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# Rapid reduction in gelation time and impregnation of hydrophobic property in the tetraethoxysilane (TEOS) based silica aerogels using $NH_4F$ catalyzed single step sol–gel process

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ABSTRACT

The experimental results on the synthesis and physical properties of tetraethoxysilane (TEOS) based superhydrophobic silica aerogels, obtained by single step sol–gel process, are reported and discussed. Superhydrophobic silica aerogels were prepared by varying the molar ratio of MeOH/TEOS ($M$) from 11 to 275, molar ratio of $NH_4F$/TEOS ($A$) from 1.2 to 9.6 and concentration of $NH_4F$ from 0.001 to 1 M, respectively. All the alcogels were dried under supercritical conditions. The remarkable results were obtained in terms of drastic reduction in the gelation time which is less than 1 min, using single step sol–gel process. Further, the obtained aerogels are hydrophobic ($\theta = 155^\circ$) without use of any hydrophobic reagents. The obtained hydrophobic property of the aerogels was improved using mono, di and tri-functional methoxysilanes as co-precursor such as, trimethylmethoxysilane (TMMS), dimethyldimethoxysilane (DMMS) and methyltrimethoxysilane (MTMS), respectively. It was observed that as the order of functional groups of methoxysilane decreases, the contact angle of the water droplet on the aerogel surface increases, indicating the aerogel become more hydrophobic. The highest contact angle of ($\theta = 168^\circ$) was observed for trimethylmethoxysilane as a co-precursor. The aerogels were characterized by bulk density, volume shrinkage, porosity, optical transmission and thermal conductivity measurements. The effect of humidity on the aerogel samples was studied using programmable environmental test chamber. The hydrophobicity of the aerogels was quantified by contact angle measurements and FTIR studies while microstructural studies were done using Transmission Electron Microscopy (TEM).

## 1. Introduction

Sol–gel processing is a novel route which has gained an importance in the preparation of a variety of porous solids. It is well known that porous solids are finding numerous applications both in science and technology because of their fascinating properties which are mostly determined by their low density, high porosity and large surface area. Out of all resulting structures of sol–gel processing, aerogels are particularly known for their small pore size (<10 nm), large specific surface area (>1000 m$^2$/g) and the best optical transmission (~99% in the visible region). Amongst all aerogels, silica aerogels have become quite popular because of their numerous and special applications such as shock-wave studies at high pressures [1], Inertial Confinement Fusion (ICF) targets [2], Cerenkov radiation detectors [3,4], micrometeorites [5], radioluminescent devices [6], light weight thermal and acoustic insulating systems [7,8], containers for liquid propellants [9], adsorption and catalytic support [10] and for super capacitors [11,12].

Silica aerogels produced using tetraalkoxysilanes, such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS), are inherently hydrophilic in character [13–15]. Furthermore, aerogels produced using TEOS precursor, have large gelation time of greater than 3 days, higher volume shrinkage (~40%), low optical transmission (~45%) and higher densities (~0.2 mg/cc) using strong acid catalyst such as HCl [16]. A few results on acid–base catalysed aerogels using two step process involves time consuming factor for their synthesis [17,18]. Though, TEOS has been widely used as a cheaper and less toxic precursor, it has very poor reactivity in the sol–gel reaction. The acid catalysed gelation of TEOS could be drastically accelerated using ammonium fluoride ($NH_4F$) [19]. So far, there are very few reports on the $NH_4F$ catalysed TEOS based hydrophobic silica aerogels, attempts have been made to synthesize TEOS based hydrophobic silica aerogels using single step sol–gel process by taking into account the fluoride anions catalyst which are known to be effective for reducing the gelation time from hours or even days

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to minutes and enhance the hydrophobic property of the aerogels [20].

## 2. Materials and methods

Silica alcogels were prepared by single step sol–gel process using tetraethoxysilane (TEOS) as the precursor. The hydrolysis and condensation reactions were carried out under the acidic condition ($NH_4F$ in water). The chemicals used were of "Purum" grade from Fluka Company, Switzerland. Double distilled water was used for the preparation of required concentration of $NH_4F$. The alcogels were aged for 24 h at ambient temperature (25 °C) and then kept in an autoclave above the critical temperature (Tc = 243 °C) and critical pressure (Pc = 7.9 MPa) of methanol under an inert atmosphere for supercritical drying. Finally, system was allowed to cool down to room temperature naturally and the aerogels were taken out for the characterization.

In order to get the best quality aerogels in terms of low density and good hydrophobicity, the molar ratio of MeOH/TEOS, *M*, was varied from 11 to 275 and then *M* value was kept constant at 33 by considering the better results as compared to the other *M* values. Effect of $NH_4F$ concentration (*A*) was studied by keeping the molar ratio of TEOS: MeOH: $NH_4F$ constant at 1: 33: 3.6, respectively, and varying the *A* value from 0.2 to 1 M. Further, the molar ratio of $NH_4F$/TEOS was varied from 1.2 to 9.6. In addition, the obtained hydrophobicity of the aerogels was improved using mono, di and tri-functional methoxysilanes as co-precursors such as, trimethylmethoxysilane (TMMS), dimethyldimethoxysilane (DMMS) and methyltrimethoxysilane (MTMS) at a molar ratio of TEOS:TMMS::1:0.33, TEOS:DMDMS::1:0.32 and TEOS:MTMS::1:0.31, respectively.

The aerogels were characterized by bulk density, porosity, volume shrinkage, thermal conductivity and contact angle measurements which all were well discussed in our earlier research papers [21–23]. The thermal conductivity was measured using C–T meter (Teleph Company, France) as per the equation:

$$\Delta T = \frac{RI^2}{L}\frac{1}{4\pi K}[\ln(t) + C^{te}] \qquad (1)$$

where, R = Resistance of the ring probe (Ω), *K* = Thermal conductivity (W/m K), *I* = Current (A), *t* = Pulse Time (s), *L* = Length of the ring probe (m) and $c^{te}$ = Integration constant.

The hydrophobicity of the aerogels was measured using the contact angle meter (rame-hart Company, Model 500-F1, U.S.A.) by putting a water droplet of 2.4 mm diameter on the aerogel surface. The same was confirmed by the measurement using a traveling microscope using the formula:

$$\theta = 2\tan^{-1}\left(\frac{2h}{\Delta}\right) \qquad (2)$$

where, *h* is the height and *Δ* is the base width of the water drop. The thermal stability of the aerogels, in terms of retention of hydrophobicity, was tested by the Thermo Gravimetric and Differential Thermal Analyses (TG-DTA) using 2960 TA universal instruments, made in U.S.A. The Fourier Transform Infrared (FTIR) investigations were carried out for confirming the evidences of Si–CH, Si–OH, C–H and Si–O–Si bondings. The optical transmission of the aerogels was measured using visible spectrophotometer (Chemito Company, India, Model No. 215-D). At a fixed wavelength in the visible range, the percentage of optical transmission for the reference block was adjusted to 100% and the optical transmission of the aerogel was measured. An extent of hydrophobicity of the aerogel samples was studied using programmable environmental test chamber. All the samples were kept at 80% humidity at 30 °C and the observations were made for continuous 15 days. Microstructural studies of the aerogel samples were carried out by Transmission Electron Microscopy (TEM).

## 3. Results and discussion

### 3.1. Gelation time

It is very difficult to set the TEOS based gels using single step sol–gel route. In case, if they set, their gelation time is very high [24]. However, using $NH_4F$ as a acid catalyst, TEOS based alcogel sets easily by single step sol–gel route in less gelation time which is about few minutes. The rapid reduction in the gelation time of the alcogels is due to the use of fluoride catalyst which is known for the ability to boost the gelation mechanism [25,26]. When $NH_4F$ was added in the single step sol–gel process, the hydrolysis and condensation reactions occurred simultaneously, as shown below.

Hydrolysis :

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

**Table 1**
Dependence of gelation time on the MeOH/TEOS molar ratio (*M*).

| Sr. No. | MeOH/TEOS molar ratio | Gelation time |
|---|---|---|
| 1 | 11 | 1 min |
| 2 | 22 | 2 min |
| 3 | 33 | 10 min |
| 4 | 44 | 25 min |
| 5 | 55 | 30 min |
| 6 | 66 | 45 min |
| 7 | 82 | 1 h |
| 8 | 110 | 3 h 35 min |
| 9 | 137 | 6 h |
| 10 | 165 | 1 day |
| 11 | 220 | 2 days |
| 12 | 275 | 3 days |

Condensation :

$$n[Si(OH)_4 + (OH)_4Si] \rightarrow n[(OH)_3Si{-}O{-}Si(OH)_3 + nH_2O$$

The $F^-$ ion from the $NH_4F$ has an ability to promote ripening process. The catalytic effect of fluorine involves the displacement of $-OC_2H_5$ groups from the TEOS via bimolecular nucleophillic attack which is impairing in case of HCl acid in single step sol–gel process. Therefore, the fluoride anions dramatically shorten the gelation time. This reduction in gelation time is more pronounced than that affected by hydroxyl ions.

Dependence of gelation time on the MeOH/TEOS molar ratio (*M*) was studied and the results were tabulated in Table 1. It was observed that the gelation time increased from 1 min to 3 days with an increase in *M* value from 11 to 275. This is due to the fact that as the dilution of TEOS in the methanol increases, the dispersion of TEOS molecules takes place to the greater extent. Therefore, this would take a longer time to form the 3D network structure of the silica particles. Furthermore, an increase in the gelation time is caused by the fact that higher dilution of TEOS in methanol lowered down the concentration of catalyst during the sol–gel reactions. Also, the gelation time was found to depend on the molar ratio of catalyst/precursor. Fig. 1 shows the reduction in the gelation time from 25 min to almost instantaneously with an increase in the $NH_4H$/TEOS molar ratio from 1.2 to 9.6 at constant *M* = 33. The decrease in the gelation time is due to the fact that an increase in the $NH_4F$ enhances the condensation process and the gel would set early. Since the molecular complexity of the gel network depends on the chemical parameters such as solvent content (MeOH), catalyst

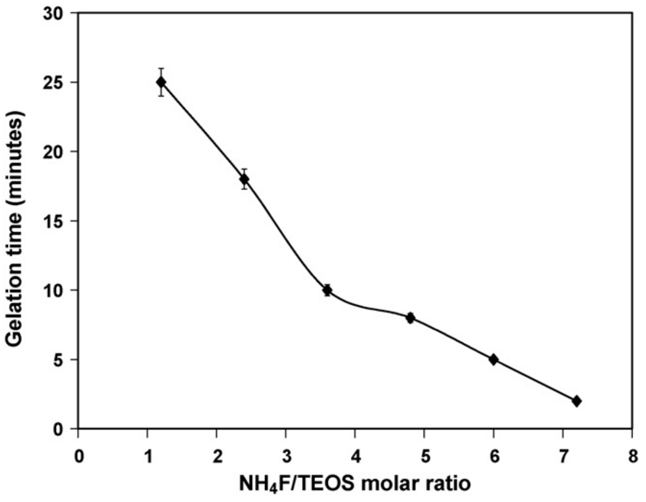

**Fig. 1.** Gelation time as a function of $NH_4F$/TEOS molar ratio.

**Table 2**
Physical properties of the as prepared aerogels.

| Sr. No. | Variations | Bulk density (g/cm$^3$) | Volume shrinkage (%) | Porosity (%) |
|---|---|---|---|---|
| MeOH/TEOS (*M*) molar ratio variation | | | | |
| 1 | 11 | 0.092 | 19 | 92 |
| 2 | 22 | 0.079 | 17 | 95 |
| 3 | 33 | 0.064 | 11 | 97 |
| 4 | 44 | 0.073 | 13 | 96 |
| 5 | 55 | 0.084 | 17 | 95 |
| 6 | 110 | Aerogels are not at all in characterizing conditions because of large shrinkage in volume | | |
| 7 | 165 | | | |
| 8 | 220 | | | |
| 9 | 275 | | | |
| $NH_4F$/TEOS (*A*) molar ratio variation | | | | |
| 10 | 1.2 | 0.070 | 14 | 94 |
| 11 | 2.4 | 0.067 | 12 | 96 |
| 12 | 3.6 | 0.064 | 11 | 97 |
| 13 | 4.8 | 0.065 | 12 | 96 |
| 14 | 6. | 0.068 | 13 | 95 |
| 15 | 7.2 | 0.069 | 14 | 95 |
| 16 | 8.4 | 0.071 | 16 | 94 |
| 17 | 9.6 | 0.071 | 16 | 93 |

concentration and steric hindrance of alkoxide, the gel did not set for the MeOH/TEOS molar ratio greater than 275. Large increase in the solvent content inhibited the polymerization process and hence the network structure.

### 3.2. Bulk density and volume shrinkage

In order to study the effect of sol–gel parameters on the physical properties such as bulk density, volume shrinkage of the aerogels, the molar ratios of MeOH/TEOS (*M*), $NH_4F$/TEOS (*A*) were varied from 11 to 275 and from 1.2 to 9.6, respectively. Table 2 illustrates the physical properties of the as prepared aerogels. It was found that the bulk density of the aerogels decreased significantly from 0.092 to 0.064 g/cm$^3$ with an increase in MeOH/TEOS molar ratio from 11 to 33. However, with further increase in the *M* value to 55, the bulk density was found to increase to 0.084 g/cm$^3$. The aerogels prepared at $M > 55$ are not at all monolithic and not in measurable form. It is due to the fact that the oxide content is greatly reduced because of higher dilution of TEOS in the methanol. From the TEM images shown in the Fig. 2a and b, it is very clear that the network densification at $M = 11$ (Fig. 2a) is higher than at $M = 33$ (Fig. 2b). Furthermore, at much higher dilution ($M > 55$), the increase in the bulk density is due to the volume shrinkage during the drying process than the extent of dilution.

The molar ratio of $NH_4F$/TEOS (*A*) was varied systematically from 1.2 to 9.6. It was found that the bulk density of the aerogels depends upon the *A* value. At constant $M = 33$, the bulk density of the aerogels was decreased from 0.070 to 0.064 g/cm$^3$ with an increase in the *A* value from 1.2 to 3.6. With the further increase in *A* value up to 9.6, the bulk density also increased up to 0.071 g/cm$^3$. This is due to the fact that since the catalyst ($NH_4F$) hydrolyses the alkoxide, lower *A* value results in the few number of hydrolyzed silanol groups and hence the limited cross linkage. Therefore, final aerogels became denser because of more shrinkage during the supercritical drying. On the other hand, at higher *A* value, aerogels are of larger pore diameter due to an increase in the amount of water that enhances the pore diameter [27]. This excess amount of catalyst causes shrinkage and hence the bulk density increases. An appropriate amount of catalyst ($A = 3.6$) hydrolyses almost all the alkoxide groups and forms highly branched polymeric network with smaller pores which minimizes the volume shrinkage and hence the bulk density [28].

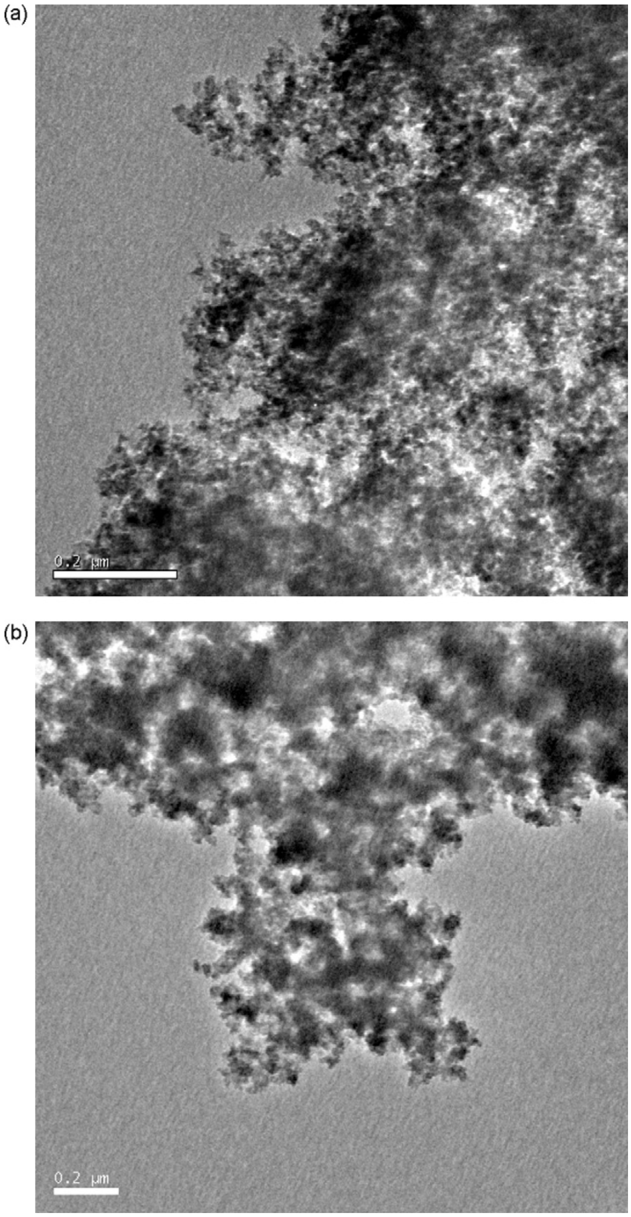

**Fig. 2.** (a) Transmission Electron Micrographs showing the microstructure of the aerogel samples prepared at $M = 11$. (b) Transmission Electron Micrographs showing the microstructure of the aerogel samples prepared at $M = 33$.

The volume shrinkage of the aerogels decreased from 19 to 11% with an increase in the *M* value from 11 to 33. For $M > 33$, the volume shrinkage was found to increase to 17%. This is due to the fact that at lower *M* value, the hydrolysis and condensation reaction rates are higher than at higher *M* values. Lower dilution of TEOS in methanol enhances higher catalyst concentration in the sol which led to rapid hydrolysis and condensation. Therefore, in short period of time, smaller clusters are formed and branched together to form gel network [29]. The as developed silica network consists of relatively small and uniform particles and pore sizes and therefore the drying stresses are minimum [30]. This led to the minimum volume shrinkage in the gel. But, the further dilution of TEOS lowers down the oxide content which led to the alcogels with uneven silica particles and pores which easily shrinks during supercritical drying process due to the differential pressure gradients. Hence, an increase in the volume shrinkage was observed. The aerogels prepared at $M > 55$ are not at all monolithic where the large volume shrinkage was observed.

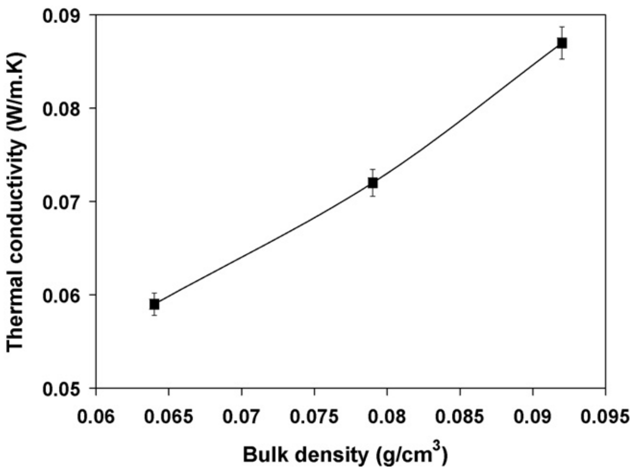

**Fig. 3.** Variation in the thermal conductivity with respect to the bulk density of the as prepared aerogels.

### 3.3. Thermal conductivity, TG-DTA and optical transmission studies

Fig. 3 shows the variation of thermal conductivity with the bulk density of the aerogels. It was found that the thermal conductivity ($K$) of the as prepared aerogel sample depends upon the bulk density of the corresponding aerogels. The thermal conductivity ($K$) decreased from 0.087 to 0.065 $\mathrm{W\,m^{-1}\,K^{-1}}$ with decrease in the bulk density from 0.092 to 0.064 $\mathrm{g/cm^3}$. This is due to the fact that as the bulk density of the aerogels decreases, the silica network becomes more porous leading to less solid content. Therefore, heat dissipation through such aerogels is less and therefore the thermal conductivity is also less. On the other hand, for higher density aerogels, the heat conduction is high and therefore the thermal conductivity is higher.

The thermo gravimetric and differential thermal analyses (TG-DTA) for the aerogel were depicted in Fig. 4. The TGA curve gave the 6.2% weight loss with respect to an increase in the temperature in the range of 330 to 640 °C for the aerogel at $M = 33$. The strong exothermic peak which corresponds to the oxidation of organic groups was resolved in the DTA curve at 300 °C temperature. Further increase in the temperature caused more weight loss indicating hydrophilic nature. The thermal stability was revealed by heating the aerogels in an oven at different temperatures and pouring them in the water until they turned to hydrophilic. The TEOS based aerogels catalysed with $NH_4F$ were thermally stable up to 300 °C and above this temperature, they lost the hydrophobic property and turned into hydrophilic aerogels. According to Rayleigh, the scattered intensity of light (I) is given by the relation [31]:

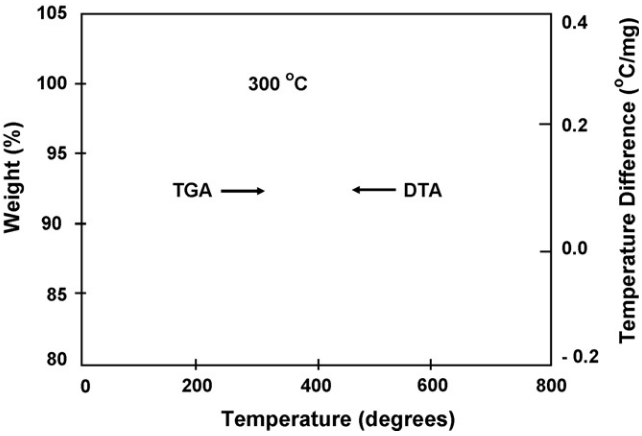

**Fig. 4.** Thermo gravimetric and differential thermal analyses (TG-DTA).

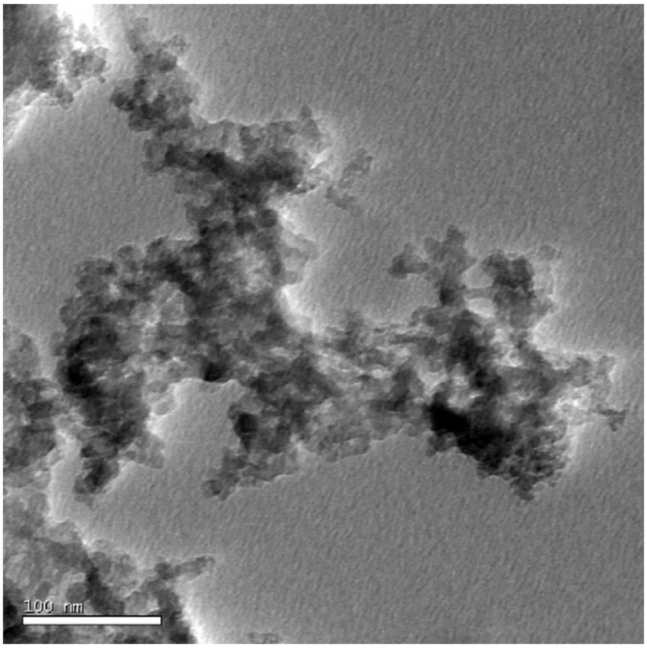

**Fig. 5.** Transmission Electron Micrograph showing the bigger pore size of the aerogel sample.

$$I = \frac{8\pi^4 r^6}{d^2\lambda^4}\frac{n^2-1}{n^2-2}(1+\cos^2\theta) \tag{5}$$

where $\theta$ is the scattering angle, $d$ is the distance from the particle to the detector, $n$ is the refractive index, $r$ is particle or the pore size and $\lambda$ is the wavelength of light. In case of $NH_4F$ catalyzed aerogels, the particles and pore sizes are large. Therefore, as $r$ is large, most of the incident light gets scattered. From the TEM image shown in the Fig. 5, the pore sizes are larger. As a result, these aerogels show very little transparency (<8%) in the visible region.

### 3.4. Hydrophobic property and FTIR studies

Under equilibrium conditions, the relation between the solid–vapour ($\gamma_{SV}$), solid–liquid ($\gamma_{SL}$) and liquid–vapour ($\gamma_{LV}$) interactions at the intersection of the three phases, is given by the Young's equation [32]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{6}$$

For a hydrophobic surface, $\theta > 90^\circ$ and therefore, from the above equation it follows that solid–liquid ($\gamma_{SL}$) interaction is greater than solid–vapour ($\gamma_{SV}$) interaction.

As mentioned in the introduction that the TEOS aerogels are inherently hydrophilic. But, it was observed that the pure TEOS alkoxide catalyzed with $NH_4F$ resulted into hydrophobic aerogels. Fig. 6a and b shows the photographs of the aerogel samples catalyzed with $NH_4F$ and catalyzed without $NH_4F$ (with $NH_4OH$), immersed in the water, respectively. The aerogel catalyzed with $NH_4F$ are hydrophobic; however, the aerogels without $NH_4F$ (with $NH_4OH$) as catalyst are hydrophilic in character. An impregnation of the hydrophobic property is due to the use of fluoride ions which are having high water repellant characteristic.

Also, the hydrophobicity of the aerogel samples was studied by measuring the contact angle of the water droplet on the aerogel surface and the results are tabulated in Table 3. It was observed that $\theta$ reduced from 155 to 144° with an increase in $M$ from 11 to 55. An enhancement in the hydrophobicity of the aerogels was stud-

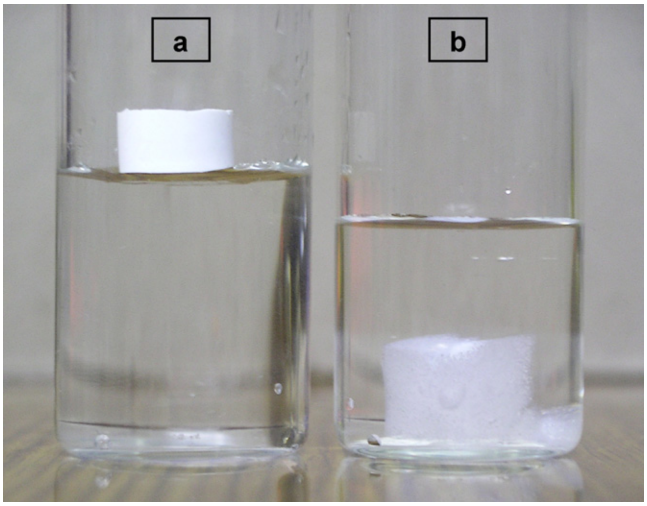

**Fig. 6.** The photograph shows the aerogel sample immersed in the water (a) catalyzed with $NH_4F$ and (b) catalyzed without $NH_4F$ (with $NH_4OH$).

ied by adding the co-precursors such as MTMS, DMMS and TMMS, respectively. It was found that as the order of functional groups of methoxysilane decreases from tri to mono, the contact angle of the aerogel surface increases, indicating the aerogel more hydrophobic. An increase in the hydrophobicity is due to the attachment of hydrolytically stable –Si–$(CH_3)$ groups by replacing surface H from –OH groups from the silica surface. As the co-precursor varies from MTMS to TMMS, the number of non-polar $CH_3$ group increases and the surface becomes highly superhydrophobic. The highest contact angle of ($\theta = 168^\circ$) was observed for trimethylmethoxysilane as a co-precursor. The sphericity of a water drop on the aerogel surface is characterized by the contact angle ($\theta$). From Fig. 7a, b and c, showing the photograph of the contact angles, it is clear that the sphericity of the water droplet is increasing from MTMS to TMMS treated aerogels. Therefore, higher the contact angle, greater the sphericity of the water drop on the superhydrophobic surfaces.

The hydrophobicity was also confirmed with Fourier Transform Infrared (FTIR) spectroscopy studies, as shown in Fig. 8 (aerogel catalyzed without $NH_4F$) and Fig. 9 (aerogel catalyzed with $NH_4F$). The Fig. 8 shows an intense peak at 3400 and 1670 $cm^{-1}$ corresponding to O–H bonds and very small peaks at 2950 and 1450 $cm^{-1}$ corresponding to C–H bonds, clearly indicating that the surface is hydrophilic. However, Fig. 9 shows the decrease in the intensity of the O–H peak at 2950 and 1450 $cm^{-1}$ with the corresponding increase in the Si–O–Si and Si–C peaks at 1090 and 805 $cm^{-1}$, respectively, which indicates that the surface is comparatively hydrophobic.

**Table 3**
Variation in the contact angle of the water droplet on different aerogel surfaces.

| Sr. No. | Variation | Contact angle (degrees) |
|---|---|---|
| MeOH/TEOS (*M*) molar ratio variation | | |
| 1 | 11 | 155 |
| 2 | 22 | 153 |
| 3 | 33 | 151 |
| 4 | 44 | 148 |
| 5 | 55 | 144 |
| Use of co-precursor | | |
| 6 | MTMS/TEOS = 0.31 | 160 |
| 7 | DMMS/TEOS = 0.32 | 165 |
| 8 | TMMS/TEOS = 0.33 | 168 |

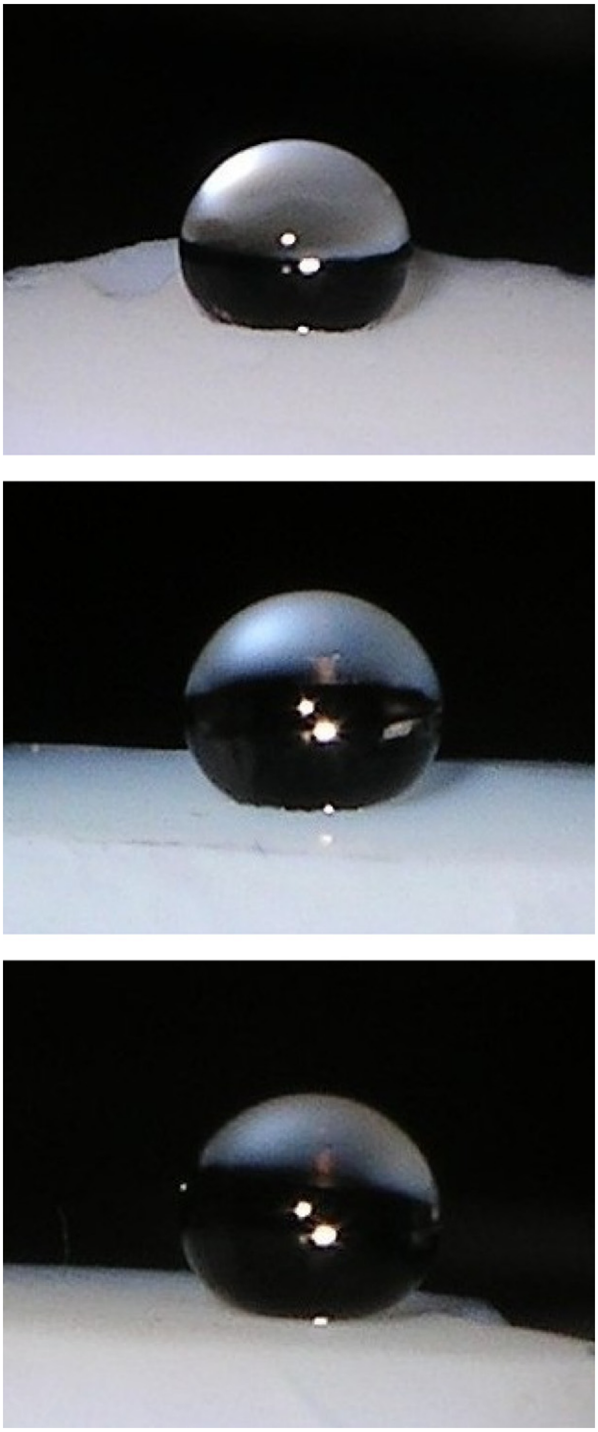

**Fig. 7.** The photograph showing an increase in the sphericity of the water droplet from MTMS to TMMS treated aerogels.

### 3.5. Humidity measurement studies

As the humidity is a measure of the amount of water vapours in the atmosphere, an influence of humidity on the as prepared aerogels was studied. Hydrophilic aerogels contain polar –OH groups on the surface that react with atmospheric moisture and network structure gets deteriorated. For the long-term applications of the aerogels, they should have water repellent property. Therefore, the as prepared aerogels were tested for extent of hydrophobicity by exposing them to water-saturated-air atmosphere, i.e. 80% humidity at 30 °C using programmable environmental test chamber. More

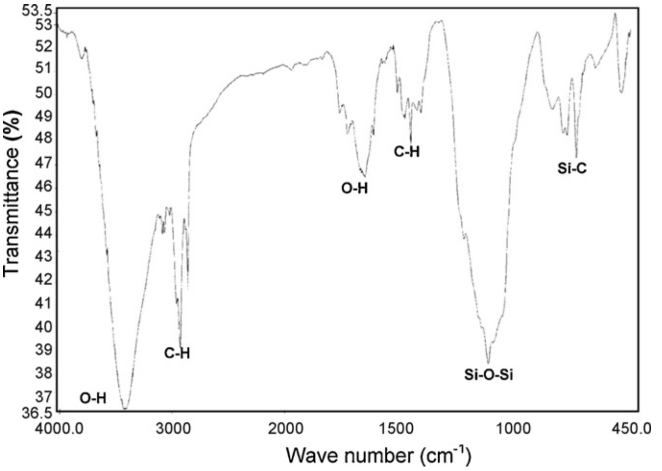

**Fig. 8.** FTIR spectrograph of an aerogel sample catalyzed without $NH_4F$ (with $NH_4OH$).

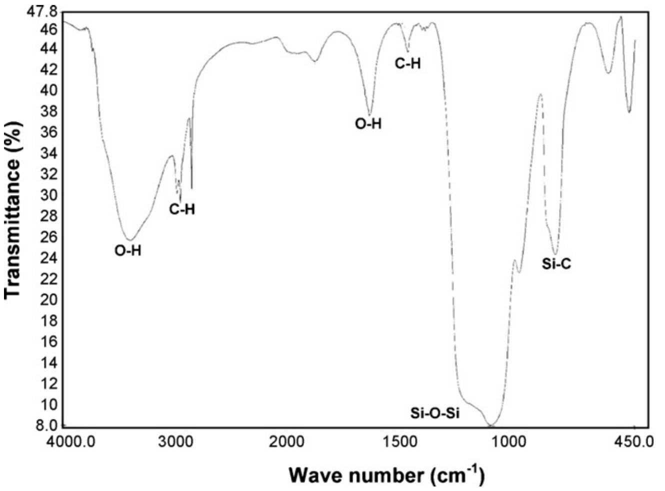

**Fig. 9.** FTIR spectrograph of an aerogel sample catalyzed with $NH_4F$.

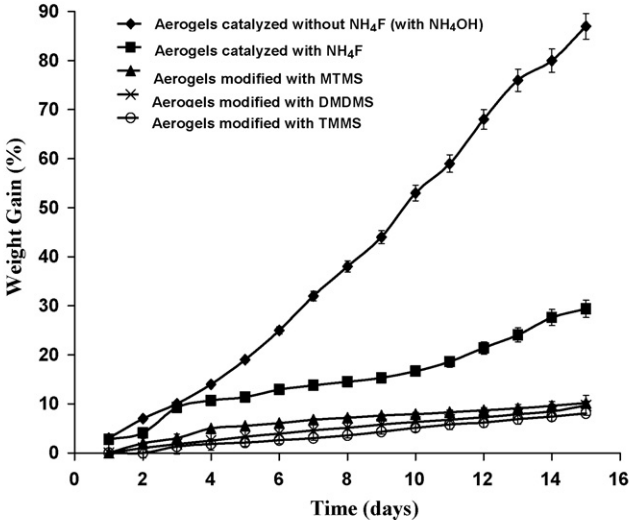

**Fig. 10.** Variation in the percentage of weight gain by the different aerogels. (a) Aerogels catalyzed without $NH_4F$, (b) aerogels catalyzed with $NH_4F$, (c) aerogels modified with MTMS, (d) aerogels modified with DMMS and (e) aerogels modified with TMMS.

the hydrophilic surface, more is the weight gain under the treatment of humidity environment. Fig. 10 shows the percentage of weight gain by the different aerogels such as TEOS aerogels without and with $NH_4F$, TEOS aerogels modified with MTMS, DMMS and TMMS, respectively. All the samples were kept in the mentioned humid surrounding for 15 days. It was observed that the aerogels catalysed without $NH_4F$ exhibited a much greater weight gain than the aerogels catalysed with $NH_4F$, over an entire period of humid exposure. The aerogels treated with MTMS, DMMS and TMMS were not considerably affected by the humid atmosphere.

## 4. Summary

Synthesis and physical properties of tetraethoxysilane (TEOS) based superhydrophobic silica aerogels were studied. The following are the major findings of the present experimental investigations:

1. TEOS based aerogels were obtained by single step sol–gel process using $NH_4F$ as a catalyst. Also, the $NH_4F$ catalyst formulation with TEOS resulted in reduction in the gelation time prominently in the single step sol–gel process.
2. The parent TEOS aerogels showed hydrophobic property due to the incorporation of $NH_4F$ as a catalyst for the gel formation. The hydrophobicity of the aerogels was increased using co-precursors such as MTMS, DMMS and TMMS, respectively. Further, the contact angle of the water droplet of the aerogel surface increased as the order of functional groups of methoxysilane decreased.
3. The aerogels obtained were totally opaque.
4. The TEOS based aerogels catalyzed with $NH_4F$ were thermal stable up to 300 °C and above this temperature, they lost the hydrophobic property and turned into hydrophilic aerogels.
5. The percentage of weight gain in the humid atmosphere by the different aerogels such as TEOS aerogels without and with $NH_4F$, TEOS aerogels modified with MTMS, DMDMS and TMMS, were studied.

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