

Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor

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Abstract

The experimental results on the synthesis of flexible and superhydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor by a two-step (acid–base) sol–gel process followed by the supercritical drying, are reported. The effects of various sol–gel parameters on the flexibility of the aerogels have been investigated. The aerogels of different densities were obtained by varying the molar ratio of MeOH/MTMS (S) from 14 to 35, with lower densities for larger S values. It has been observed that the Young's modulus (Y) decreased from 14.11×10^4 to 3.43×10^4 N/m² with the decrease in the density of the aerogels from 100 to 40 kg/m³. Simultaneously, the aerogels are superhydrophobic with a contact angle as high as 164°. The superhydrophobic aerogels are thermally stable up to a temperature of 530 K, above which they become hydrophilic. The aerogels have been characterized by bulk density, percentage volume shrinkage, and porosity measurements. The microstructures of the aerogels have been studied using the transmission electron microscopy (TEM). The Young's modulus of the aerogels has been determined by an uniaxial compression test. The variation of physical properties of the aerogels has been explained by taking into consideration the hydrolysis, condensation reactions, the resulting colloidal clusters and their network formation.

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1. Introduction

Silica aerogels are sol–gel-derived materials consisting of interconnected nano-particle building blocks, which form an open and highly porous three-dimensional silica network. Typical silica aerogels have high surface area (~ 1000 m²/g), high optical transmission ($\sim 93\%$), low density (40 kg/m³) and low thermal conductivity (0.02 W/mK) [1–4]. These features have led the aerogels for various applications such as super thermal insulation [5,6], acoustic insulation [7], in Cerenkov radiation detectors [8,9], low dielectric constant aerogel films in ultra large scale integrated circuits [10,11], superhydrophobic aerogels for oil-spill cleanup [12], in catalysis [13], and inertial

confinement fusion (ICF) targets in thermonuclear fusion reactions [14].

Despite having these fascinating properties, the aerogels have major drawbacks that they are fragile, brittle and moisture sensitive, which limit their applications in various fields. Due to the fragility and the brittleness, aerogels easily break and become into pieces and powder with the application of a small stress. Therefore, in the present studies, attempts have been made to synthesize highly flexible and superhydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor by a two-step acid–base sol–gel process [15]. The aerogels consist of cross-linked network of silica polymer chains extended in three dimensions as can be seen from Fig. 1. Due to the presence of non-polar alkyl groups (i.e. methyl) attached to the silica polymer chains, the inter-chain cohesion is minimized resulting in the elastic and flexible three-dimensional network. Also, the higher dilution of the MTMS precursor with methanol solvent yielded silica network with a low degree of polymeriza-

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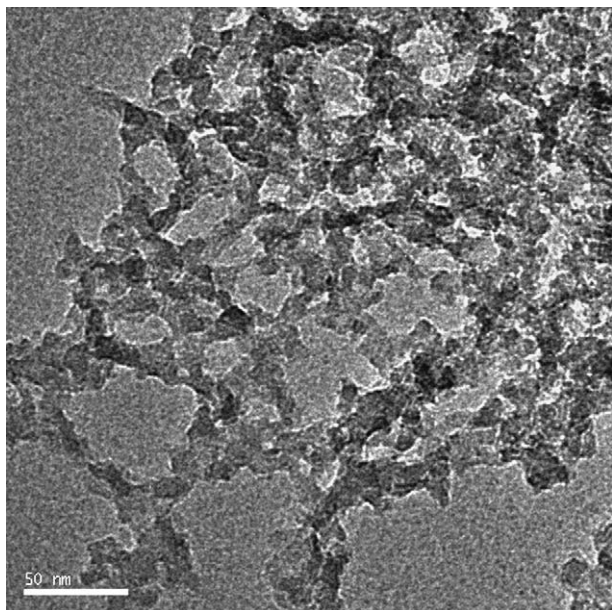


Fig. 1. Transmission electron micrograph of silica aerogel showing three-dimensional cross-linked network of silica chains.

tion exhibiting higher flexibility. Whereas, for lower dilution of the MTMS precursor, an extensive polymerization resulted in dense and rigid structures. Because of the new property, i.e. flexibility in the aerogel, it can be bent to any shape and acts as a good shock absorber as well.

2. Experimental procedures

2.1. Sample preparation

Silica aerogels were produced by a two-step, acid–base, catalyzed sol–gel process followed by the supercritical drying. The chemicals used were: methyltrimethoxysilane (MTMS, $\text{H}_3\text{C}-\text{Si}-(\text{OCH}_3)_3$) and ammonium hydroxide (NH_4OH) of purum grades (from Fluka Company, Switzerland), methanol (MeOH, CH_3OH) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) of ExcelR and SQ grades, respectively (from Qualigens Company, India). Double distilled water was used to prepare both the acidic and basic catalysts.

Silica alcossols were prepared in a 150-ml beaker in two steps (acidic and basic): (i) by mixing and stirring the methyltrimethoxysilane (MTMS), methanol (MeOH) and water (half of the total amount) in the form of oxalic acid catalyst, for 30 min, and (ii) after 24 h, the base catalyst (NH_4OH) in the form of H_2O (the remaining half amount) was added drop by drop while stirring for 30 min. The total molar ratio of $\text{H}_2\text{O}/\text{MTMS}$ was kept constant at 8. The molar ratio of MeOH/MTMS (S) was varied from 14 to 35. The oxalic acid catalyst and NH_4OH catalyst concentrations were varied from 0.0005 to 0.1 M and 6 to 13.36 M, respectively. The sols were transferred to Pyrex test tubes of 15 mm outer diameter and 125 mm height. The test tubes were made air-tight using wooden corks and kept for gelation at 300 K. After the sols were set, methanol was added over the gels in order to prevent shrinkage and cracks. The alcogels were aged for two days at 300 K. Silica aerogels were obtained by the supercritical drying of the alcogels

(at 538 K and 10 MPa) in an autoclave of 600 ml capacity (Parr Instrument Company, Moline, IL, USA). An excess amount of methanol (MeOH) was added into the autoclave (total filling of the autoclave with MeOH is 25% by the volume including in the gels). After reaching the temperature and pressure well above the critical points of methanol solvent ($T_c \sim 516$ K and $P_c \sim 7.9$ MPa), the methanol vapors were released from the autoclave and finally flushed with 0.3 MPa dry nitrogen. The autoclave was then cooled to an ambient temperature and the aerogels were taken out for characterization.

2.2. Methods of characterization

The bulk densities of the aerogels were calculated by their mass to volume ratios. The percentage of porosity (P %) of the aerogels was calculated using the equation:

$$P \% = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100, \quad (1)$$

where ρ_b is the bulk density and ρ_s is the skeletal density of the aerogels which was measured using helium pycnometry and its value was found to be 1900 kg/m^3 . The percentage of volume shrinkage (V_s %) was determined from the change in the volumes of the alcogel and the aerogel using the equation:

$$V_s \% = \left(1 - \frac{V}{V^1}\right) \times 100, \quad (2)$$

where V is the volume of the aerogel and V^1 is the volume of the alcogel.

To quantify the degree of hydrophobicity, the contact angle (θ) of a water droplet placed on the hydrophobic aerogel surface, was calculated using the equation [16]:

$$\tan(\theta/2) = (2h/W), \quad (3)$$

where the base contact length W and height h of the droplet were measured using a traveling microscope. Also, the contact angle (θ) was measured by contact angle meter (Tantec Company, USA). Good agreement has been observed by both the methods in the measurement of θ .

The microstructure of the aerogels was studied using the transmission electron microscope (TEM, Philips, Tecnai F20 model). The thermal stability of the hydrophobic aerogels was investigated by heating them in a furnace at various temperatures ranging from 320 to 773 K. Here, the term thermal stability refers to the threshold temperature up to which the aerogel retains its hydrophobic property, and above which it becomes hydrophilic.

The elastic constant called the Young's modulus (Y) or modulus of elasticity, is a measure of hardness, stiffness, rigidity (or softness, flexibility, or pliability) of the solid. It is also defined as the resistance to any deformation in the solids. It means that the lesser the value of Y , the more flexible is the solid. The Young's modulus (Y) of the aerogels has been determined by an uniaxial compression test as shown in Fig. 2. In this test, the aerogel sample under the testing was kept in a glass tube fixed with a rigid support and having a little bigger diameter than that of the aerogel sample. Various loads (e.g., 0.01, 0.02, 0.03 kg,

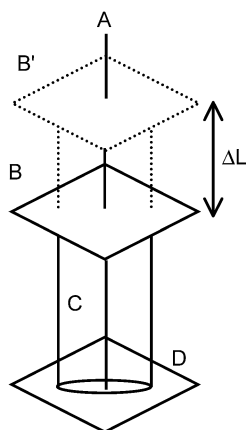


Fig. 2. Schematic diagram of the experimental set-up for the Young's modulus measurements of the silica aerogels. A: vertical axis; B: platform for the application of the stress; C: silica aerogel cylinder; D: flat bottom surface; ΔL : change in length after the application of the stress.

etc.) were placed on the cylindrical aerogel samples and as a result, the aerogel undergoes compression which was characterized by measuring the corresponding change in length (ΔL) using the traveling microscope with an accuracy of ± 0.0001 m. The graphs of the change in length (ΔL) against the mass applied, m , were plotted and the slopes ($\Delta L/m$) of these graphs were used to calculate the Young's modulus of the aerogels by using the equation:

$$\text{Young's modulus } (Y) = mgL/\pi r^2 \Delta L = (Lg/\pi r^2)/\text{slope}, \quad (4)$$

where m is the mass placed on the aerogel sample, g is the acceleration due to gravity. L is the original length of the aerogel before deformation and r is the radius of the aerogel.

The root mean square (RMS) error values have been measured using the formula:

$$\left[\left(\sum x - \bar{x} \right)^2 / 5 \right]^{1/2}, \quad (5)$$

where x and \bar{x} represent the actual and mean values, respectively. The number of samples used for each measurement are 5.

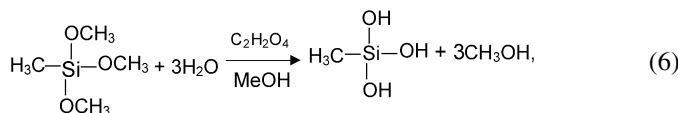
3. Results and discussion

Generally, hydrophilic or hydrophobic silica aerogels were produced by the sol-gel process and supercritical drying of silica aerogels based on the organosilane compound precursors and co-precursors of the type $R_n\text{SiX}_{4-n}$ (where R = alkyl or aryl or vinyl groups, X = Cl or alkoxy groups, $n = 0$ to 3) [17]. Therefore in the present studies we have selected the trifunctional organosilane compound of the type $R_1\text{SiX}_3$, namely the methyltrimethoxysilane (MTMS, $\text{H}_3\text{C-Si-(OCH}_3)_3$) with an idea that both the methyl and the methoxy groups are the smallest among all the alkyl and alkoxy groups which would therefore facilitate the hydrolysis and condensation reactions leading to the superhydrophobic and flexible aerogels. We have not tried the chloro-compounds because they corrode the autoclave systems.

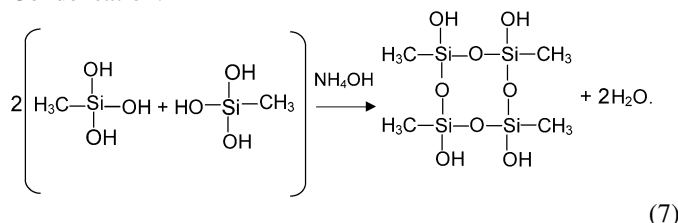
Each monomer of the MTMS precursor has one non-hydrolyzable methyl group (CH_3) and three hydrolyzable methoxy

groups (OCH_3). The three methoxy groups undergo hydrolysis and condensation reactions as per the following chemical reactions:

Hydrolysis:



Condensation:



As the condensation and hence the polymerization progresses, the number of hydrophobic $\equiv\text{Si-CH}_3$ groups increases compared to the number of hydrophilic $\equiv\text{Si-OH}$ groups leading to an inorganic-organic hybrid silica network which is superhydrophobic and highly flexible.

We have used both the single-stage (base catalyzed) and two-stage (acid-base catalyzed) sol-gel processes. In the single-stage process, the condensation takes place before the hydrolysis is fully completed and therefore the network formation is not continuous leading to less flexible aerogels (less than 5%, compressible by volume). On the other hand, in the two-stage process, first the hydrolysis reaction is complete under the acidic conditions and then, after 24 h when the base catalyst is added, the condensation takes place leading to the build-up of systematic, complete and continuous network formation leading to highly flexible aerogels with compression as high as around 60% by volume.

3.1. Effect of MeOH/MTMS molar ratio (S)

The effect of MeOH/MTMS molar ratio (S) on the elastic and other physical properties of the silica aerogels has been studied by keeping the molar ratio of $\text{H}_2\text{O/MTMS}$ constant at 8. The H_2O was added in the form of oxalic acid and ammonium hydroxide. The oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and ammonium hydroxide (NH_4OH) catalyst concentrations were kept constant at 0.001 and 10 M, respectively. It has been observed that the gelation time increased from 2 to 16 h with an increase in S value from 14 to 35. This is due to the fact that the increase in the S value increases the separation between the MTMS monomers and also between the reacting silica oligomers in the sol and hence the gelation time increased [18]. All the aerogel samples are opaque.

The Young's moduli (Y) of the aerogels vary with the bulk density. It has been observed that with an increase in S value from 14 to 35, the volume shrinkage and hence the bulk density of the aerogels decreased from 28 to 7% and from 100 to 40 kg/m^3 , respectively. Fig. 3 shows the variations of the change in length (ΔL) against the mass (m) applied for the calculation of Y . The Y was found to decrease from 14.11×10^4

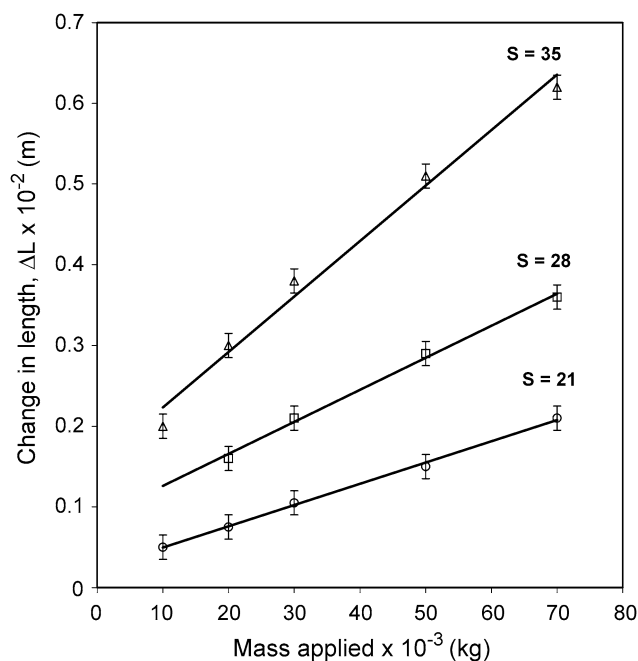


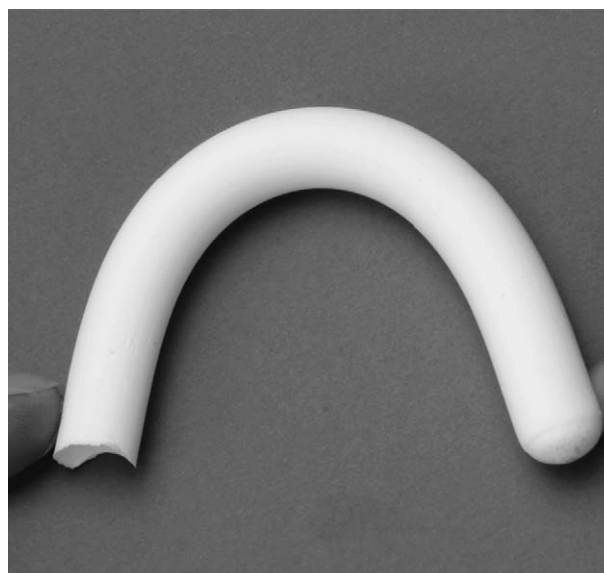
Fig. 3. Plots of change in length against mass applied for the silica aerogels prepared at various MeOH/MTMS molar ratios.

to $3.0 \times 10^4 \text{ N/m}^2$ for S values of 14 and 35, respectively, resulting in an increase in the flexibility of the aerogels. Figs. 4a and 4b show the maximum possible bending of the aerogels (further bending resulted in breaking of the aerogel samples) prepared at two different S values of 28 and 35, respectively. It is clearly seen from Fig. 4 that the aerogel with $S = 35$ can be bent to a greater extent than the aerogel with $S = 28$. Figs. 5a and 5b show the transmission electron micrographs of the aerogel samples prepared at two different S values of 14 and 35, respectively. Since the silica chains of the aerogel with $S = 35$ are quite separated from each other and large empty spaces (pores) are seen in the network, the aerogel undergoes more flexibility when the stress is applied. However, if the S value is decreased, i.e. for $S = 14$, the degree of polymerization increased and the extensive cross-linking in three dimensions resulted in the rigid structure leading to less flexibility of the aerogels.

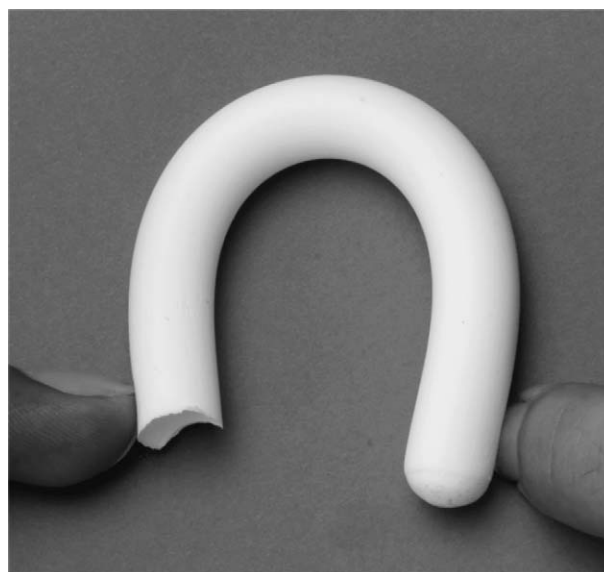
Keeping this in view, to obtain the aerogels with the low Young's modulus, low density, less volume shrinkage, the MeOH/MTMS molar ratio was kept at 35 for further experiments.

3.2. Influence of acid and base catalyst concentrations

Generally, in the case of single-step sol–gel process, the gelation time increases with increase in the solvent amount (methanol in the present case) in the sol. This problem of longer gelation time was overcome by using the two-step acid–base sol–gel process. The effect of oxalic acid concentration (A) on the physical and elastic properties of the silica aerogels was studied by varying it from 0.0005 to 0.1 M. The S and the NH_4OH catalyst concentration were kept constant at 35 and 10 M, respectively. It was observed that the gelation time de-



(a)

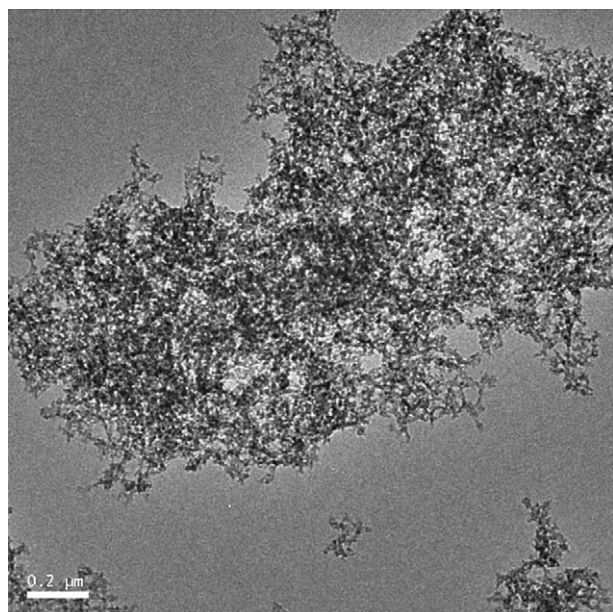


(b)

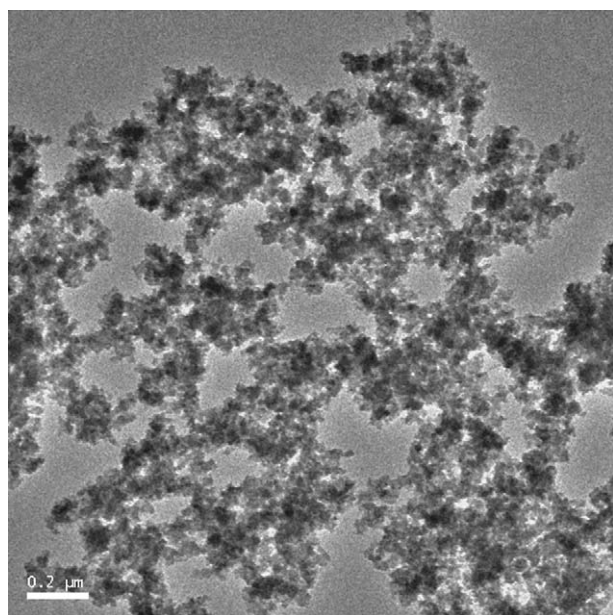
Fig. 4. Flexible silica aerogels prepared at two different MeOH/MTMS molar ratios: (a) $S = 28$ and (b) $S = 35$.

creased from 16 to 8 h with an increase in the A value from 0.0005 to 0.1 M. This is due to the fact that the increase in A value increases the rate of hydrolysis reaction resulting in the faster gelation [19].

The elastic property measurements revealed that the Young's modulus (Y) of the aerogels decreased from 6.2×10^4 to $3.4 \times 10^4 \text{ N/m}^2$ with an increase in A value from 0.0005 to 0.01 M. As described in the earlier section, the graphs of the change in length against the mass applied were plotted (Fig. 6) to determine the Young's moduli of the aerogels using Eq. (4). The decrease in the Y can be explained by taking into consideration the microstructure of the aerogels. Figs. 7a and 7b show the transmission electron micrographs of the aerogel samples prepared at two different A values of 0.0005 and 0.01 M, respectively. It is clearly seen from Fig. 7 that the silica network



(a)



(b)

Fig. 5. Transmission electron micrographs of MTMS based aerogels prepared with (a) $S = 14$ and (b) $S = 35$.

consists of larger particles and pores and the network is less connected for $A = 0.0005$ M, and whereas for $A = 0.01$ M, the network consists of smaller silica particles and pores with well connected network. Moreover, the bulk density was also found to decrease from 61 to 42 kg/m³ with increase in the A value from 0.0005 to 0.01 M.

Therefore, the Young's modulus (Y) decreased with increased oxalic acid concentration (A). Fig. 8 shows the three states of the flexible aerogel sample, prepared with $A = 0.01$ M: (a) without stress, (b) with an applied stress, and (c) after releasing the applied stress. From Fig. 8, it is clear that the aerogel sample could be compressed up to around 60% of its volume and regained its original dimension after the stress is

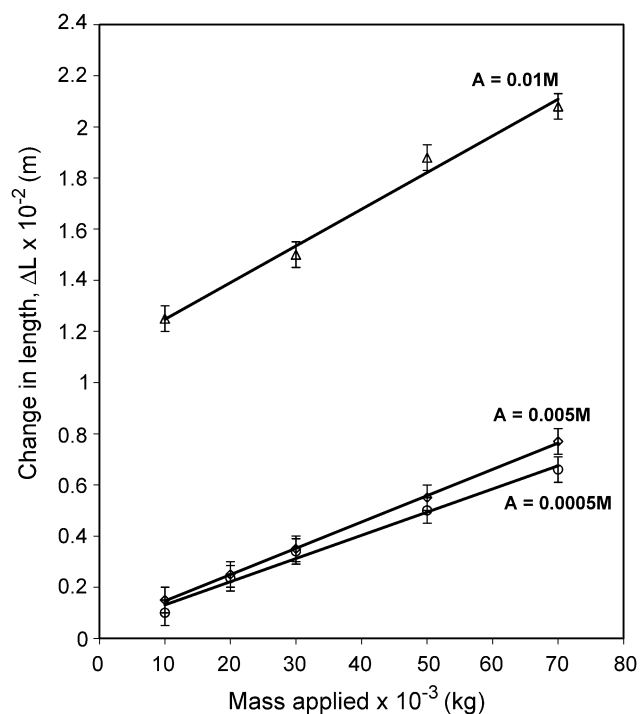


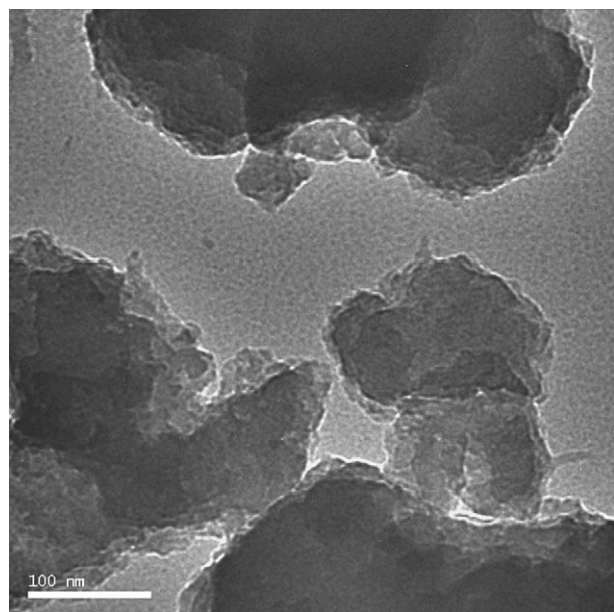
Fig. 6. Plots of change in length against mass applied for the silica aerogels as a function of oxalic acid concentration (A).

released. The experiments on the repeated compression and re-expansion of the aerogels were carried out at least 20 times and the elastic properties (the Young's moduli) have been found to be the same. In addition, it has been observed that the aerogel maintain the same microstructural properties even after 20 times compression and re-expansion. This has been confirmed by the TEM studies before and after the load was applied and therefore aerogel properties do not degrade after bending or compression. The physical properties are quite reproducible because the aerogels have both the inorganic and organic components. Each monomer of MTMS contains one non-hydrolyzable organometallic $\equiv\text{Si}-\text{CH}_3$ (R) group leading to the R/Si ratio of 1. Therefore, the final aerogel contains 75% oxide content (i.e. $\text{SiO}_{1.5}$) and 25% carbon content (i.e. CH_3 groups) resulting in superhydrophobicity (contact angle 164°) and flexibility (the Young's modulus $\sim 10^4$ N/m²).

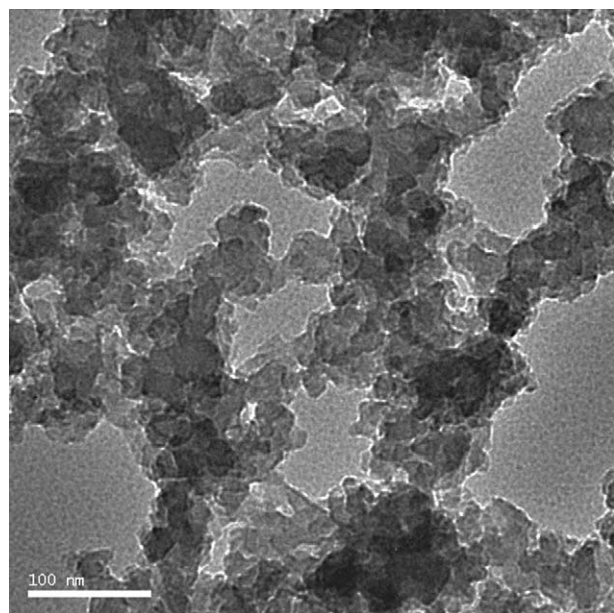
The effect of base catalyst concentration (B) on the physical properties of the silica aerogels has also been studied by varying it from 6 to 13.3 M. It was observed that for $B < 10$ M, the gel could not be obtained because of the sedimentation due to an insufficient base catalyst for the complete condensation. For the $B > 10$ M, the volume shrinkage and hence the bulk density of the aerogels increased from 20 to 30% and from 45 to 63 kg/m³, respectively. The volume shrinkage and the bulk density were found to be optimum at $B = 10$ M.

3.3. Hydrophobicity and thermal stability of the aerogels

The precursor, i.e. MTMS, used in the present studies, contains one hydrolytically stable methyl group, which is responsible for the hydrophobicity in the silica aerogels [20]. The



(a)



(b)

Fig. 7. Transmission electron micrographs of MTMS based aerogels prepared with (a) $A = 0.0005$ M and (b) $A = 0.01$ M.

hydrophobicity was characterized by measuring the contact angles (θ) of the water droplet placed on the aerogel surfaces under investigation. The contact angle (θ) measurements revealed that all the aerogels are superhydrophobic with θ values ranging from 158° to 164° .

The alkyl groups (e.g., methyl in the present studies) responsible for the hydrophobicity are thermally stable up to a threshold temperature of 530 K. Above this temperature they get detached from the surface making it hydrophilic. This threshold temperature for the methyl groups was investigated by heating the aerogels up to temperature of 773 K and testing them with water. It has been observed that the MTMS based aerogels are thermally stable up to a temperature of 530 K and

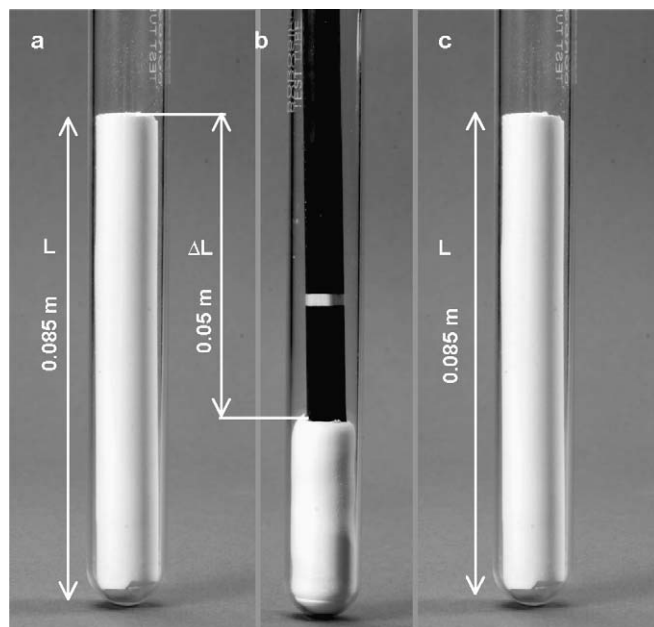


Fig. 8. A photograph showing the three states of the flexible aerogel sample: (a) without stress, (b) with stress, (c) after releasing the applied stress.

above which the aerogels become hydrophilic and absorb water.

4. Conclusions

Highly flexible and superhydrophobic silica aerogels could be obtained using methyltrimethoxysilane (MTMS) precursor by two-step acid–base sol–gel process for the molar ratio of MTMS:MeOH:H₂O at 1:35:8, respectively. The Young's modulus of the aerogel increased with an increase in the bulk density. Very high dilution of the MTMS precursor in the methanol solvent (ten times) and the presence of non-polar methyl groups in the silica polymer chains resulted in the flexible silica aerogels with compressibility as high as $\sim 60\%$ of the original length. The MTMS based aerogels were superhydrophobic with water contact angle as high as 164° . The hydrophobic aerogels were found to be thermally stable up to a temperature of 530 K. Since the aerogels are highly compressible, large volumes of the aerogels can easily be transported.

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