent mechanical property without sacrificing much thermal insulating performance. But the raw sepiolite fiber needs to be treated with ammonia and nitric acid before being added to the silica sol to prepare composite silica aerogels. Recently, He et al. [20] developed a high-strength mullite fibers reinforced ZrO_2–SiO_2 aerogels by a rapid gelation process. The ZrO_2–SiO_2 aerogels exhibit high compressive strengths and excellent thermal insulating performance. Al_2O_3–SiO_2 aerogel composites reinforced by mullite fibers were prepared by soaking with polycarbosilane solution and the pysrolysis which can be used as thermal insulations because of good thermal insulating property. Also, the mullite fibers was coated with SiC by using polycarbosilane as a precursor [21]. Ślosarczyk et al. [22,23] reported a carbon microfibers based composite silica aerogel dried in supercritical and ambient pressure conditions. The properties of the composite silica aerogels dried in supercritical and ambient pressure conditions were compared. The carbon fibers need to be treated chemically in hot nitric acid before being introduced to TMOS solution.

Fiber reinforcement contributes to the improvement of the mechanical property and integrity of the composite aerogels. Meanwhile, their thermal insulation property and density would be deteriorated. Furthermore, a surface modification of these materials was necessary to improve the compatibility between the added materials surface and the silica interface. The problem can be solved perfectly by introducing SiO_2 nanowires as a secondary phase into the silica matrix. This method has several advantages, namely (i) the SiO_2 nanowires and silica aerogel matrix have excellent compatibility and dispersibility because the components of nanowire and aerogel matrix all are silica. (ii) The SiO_2 nanowires need not to be modified before being used to prepare composite silica aerogels. (iii) The properties (e.g. thermal insulation property, mechanical property) can be improved highly because of the good compatibility. And the outstanding mechanical property would have a profound and positive effect on the practical application of aerogels.

In this work, we prepared composite silica aerogel**s** by introducing SiO_2 nanowires into the system to overcome the poor mechanical property and to achieve good thermal insulting properties of silica aerogel. The SiO_2 nanowires, without any modification, was added to the silica sol directly to prepare SiO2 nanowires based composite silica aerogel because of the excellent compatibility. Besides, the SiO_2 nanowires can exist in the silica sol stably for a long time. The SiO_2 nanowires based composite silica aerogel is characterized by scanning electron microscope and Fourier transform infrared spectroscopy. The mechanical and thermal properties of the SiO_2 nanowires based composite silica aerogel are also be investigated and discussed in detail.

2. Experimental

2.1. Raw material

Tetraethyl silicate (AR), 1-pentanol (AR), Ethanol (AR), Hydrogen chloride (36–38%, AR) and Trisodium citrate dihydrate (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Polyvinylpyrrolidone (PVP, molecular weight 40 kg/mol) was purchased from Sigma-Aldrich. $NH_3 \cdot H_2O$ (25–28%, AR), *N*-hexane (>99.0%) and Trimethylchlorosilane (TMCS) (>98.0%) were purchased from Aladdin Chemicals, China. All chemicals were used as received without further purification. The water (>18.2 MΩ cm) was obtained from a Millipore-Q water purification system (Millipore, USA) in this work.

2.2. Preparation of SiO_2 nanowires

SiO_2 nanowires were prepared through the simple one-pot method [28,29]. In a typical synthesis, polyvinylpyrrolidone (15 g) was added to 1-pentanol (150 ml) in a 250 ml glass flask. After sonicating for 2 h, absolute ethanol (15 ml), deionized water (4.2 ml), and 0.18 M sodium citrate dihydrate solution in water (1.5 ml) were added to the mixture. The flask was shaken by hand to mix its contents. Then, ammonia (3 ml) was added, the flask was shaken again and tetraethylorthosilicate (1.5 ml) was added to the mixture. After shaking again the solution, the flask was left to rest at 90 °C for 15 min, 30 min, 90 min or 180 min to get SiO_2 nanowires with different lengths. Finally, the reaction mixture was centrifuged and washed with ethanol and water for several times.

2.3. Preparation of SiO_2 nanowires based composite silica aerogel

In this work, SiO_2 nanowires based composite silica aerogel was prepared based on the two-step surface modification and ambient pressure drying route of SiO_2 nanowires based composite silica aerogel as described previously [30]. A flowchart of synthesis of SiO_2 nanowires based composite silica aerogel is presented in Fig. 1. The experimental parameters have been modified to prepare silica aerogel. Briefly, a certain amount of SiO_2 nanowires were dissolved in absolute ethanol (11.7 ml) by sonication for 10 min. When all SiO_2 nanowires have been dissolved, deionized water (1.8 ml) and tetraethylorthosilicate (5.6 ml) were added to the mixture. Hydrogen chloride was added to the solution to adjust its PH value about 2 before magnetic stirring for 30 min. Then, the ammonia was added to the solution to form silica wetgel. After gelation, SiO_2 nanowires based composite silica wetgel was immersed in ethanol at 55 °C for 48 h. And then was immersed in TMCS/ethanol/*n*-hexane mixture at 35 °C for 48 h. Finally, the wetgel was washed by n-hexane and dried in an oven at atmospheric pressure at 55 °C, 85 °C, and 135 °C for 24 h, 12 h, and 6 h, respectively. SiO_2 nanowires reinforced silica aerogels with varying amount of SiO_2 nanowires (3.5, 7, 10.5 and 14 wt% of SiO_2 nanowires with respect to the total silica content) have been prepared in this study.

2.4. Characterization

The morphology of the SiO_2 nanowires and the composite silica aerogel were characterized with a field-emission scanning electron microscope (FESEM, Hitachi S-4800). Intelligent Fourier transform infrared spectrometer (NICOLET 6700) was used to record Fourier transform infrared spectrum (FTIR) of the SiO_2 nanowires based composite silica aerogel. And its photos were recorded with a Canon EOS 500D digital camera. Water contact angles were measured on an OCA20 system (Data-physics, Germany) at room temperature. The