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Facile fabrication of graphite-doped silica aerogels with ultralow thermal conductivity by precise control

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ABSTRACT

Graphite-doped silica (G/SiO_2) aerogels for thermal insulation were prepared through doping colloidal graphite (G) into silica (SiO_2) sol, followed by aging, washing and supercritical drying. The morphology and structure of the as-prepared composite aerogels were characterized by means of scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectrum, and nitrogen adsorption/desorption measurement. It was found that all the composite aerogels had the typical three-dimensional porous structure and high specific surface areas (~1500 m^2/g). The thermal conductive property of the composite aerogels was studied by SHT-P transient automatic measurement. The results indicated that the thermal conductivity of the G/SiO_2 composite aerogel with G/SiO_2 mass ratio of 0.4% was 0.017 W/(m·K) at room temperature, which was lower than that of pure SiO_2 aerogel (0.02 W/(m·K)) and endowed the G/SiO_2 composite aerogel good thermal insulation performance.

1. Introduction

Silica aerogel is a kind of amorphous solid material with nanoporous structure, high porosity, large surface area, and low thermal conductivity [1–7]. Therefore, it is successfully applied in thermal, optics, electricity, acoustics and many other domains [8–14]. In particular, functional composite materials (especially high-surface-area materials such as mesoporous materials) have attracted increasing interest with many functions developed in the recent years [15–20].

It has been reported that the thermal conductivity of pure silica aerogel could be about 0.02 W/(m·K) under ambient conditions [21]. However, the radiative thermal conductivity of pure silica aerogels increases drastically with the increase of temperature, which is attributed that pure silica aerogels are infrared-transparent with the wavelength of 3–8 μm [22]. Thus, a great deal of methods, such as the introduction of opacifiers, had been done to reduce heat transfer by radiation and further improve thermal insulation property of silica aerogels [23–26]. Kuhn et al. produced the composite of SiO_2 aerogel and micrometer-sized mineral powders, such as SiC, TiO_2, Fe_3O_4, and B_4C, in order to develop opacified thermally insulating materials [27–29]. These results showed that SiC and TiO_2 were optimum opacifiers at higher temperatures. Feng et al. used fumed silica, opacifier SiC, and fiber to prepared nanoporous thermal insulating aerogels by a dry molding method [30]. It was found that when the SiC powder was adopted with the average size of 0.877 μm and mass ratio of 25%, thermal conductivity of the composite was 0.027 W/(m·K) at ambient temperatures. Wu et al. developed a new convenient method to facilitate the fabrication of Al_2O_3–SiO_2 composite aerogels, thermal conductivities of which were 0.023, 0.029 and 0.025 W/(m·K) with the Al/Si molar ratios of 2, 3 and 8, respectively, at room temperature [31].

However, it was found that although these composite aerogels, such as Al_2O_3, had thermal conductivities as low as 0.023 W/(m·K), the value for thermal insulation was still higher than that of pure silica aerogel (0.020 W/(m·K)). Meanwhile, the high density and doping mass of the mineral opacifiers also limited their applications for spacecrafts. As a low-density material, carbon materials could be also used as opacifiers. For example, carbon black was added into SiO_2 aerogel to reduce the radiative heat transfer. However, carbon black was not stable under the high temperature. Therefore, it could be seen that the pre-research on the introduction of opacifiers could not meet the needs totally and a novel opacifier should be found for optimizing the thermal insulation property of SiO_2-based composite aerogels. Due to its low density, good thermal stability and absorption capacity of infrared ray, graphite would be an efficient opacifier to reduce the heat transfer by radiation

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in SiO_2 aerogels. Meanwhile, graphite also had native thermal conductivity. Thus, it is a significant investigation on the precise control of graphite content and its dispersion state in the SiO_2-based composite aerogel for the excellent thermal insulation performance. To the best of our knowledge, there had been no the report so far to precisely use colloidal graphite as an efficient opacifier for the thermal insulation performance of SiO_2-based composite aerogels.

In this work, we used a sol-gel method via dopping colloidal graphite into silica sol to produce graphite-doped silica (G/SiO_2) aerogels with good formability, high specific surface area, and low thermal conductivity at room temperature. Furthermore, the effects of the components of precursor solution and graphite contents on the structure and thermal insulation performance of G/SiO_2 composite aerogels were also discussed in details.

2. Experimental

2.1. Reagents and chemicals

Ethanol (EtOH, purity ≥ 99.7%), tetraethoxysilane (TEOS), ammonium hydroxide and acetone (purity ≥ 99.5%) were purchased ChengDu Kelong Chemical Reagent Company. Hydrochloric acid was supplied by Tianjin Kermel Chemical Reagent Company. Colloidal graphite was provided by Qingdao Risheng Graphite Co., LTD.

2.2. Preparation of graphite-doped silica aerogels

The preparation process of G/SiO_2 composite aerogels had two steps. In the first step, the precursor solution was prepared by mixing with TEOS, EtOH and deionized water in a certain volume ratios (1:2:1–1:5:1) under magnetic stirring at room temperature for 90 min. Then, the pH of the precursor solution was adjusted to 3–4 by hydrochloric acid. In the second step, a certain quantity of colloidal graphite powders (G/SiO_2 mass ratios = 0.2%, 0.4%, and 0.6%, respectively) dissolved in ethanol was added into the precursor solution. Then, after magnetic stirring in a few min, the ammonium hydroxide (0.2 M) was added into the above stock solution until the pH value was adjusted to 6–7. In order to avoid sedimentation of graphite powders, the following gelation period was limited in about 2–3 min by controlling the amount of ammonium hydroxide. After pouring the sol into the ampoules and aging at room temperature, the wet gel was placed in the ethanol bath at room temperature to remove any impurities or water remaining in it. At last, the G/SiO_2 composite aerogels were obtained after supercritical CO_2 drying. Especially, when the H_2O/EtOH/TEOS volume ratio of precursor solution was 1:4:1, the related composite aerogels were named as G/Si-1, G/Si-2 and G/Si-3 with the corresponding G/SiO_2 mass ratios of 0.2%, 0.4% and 0.6%, respectively.

2.3. Characterization

The microstructure of the composite aerogel was characterized by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS, Ultra 55, Zeiss) and transmission electron microscopy (TEM, JEOL JEM-2010). Nitrogen adsorption-desorption analysis (Quadrasorb SI) at 77 K was used to indicate the specific surface area and pore size distribution of the composite aerogel. Fourier transform infrared (FTIR, Nicolet 6700 Thermo Fisher) spectroscopy was used to identify the chemical compositions of composite aerogels. Thermal conductivity of the composite aerogel was measured by using SHT-P transient automatic measurement at room temperature.

3. Results and discussion

As seen from Scheme 1, it showed the schematic illustration for the synthesis of G/SiO_2 composite aerogels. It could be seen that TEOS, EtOH and deionized water were mixed in a certain volume ratios to prepare the precursor solution. Subsequently, a certain quantity of colloidal graphite powders was added into the precursor solution. After that, the sol was poured in a sealed ampoule and held to form a gel, which was then subjected to supercritical CO_2 drying. It was known that the key issue of synthesizing the composite aerogels was the present of well-dispersed state for graphite powders to prevent sedimentation. Thus, in our preliminary work, the effect of the components of precursor solution on the morphology and structure of pure SiO_2 aerogels was discussed and the optimum component volume ratio for SiO_2 gel network was chosen to further well disperse graphite powders. As shown in Fig. S1, from SEM images of pure SiO_2 aerogels with different H_2O/EtOH/TEOS volumetric ratios, it was noted that all the pure SiO_2 aerogels had the typical three-dimensional porous network. Among them, the pure SiO_2 aerogel with the H_2O/EtOH/TEOS volumetric ratio of 1:4:1 (Fig. S1d) had the relatively uniform pore structure and few aggregations or collapse occurred. Therefore, according to the preliminary trying, the H_2O/EtOH/TEOS volumetric ratio in precursor solution was optimized at 1:4:1.

Besides, the present of well-dispersed state for graphite powders was also influenced by their deflocculation and stability, which could be achieved by controlling the doping content of graphite powders, its mixing time in precursor solution and the gel time of the sol. In this work, in order to avoid sedimentation of graphite powders, the mixing time and gelation period were limited in about 25 min and 2–3 min, respectively. On this basis, Fig. 1a showed the photos of composite aerogels with different G/SiO_2 mass ratios in appearance. As seen from Fig. 1a, it could be seen that the as-prepared G/SiO_2 composite aerogels exhibited good formability and crackfree in appearance. The uniform gray color of the G/SiO_2 composite aerogels would endow the well dispersion of graphite powders in the SiO_2 gel network. Furthermore, Fig. 1b–d showed the micrographs of the G/SiO_2 composite aerogels. From SEM images, it was found that compared with the pure SiO_2 aerogel (Fig. S2), all the G/SiO_2 composite aerogels still kept the original three-dimensional porous structure and there was no distinct agglomeration. The result visually demonstrated that in the G/SiO_2 composite aerogels, graphite powders had evenly dispersed in the SiO_2 matrix to form uniform porous structure, which was well consistent with their uniform gray color in appearance (Fig. 1a).

In order to investigate chemical compositions of aerogels, FTIR analyses of pure silica aerogel and G/SiO_2 composite aerogels were shown in Fig. 2. It was seen that for pure SiO_2 aerogel, the absorption bands at 469 and 962 cm^{-1} were assigned to the Si—O—Si and Si—OH bending vibrations, respectively. The peaks at 800 and 1090 cm^{-1} were corresponded to the symmetric and antisymmetric Si—O—Si stretching vibrations, respectively. The absorption bands at 3434 and 1638 cm^{-1} derived from the —OH stretching and bending vibrations, respectively, which were caused by physically absorbed water molecules. It could be seen that all the G/SiO_2 composite aerogels showed the similar FTIR spectra as that of pure SiO_2 aerogel, suggesting there was no new absorption bonds. Thus, it showed the physical interaction between graphite powders and SiO_2 matrix in G/SiO_2 composite aerogels.

Nitrogen adsorption/desorption measurements were employed to characterize the surface area and pore structure of the samples. The pore size distribution and specific surface area of samples were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods (Fig. 3). The composite aerogels showed the typical IV isotherms according to the IUPAC classification, which is characteristic of the mesoporous structure. The desorption cycles of the isotherms showed a hysteresis loop for all the samples, which is generally attributed to the capillary condensation that occurs in the mesopores. As is shown in Table 1, it was obvious that the G/Si-2 composite aerogel had the highest specific surface area of 1504 m^2/g and pore volume of 15.2 cm^3/g. On the whole, it was seen that the specific surface area as well as the pore volume underwent a