

# High specific surface area TEOS-based aerogels with large pore volume prepared at an ambient pressure

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## Abstract

The experimental results on the synthesis of tetraethoxysilane (TEOS)-based silica aerogel with high specific surface area and large pore volume, via ambient pressure drying (APD) route, are reported. The silica aerogels were prepared by the acid–base sol–gel polymerization of TEOS precursor followed by the drying of the alcogels at an ambient pressure. The solvent present in the alcogel (i.e. ethanol) was replaced by a non-polar solvent such as hexane prior to the surface modification step. In order to minimize the drying shrinkage, the surface of the gels was modified using trimethylchlorosilane (TMCS) before the APD. The FTIR spectra of the surface modified aerogels showed Si–CH<sub>3</sub> peaks at 2965 and 850 cm<sup>−1</sup>. The effect of the base catalyst (NH<sub>4</sub>OH) addition to the sol, at different time intervals (*T*), on the physical and textural properties of the resulting aerogels has been investigated. It has been observed that the surface area and the cumulative pore volume of the aerogels enhanced considerably from 819 to 1108 m<sup>2</sup> g<sup>−1</sup> and 2.65 to 4.7 cm<sup>3</sup> g<sup>−1</sup>, respectively with an increase in the *T* value from 6 to 48 h. Silica aerogels with very low bulk density (0.06 g cm<sup>−3</sup>), extremely high specific surface area (1108 m<sup>2</sup> g<sup>−1</sup>) and large cumulative pore volume (4.7 cm<sup>3</sup> g<sup>−1</sup>) could be synthesized by drying the alcogels at the ambient pressure. The aerogels were mesoporous solids with the average pore size ranging from 12 to 17 nm. The results have been discussed by taking into consideration the hydrolysis and condensation reactions during the sol–gel polymerization of the TEOS precursor.

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## 1. Introduction

Silica aerogels are the nano-porous form of silica which exhibits extremely high specific surface area ( $\sim 1500 \text{ m}^2 \text{ g}^{-1}$ ), low density ( $\sim 0.03 \text{ g cm}^{-3}$ ) and high porosity (98%) [1,2]. Because of their nano-porous nature and tenuous solid silica network, aerogels proved themselves as an ideal candidate for variety of applications such as thermal super-insulators in solar energy systems, refrigerators, thermos flasks [3], Internal Confinement Fusion (ICF) targets for thermonuclear fusion reactions [4], very efficient catalysts and catalytic supports [5],

storage media for liquid rocket propellants [6], as Cerenkov radiation detector media [7] and in radio luminescent devices [8].

Despite these fascinating properties, the use of silica aerogels in various applications has been hindered greatly by the supercritical drying method that is generally used to preserve the porous silica gel network during the drying [9]. Further, the supercritical drying involves risks and complications. Several attempts have, therefore, been made to synthesize silica aerogels by drying the gels at an ambient pressure. During this process, the surface of the gel is modified by an organosilane compound which avoids the condensation reactions between the silica clusters and thereby the irreversible shrinkage of the gel during the ambient pressure drying [10].

In the present studies, by using two step acid–base sol–gel process, we could control effectively the pore sizes of the TEOS-based alcogels and the aerogels with extremely high surface area ( $1108 \text{ m}^2 \text{ g}^{-1}$ ) and large pore volume ( $4.7 \text{ cm}^3 \text{ g}^{-1}$ ) could be synthesized at the ambient pressure.

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The water glass being the cheapest source of silica it has widely been used for the preparation of silica aerogels via ambient pressure drying [11]. However, the huge consumption of expensive silylating agent for the surface modification of the hydrogels and solvent used for the water replacement makes this route quite expensive [12,13].

## 2. Experimental

### 2.1. Aerogel preparation by two step sol–gel process

Silica aerogels were prepared by a two step acid–base catalyzed sol–gel process followed by ambient pressure drying [18]. The experimental steps followed for the aerogel synthesis have been shown in Fig. 1. The chemicals used for the preparation of alcossols were tetraethoxysilane (TEOS), Si-(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (ALDRICH), ammonium hydroxide (NH<sub>4</sub>OH, from Duksan chemical), ethanol (EtOH, C<sub>2</sub>H<sub>5</sub>OH) and oxalic acid (Dihydrate) (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, from Duksan chemical). Double distilled water was used to prepare the desired concentrations of oxalic acid and NH<sub>4</sub>OH catalysts.

Silica alcossols were prepared in a 250 ml beaker in two steps as follows: in the first step, tetraethoxysilane (TEOS), ethanol (EtOH) and oxalic acid were mixed under constant stirring conditions for 15 min. In the subsequent step, the base catalyst (NH<sub>4</sub>OH) was added drop by drop while stirring at different time intervals (*T*) to the acid catalyzed sol. In order to compare the physical and hydrophobic properties of the aerogels, the time interval before the base catalyst addition was varied from 6 to 48 h. The molar ratio of TEOS:EtOH:H<sub>2</sub>O (acidic):H<sub>2</sub>O (basic): was kept constant at 1:6.9:3.5:2.2, respectively, along with the oxalic acid and NH<sub>4</sub>OH concentrations constant at 0.01 and 0.5 M, respectively. The

alcossols were then transferred to 150 ml beakers and they were made air-tight and were kept for gelation at room temperature. After the sols were set (i.e. gelation), a small quantity of ethanol was added over the gels in order to prevent the evaporation of pore solvent and thereby the shrinkage and or cracking of the gel. The alcogels were aged for 6 h in ethanol at room temperature (~27 °C).

Before the surface modification of the gel was carried out, the ethanol present in the alcogels was exchanged with a non-polar solvent such as hexane in order to avoid the reverse reaction of surface modification, which generally occurs in polar solvents. For this purpose, the alcogels were kept in hexane solvent (50 ml) for 12 h. The surface modification was then carried out by immersing the alcogels in a hexane bath containing Trimethylchlorosilane (TMCS). The molar ratio of TEOS/TMCS was kept constant at 2. Silica aerogels were obtained by the atmospheric drying of the gels in an oven at 65 °C for 4 h, 80 °C for 2 h and at 120 °C for 2 h. For a complete evaporation of the pore liquid, the gels were finally dried at 200 °C for an hour. The aerogel samples were allowed to cool to room temperature and they were characterized by various techniques.

### 2.2. Characterization methods

The pore size distributions (PSDs) were measured using a multiple point nitrogen gas adsorption BET surface area analyzer (Model ASAP 2000) made by Micromeritics. A BET analysis from the amount of N<sub>2</sub> gas adsorbed at various partial pressures (five points  $0.05 < p/p_o < 0.3$ , nitrogen molecular cross-sectional area = 0.162 nm<sup>2</sup>) was used to determine the surface area, and a single condensation point ( $p/p_o = 0.99$ ) was used to find the pore size and pore volume. Pore size distributions were calculated from the desorption isotherms [14].

In order to study the thermal stability, hydrophobic nanoporous silica aerogels of 10 mg in weight were heat-treated in air, from room temperature (25 °C) up to 400 °C with controlled heating rate of 1.5 °C min<sup>-1</sup> using a microprocessor based Parr temperature controller (Model 4846) connected to a muffle furnace (A.H.JEON Industrial Co. Ltd., Korea). Here the thermal stability refers to the temperature up to which the nano-porous silica aerogel retains its hydrophobicity [15].

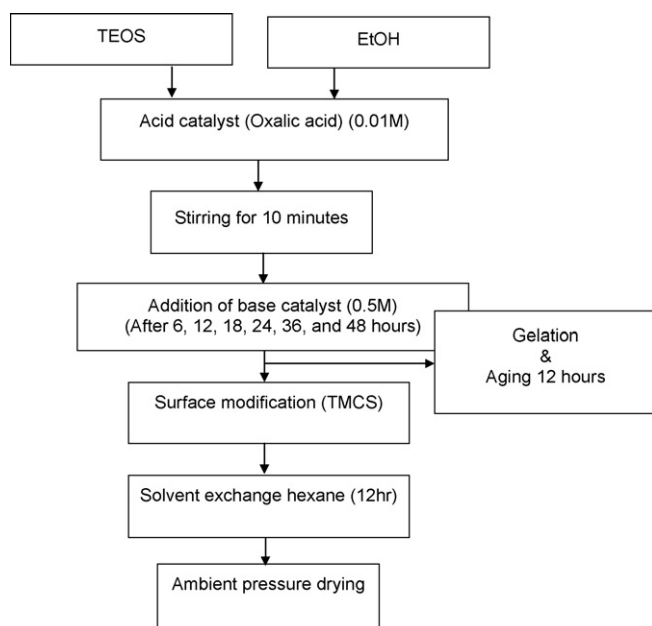


Fig. 1. Flow chart of the production of TEOS-based silica aerogel through two step sol–gel process at ambient pressure.

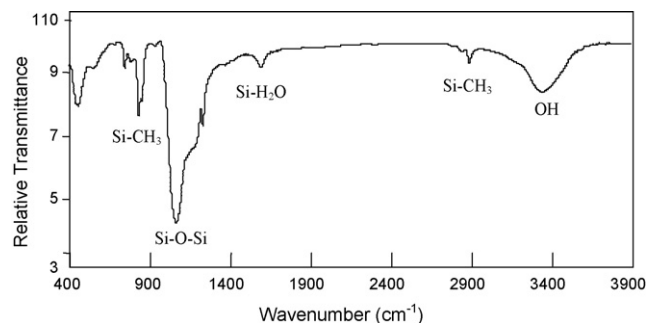


Fig. 2. FT-IR spectra of TMCS surface modified silica aerogel.

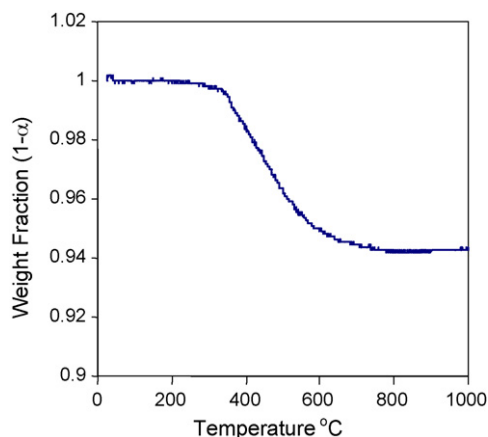


Fig. 3. TGA curves of TMCS modified nano-porous silica aerogel.

The surface modification was confirmed using Infrared (IR) spectroscopy using Perkin-Elmer (Model No. 783) IR spectrophotometer. For this purpose, the as produced silica aerogel powder was used for analysis with KBr reference. The microstructure (morphology) of nano-porous silica aerogel was observed using scanning electron microscopy (SEM) analyzer (Model Philips XL-30).

The packing bed density of the aerogel sample was obtained by filling them in a cylindrical column of known volume and the density was calculated from its mass to volume ratio. All the observations were taken for six times for each sample and the average value was taken as the packing bed density of the aerogels.

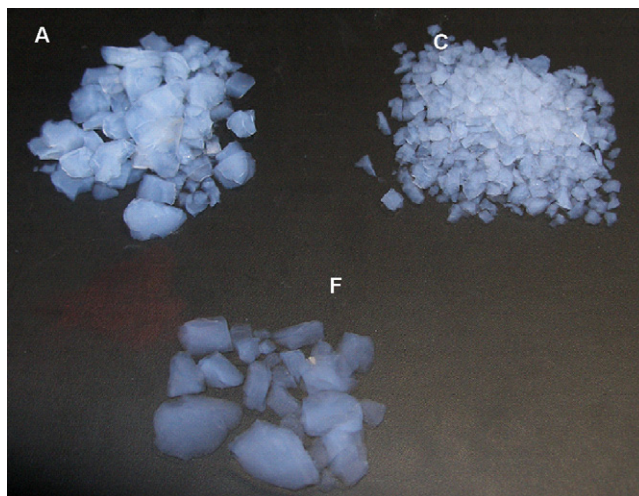


Fig. 4. Photograph of nano-porous silica aerogel prepared at different  $T$  value: (a)  $T = 6$ , (c)  $T = 18$ , and (f)  $T = 48$ .

### 3. Results and discussion

#### 3.1. Surface modification and hydrophobic properties of the TEOS-based aerogels

The surface modification of the alcogels by non-polar groups such as alkyl/aryl is an indispensable step before the ambient pressure drying as it prohibits the formation of new siloxane bonds between the adjacent silica clusters and thereby the irreversible shrinkage of the gel [16]. In the present studies the

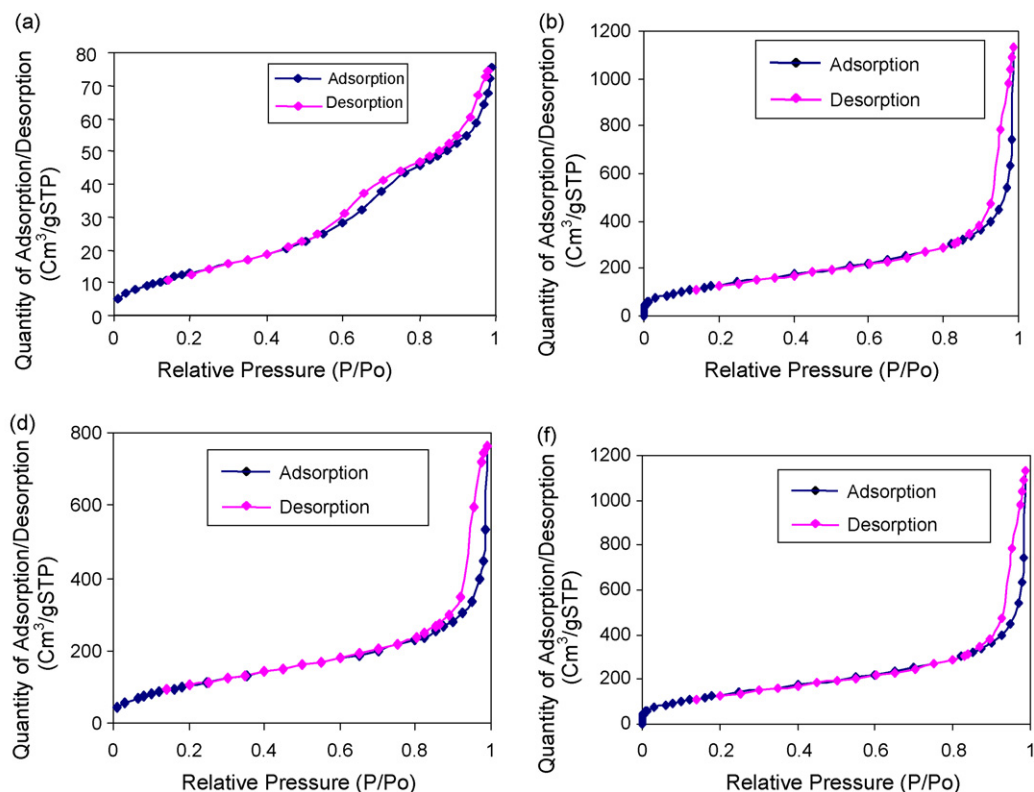
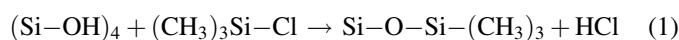


Fig. 5.  $N_2$  adsorption/desorption isotherms of silica aerogel prepared at different  $T$  value: (a)  $T = 6$ , (b)  $T = 12$ , (d)  $T = 24$  and (f)  $T = 48$ .

Table 1

No.	TEOS/EtOH:acidic(H <sub>2</sub> O)/basic(H <sub>2</sub> O) molar ratio	TEOS/TMCS molar ratio	Base addition time interval (h)	Gelation time (min)
a	1:6.9:3.5:2.2	2	6	15
b	1:6.9:3.5:2.2	2	12	10
c	1:6.9:3.5:2.2	2	18	8
d	1:6.9:3.5:2.2	2	24	5
e	1:6.9:3.5:2.2	2	36	4
f	1:6.9:3.5:2.2	2	48	2

surface of the alcogels was organically modified by tri-methyl groups present in the trimethylchlorosilane according to the following chemical reaction:



The surface modification of the gels according to the reaction (1) was confirmed by means of Fourier Transform Infrared Spectroscopy (FT-IR). Fig. 2 shows the FTIR spectra of the TMCS modified TEOS-based silica aerogel. The presence of Si-CH<sub>3</sub> peaks at 2965 and 850 cm<sup>-1</sup> clearly confirms the surface modification of the aerogels. As a consequence of the surface modification process the aerogels exhibited hydrophobic behavior, as expected. The aerogels were heated in a furnace at various temperatures in order to investigate the thermal stability of the hydrophobic nature. It has been observed that the aerogels retain their hydrophobic behavior up to a maximum temperature of 320 °C and above which they become hydrophilic. This is because of the fact that at this temperature the surface -CH<sub>3</sub> groups, which are the cause for aerogel hydrophobicity, get oxidized leaving behind

the hydrophilic aerogels. This type of phenomena has previously been observed by many aerogel researchers and they also found similar results [17]. In addition to this, Thermo gravimetric (TG) analysis of the TMCS modified aerogels was performed to confirm the oxidation temperature for the -CH<sub>3</sub> groups. Fig. 3 depicts the TG curve obtained for the TMCS modified aerogel in the temperature range of 25–1000 °C, in air atmosphere. It is clearly seen from Fig. 3 that the sample exhibited a negligible weight loss up to a temperature of 320 °C and beyond which the aerogel underwent significant loss in its weight. This refers to the oxidation of the -CH<sub>3</sub> groups from the surface of the modified silica aerogel.

### 3.2. Physical properties of the TEOS-based aerogels

In order to investigate the effect of the time interval before the base catalyst (NH<sub>4</sub>OH) addition on the physical properties of the resulting silica aerogels, it was varied from 6 to 48 h. The TEOS: EtOH:acidic(H<sub>2</sub>O):basic(H<sub>2</sub>O) molar ratio was kept constant at 1:6.9:3.5:2.2, respectively. The gelation time of the TEOS-based

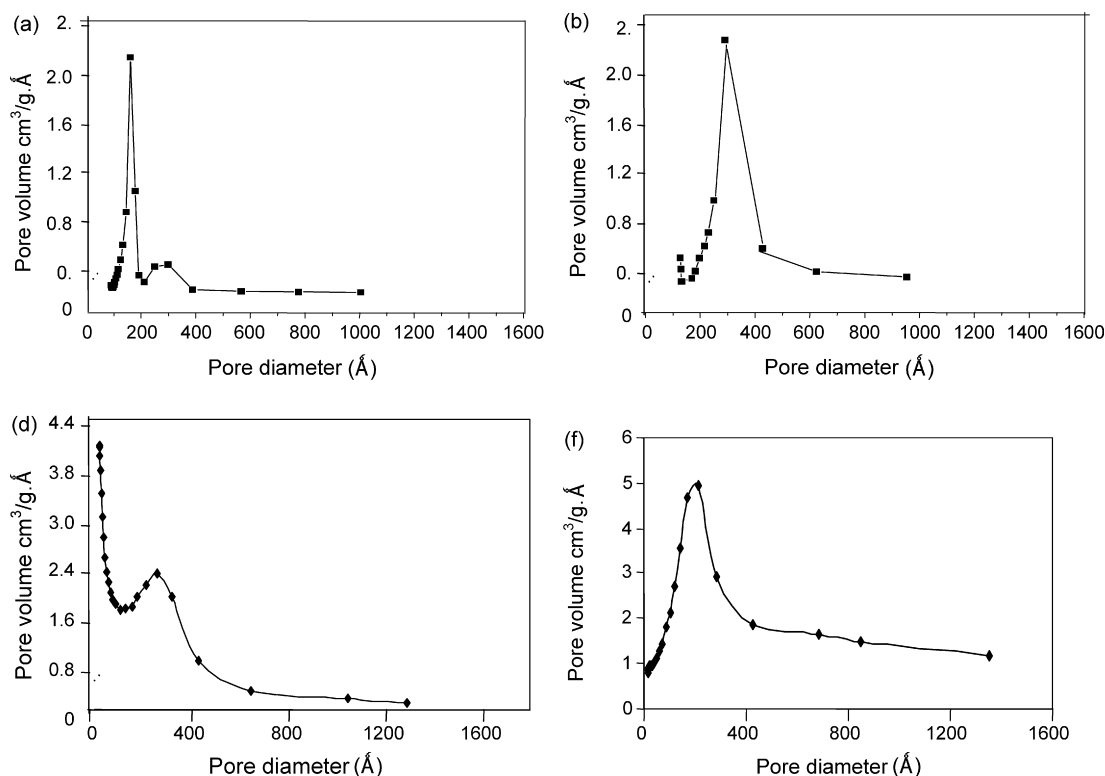


Fig. 6. BET Pore size distributions of silica aerogel prepared at different  $T$  value: (a)  $T = 6$ , (b)  $T = 12$ , (d)  $T = 24$  and (f)  $T = 48$ .



Table 2

No.	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Specific pore diameter (nm)	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Density ( $\text{g cm}^{-3}$ )
a	819	12.0	2.65	0.110
b	826	12.8	2.78	0.097
c	875	13.2	3.16	0.089
d	911	14.3	3.71	0.082
e	1088	15.3	4.05	0.071
f	1108	17.5	4.7	0.060

alcosols was dramatically short (maximum 15 min) which in general takes at least three days for the acid catalyzed TEOS-based sols [18]. This drastic reduction in the gelation time can be attributed to the two step acid–base sol–gel process in which the TEOS precursor is hydrolyzed in the first step by the addition of the acid catalyst and the rapid condensation of the hydrolyzed species is carried out by the addition of base catalyst in the subsequent step. Whereas, in case of the acid catalyzed (single step) TEOS sols the hydrolysis and condensation reactions cannot be controlled in a better way.

The bulk density of the aerogel decreased from 0.11 to  $0.06 \text{ g cm}^{-3}$  with an increase in the  $T$  value from 6 to 48 h, respectively (Tables 1 and 2). In addition, the optical transmission of the obtained aerogel samples increased with an increase in the  $T$  value which could be observed in Fig. 4. This is because, with an increase in the  $T$  value, the hydrolysis of TEOS precursor approaches completeness leading to the systematic building up of the silica network that can withstand the drying stress and thereby reducing the drying shrinkage of the gel and hence the bulk density of the resulting aerogels. Whereas, the gel network obtained for lower  $T$  values is relatively weaker because of the incomplete hydrolysis of the TEOS precursor.

### 3.3. Textural properties of the TEOS-based aerogels

The specific surface area and porosity properties of the aerogels have been given in Table 1. It has been observed that the TMCS modified TEOS-based aerogels exhibited extremely high specific surface area in the range of  $819\text{--}1108 \text{ m}^2 \text{g}^{-1}$ . This is because of the efficient surface modification of the gels by the tri-methyl groups, before the ambient pressure drying. The average pore diameter ( $P_d$ ) of the aerogels could be varied from 12 to 17 nm by varying the time interval before the base catalyst addition. The enhancement in the surface area and the average pore diameter with an increase in the  $T$  value can be attributed to the fact that the gels with higher  $T$  values shrink less than those obtained for the lower  $T$  values, as discussed in the previous section.

The nitrogen adsorption–desorption isotherms obtained at 77 K are depicted in Fig. 5(a, b, d and f). It presents the amount of the gas adsorbed at equilibrium as a function of the partial pressure ( $p/p_0$ ). The maximum amount of the  $\text{N}_2$  gas adsorbed increased with an increase in  $T$  value. This is due to the fact that the pore volume increased with an increase in  $T$  value and thus absorbing more volume of  $\text{N}_2$ . The physisorption isotherms obtained for all the aerogels are Type IV which is the characteristic feature of the mesoporous materials [19]. The

desorption cycle of the isotherms showed hysteresis loop for all the samples which is generally attributed to the capillary condensation occurring in the mesopores. Fig. 6(a, b, d and f) illustrates the PSD profiles of the TEOS-based aerogels

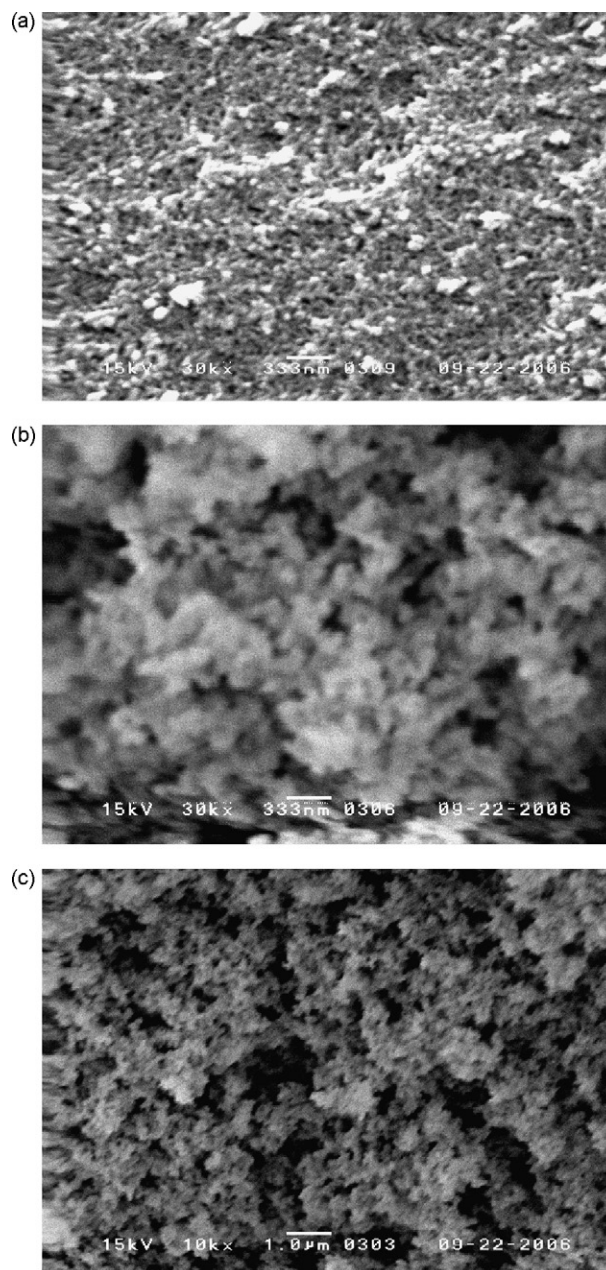


Fig. 7. SEM microstructure of nano-porous of silica aerogel prepared at different  $T$  value: (a)  $T = 6$ , (c)  $T = 18$  and (f)  $T = 48$ .

synthesized at the ambient pressure. A significant change has been observed in the PSD profiles of the aerogels obtained at various  $T$  values. The peak pore diameter shifted to higher value as the  $T$  value increased from 6 to 48 h. As per the IUPAC classification of the pores [20], all the aerogels showed a pronounced peak in the mesopore region (20–500 Å) which signifies that the aerogels maintain mesopores in their structure even after drying them at the ambient pressure. This fact could also be observed from the scanning electron micrographs of the aerogels shown in Fig. 7(a, c and f).

#### 4. Conclusions

The silica aerogels with extremely high specific surface area ( $1108 \text{ m}^2 \text{ g}^{-1}$ ) and large pore volume ( $4.7 \text{ cm}^3 \text{ g}^{-1}$ ) could be synthesized by the two step acid–base sol–gel polymerization of tetraethoxysilane (TEOS) followed by the ambient pressure drying. The time interval before the base catalyst addition strongly influenced the physical and textural properties of the resulting aerogels. The bulk density of the aerogels decreased from 0.11 to  $0.06 \text{ g cm}^{-3}$  with an increase in the  $T$  value from 6 to 48 h. The surface area and the cumulative pore volume of the aerogels increased significantly from 819 to  $1108 \text{ m}^2 \text{ g}^{-1}$  and 2.65 to  $4.7 \text{ cm}^3 \text{ g}^{-1}$ , respectively with an increase in the  $T$  value from 6 to 48 h. The aerogels were mesoporous solids with the average pore size ranging from 12 to 17 nm depending on the synthesis conditions. The TG analysis revealed that the aerogels retain their hydrophobic nature up to a maximum temperature of  $320^\circ\text{C}$  and heating them above this temperature resulted in oxidation of the surface  $\text{Si-CH}_3$  groups responsible for the aerogel hydrophobicity.

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