Synthesis of low-density silica gel at ambient pressure: Effect of heat treatment

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A silica gel with the density of 0.2 g/cm^3 and porosity of 90% was synthesized. The silica wet gel was dried and heat-treated under the ambient pressure after modification of the surface by TMCS. The specific surface area and total pore volume of the dried gel increased with increasing heat treatment temperature and represented the maximum value of 1050 m^2/g and 3.2 cm^3/g, respectively, under 350 °C. The surface characteristic of the gel was hydrophobic when heat-treated in nitrogen and converted to hydrophilic after heat-treatment in air. As the result of pore characteristics, and microstructure of gel, the properties of the gel were considered to be similar to those of conventional aerogel.
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1. Introduction
The aerogel is a nanoporous material which shows unique properties due to its low density and high porosity [1, 2]. Especially, numerous applications for using electronic, optical and thermal properties etc. have been investigated intensively for silica aerogels with properties such as ultralow dielectric constant, low refractive index and low thermal conductivity [3, 4].

Conventionally aerogel has been made through a supercritical drying method, which needs high costs. This caused the commercial viability of aerogels to be so limited that many researchers in the world have studied synthetic processes for making aerogels at ambient pressure [5].

In 1992, Deshpande *et al*. prepared low density silica gel at ambient pressure and suggested the possibility of making aerogel at ambient pressure [6]. In this study, we synthesized and heat-treated the silica gel in order to modify the properties similar to conventional aerogel.

2. Experimental procedure
Silica sol was prepared from tetraethoxysilane (TEOS; Fluka, Switzerland) dissolved in ethanol using a two-step acid/base catalyzed procedure. In the first step, TEOS, EtOH (Ethanol; Duksan Chem. Co. Ind., Korea), H$_2$O and HCl were mixed and stirred at room temperature for 90 min. (stock solution). In the second step, EtOH and NH$_4$OH were added to the stock solution and mixed at room temperature for 30 min. The overall ratio of sol was shown in Table I. The sol was allowed to gel and aged in polyethylene mold at room temperature for 24 hrs. After pulling the gel from the mold, the gel was washed with excess EtOH and subjected to a pore fluid-exchange procedure using *n*-hexane (Duksan Chem. Co. Ind., Korea). After pore fluid-exchange, the surface of gel was modified with Trimethyl -chlorosilane (TMCS; Lancaster Co. Ltd., England) in TMCS and

n-hexane solution (6 vol% TMCS in *n*-hexane) at room temperature for 24 hrs. The surface modified gel was dried at room temperature for 48 hrs followed by 60 °C for 24 hrs.

The heat-treatment of dried gel was performed up to 600°C under air and nitrogen atmosphere using electrical furnace.

The microstructural change of the gel according to heat treatment was observed by scanning electron microscopy (SEM: Hitachi, H600, Japan). The change of surface properties was investigated by using Fourier transformation infrared spectroscopy (FTIR; Jasco, FT-IR-300E, Japan), Differential Thermal Analysis (DTA; TG/DTA-92, Setaram, France), and nitrogen/BET analysis (Micrometrics Co., Gemini 2375, USA). The surface characteristics of the gel was tested by placing it on water for 24 hrs.

3. Results and discussion
3.1. Properties of dried-gel after modification
During drying, in general, wet gel experiences so enormous shrinkage that the gel lost most of features, and dried irreversibly. Main driving force of this phenomenon was believed to be continuous additional condensation between surface -OHs due to the capillary force during drying [7]. No additional condensations, however, were expected for the gel prepared in this study because the surface -OH of wet gel was modified

TABLE I Starting composition of silica sol prepared in this study

	TEOS	EtOH	H$_2$O	HCl	NH$_4$OH
			Mol. ratio.		
1st Step	1	3	1	0.0007	-
2nd Step	-	10.5	2.6	-	0.002
Total	1	13.5	3.6	0.0007	0.002

with TMCS into non-reactive -CH₃ [6] as shown in Fig. 1. So this gel was expected to dry reversibly, which means the modified gel may recover the wet gel feature after drying.
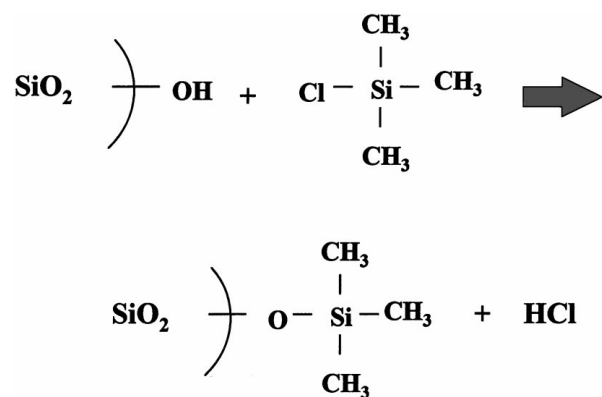
The general properties of dried gels with and without modification in this study was shown in Table II. The surface modified gel showed lower density, higher surface area and pore volume than that of non-modified gel. The microstructure of dried gels with and without modification was exhibited in Fig. 2. It was shown that modified gels had many visible pores in comparison with non-modified gel. From this result, it was confirmed that the surface modified gel could maintain the feature of the wet gel to a degree during drying and

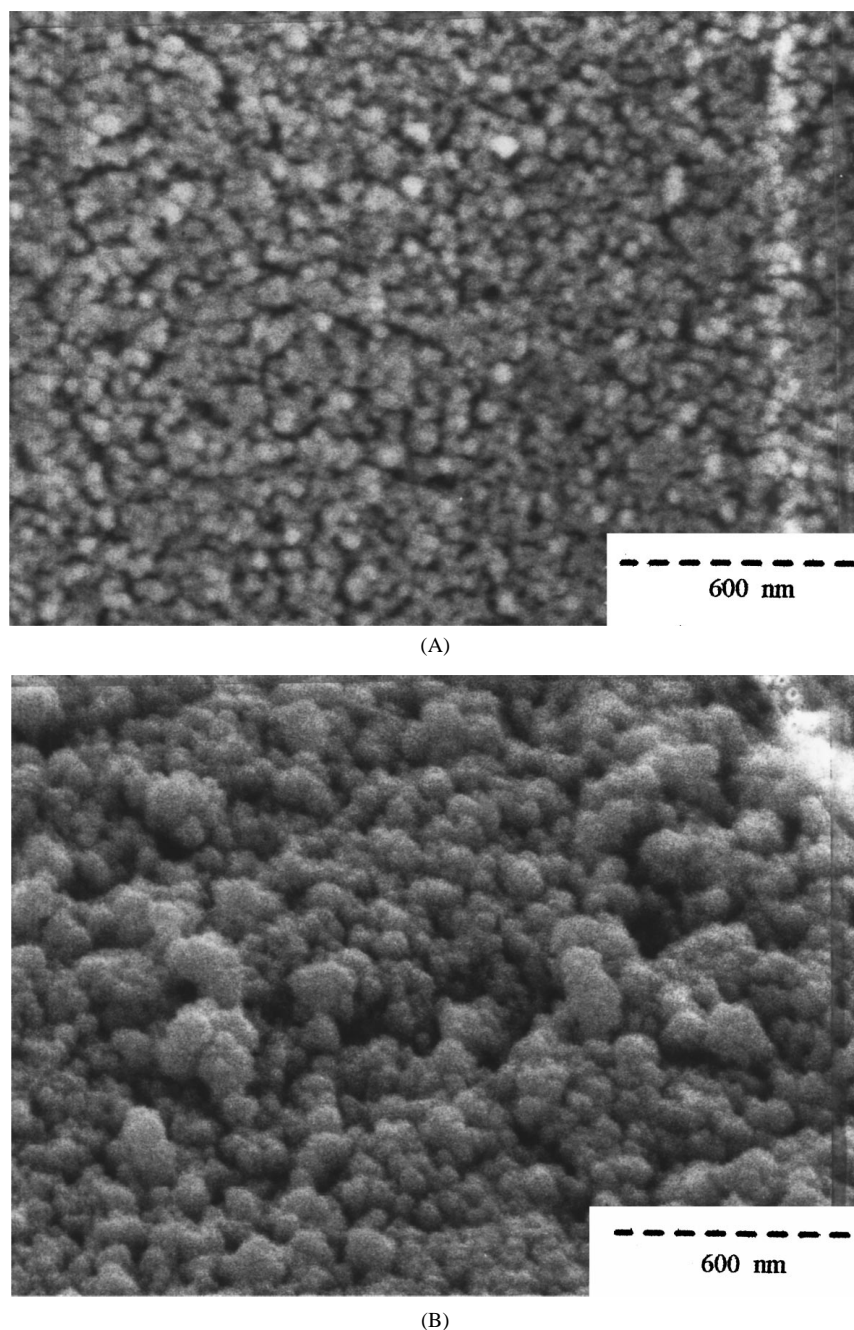*Figure 1* Illustration of surface modification in this study.

(A)

(B)

Figure 2 Microstructures of dried-gel with and without modifications. (A): without modification; (B): with modification.
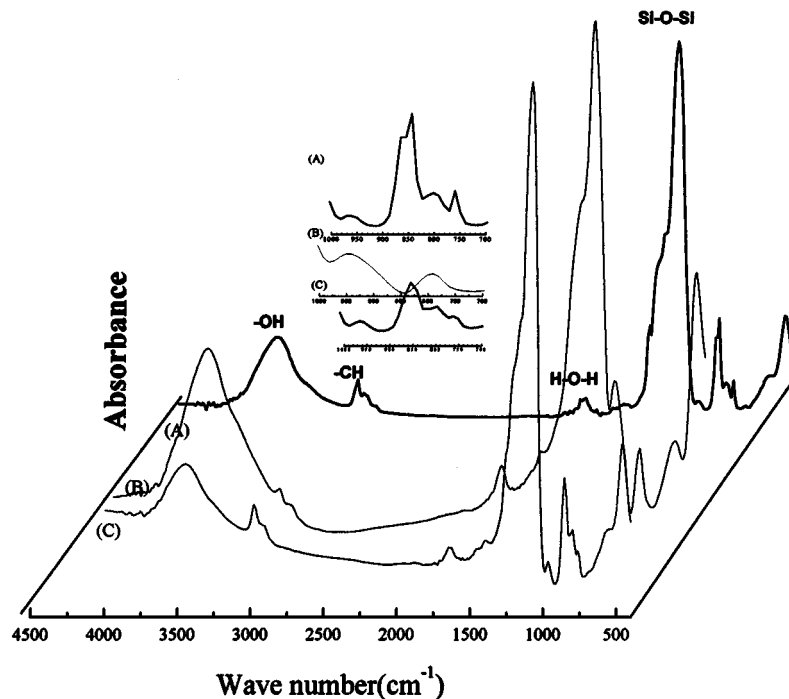
Figure 3 FT-IR spectra of dried-gels prepared in this study. (A): with modification; (B): without modification; (C): with modification and water vapor treatment.

therefore shrink reversibly followed by "Spring Back" to wet gel-like structure after drying.

Fig. 3 showed the FTIR spectra of the dried gels with and without surface modification. Although the OH and SiOH peaks were quite notable for the dried gel with and without modification, the intensity of CH peak at $\sim$2950 cm^{-1} of the dried gel after modification was greater than that of before modification. CH peak at $\sim$850 cm^{-1} appeared only for dried gel after modification. CH peak at $\sim$2950 cm^{-1} in FTIR spectra of gels without modification disappeared after water vapor treatment, whereas that of gel after modification still remained. In general, TEOS based-gel has -CHs originated from -OC$_2$H$_5$ on its surface [8] and they are converted to -OH at the contact of H$_2$O by the reaction as follows [9].

$$-OC_2H_5 + H_2O \rightarrow -OH + C_2H_5OH$$
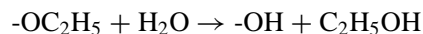
On the contrary, -CHs originated from -CH$_3$ did not react with H$_2$O [9] and showed any changes. As a result of Fig. 3, the dried gels after modification had -CH on their surface, which was originated from TMCS used for surface modification in this study.

3.2. Effect of heat treatment

Fig. 4 represented the result of the differential thermal analysis of dried gels after modification. Endothermic peak in the vicinity of 120 °C was observed due to
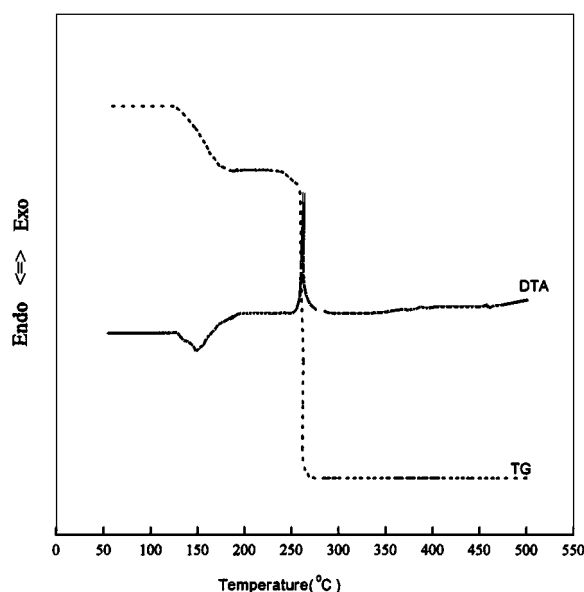

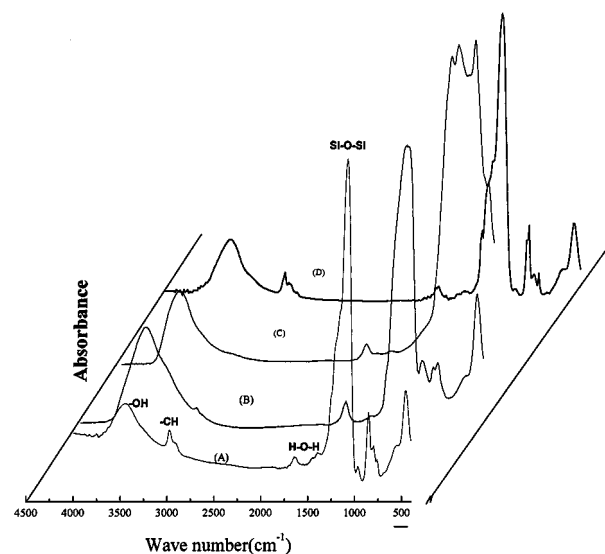*Figure 4* TG/DTA curves for 60°C-dried with modification.

Figure 5 FT-IR spectra of gel according to heating temperature and atmosphere. (A): 60 °C; (B): 350°C in air; (C): 450°C in air; (D): 450°C in nitrogen.
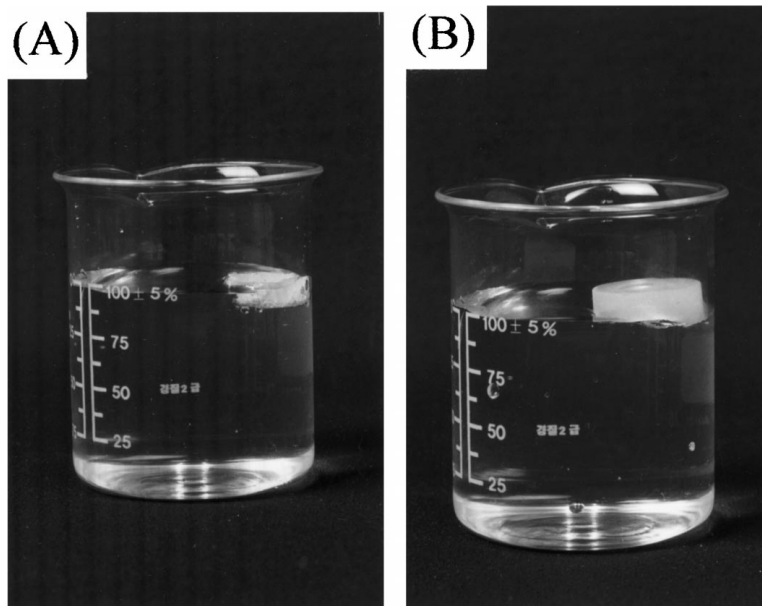
Figure 6 Illustrations of hydrophobicity or hydrophilicity of heat treated-gels at 350°C in this study. (A): heated in air; (B): heated in nitrogen.
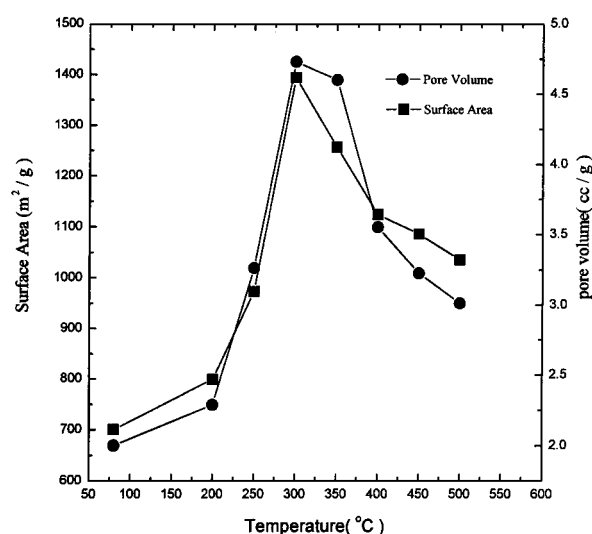

Figure 7 Change of specific surface area and pore volume of dried-gel as a function of heat treatment temperature.

the evaporation of absorbed water. Sharp exthothermic peak at 260 °C was also seen due to oxidation of surface -CH$_3$ and residual organics [10].

Fig. 5 showed the FTIR spectra of the gels with heat-treatment temperature and atmosphere. -CH peaks disappeared in air after 300 °C, however still existed in nitrogen even after 400 °C. In air, the -CH was oxidized into -OH after 260 °C as shown in Fig. 4, while the oxidation of -CH did not occur in nitrogen. As a result, it is expected that the gel heat-treated above 300 °C in air has the hydrophilic surface and heat-treated in nitrogen has hydrophobicity.

Fig. 6 illuminates the photographs of the gel heat-treated in air and nitrogen. The gel heat-treated in air was immersed when put on the water, but the gel heated in nitrogen floated on. This is important to the application of aerogel. Generally, water absorbed gel degraded the unique properties of aerogel such as low thermal conductivity, low dielectric constant, and low
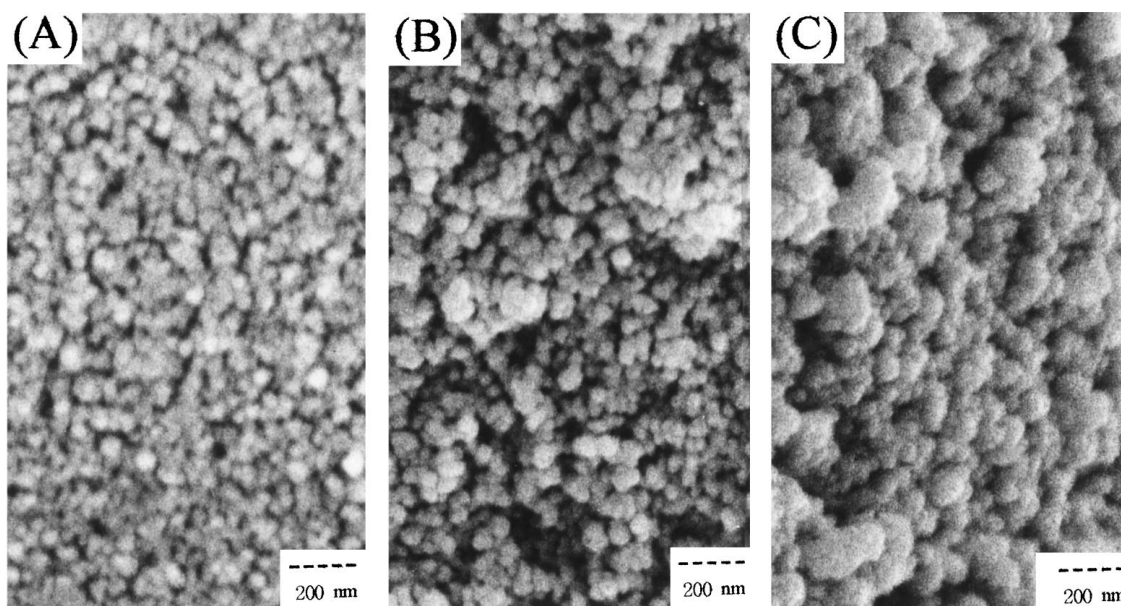

Figure 8 SEM pictures of gels according to heat treatment temperature. (A): dried at 60°C; (B): heat treated at 350 °C; (C): heat treated at 600 °C.

transparency so the hydrophobic surface of gel must be maintained even after heat treatment [8, 11].

Fig. 7 showed the change of surface area and pore volume of dried gels after modification as a function temperature in air. The surface area and pore volume of gels after modification increased up to their maximum values of 1050 m^2/g and 3.2 cm^3/g, respectively, in the range of 300 °C–350 °C with increasing temperature. Beyond this temperature range, the surface area and pore volume of gel decreased gradually. Due to the expansion of gas inside the gel by heat-treatment and the low permeability of the gel [12], it is difficult to escape the expanded gas from the gel, and the gas compresses the gel network. This is supposed to be the main reason of increment the surface area and pore volume of gel after heat-treatment.
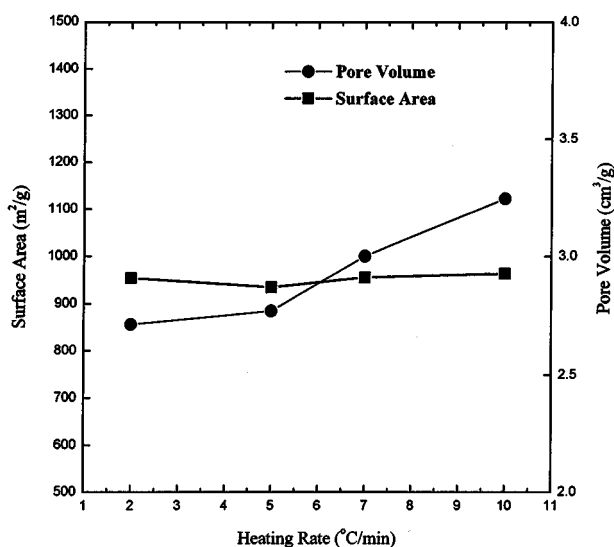
Fig. 8 showed SEM photographs of the gel heat-treated at various temperature. It showed that pore size increased after heat-treatment at 350 °C and decreases at 600 °C, which means the densification of structure seems to start after this temperature. At 350 °C, where the maximum pore volume appears, the 3-dimensional solid network structure was observed and pore size was in the range of 1–100 nm. As a whole, the gel heat-treated at 350 °C had the identical microstructure to that of aerogel by supercritical drying.

Higher heating rate caused the rapid gas expansion in the gel and inhibited to escape gas from the gel. From this reason, the gas will compress the gel and make it expand under high heating rate.

Fig. 9 showed the changes of surface area and pore volume of gel with heating rate. Surface area was constant and pore volume was increased with increasing heating rate. It shows that the extent of expansion of gel depends on the heating rate, and the properties of gel can be controlled by heating rate.

The photograph of crack-free gel heated at 350 °C in air was shown in Fig. 10 and the result of their texture evolution was given in Table III with comparison of dried gel. The crack-free gel can be obtained only by following heating schedule: 2 °C/min to 250 °C, soaking for 120 min and then 1 °C/min to 350 °C, soaking for 120 min. The final heat-treated gel was transparent

Figure 9 Change of surface area and total pore volume of gel according to heating rate.

TABLE II The comparison of properties of dried and heat-treated gel

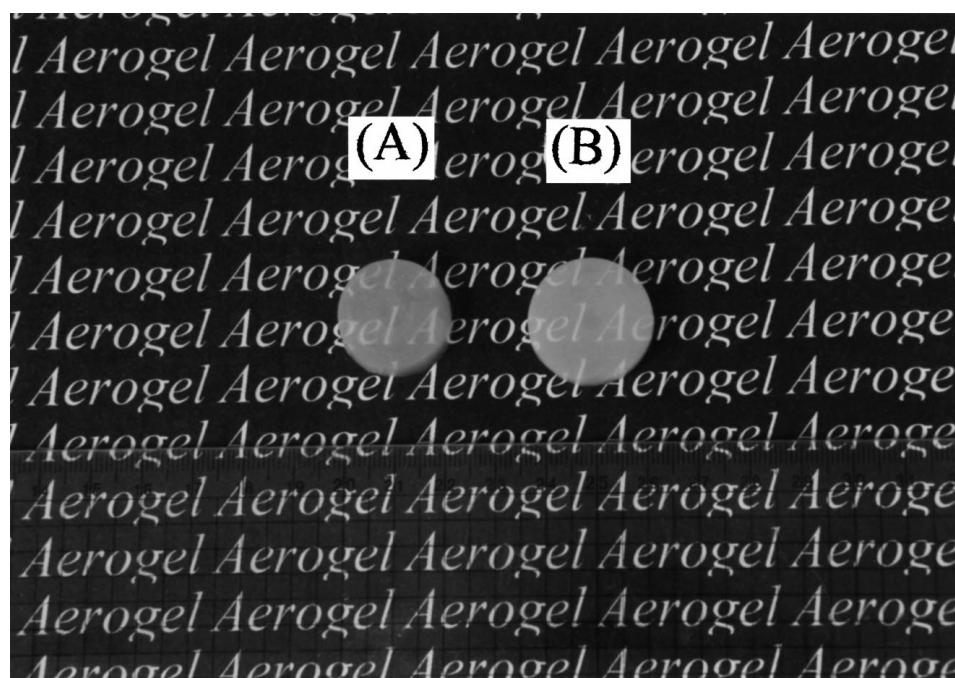| Properties	Density (g/cm^3)	Specific Surface Area (m^2/g)	Total Pore Volume (cm^3/g)
Dried Gel (60 °C)	0.45	750	2.1
Heat-treated Gel (350 °C)	0.24	1050	3.2

Figure 10 Photographs of crack-free gel prepared in this study. (A): dried at 60°C; (B): heat treated at 350 °C.

blue and bigger than dried gel, showing more similar feature to aerogel by supercritical drying. Surface area and pore volume of heated gel were higher than those of dried gel, and its density was lower.

4. Conclusions

Transparent low-density silica gels with aerogel-like properties were prepared by surface modification and heat-treatment at ambient pressure. Their properties such as surface area, pore volume showed maximum values of 1050 m^2/g and 3.2 cm^3/g, respectively, in the range of 300 °C–350 °C and decreased gradually beyond this temperature range. The surface of the gel was hydrophilic when heat-treated in air, hydrophobic in nitrogen. The pore structure of gel could be controlled by heating condition.

Acknowledgement

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