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# Synthesis of silica aerogels from waterglass via new modified ambient drying

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A new modified ambient drying process for synthesizing silica aerogels cost-effectively from waterglass has been developed. Crack-free silica aerogels were obtained via solvent exchange/surface modification of wet gels using IPA/TMCS/*n*-Hexane solution. Silica aerogels were heated at different temperatures. The effects of heating temperature on chemical bonding state of aerogels were investigated by means of DTA and FTIR. The surface characteristic of the aerogel was hydrophobic when heat-treated under 350°C. The porosities, densities, and specific surface areas of the silica aerogels were in the range of 93–94%, 0.12–0.15 g/cm$^3$, and ~630 m$^2$/g, respectively. Distinct spring back phenomena were observed in surface modified wet gels during drying.

## 1. Introduction

Silica aerogel is a nanostructure material with high surface area (500–1200 m$^2$/g), high porosity (~99.8%), low density (0.003–0.35 g/cc), low dielectric constant (<2.0), and low thermal conductivity (0.01–0.015 W/m · K). Particularly, because of their excellent heat insulation properties, silica aerogels have received significant attention. However, conventional production of silica aerogels includes expensive raw materials like tetraethoxysilane (TEOS) and supercritical drying which prohibit commercialization. For successful large-scale commercialization of aerogels, it is clear that costs and risks must be dramatically reduced. To achieve this goal, requirements include (1) the use of inexpensive precursors such as sodium silicate (waterglass) and (2) the development of continuous ambient drying technology that does not require high pressure [1–3].

Ambient drying is possible through the surface modification of wet gels. Using this modification, the —OH species of the surface that lead gel to collapse by condensation reaction are modified into non-reactive groups. However, in order to perform surface modification, at least one solvent exchange process is required as a prerequisite [4, 5]. Conventionally, the solvent exchange process relies only on the concentration gradient between solvents, and so a very long diffusion time and the recycling of the solvent cause considerable costs and disadvantages in the process.

In order to solve these problems, recently, F. Schwertfeger *et al.* [3] developed a process for waterglass based silica aerogels in which solvent exchange and surface modification using HMDSO/TMCS solution were simultaneously progressed by chemical reactions and a phase separation mechanism.

This paper describes a new modified technique for the synthesis of waterglass based silica aerogel bulk via an ambient drying process which uses IPA/TMCS/*n*-Hexane solution as solvent exchange/modification agents. IPA/*n*-Hexane is cheaper than HMDSO and IPA reacts with TMCS to yield isopropoxytrimethylsilane as silane agent. The properties of silica aerogels with various process conditions are also discussed.

## 2. Experimental procedure

### 2.1. Preparation of silica wet gels

The procedure for synthesizing silica aerogel is shown as a flow chart in Fig. 1. Silica wet gels were prepared with waterglass (Young-il Co., Korea) as starting materials. About 0.7 liter of waterglass solution ($SiO_2$ contents 8 wt%, $Na_2O : SiO_2$ mole ratio 1 : 3.3) went through an ion exchange column (8 cm in diameter, 40 cm in length) filled with 1 liter of Amberlite (Rohm & Haas, France). The collected silica sol had a pH in the range of 2.7. For gelation, 1.0 M $NH_4OH$ solution was added to the silica sol. The sols, which had pH values ranging from 3.5 to 5.0 with increments of 0.5, were stirred for 30 seconds respectively, and then transferred into polypropylene vessels (30 mm in diameter). After gelation in closed vessels, the wet gels were aged for 1 day in deionized (D.I.) water in order to strengthen the gel structure.

### 2.2. Solvent exchange/surface modification and drying of wet gels

In this experiment, three solvents [isopropyl alcohol (IPA; Yakuri, Japan), trimethylchlorosilane (TMCS; Lancaster, U.K.), *n*-Hexane (Duksan Co., Korea)] were used for the solvent exchange/modification.

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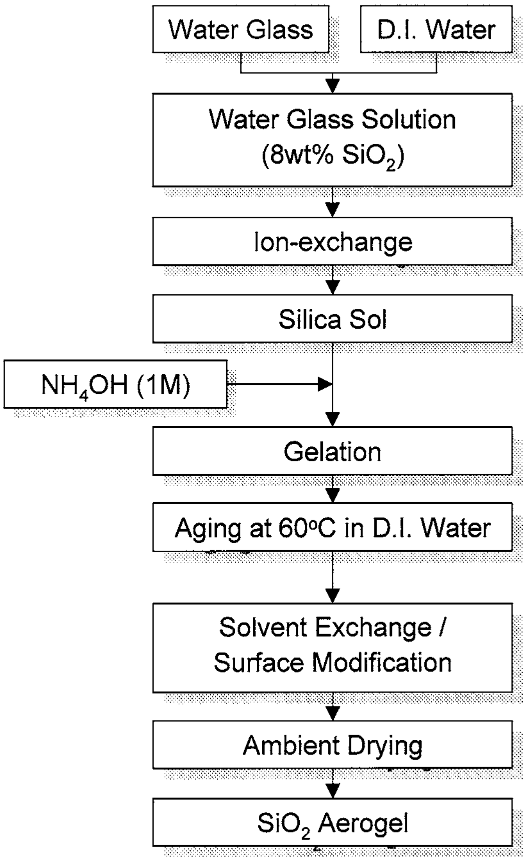


*Figure 1* Overall experimental flowchart.

The aged wet gels were immersed in IPA/TMCS/*n*-Hexane solution. After preparative experiments, the optimum conditions for modification were adopted as follows: the mole ratio of TMCS : pore water : IPA = 0.4 : 1 : 0.4 and the volume ratio of *n*-Hexane/TMCS = 10. The modified wet gels were dried at room temperature for 15–20 h, then heat-treated at 40°C for 1 h and at 230°C for 1 h in air.

## 2.3. Characterization

The X-ray photoelectron spectroscopy (XPS) (Model ESCALAB 2201-XL, Thermo VG Scientific, England) measurement was carried out to characterize the ion-exchanged silica sol composition. Apparent density was determined by weighing samples of known dimensions. The microstructure of silica aerogel was observed by scanning electron microscopy (SEM) (Model H4200, Hitachi, Tokyo, Japan). The surface area of silica aerogel was determined using the Brunauer-Emmitt-Teller (BET) method (Model Gemini 2375, Micromeritics Instrument Group, Norcross, GA). Differential thermal analysis (DTA) (Model TG/DTA-92, Setaram, France) was used to predict the reaction inside gel during heat treatment. Fourier transform infrared spectroscopy (FTIR) (Model FTIR-300E, Tokyo, Japan) was employed to investigate the change of chemical bonding state of aerogel according to heating temperature.

## 3. Results and discussion

## 3.1. Characteristics of silica sols

In order to confirm termination of ion-exchange reaction, waterglass and ion-exchanged silica sol composition were investigated using XPS under vacuum of $8 \times 10^{-9}$ Torr after heating at 700°C for 2 hr. As shown in XPS wide/narrow scan spectra, sodium ions were fully removed through ion-exchange process (as shown in Figs 2 and 3).

TABLE I Gelation properties of silica sols prepared from waterglass

| pH of starting sol | Gelling time (min) at 60°C | Radical shrinkage (%) with aging time | |
|---|---|---|---|
| 3.5 | 45–50 | 24 hr | 10.0 |
| | | 48 hr | 11.6 |
| | | 72 hr | 12.6 |
| 4.0 | 23–28 | 24 hr | 10.3 |
| | | 48 hr | 12.3 |
| | | 72 hr | 13.3 |
| 4.5 | 15–18 | 24 hr | 13.0 |
| | | 48 hr | 13.3 |
| | | 72 hr | 13.6 |
| 5.0 | 8–10 | 24 hr | 13.3 |
| | | 48 hr | 13.3 |
| | | 72 hr | 14.0 |

The gelation properties, with respect to the pH, gelation time, and syneresis, were observed to determine the optimum conditions for gelation; the results are shown in Table I. The optimum pH, gelling temperature, and aging time were 3.5, 60°C, and 24 hr, respectively.

## 3.2. Mechanism of solvent exchange/surface modification

During the solvent exchange/surface modification process, transparent liquid came out from the wet gel and formed under the *n*-Hexane phase. The resulting modified wet gels were located on top of the built solution, the bottom of the upper *n*-Hexane solution. These phenomena could be explained by the following seven different reactions that can occur during the solvent exchange/modification of wet gel.

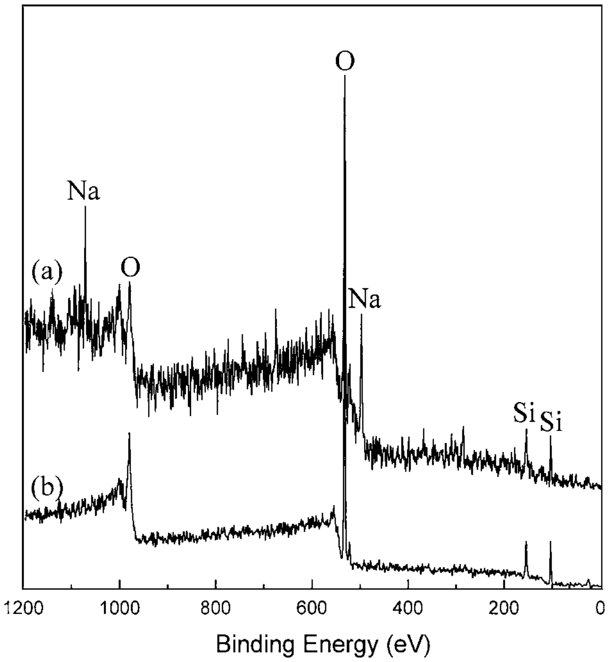
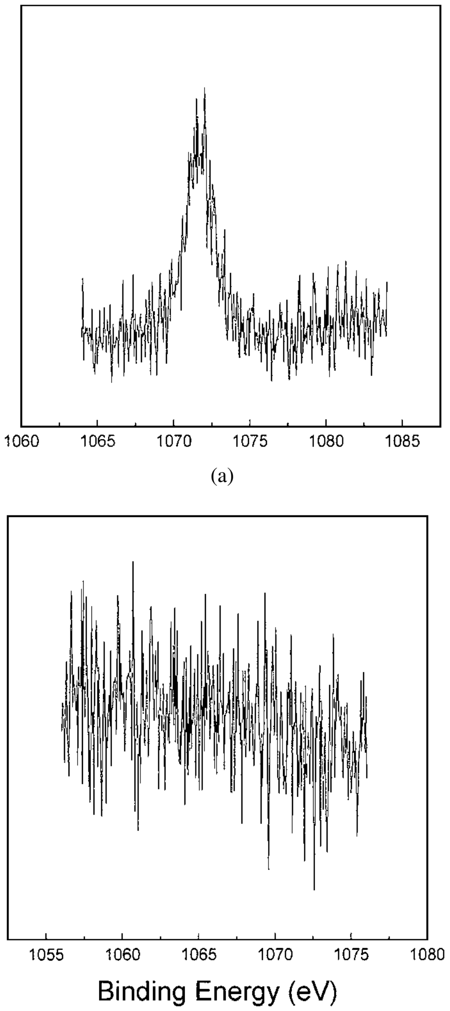


*Figure 2* XPS spectra of (a) waterglass as received and (b) ion-exchanged gel after drying.



(a)

(b)

*Figure 3* XPS narrow scan spectra (Na 1s) of (a) waterglass and (b) ion-exchanged gel after drying.

$$2\mathrm{TMCS} + \mathrm{H_2O} \rightarrow \mathrm{HMDSO} + 2\mathrm{HCl} \tag{1}$$

$$\mathrm{TMCS} + \mathrm{IPA} \rightarrow \mathrm{(CH_3)_3Si{-}O{-}CH(CH_3)_2} + \mathrm{HCl} \tag{2}$$

$$2\mathrm{(CH_3)_3Si{-}O{-}CH(CH_3)_2} + \mathrm{H_2O} \rightarrow \mathrm{HMDSO} + 2\mathrm{IPA} \tag{3}$$

$$\mathrm{HMDSO} + 2\mathrm{HCl} \rightarrow 2\mathrm{TMCS} + \mathrm{H_2O} \tag{4}$$

$$\mathrm{(CH_3)_3Si{-}O{-}CH(CH_3)_2} + \mathrm{HCl} \rightarrow \mathrm{TMCS} + \mathrm{IPA} \tag{5}$$

$$\mathrm{TMCS} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O{-}Si(CH_3)_3} + \mathrm{HCl} \tag{6}$$

$$\mathrm{(CH_3)_3Si{-}O{-}CH(CH_3)_2} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O{-}Si(CH_3)_3} + \mathrm{IPA} \tag{7}$$

As described in reactions (1)–(3), TMCS reacts with $H_2O$ and IPA to yield HMDSO, isopropoxytrimethylsilane [$(CH_3)_3Si{-}O{-}CH(CH_3)_2$], and HCl spontaneously in pore. Isopropoxytrimethylsilane, a moisture sensitive agent, reacts violently with the pore water to generate HMDSO and IPA as in reaction (3), and also reacts with the —OH of the internal surface according to reaction (7). Because HMDSO can again react with TMCS and HCl as in reaction (4) and isopropoxytrimethylsilane can react with HCl as in reaction (5) to form TMCS, TMCS still exists in solution, so the surface modification by TMCS and isopropoxytrimethylsilane such as in reaction (6) and (7) takes place. This modification mechanism can be illustrated as in Fig. 4 in which Schwerfeger's principle [3] is applied. At the beginning of the modification, the hydrophilic property of the internal surface was modified to hydrophobic by isopropoxytrimethylsilane and TMCS that react with the —OH of the internal surface. Thus, hydrophobic areas of the pore surfaces were formed and the newly generated IPA/HMDSO solution was able to collect on the hydrophobic parts of the surface. (IPA is soluble in HMDSO or aqueous HCl. But IPA/HMDSO solution cannot mix with aqueous HCl/IPA solution.) The hydrophobic areas and adjacent layer grew into the gel while the reactions proceeded. As a result, aqueous HCl/IPA solution, that separated from the IPA/HMDSO phase, pressed out of the gel pore. And outside of the wet gel, a phase separation between *n*-Hexane and aqueous HCl/IPA occurred.

### 3.3. Properties of silica aerogels

Fig. 5 shows DTA curve of room temperature-dried silica gel that experienced surface modification. It is believed that the exothermic peak in the vicinity of 420°C is attributed to oxidation of $-CH_3$ developed from modification and residual organics ($-OC_2H_5$) [4, 5].

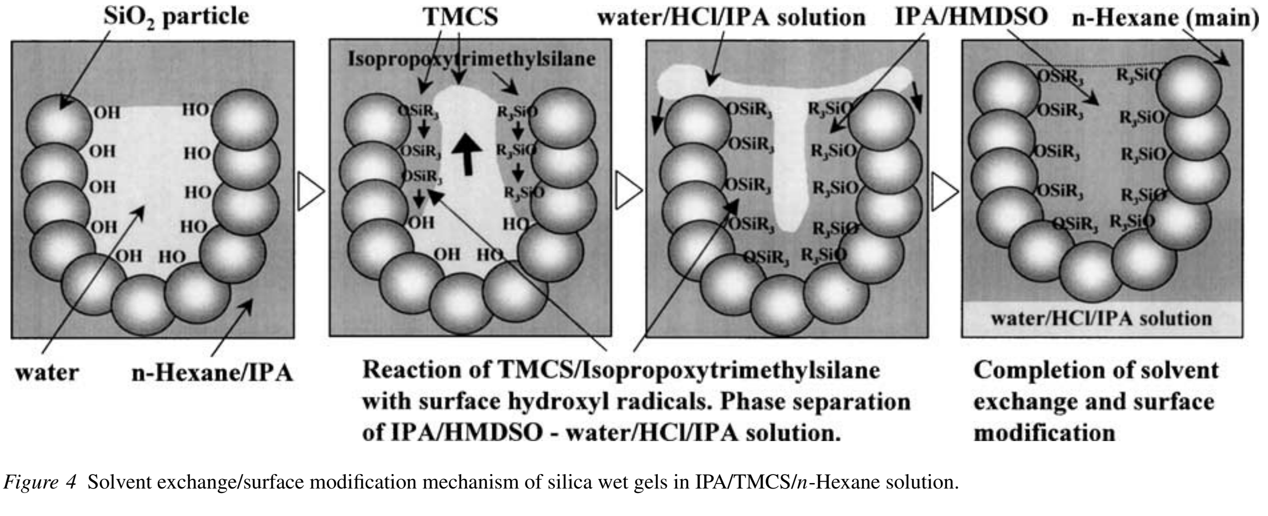


*Figure 4* Solvent exchange/surface modification mechanism of silica wet gels in IPA/TMCS/*n*-Hexane solution.

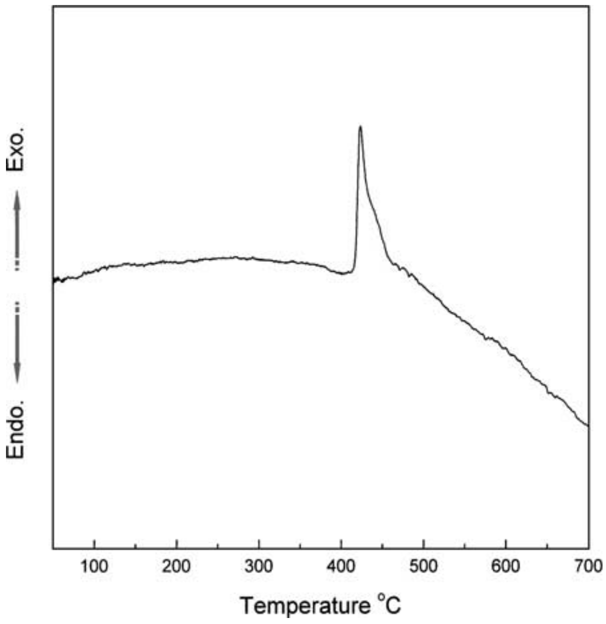


*Figure 5* DTA curve for a silica gel prepared by the IPA/TMCS/*n*-Hexane method and dried at room temperature.

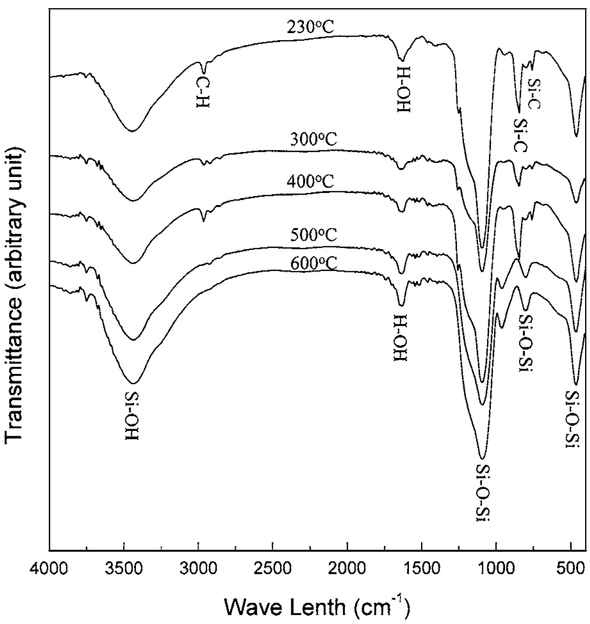


*Figure 7* FT-IR spectra of silica aerogels modified in IPA/TMCS/*n*-Hexane solution and heat-treated at various temperatures.

Fig. 6 illuminates the photographs of hydrophobicity-hydrophilicity transition according to temperature variation. This is important to the application of aerogel. As we know, water absorption degraded the unique properties of aerogel such as low thermal conductivity, low dielectric constant, and so on. Therefore the hydrophobic surface of aerogel must be maintained even after heat treatment. Fig. 7 shows the FT-IR spectra of modified dry gels treated at various temperatures (100–600°C). The spectrum of the sample heat-treated at 230°C shows that the wet gels were modified with trimethlysilyl [$Si(CH_3)_3$] groups on the internal surface (At about 3500 cm$^{-1}$, the Si—OH signal is a background peak caused by KBr that is added for measurement and at about 1600 cm$^{-1}$, the H—OH peak is caused by physically adsorbed water). That the wet gel was modified with trimethyl groups indicates the hydrophobicity of the aerogels. The property of hydropobicity is maintained up to 350°C.

As seen in Fig. 8, the microstructure of silica aerogels was a 3-dimensional nanoporous structure. As the pH of starting sols increased, the silica aerogel network became close gradually, because of the more intensive condensation reaction, and so the values of specific surface areas decreased (see Table II). In Table II, the important properties of silica aerogels are listed. It shows that the silica aerogels based on waterglass using IPA/TMCS/*n*-Hexane method have no great differences in comparison to aerogels synthesized by the general method—via supercritical drying technique from silica alkoxide.

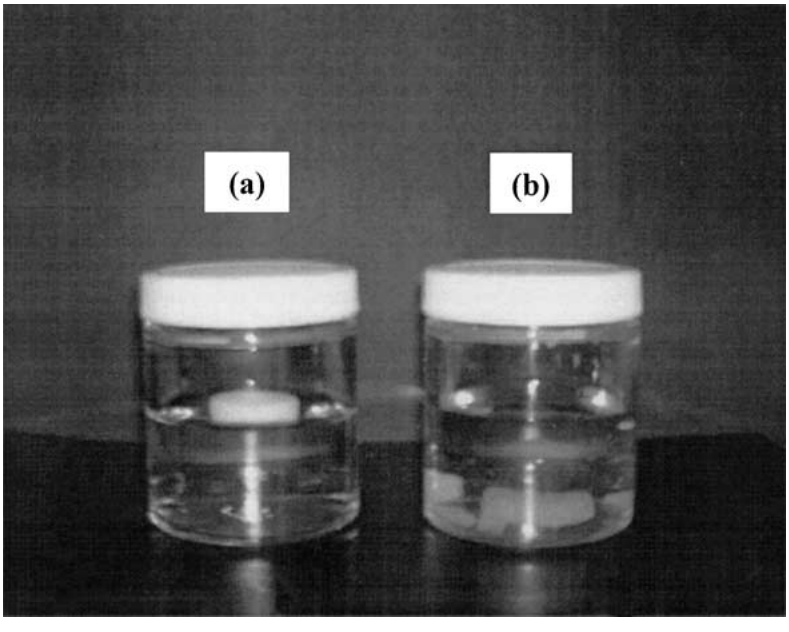


*Figure 6* Hydrophobic and hydrophilic properties of a silica aerogel prepared by the IPA/TMCS/*n*-Hexane method and heat-treated at: (a) 350 and (b) 400°C.

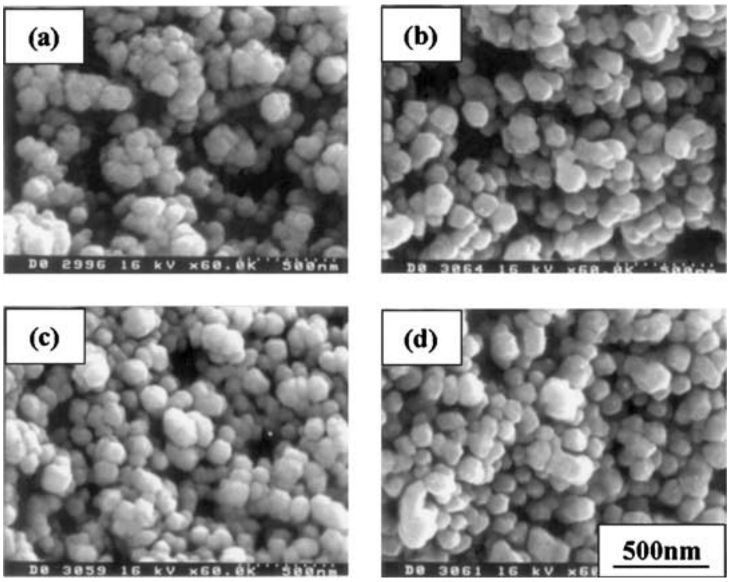


*Figure 8* SEM micrographs of silica aerogels from different pH sols synthesized by the IPA/TMCS/$n$-Hexane method: (a) 3.5, (b) 4.0, (c) 4.5, and (d) 5.0 pH.

TABLE II Effect of starting sol pH on properties of silica aerogels

| pH of staring sols | Bulk density (g/cm$^3$) | Porosity (%) | Specific surface area (m$^2$/g) |
|---|---|---|---|
| 3.5 | 0.123 | 94.3 | 630 |
| 4.0 | 0.132 | 94.0 | 541 |
| 4.5 | 0.138 | 93.7 | 507 |
| 5.0 | 0.151 | 93.1 | 439 |

## 4. Conclusions

The main findings from our research on the synthesis of silica aerogels from waterglass by the ambient drying technique using IPA/TMCS/$n$-Hexane solution are as follows:

1. Solvent exchange and surface modification of silica wet gels, obtained by ion-exchange from waterglass, were simultaneously accomplished in IPA/TMCS/$n$-Hexane solution.
2. Porosities, densities, and surface areas tended to decrease with the increase of the sol pH.
3. The modified dry gel showed distinct ‘spring back’ phenomena during drying and crack-free aerogels were obtained.
4. Silica aerogels synthesized by the new ambient drying technique using IPA/TMCS/$n$-Hexane solution showed properties of 0.12–0.15 g/cm$^3$ density, 93–94% porosity, $\sim$630 m$^2$/g specific surface area, and in particular the hydrophobic property was maintained up to 350°C.

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