

Study on the Properties of Silicon Aerogel Prepared by Lotion System

Zhang Yupeng, Zhao Hongkai, Zang Xulong, Zhao Jiaming

College of Materials Science and Engineering, Jilin Jianzhu University, Changchun, 130118, China

Keywords: Emulsion; Aerogel; Temperature; Emulsifier concentration; Stirring rate; Modifier

Abstract: In this chapter, aerogel particles are prepared from W/O lotion, the emulsification mechanism of lotion is briefly described, and the factors affecting the preparation of aerogel microspheres are studied. Through a series of characterization and tests, it is known that: properly increasing the temperature can accelerate the gel reaction rate and shorten the gel time; The stirring rate and surface modifier have certain effects on the density and porosity of aerogel. The preparation of silicon aerogel by lotion method reduces the tedious steps of solvent replacement, shortens the preparation cycle, and greatly reduces the preparation cost.

1. Introduction

Aerogel is a three-dimensional network cross-linked porous solid material, and it has high porosity, high specific surface area, low density and other excellent properties. These characteristics make aerogel have a better development prospect than other materials. Now aerogel has been paid^[1-2] attention to in various industries. The Preparation of aerogel requires a lot of time, high equipment requirements and cost. Many scholars have made great adjustments and changes in the selection of silicon source, preparation process and subsequent drying conditions, in order to reduce the production cost of aerogel and pave the way for large-scale production. The emulsion system for preparing silicon aerogel has the advantages of short cycle, strong operability, and drying under normal pressure, which are favored^[3-5] by many scholars. Up to now, great progress has been made in the preparation of aerogels by emulsion system. In this paper, the performance of the preparation of aerogels by emulsion system was studied.

2. Experimental part

2.1 Experimental Ingredients

Basic silica Sol analysis pure, CH₅NaO₃Si analysis pure, H₂O analysis pure, CTAB analysis pure Tianjin Guangfu Fine Chemical Research Institute, CH₃ (CH₂)₃ analysis pure Tianjin Xinbote Chemical Co., LTD., CH analysis pure Xilong Science C₆H₁₄., LTD., HCl analysis pure Beijing Chemical Plant, TMCS analysis pure Nanjing Chuangzhi Chemical Additives Co., LTD.

2.2 Experimental Instruments

The sources of the experimental instruments are: scanning electron microscope American FEI company, electric heating constant temperature blast drying oven Tianjin Test Co., Ltd., digital display constant temperature water bath pot Bangxi Instrument Technology Co., Ltd., digital display electric stirrer American Selo Czech Co., Ltd., thermogravimetric Shanghai SMAO Analytical Instrument Co., Ltd., Specific Surface Area and Porosity Analyzer Jinapu Technology Co Ltd.

2.3 Raw material preparation

The process of raw material preparation first is the alkaline silica sol was diluted with deionized water to 5% ~ 7% as water phase, n-hexane as oil phase and CTAB as emulsifier. N-butanol is dissolved in the oil as an emulsifier, the water phase was gradually added into the oil phase at 30 °C and 1 mol / L hydrochloric acid solution was added to reduce the pH to 7 ~ 8. Continue stirring for about 15 minutes, wait for the emulsion gel phenomenon to stop stirring.

2.4 Experimental Procedure

Emulsifier and n-hexane were added into the silica sol solution to generate W/O emulsion, and then hydrochloric acid solution was added to generate SiO₂ wet gel microspheres. Finally, SiO₂ aerogel microspheres were generated after a series of experiments including aging, solvent exchange and surface modification.

3. Preparation of aerogel microparticles by emulsion method and performance analysis

3.1 Influence of drying temperature on aerogel

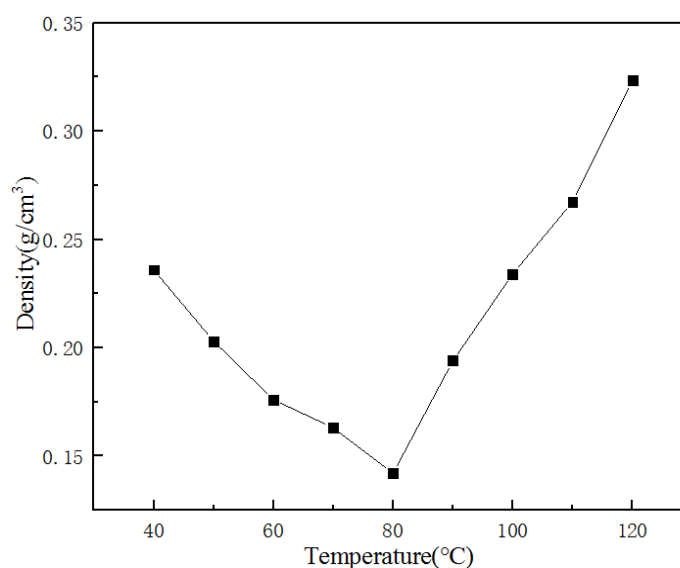


Figure 1: Effect of temperature on aerogel density

It can be seen from Figure 1 that the density of SiO₂ aerogel continues to decrease when drying at 0-80°C, and the density reaches the lowest when drying at 80°C. At this time, the inside of SiO₂ particles is full of a large number of pores. The aerogel density continues to increase with the increase of temperature, which is due to the gradual increase of temperature, the evaporation rate of

n-hexan and TMCS in the emulsion accelerates. Part of TMCS is volatilized into the air before fully reacting, resulting in the results shown in Figure 2.

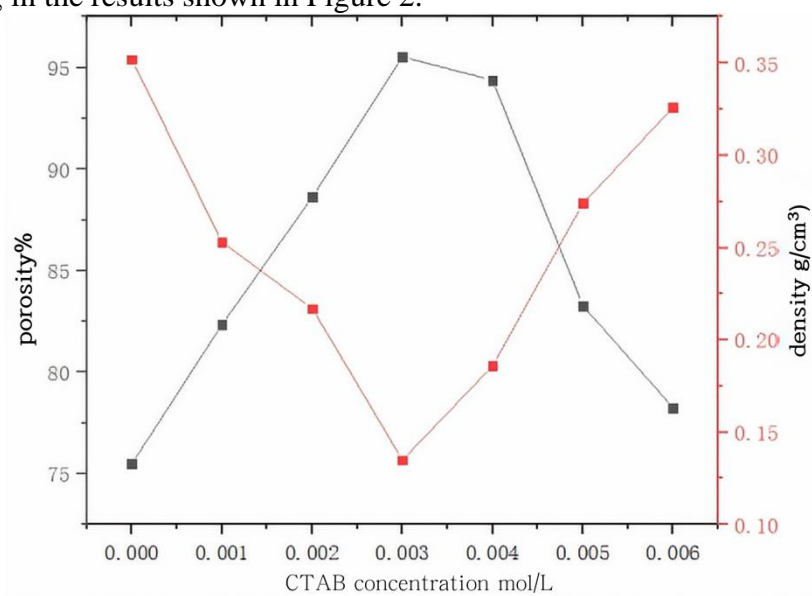


Figure 2: Influence of CTAB concentration on the porosity and density of aerogel

It can be seen from Figure 2 that with the increase of CTAB concentration, the density of aerogel decreases first and then increases, as shown in the figure, and the density is 0.125g/cm³ at 0.003mol/L. The reason for this phenomenon is that when no emulsifier is used, the oil-water interface of the aerogel is difficult to blend, and there maybe emulsion droplets that are not evenly stirred during the reaction, or even many droplets do not form W/ O-shaped particles. This is due to the fact that the interfacial tension is not effectively reduced due to drying, which leads to the high density of the aerogel. When the concentration of CTAB continues to increase to a large enough amount, the steric hindration between the molecules of the aerogel makes it difficult to carry out the gel reaction, the skeleton strength becomes smaller, the reaction time increases, and the contraction of the aerogel becomes more serious.

3.2 Influence of emulsifier on the pore size and morphology of aerogel

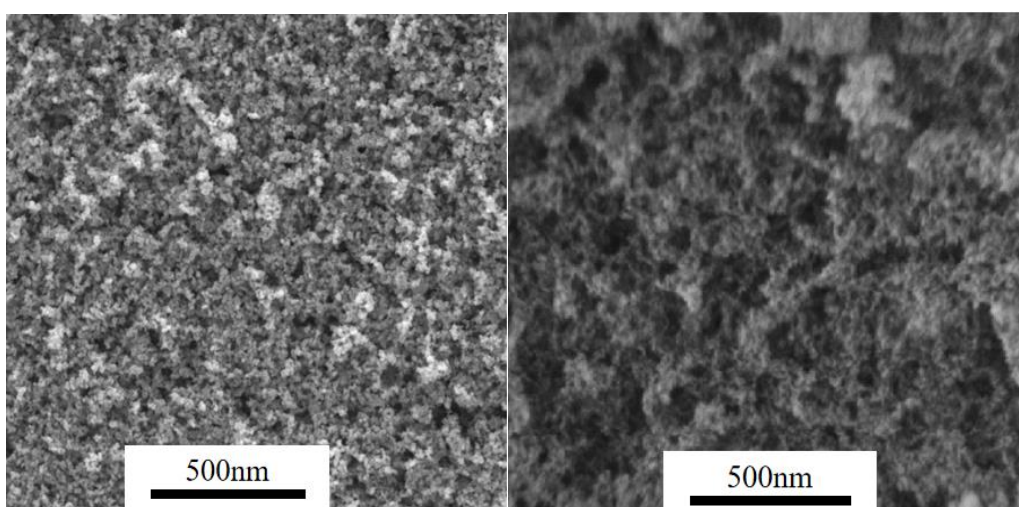


Figure 3: SEM images of aerogel pore size changes

In this experiment, CTAB was used as emulsifier. As CTAB dissociated quaternary ammonium cation and Br ion with strong negative charge in solution, OH- and Br ions jointly attacked Si nucleus, and Si-O bond was broken. In this study, the structural characteristics of porous SiO₂ materials (the changes of surface area and pore size with aerogels are shown in Figure 3) are difficult to approach each other and form micelles due to the existence of electrostatic repulsion between hydrophilic groups. Micelle formation process occurs when the emulsifier concentration is high enough, effective bonding occurs and micelles are gradually formed. Meanwhile, due to dehydration, the SiO₂ particles between hydroxyl groups on the surface of silica sol particles are connected to each other to form a three-dimensional structure. At this time, the surface of the particles is negatively charged, and CTAB is a cationic emulsifier. The charged end is adsorbed on the surface of the particles to "shield" the hydroxyl group surface on the gel and prevent the cross-linking of the particles. When the gravity decreases and the sol particles appear as enlarged gel pores, they are in a very loose state.

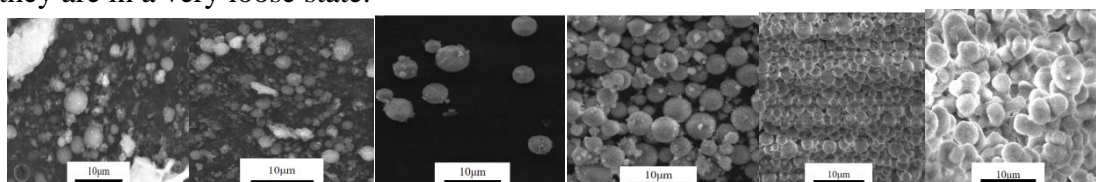


Figure 4: SEM images of aerogel under different concentrations of emulsifiers

Figure 4 shows the SEM images of aerogel under different concentrations of emulsifiers, and a~f corresponds to the SEM photos when the concentration is 0.001~0.006mol/LCTAB respectively. The emulsifier is too low. The surface of each droplet becomes smaller, and as it becomes smaller, the boundary mask formed becomes weaker and easily broken under high speed mixing, reducing the overall stability of the emulsion. As the CTAB increases, the agglomeration of aerogel microspheres will become more pronounced.

3.3 Effect of stirring



Figure 5: Macroscopic delamination of emulsion after gelation

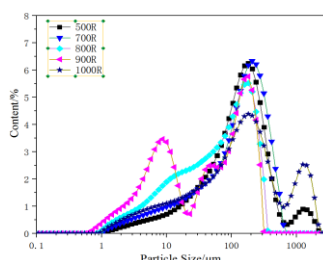


Figure 6: Effect of stirring rate on particle size of emulsion

As can be seen from Figure 5, stirring rate has an important effect on the particle size of aerogel. The larger the stirring rate is, the smaller the droplets will be formed, while too small the stirring

rate will lead to uneven dispersion of the droplets and fail to form a stable structure.

As can be seen from Figure 6, with the gradual increase of the stirring speed, the small particles in the range of 0.1 micron to 10 micron are greatly increased. However, when the stirring speed reaches 1000 r/min, the overall particle size tends to decrease, which maybe due to the crack of gelparticles caused by the too fast stirring speed. With the increase of diameter, the shape of aerogel particles becomes irregular, and the particle size distribution becomes wider.

3.4 Effects of modifiers on aerogel changes

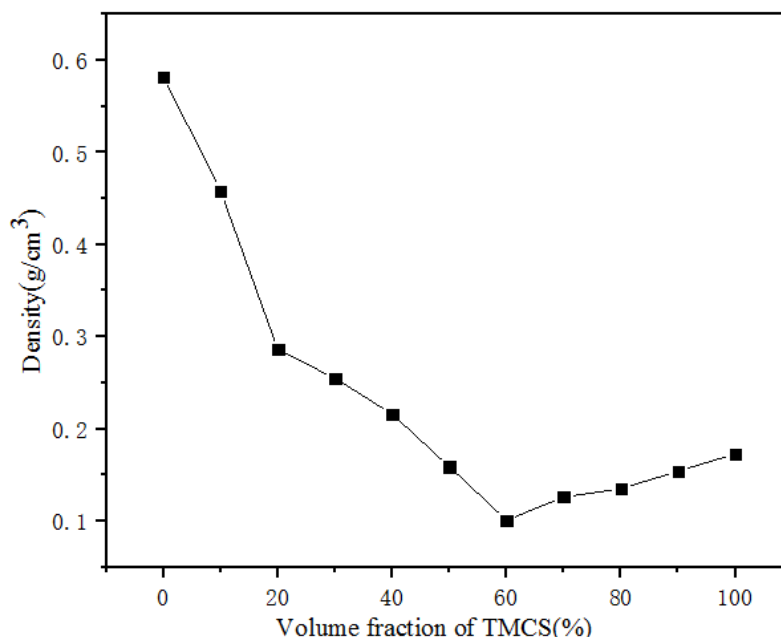


Figure 7: Effect of TMCS change on aerogel density

As can be seen from Figure 7, the density of aerogel decreases first and then increases with the increase of TMCS volume fraction, because the products of TMCS reaction process react with the water in the gel and the hydroxyl group on the surface. Under the same conditions, it has a faster reaction rate than other solvents, and can replace most of the hydroxyl groups in the gel, which greatly reduces the shrinkage damage caused by surface tension during drying. However, the higher the concentration of TMCS, the higher the density of the aerogel, because the higher the concentration of TMCS, the faster the reaction rate, and then produce a large number of HCl solution, destroy the internal structure of the aerogel. The gel undergoes local collapse and an^[7] increase in density. As can be seen from the figure, the aerogel density is lowest when the amount of TMCS is 60% of the gel volume.

3.5 Performance Characterization

After grinding into powder according to the mass ratio of potassium bromide to sample of about 0.1:0.001, the powder was put into the mold to make transparent sheet under medium pressure. Finally, the functional groups of SiO₂ aerogel samples were analyzed in the Perkin-Elmer Spectrum GX intelligent Fourier infrared Raman spectrometer. The wave number range of 4000~500cm⁻¹ was measured.

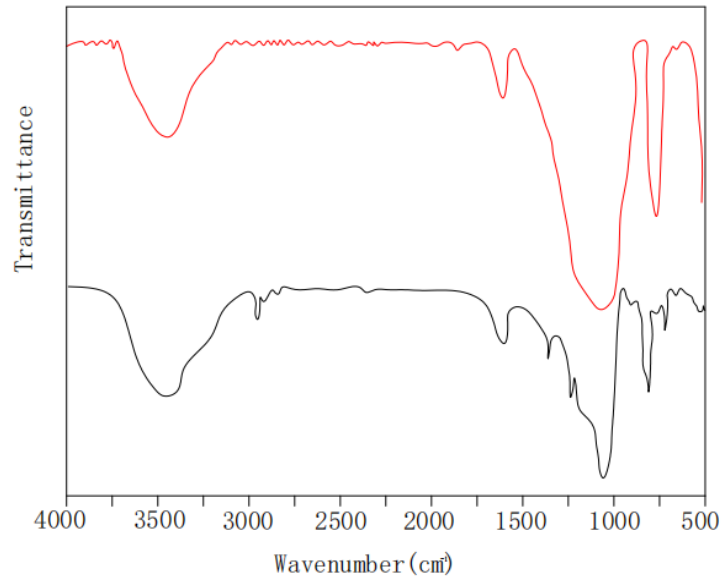


Figure 8: Infrared spectra of modified and unmodified SiO₂ aerogel microspheres

Figure 8 shows the infrared analysis diagram of the sample before and after the modification of aerogel particles. In the figure, obvious diffraction peaks appear at 1096.24 cm^{-1} and 813.23 cm^{-1} , which are caused^[6] by the antisymmetric stretching vibration and bending vibration of Si-O-Si. At the wavelength of 3423.56 cm^{-1} and 1635.82 cm^{-1} , Si-OH bond stretching vibration and bending vibration appeared.^[7] The diffraction peak at 2965.26 cm^{-1} is the modified -Si-CH₃ by TMCS, so the aerogel prepared has high hydrophobicity.

The test sample was dried in the oven to remove the surface moisture of the sample, and then put into the SDTQ600 thermogravimetric analyzer of Shanghai SMaio Analytical Instrument Co., Ltd. to test the thermal stability of the sample. The TG curve of the sample was tested by the analyzer. Nitrogen was used as the atmosphere medium, the temperature rise rate was 10 $^{\circ}\text{C}/\text{min}$, and the temperature rise range was between 25 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$.

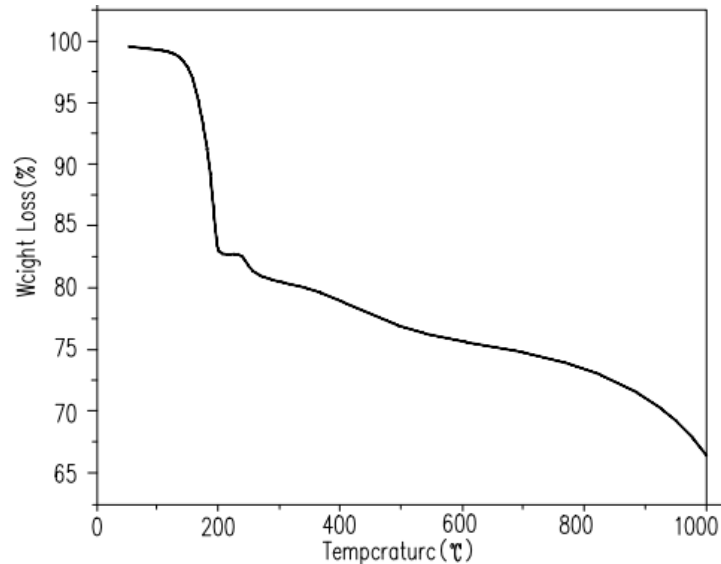


Figure 9: TG curve of SiO₂ aerogel

The thermogravimetric curve of SiO₂ aerogel particles in nitrogen environment is shown in Figure 9. It can be seen from the analysis of the figure that the overall thermal stability of SiO₂

aerogel is good, and there is a mass loss of 17.5% between 50°C and 220°C, which is mainly due to the desorption of water adsorbed on the surface of the dry aerogel and the further condensation of hydroxyl and alkyl groups on the surface.

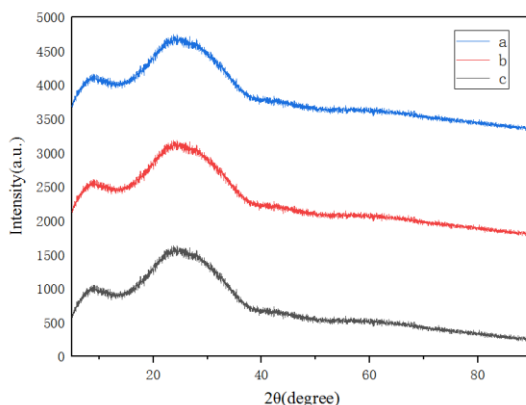


Figure 10: XRD patterns of SiO₂ aerogel microspheres with different concentrations of Modifier

(a) 20% TMCS; (b) 40% TMCS; (c) 60% TMCS

As can be seen from Figure 10, $2\theta=20^{\circ}\sim 35^{\circ}$ has a gentle dispersion peak, which corresponds to the SiO₂ [8] of disordered amorphous structure, and the image as a whole shows disordered amorphous morphology. Moreover, there are no obvious characteristic peaks in the aerogel XRD diffraction patterns of a, b and c with different concentrations of modifier ratio, as shown in Figure 11.

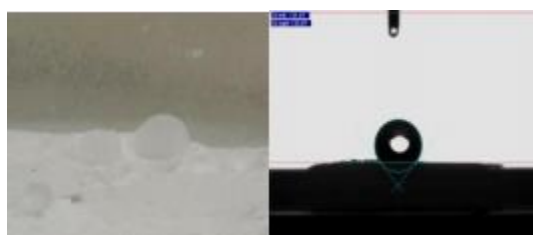


Figure 11: Macroscopic and microscopic hydrophobic effects of aerogel

The contact Angle of the sample is 131.6. On the left and 132.0° on the right, showing high hydrophobicity and the liquid can flow on the surface, indicating that the modification effect of the aerogel group is obvious.

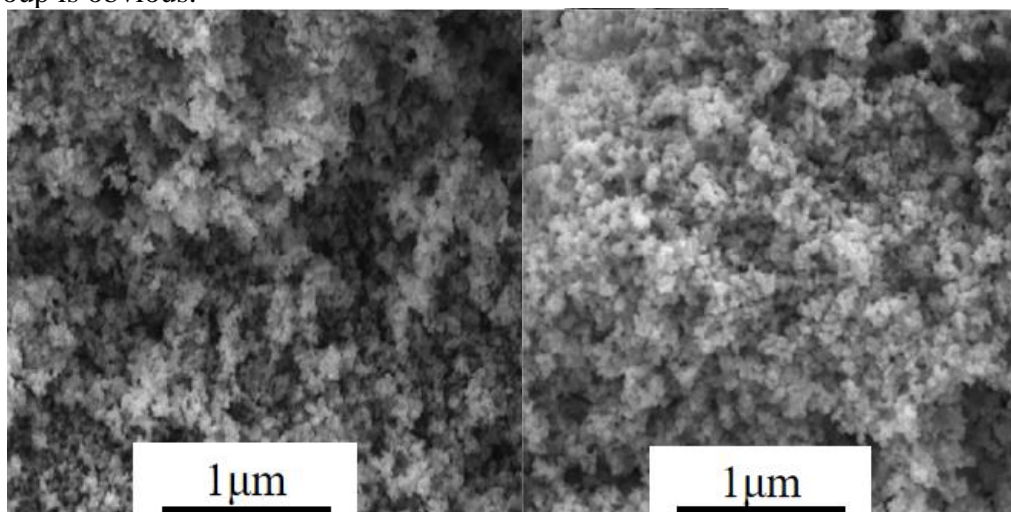


Figure 12: SEM image of aerogel micromorphology

FIG. 12 is the SEM image of the aerogel microspheres, indicating that the aerogel particles are a three-dimensional network structure composed of nanoparticles, which better maintains the nanovoid structure.

4. Conclusion

The effects of important parameters in the preparation of aerogel on the properties of the product were analyzed in this experiment. Temperature, emulsifier concentration, stirring rate and surface modifier content all affect the key properties of aerogels such as density, particle size and porosity. Increasing the temperature can speed up the reaction rate and shorten the experiment time; The concentration of emulsifier has a non-monotone change on the density of aerogel, and the optimal density is when the concentration is 0.003 mol/L and the content of surface modifier is 60% of the gel volume, while the stirring rate will have a significant effect on the particle size of aerogel, and when it reaches a certain degree, the phenomenon of microspheres rupture will occur, resulting in the increase of particle size. In addition, with the increase of the emulsifier concentration, the porosity increased first and then decreased, and the highest rate was 95.54%. These conclusions can provide guidance for the preparation of aerogel.

Acknowledgement

This work was supported by JJKH20220267CY of Education Department of Jilin Province, 20210203206SF of Science and Technology Department of Jilin Province, S202210191019X of Innovation and Entrepreneurship Training Program for College Students of Jilin Province.

References

- [1] Pajonk G M. Some applications of silica aerogels [J]. *Colloid and Polymer Science*, 2003, 281(7):637-651.
- [2] Qin Guotong, Men Weiwei, Wei Wei, et al. Advances in aerogel research, *Chinese Journal of Materials Science and Engineering*, 2005, 23(2):293-296.
- [3] Song L, Ge X, Wang Jinshu. Direct preparation of silica hollow spheres in a water in oil emulsion system: The effect of pH and viscosity [J]. *Journal of Non-Crystalline Solids*, 2006, 352(21-22):2230-2235.
- [4] Kyoung-Jin Lee, Kim Y H, Lee J K, et al. Fast Synthesis of Spherical Silica Aerogel Powders by Emulsion Polymerization from Water Glass [J]. *Chemistryselect*, 2018, 3(4). 1257-1261.
- [5] Hong S K, Yoon M Y, Hwang H J. Fabrication of Spherical Silica Aerogel Granules from Water Glass by Ambient Pressure Drying [J]. *Journal of the American Ceramic Society*, 2011, 94(10). 3198-3201.
- [6] Ingale S V, Wagh P B, Tripathi A K, et al. Physico-chemical properties of silica aerogels prepared from TMOS/MTMS mixtures [J]. *Journal of Porous Materials*, 2011, 18(5):567-572.
- [7] Ren C, Qiu W, Chen Y, et al. Physico-chemical properties and photocatalytic activity of the TiO₂/SiO₂ prepared by precipitation method [J]. *Separation & Purification Technology*, 2013, 107:264-272.
- [8] Kwon Y G, Choi S Y, Kang E S, et al. Ambient-dried silica aerogel doped with TiO₂ powder for thermal insulation [J]. *Journal of Materials Science*, 2000, 35(24):6075-6079.