Original Research Paper

Rapid synthesis of sodium silicate based hydrophobic silica aerogel granules with large surface area

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A B S T R A C T

In this study, we tried to synthesize ultralow density and super hydrophobic silica aerogel with extra high specific surface area, by using absolutely cost effective processing from sodium silicate. Hydrosol was obtained through ion exchange. To reduce the processing time, the gels were mechanically agitated to granules before solvent exchange. N,N-Dimethylformamide (DMF), serving as drying control chemical additive (DCCA), was introduced to reduce shrinkage. When the molar ratio of Si in sodium silicate to DMF is 0.31, the pore size distribution is the narrowest. Before dried under ambient pressure, the gels were surface modified by Trimethylchlorosilane (TMCS) in order to make sure the aerogels are hydrophobic. And the proper molar ratio of TMCS to pore water is 0.0233 which is much lower than that in previous experiments. The resulting aerogels have well-developed mesoporous structure with extremely high specific surface area (817 m^2/g) and super hydrophobicity (contact angle of 165°).

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1. Introduction

Silica aerogels are translucent and thermal insulating material consisting of nanoparticle building blocks, networked together to form an open, highly porous structure. They have large surface area (500–1500 m^2/g), high porosity (80–99%), low bulk density (0.03–0.35 g/cm^3). Due to these excellent properties, silica aerogels have attracted much attention for they have potential to be applied in many fields. Silica aerogels can serve as thermal super-insulators in solar energy systems, refrigerators, thermal flasks [1], internal confinement fusion (ICF) targets for thermonuclear fusion reactions [2], very efficient catalysts and catalytic supports [3]. The extremely low density and high surface area of monolithic aerogels provide an opportunity to improve the performance of various metal-oxide-based devices, including gas-and bio-sensors, batteries, heterogeneous catalysis devices, and low dielectric constant materials for integrated circuits (low-k dielectrics) [4].

Silica aerogels are produced by removing entrapped solvent from wet gel while maintaining its nanostructure. Several researchers have used supercritical organic solvents for drying [5,6] to synthesize silica aerogel, which avoids the collapse and shrinkage

during drying. However, supercritical drying, requiring high pressures (5–10 MPa), is cost-expensive. Some other researchers have prepared silica aerogel using tetraethoxysilane (TEOS) under ambient pressure [7,8]. However, TEOS is expensive in price. To further reduce the cost, the sodium silicate (a more inexpensive precursor) based aerogel has been synthesized. To remove Na$^+$ in the sol, Bangiet et al. [9] soaked the gel in water after a two-step sol–gel process, but the surface area of synthesized silica aerogel is just 425 m^2/g. Watervapor passing through the gel was employed by Gurav [10], but it costs too much energy to make vapor. Besides, the aerogels' surface area is 510 m^2/g. Through ion exchange, Fei Shi et al. [11] have prepared sodium silicate based silica aerogels with surface area of 618 m^2/g. Hwang et al. [12] have synthesized sodium silicate based silica aerogels via single step solvent exchange/surface modification with help of ion exchange in more than 5 days. Large amount of Trimethylchlorosilane (TMCS) was used to complete the modification where the molar ratio of TMCS to pore water ranged from 0.25 to 0.4. However TMCS is expensive, which will largely increase the production cost. In addition, the areogels' surface area increased to 625 m^2/g.

The present study introduces two step solvent exchange and surface modification method, in which the TMCS consumption is less than one tenth of that needed in single step solvent exchange/surface modification method. It largely reduces the production cost. To control the pore size distribution, DMF, serving as DCCA, has been used to study the effect on properties of organic

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silicon source TEOS or TMOS based silica aerogels [13,14]. In this work, DMF has been introduced in the synthesis of sodium silicate based silica aerogel, aiming to act as DCCA and to obtain a well distributed pore structure. Its effect on the properties of this aerogel was studied for the first time as far as we know. In addition, by mechanically agitating the gels from pieces to small granules, the contact area between the gels and liquid agents (exchange solvent and modification agent) increased, and thus the preparation period reduced to ∼2 days.

2. Experimental procedure

2.1. Sample preparation

Silica aerogels were prepared by a single-step sol–gel process followed by ambient pressure drying. The precursor used for preparation of hydrogels was sodium silicate (wt 32%, QDSS, China, $n(Na_2O): n(SiO_2) = 1:3.55$). Other agents, including ammoniumhydroxide (NH_4OH) as base catalyst, DMF as DCCA, ethanol (EtOH) and n-hexane as exchanging solvents and TMCS as a silylating agent, are the same as our previous work [15].

The sodium silicate was diluted with deionized water (DI·H_2O). To avoid the effect of NaCl, a strong acidic cation resin (732# resin, SCRC, China) of the sulphonated polystyrene type was selected to remove sodium ions in the sodium silicate solution. The collected silica sol had a pH ranging 3–4. Then 0.5 mol/L aqueous NH_4OH solution was added to modify the pH of the solution to 6 and various amount of DMF was added to the solution if necessary. The gelation occurred and porous network formed. DI·H_2O was added to age the gel for 12 h. Then the gel with EtOH was mechanically agitated to granules at ∼400 r/min for 5 min followed by the solvent exchange and surface modification process at stirring of ∼30 r/min. EtOH was used to exchange water within the pores of hydrogel twice within 12 h and the ethanol was replaced by n-hexane twice in 12 h. All of the age and exchange process was carried out in 45 °C water bath. The surface modification of the gel was carried out by adding the silylating mixture of TMCS: hexane in the volume ratio of 15% under condition of 45 °C water bath in 12 h. Then the silylated gel was dried in ambient pressure at 60 °C for 2 h and finally dried at 100 °C for 4 h to get silica aerogel.

2.2. Characterization

The bulk density of the aerogel sample was calculated by measuring its mass to volume ratio. The porosity of the aerogels was calculated using the following formula:

$$\text{porosity} = \left(1 - \frac{\rho_a}{\rho_s}\right) \times 100\% \tag{1}$$

where ρ_a is the bulk density of aerogel and ρ_s is the skeleton density of the silica aerogels, generally the value of ρ_s is 2.2 g/cm³.

The contact angle measurements were performed using a KSV (Helsinki, Finland) CAM 200 contact angle goniometer at ∼20 °C. The thermal stability of aerogel sample was studied by the thermal gravimetric and differential thermal analysis (TG-DTA) using SDT Q600 (TA Instruments, USA). TG-DTA can also help to decide oxidation temperature of –CH_3 group contained in the aerogel. It is the temperature up to which the silica aerogel samples retain its hydrophobicity. The hydrophobic nanoporous silica aerogels with a weight of 6 mg were heat-treated in air, from room temperature (25 °C) up to 800 °C, with a controlled heating rate of 10 °C min⁻¹. The microstructure and morphology of the aerogels were studied using Scanning Electron Microscope (SEM) (SIRION 200, FEI, USA). The specific surface areas were determined by nitrogen sorption isotherms with standard Brunauer–Emmett–Teller (BET)

analysis (Tristar II 3020M, Micromeritics Instrument Corporation, USA). The pore size distributions (PSD) were estimated by the Barrett–Joyner–Halenda (BJH) method (Tristar II 3020M, Micromeritics Instrument Corporation, USA). The surface chemical modification of aerogels was studied using Fourier Transform Infrared Spectroscopy (FT-IR) (Nicolet 8700, Thermo Fisher Scientific, USA), which gave the information about various chemical bonds such as O—H, C—H and Si—O—Si.

3. Results and discussion

Silica hydrogels were prepared by sol–gel process. The sol process was completed in the exchange column and the gelation was catalyzed by NH_4OH as shown in the following reactions:

$$\text{Condensation}: \quad Si(OH)_4 + (OH)_4Si$$
$$\rightarrow (OH)_3Si—O—Si(OH)_3 + H_2O \tag{2}$$
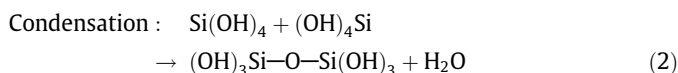
When the liquid within the pores of gel is evaporated, the capillary pressure gets stronger, the difference of which can lead to pore collapse. And it can be calculated with the following Eq. (3):

$$p = 2\sigma \cos\theta/r \tag{3}$$

where p is capillary pressure, σ is surface tension of solvent, θ is contact angle and r represents capillary radius. To minimize the capillary pressure, the solvent exchange and surface modification process is necessary. A polar solvent should be chosen to exchange pore water, and a non-polar solvent was used to exchange the polar solvent. Through comparison (Table 1), ethanol and n-hexane were chosen to be the polar solvent and non-polar solvent, respectively.

3.1. Effect of DI·H_2O: sodium silicate molar ratio on silica aerogels

The solvent deionized water (DI·H_2O) is a key factor that affects the properties of silica aerogels. Various volume ratios of DI water to 32% sodium silicate were selected to study the influence on the aerogels. To determine the proper volume ratio of DI·H_2O to sodium silicate (denoted with symbol V), V was set from 2 to 5 during which sufficient modification agent was applied. It can be seen in Table 2 that the bulk density of the silica aerogels decreases from 0.142 g/cm³ to 0.103 g/cm³ when V increases from 2 to 4. However, with the further increase of V from 4 to 5, the aerogel density rises from 0.103 g/cm³ to 0.146 g/cm³. The specific surface area and pore volume present the same variation tendency with the bulk density. When small amount of DI·H_2O is used to dilute sodium silicate, the volume of the whole hydrosol system is small. After gelation, the pores grouped by secondary particles will have a small diameter for the total volume of the hydrogel is limited by the solvent DI·H_2O. And the smaller pores will have stronger ability against the capillary pressure, so they are hard to be destroyed during drying process under ambient pressure. The average pore diameter increases with enlargement of the volume of whole hydrosol system. On one hand, the silica aerogels, with small V value, can resist the capillary pressure better. Nevertheless, their whole volume is small and their bulk density is relatively high. On the other hand, too much DI·H_2O diluting sodium silicate will result in loose linkages between the silica particles. The loose linkage causes the poor mechanical strength of the gel network and the pores will collapse under ambient pressure drying.

Table 1
Surface tension of several solvents at 20 °C [16] (10^{-3} N m⁻¹).

Solvent	Isopropanol	n-Hexane	Acetone	Ethanol	Water
Surface tension	21.7	18.4	23.7	22.3	72.8