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Continuous adjustment of fractal dimension of silica aerogels

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ABSTRACT

In previous study, it was found that the fractal dimension of the silica aerogel could be only controlled by adjusting the catalysts. In this work, we used the aging process investigated by Hæreid et al. to continuously adjust the fractal dimension of silica aerogel. The fractal structure of the silica aerogels were analyzed by small angle x-ray scattering (SAXS). The SAXS measurements show linear increases in the volume fractal dimension (2.32–2.64) of the secondary particles with aging time (0–72 h). This linear behavior is due to the silica precipitated from the aging solution to the secondary particles is at a constant rate. In the meantime, the light transmittances was obtained by ultraviolet–Visible–infrared spectrophotometer, extinction coefficient were obtained by fitting the curve of light transmittances. We developed a new model to build a connection between the extinction coefficient and the fractal dimension of the silica aerogel obtained by SAXS. From new model, it was found it is due to the increases in volume fractal dimension (D_f) that result in increases of extinction coefficient and decreases of light transmittances. The optical transparency of silica aerogel is strongly affected by the volume fractal dimension (D_f) of the secondary particles of silica aerogel.

1. Introduction

Silica aerogel is considered as a unique class of silica materials, which has been widely applied in Cherenkov radiators [1–3], acoustic barrier material [4],heat storage devices [5]. In the past decades, silica aerogel has gained a lot of attention for its fascinating properties, such as very low density, high inner surface area, high optical transparency, low refractive index and extremely low thermal conductivity [6–12].

The proprieties of silica aerogel are strongly affected by the nanostructure features such as the fractal range, fractal dimension and mean particle size [13, 14]. In previous researches, the nanostructure features of silica aerogel can be only controlled by adjusting the catalysts, solvents, and precursors in the sol-gel processes [15–20]. It should be noted that the fractal dimension of silica aerogel is independent of the starting concentration of solution and only dependent on the nature of the catalyst [21].

The aging process also has a great effect on the microstructure of the silica aerogel. Due to dissolution and re-precipitation of silica from the primary particle surfaces to the contact point of minimize negative radius of the curvature, it can increase the strength and stiffness of wet gels and reduce the cracking and shrinkage during drying [22].

However almost no work studies the continuous control of the fractal dimension or the microstructure evolution on the aging process. Thus in this work, we aimed to study the effects of the aging process on the fractal dimensions of the silica aerogels. The Hæreid's aging process was used since it was a mature and standard method [23]. Furthermore, we tried to use the aging process to continuously adjust the fractal dimensions and microstructures of silica aerogels.

On the other hand, a new model was built to understand the relationship between the extinction coefficient and the nanostructure parameters of the silica aerogel obtained by SAXS. In previous study, it was found that the isotropic scattering is induced by the nanoscale inhomogeneity of the aerogel network and the spectra could be fitted well with the Rayleigh scattering theory [14]. We use this model to analyze the microstructure evolution during the aging process. Since the properties of the silica aerogels are mainly determined by their microstructure, we believe that this work will facilitate the understanding of physics properties and provide a novel way to precisely control the microstructure of different type of the aerogels.

2. Experimental

2.1. Chemicals

Tetraethylorthosilicate (TEOS), ethanol (EtOH), hydrochloric acid (HCl), and ammonium hydroxide (NH_4OH) were analytical reagents

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and purchased from National medicines Co., China. Deionized water was used for synthetic reactions.

2.2. Synthesis of silica gel

The method of synthesis for silica gel is similar to the process described in previous research [24, 25]. First, a solution was prepared by the sequential addition of TEOS, ethanol, deionized water, and hydrochloric acid in the molar ratio of TEOS: EtOH: H_2O: HCl = 1:2.4:1.5:10^{-5}. The mixture was stirred at room temperature for 30 min, and then refluxed for > 20 h at 95 °C. After refluxing, the EtOH produced by reaction and initially added to keep the mixture single phase was distilled off for 4 h at 105 °C. Condensed Silica (CS) was obtained. At the second step, CS was diluted by EtOH, H_2O and NH_4OH was added to the solution as catalyst. The volume ratio of CS: EtOH: H_2O: NH_4OH was 1:20:1:0.01. The sol was gelled inside PE tube with an inner diameter of 4.4 cm at room temperature (25 °C).

2.3. Aging process

In this work, we applied the procedure as proposed by Hæreid et al. [23]. After all the gels were prepared, some of the gels were first soaked in a washing solution (20 vol% H_2O/ethanol) for 24 h at 60 °C and second in an aging solution 70 vol% TEOS/ethanol) for times from 0 to 72 h at 70 °C. Some of the gels were kept directly for supercritical drying for comparing. All of the gels were subjected to ethanol supercritical drying (265 °C, 10 MPa). Fig. 1 shows the flow chart of experiment.

2.4. Characterization of the samples

The density of aerogel was determined by measuring the dimensions and mass of monoliths. The linear shrinkage is determined by measuring the gel diameter and the aerogel diameter. The skeletons are the main source of scattering light. The morphology of the skeletons of the aerogels were investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM, JEOL-1230). The samples for TEM imaging was prepared in this way; first the sample was ground into powder, then dispersed in ethanol, sonicated for 1 h and the supernatant of the ethanol was taken for observation. SAXS experiments were performed at Yangzhou University (NanoSTAR). In addition to small-angle X-ray scattering, the aerogels were characterized by nitrogen sorption at 77 K (Quantachrome Autosorb-1; software Autosorb-1). The directional light transmittances were measured by UV-VIS-IR spectrophotometer (JASCO V-570).

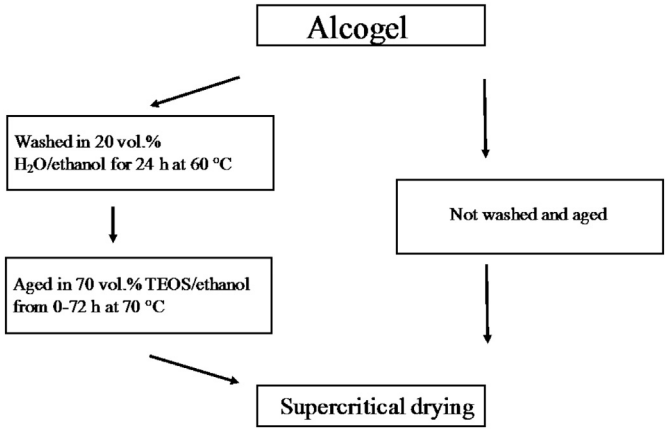

Fig. 1. The flow chart of the experiment.

Table 1
Details of all the samples.

	Mass/g	Density/mg*cm^{-3}	Linear shrinkage/%	Thickness/mm
Not washed and aged	2.00	172	~23.5	9.4
Washed-aged-0 h	1.96	99	~8.9	11.2
Washed-aged-4 h	2.00	102	~8.9	11.2
Washed-aged-24 h	2.24	86	~0	12.3
Washed-aged-48 h	2.47	95	~0	12.3
Washed-aged-72 h	2.81	108	~0	12.3

3. Results and discussion

3.1. Density and liner shrinkage

The details of the samples are shown in Table 1. It can be seen from Table 1 that the linear shrinkage is greatly reduced by the washing and the aging step. Fig. 2 shows the linear fit of mass versus aging time in the TEOS/ethanol solution. It is shown in Fig. 2 that the mass of aerogels is linear increasing with the aging time from 1.96–2.81 g. The apparent densities of the aging samples almost remain the same is due to the different shrinkage. The Washed-aged-0 h has a linear shrinkage of 8.9%. The Washed-aged-72 h has nearly no linear shrinkage due to the strengthening effect. Although its mass increases from 1.96 to 2.81 g, the density is not greatly increased.

3.2. TEM analysis

Fig. 3 shows the TEM images of all the aerogels. The TEM images display typical silica aerogel morphologies with mesopores enclosed by secondary particle aggregates of ~10 nm in diameter. TEM images show a rather traditional branched structure. But no systematic microstructural variations of particle size could be discerned for the different aging times. On the other hand, the pore size of the aerogels may increase with aging time.

3.3. Continuous increasing of fractal dimension

Small-angle X-ray scattering (SAXS) is an effective way to learn the

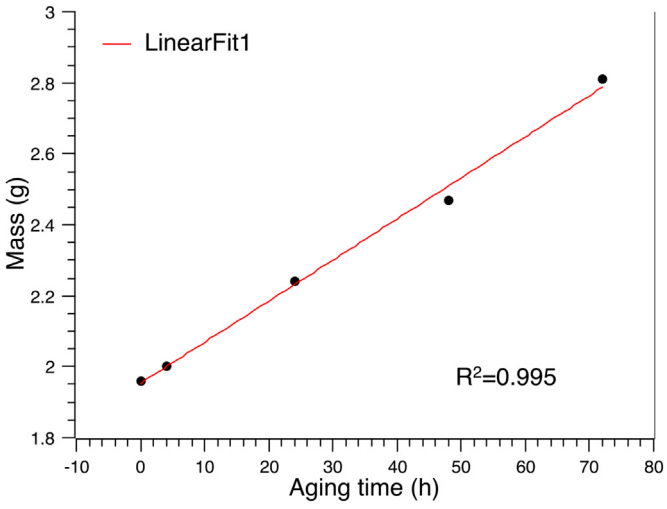

Fig. 2. Mass versus aging time in the TEOS/ethanol solution.