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Effect of different sizes of graphene on thermal transport performance of graphene paper

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ABSTRACT

As a two dimensional materials, graphene attracts great attention as heat dissipation material due to its excellent thermal transport property. Herein, three kinds of graphene papers were fabricated with three different thickness graphene nanoplatelets (GNP) via simple vacuum filtration method. The effects of the different size of GNP on the thermal conductivity of graphene papers are investigated systematically. The in-plane thermal conductivity of GNP-7 (the thickness of GNP approximately 7 nm) paper achieves 149.2 $Wm^{-1}K^{-1}$, is about 7 times compared to that of GNP-3 (3 nm) and GNP-5 (5 nm), which indicates that thermal conductivity of graphene film increased with increasing the thickness of GNP. Furthermore, the in-plane thermal conductivity of GNP-7 can increase by 25% and raise up to 187.4 $Wm^{-1}K^{-1}$ after cold-compaction as cold-compaction will further tighten the loose stacked layers, making the paper more anisotropic in heat conduction. The excellent heat conductive properties of the paper are expected to use as efficient heat spreader for thermal management applications.

1. Introduction

Efficient thermal transport and heat removal play a vital role for the long service life and high performance of electronic devices [1–3]. In recent years, lightweight composites with superior thermal transport properties promise great application potential. Graphene, a sp^2-bonded two dimensional material has attracted tremendous attentions since its first discovery in 2004 [4,5]. Now, graphene is regarded as a superstar material because of its outstanding physical and chemical properties, such as high carrier mobility [6], large surface area [7], good mechanical scalability [8] and super thermal conductivity [9,10]. Thus, graphene has a variety of applications in electrical and energy devices, catalysts, sensors, biomedicine, composite materials and solar cells, etc [11–20]. For instance, the in-plane thermal conductivity of graphene has been reported to be 5300 $Wm^{-1}K^{-1}$ at room temperature [9], which is much higher than that of the basal planes of graphite [21–23]. Renteria and co-author [23] reported their results that annealing of the free-standing graphene oxide (GO) films at temperature (1000 °C) increase the in-plane thermal conductivity of the GO films from 3 $Wm^{-1}K^{-1}$ to 61 $Wm^{-1}K^{-1}$. Xiang and co-author [24] reported the thermal conductivity of neat exfoliated graphene nanoplatelets is about 70 $Wm^{-1}K^{-1}$. Tian and co-author [25] reported the thermal diffusivity of all-carbon nanocomposites of graphene oxide and few-layer graphene is up to 80 mm^2/s, which was competitive to those well-known thermally conductive metals. Xiang et al. [26] prepared graphite nanoplatelet paper using exfoliated graphite nanoplatelets by vacuum filtration. The thermal conductivity of the flexible, lightweight paper-like materials was 178 $Wm^{-1}K^{-1}$. Kong et al. [27] prepared flexible graphene–carbon fiber composite paper by depositing graphene oxide into the carbon fiber precursor followed by carbonization. The as-obtained hierarchical graphene/carbon fiber composite paper possessed ultra-high in-plane thermal conductivity of 977 $Wm^{-1}K^{-1}$. Xin et al. [28] reported an approach to fabricate large area freestanding graphene paper by direct deposition of graphene films and water exfoliation from highly hydrophilic substrates. The graphene paper by high temperature annealing displayed superior thermal conductivity (up to 1434 $Wm^{-1}K^{-1}$). Zhang and co-authors [29] proposed a way improved heat spreading performance of graphene based film and the in-plane thermal conductivity reaches up to 1642 $Wm^{-1}K^{-1}$. Shen et al. [30] reported an approach to fabricate large-area GO film by direct evaporation of GO suspension under mild heating, and the in-plane thermal conductivity reaches up to 1100 $Wm^{-1}K^{-1}$.

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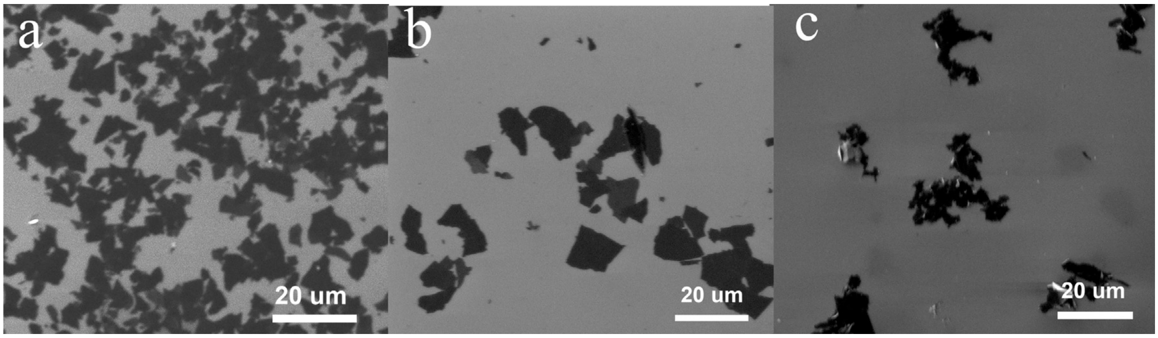

Fig. 1. SEM images of (a) GNP-3, (b) GNP-5 and (c) GNP-7.

Though, many efforts have been focused on preparation the graphene paper to improve the heat transport performance and other properties [31–34]. Few works have done about the effect of the dimensions of graphene on thermal conductivity of graphene paper. The dimensions of graphene, including the number of layers and the lateral size, often show a significant impact on the electrical and mechanical properties of graphene papers and the composites [35–37], rare attentions have been attracted to their effects on thermal conductivity. It is found that the thermal transport in two-dimensional graphene was greatly affected by its size and thickness. Because of the long phonon mean free path, the in-plane thermal conductivity of graphene depends on its length along the heat flow direction with increasing thermal conductivity as the length increases [38].

Herein, we fabricated three kinds of graphene papers via simple vacuum filtration method with the different dimensions of graphene and then the thermal transport properties of graphene papers are investigated. Compared the previous works, we systematically studied the effect of graphene thickness on the thermal conductivity of graphene films, which was not reported previously [39–41]. The effect of the dimensions of graphene on thermal conductivity of graphene paper has great implications for the next generation thermal management applications.

2. Experimental

2.1. Materials

Few-layer graphene nanoplatets (GNP) (Ultraphene^{TM} EX) with a lateral size of 5–10 µm and average thickness of 3 nm (denoted as GNP-3) were purchased from Nitronix Nanotechnology Corporation (Taiwan, China). And few-layer GNP (Ultraphene^{TM} S) with the average size of 10–30 µm and average thickness of 5 nm (denoted as GNP-5) were also supplied by Nitronix Nanotechnology Corporation (Taiwan, China). Morsh graphene nanoplatets with a diameter of 7–25 µm and average thickness of 7 nm (denoted as GNP-7) was produced by Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences (China). All the chemicals were of analytical reagent grade and used without further purification.

2.2. Preparation of GNP paper

Firstly, 25 g GNP-3 was dispersed in 500 ml ethanol and bathed for 15 min under constant stirring. Secondly, it was washed by filtering via the polyether sulfone (PES) (0.22 µm, 50 mm) filter paper and repeated three times. Finally, it was re-dispersed in ethanol. A PES membrane (0.22 µm, 50 mm) was used for paper making through vacuum filtration. A controlled multi-filtration process (5 ml at a time) was used to minimize the disordered layering structure caused by water flow. Forty milliliters of the suspension was filtered to make one paper. The paper was then suction dried for 3 h and then put into a vacuum oven and dried at 200 °C for several hours before peeling the GNP-3 paper off the membrane. Then some GNP-3 film were chosen to pressed with a flat vulcanizer (10 Mpa 10 min) to remove air bubbles and make the sample denser. GNP-5 paper and GNP-7 paper were also prepared via the same method.

2.3. Characterization

The sample surface of three kinds of graphene were examined with a Quanta FEG250 field emission scanning electron microscopy (FE-SEM, FEI, USA) at an acceleration voltage of 20 kV. Samples were broken and the fractured surface were coated with a thin layer of gold powder to avoid the accumulation of charge and improve the conductivity. Transmission electron microscopy was take by JEM-2100 (TEM, Jeol, Japan) with an acceleration voltage of 200 kV. The samples were dispersed in ethanol using ultrasonic mixing for 15 min and some pieces were collected on 200 mesh carbon coated copper grids. Atomic force microscope (AFM) measurement was conducted on a Multimode SPM from Digital Instruments with NanoscopeIa controller. X-ray photoelectron spectroscopy (XPS) was carried out with Kratos AXIS ULTR DLD spectrometer. Raman spectra were obtained by Raman spectrometer with laser wavelength of 532 nm (Renishaw plc, Wotton-under-Edge, UK). Thermal conductivities of the composites were determined with laser flash apparatus (LFA, NETZSCH 447, Germany) at room temperature. The sample size for in-plane and out-of plane measurement was round with a diameter of 25.4 mm and 12.7 mm, respectively. The IR-photos were captured by infrared camera (Fluke, Ti400, U.S.A.).

3. Results and discussion

3.1. Characterizations of GNPs

The microscopic morphology of three types exfoliated graphene nanoplatelets are shown in Fig. 1. Fig. 1**(a)** shows that the SEM image of GNP-3 with a flaky sheet structure in shape and the average platelet size is around 15 µm. The SEM image of GNP-5 is shown in Fig. 1**(b)**. The average particle dimension is close to 22 µm. For comparison, we can concluded from Fig. 1**(a)** and **(b)** that the size dimension of GNP-3 is smaller than GNP-5 under the same magnification. From Fig. 1**(c)**, we can find GNP-7 has the similar dimension with the GNP-5 and the average particle dimension of GNP-7 is close to 20 µm.

Fig. 2**(a–c)** shows the TEM images of GNP-3, GNP-5 and GNP-7. From Fig. 2**(a–c)**, the edge of the graphene sheet appeared to be rolled up. It was obviously shown that the transparency of GNP decreased with the increasing thickness of graphene sheets. Hence, further demonstrates data are showed in AFM. The graphene nanosheets were picked up from the solution with a silicon substrate and then dried in air. Fig. 2**(d–f)** shows typical AFM images and the height profiles of graphene platelets dispersed in ethanol. The average thickness of GNP-3 was determined to be about 3.65 nm from the AFM image in Fig. 2**(d)**, which is consistent with Liu's work [42]. The average thickness of GNP-