SIO GRAFEN

Highly thermally conductive graphene/polymer composites

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Abstract

Highly thermally conductive materials have attracted great interest in both industry and academia. In this project we have developed a scalable fabrication technique to prepare high-loading graphene/polymer composite (containing more than 50% of graphene by weight) with thermal conductivity around 100 W m^{-1} K^{-1}. In addition, generic knowledge is obtained about the effects of different processing conditions on the final composite conductivity. The fabrication technique and the generic knowledge are anticipated to facilitate the research and development in the field of graphene/polymer composite-based thermal management.

Contents:

1. Introduction

Thermal management is becoming more and more important in a wide variety of household and industrial applications, such as computers, electronics, high-power lasers, lighting equipment, automotive equipment, communication devices and energy storage devices. For example, with the continuously increasing level of integration, miniaturization and hence power density of electronic devices and equipment, it is crucially important to quickly dissipate the generated heat to improve the reliability, efficiency, and lifetime of the systems [1]. High-rate batteries also generate enormous heat during the charging/discharging process and require effective separators to quickly dissipate the heat. Thermal energy storage technologies need to increase the thermal conductivity of the heat storage materials to ensure fast charging and discharging processes. Thereby, materials of high thermal conductivity and excellent integrability with various devices and systems are highly desired.

Due to its super-high thermal conductivity (up to 5000 W m^{-1} K^{-1} [2]), the material graphene is receiving significant interest from both academia and industry. The present efforts in pushing graphene towards industrial applications can be divided into two directions. One is high-end applications which rely on pure free-standing graphene films with thermal conductivity up to 1500-3200 W m^{-1} K^{-1} [3,4], approaching the property of high-quality individual graphene flakes. The fabrication, however, usually necessitates high-temperature (>2000 ^{o}C) annealing process, which restricts the applicability and integrability of such high-performance graphene films.

The other direction is the low-end applications based on the graphene-polymer composites. In general, polymers possess multiple advantages, including lightweight, low cost, excellent processability and good corrosion resistance, but suffer from low thermal conductivity < 0.5 W m^{-1} K^{-1} [1]. Therefore, the combination between graphene and polymers have been anticipated as an ideal solution to a new kind of thermally conductive materials with wide applicability. Recent reviews [1, 5] indicate that in the past decade thermally conductive graphene/polymer composites have been extensively studied, ranging from mechanism to fabrication processing to applications. Most composites have attained significantly improved thermal conductivity ranging from 1 to 10 W m^{-1} K^{-1} (as compared with pure polymers). The graphene-polymer composites are often fabricated through three methods: solution blending, melt mixing and in-situ polymerization [1]. Solution blending produces homogeneous dispersion at low graphene loading while high loading of graphene causes sediment shortly after processing. Melt mixing produces high graphene loading but the high viscosity of melt polymer makes it difficult to disperse graphene uniformly. In-situ polymerization adds insulating coating to graphene flakes and results in low conductivity. All these make it challenging to attain higher conductivity >10 W m^{-1} K^{-1}. It is widely accepted that processing conditions evidently affects the composites' conductivity. In general, large graphene flakes, intact flake surface, high graphene loading (concentration of graphene with respect to dry materials), aligned flakes, additional fillers (e.g., metal nanoparticles, boron nitride), and uniform dispersion are all favored factors for the conductivity improvement [1, 5]. It has also been demonstrated that high graphene loading around 20% is a scalable and feasible method to increase the conductivity beyond 10 W m^{-1} K^{-1} [6], but further higher loading may cause severe aggregation of graphene flakes and instead degrade the conductivity.

In this project, we have developed a scalable technique to prepare high-loading graphene/polymer composite with thermal conductivity about 100 W m^{-1} K^{-1}. The fabrication involves medium-temperature (250-400 ^{o}C) annealing process, and thereby fills well the gap between the present high-end and low-end techniques for graphene-based thermally conductive materials to provide complementary applicability and integrability. In addition, systematic studies have been conducted to acquire generic knowledge about the effects of various processing conditions on the conductivity graphene/polymer composites.

2. Experimental details

In this project, the graphene/polymer composites were generally prepared through casting of graphene inks with compatible thermal treatment. Electrical and thermal conductivity was characterized to investigate the effects of different processing conditions.

2.1 Ink formulation

The graphene inks were prepared through a solvent exchange process [7]. First, graphene was exfoliated from graphite foil through an electrochemical exfoliation process [8] followed by dispersing in an organic solvent, dimethylformamide (DMF) to obtain ~2 mg/mL dispersion. Then, graphene was separated from DMF through ultracentrifugation of dispersion at 10,000 rpm for 30 mins to remove the DMF supernatant. Finally, the graphene was re-dispersed into a target polymer/solvent solution through sonication or magnetic stirring to obtain the graphene/polymer inks, that is to say, the solvent has been exchanged from the toxic DMF to the final solvent. In our technique, the polymer can be ethyl cellulose (EC) or polyvinylpyrrolidone (PVP), while the solvent is ethanol, water or mixture of ethanol and butyl acetate. This solvent exchange technique is superior to the solution blending method. On the one hand, throughout the fabrication, graphene is in liquid phase which greatly increases its dispersability. On the other hand, both the graphene concentration and loading (the mass ratio of graphene to polymer) can be well adjusted through tailoring the concentration and volume of the target polymer/solvent solution. As a result, at high graphene concentration around 100 mg/mL, stable and viscos graphene/polymer composite inks can be obtained at high graphene loading of 90%. The mechanism of the ink stability is likely similar to that of hydrogels or organogels, but further studies are needed for confirmation.

2.2 Film casting

2.2.1 Direct drop casting

The viscos graphene inks have great processability, which allows us to readily fabricate uniform patterns simply through drop casting. Figure 1 shows some examples of the drop-cast graphene/polymer films where the profilometry (Figure 1b) indicate good thickness uniformity.

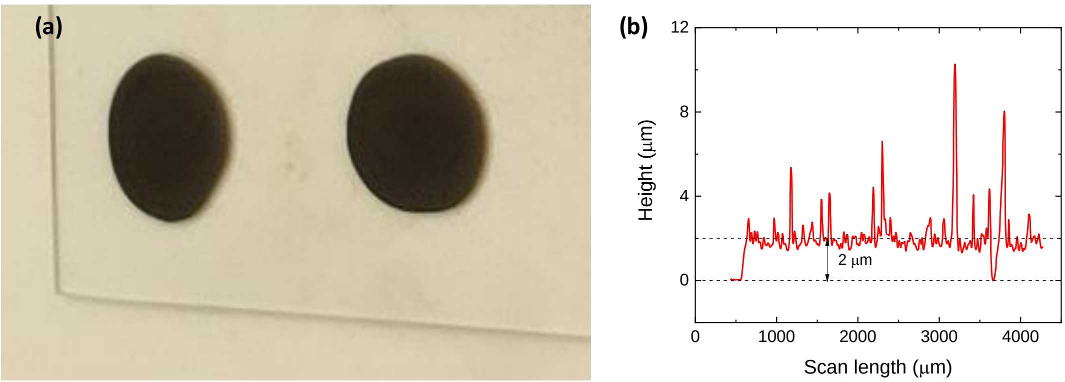
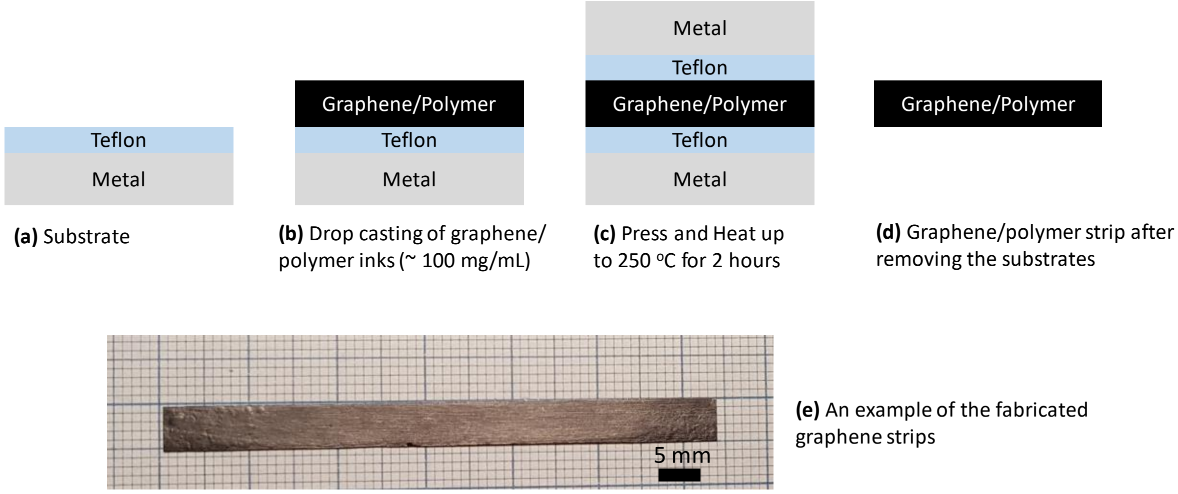


Figure 1. *Drop-cast graphene films. (a) Photograph of two drop-cast graphene/EC composite patterns. (b) Profile of a drop-cast graphene/EC composite pattern.*

1.1.1 Free-standing thick films



(a) Substrate

(b) Drop casting of graphene/ polymer inks (~ 100 mg/mL)

(c) Press and Heat up to 250 °C for 2 hours

(d) Graphene/polymer strip after removing the substrates

(e) An example of the fabricated graphene strips

Figure 2. *(a-d) Schematic of fabrication procedure of thick free-standing graphene films based on drop casting of graphene inks. (e) is the photograph of a final high-loading graphene/polymer strip.*

Benefitting from the good thickness uniformity of drop-cast graphene/polymer composite films, we have also developed a process to fabricate free-standing thick graphene films (up to 200 microns thick) to facilitate thermal conductivity measurement. As illustrated in Figure 2, on top a Teflon-coated metal substrate (Figure 2a), high-concentration (viscos) graphene inks were drop cast (Figure 2b). After drying, the graphene films were pressed with another Teflon-coated metal substrate and heated up to 250 °C to increase the flake contacts (Figure 2c). Finally, the two metal substrates were taken apart to obtain thick free-standing graphene films (Figure 2d,e).

2.3 Conductivity characterization

Thermal conductivity and/or electrical resistivity was characterized for the graphene/ polymer composite films with the techniques detailed below.

2.3.1 Electrical resistivity

For directly drop-cast graphene/polymer films on substrates, the four-point probe technique was used to measure the sheet resistance R_s and a profilometer was used to measure the thickness t (as in Figure 1b). The electrical resistivity ρ is given by

$$\rho = R_s \cdot t. \qquad (1)$$

For free-standing graphene/polymer films, both resistance and dimension (length, width and thickness) were directly measured to calculate the electrical resistivity.

2.3.2 Thermal conductivity

To measure the thermal conductivity for the free-standing graphene/polymer films, a home-made apparatus was set up according to a self-heating method [9], as illustrated in Figure 3.

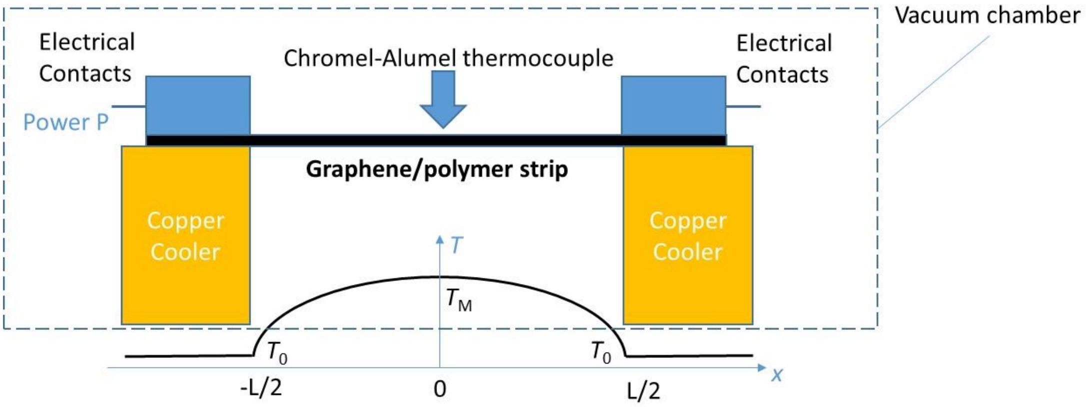


Figure 3. *Schematic of the apparatus for thermal conductivity measurements based on a self-heating technique [9]. The bottom illustrates the temperature distribution on the free-standing graphene/polymer strip during self-heating.*

In brief, the graphene/polymer samples were prepared in long strip shape (as in Figure 2d) with length L, width w and thickness t, and suspended across two copper coolers. The copper coolers and electrical contacts (silver paste) are both efficient heat sinks, which maintain the temperature of the ends of the graphene strip at T_0. When the temperature rise is not high (< 40 °C in this project), the graphene sample was almost uniformly heated by electricity with total power P [9]. When the length of the graphene strip is much longer than its width and thickness, the thermal conduction can be viewed as one-dimensional and the thermal conductivity κ of the graphene/polymer can be calculated as [9]

$$\kappa = \frac{PL}{8wt(T_M - T_0)}, \tag{2}$$

where T_M is the temperature at the middle of the strip.

In this project, the sample length to width ratio was kept as 10:1. The whole setup was installed in a vacuum chamber at a pressure of 10^{-5} Torr. T_M was measured by a Chromel-Alumel thermocouple (diameter is 0.075 mm) with differential connection.

The system was calibrated by measuring two reference samples: a lead sheet and a commercial Panasonic Pyrolytic Graphite Sheet PGS 700, with known thermal conductivity of 34.7 and 700 W m^{-1} K^{-1}, respectively. Our measured values are 38 and 560 W m^{-1} K^{-1}, with a deviation of less than 20% from the expected values.

3. Results and Discussion

In order to obtain the generic knowledge about the optimal processing conditions for fabricating high-conductivity graphene/polymer composites, we conducted systematic studies on the effects of various processing conditions. Because the sample preparation for thermal conductivity measurement requires a large amount of graphene materials, to simplify the project, we started with characterizing electrical resistivity of directly drop-cast graphene/EC composite on glass slides. Although the electrical conductivity is not always in line with thermal conductivity, the influence of the processing parameters on the two conductivities is typically similar to each other. The most critical processing parameters for the electrical resistivity were taken into account during sample preparation for the final thermal conductivity measurement.

3.1 Directly drop-cast graphene/polymer composites

With the electrical resistivity characterization of directly drop-cast graphene/EC composites, we studied the effects on five processing parameters. They are graphene concentration in the inks, stirring time and sonication time of the inks before drop casting, annealing temperature and time after drop casting. In this section, each of the reported data is based on the statistics over 5 samples. In order to obtain high-loading graphene in the final composites, the mass ratio of graphene to polymer (EC) is 2.5:1, corresponding to the graphene loading of 71.4% (with respect to dry materials). The ink solvent is the mixture of ethanol and butyl acetate with volume ratio of 4:1.

3.1.1 Graphene concentration

We first investigated the effects of graphene concentration in the inks on the electrical resistivity of the drop-cast graphene/polymer films. In this study, the other four parameters were kept constant, i.e., the inks were used for drop casting shortly after preparation without any stirring or sonication, and after drop casting, the samples are annealed at 100 ^{o}C for half an hour. The results are plotted in Figure 4.

From Figure 4, one can see that the resistivity decreases with the graphene concentration. However, such dependence may not be straightforward. Low graphene concentration gives rise to high resistivity, but also large variation of resistivity and thinner films. The latter may imply that a low graphene concentration makes the drop-cast graphene/polymer films below percolation threshold, which significantly increases the resistivity and variation. Therefore, in order for high-conductivity graphene/polymer composites, inks of high graphene concentration are favored due to large film thickness and small sample-to-sample deviation.

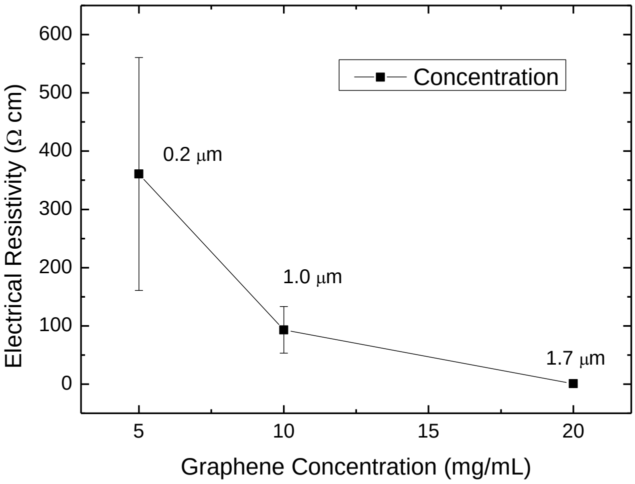


Figure 4. *Dependence of electrical resistivity of the directly drop-cast graphene/EC composites on the graphene concentration in the inks. The numbers at the data points indicate the film thickness. For some data points, the error bar is smaller than the symbol.*

3.1.2 Stirring time and sonication time

In this section, all the graphene/polymer composite films were prepared with the graphene inks of concentration of 20 mg/mL, and after drop casting, the samples are annealed at 100 ^{o}C for half an hour. To study the effects of stirring time, before drop casting, the inks were stirred by magnetic stirring at 500 rpm for different times.

For the study of sonication time, the inks were sonicated at bath sonication (at a power of 80 W) for different times. The results are plotted in Figure 5.

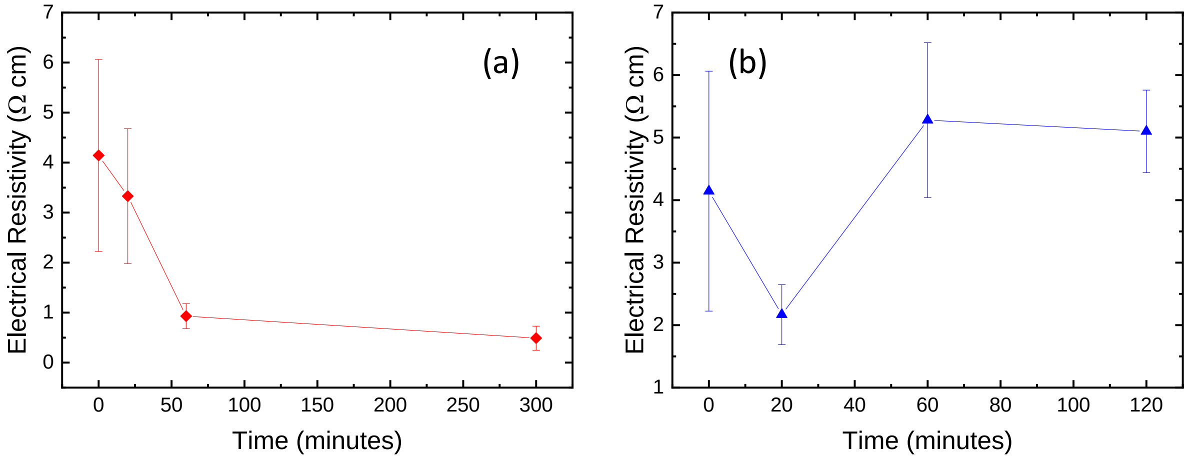


Figure 5. *Dependence of electrical resistivity of the directly drop-cast graphene/EC composites on (a) the stirring time and (b) sonication time of the inks before drop casting.*

In Figure 5(a), it is clear that the resistivity monotonically decreases with stirring time, whereas in Figure 5(b), the electrical resistivity decreases at short sonication time (< 20 minutes) but increases at longer sonication time. The reason could be during stirring, the inks become more and more uniform which thereby improve the uniformity of graphene/polymer films so as to decrease the resistivity. But one should note that after being stirred for around 1 hour, the ink uniformity is maximized so that further longer stirring time will not decrease the resistivity significantly. Similarly, during short-time sonication, the graphene inks also become uniform and the resistivity decreases accordingly. However, long-time sonication could likely break down the graphene flakes into smaller ones, which on the contrary will increase the resistivity. Therefore, for high-conductivity graphene/polymer films, stirring with long enough time is preferred for better ink uniformity. If sonication is used to increase ink uniformity, the side effects of the breakdown of graphene flakes should be considered.

3.1.3 Annealing temperature and annealing time

In this section, the effects of annealing temperature and annealing time are investigated. All the graphene/polymer composite films were prepared with the graphene inks of concentration of 20 mg/mL without any stirring or sonication. The results are plotted in Figure 6.

At low annealing temperature of 50 ^{o}C as in Figure 6(a), the resistivity decreases with increasing annealing time. In contrast, at high annealing temperature of 250 ^{o}C as in Figure 6(b), the resistivity does not evidently change with the annealing time when it is longer than 0.5 hour. Therefore, low temperature and long time, and high temperature and short time are both effective ways for annealing to obtain high conductivity. However, it is temperature that predominates the annealing process. As shown in Figure 6(c), the conductivity increase (or resistivity decrease) due to longer annealing time is less than one order of magnitude, whereas when the annealing temperature increases from 50 ^{o}C to 250 ^{o}C, the conductivity increases about four orders of magnitude. As a matter of fact, the annealing temperature is the most predominating factor throughout the overall fabrication process because no other factors (graphene concentration, stirring time and sonication time) could generate comparable effects.

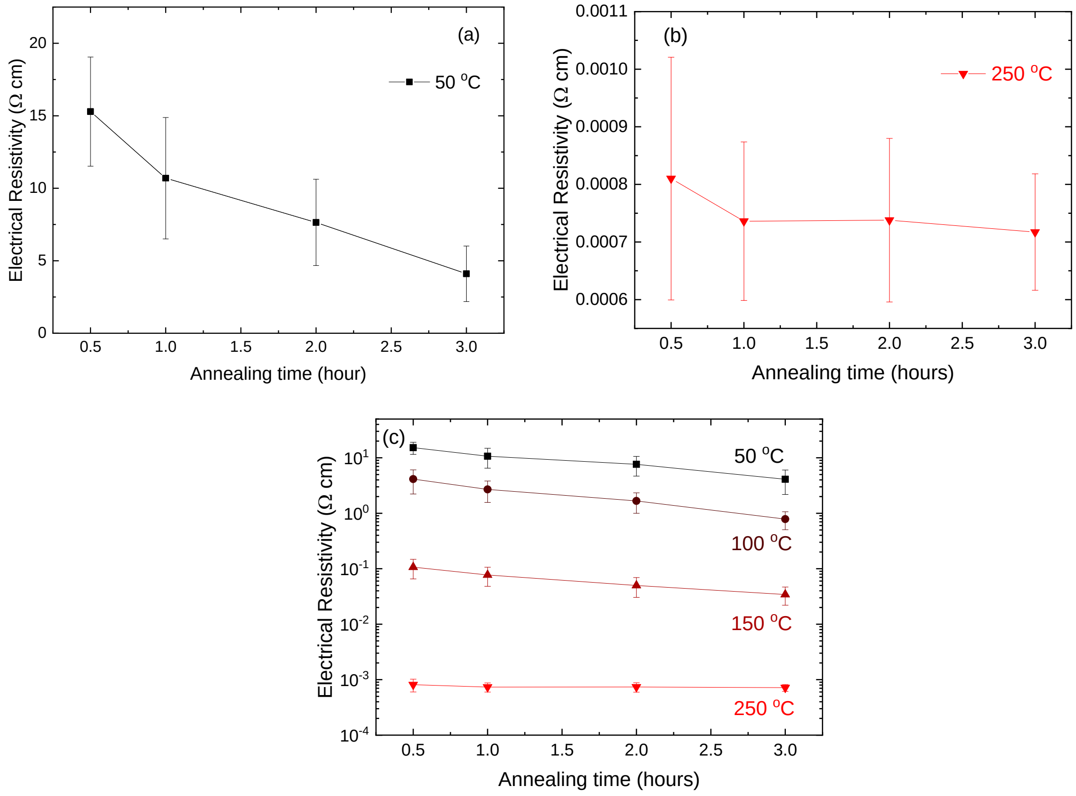


Figure 6. *Dependence of electrical resistivity of the directly drop-cast graphene/EC composites on the annealing time at (a) 50 ^{o}C, (b) 250 ^{o}C and (c) a range of temperatures.*

3.2 Free-standing graphene/polymer composite films

In this section we prepared free-standing graphene/polymer composite strips for characterization of thermal conductivity. Based on the generic knowledge obtained in Section 3.1 about the effects of processing conditions, the graphene/polymer strips were prepared with high-concentration (~ 100 mg/mL) graphene inks. Before drop-casting the inks were stirred for a long time, and after the ink dried, the samples were pressed by two Teflon-coated metal plates and annealed at 250 ^{o}C for 2 hours. After taking away the metal plates, the "as-prepared" free-standing strips were characterized with the self-heating technique for thermal conductivity measurement. The results are listed in Table 1. In order to further improve the thermal conductivity, the strips were pressed in-between two BN plates and heated to > 375 ^{o}C for 1 hour. The properties of these "post-treated" samples are also listed in Table 1.

Table 1. Conductivity characterization of free-standing graphene/polymer composites. In the table, t, ρ, and κ stand for graphene/polymer strip thickness, electrical resistivity and thermal conductivity, respectively. Gra, PVP and EC mean graphene, polyvinylpyrrolidone and ethyl cellulose, respectively. The graphene:polymer ratio is the mass ratio.

Sample (ink solvent)	**As prepared**			**Post treated**		
	t (μm)	**ρ (mΩ cm)**	**κ (W m^{-1} K^{-1})**	**t (μm)**	**ρ (mΩ cm)**	**κ (W m^{-1} K^{-1})**
Gra:PVP=5:1 (water)	198	2.8	80	175	2.5	103
Gra:PVP=10:1 (water)	100	1.8	65	70	1.2	100
Gra:EC=5:1 (Ethanol)	80	2.1	85	75	1.6	115
Gra:EC=1:1 (Ethanol)				128	9.9	67

From Table 1, it is clear that high-loading (>80%, the first three samples in Table 1) graphene/polymer strips have been successfully fabricated and the as-prepared samples have attained high thermal conductivity of 65-85 W m^{-1} K^{-1}. With further post treatment at higher temperature (note the post treatment may significantly degrade the properties of polymer, especially EC), the thermal conductivity can increase to be over 100 W m^{-1} K^{-1}. The samples, graphene/PVP (5:1) and graphene/EC (5:1), attain very similar thermal conductivity, implying the thermal conductivity of the composites is not sensitive to the included polymers. Surprisingly, although the graphene/PVP (10:1) composite has higher graphene loading, its thermal conductivity is lower than the sample graphene/PVP (5:1). The reason could be too high graphene loading in the composite graphene/PVP (10:1) may induce significant aggregation and reduce the film uniformity, which cause degradation in thermal conductivity. On the other hand, the too low graphene loading in the composite Graphene/EC (1:1) result in low thermal conductivity so that the value of the as-prepared sample can hardly be measured by our self-heating setup. A post treatment at high temperature of 375 ^{o}C, which burns out a considerable amount of polymer, lead to a thermal conductivity of 67 W m^{-1} K^{-1}.

Finally, it is worthy of emphasizing that the high-loading graphene/polymer composites developed in this project have attained thermal conductivity (~ 100 W m^{-1} K^{-1}), which lies in between that of the present low-loading graphene/polymer composite (< 10 W m^{-1} K^{-1}) and the high-end free-standing graphene films (1500-3000 W m^{-1} K^{-1}). And meanwhile, only medium temperature (200-400 ^{o}C) is needed. These features may bring complementary applicability to the present applications of graphene/polymer and pure graphene films. For example, in another project also supported by SIO Grafen, we used the high-loading graphene composites as an effective coatings on thinned aluminum substrates to obtain similar thermal performance to the original aluminum substrates while reduce the overall weight. That is to say, the high-loading graphene/polymer composites could provide an effective lightweight solution to the present aluminum-based thermal management industry.

4. Conclusion

In summary, in this project we have developed a scalable fabrication technique based on a solvent exchange process to prepare high-loading (> 50% concentration by weight) graphene/polymer composite inks which enable easy fabrication of graphene/polymer composite coatings and films simply through drop casting. In addition, generic knowledge is obtained about the effects of different processing conditions on the final composite conductivity: High-concentration graphene/polymer composite inks have better processability and facilitate the production of thick graphene/polymer films surpassing percolation threshold so as to obtain high conductivity. Longer stirring time and relatively shorter sonication time are preferred for higher conductivity. Higher annealing temperature significantly increases the conductivity, while the effect of annealing time is limited. In particular, the annealing temperature predominates all the processing parameters because the conductivity could increase by four orders of magnitude when the temperature increases from 50 ^{o}C to 250 ^{o}C. Finally, it has been demonstrated that high-loading graphene/polymer composites can have high thermal conductivity around 100 W m^{-1} K^{-1} with weak dependence on the ink composition or polymer type. This value is significantly superior to most of the reported performance of less than 10 W m^{-1} K^{-1} for low-loading graphene/polymer composites in the publications to date. We hope our fabrication technique and the obtained generic knowledge are useful for the research and development in the field of graphene/polymer composite-based thermal management.

5. Acknowledgement

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