



Thermal conductivity of aerogel composites with oriented nitrogen-doped graphene



Chenwu Yue, Jian Feng*, Junzong Feng, Yonggang Jiang

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, China

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ABSTRACT

Aerogels with oriented sheets show better thermal insulation properties. However, it is difficult to prepare bulk oriented aerogels. In this paper, we prepared this kind of aerogels by using aligned fibers as the wall of galleries. This simple method makes the N-doped graphene sheets align along the in-plane orientation during impregnating. The as-prepared aerogel composites not only show much lower through-plane thermal conductivity ($26.6\text{--}29.8\text{ mW m}^{-1}\text{ K}^{-1}$) compared to their in-plane thermal conductivity ($44.9\text{--}55.1\text{ mW m}^{-1}\text{ K}^{-1}$), but also exhibit high tensile strength (higher than 3 MPa). After being heat treated at $300\text{ }^\circ\text{C}$, the through-plane thermal conductivity ($23.3\text{ mW m}^{-1}\text{ K}^{-1}$) is even lower than the thermal conductivity of pure aerogels. These properties significantly contribute to their applications in thermal insulation. Besides, the simple method is also useful in preparing other materials with oriented sheets and high strength.

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1. Introduction

Graphene, a single atomic layer of sp^2 carbon atoms [1,2], has received much attention since first obtained by mechanical exfoliation [2] for its excellent electrical [3], thermal [4], optical [5] and mechanical [6] properties. Its measured in-plane thermal conductivity at room temperature for suspended samples are as high as $2500\text{--}5300\text{ W m}^{-1}\text{ K}^{-1}$ [4,7,8], while the out-of-plane thermal conductivity between graphene sheets is less than $50\text{ W m}^{-1}\text{ K}^{-1}$ [9], which has been regard as one of the most significant factors that limit the thermal transportation properties of graphene-based materials for thermal management [10–12]. However, this unique and seemingly disadvantageous property may become fascinating under certain circumstance.

Graphene aerogels (or reduced graphene oxide aerogels, rGO aerogels) have attracted much attention in catalyst [13], battery [14], sensor [15], supercapacitor [16], adsorption [17], thermal management [12]. et al. for their outstanding properties. Recently, it is found that this kind of materials can also be used in thermal insulation. The thermal conductivity under vacuum reaches $2\text{--}4 \times 10^{-4}\text{ W m}^{-1}\text{ K}^{-1}$, which is the lowest thermal conductivity ever measured [18]. Besides, by introducing defects and decreasing

pore size, the thermal conductivity at room temperature under atmospheric pressure is only $23.2\text{ mW m}^{-1}\text{ K}^{-1}$, which is even lower than that of static air and not higher than that of SiO_2 aerogels [19]. Since their density is much lower than traditional thermal insulation materials, this kind of materials are more advantageous for thermal insulation to some extent.

However, the sheets in the aerogels are randomly connected, which takes little advantage of the anisotropic thermal conductivity of graphene. If the sheets orientedly distribute along the in-plane orientation, the in-plane thermal conductivity may increase, while the through-plane thermal conductivity may be suppressed. The higher in-plane thermal conductivity will contribute to the heat transfer along the in-plane orientation, avoiding the overheating in certain position. And the lower through-plane thermal conductivity can help suppress the heat transfer through the aerogels, protecting the stuff in the other side. So the orientation of the sheets may further improve the thermal insulation properties of the aerogels.

The graphene-based materials with interior sheets alignment have been prepared from graphene oxide liquid crystals [20,21]. But the GO liquid crystals can not be used to prepare the thermal insulation aerogels for their random and diverse orientations. The flow of the GO suspension can also make the sheets align complying with the flowing direction since the existence of shear force [22]. But the thickness is limited. To obtain bulk oriented aerogels for thermal insulation, the GO suspension must flow throw many parallel narrow galleries. This process is complicated

* Corresponding author.

E-mail address: fengj@nudt.edu.cn (J. Feng).

and costly.

In this paper, we prepared aerogel composites with oriented N-doped graphene sheets by using ultrafine quartz fibers as the wall of galleries. The ultrafine quartz fibers not only contribute to the orientation of the sheets, but also act as the reinforcements of the aerogels. The as-prepared composites show much lower through-plane thermal conductivity compared to in-plane thermal conductivity and high strength.

2. Experimental section

2.1. Synthesis of as-prepared aerogel composites

The ultrafine quartz fibers with diameter of 5 μm were stacked parallel to the in-plane orientation. Then, the stacked quartz fibers were clamped with two stainless steel plates to obtain a desired thickness (10–50 mm) and desired bulk density (0.03–0.07 g cm^{-3}). A 1000 ml graphene oxide (GO) suspension (12 mg ml^{-1}) was commixed with 48 g paraphenylene diamine (PPD) and 9 ml concentrated ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$). Subsequently, the fixed fibers were impregnated from a certain side with the mixture under vacuum (Fig. 1). After been sealed, the ultrafine quartz fibers containing GO mixture were heated at 90 $^\circ\text{C}$ for 8 h to get hydrogel. Then the solvent in the hydrogel was exchanged 5 times with water and ethanol. Finally, the gel was dried with supercritical CO_2 to obtain aerogel composites with oriented N-doped graphene sheets. The pure aerogels were prepared under the same conditions without fibers as reinforcements.

2.2. Heat treatment of as-prepared aerogel composites

To investigate the heat resistance properties under air atmosphere, the as-prepared aerogel composites were placed in a muffle furnace, heated under air atmosphere at certain temperature (300 or 400 $^\circ\text{C}$) for 2 h with heating rate of 3 $^\circ\text{C min}^{-1}$. After natural cooling in the furnace, the aerogel composites were characterized.

2.3. Characterization

The bulk density was calculated from the mass and corresponding volume. The microstructure was observed with Hitachi S4800 field emission scanning electron microscope (SEM). The Raman spectra were performed with Renishaw inVia Raman microscope using an excitation wavelength of 514.5 nm. The thermogravimetry and differential scanning calorimetry (TG-DSC) test was taken on SDT Q600 thermogravimetric analyzer. The nitrogen adsorption–desorption tests were carried out at 77 K in an autosorb-1 physical adsorption instrument after 16 h of sample outgassing in vacuum, and the specific surface area and pore size distribution were

calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The thermal conductivity was measured with samples $\Phi 40 \times 15$ mm for aerogels and $45 \times 45 \times 15$ mm for composites using Hot disk TPS2500 apparatus. The isotropic and anisotropic thermal conductivity were tested by using 5465 and 5501 sensors, respectively. The specific heat capacity for anisotropic thermal conductivity test was characterized with Hot disk TPS2500 apparatus by heat capacity module. The tensile strength of the composites was tested with sample like dumbbell.

3. Results and discussion

The ultrafine quartz fibers act as wall of galleries, dividing the space in the fixed fibers into numbers of galleries parallel to the in-plane orientation. During impregnating, the GO suspension flows through the galleries (the space among the fibers). The sheets align along the flowing direction, namely, distribute along the in-plane orientation to some extent. After heated at 90 $^\circ\text{C}$, the hydrogel and corresponding aerogel show oriented sheets (Fig. 2). The oriented sheets connect with each other, but are not closely stacked (Fig. 2). They form numbers of pores with diameter from dozens of nanometers to hundreds of nanometers, which is greater compared to that of pure aerogels. Meanwhile, different from that of pure aerogels, the microstructure is not homogeneous.

The N_2 adsorption–desorption isotherm curve and BJH pore size distribution of pure aerogels and as-prepared aerogel composites are shown in Fig. 3. Both the isotherm curves belong to typical type III; adsorption–desorption isotherm [23], revealing plenty of pores with size more than 5 nm and wide range of pore sizes. But the pore volume and BET surface area of pure aerogels are much higher than that of as-prepared composites (Table S1). This attributes to the introduction of ultrafine quartz fibers, which own negligible pore volume and BET surface area compared to the aerogels. At the same time, since the oriented sheets form greater pores, more pores can not be characterized by the N_2 adsorption–desorption method. From the BJH pore size distribution, the ratio of pores with diameter larger than 20 nm in the pure aerogels is much greater than that in as-prepared aerogel composites. Obviously, a sharp peak at about 4 nm is observed in the BJH pore size distribution of as-prepared aerogel composites, while that of the pure aerogels is almost negligible. These pores attribute to the wrinkles when 2 sheets contact with each other (Fig. 2f, l). The oriented sheets always own more overlap positions compared to the pure aerogels. So the as-prepared aerogel composites show more pores with diameter of 4 nm, which in turn illustrates the orientation of the sheets in as-prepared aerogel composites. The difference of microstructure (Fig. 3c and d) also illustrates that the alignment of sheets is affected by the fibers. Since most of the fibers are stacked parallel to the in-plane orientation, and the suspension flows along the orientation. The sheets tend to align along the in-plane orientation.

Theoretically, the solid thermal conductivity is in direct proportion to the density [24]. So, the introduction of fibers will increase the thermal conductivity, especially the solid thermal conductivity. But, since the alignment of graphene sheets suppresses the contact of graphene sheets, the thermal resistance increases. From Fig. 4, the solid thermal conductivity (since the radiative thermal conductivity is negligible at room temperature, the thermal conductivity at 3 Pa is regard as the solid thermal conductivity) almost does not show any change. As for the thermal conductivity under atmospheric pressure, the as-prepared aerogel composites show higher thermal conductivity. This is mainly due to the increase of gaseous thermal conductivity. The greater pore diameter allows more gas molecules collide with each other, increasing the gaseous thermal conductivity. Meanwhile, since the pore diameter is still relatively small, the gaseous thermal

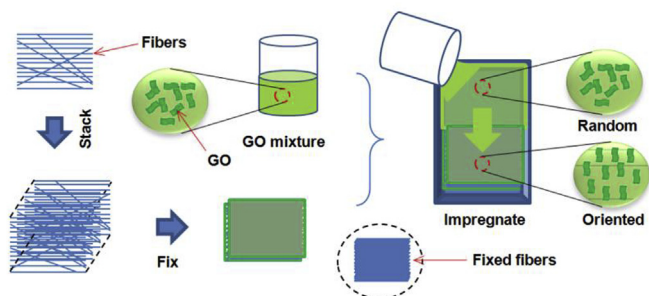


Fig. 1. Schematic illustration of stacking and impregnating process of as-prepared aerogel composites.

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