Enhancement of electrical and thermal properties of graphene by aligned carbon nanotubes

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Abstract
In order to explore the composite effects of graphene (GR) and carbon nanotubes (CNTs), GR/CNTs aerogels and GR/CNTs coatings were fabricated. Aligned carbon nanotubes (ACNTs) and twining carbon nanotubes (TCNTs) were comparatively examined by integrating them with graphene, which has seldom been studied in detail. Freeze drying was newly adopted to retain the liquid distribution in GR/CNTs mixture. Fourier Transform Infrared Spectroscopy (FTIR) analysis demonstrated that OH group and carboxylic acid groups were effectively induced onto CNTs via chemical modification. Scanning electron microscopy (SEM) showed that ACNTs achieved better dispersion and homogeneity in graphene than TCNTs. GR/CNTs hybrid composite with various loading of ACNTs or TCNTs were examined by electrical/thermal conductivity tests and practically evaluated for thermal management in LEDs. Results revealed that the electrical and thermal properties of graphene can be dramatically enhanced by the proper addition of ACNTs due to the formation of effective conductive bridges. The GR/ACNTs aerogel with 10 wt% ACNTs attained a high electrical conductivity of $2.08 \times 10^4 \, \text{S} \, \text{m}^{-1}$, elevated to $2.76 \times 10^4 \, \text{S} \, \text{m}^{-1}$ after annealing treatment. The eco-friendly and low-cost GR/ACNTs coating with 10 wt% ACNTs prominently reduced the operating temperature of LEDs by 8.6 °C, acting as potential thermal management materials in practical applications.

1. Introduction
Carbon nanotubes (CNTs) and graphene (GR) have received much attention due to their unique structure and outstanding properties such as superior electrical and thermal conductivities [1–8]. The synergistic effects of electrical and thermal properties have been pursued by combinations of One-dimensional CNTs and two-dimensional graphene [9–13]. There are many potential applications in various fields based on these synergistic effects, such as GR/CNTs hybrid aerogels [14, 15] and GR/CNTs hybrid materials for thermal management [16, 17].

Graphene aerogels (GAs) and graphene hydrogels have been frequently studied as promising materials in many fields [18–21], in which the electrical properties often play a significant role. Incorporating CNTs into the GAs could enhance the electrical conductivity, since CNTs can provide more channels for efficient electron transfer between graphene sheets. It was reported that the addition of CNTs enhanced the electrical conductivity up to 0.56 S m$^{-1}$, i.e. 2.8 times compared to the pure Gas [22].

Nowadays, there is an increasing demand to overcome the heat dissipation problem of high-power LEDs. Graphene-based composites has been intensively explored as thermal management materials for LEDs [23–25]. However, high-quality & low-cost products which could be commercially available still need to be developed.

There are aligned carbon nanotubes (ACNTs) and twining carbon nanotubes (TCNTs) distinguished by the order degree of CNTs. ACNTs have the advantage of high order degree, good controllability, and easy manipulation [26], showing excellent electrical and thermal properties [27–30]. The specific capacity of ACNT
arrays was 350 mAh g\(^{-1}\) after 50 cycles in Li-battery, while the battery with the TCNTs achieved 197 mAh g\(^{-1}\) only\(^{[30]}\). The cooling efficiency of multilayer ACNT films could be about 13.3\% higher than pure copper\(^{[31]}\). The heat dissipation efficiency of the flexible aluminum-ACNTs composites was higher than that of aluminum foil, copper sheet, and graphite sheet by up to 56\%, 40\%, and 20\%, respectively\(^{[32]}\).

To the best of our knowledge, the integrating effect between graphene and ACNTs or TCNTs has seldom been studied in detail. Here we report on the impact of different amounts of ACNTs or TCNTs on the electrical and thermal properties of graphene. Freeze drying was novelty adopted to retain the liquid distribution in GR/CNTs mixture. GR/CNTs hybrid aerogels were fabricated, investigating the electrical conductivity and the dispersion state of hybrid particles. Eco-friendly aqueous GR/CNTs hybrid coatings of low cost were fabricated for LED heat sinks, exploring their thermal conductivity and thermal management.

2. Experimental

2.1. Materials

Water-based graphene paste was provided by SuperC Technology Ltd, China. The weight ratio of GR: water: dispersant was about 2.5:96.5:1 in the paste.

Twining MWCNTs were purchased from Timesnano, China, with a diameter ranging from 10 to 20 nm and a length ranging from 10 to 30 μm.

Sulfuric acid(H\(_2\)SO\(_4\)), nitric acid(HNO\(_3\)): analytical grade, Aladdin; defoamer BYK-028: analytical grade, BYK\(_{\text{c}}\); leveling agent BYK-378: analytical grade, BYK; styrene-acrylic latex : analytical grade, DongLian Ltd, China, were used.

2.2. Preparation of CNTs suspension

ACNTs were synthesized by vacuum chemical vapor deposition according to Chen’s and Li’s work\(^{[33, 34]}\), growing on an Al foil with an average diameter of 15 nm and a height of about 20 μm. The Al foil was etched by H\(_2\)SO\(_4\) solution to separate ACNTs from it, which then collected and washed.

The purchased TCNTs and self-made ACNTs were purified and functionalized using H\(_2\)SO\(_4\) and HNO\(_3\). They were dispersed in an acid solution consisting of 3:1 concentrated H\(_2\)SO\(_4\)/HNO\(_3\) mixture and were refluxed for 24 h at 80 °C. The solution was filtered with distilled water until the pH reached 6–7, and then CNTs were collected and dispersed in distilled water to obtain an aqueous CNTs suspension with the concentration of 2.5 wt%.

2.3. Preparation of GR/CNTs aerogel

The fabrication process of GR/CNTs aerogel is shown in figure 1(a). GR paste and CNTs suspension were mixed in a specific ratio and bead milled for one hour to obtain a homogenous GR/CNTs slurry. CNTs% (based on the weight of graphene) was selected to be 5 wt%, 10 wt% and 15 wt%. The slurries were freeze dried under −60 °C and at 1 mbar pressure to obtain aerogels. Graphene aerogel without CNTs was also produced for comparison. Tablets with a diameter of 2 cm were made of the aerogels by powder compressing machine (YP-40T). Some tablets were annealed in argon atmosphere at 800 °C and 1000 °C for 2 h.

2.4. Preparation of GR/CNTs coating

The fabrication process of GR/CNTs coating is shown in figure 1(b). GR/CNTs slurry was fabricated as described above, then it was mixed with 40 vol% styrene acrylic emulsion, 0.1 wt% defoamer BYK-028 and 0.05 wt% leveling agent BYK-378 to prepare the GR/CNTs coating. Styrene acrylic emulsion is very cheap and environmentally-friendly as compared to other coating materials. Al-based heat sinks were coated with the GR/CNTs coating to test the thermal management for LED.

2.5. Characterization

Scanning electron microscopy (SEM, Zeiss Sigma 500, Germany) was conducted to examine the dispersion of hybrid particles in the GR/CNTs aerogel.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out with Bruker TENSOR II (Germany) in the range of 400–4000 cm\(^{-1}\).

Electrical conductivity measurements of the GR/CNTs tablets were carried out in a four-probe resistivity tester (RTS-9, Guangzhou 4-probe technology Co., Ltd China) at room temperature.

The thermal conductivity of GR/CNTs coating was determined in a thermal conductivity analyzer (Hot Disk TPS 2500, Sweden) using transient plate heat source method referred to ISO22007-2 at room temperature. Al-based heat sinks with and without the coating were compared taking into account the heat dissipation results.
for 50W-power LEDs, by analyzing the steady temperature of LEDs obtained by infrared radiation thermometer (Fluke 59E+) after 2-hour lightening.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy is one of the most important tools to investigate the surface modification of carbon allotropes. Figure 2 shows the FT-IR spectra of ACNT, TCNT and GR. Typical O–H stretching vibrations (3420 cm$^{-1}$) were detected in ACNT, TCNT and GR, attributed to the oxidation during the purification process [35]. The peak at 1638 cm$^{-1}$, 1383 cm$^{-1}$, and 1117 cm$^{-1}$ represents the stretching vibration of C=O, and the non-symmetric stretching vibration of C–O–C, respectively [36]. These results demonstrate that OH group and carboxylic acid groups were effectively induced via chemical modification, which could contribute to the uniform dispersion of CNTs and GR in aqueous solution.

3.2. Scanning electron microscope (SEM)

The dispersion and compatibility of GR and CNTs in the aerogels are obtained by Scanning Electron Microscope (figures 3(c)–(f) for GR/ACNTs and h-j for GR/TCNTs). Freeze drying helped to retain the original shape and distribution state of the materials in aqueous solution using fast cooling rate, so the dispersion of GR/CNTs mixture in the liquid phase could be investigated from the SEM images of the freeze-dried aerogels. It can be observed that ACNTs shows better dispersion and homogeneity in graphene than TCNTs.

The image of GR aerogel without CNTs in figure 3(a) reveals the multilayered, wrinkled and paper-like structure of graphene. The SEM image of self-produced ACNTs (figure 3(b)), shows that the carbon nanotubes with an average diameter of 15 nm and a height of about 20 μm are highly aligned and seldom tangled. In contrast, the bought CNTs with a diameter ranging from 10 to 20 nm and a length ranging from 10 to 30 μm are twisted together and randomly oriented (figure 3(g)).

The morphology of GR integrated with different amount of ACNTs is shown in figures 3(c)–(f). No agglomeration of CNTs at loading of 5 wt% (figure 3(c)) and 10 wt% (figures 3(d), (e)) is observed. ACNTs are embedded into GR sheet uniformly on the top view (figure 3(d)), and penetrated into the interlayers of GR to
construct a hierarchical GR/CNTs architecture on the cross section view (figure 3(e)). These tubes act as bridges for connecting different layers [37]. When the loading of ACNTs increased to 15 wt%, CNTs are agglomerated covering the GR sheet (figure 3(f)).

As for TCNTs combined with GR, a slight agglomeration of CNTs is observed at CNTs loading of 5 wt% (figures 3(h)), which, however, is exacerbated as the CNTs loading raised from 10 wt% (figure 3(i)) to 15 wt% (figure 3(j)). The latter implies the higher difficulty of TCNTs, as compared to ACNTs, to uniform dispersed into graphene.

Figure 2. FTIR of (a) ACNT, (b) TCNT, (c) GR.
3.3. Electrical properties

The electrical properties of the GR/CNTs composites were determined by means of four-electrode probe method. Figure 4(a) displays the electrical conductivity of the aerogel tablets formed at 10MPa compression with different CNTs content. The electrical conductivity of pure graphene is $1.79 \times 10^4$ S m$^{-1}$. The addition of ACNTs into the GAs enhanced the electrical conductivity, reaching $1.91 \times 10^4$ S m$^{-1}$ with 5 wt% ACNTs, $2.08 \times 10^4$ S m$^{-1}$ with 10 wt% ACNTs, and $1.85 \times 10^4$ S m$^{-1}$ with 15 wt% ACNTs. The GR/ACNTs composite with 10 wt% ACNTs has attained the highest value, attributed to the good dispersion and the

![Figure 3](image-url)

**Figure 3.** SEM images of (a) graphene aerogel; (b) ACNTs; GR/ACNTs aerogels with ACNTs loading of (c) 5 wt%, (d) (e) 10 wt%, (f) 15 wt%; (g) TCNTs; GR/TCNTs aerogels with the TCNTs loading of (h) 5 wt%, (i) 10 wt%, (j) 15 wt%.
formation of 3D electrically conducting paths that facilitate the transport of electrons. The electrical conductivity decreased when the ACNTs loading increased to 15 wt%, probably due to the local agglomeration of CNTs. CNTs agglomerates were tend to block the electrically conduction paths and increase the electron transmission resistance, thus decreasing the electrical conductivity.

The conductivity of GR/TCNTs composites is $1.83 \times 10^4$ S m$^{-1}$ at the TCNTs loading of 5 wt%, which is slightly higher than that of pure GA. Afterwards, it drops to $1.71 \times 10^4$ S m$^{-1}$ at TCNTs loading of 10 wt% and $1.56 \times 10^4$ S m$^{-1}$ at 15 wt%. It is speculated that the severe agglomeration of TCNTs (shown in figures 3(i), (j)) blocked the electrically conducting paths and reduced the electrical conductivity.

The changes in electrical conductivity upon compression and calcination temperature of GR/ACNTs composite with 10 wt% ACNTs are exhibited in figure 4(b). The electrical conductivity increased as the forming pressure and calcination temperature increased. The increasing forming pressure could make the aerogel more condensed, leading to the elimination of air voids. Moreover, the thermal annealing could remove the functional groups, leading to stronger $\pi$-$\pi$ interactions [22]. Hence, the compression and annealing treatment dramatically increased the electrical conductivity of GR/ACNTs aerogels, offering very high conductivity values compared to that previously reported [22, 38, 39].

3.4. Thermal properties

The thermal conductivity of different GR/CNTs coatings was measured using the transient plate heat source method (figure 5(a)). The thermal conductivity of the GR coating is 1.13 W mK$^{-1}$, increased to 1.34 W mK$^{-1}$ with 5 wt% ACNTs, and reaching a maximum of 1.56 W mK$^{-1}$ with 10 wt% ACNTs (38% increase compared to the GR coating). At higher ACNTs loadings of 15 wt%, the thermal conductivity declines to 0.98 W mK$^{-1}$. The thermal conductivities of GR/TCNTs coating decreased with increasing TCNTs loading, following the order: $0.91 \text{ W mK}^{-1}$ at 5 wt% TCNTs > $0.74 \text{ W mK}^{-1}$ at 10 wt% TCNTs > $0.69 \text{ W mK}^{-1}$ at 15 wt% TCNTs. These results can be interpreted as follows.

The thermal conductivity $K$ is considered to be the sum of phonon and electronic heat conductivity, that is: $K = K_p + K_e$, where $K_p$ and $K_e$ are the phonon and electronic heat conductivity in solid materials [6].

![Figure 4. Electrical conductivity of (a) GR/CNTs aerogels with different CNTs loading, (b) GR/ACNTs aerogels with 10 wt% CNTs loading at different calcination temperature and forming pressure.](image)
When a proper amount of CNTs is embedded into GR sheets uniformly, it could be acted as an effective interconnector and heat conductive bridge, forming 3D heat conduction paths, which in turn improved the thermal properties. On the contrary, CNTs agglomerates would block the heat conduction paths, leading to an increased phonon scattering density, thus decreasing the thermal conductivity [40].

To practically evaluate the thermal management of the GR/CNTs coatings, the steady temperature of LED using Al-based heat sinks with and without the coating was determined by infrared radiation thermometer after 2-hour lightening. The surface temperature of LED using the pristine heat sink was 39.1 °C. The corresponding temperature for GR/ACNTs coatings was 33.6 °C at 5 wt% ACNTs, 30.5 °C at 10 wt% ACNTs, 34.9 °C at 15 wt% ACNTs, whereas for TCNTs-containing coatings was 36.7 °C at 5 wt% TCNTs, 37.9 °C at 10 wt% TCNTs, 38.4 °C at 15 wt% TCNTs and 35.8 °C for pure GR. The thermal management results in combination with the thermal conductivity results, reveal that the coatings with better thermal conductivity attained lower LED temperature.

The GR/ACNTs coating with 10 wt% ACNTs, which offers the highest thermal conductivity, reduced the operating temperature of LEDs by as much as 8.6 °C. This can be considered as an adequate performance in the field of LEDs thermal management [23–25]. At the same time, the coating is low-cost and environmentally-friendly, showing great potential as thermal management material for practical applications.

4. Conclusions

In this study, GR/CNTs hybrid aerogels and GR/CNTs hybrid coatings were fabricated, introducing various loading of ACNTs or TCNTs into graphene. ACNTs showed better dispersion and homogeneity in graphene than TCNTs. The electrical and thermal properties of graphene were dramatically enhanced by the proper incorporation of ACNTs. On the other hand, TCNTs were tend to agglomerate and block the conducting paths, thus reducing the thermal/electrical conductivity. The Eco–friendly and low-cost GR/ACNTs coating demonstrated satisfactory performance in the thermal management for LEDs, showing great potential for practical applications.

Acknowledgments

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