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Fabrication of a silica aerogel and examination of its hydrophobic properties via contact angle and 3M water repellency tests

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Abstract. Aerogels are dry gels with a very high specific pore volume. Aerogels with increased hydrophobicity have significant potential to expand their use as lightweight materials. Considering its special nanostructure and exceptional properties, this paper focuses on the synthesis and hydrophobic evaluation of a silica aerogel. The structural properties were investigated by measuring density, SEM micrographs, and BET analyses. Also, the hydrophobic evaluation was carried out by measuring 3M water repellency and water/alcohol contact angle. The BET analysis showed successful synthesis of the nanoporous silica aerogel with a pore size of 24 nm and porosity of 89%. The synthesized aerogel showed 3M water repellency of 3 and water contact angle of 129.6˚. Also, it is worth-mentioning that as the alcohol content of the drops in 3M water repellency test is increased, the drop contact angle is decreased due to its lower surface tension. Thus, the contact angle reaches the zero at 3M water repellency test number of 4 (water/alcohol 60/40).

Introduction

The word aerogel was firstly presented by Kistler in 1932 to title gels in which the liquid was replaced with a gas, without collapsing the gel solid network [1]. Aerogels are dry gels with a very high specific pore volume. Aerogels, known as frozen smoke or air-glass, are contained of nanoparticles with usual dimensions of less than 10 nm and pore sizes of less than 50 nm in diameters [2-4]. If aerogels are sensitive to moisture, it causes them to lose their structural network integrity during their application. Thus, aerogels with increased hydrophobicity have significant potential to expand their use as lightweight structural, insulating or shock absorbing materials especially in aeronautics, microelectronics, and sensing applications.

There are three primary techniques used to make hydrophobic silica aerogels which involve vapor phase after treatment, co-precursor techniques, and derivatization methods [5].

The majority of the work reported in the literature has focused on the use of organosilanes specially methytrimethoxysilane (MTMS) or trimethylethoxysilane (TMES) as a co-precursor to make hydrophobic gels. They achieved a water contact angle up to 180˚. For example, Standeker et al. [6] studied the effects of MTMS and TMES on hydrophobicity and achieved contact angles of 42–173˚ for MTMS/TMOS molar ratios of 0.5–5 and contact angles of 100–180˚ for TMES/TMOS molar ratios of

0.5–5. Additional studies were performed by Rao and coworkers [7] in which the monolithic aerogels with contact angle up to 140˚ were fabricated. On the other hand, silylation especially with (trimethylchlorosilane) TMCS has been performed using a variety of precursor materials to form hydrophobic gels which are able to use ambient drying. For example, Jeong et al. [8] provide a direct comparison of TEOS-based, ambient-dried aerogel powders with and without silylation and show an increase in contact angle from near zero to 158 when silylation was used. Different from these works, no research has been done on the surface energy investigation of the aerogel material via 3M water repellency test.
This paper focuses on one of the most studied aerogel materials, silica aerogels and investigates its synthesis and hydrophobic properties containing surface energy in a new way.

Experimental

Aerogel synthesis. The schematic procedure for synthesizing the silica aerogel is shown in Fig. 1. According to fig.1, the silica sol was prepared with a waterglass or sodium silicate solution with a specific gravity of 1.39 which was diluted to 1:4 (v/v) with water. The sodium ions were exchanged with proton ones by going through an Amberlite IR 120 H ion exchange resin-filled column. The gelation was occurred via addition of the ammonia solution (1%) to the collected silicic acid with pH values of 2.4–2.7 in a plastic vessel. The wet gels were aged for 3 h to strengthen their structures. The aged hydrogel was immersed in the propone-2-ol, n-Hexane, and TMCS/n-Hexane (1:5 V/V) mixture for 24 h to be changed to alcogel, organogel, and modified organogel, respectively. The resulted modified gels were dried at room temperature for 24 h. The dried gel was heat treated at 50 and 230ºC for 1 h to make the aerogel granules.

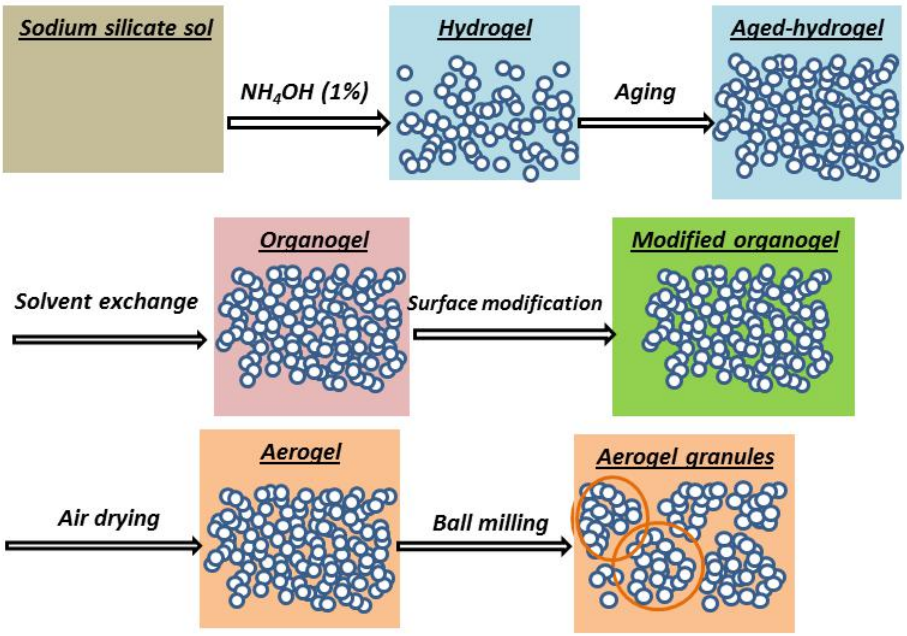

Figure. 1 A schematic of aerogel synthesis.

Hydrophobic properties. To study the level of the samples' hydrophobicity, both sliding angle and 3M water repellency [9] tests were examined. The samples were tested for water repellency using the water/alcohol drop test. The samples are placed flat on a smooth, horizontal surface. Beginning with the lowest numbered test liquid, three small droplets (approximately 5mm in diameter) are placed onto the sample using a pipette. The droplets are observed for 10 s. If after 10 s, two of the three droplets are still visible as spherical to hemispherical, the fabric passes the test. Samples are rated as pass or fail of the appropriate test liquid, W–10. The rating given to a sample is for the highest test liquid remaining visible after 15 s. 3M water repellency liquids

number and content is indicated in Table 1. In general, water repellency rating of 2 or greater is desirable. The location of a droplet on the surface of the hydrophobic treated samples allows evaluating the water contact angle. The images were taken using a USB digital microscope, Digi Micro Scope. The angles between the liquid/solid and liquid/vapor interfaces were measured using the Digimizer software.

Table 1 3M water repellency liquids number and content.

Test number	Water/ alcohol ratio
0 (water)	100/0
1	90/10
2	80/20
3	70/30
4	60/40
5	50/50
6	40/60
7	30/70
8	20/80
9	10/90
10 (alcohol)	0/100

SEM and BET. The SEM images were obtained using a KYKY-EM3200 microscope.
The BET analysisto evaluate the specific surface areas, total pore volume, and mean pore diameter and distribution was carried out using a Belsorp mini IIapparatus (ISO 9277).
Density and porosity. The porosity of the manufactured silica aerogel was calculated using Eq. 1[9].

Where, P, ρ_b, and ρ_s, represent the porosity (%), bulk density (g/cm^3), and skeletal density of the amorphous silica (g/cm^3), respectively. The bulk density and total pore volume were calculated by Eq. 2.

Where, m is the mass (g), V_α is the apparent volume (cm^3), and v is the total pore volume (m^3/g).

Result and discussion
Aerogel synthesis. Fig. 2 shows the primary hydrogel before and the resulted aerogel granules. As shown in Fig. 2, the initial transparent gels were changed to the opaque hydrophobic aerogel during the surface modification process. Two phases containing of water/HCl phase under the *n*-Hexane phase, obtained after successful treatment of the gel with TMCS is indicated in Fig. 2 (B). The hydrophobic modified gel was floated in the *n*-Hexane phase. This phenomenon is explained by the following main reaction (1) that can occur during the solvent exchange/modification of the wet gel [10].

$$TMCS+\equiv Si-OH \rightarrow \equiv Si-O-Si(CH_3)_3+HCl \quad (1)$$

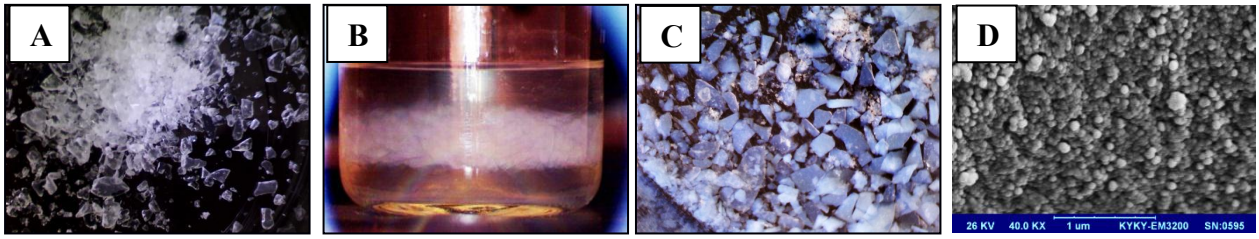

Figure. 2 (A) The hydrogel, (B) two phases formed at the end of surface modification step, (C) the aerogel granules, and (D) SEM micrographs

Also, the structure of the synthesized aerogel in a nanoscale form is shown in a SEM micrograph in Fig. 2 (D).
Table 2 shows the structural parameters of the synthesized aerogel obtained by the BET analysis. It is clear that the porous powder is successfully synthesized with a surface area of 815 m^2/g, a mean pore diameter of 24 nm, and a total pore volume of 3.5 m^3/g. Thus, the obtained dried gel in this work can be called an aerogel because all aerogels have nano-pores with diameters of less than 50 nm [11].

Table 2 Aerogel characteristics

Density (g/cm^3)	Total pore volume (m^3/g)	Mean pore diameter (nm)	Porosity (%)	Water contact angle (º)	3M water repellency
0.25	3.5	24.0	89	129.6	3

Hydrophobic properties. Surfaces are known to interact with their environment in a variety of ways. One central concept governing such interactions is the minimization of the interfacial surface-free energy [12]. The resulted aerogel shows the 3M water repellency value of 3. It indicates the silylation of the OH groups to the O–Si $(CH_3)_3$ groups with TMCS. So, it can be concluded that TMCS successfully reacted with Si–OH groups which are the main source of hydrophilicity of the aerogels. Water/alcohol drops, used in 3M water repellenct test, on the aerogel surface is shown in fig. 3. Also, water/alcohol drops contact angles on the aerogel surface is indicated in Table 3. The aerogel granules exhibit a water contact angle usually associated with that of high hydrophobic gels modified by the TMCS hydrophobic agent.
Also, there is an indirect relation between the water/alcohol number and its contact angle as shown in fig. 3 and Table 3. Thus, as alcohol content of the test droplet is increased, its contact angle is decreased until it reached the Zero at test number of 4 (water/alcohol 60/40). This is due to this fact that the addition of alcohol to the water phase decrease it surface tension leading to easier penetration of the drops to the surface.

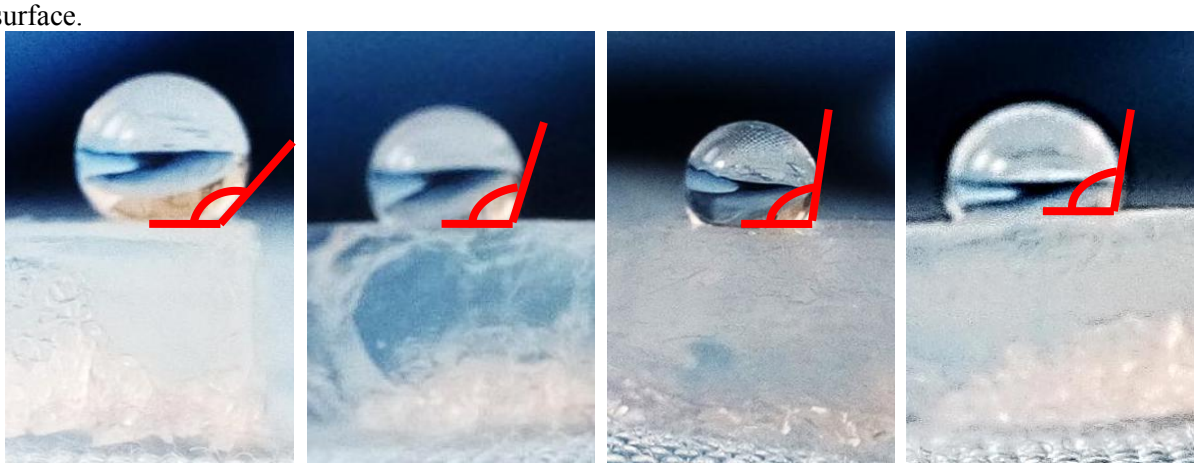

Figure. 3 3M water repellency solutions. (A) 100/0, (B) 90/10, (C) 80/20, (D) 70/30 water/alcohol drops on the aerogel surface

Table 3 Contact angle of water/alcohol drops used in 3M water repellency test on the aerogel surface

Test number	W	1	2	3	4
Contact angle	129.6	126.3	118.1	108.2	0

For better comparison, the colour water drop and 60/40 water/alcohol drop on the aerogel surface is indicated in fig. 4. It is clearly obvious that the 60/40 water/alcohol drop spreads on the aerogel surface and wet it completely.

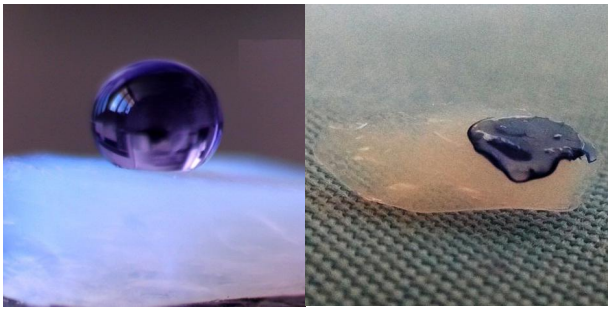

Figure. 4 (A) A (100%) water droplet, and (B) (60/40) water/Isopropan 2-ol drop on the synthesized aerogel surface.

Conclusion

In this research, waterglass based aerogel granules were prepared by a sol–gel process and ambient pressure drying. According to the results, the silica aerogel was fabricated with a mean pore diameter of 24 nm, atotal pore volume of 3.5 m^3/g, and porosity of 89%. The silica aerogel showed hydrophobic properties by a water contact angle of 129.6° and 3M water repellency of 3 with water/alcohol mixture with volumetric ratio of 70/30. Thus, the liquids with surface energy of less than 3M water repellency value of 4 cannot be absorbed on the aerogel surface which can be investigated in further studies.

Acknowledgment

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