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Effect of different chemical additives and heat-treatment on ambient pressure dried silica aerogels

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The experimental results on the physical and super-hydrophobic properties of the ambient pressure-dried silica aerogels doped with different chemical additives (CAs) and heat-treated at 350°C for 2 h in air are reported. N,N-dimethylformamide (DMF), glycerol (GLY) and ethylene glycol (EG) were doped as CAs to the tetraethyoxysiliane (TEOS) precursor prepared aerogels. The molar ratio of CAs/TEOS (G) was varied from 0 to 1.2. DMF-doped aerogel at $G = 0.8$ possessed minimum shrinkage (≈6%) and low bulk density (≈0.2 $\mathrm{g\,cm^{-3}}$). The contact angle (θ) at $G = 0.8$ DMF-doped aerogel was ~178°, which decreased a little ($\theta \approx 162°$) when heat-treated at 350°C in air, but the super-hydrophobic property was retained. The small angle X-ray scattering testing results showed that DMF-doped aerogel had the most uniform and smallest particles and particle size distributions compared with GLY- and EG-doped aerogels. But the CAs doping had a little influence on the degree of surface roughness of the particles.

Keywords: silica aerogels; super-hydrophobic; heat treatment; SAXS; DCCA

1. Introduction

The addition of drying control chemical additives (DCCAs) can result in uniform pore and particle sizes, thus reducing the differential drying stresses by minimising the variation rates of evaporation [1]. Thus, the important physical property of DCCAs is to possess low surface tension and high boiling point, because the mixture of the final liquids in the pores must contain DCCAs, which will decrease the capillary pressure during drying process. The Si–OH groups present in the aerogel pore surfaces are the main source of hydrophilicity because they promote the adsorption of water. Owing to the limited contact area of the solid surface with water, chemical reactions or bond formation through water are inhibited on a hydrophobic surface. The hydrophobicity of a solid surface is commonly determined by a contact angle measurement [2], which is calculated by

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Young's equation [3]. Hydrophobicity refers to a contact angle higher than 90°, while super-hydrophobicity refers to a contact angle higher than 150°. There are merely two techniques to create super-hydrophobic surfaces, i.e. making a rough surface from a low surface energy material and modifying a rough surface with a material of low surface energy. So, adopting surface modification methods are prerequisite to obtain hydrophobic silica aerogels and thereby keep their excellent properties [4–6]. In our previous work [7], we reported a surface modification method where *n*-hexane was used as the solvent and became the only liquid left in the pores before drying. So the DCCAs-doping in this process is only applicable during gel formation. Temperature stability of silica aerogels is very important owing to the deterioration of the properties above a certain temperature. It is confirmed that the surface-modified gels can maintain the feature of the wet gels to a degree during drying, and therefore shrink reversibly followed by 'Spring Back' to wet gel-like structure after drying [8].

Because a surface modification method was adopted to obtain hydrophobic aerogels, we call chemical additives (CAs) to replace the DCCAs in other's paper considering their working process. In this article we report the effect of three kinds of CAs, i.e. N,N-dimethylformamide (DMF), glycerol (GLY) and ethylene glycol (EG) and heat-treatment on the property of silica aerogels. The solution of isopropyl alcohol (IPA), trimethylchlorosilane (TMCS) and *n*-hexane is adopted to modify the surface of the samples at 60°C. The influence of CAs/tetraethyoxysiliane (TEOS) molar ratio (*G*) on volume shrinkage, bulk density and fractal dimension is studied. The aerogels have been characterised by scanning electron microscopy (SEM), contact angle measurement and small angle X-ray scattering (SAXS) testing.

2. Experimental procedures

2.1. *Sample preparation*

Silica alcogels were prepared via a two-step acid/base process by keeping the molar ratio of TEOS, ethanol (EtOH), water (H_2O), hydrochloric acid (HCl) and ammonia (NH_4OH) constant at $1:6:8:1.0\times10^{-3}:1.1\times10^{-2}$, respectively, and varying the molar ratio of CAs/TEOS (*G*) from 0 to 1.2. The total volume of the starting sols was kept constant and all compositions were measured by the volume ratio calculated by their molar ratio above. The measurement of the liquid volume was repeatable within a maximum deviation of ±0.05 ml. The oven temperature had an uncertainty of 1°C, and the measurement temperature was found to be repeatable within a maximum deviation of ±3°C. The TEOS, EtOH, H_2O and HCl were mixed in the molar ratio of $1:4:1:1.0\times10^{-3}$ and stirred at 60°C for 1 h in the acid catalysed procedure. In the following base catalysed procedure, the remaining H_2O, EtOH, NH_4OH and CAs were added to the stock solution and stirred at room temperature for 10 min. After gelation, the alcogels were held at 50°C for 1 h. Two aging treatment steps were conducted by soaking the alcogels in 30 vol%H_2O/EtOH solution for 24 h at 60°C and in 70 vol%TEOS/EtOH solution for 16 h at 70°C. The volume ratio of alcogel : treatment solution was 1 : 3.1 [9]. The aged alcogels were immersed in IPA/TMCS/*n*-hexane solution for 36 h at 60°C subsequently. The molar ratio of TMCS : pore water : IPA = 0.4 : 1 : 0.4 and the volume ratio of *n*-hexane : TMCS = 10 [10]. The modified gels were dried at room temperature for 8 h and then at 60°C for 24 h.

Heat-treatment process was executed by the following heating schedule: 2°C min^{-1} to 250°C, soaking for 60 min, and then 1°C min^{-1} to 350°C, soaking for 120 min.

2.2. *Characterisation*

The bulk density of the aerogels was measured directly from the weight to volume ratio. The weight was measured using a microbalance having 10^{-4} mg accuracy. The percentage of volume shrinkage ($V_s(\%)$) of the aerogels was determined from the change in the volume of alcogel and aerogel using the formula

$$V_s(\ \%) = \left[1 - \frac{V}{V^1}\right] \times 100, \tag{1}$$

where V is the volume of the aerogel and V^1 the volume of the alcogel. The volume and density of the aerogels were determined through repeatability tests. The actual results were represented as mean ± standard deviation. The hydrophobicity of the aerogels was tested by measuring the contact angle (θ) of a water droplet on the horizontal sample surface. From the measurement of base length (Δ) and the height (h) of the droplet [11] (Figure 1), θ was calculated using the formula

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

The microstructural change of the aerogels caused by CAs-doping and heat-treatment in air at 350°C was observed by SEM. The SAXS testing was adopted to analyse the fractal structure of the aerogels. Linear fitting of the SAXS results were used to calculate the fractal dimension of the aerogels.

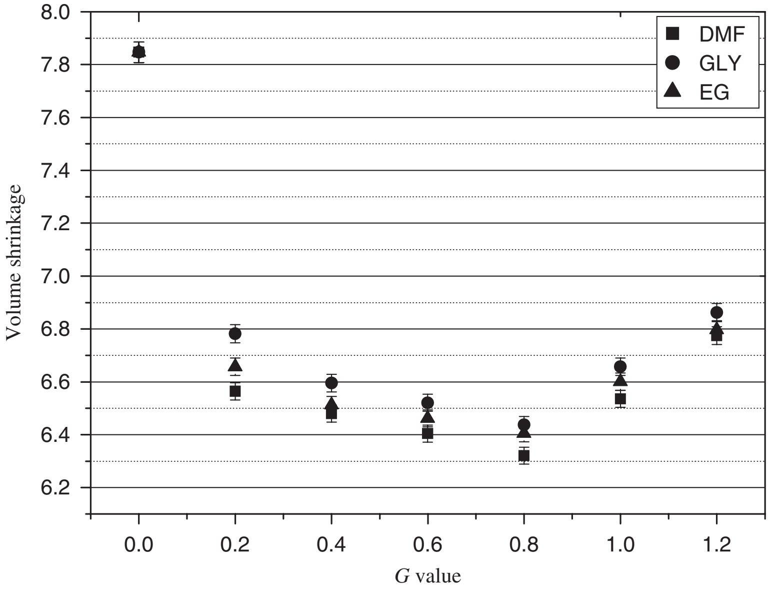

Figure 1. Volume shrinkage of silica aerogels doped with CAs at different G values.

3. Results

3.1. *Volume shrinkage and bulk density of the aerogels*

Figure 1 shows that the aerogels doped with CAs possess less shrinkage than undoped one and the minimum shrinkage is obtained at $G = 0.8$. It was also indicated that the shrinkage of the samples doped with DMF were comparatively smaller. On the other hand, the corresponding bulk density of the aerogels doped with CAs was lower than the undoped one. The respective bulk density at $G = 0$ and $G = 0.8$ doped with DMF, GLY and EG was 0.32 ± 0.02, 0.21 ± 0.02, 0.24 ± 0.02 and $0.23 \pm 0.02\,\mathrm{g\,cm^{-3}}$, respectively.

3.2. *SEM analysis*

Figure 2(a–d) shows the SEM microstructure of the aerogels doped with different CAs. It is clear from the figure that the undoped samples possess bigger particles and pores with non-uniform sizes, whereas smaller clusters with almost uniform pore size were observable in the SEM of CAs-doped aerogels. Besides, DMF-doped aerogels had the smallest particle sizes and more uniform pores than the other two. Figure 2(e) indicates the SEM photographs of the aerogel heat-treated in air at 350°C. Comparing with Figure 2(b), it showed that pore sizes and the particles increased after heat-treatment at 350°C.

3.3. *Effect of heat-treatment*

Figures 3 and 4 illuminate the photographs of the silica aerogels with and without heat-treatment. Figure 3 indicates the contact angles of samples obtained at $G = 0.8$, DMF-doped aerogels. The θ value was calculated by Equation (1). It is clear that super-hydrophobic aerogels were prepared with $\theta \approx 178^\circ$, but the contact angle had a little decrease in the value ($\theta \approx 162^\circ$) when heat-treated at 350°C. Figure 4 demonstrates that the aerogel heat-treated in air at 350°C is immersed a part when put on the water, but the aerogel without heat-treatment floats on. Thus, the super-hydrophobicity could be retained at almost 350°C heat-treatment in air.

3.4. *SAXS testing*

The SAXS experiment was performed using synchrotron radiation as an X-ray source with a long-slit collimation system. The incident X-ray wavelength (λ) was 0.154 nm and the scattering angle (2θ) was approximately 0.1–3°. The scattering wave vector (h) was calculated using the formula

$$h = \frac{4\pi \sin\theta}{\lambda}. \tag{3}$$

In systems without distinct surfaces, the scattering intensity (I) often obeys a power law in the magnitude of the scattering vector according to the following formula:

$$I(h) \propto h^{-D}. \tag{4}$$

Objects obeying Equation (4) are called possessing volume fractal structure [12], while D is the volume fractal dimension ($1 < D < 3$). The SAXS intensity of an aerogel with a surface fractal structure is shown in Equation (5), where D_s is the surface fractal

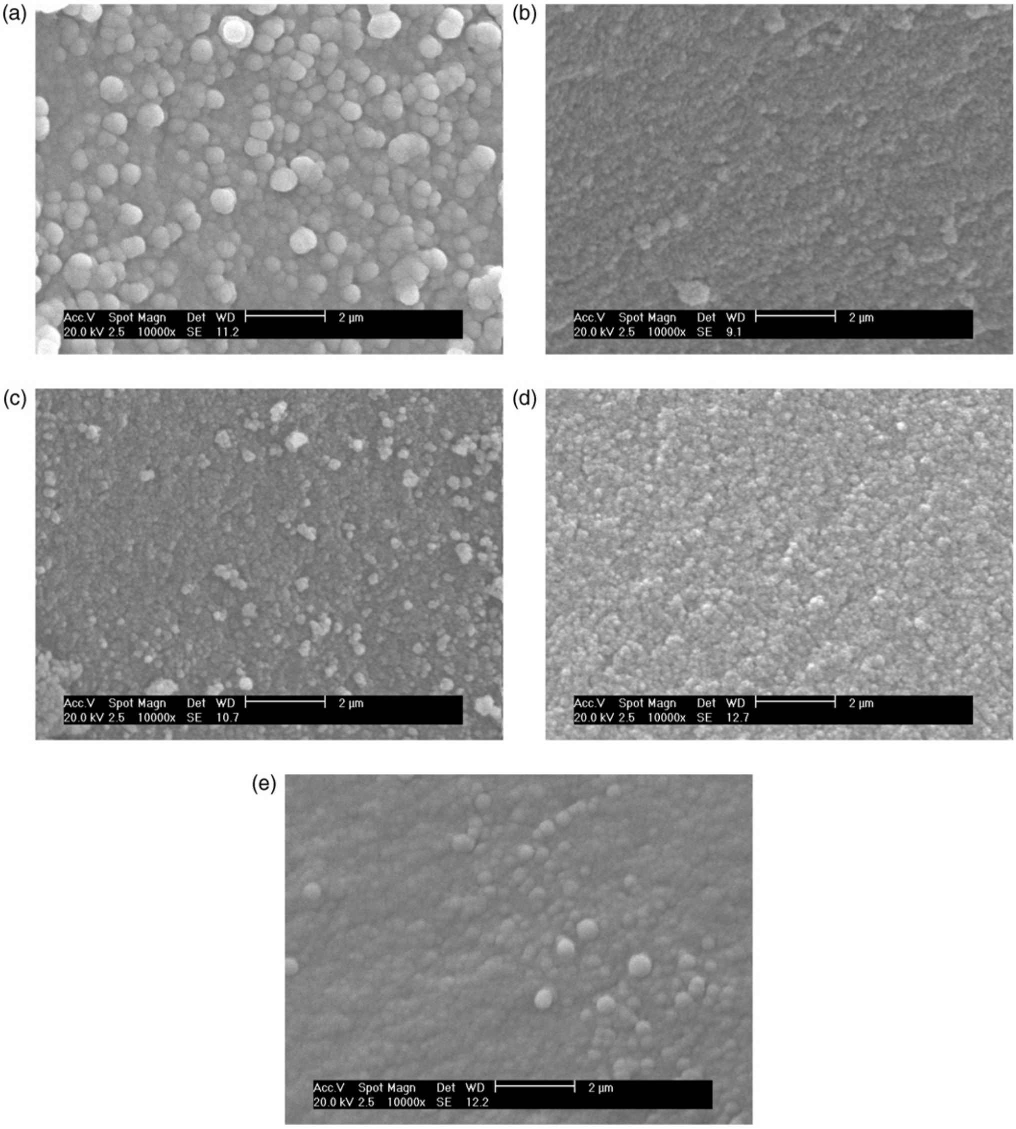

Figure 2. SEM microstructure of aerogels doped with different CAs and heat-treated at 350°C in air: (a) $G=0$; (b) DMF-doped, $G=0.8$; (c) GLY-doped, $G=0.8$; (d) EG-doped, $G=0.8$ and (e) heat-treated at 350°C, DMF-doped, $G=0.8$.

dimension ($2 < D_s < 3$). A perfectly smooth surface presents $D_s=2$, so the intensity of Equation (5) becomes the well-known Porod's law ($I(h) \infty q^{-4}$)[13],

$$I(h) \propto h^{D_s-6}. \tag{5}$$

Figure 5 shows the effect of CAs on the typical scattering curve obtained by SAXS. The parameter D or D_s could be easily calculated from the slopes of log $I(h)$ versus log h plots.

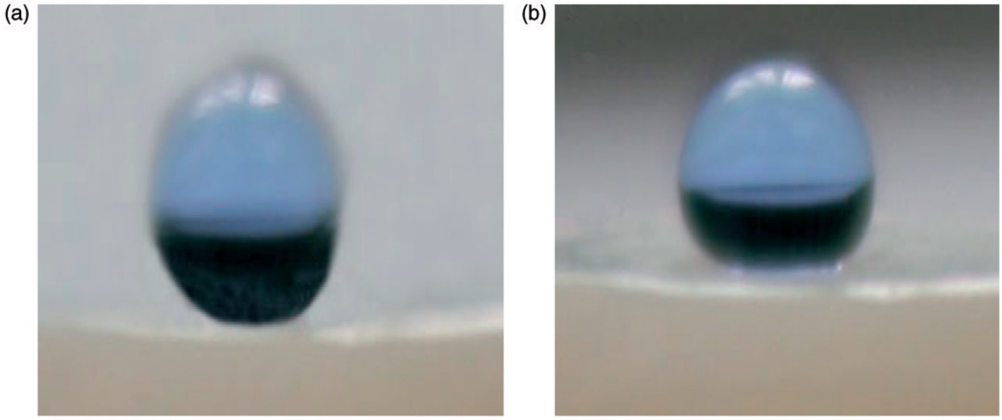

Figure 3. The contact angles of silica aerogels doped with DMF at $G = 0.8$: (a) without heat-treatment, $\theta \approx 178^\circ$ and (b) heat-treatment in air at 350°C, $\theta \approx 162^\circ$.

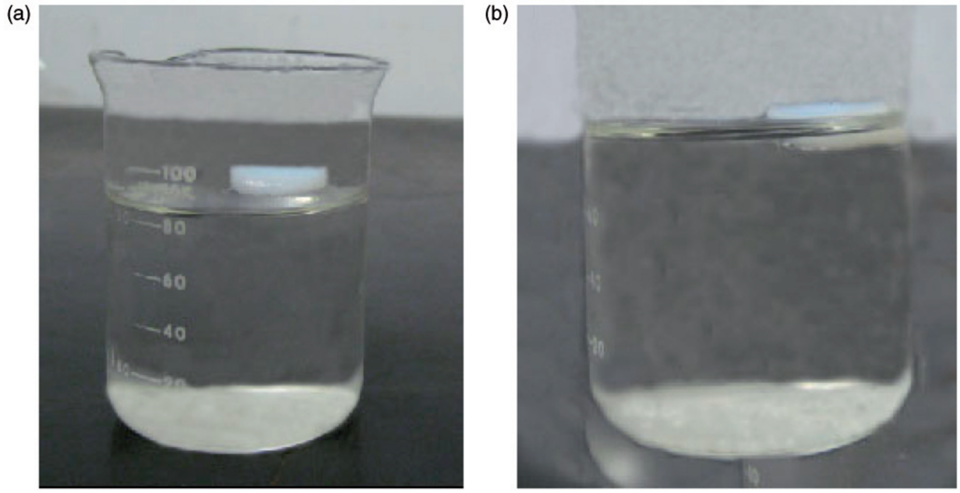

Figure 4. Illustrations of hydrophobicity of silica aerogels doped with DMF at $G = 0.8$: (a) without heat-treatment and (b) heat-treatment at 350°C.

It was clear that the intensity curves could be divided into three regions whether CAs are doped or not. At very small h region, the materials became homogeneous (non-fractal). In the intermediate region, $I(q)$ is dependent on the volume fractal dimension of the network, while in the large h region measurement showed the particle surface fractal dimension. The positions of the two crossovers were related to the size of the primary-particle diameter, a (large h), and correlation length, ξ (small h). The values of the correspondingly fractal characteristics of the aerogels doped with and without CAs are listed in Table 1. The correlation length, ξ, of the volume fractal property decreased, the fractal range, ξ/a, shortened and the surface fractal dimension, D_s, slightly decreased with the CAs-doping, while the doping influence on the volume fractal dimension seemed to be more complex.

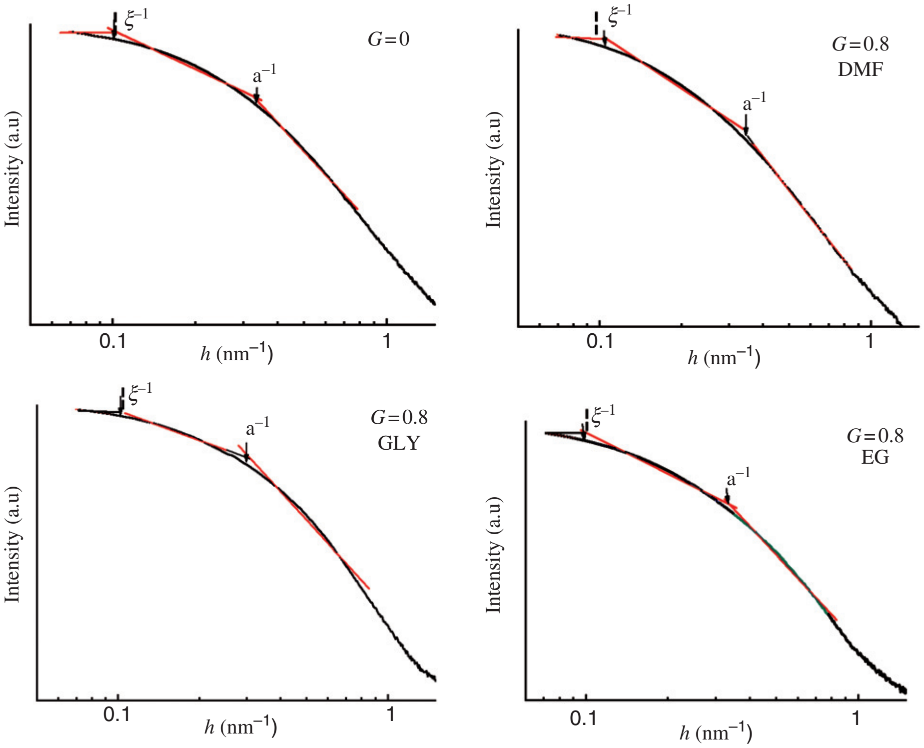

Figure 5. SAXS curves for samples doped with different CAs at different G values.

Table 1. The fractal characteristics of the aerogels doped with and without CAs.

G	D	a (nm)	ξ (nm)	ξ/a	D_s
$G=0$	1.44 ± 0.03	≈ 2.86	≈ 10.59	≈ 3.70	2.75 ± 0.01
$G=0.8$, DMF	1.75 ± 0.03	≈ 3.77	≈ 10.26	≈ 2.72	2.71 ± 0.01
$G=0.8$, GLY	1.07 ± 0.03	≈ 3.19	≈ 10.36	≈ 3.25	2.65 ± 0.03
$G=0.8$, EG	1.50 ± 0.03	≈ 3.30	≈ 10.17	≈ 3.08	2.52 ± 0.02

4. Discussion

When without a surface modification process, the doping of DCCAs could decrease the capillary pressure exerted on the pores of aerogels because of their low surface tension and high boiling point. Table 2 lists the boiling point and surface tension of the liquids used in this experiment, i.e. EtOH, H_2O, DMF, GLY and EG. The main effect of CAs here in the gel formation process is to reduce the surface tension and thereby modify the pore size distribution (PSD) of the aerogels. The shrinkage of the alcogels without CAs occurred owing to the tensile force caused by the surface tension of EtOH/H_2O liquid. These forces could be decreased when doped with CAs and the shrinkage of aerogels

Table 2. Some standard physical properties of EtOH, H_2O, DMF, GLY and EG [14].

Reagent	Boiling point (°C)	Surface tension at 20°C (10^{-3}N m^{-1})
EtOH	78.3	24.1
H_2O	100	72.9
DMF	153.0	36.8
GLY	182	63.3
EG	179.0	48.4

was simultaneously decreased. But the TEOS concentration was decreased slightly with the increase of G value, which caused the tendency of increasing the shrinkage. Thus the minimum shrinkage of the samples was obtained at $G = 0.8$. Because DMF possessed the lowest surface tension, the shrinkage of aerogels doped with DMF was the lowest among the three. CAs could form strong hydrogen bonds with the silanol groups of the silica alcogels. The active participation of CAs in steric shielding around Si caused decrease in the colloid particle size and shifted the PSD to the minor pore width region. Therefore, smaller particles and PSDs could be obtained when doped with CAs, which was coincident with the SEM photographs.

During drying, in general, wet gel experienced some shrinkage that the gel lost many features of their porous property. When heat-treated at certain temperature, the shrinkage was reversible followed by a 'Spring Back' process to become a wet-gel-like structure. In this experiment, the aerogels doped with DMF at $G = 0.8$ decreased the shrinkage of ~3% after heat-treatment at 350°C. High heating rate caused the rapid gas expansion in the gel and inhibited to escape gas from the gel. So the gas would compress the gel and make it expand under high heating rate. But if the compress force was too big, the porous structure of the gel might be destroyed. Due to this reason, we adopted this heating schedule in this experiment. Besides, some hydrophobic groups on the surface of the gels might disappear after 350°C heat-treatment in air. As a result, the hydrophobicity of the aerogel degraded, but also possessed the super-hydrophobic property.

SAXS results could explain the fractal structure of porous materials [15] and show the connectivity of a polymeric network [16]. The surface fractal dimension decreased a little when doped with different CAs, so their doping had little influence on the degree of surface roughness of the particles. But the volume fractal dimension was changed more prominent. GLY-doped aerogel decreased the D value, EG-doped aerogel increased it a little and DMF-doped aerogel increased it obviously. Therefore, the DMF-doped aerogel possessed the most uniform and smallest particles and PSDs, which could also be seen from their SEM photographs.

5. Conclusions

Silica aerogels of hydrophobic property have been obtained using three different CAs, namely DMF, GLY and EG. The doping of CAs could reduce the tension forces and thereby modify the PSD of the aerogels. According to the difference of their surface tension, DMF-doped aerogels had less shrinkage (≈6%) and lower bulk density (≈$0.2\,\mathrm{g\,cm^{-3}}$). The super-hydrophobic property was retained even if the aerogel was heat-treated at 350°C in air ($\theta \approx 162^\circ$). The CAs-doped aerogels possessed smaller and more uniform particle sizes and PSDs. The SAXS curves indicated that the doping of CAs had a little effect on the surface fractal dimension, while it had more complex influence on volume fractal dimension. DMF-doped aerogels possessed the most uniform and the smallest particles and PSDs.

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