

# Influence of various processing parameters on water-glass-based atmospheric pressure dried aerogels for liquid marble purpose

Uzma K. H. Bangi · Sunetra L. Dhere ·  
A. Venkateswara Rao

Received: 5 November 2009 / Accepted: 30 January 2010 / Published online: 17 February 2010  
© Springer Science+Business Media, LLC 2010

**Abstract** Experimental results on the influence of various processing parameters on water-glass-based atmospheric pressure dried aerogels for liquid marble purpose are reported. Silica aerogels were prepared by varying the parameters namely washing temperature of the gels with water, washing period of the gels, protic solvents, and drying method. The physical properties of silica aerogels were studied by measuring granular bulk density, contact angle with water, thermal conductivity, and thermal stability in the furnace. The elemental analyses were carried out using Atomic Absorption Spectroscopy (AAS) and FT-Raman spectroscopy. The structural studies were carried out using Transmission Electron Microscopy (TEM). Also, the effect of humidity on the silica aerogels was studied in humidity chamber. Opaque silica aerogels with hydrophobicity ( $150^\circ$ ), low density ( $0.053 \text{ g/cm}^3$ ), and low thermal conductivity ( $0.068 \text{ W/mK}$ ) have been obtained for the molar ratio of  $\text{Na}_2\text{SiO}_3$ :  $\text{H}_2\text{O}$ : citric acid: TMCS at 1:146.67:0.72:9.46. The hydrophobic powder of silica aerogels can form the liquid marbles.

## Introduction

Silica aerogels are a class of extremely low density ( $0.004$ – $0.500 \text{ g/cm}^3$ ) materials characterized by an open cross-linked silica network with particles usually  $<10 \text{ nm}$  and pore size usually  $<50 \text{ nm}$  in diameter. They have low thermal conductivity ( $\sim 0.005 \text{ W/mK}$ ) with high porosity ( $80$ – $99.8\%$ ) and large inner surface area ( $500$ – $1200 \text{ m}^2/\text{g}$ )

[1, 2]. Therefore, they have wide potential applications in many fields such as Cerenkov detector [3], thermal insulation [1], catalysts [4], gas filters and electronics [5], and so on.

Conventionally, silica aerogels were prepared by Kistler via sophisticated and energy intensive supercritical drying process which restricts the growing technology of the aerogels [6]. Afterward, Teichner and Nicolaon [7] produced the silica aerogels using expensive precursors as TEOS or TMOS. With the advancement in the aerogels research, in 1995, Prakash et al. [8] reported the synthesis of silica aerogel films using water-glass followed by silylation of wet silica gels at atmospheric pressure. Therefore, recently many groups are interested in the preparation of the silica aerogels at atmospheric pressure using water-glass and tetraethoxysilane (TEOS) precursors [9–12]. In the atmospheric pressure drying method of the preparation of silica aerogels, the silylation (surface chemical modification) is the main step to reduce the capillary pressure exerted by the liquid present in the pores of gel. In silylation process, the surface silanol groups are replaced by the alkyl groups so that gel springs back to its original shape after shrinkage due to repulsion between the alkyl groups [9]. It is accompanied by using the hydrophobic reagent like trimethylchlorosilane (TMCS). Moreover, TMCS causes the decrease in the surface tension of the solvent and contact angle between the solvent and surface of silica network [13]. The prerequisite of this step is to wash the gel with protic solvents, because the protic solvents (alcohols) have low surface tension. Hence, the overall effect is the reduction in the capillary pressure that arises in the pores of gel during evaporation [14]. The as-prepared aerogels are opaque in nature due to trapping of sodium citrate formed by crystallization of sodium ion from water glass and citrate ion from citric acid in the

U. K. H. Bangi · S. L. Dhere · A. Venkateswara Rao (✉)  
Air Glass Laboratory, Department of Physics, Shivaji University,  
Kolhapur 416004, Maharashtra, India  
e-mail: avrao2012@gmail.com

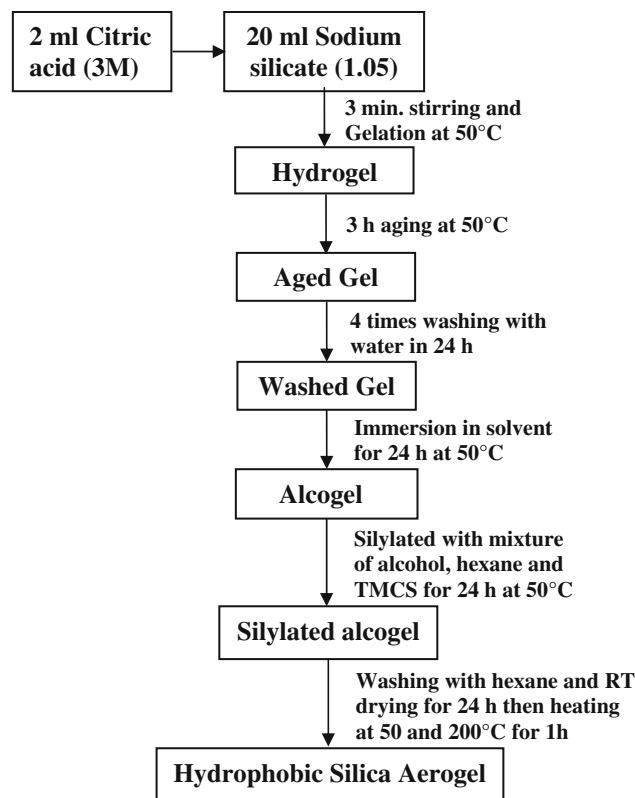
pores of gel. Therefore, the attempts have been made to minimize the opacity by varying the temperature and period of washing the gels with water. So, to produce low density hydrophobic silica aerogels to form liquid marbles, in the present paper, we have studied the influence of various processing parameters on water-glass-based atmospheric pressure dried aerogels.

Droplets capture both hydrophilic and hydrophobic components, owing to capillarity if no stronger force such as gravity is acting against it. For a liquid droplet, there may be two possible motions: (1) if the droplet partially wets the surface, it slides along it; (2) if the droplet is in superhydrophobic state, it can roll on the surface [15], much like a marble on a rough inclined plane, both needing an external driving force such as gravity. It is known that there are typically two states in which a droplet can reside on a given surface [16] as explained by Cassie model [17] and Wenzel model [18]. Generally, a droplet tends to reside in the lowest energy state, i.e., the state in which apparent contact angle is minimal. However, an energy barrier separates the two states so that a droplet may reside in Cassie state even though Wenzel state has a low energy, and inversely [19]. He et al. [20] have demonstrated that the Cassie state shows much less hysteresis compared to Wenzel state and is therefore preferred for moving droplets application. An interesting alternative to achieve these is to encapsulating a liquid droplet with a hydrophobic powder. The resulting liquid marbles are found to behave like a soft solid showing dramatically reduced adhesion to a solid surface [21]. Such extreme contact angles dramatically reduce both hysteresis and viscous friction giving very high speeds of motion to droplets which are theoretically possible. However, the solid–liquid area of droplets tends toward zero so that one cannot exploit the surface energy as a driving force. Therefore, the moving droplets are an efficient way of transporting and/or collecting sensitive and fragile material such as cells, nanotubes, and different micro-/nano-objects. Taking these facts into account, we prepared liquid marbles from superhydrophobic powder of silica aerogel.

## Experimental

### Preparation of silica aerogels

The schematic presentation of the preparation of water-glass-based atmospheric pressure dried silica aerogels is shown in Fig. 1. Chemicals used were water-glass ( $\text{Na}_2\text{SiO}_3$ , s-d fine chemicals, India,  $\text{Na}_2\text{SiO}_3$  content 36 wt%,  $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.33$ ), citric acid-hydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ), methanol (MeOH), ethanol (EtOH), propanol (PrOH), butanol (BuOH), hexane (Merck, India), and trimethylchlorosilane



**Fig. 1** Schematic presentation of the preparation of hydrophobic silica aerogels

(TMCS, Fluka, Pursis grade, Switzerland). Double distilled water was used for the preparation of solutions and for washing the gels. Silica hydrosols were prepared by catalyzing the water-glass precursor of specific gravity 1.05 (diluted from 1.39) with citric acid (3 M) in 125 mL glass beaker using the molar ratio of  $\text{H}_2\text{O}:\text{Na}_2\text{SiO}_3$  at 0.67 as following the earlier work [22]. The role of alcohol present in the pores of alcogel is to reduce the surface tension causing the shrinkage during drying. The modified alcogels were just washed with hexane and then subjected to drying. Two methods are followed for drying purpose viz. method A (drying at room temperature (RT) for 24 h followed by heating at 50 and 200 °C for 1 h each) and method B (heating at 50 and 200 °C for 1 h each). The resulting hydrophobic silica aerogels were used for the characterization after cooling of oven to atmospheric temperature.

### Method of characterizations

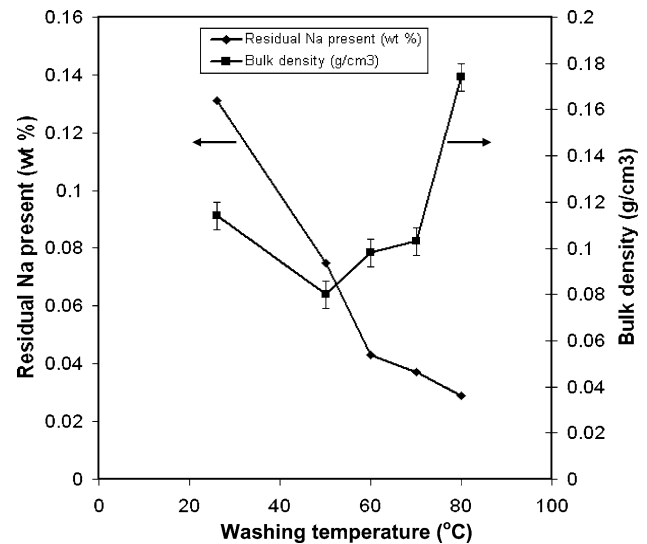
The granular bulk density of aerogels was calculated by ratio of mass of aerogel to its volume where mass is measured by microbalance (Dhona 100 DS,  $10^{-5}$  accuracy) and volume is measured by filling the granules of aerogel in a cylinder of known volume. The % of volume shrinkage, % of porosity, and pore volume were calculated from

the formulae, which have been reported elsewhere [23]. The thermal conductivity of the aerogel sample was measured using C-T meter (Teleph Company, France, accuracy  $10^{-3}$  W/mK). The hydrophobicity of the aerogels was tested by measuring the water contact angle using contact angle meter (Rame-Hart, Model 500-F1, USA). Also, it is confirmed by the FT-Raman spectroscopy (BRUKER MultiRAM, Australia). The estimation of the sodium present in the pores of the aerogels is carried out by using the Atomic Absorption Spectroscopy (AAS, Perkin Elmer, USA). The microstructure of the aerogels was studied using Transmission Electron Microscopy (TEM, using FEI TECNI SPRIT, accelerating voltage: 120 kV). The thermal stability of aerogel was checked in the controlled furnace (Vulcan TM 3-550, Norway). The humidity effect on hydrophobicity of aerogels was carried out in humidity chamber (Model CHM-38, REMI Instrumentation Ltd.) at a relative humidity of 85% at 30 °C for 30 days.

## Results and discussion

### Influence of washing temperature of the gels with water ( $T$ )

The washing temperature ( $T$ ) of the gels with water predominantly affects in the exclusion of sodium salt from the pores of the gel network. The influence of washing



**Fig. 2** Influence of washing temperature on the residual Na present and packing density of silica aerogels

temperature of the gels with water on the physical properties of silica aerogels is studied by varying it from 30 to 80 °C (Table 1). Figure 2 shows the influence of washing temperature of the gels on residual Na present (wt%) and granular bulk density of the silica aerogels. It is observed that as  $T$  increased, the residual Na present (wt%) decreased from 0.14 to 0.03 wt%. The reason behind this is, the movement of sodium citrate within the gel body is

**Table 1** Effect of various processing parameters on physical properties of silica aerogels

Variations	% of volume shrinkage	% of porosity	Pore volume (cm <sup>3</sup> /g)	Thermal conductivity (W/mK)	Contact angle (deg)
Variation in washing temperature of the gels with water (°C)					
30 °C	47	94	8.2	0.108	140
50 °C	31	95.7	11.8	0.087	145
60 °C	45	94.8	9.6	0.097	142
70 °C	50	94.5	9.1	0.1	140
80 °C	70	90.8	5.2	0.116	130
Variation in washing period of gel with water (hours)					
8 h	70	93.7	7.9	0.11	130
16 h	70	94	8.2	0.108	130
24 h	31	95.7	11.8	0.087	145
32 h	43	95	10	0.097	142
Variation in protic solvents					
MeOH	31	95.7	11.8	0.087	145
EtOH	68	91	5.4	0.114	130
PrOH	77	87.6	3.7	0.139	128
BuOH	77	87.5	3.4	0.144	128
Variation in drying method					
Drying method A	22	96.2	13.5	0.083	146
Drying method B	9	97.2	18.3	0.068	150

considered to proportional to proceed through diffusion as given in the following equation.

$$D = kT/6\pi\eta r \tag{1}$$

where  $D$  is diffusion coefficient,  $k$  is Boltzmann constant,  $T$  is temperature,  $\eta$  is viscosity of the medium,  $r$  is the particle radius. Since,  $D$  is directly proportional to  $T$ , therefore, as  $T$  increases, the diffusion is faster, i.e., permeability of salt and water through gel increases with temperature. Also, the solubility of sodium citrate is 72 g/100 g of water at room temperature, therefore, as  $T$  increases, more Na will come out from the gel network. From Fig. 2, it is observed that as  $T$  increased up to 50 °C, the bulk density of the silica aerogels decreased then further increased for  $T > 50$  °C. This is because, the elevated temperature crumbles the gel network which causes the shrinkage during drying producing dense aerogels. Hence, washing the gels at 50 °C produced the low density (0.080 g/cm<sup>3</sup>) silica aerogels. Figure 3 shows the TEM images of the silica aerogels for the gels washed with water at 50 and 80 °C which clarifies that for the gels washed at 80 °C, aerogels have shrunk and dense network (Fig. 3b) whereas for the gels washed at 50 °C, they have porous network (Fig. 3a).

**Influence of washing period of gel with water ( $t$ )**

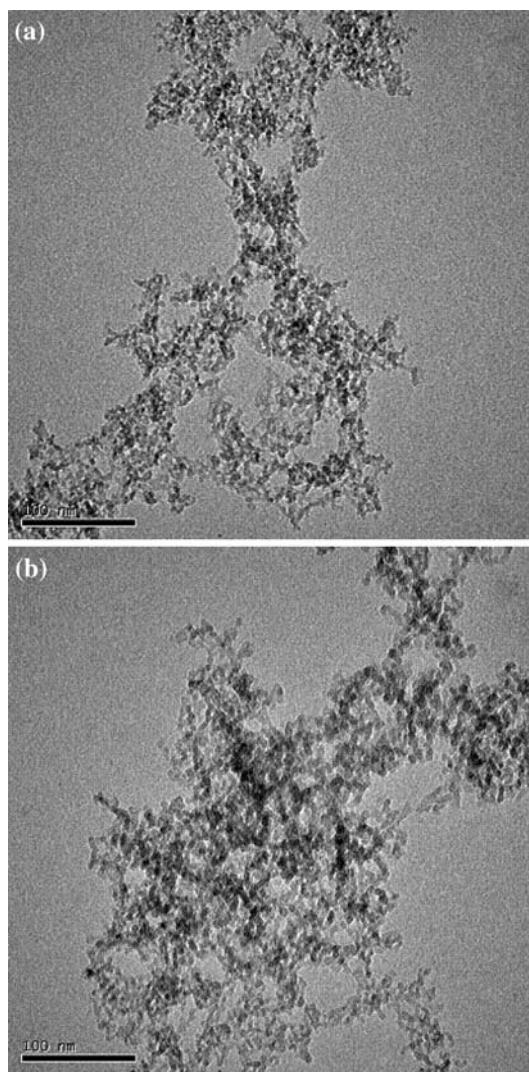
The influence of washing period ( $t$ ) of gel on the physical properties of silica aerogels is studied by varying it from 8 to 32 h as shown in Table 1. Figure 4 shows the influence of washing period ( $t$ ) on the residual Na present (wt%) and granular bulk density of the silica aerogels. It is observed that as  $t$  increased, the residual Na present decreased from 0.12 to 0.05 wt%. Again, the reason for this is explained by diffusion process and it takes longer time to exclude sodium citrate enough. The washing process is described as the change in the concentration of sodium citrate, therefore, the average concentration,  $C_{av}$ , of sodium salt in the gel is given by the following equation.

$$\frac{C_{av}}{C_o} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left( \frac{1}{(2n+1)^2} \exp \left\{ \frac{-(2n+1)^2 \pi^2 Dt}{4l^2} \right\} \right) \tag{2}$$

where  $C_o$ ,  $t$ ,  $2l$  are initial concentration of sodium salt, time, and thickness of the gel plate, respectively [24]. Hence, the washing period ( $t$ ) necessary to remove sodium salt enough as a function of the thickness ( $l$ ) of the gel plate is,

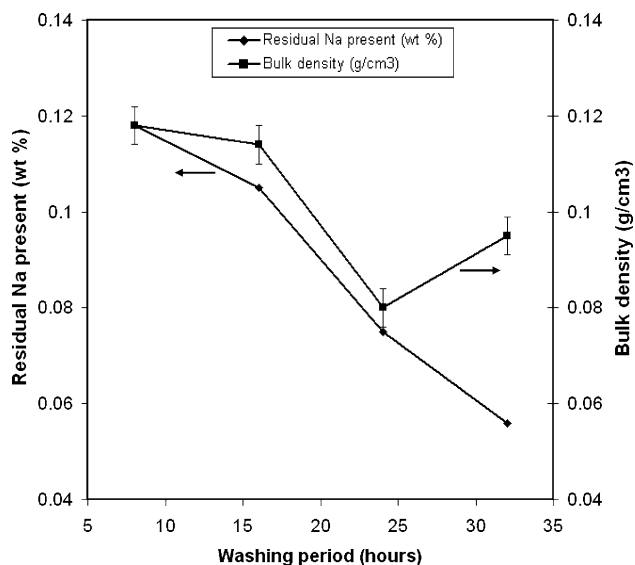
$$t \propto \frac{l^2}{D} \tag{3}$$

Since, the washing period is directly proportional to thickness of the gel plate as a second order function and



**Fig. 3** TEM images of the silica aerogels washed with water at **a** 50 °C, **b** 80 °C

inversely proportional to diffusion coefficient, means as the thickness of the gel increases, the washing period increases. Also, it takes long time to come out the salt from the gel network. From Fig. 4, it is observed that as  $t$  increased from 8 to 24 h, the bulk density of the silica aerogels decreased. This is because, the gel washing leads to an increase in the stiffness accompanied by increase in the pore radius of the gel network [25], which enables the gel to withstand the capillary pressure better during the drying stage. This leads to minimum shrinkage during drying and hence low density silica aerogels. But, as washing period increased to 32 h, the bulk density of aerogels increased. The is due to, the excess washing with water may weakened the gel network which causes the shrinkage of network during drying, which is dependent on the stiffness of the gel network [26]. Hence, washing the gels for 24 h produced low density silica aerogel.

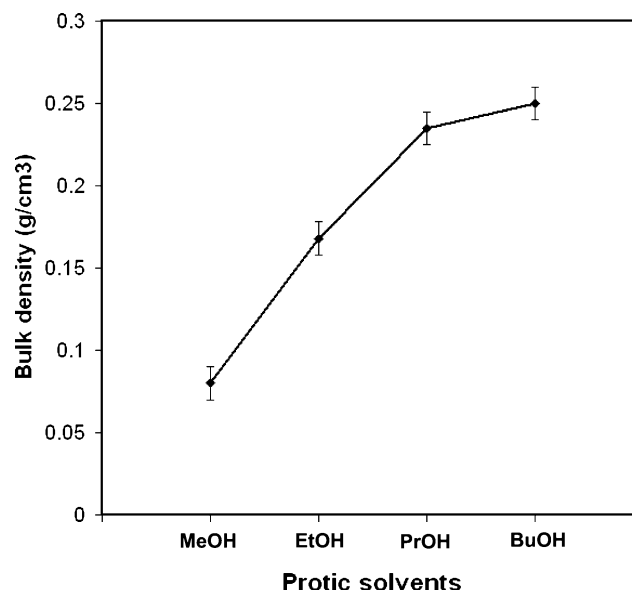


**Fig. 4** Influence of washing period on the residual Na present and packing density of silica aerogels

#### Influence of various protic solvents (alcohols)

Gel washing with the alcohol prior to silylation enormously affects the physical properties of silica aerogels. The solubility of alcohols in water is affected by the presence of hydroxyl groups. Because the hydroxyl groups participate in the hydrogen bonding with water molecules. Alcohols are both hydrogen bond donors and hydrogen bond acceptors. By participating in hydrogen bonds with water, the solubility of alcohols increases immensely. So, the water is completely replaced by alcohol which is required for appropriate silylation.

The influence of the various alcohols on the physical properties of silica aerogels is shown in Table 1 and the physical properties of alcohols are shown in Table 2. From the Fig. 5, it is observed that the granular bulk density of silica aerogels increased with increase in the chain length of alcohol. This is because, as the chain length increases, the hydrophobic part (non-polar part) becomes dominant over hydrophilic (polar part) one causing the decrease in the solubility and increase in the viscosity as given in Table 2. Also, it depends on the surface tension of the solvent. It was observed that the aerogels prepared using methanol have low density ( $0.080 \text{ g/cm}^3$ ). Because, the



**Fig. 5** Influence of various protic solvents on the packing density of silica aerogels

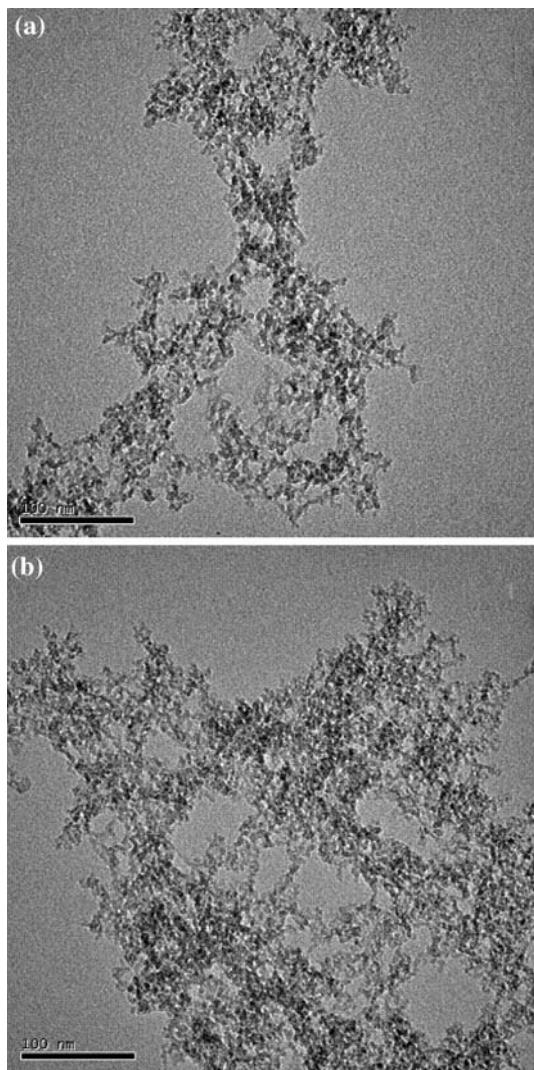
surface tension of methanol is lower, therefore the gel will not experience shrinkage as long as capillary pressure (in Eq. 1) is lower or equal to pristine gel strength assuming that contact angle of pore liquid with pore wall is zero. Figure 6 shows the TEM images of the silica aerogels prepared using methanol and butanol solvents. It is observed that for the aerogels prepared with methanol, the network is porous (Fig. 6a) while with butanol the network is shrunk and dense (Fig. 6b). The reason behind this is the surface tension of solvent which affects the silylation of alcogel and hence the density of silica aerogel.

#### Influence of drying method

Drying involves the evaporation of water, alcohols, and other volatile components present in the pores of gel network. Drying at high temperature causes the spring back of the silylated gels and hence lowers the density of the silica aerogels. The influence of drying methods on the granular bulk density and thermal conductivity of silica aerogels is compared in Fig. 7. From the Fig. 7 it is clear that method B produced lower density ( $0.053 \text{ g/cm}^3$ ) and lower thermal conductivity ( $0.068 \text{ W/mK}$ ) silica aerogels as compared to

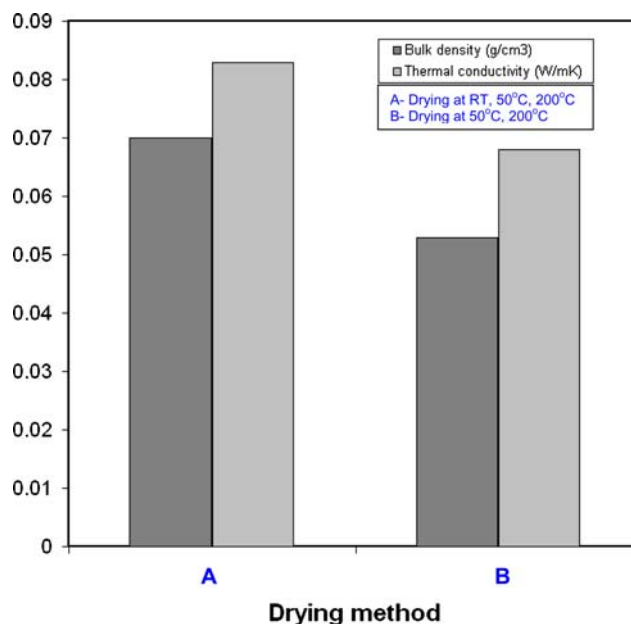
**Table 2** Physical properties of protic solvents (alcohols)

Serial no.	Protic solvents	Solubility in water	Viscosity (cP)	Surface tension (mN/m)
1	Methanol	Fully miscible	0.54	22.5
2	Ethanol	Fully miscible	1.07	22.3
3	Propanol	Fully miscible	1.93	23.78
4	Butanol	9.1 mL/100 mL	3	24.6

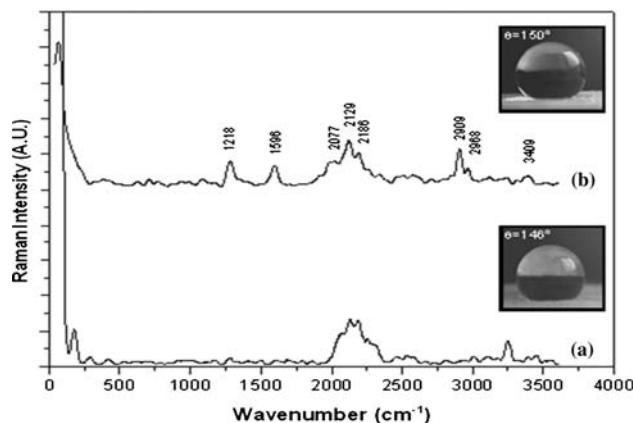


**Fig. 6** TEM images of the silica aerogels prepared using **a** methanol, **b** butanol

aerogels resulting from method A having density  $0.070 \text{ g/cm}^3$  and thermal conductivity  $0.083 \text{ W/mK}$ . The reason for the change in density and thermal conductivity is the rapid expansion of pore gas in gel and lower gel-permeability [27] in the drying method B. It is difficult to escape the expanded gas from the gel, and the gas compresses the gel network leading to increase in the pore volume and hence decrease of the density of silica aerogels. While for method A, the gels shrink due to the loss of pore fluid maintaining the liquid–vapor interface at the exterior surface of gel and they are affected by the moisture leading to increase in the density of aerogels. Figure 8 depicts the FT-Raman spectra of the aerogels dried by method A (a), and method B (b) along with photograph of water droplets placed on hydrophobic silica aerogel surface. The spectra clearly demonstrate the differences of the vibrational behavior depending on drying method of the aerogels. The peaks at

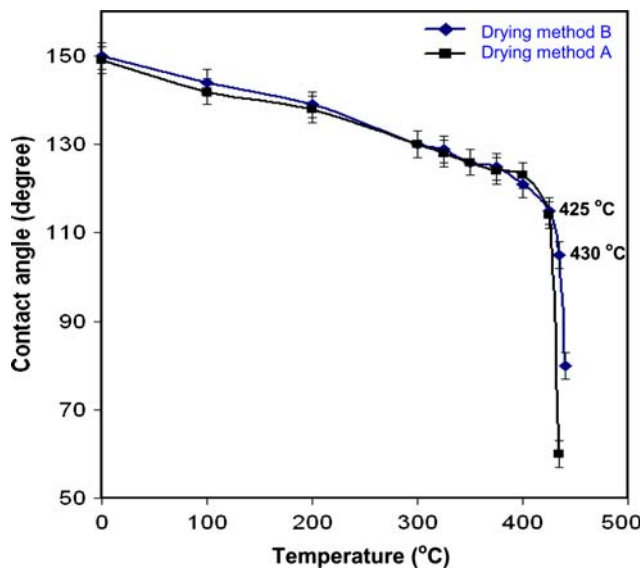


**Fig. 7** Influence of drying methods A and B on the packing density and thermal conductivity of silica aerogels



**Fig. 8** FT-Raman spectra of the silica aerogels dried by method B (a), and method A (b)

$1596, 3409,$  and  $1218 \text{ cm}^{-1}$  arisen from H–OH [28], Si–OH [29], and Si–O [30] stretching modes. The scattering modes at  $2909$  and  $2968 \text{ cm}^{-1}$  are due to C–H stretching [31]. The broad peak in between  $2000$  and  $2500 \text{ cm}^{-1}$  is considered as a result of shifting of C–H stretching band [32]. The OH peak intensity is weak and C–H peak intensity is strong in the aerogels dried by method B as compared to those by method A, indicating that they are sufficiently silylated. Therefore, the aerogels dried using methods A and B show contact angles  $146$  and  $150^\circ$ , respectively as seen from Fig. 8. The thermal stability of these aerogels was checked by heating them in temperature controlled furnace and putting the aerogel pieces in water. From Fig. 9, it is clear that beyond the temperature  $425$  and  $430 \text{ }^\circ\text{C}$ , the aerogels dried by



**Fig. 9** Measurement of thermal stability of the silica aerogel

**Table 3** Effect of humidity on silica aerogels dried by methods A and B

Serial no.	No. of days	Weight gain in the silica aerogels (mg) dried using	
		Method B	Method A
1	0	–	–
2	10	1.03	1.17
3	20	2.59	2.28
4	30	3.96	3.28

methods A and B, respectively, transform to hydrophilic nature. This is because of the decomposition of surface methyl groups which are responsible for the hydrophobicity of aerogels. It means that the aerogels dried by method B are retaining their hydrophobicity up to 430 °C. The influence of humidity on the as-prepared aerogels was studied by exposing them to the water saturated air atmosphere, i.e., 85% humidity at 30 °C (Table 3). As seen from the Table 3, it is observed that with an increase in number of days, the weight of aerogels increased causing an increase in the density of aerogels. This is due to the fact that, with an increase in the humidity period, the percentage of silanols on the surface of aerogels increases causing absorption of water from the humid surrounding. Therefore, the weight of aerogels increased leading thereby density and slight decrease in the hydrophobicity.

#### Formation of liquid marbles

Liquid marbles are liquid drops covered with micro- or nano-particles with a low surface energy. They are formed when hydrophobic grains self-organize on the liquid–vapor

interface of hydrophilic liquid [21, 33, 34]. From the work carried out by Aussillous and Quere [21, 35] it is known that hydrophobic powder particles can spread over a liquid creating a surface film. The tendency of solid to spread over or adhere to a liquid binder is called solid spreading nucleation [36–38]. Liquid marbles are obtained by trying to mix a hydrophobic powder with water, or with a solution of water and glycerol. Liquid marbles could be used for microfluidic applications [35]. Here, we chose the mixture of water and glycerol in 1:1 volume ratio for the formation of liquid marbles and hydrophobic powder of silica aerogel. The granular aerogels were crushed and made in a fine powder then the mixture of water and glycerol was dropped into the as-prepared fine aerogel powder. The grains continuously coat the drop and form the spherical-shaped liquid marble with planar contact zone as shown in Fig. 10. The exact shape of the drop results from a balance between gravity (which favors the contact) and capillarity (which opposes it because of the deformation it induces). For  $R \ll \kappa^{-1}$ , gravity is negligible and drop looks like a sphere, where  $R$  is the radius of droplet and  $\kappa^{-1}$  is capillary length. The size  $l$  of the contact between the marble and solid is given by [35],

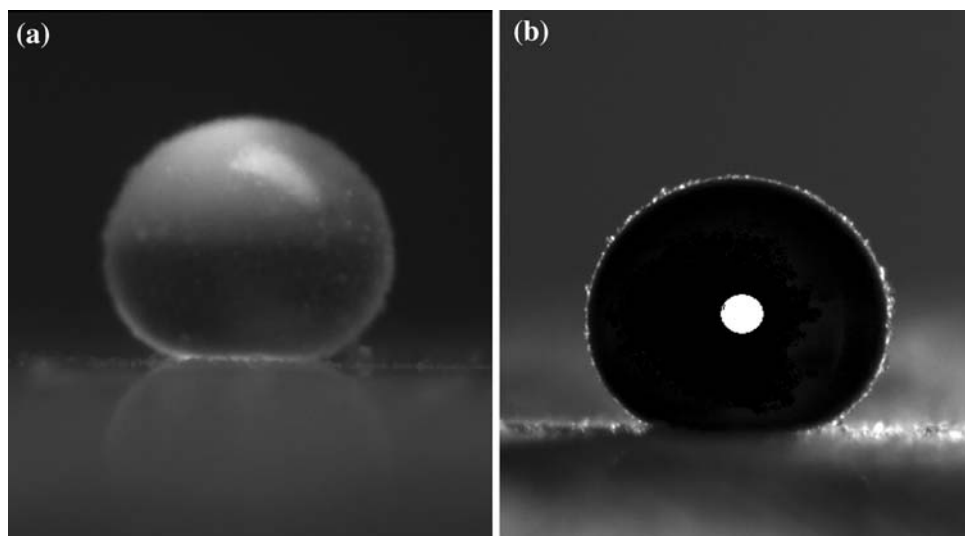
$$l = \sqrt{2/3} R^2 \kappa \quad (4)$$

It shows that the size  $l$  of contact between marble and solid increases as  $R^2$ , much quicker than for an uncoated droplet of liquid in partial wetting, for which  $l$  increases as  $R$  ( $l = R \sin\theta$ , where  $\theta$  is contact angle). Since, on the superhydrophobic surfaces, the water cannot enter the microscopic charms in the roughness because the pressure required is too high. Therefore, it was considered that there is no direct contact between liquid and solid and the liquid marble really sits on the hydrophobic particle [21, 39, 40]. The force needed to move these marbles is extremely small. The angle of inclination of the plane for liquid marble to roll-off is measured to be  $\sim 3^\circ$  which reveals the least contact with the substrate to avoid contamination problems and produces high displacement velocities, even for viscous liquids like glycerol.

#### Conclusions

The TEM images of the silica aerogels clearly indicate the influence of washing temperature and protic solvents on the porosity. FT-Raman spectra of the silica aerogels dried at RT, 50, 200 °C and 50, 200 °C clarify the difference in the hydrophobicity. The opaque silica aerogels with low granular density (0.053 g/cm<sup>3</sup>), low thermal conductivity (0.068 W/mK), and better hydrophobicity (150°) were obtained for the molar ratio of Na<sub>2</sub>SiO<sub>3</sub>: H<sub>2</sub>O: citric acid:

**Fig. 10** Photographs showing **a** liquid marble on a glass plate and **b** hydrophobic powder coat on the surface of droplet to form liquid marble



TMCS at 1:146.67:0.72:9.46 by washing the gels with water at 50 °C for 24 h, using methanol as a solvent and drying the silylated alcogels washed with hexane at 50, 200 °C. These aerogels were thermally stable up to 430 °C and showed slight decrease in hydrophobicity after 1-month storage in 85% humidity at 30 °C. The hydrophobic powder of these aerogels forms the liquid marbles.

**Acknowledgements** The authors are grateful to the Department of Science and Technology (DST), New Delhi, Government of India, for the financial support for this work through a major research project on “Aerogels” (No.SR/S2/CMR-67/2006). One of the authors Uzma K. H. Bangi is highly grateful to DST for providing the Senior Research Fellowship (SRF).

## References

1. Ayen RJ, Iacobucci PA (1988) *Rev Chem Eng* 5:157
2. Fricke J (1988) *J Non-Cryst Solids* 100:169
3. Pinto da Cunha J, Neves F, Lopes MI (2000) *Nucl Instrum Methods A* 452:401
4. Schneider M, Baiker A (1995) *Catal Rev Sci Eng* 37:515
5. Mezza P, Phalippou J, Sempere R (1999) *J Non-Cryst Solids* 243:75
6. Kistler SS (1931) *Nature* 127:741
7. Teichner SJ, Nicolaon GA (1968) *Bull Soc Chem Fr* 5:1900
8. Prakash SS, Brinker CJ, Hurd AJ (1995) *J Non-Cryst Solids* 190:264
9. Deshpande R, Smith D, Brinker CJ. US Patent No. 5, 565, 142 issued 1996
10. Kwon YG, Choi SY, Yang ES, Baek SS (2000) *J Mater Sci* 35:6075. doi:10.1023/A:1026775632209
11. Parvathy Rao A, Venkateswara Rao A, Bangi Uzma KH (2008) *J Sol-Gel Sci Technol* 47:85
12. Gurav JL, Rao AV, Nadargi DY (2010) *J Mater Sci* 45:503. doi: 10.1007/s10853-009-3968-8
13. Smith DM, Scherer GW, Anderson JM (1995) *J Non-Cryst Solids* 188:191
14. Deshpande R, Hua D, Smith D, Brinker CJ (1992) *J Non-Cryst Solids* 144:32
15. Mahadevan L, Pomeau Y (1999) *Phys Fluids* 11(9):2449
16. Bico J, Marzolin C, Quere D (1999) *Europhys Lett* 47(2):220
17. Cassie A (1948) *Discuss Faraday Soc* 3:11
18. Wenzel TN (1949) *J Phys Colloid Chem* 53:1466
19. Ishino C, Okumura K, Quere D (2004) *Europhys Lett* 68(2):419
20. He B, Lee J, Patankar NA (2004) *Colloid Surf A* 248:101
21. Aussillous P, Quere D (2001) *Nature* 411:924
22. Bangi Uzma KH, Parvathy Rao A, Hirashima H, Venkateswara Rao A (2009) *J Sol-Gel Sci Technol* 50:87
23. Parvathy Rao A, Pajonk GM, Rao AV (2005) *J Mater Sci* 40:3481. doi:10.1007/s10853-005-2853-3
24. Takahashi R, Sato S, Sodessawa T, Kamomae Y (2000) *Phys Chem Chem Phys* 2:1199
25. Einarsrud MA, Nilsen E, Rigacci A, Pajonk GM, Buathier S, Valette D, Durant M, Chevalier B, Nitz P, Ehrburger-Dolle F (2001) *J Non-Cryst Solids* 285:1
26. Brinker CJ, Scherer GW (1985) *J Non-Cryst Solids* 70:301
27. Zeng SQ, Hunt A, Grief R (1995) *J Non-Cryst Solids* 186:264
28. Babou F, Coudurier G, Vedrine J (1995) *J Catal* 152:341
29. Signoretto M, Pinna F, Strukul G, Chies P (1997) *J Catal* 167:522
30. Walrafen GE, Hokmabadi MS, Holmes NC, Nellis WJ, Henning S (1985) *J Chem Phys* 82:2472
31. Kim CY, Jang AR, Kim BI, Suh DH (2008) *J Sol-Gel Sci Technol* 48:336
32. Nie S, Marzilli LG, Yu N-T (1989) *J Am Chem Soc* 111:9256
33. Mahadevan L (2001) *Nature* 411:924
34. McEleney P, Walker GM, Larmour IA et al (2009) *J Chem Eng* 147:373
35. Aussillous P, Quere D (2006) *Proc R Soc* 462:973
36. Farber L, Hapgood KP, Michaels JN (2006) Hydrophobic nucleation in particle agglomeration, World Congress of Particle Technology 5, April 2006, Orlando, Florida, AIChE
37. Hapgood KP, Farber L, Michaels JN (2009) *J Powder Technol* 188:248
38. Eshtiaghi N, Liu JS, Shen W et al (2009) *J Powder Technol* 196:126
39. Bormashenko E, Bormashenko Y, Musin A, Barkay Z (2009) *Appl Surf Sci* 255:6429
40. Bormashenko E, Pogreb R, Whyman G et al (2009) *Colloids Surf A Physicochem Eng Asp* 351:78