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# Preparation and Characterization of Nanoporous Silica Aerogel Granules on The Basis of Water Glass Via Ambient Pressure Drying Method

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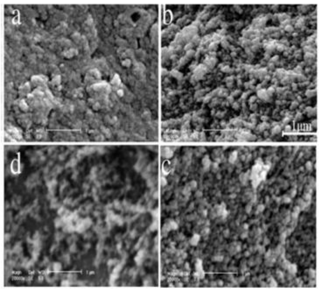
**Graphical abstract**



**Abstract**

A crack-free silica aerogel monolith is a nanostructured material with so many surprising properties such as high specific surface area, high porosity, low dielectric constant, low density and outstanding heat insulation properties that were fabricated from a cheap water glass derived silicic acid solution.In this research , the OH surfaces of the wet gel were modified using a HMDZ/n-hexane or TMCS/n-hexane mixture followed by solvent exchange from water to n-hexane. The obtained surface modified wet gel was dried at different temperature under ambient pressure.The properties of hydrophobic silica aerogels synthesized by this new route were investigated by scanning electron microscopy (SEM), differential temperature analysis (DTA) and Fourier-transform infrared spectroscopy (FT-IR).The results showed that 20 wt% HMDZ as surface modifier and 75 °C as drying temperature resulted an acceptable hydrophobic silica aerogel with the density of 0.15 gr/cm³ and specific surface area of about 520 m²/gr.

*Keywords*: Hydrophobic silica aerogel; ambient pressure drying; water glass

## ■1.0 INTRODUCTION

Silica aerogels are nanostructured porous materials achieved by removing the liquid from a wet gel without or minimum shrinkage. They are formed from highly cross-linked network of silica particles. These unique materials exhibit many captivating properties, which include a very low density (~3 kgm$^{-3}$), low thermal conductivity (~0.02WmK$^{-1}$), a low refractive index (~1.01 to 1.1), high optical transparency (~90%) and a high surface area (~1600m$^2$ g$^{-1}$) [1, 2].

Because of these properties, silica aerogels are employed in nuclear reactors as Cerenkov radiation detectors, containers for liquid rocket propellants, thermal superinsulators for solar energy systems, refrigerators, windows and air conditioning systems (3–4).

Graham showed that water in silica gel could readily be replaced by organic liquids. This fact led Kistler [5] to explore replacing the liquid in a wet gel with gas by extracting the liquid from the gel at a high temperature and high pressure. He produced aerogels in an autoclave, which was an expensive process.

Since the drying takes place at a high temperature and pressure, it is a very difficult and unreliable method. Furthermore, the Kistler method was very tedious and time-consuming. In 1968 a team of researchers headed by Teichner developed a method for producing silica aerogels within one day using (albeit costly) silicon alkoxide precursors [6].

For commercial production, however, it is desirable to produce the silica aerogels using a low-cost precursor such as sodium silicate and to dry the wet gels at ambient pressure. Pure silica aerogels are hydrophilic and adsorb atmospheric moisture. Thus, the aerogels deteriorate with time in humid environments due to the adsorption of water molecules because of the polar –OH groups on their surface that can take part in hydrogen bonding with $H_2O$. The replacement of H from Si-OH groups with hydrolytically stable Si-R groups through the oxygen bond prevents the adsorption of water and hence results in hydrophobic aerogels [7].

In continuation of research on the hydrophobic aerogels, Schwertfeger and co-workers [8] have produced the silica aerogels using a water glass precursor with ion-exchange resin by surface modification and drying at ambient pressure. They passed sodium silicate solution through an ion-exchange resin to replace Na+ ions from the solution with H+ ions. However, ion-exchange resin is costly and requires repeated washing with water. To regenerate the resin, repeated washing with HCl is needed to replace Na+ ions with H+ ions, which is a lengthy and time-consuming process. Kang and Choi [9], Jeong et al and Wei et al have prepared silica aerogels by employing surface modification and drying at ambient pressure. Kim and Hyun have synthesized the silica aerogels employing the similar method.

Production of monolithic crack free structure with low density is the main problem in ambient pressure drying procedure.We reported the synthesis of hydrophobic silica aerogels modified with HMDZ(hexamethyle disilazan) and TMCS(tree methyl cholorosilane) from a water glass precursor using an inexpensive and simple method involving the aging of a gel, washing with water, the subsequent surface modification of the gel, and finally drying in different temperature at ambient pressure.

## ■2.0 EXPERIMENTAL PROCEDURE

A sodium silicate solution (water glass) was used as a precursor to prepare the silica sol. Water glass (Merck company, Germany; silica content 26–28 wt%, $SiO_2$:$Na_2O$ = 3.3:1) was mixed with distilled water to make an 8 wt% silicate solution. The diluted silicate solution was then passed through a column filled with an ion exchange resin (Amberite, H. Rohm & Hass Co., PA).

The prepared silicic acid has a pH ranging from 2.4 to 2.8. Glycerol at 3, 4, and 5 wt% were added to the silica sol. A base catalyst ($NH_4OH$) was then used to bring the pH of the silica sol to 4.0. The silica sol was poured into 30 ml polypropylene molds. The molds were sealed and placed in an oven at 50 °C for 3 h.

The obtained wet gels were washed in 30% $H_2O$/EtOH for 24 h at 70 °C. The samples subsequently were aged in double distilled water (with 5 micro Siemens hardness) for 24 hours in 60 °C to induce more strength to the gel network. The aged wet gels were washed in hexane (99%, Merck Company, Germany) for 21 h at 50 °C, with the hexane being replaced every 7 h.

After washing, the surfaces of the wet gels were chemically modified in a 5% TMCS (trimethylchlorosilane, $Si(CH_3)_3Cl$, 98% Fluka) /hexane and 10, 20 and 30 wt.% HMDZ (hexamethidisilazane, 97% Fluka) /hexane solution for 24 h at 50 °C. Finally, the surface-modified wet gels were washed repeatedly in hexane for 24 h at 50 °C in order to remove the remaining surface modification agents and reaction products, such as hydrochloric acid. The obtained wet gels were stored in an oven and dried at 75, 90 and 120 °C under ambient pressure.

The bulk density of the aerogels was determined by using the Archimedes method in ethanol at room temperature. Fourier transform infrared (FT-IR) spectroscopy was used to confirm the surface chemical structure of the aerogels in the wave number range of 400– 4000 cm-$^1$ .

The surface area was determined by BET analysis from the amount of $N_2$ gas adsorbed at various partial pressures. The microstructure of the aerogels was observed by field emission scanning electron microscopy.

## ■3.0 RESULTS AND DISCUSSION

Table 1 shows the bulk density, porosity and specific surface area of the aerogels fabricated at different condition. The results reveal that by increasing the percentage of HMDZ from 10 to 20 wt%, the density decreases to 0.15gr/$cm^3$. It is due to the better modification of microstructure to gain a more homogeneous pore size distribution [10]. Further increasing in HMDZ cause to increase in density[10]. This is because that excess contents of modifier lead to damage the silica network due to remain of the different agents and their reaction products in the pores [11].

**Table 1** Density, porosity and specific surface area of fabricated aerogels

| **Sample no.** | **Percentage of HMDZ (wt %)** | **Drying temperature( °C)** | **Density(gr/c $m^3$)** | **Porosity (%)** | **Specific surface area($m^2$/gr)** |
|---|---|---|---|---|---|
| A | 0 | 75 | 0.82 | 16 | 102 |
| B | 10 | 75 | 0.19 | 87 | 496 |
| C | 20 | 75 | 0.15 | 93 | 520 |
| D | 30 | 75 | 0.22 | 84 | 485 |
| E | 20 | 90 | 0.20 | 89 | 508 |
| F | 20 | 120 | 0.24 | 82 | 478 |

Furthermore, it is clear that the density increases gradually with increasing the drying temperature from 75 to 120 °C. This is because of the additional gas pressure induced throughout the silica network and may destroy the thin walls separated the nanoscale pores. As revealed in table 1, the specific surface area for samples confirms the difference final densities and porosities. The maximum value of specific surface area (520 $m^2$/gr) is corresponded to the sample C which has the optimum properties. Figure 1 shows the $N_2$ adsorption-desorption isotherm of the sample C. The graph shows a typical type IV isotherm, which indicates the mesoporous structure of the aerogel [12].

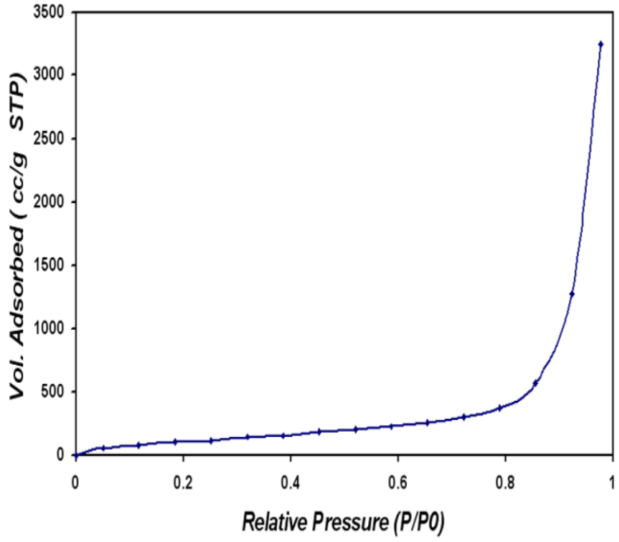


**Figure 1** N2 adsorption–desorption isotherms for sample C

Figure 2 shows the FT-IR spectra of aerogels synthesized with 10, 20 and 30 wt% HMDZ as modifier. The strong absorption peaks near 1100 and 1220 cm$^{-1}$ and the weak peak around 800 cm$^{-1}$ were assigned to the asymmetry and symmetry bending modes of Si–O–Si, respectively. The strong peak near 460 cm$^{-1}$ was assigned to the Si–O–Si bending stretching mode. These peaks are characteristic peaks showing a typical silica aerogel network structure.

On the other hand, the weak peak around 2900, 1260, 1150, and 850 cm$^{-1}$ were assigned to the $CH_3$ terminal, which originates from the TMCS-modified silica surface. The peaks at 1260, 1150 and 850 cm$^{-1}$ indicate the presence of Si–C, while the peak at 2900 cm$^{-1}$ is due to C–H stretching [13–16]. These peaks show that the aerogels are modified into a hydrophobic form. All of spectra indicated that modification agents converts the aerogels into hydrophobic form.

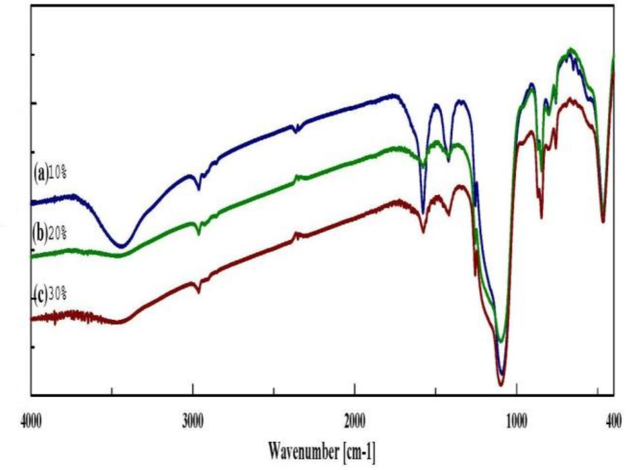


**Figure 2** FT-IR spectra of the aerogels synthesized with (a) 10wt% HMDZ (b) 20wt% HMDZ and (c) 30wt% HMDZ

Figure 3 shows the differential thermal analysis(DTA) and thermogravimetery(TG) graphs of 75 °C dried aerogel containing 20 wt.% HMDZ (sample C). The weight loss in the range of 330 to 550 °C in TG graph indicates the gradual remove of the surface -$CH_3$ groups and residual organic components. Exothermic peaks near 460 and 600 °C in DTA graph are related to the phase transformation of silica.

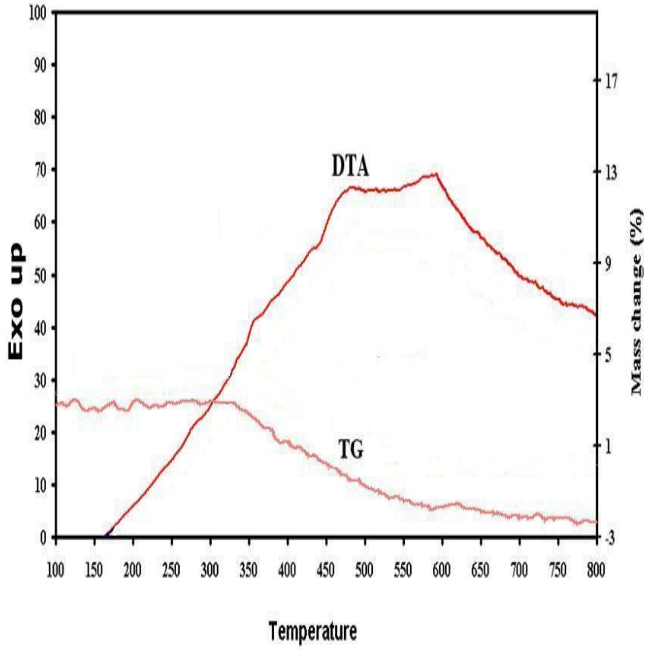


**Figure 3**. TG/DTA curves of 75 °C dried silica aerogel that experienced modification by 20wt% HMDZ solution

Figure 5 a-d shows the SEM micrograph of the different samples. Figure 5.a shows the microstructure of alchogel dried without surfactant modifier (HMDZ). It is illustrated that the absence of HMDZ cause to the destruction of the pore skeleton and hence notably increase the density. Figure 5.b, c and d correspond to samples with 20, 10 and 30 wt% HMDZ respectively. It is obvious that the pore size and distribution are more homogeneous in the sample C (figure 5.b that related to the aerogel modified with 20 wt% HMDZ). As shown in Figure 5.d, the more content of HMDZ (30 wt%) leads to a non-uniform pore size and microstructure.

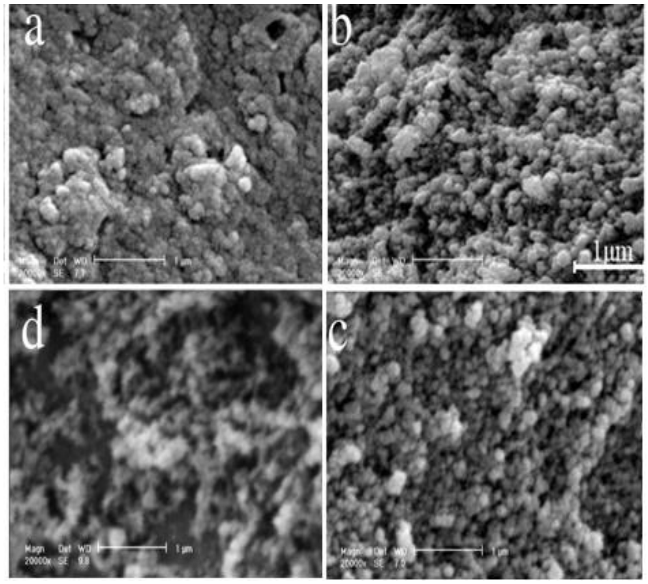


**Figure 4** SEM images of the aerogels: (a) alcogel without HMDZ, (b) aerogel with 20 wt% HMDZ, (c) Aerogel with 10 wt.% HMDZ, (d) aerogel with 30 wt.% HMDZ

As shown in Figure 5, a monolithic crack-free aerogel obtained with 20 wt% HMDZ as modifier at 75 °C drying temperature. The sample showed a remarkable hydrophobicity at room temperature.

**Figure 5** **M**onolithic crack-free aerogel

## 4.0 CONCLUSION

Hydrophobic, monolithic, low density and semitransparent silica aerogels were produced during ambient drying with the aid of HMDZ surface modifier. Both percentage of HMDZ and drying temperature showed effective role in final properties of prepared aerogels. The results indicates that the optimum condition (20 wt% HMDZ and 75 °C as drying temperature) deliver the most favorable properties. In the situation, samples have a bulk density about 0.15 gr/cm³, specific surface area of about 520 m²/gr and the most uniform microstructure. Further increasing in drying temperature (more than 75 °C) cause to lower the final quality of produced aerogels.

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