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Thermoelectric behavior of aerogels based on graphene and multi-walled carbon nanotube nanocomposites

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A B S T R A C T

In this work, we presented that the Seebeck coefficient and electrical conductivity can be increased simultaneously in aerogels based on graphene and multi-walled carbon nanotube (graphene-MWCNT) nanocomposites, and at the same time the thermal conductivity is depressed due to 3D porous skeleton structure. As a result, graphene-MWCNT aerogels possess ultra-low thermal conductivities (~0.056 W m^{-1} K^{-1}) and apparent density (~24 kg m^{-3}), thereafter the figure of merit (*ZT*) of ~0.001 is achieved. Although the ZT value is too low for practical application as a thermoelectric (TE) material, the unique structure in this project provides a potential way to overcome the challenge in bulk semiconductors that increasing electrical conductivity generally leads to decreased Seebeck coefficient and enhanced thermal conductivity.

1. Introduction

Being able to convert waste heat and solar energy directly into useable electricity by TE effect, TE materials have attracted considerable interests devoted to energy research, and the past years have also witnessed their remarkable progress [1–5]. The ability of interconversion between heat and electricity depends on the thermoelectric figure of merit (ZT), which is the most important parameters for the selection of TE materials, $ZT = \alpha^2\sigma T/\kappa$, where α, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Traditionally, TE materials are inorganic semiconductors, such as bismuth, tellurium and lead [6–8]; because of high cost, instability, potential toxicity and scarcity of some elements, the commercially available inorganic TE materials have still limited applications. Polymer and polymer-inorganic TE materials are increasing studied due to low density, low thermal conductivity, and versatile processability [9,10], meanwhile, doping and hybrid are used to increase electrical conductivity of polymers [11–17]. Nevertheless, increasing electrical conductivity of polymers is generally accompanied with a tremendous decrease in the Seebeck coefficient. This tradeoff contributes little rise in the power factor ($\alpha^2\sigma$). As a favour of nanostructure materials with high electrical conductivity [18–21], graphene and carbon nanotube (CNT) have attracted tremendous attention because they have potential applications in TE materials [22–24]. However, because of low Seebeck coefficient and high thermal conductivity [25–29], it is difficult for graphene [30–32] and CNT [33–37] to be used as TE materials without being hybrid with other materials.

In this paper, conducting carbon aerogels [38–40] are considered as a selective type of promising energy-conversion materials on account of their unique properties. Conducting carbon aerogels have highly open-cell foam structure and a tenuous solid skeleton which strongly block phonon transport, resulting in ultra-low thermal conductivity [41]. With a 3D network structure, conducting carbon aerogels can provide multiple paths for electrons transport, leading to electrical conductivity increased [42]. Abundant junctions and interfaces exist in the conducting carbon aerogels, which may affect electron filtering [43], thereafter the electrical conductivity and the Seebeck coefficient can be decoupled and simultaneously enhanced. Except the advantages

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mentioned above, conducting carbon aerogels have an extremely low density (~40 kg m^{-3}) compared to traditional materials, which can provide higher power density in the same condition.

Herein, conducting carbon nanocomposite aerogels consisting of graphene and MWCNT were prepared by the self-assembling during the reduction of graphene oxide (GO) to form a highly cross-linked hydrogel, and MWCNT was well dispersed in GO solution in advance, as shown in Fig. 1. The reason for introducing graphene into CNT is that a unique synergistic effect of one dimensional CNT and two-dimensional graphene sheets has been observed in hybrid materials [44–47], and it is found CNT has bridged the defects for electron transfer as well as increased the layer spacing between graphene sheets [46]. We demonstrate that graphene-MWCNT aerogels have the high porosity, the tenuous 3D solid skeleton and the open-cell foam structure, and the unique structure depresses the thermal conductivity strongly. Moreover, the huge interfaces and junctions in the nanocomposite aerogels have an energy-filtering effect, as shown in the middle of Fig. 1, which results in an enhanced Seebeck coefficient. Thus, we show that the three thermoelectric parameters (α, κ and σ) can be tuned independently in the conducting nanocomposite aerogels, which results in an improvement in the ZT value. Furthermore, this method is simpler to fabricate, low-cost and scalable, and these observations we found may be extended to be a facile and general strategy to prepare nanocomposite TE materials with enhanced thermoelectric properties.

2. Experimental section

2.1. Materials

Natural graphite flakes (40 μm) were provided by Qingdao Ruisheng Company (China), and multi-walled carbon nanotubes (MWCNT, Nanocyl NC7000) were offered by Nanocyl (Belgium), and other chemicals were purchased from Chengdu Kelong Company (China).

2.2. Preparation of graphene oxide

Graphene oxide (GO) was prepared using a modified Hummers method. In the typical experiment, graphite (10 g) with sodium nitrate (5 g) was put into a 1 L flask at 0 °C, and then concentrated H_2SO_4 (230 mL) was added slowly into the flask under stirring for 0.5 h. In this process, the temperature of mixture should be kept under 10 °C. Subsequently 30 g of $KMnO_4$ was added into the flask little by little in 1.5 h to prevent the rapid temperature increase, and the temperature was kept at ~10 °C with continuously being stirred for 2 h. Then, the reaction temperature was increased to 35 ± 3 °C and maintained for 2 h under agitation. After the reaction completing, 460 mL of deionized water was slowly poured into the solution under vigorous stirring with the temperature keeping around 98 °C, and a dark brown suspension was achieved. The suspension should be further treated by adding 150 mL of H_2O_2 (5%) to convert the residual permanganate and MnO_2 into a soluble $MnSO_4$, and then it was diluted to approximately 1.4 L. Upon treatment, the target suspension became bright yellow. The GO aqueous suspension was washed for times using diluted HCl (3%) and deionized water till it was neutral.

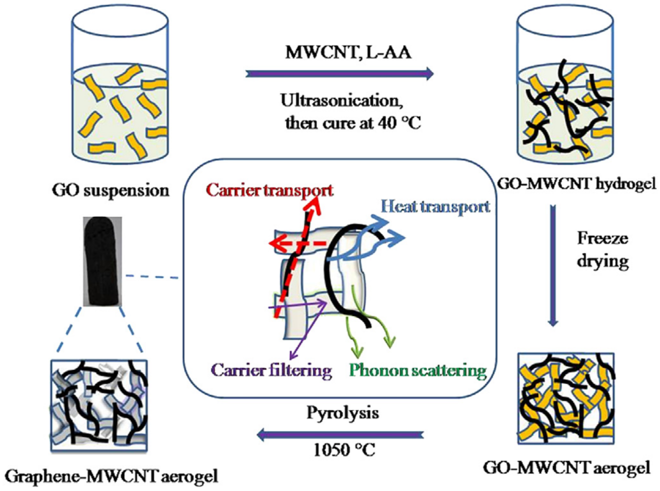

Fig. 1. The synthesis route of graphene-MWCNT aerogels.

2.3. Preparation of nanocomposite aerogels

In a typical procedure as shown in Fig. 1 and, 20 mL 2.0 mg/mL^{-1} GO aqueous solution mixed with different amounts of MWCNT were under ultrasonication for 0.5 h in a glass tube, and the amounts of MWCNT were 0.002 g, 0.006 g, 0.01 g, 0.02 g, 0.03 g, 0.04 g, and 0.05 g, respectively. Thus, the mass ratio between MWCNT and GO was 0.05, 0.15, 0.25, 0.5, 0.75, 1, and 1.25, respectively. Then 0.2 g L-ascorbic acid (L-AA) was added into the glass tube. The mixture was heated up to 40 °C and then left to stand for 24 h to form graphene-MWCNT nanocomposite hydrogel. The hydrogel was purified first in a large amount of distilled water and quenched with liquid nitrogen and then freeze dried for 24 h to obtain the graphene-MWCNT aerogels. The graphene-MWCNT nanocomposite aerogels was pyrolysis at 1050 °C. As a comparison, we also prepared GO aerogel, which was quenched with liquid nitrogen from an aqueous suspension with 1.86 wt % GO and then freeze dried.

3. Characterizations

Atomic force microscopy (AFM, SPA400/SPI4000, Seiko Instruments Inc. Japan) was carried out using a Nanoscope multimode V8 to characterize the thickness and the morphology of GO layers. X-ray diffraction (XRD) patterns of graphite and aerogels were achieved using a Philips X'Pert Graphics & Identify with Ni-filtered CuKa radiation ($k = 0.154$ nm) at a tube current of 30 mA and a generator voltage of 40 kV. Scanning was at a speed of 2.4 °C min^{-1}, from 5 to 50° of 2θ. X-ray photoelectron spectroscopy (XPS) spectra of aerogels were obtained with a EURO EA3000 spectrometer. After correcting the sensitivity factor for each element, the elemental compositions were acquired from peak area ratios. Raman spectra of aerogels were recorded using a LABRAM HR800 confocal micro-Raman spectrometer with a 532 nm ND: YAG laser. The microstructures of aerogels were examined in a scanning electron microscopy (SEM: Quanta250) after coating gold nanoparticles on the samples.

Apparent density of each aerogel was determined using its physical dimensions and weight. The thermal conductivity of aerogels was examined on a transient plane source method with a Hot Disk 2500-OT. The electrical conductivity of aerogels was obtained via a four-probe method using a RTS-8 ohmmeter (Four-probe Technology Company, Guangzhou). The current transmitted through the samples was set at 100 mA during measurement. The Seebeck coefficient was determined by placing the samples between two copper cylinders attached to two Peltier modules, one for cooling and the other for heating. There generated the temperature gradient across the samples and meanwhile induced thermal voltage. The temperature gradient (ΔT) was accurately