A Simple and Efficient Approach to Cellulose/Silica Composite Aerogel with High Silica Utilization Efficiency

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Abstract: Cellulose aerogel is a fascinating material with high porosity, low density and biocompatibility. However, cellulose aerogel lacks sufficient thermal stability. Recombination between cellulose aerogel with silica is efficacious for enhance the cellulose aerogel's thermal stability. This work described a simple and efficient approach to the cellulose/silica composite aerogel *via* a dropwise manner, using tetraethoxysilane as silicon source and NaOH solution as cellulose solvent. The result showed that the thermal stability of cellulose aerogel was enhanced by introducing silica. And by this manner, the utilization efficiency of silica was up to 95%. The composite aerogel had a low density and a high porosity, which promised the material a good heat insulation performance, and the thermal conductivity of the composite aerogel was low to 0.0161W/(m·K). Moreover, by adjusting cellulose concentration and tetraethoxysilane amount, the density, porosity and thermal conductivity of the composite aerogel could be controlled. This work contributed to improving the utilization efficiency of silica for the composite aerogel with better performances.

Keyword: Cellulose, Silica, Aerogel, Dropwise, Utilization efficienc, Heat insulation.

1. INTRODUCTION

Aerogel is a kind of materials prepared by replacing the liquid solvent in a gel by air without substantially altering the network structure or the volume of the gel body [1, 2]. As the new third-generation material, cellulose aerogel possesses features of traditional aerogel [3, 4]. Cellulose aerogel, known for high porosity and large internal surface, low density, comparatively high ductility, and biocompatibility, is a fascinating materials compared to other inorganic or synthetic organic aerogel [5-7]. However, in spite of their intriguing properties, cellulose aerogel lacks sufficient thermal stability. Therefore, a couple of scientific studies have been performed, aiming at the improvement of the cellulose aerogel's thermal stability [8]. And it has been demonstrated that recombination between cellulose aerogel with silica is efficacious for improvement of thermal stability [9-11]. Due to the quantum tunneling effect, the volume effect of SiO_2 and the action of swimming permeability of cellulose, SiO_2 particulates can penetrate into the nearby π-bond of cellulose, and the electron cloud occurs to interlapping. The composited SiO_2 improves the heat endurance, resistance to wear, toughness, hydrophobicity [12].

There were so many reported methods to synthesis cellulose/silica composite aerogel. *In-situ* formation method attracted a lot of attention [13]. By this way, silica was introduced into cellulose aerogel to improve the thermal stability and mechanical stability. However, there exists significant disadvantage to the in-situ formation method. For example, the amount of composited silica cannot be determined accurately, and the utilization efficiency of silicon source was low [14]. These defects result in the waste of silicon source. When the silica is used excessively, the phenomenon of powder out happen to the cellulose/silica composite aerogel, thereby affects the performance of the material.

In this paper, cellulose and silica was composited by dropping the TEOS hydrolyzate in the cellulose/NaOH solution. By the dropwise manner, the silica content in the composite aerogel was adjusted by controlling the added silica amount, thereby led to the performance of the composite aerogel controllable. The improved utilization efficiency of silica was the greatest advantage of this approach. And it avoid silicon source wasted effectively.

2. EXPERIMENTAL

2.1. Materials

Cotton linter cellulose was provided by Hubei Chemical fiber group co., Ltd. Cellulose was used without further purification. Sodium hydroxide, absolute ethanol, tetraethoxysilane (TEOS), and acetic acid were purchased from Guangzhou chemical reagent factory. All the chemical reagents were analytical grade and directly used.

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2.2. Preparation of Cellulose Aerogel and Cellulose/Silica Composite Aerogel

At first, TEOS, H_2O and ethanol were mixed at the molar ratios of 1.0 : 3.4 : 8.5. Constant reflux condensation was taken for 90min at 60°C, until the hydrolysis was equilibrium. Thus the TEOS hydrolyzate was obtained. According to the ratio of TEOS, water and ethanol, the silica mass of per milliliter TEOS hydrolyzate was 0.07462g.

Second, cellulose was mixed with water, and the mixture was cooled to 5°C 30 min. The NaOH/water solution was precooled at -20°C 1h before being mixed with the cellulose/H_2O mixture. Cellulose was mixed with aqueous NaOH in such proportion that in 100.0 g solution there was X g cellulose, 7.6 g NaOH, (92.4 - X) g water. X was varied from 2.0 to 3.0 g. The cellulose/NaOH mixture was exposed to stir for 5 min, ultrasonic for 20 min until cellulose was dissolved. Solution was poured into a cylindrical mold. Then the solution was kept for a few hours for complete gelation. The cellulose hydrogel was obtained. The cellulose hydrogel was washed with 5wt% acetic acid solution to eliminate NaOH. The cellulose hydrogel was dried by freeze-drying to eventually produce the cellulose aerogel.

In order to obtain the composite aerogel, the TEOS hydrolyzate was added in drop by drop when the cellulose/NaOH solution was stirred. With the same subsequent treatment as cellulose aerogel, the cellulose/silica composite aerogel was obtained. The number following the sample name denoted cellulose concentration and TEOS amount. For instance the sample Aerogel-3-2 meant 2ml TEOS hydrolyzate and 3% cellulose concentration.

2.3. Characterization

2.3.1. Utilization Efficiency of Silica and Silica Content

The utilization efficiency was calculated by the ratio between the mass of silica in the composite aerogel and the mass of added silica (m_0). The mass of silica in the composite aerogel was obtained by the following experiment. After the sample was dried at 100°C for 5 h, weighed and recorded as M. The sample was sintered at 800°C for 24 h by Electrical Resistance Furnace (model: YFX111012) from Shanghai Y-Feng Electrical Furnace Co., Ltd. Weighted the residuum and recorded as m_1. The residue component was just SiO_2 after cellulose was burnt away. The utilization efficiency (S) was calculated by Equation 1. And the silica content (Q) was calculated by Equation 2.

$$S(\%) = \frac{m_1}{m_0} \times 100\% \tag{1}$$

$$Q(\%) = \frac{m_1}{M} \times 100\% \tag{2}$$

2.3.2. Density

The cellulose/silica composite aerogel was dried for 5 h. Its weight was marked as m. In order to get volume V, its height and diameter were measured by the caliper and recorded, respectively. The measurement of each sample was repeated three times to take the average. Density (ρ, g/cm^3) was calculated by the following Equation 3.

$$\rho = \frac{m}{V} \tag{3}$$

2.3.3. Porosity

The porosity (*P*) was calculated by Equation 4 [15]. Here, ρ_m was the bulk density of the material and ρ_t was the skeletal density cellulose. The skeletal density of regenerated cellulose is 1.592 g/cm^3 [16].

$$P = (1 - \frac{\rho_m}{\rho_t}) \times 100\% \tag{4}$$

2.3.4. SEM

Scanning electron microscopy (SEM) images of samples were obtained by a Hitachi S-3000N scanning electron microscope of Japan’s Hitachi. Operated at 15 KV after metallisation with Au.

2.3.5. Measurement of Thermal Stability

Thermogravimetric analysis (TGA) was carried out on a simultaneous thermal analyzer (NETZSCH STA-449C) under atmosphere in the range of 50-650°C, with a heating rate of 10°C /min.

2.3.6. Measurement of Thermal Conductivity

In order to investigate the heat insulating property of composite aerogel, thermal conductivity was evaluated by the guarded hot plate method on a Conductometer (model: DZDR-PL) of Nanjing Dazhan Institute of Electrical Technology. Considering the low decomposition temperature of cellulose, cellulose aerogel can be used in normal and low temperature environment. In the measurement, the temperature of hot plate and cold plate were set at 50 and -15°C,

Table 1: The Silica Content and Utilization Efficiency of Different Composite Aerogels

Sample	Aerogel-3-2	Aerogel-3-4	Aerogel-3-6	Aerogel-3-8	Aerogel-3-10	Reported Sample
Silica Content	5.28	9.89	14.1	14.16	15.03	2%
Silica Utilization Efficiency	95.53%	89.64%	95.28%	95.75%	95.56%	52.4%

respectively. All of the samples were dried at 100°C for 5 h in advance.

3. RESULTS AND DISCUSSION

3.1. The Utilization Efficiency of Silica

The utilization efficiency and silica content of different composite aerogels were shown in Table **1**. It could be clearly seen that the silica content of composite aerogel increased with the increase of TEOS amount, and the utilization efficiency of silica was kept to about 95% high level. It was far higher than the reported utilization efficiency [14]. Therefore, this method improves the composite efficiency of silica effectively, and avoids the silicon source wasted.

Figure **1** showed representative SEM micrographs of the cellulose aerogel and composite aerogels. In the cellulose aerogel and cellulose/silica composite aerogels, the diameter of cellulose fiber was about 15μm. At the same time, silica compounds deposited on the surface of cellulose fibers in the form of thin film, isolated/grouped nanoparticles, as well as relatively large-scale particles. The silica compounds, which located at the intersection of adjacent fibers, could create crosslink between fibers and lead to the composite aerogels reinforced. It could be clearly observed that the deposition amount of silica in the composite aerogel increased with the increase of the TEOS amount.

3.2. The Thermal Stability of Aerogels

The thermal properties of the cellulose aerogel and composite aerogel were evaluated with TGA and DTG. The typical TGA and DTG curves for the cellulose aerogel and cellulose/silica aerogels were presented in Figure **2**, respectively.

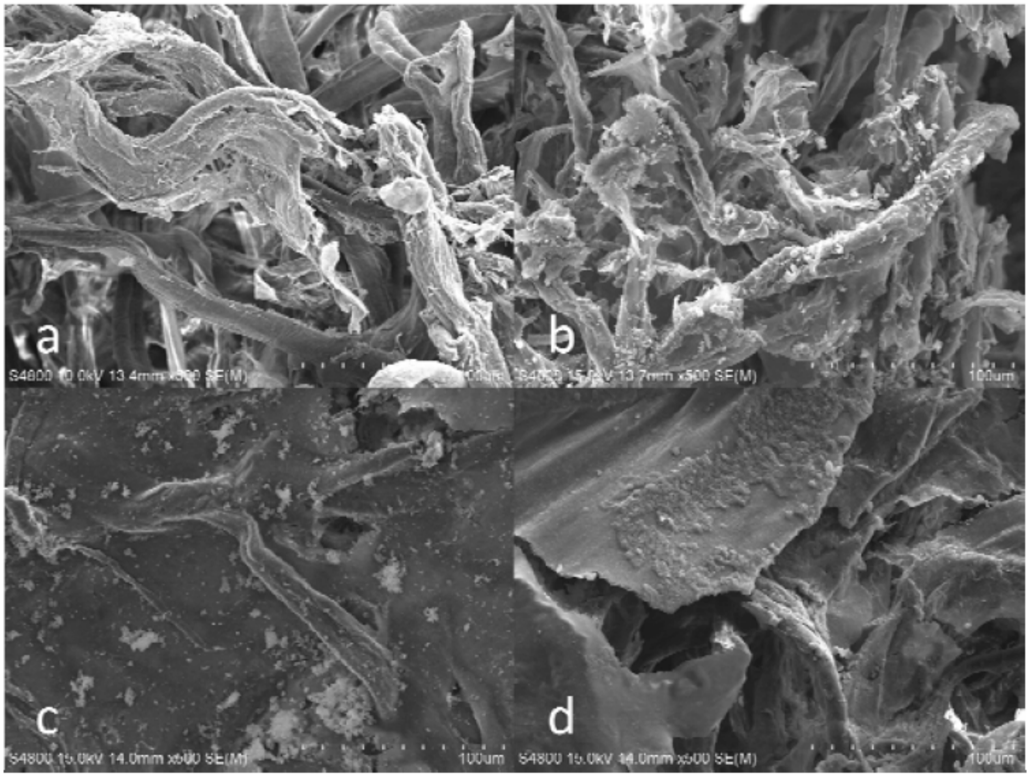

Figure 1: SEM images of Cellulose aerogel (**a**) and composite aerogels of Aerogel-3-2 (**b**), Aerogel-3-6 (**c**) and Aerogel-3-10 (**d**), respectively.

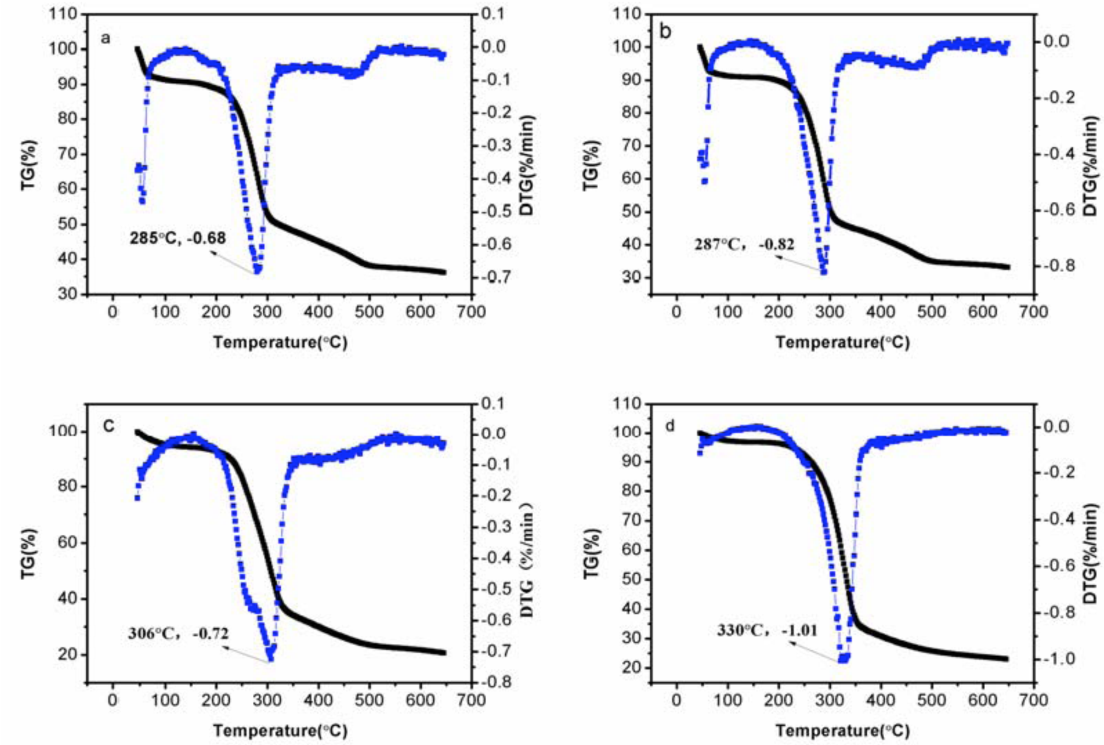

Figure 2: TGA curves of cellulose aerogel (**a**), Aerogel-3-2 (**b**), Aerogel-3-6 (**c**) and Aerogel-3-10 (**d**).

A small weight loss at approx 80°C could be corresponded to the release of water. An intensive decomposition of cellulose aerogel was typically observed at 285°C, whereas the decomposition occurred at 287°C, 306°C and 330°C for the Aerogel-3-2, Aerogel-3-6, Aerogel-3-10. The decomposition temperature increased with the increase silica content. The increase of the decomposition temperature indicated a strong organic-inorganic phase interaction which greatly improved the thermal stability of the composite material. Hence, the thermal stability of cellulose aerogel can be improved by introduction of silica. No further weight loss occurred after the temperature had reached 600°C.

3.3. Heat Insulation Performance

Density and porosity are the main factors to influence the heat insulation property of materials [17]. As shown in Figures **3** and **4**, the composite aerogel had low density and high porosity, which led to high heat insulation performance. The increase of the number of polymer molecule per unit volume caused the increase of density of polymer network. It also made hydrogel easier to form small and uniform condensed phase and caused the decrease of porosity. And as the silica content increased, the more silica was filled up the pore of the composite aerogel. When the cellulose concentration was 2% and the TEOS amount was 2ml, the density was low to 0.0415g/cm^3 and the porosity was up to 97.34%. At the same cellulose concentration, because of higher silica content, the density was increased and the porosity was decreased with the increase of TEOS amount. Hence, the control on the silica content is important to the composite aerogel.

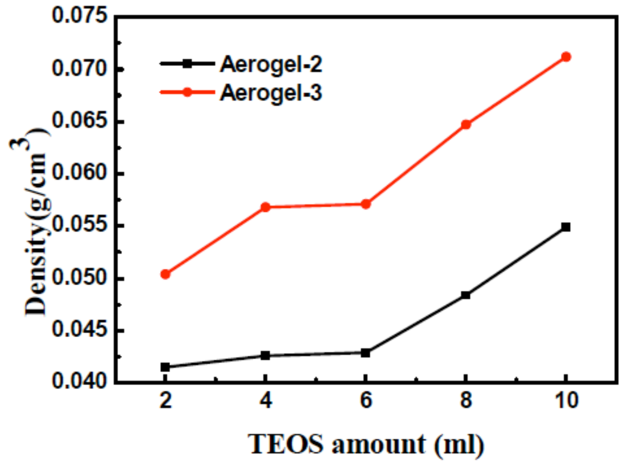

Figure 3: The effect of TEOS amount on aerogel's density.

The thermal conductivity of dense solid is always higher than that of still air. At normal temperature, thermal conductivity increases with the increase of solid matter content in unit volume. The increase of porosity can reduce the mean free energy of phonon,

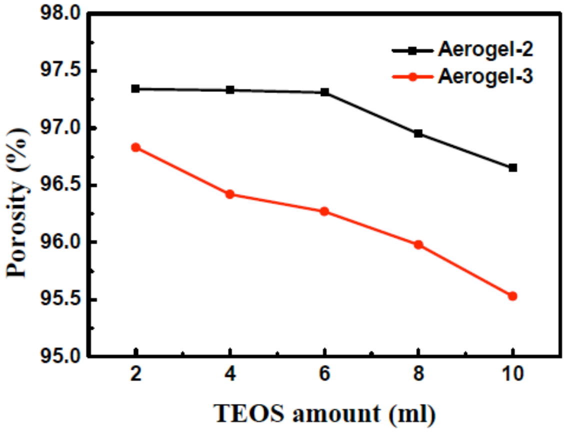

Figure 4: The effect of TEOS amount on aerogel's porosity.

and thus to reduce the thermal conductivity of materials. The effect of cellulose concentration and TEOS amount on aerogel's thermal conductivity was shown in Figure **5**. When the cellulose concentration was 2% and the TEOS amount was 6ml, the thermal conductivity was low to 0.0161W/(m·K). The smaller the density was and the higher the porosity was, the lower the thermal conductivity was. When porosity is higher, the heat transfer route increased, the heat transfer rate had greatly reduced. In the meantime, air molecules had a bigger motion space in composite aerogel. It resulted in a relatively big mean free energy of the air molecules, and caused the decrease of thermal conductivity. Therefore, we can control density and porosity to gain the expected heat insulation performance for the prepared composite aerogel *via* the adjustment of the silica content.

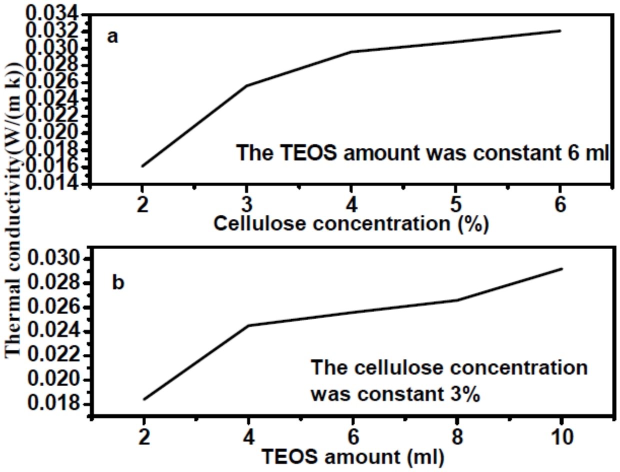

Figure 5: The effect of cellulose concentration (**a**) and TEOS amount (**b**) on thermal conductivity.

4. CONCLUSIONS

In this work, we described a simple and efficient approach to synthesis cellulose/silica composite aerogel with high silica utilization efficiency. Silica was introduced into cellulose *via* the dropwise manner. This approach led to the utilization efficiency of silica was up to 95%. Silica was existed in the form of thin film, isolated/grouped nanoparticles, as well as relatively large-scale particles. Moreover, the thermal stability and insulation properties of cellulose aerogel were enhanced. The thermal conductivity of the composite aerogel could be controlled by adjusting the cellulose concentration and the TEOS amount. When the cellulose concentration was 2% and the TEOS amount was 6ml , the thermal conductivity was low to 0.0161W/(m·K), which was far lower than the value of the classical foam insulation material for refrigerators. This work promised a way to prepare the cellulose/silica composite aerogel with high silica utilization efficiency, and better performance.

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