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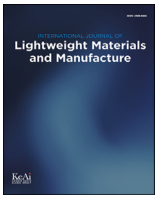

Original Article

Flexible graphene-coated carbon fiber veil/polydimethylsiloxane mats as electrothermal materials with rapid responsiveness

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ABSTRACT

Flexible electrothermal mats with rapid responsiveness were prepared by spray-coating of graphene nanoplates (GNP) acetone dispersion on carbon fiber veil and following curing of polydimethylsiloxane (PDMS) on the mats. Morphological feature, electrical property, and electrothermal behavior of the mats with different area density from 55 to 20 g m^{-2} were investigated. Scanning electronic microscope (SEM) confirmed that pristine graphene nanoplates were uniformly deposited on the surface of carbon fiber resulting in volume resistance decreased substantially. Compared with the carbon fiber veil without coated GNP, the electric heating behavior of graphene-coated carbon fiber/PDMS mats were improved largely, such as the stead-state maximum temperature reached 297 °C, the maximum heating rate reached $5^{\circ}Cs^{-1}$ tested by an infrared camera, the maximum power density reached 11.11 kW m^{-2}. The respond time from room temperature 25 °C–200 °C was only 40 s tested by infrared thermal image. Even under high twisting/bending state or continuous stepwise voltage changes, the graphene-coated carbon fiber/PDMS mats retained stable electrical heating performance in aspects of temperature responsiveness and steady-state maximum temperature.

1. Introduction

Electrothermal materials are a kind of functional electric resistors that can convert electric power into thermal energy by Joule effect [1]. In our daily life, electro-heating materials and devices have been extensively used as the thermal source in various special conditions around us, such as anti-icing/deicing devices, floor heating, vehicle window defrosters, automobile mirror defoggers, intelligent textiles and so on [2]. Traditional metal electrothermal materials such as Fe-Cr-Al compound metal, Ni-Cr compound metal, copper [3] and indium tin oxide (ITO) have been widely used and shown high thermal mechanical stability. Particularly, indium tin oxide (ITO), due to its high electrical conductivity and good transparency, has attracted significant research interests [4]. However, metal electric heaters have some disadvantages such as heavy weight, brittleness, non-uniform heating, high energy consumption, high cost, and easy to corrode by acids and base which have impeded their applications [5].

In contrast to the traditional metal-based electrothermal materials, carbon-based heaters have the advantages of ultra-light weight, high thermal conductivity, low electrical resistivity, high power energy conversion efficiency, corrosion resisting, environmental friendliness and easy available [1]. This new type of materials have been attracted wide attention and considered as the potential candidates to replace traditional ones. Generally, the carbon-based electrothermal materials can be selected from carbon fiber veil [6], carbon black powder [7], carbon nanotube [8,9], graphite [10], graphene [11–14] and graphene foam [25]. Considering the mechanism of electric energy converting to heat for carbon-based heater is mainly the collision between charged particles in the electric field, therefore the current and the intrinsic resistance of the electrothermal materials directly influence the heating performance [16].

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Furthermore, it is reported that the electrothermal transformation efficiency of the heater is mainly related to the convective heat loss. Among all the carbon-based heating materials, graphene, which is a two dimensional (2D) nanomaterial with very high current density [12] ($\approx 2 \times 10^9$ A cm^{-2}) and thermal conductivity (≈ 5300 W m^{-1} K^{-1}), has been known as an ideal conductor of both thermal and electricity [15]. The remarkable thermal conductivity guarantees that graphene has the performance of a fast temperature response and uniform temperature distribution, which is very important for heater. The graphene-based heater has a low convective heat transfer coefficient, which gives it good electrothermal property. The above mentioned advantages make graphene a promising alternative for high efficient and effective heaters. Lei Fu reported that graphene molecules structure with thicknesses at the atomic level were directly grown on the surface of ceramic substrates. Its heating performance were systematically investigated, the high heating temperature up to ≈ 600 °C at applied voltage of 7.5 V was obtained. Weiwei Zhou prepared lightweight and flexible electro-thermal films using graphite nanoplatelets (GNP) by gap coating and plastic packaging method, which were more fit for wearable/smart electronics and could work at a high heating rate of 25–65 °Cmin^{-1} under a low voltage of 3–5 V, due to the low electrical resistivity [17]. James M. Tour fabricated a conductive composite of graphene nanoribbon stacks used epoxy resin as matrix, which exhibited a conductivity >100 Sm^{-1} at 5 wt % GNR content and had been used for deicing of surfaces through Joule effect with a heating power density of 0.5 Wcm^{-2} [18].

However, most of the graphene-based heaters have the drawbacks of large sheet resistance, and require a high input voltage when a high temperature is needed, and also the graphene-based film prepared by chemical vapor deposition (CVD) is brittle and low strength, and very hard to conform to curved heating parts unless the structural encapsulation and mechanical reinforcement are sufficiently implemented. For the electrothermal materials, flexibility or shape conformability is desirable performance for many applications, such as the anti-icing/deicing of aircraft, the heating of sensors, pipes and vessel. For this application, carbon fiber veil is suitable because it is in a sheet form, can be easily incorporated in a structural composite and conform to the curved surface, and also have the performance of corrosion resistant and low resistant. But for the carbon fiber veil as heater, the heating efficiency and thermal distribution is not ideal.

In this work, lightweight, highly flexible and conductive graphene-coated carbon fiber/polydimethylsiloxane (PDMS) veils were easily fabricated by using a feasible spray-coating and curing method [19]. Defect-free graphene was evenly dispersed in acetone to obtain a uniform solution. The carbon fiber veil was spray-coated with the acetone graphene solution and dried until the acetone was volatilized completely. Thereafter PDMS was brushed on the surface of the carbon veil with coated graphene and then it was cured by hot press method. The combination of graphene and carbon fiber veil can effectively decrease the resistant of the electrothermal heaters, and assistant the dispersion of graphene on the surface of the carbon fiber because of π-πaction between carbon fiber and graphene. For comparison, the pristine carbon fiber veil/polydimethylsiloxane (PDMS) mats were also fabricated. The structure and morphology of carbon fiber/graphene mats were evaluated by scan electronic microscope and optical microscope. The electrothermal performance of the mats related to the mat thickness and applied voltage was investigated. The heating behavior, such as temperature response rapidity, electric heating power density and balanced temperature at various voltages, was evaluated. What is more, in order to validate their operational stability and reliability as electric heating devices, the electric heating performance of the mats under mechanical deformation and cyclical voltage changes was measured. The researched materials have the perspective of used as lightweight electric heater in the polymer based composite.

2. Experimental

2.1. Materials

The graphene nanoplates were commercially purchased from Institute of Coal Chemistry Chinese Academy of Sciences, which were fabricated by the method of chemical intercalation and thermal expansion, and then further reduced to remove excess oxygen functional groups. The average size of the dispersed graphene nanoplates is larger than 550 nm with about 3–5 layers, electrical conductivity is 2000–4000 Sm^{-1}, and was used without any further treatment. Carbon fiber veil with the area density of 55, 35, 20 g m^{-2} were provided by De Zhou carbon fiber Co. Ltd. PDMS including hardener (Sylgard 184 Silicone Elastomer Kit, Dow Corning) was used as a flexible and high temperature resistant polymer matrix. Highly conductive silver paint (~5×10^3 S cm^{-1}) was prepared by ourselves to prepare electrodes. Acetone was obtained from Beijing chemical reagent Co. Ltd. All the chemical agents and solvent were directly used as received without any further purification.

2.2. Fabrication of graphene-coated carbon fiber veil/PDMS mats

The electrothermal mats were prepared as follows. Firstly, graphene nanoplate solution of 2 mg ml^{-1} was prepared in acetone using ahorn-type ultrasonicator for 40 min. Subsequently, the homogeneous graphene dispersion of 50 ml was spray-coated on carbon fiber veil (20 cm × 20 cm) with different area density by a portable commercial spray gun. The spraying pressure was 0.2 MPa, the flow rate of the graphene dispersion solution out of the spraying nozzle was 1 mL/cm^2. The carbon fiber veil with coated graphene was dried at room temperature for 24 h. The content of coated graphene was about 10% of the weight of the carbon veil. Secondly, the Cu foils with thickness 0.35 μm as electrodes were adhered to across sides of carbon fiber/PDMS mats with epoxy conductive Ag paste. Finally, PDMS mixed with the hardener (the ratio of PDMA to curing agent is 10:1 by weight) was brushed on the surface of the conductive mats, and was cured at 120 °C for 1 h by hot press method with pressure of 0.2 MPa. Finally, after the conductive copper wires were linked with Cu foils, the final electrothermal device were finished. The manufacturing procedure of graphene-coated carbon fiber/PDMS mats was schematically illustrated in Fig. 1. The finished graphene-coated carbon fiber electrothermal mats with area density 55–20 g/m^2 were marked as G-CFx/PDMS, where x stands for the mean area density of the carbon fiber veil, G means the graphene-coated modification. Then CF55/PDMS stands for the mat without graphene modification.

2.3. Characterization

Scanning electron microscope (FEI Quanta 600) was used to characterize the morphology of sample and microstructure features of graphene nanoplates and flexible graphene-coated carbon veil/PDMS mats. Volume resistance was tested by Fluke F1508 insulation resistance tester. Sheet resistance of the mats was tested by four point probe meter (ST2258A, Suzhou Jingge Electronic Co., LTD). The surface temperature was recorded by a K-type thermal couple. Thermal infrared (IR) images were obtained by an imaging IR thermometer (FOTRIC 225), which can measure temperatures from −25 to 400 °C. For the heating measurement, the voltage was supplied by a single-phase contact voltage regulator (TDGC2-

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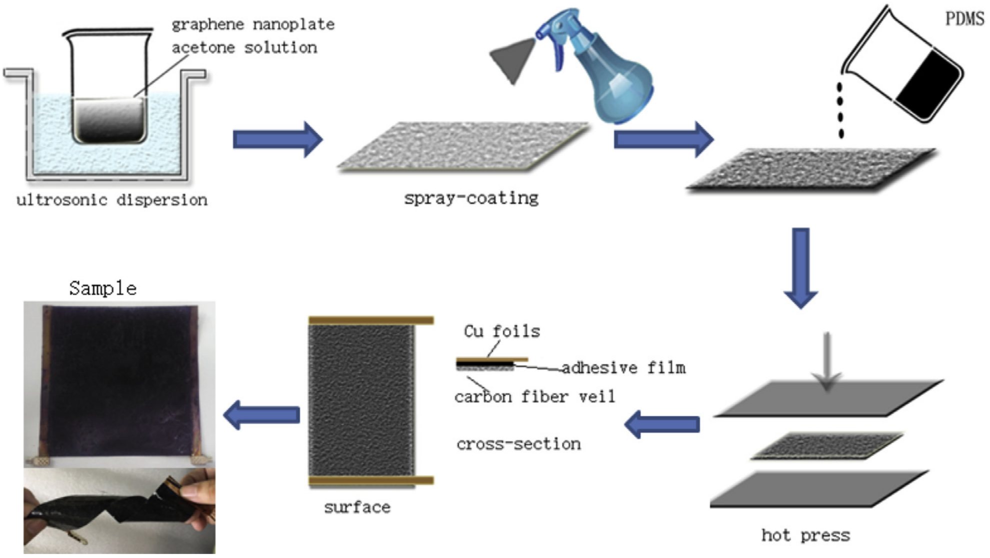


Fig. 1. Schematic procedure to manufacture graphene-coated carbon fiber veil/PDMS mats by spray-coating of graphene acetone solution and following curing of PDMS.

3KVA). Alternating current was applied to the electrothermal mats by two copper foil strips adhered to the mat edges. The electric power density (Ps) was obtained by the equation $P_s = UI/S$, where U and I means the voltage and the corresponding current, and S is the area of electro-thermal mats surface. The mats thickness (h) was recorded by micro-meter screw gauge [17].

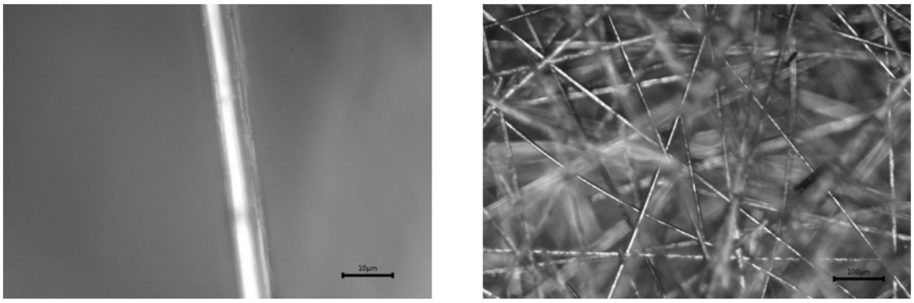
3. Results and discussion

3.1. Fabrication of graphene-coated carbon fiber/PDMS mats

Compared to other electrothermal materials or devices, the graphene-coated carbon fiber/PDMS heater has a feasible fabrication procedure, which does not rely on any expensive setting or a complex process. The fabrication process of the flexible electrically conductive mats composed of carbon fiber veil, graphene nanoplate, and PDMS is illustrated in Fig. 1. In brief, the free-standing carbon fiber veil/graphene mat is prepared by spraying homogeneous graphene acetone suspension on the surface of carbon fiber veil. After drying, the carbon fiber veil with coated graphene is brushed with PDMS to obtain the flexible carbon fiber veil/graphene electrically conductive mats. These three constituents were selected because of the following considerations: (1) carbon fiber veil possesses high electric conductivity, good electrothermal performance, shape conformability and high thermal stability. Fig. 2 shows the optical image of carbon fiber veil. The diameter of carbon fiber is about 5–10 μm, the length is about 2 cm. The carbon fiber veil can been used as the carrier of graphene and enhance the strength of graphene-coated carbon fiber mats with PDMS as matrix [20]. (2) The graphene has extremely high thermal conductivity and current density, as well as relatively low thermal loss, which endow graphene with the high efficiency as electrothermal heater. As depicted in Fig. 3, graphene nanoplates are slightly stacked layer by layer. Graphene nanoplates have a large specific area and easy to coat on the surface of carbon fiber which could greatly assist the transport of electro power and heat energy, and distribute surface heat in the form of radiation and enhance heat conduction. (3) PDMS has no toxicity, is a chemically inert, elastic, and transparent polymer, which makes it suitable for the application in stretchable and flexible electronic devices. With the aid of the side alkyl groups and inorganic Si-O backbone, PDMS bears higher stability at elevated temperatures than ordinary organic polymers. In this work, the advantages of all three kind of materials were been used, which was suitable for electrothermal heaters with high flexible, high strength and high electrothermal efficiency [7,21].

3.2. Microstructure of graphene-coated carbon fiber/PDMS mats

The microstructure and morphology of graphene-coated carbon fiber/PDMS mats were investigated by SEM microscope. Typical



(a) (b)

Fig. 2. Optical microscope images of carbon fiber veil (a)×1000 (b)×100.

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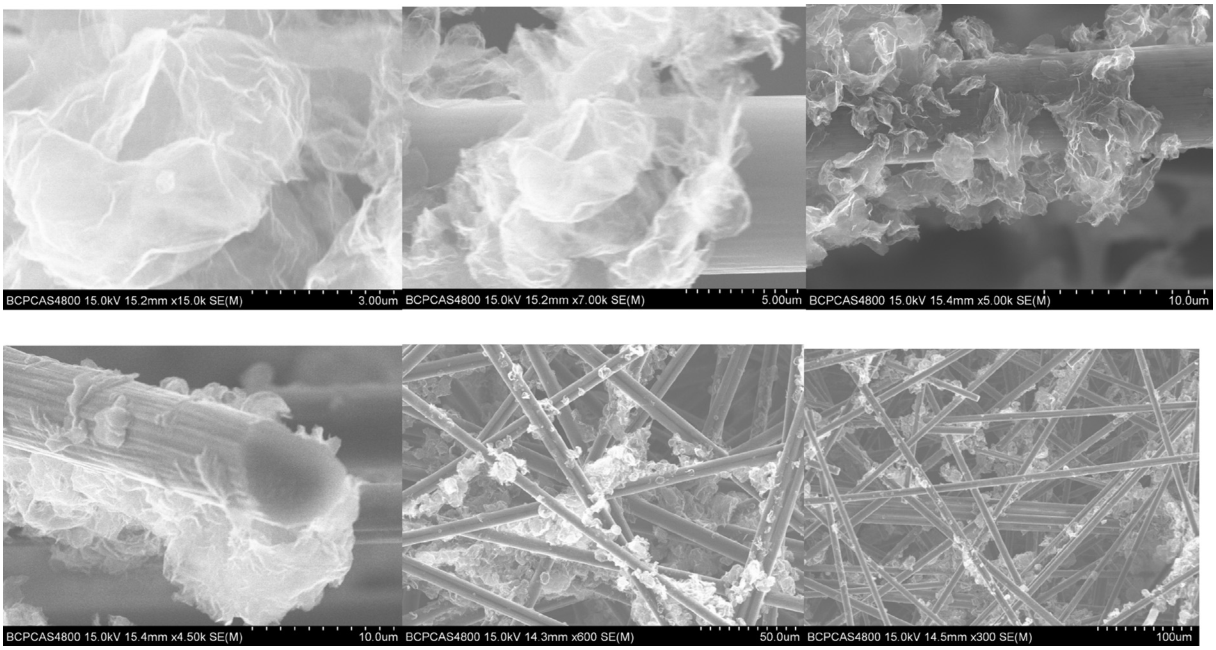

Fig. 3. Typical SEM at different magnifications of both surface and cross-section of graphene-coated carbon fiber veils.

SEM images of surface and cross-section of the G-CF/PDMS mats at different magnifications are presented in Fig. 3. Pristine GNP was found to be uniformly deposited on the surface of carbon fiber, wrapped around the surface of carbon fiber and inserted into the cross-points between carbon fibers, forming a beads-on string structure. The strong π-πaction was formed between the surface of carbon fiber and graphene sp^2 two-dimensional layered structure. The strong interface action was beneficial to the heat and electro transmission [26,27]. Fig. 4 shows the typical SEM images of both the surface morphology and transversal section morphology of G-CF/PDMS mats. It was observed that carbon fiber of the veil was wrapped by PDMS, which was mainly due to the wetting and infiltrating of the low viscosity PDMS to the interspace among carbon fiber (Fig. 4(a)). The wrapped carbon fiber as well as the interface structure between PDMS and carbon fiber were also observed from the transversal section image of the G-CF/PDMS mats (Fig. 4(b)). Therefore, it is well confirmed that the structural stability of the G-CF/PDMS mats under mechanical deformation is related to the strong interface strength between carbon fiber and PDMS. The PDMS further strength the interface action between carbon fiber and coated graphene and keeps the graphene from peeling off the surface of the carbon fiber under the deformation [7]. This microstructure of the composite with PDMS as matrix and graphene modified carbon fiber veil as reinforcement contributed to the formation of the electrically conductive mat which was beneficial to the electrical conducive and heat transmission.

Volume resistance of the compound mats were measured by insulation resistance meter. Table 1 shows the volume resistance of carbon fiber veil with or without coated graphene. It can be seen the resistance of carbon fiber veil with graphene modification

Table 1
Volume resistance of carbon fiber veil with or without coated graphene.

Item	Volume resistance(Ω)	Item	Volume resistance(Ω)
CF55/PDMS[a]	19.1 ± 0.49	G-CF55/PDMS	9.4 ± 0.47
CF35/PDMS	26.4 ± 0.52	G-CF35/PDMS	9.5 ± 0.51
CF20/PDMS	38.0 ± 0.62	G-CF20/PDMS	16.3 ± 0.58

[a] Sample size: 20 × 20 cm^2.

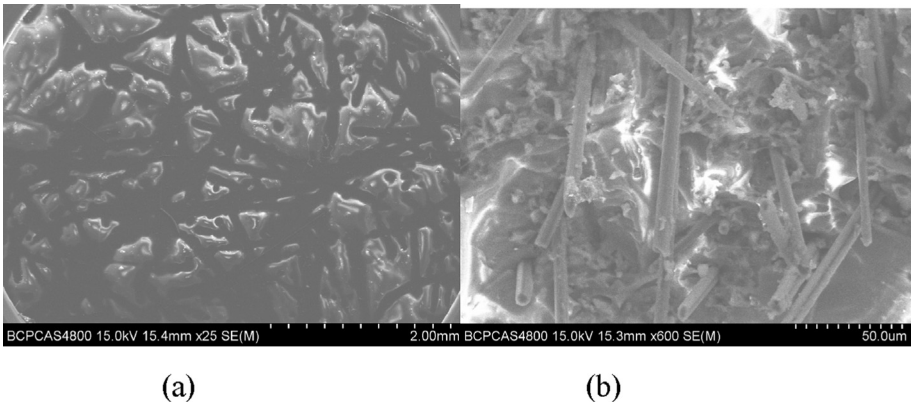

Fig. 4. Typical SEM images of surface(a) and cross-section (b) of G-CF/PDMS mats.

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decrease about 80 % compared with that of pristine carbon fiber veil, which was mainly attribute to the high conductivity of graphene [22].

3.3. Electrothermal performance of G-CF/PDMS mats and modeling the temperature elevation

The temperature change was measured with a K-type thermocouple attached on the surface of the substrate in the middle of the mat heater. The electrothermal behavior of the CF/PDMS mat with different area density with or without coated graphene was investigated under ambient condition by inputting constant voltage from 10 to 65 V. Fig. 5 shows the temperature vs time curves of the compound mat with various density (55, 35, 20 g m^{-2}) of carbon fiber veil with (d-f) or without (a-c) coated graphene, respectively. The surface temperature of the electrothermal mat increases rapidly with time above critical voltage is applied, and reaches steady-state temperature. In the second region, the surface temperature of heating mat remains unchanged. According to the energy conservation law, the heat obtaining from electric energy is equal to thermal loss by radiation and convection in this region, and then temperature decreases rapidly to ambient temperature when the inputting voltage is shut off. During the first region, it indicates that the electric heating rate of the G-CF/PDMS mats is strongly related to the electrical resistances of carbon fiber veil as well as inputting voltage. Under a specific inputting voltage, the mat with a lower electrical resistance could achieve more higher steady-state temperatures because of higher power density.

The voltage-dependent temperature curves of compound mat with the various density of carbon fiber veil with or without coated graphene in Fig. 6(a) show that the maximum temperature of each mat monotonically increases with increasing voltage. Compared with the electrothermal performance of carbon fiber veil without modification, the steady-state maximum temperatures, also the hating rate, of the G-CF/PDMS mats are more higher because of the higher electrothermal efficiency which is all ascribed to the excellent electric and thermal conductivity of graphene nano plate.

As we all known, the surface temperature of electric heating mat was mainly decided by the power density and ambient temperature [2]. And the heating power density is computed by the equation $Ps = UI/S$ or $Ps = U^2/(RS)$, where R and S refer to the resistance and area size of electrothermal mat, respectively. Fig. 6(b) shows the voltage depend power density curves of compound mat. For a specific mat, the power density also increases in line with the

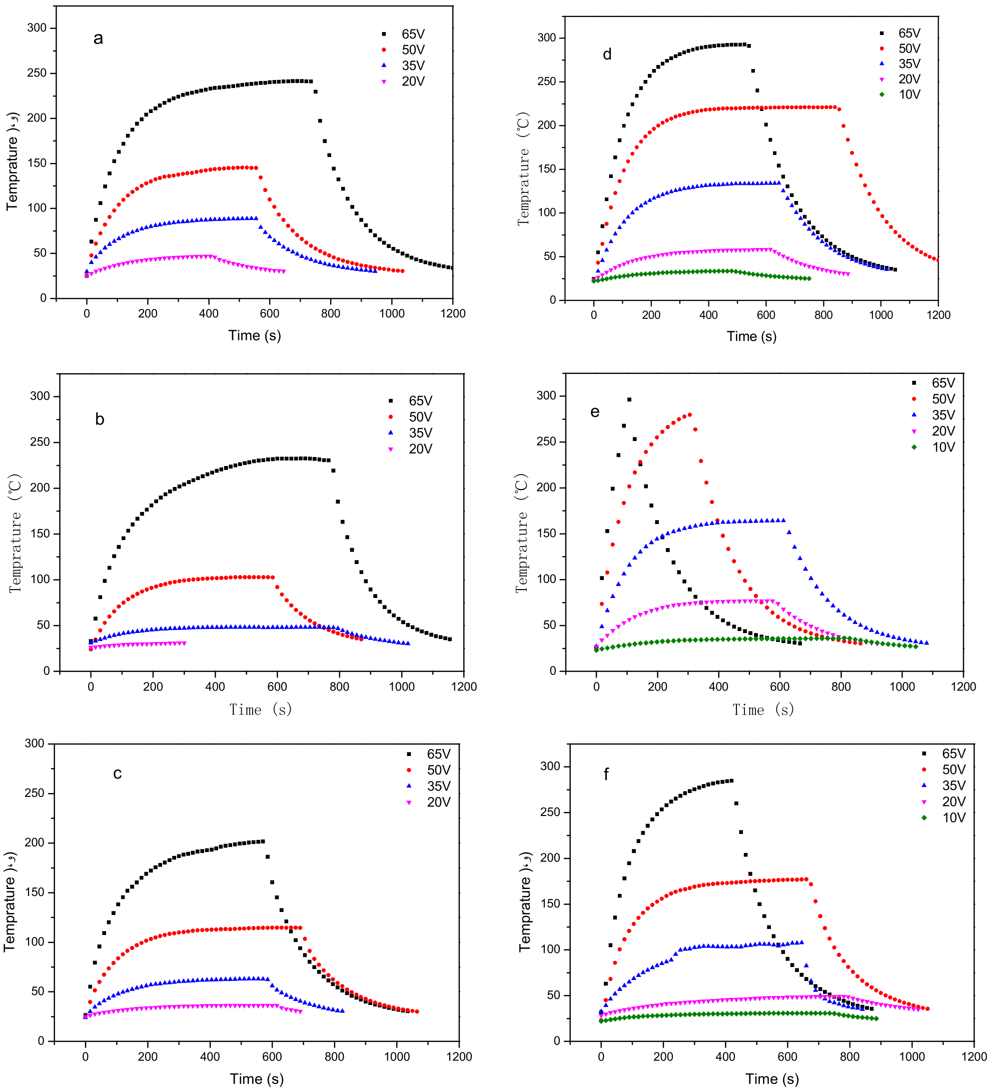

Fig. 5. Time dependent temperature profiles of the compound mat. (a) CF55/PDMS (b) CF35/PDMS (c) CF20/PDMS (d) G-CF55/PDMS (e) G-CF35/PDMS (f) G-CF20/PDMS.

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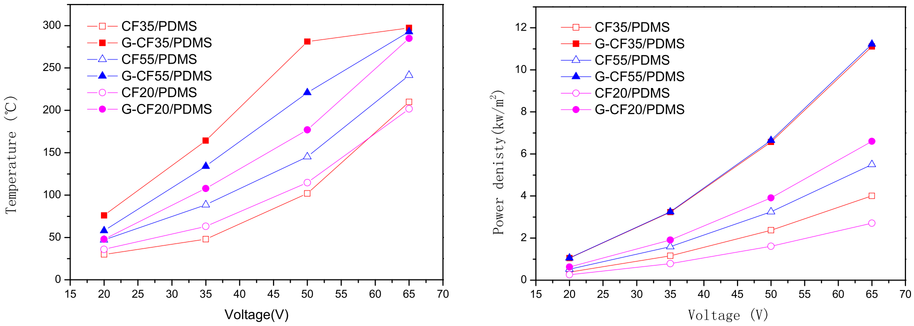

Fig. 6. Maximum temperature vs voltage curves (a) and power density vs voltage(b) of each compound mat.

voltage raise, which indicates the electric heating performance can been controlled by voltage. What is more, the power density of G-CF/PDMS mat was more larger than that of CF/PDMS mat. In all the materials, the G-CF35/PDMS mat shows the largest power density of 12 kW m^{-2} and the maximum temperature reaches 300 °C at the applied voltage of 65v. It was assumed that the current system used on the Boeing 787 (metal spray) requires a steady state temperature of 6 °C for effective anti-icing under −18 °C operational ambient conditions, expending 11.8 kWm^{-2} without considering the energy absorbed by the composite structure [23]. Then the attained power density in this work can meet the anti-icing requirements under −18 °C.

The response time is the time taken for the mat to reach a steady-state temperature from room temperature. In order to quantitatively ascertain the characteristic parameters related to hear response rapidity and energy conversion efficiency of the electrothermal performance, the three section, temperature growth section, balanced temperature section and temperature decrease section, in the time-dependent temperature curves in Fig. 5 can been calculated by empirical equation [21].

During the first section, the relationship between temperature increase and time can be empirically expressed as:

$$\frac{T_t - T_0}{T_m - T_0} = 1 - \exp(-t/\tau_g)$$

where T_0 and T_m refer to the initial ambient temperature and steady-state temperatures, respectively. T_t means the real temperature at time t. τ_g means the characteristic growth time constant and it is obtained by fitting the data of the temperature with time in the first section.

In the second section in the stead state, the maximum temperatures at fixed voltage remained stable by energy conservation law that heat gain from electric energy is equal to heat loss by radiation and convection. The heat transferred by radiation and convection, h_{r+c}, is thus expressed as:

$$h_{r+c} = \frac{I_c V_0}{T_m - T_0}$$

where I_c is the steady-state current and V_0 is the applied voltage.

In the third section, the temperature decreases with time after the voltage is off, which can be expressed by the following empirical equation:

$$\frac{T_t - T_0}{T_m - T_0} = \exp(-t/\tau_d)$$

where τ_d is the characteristic decay time constant and it could be calculated by fitting experimental time-dependent temperature curves. All the calculated τ_g,τ_d, and h_{r+c} were summarized in Table 2. Compared to the τ_g and τ_d values of the CF film, the values of G-CF are all relatively lower, which means the G-CF film have more rapid temperature responsiveness [21].

3.4. *Heating rate and stability*

Temperature uniformity is important for heating device. For traditional metal net or wire heating device, there is always overheating area or spot. In this work, the temperature distribution of as-prepared G-CF/PDMS mat was recorded by a hand held IR imager, which is an important parameter to assess the heating property of electrothermal device. The IR images of as-prepared G-CF35/PDMS mat at a fixed voltage of 35 V with different time are present in Fig. 7. The IR images give an illustration of the heating process throughout the mat. It can been seen the temperature reach about 200 °C at only 40s, the heating rate approaches 5 °C s^{-1}, which is almost two times of 2.75 °C s^{-1} tested by K-type thermocouple because thermocouple takes longer time for heat conductivity. The tested results show that the temperature uniformity of G-CF35/PDMS mat is quite ideal, and the area of uniform temperature occupies almost above 80 % of the whole heating mat. The well-distributed temperature is due to the even density of carbon fiber veil and the homogenous graphene dispersion.

Flexibility and stability are necessary property for new type electrothermal materials and devices [24]. To confirm this property, the influence of bending and twisted deformation on electrical heating property of the G-CF/PDMS mat was investigated. In order to further understand the electro-heating performance of the flexible electrothermal mat under bending state, the heating process was investigated in the bending state under a fixed voltage of 35 V (see Fig. 8). Obviously, time-dependent temperature curves in planar state coincides well with the curves in bending states, which implying the good stability of G-CF35/PDMS in mechanical deformation. The temperature distribution in bending state is similar to that of planar state (see Fig. 7).

In order to further test the electrothermal stability of the flexible mat under the mechanical deformation, the electric heating performance of the G-CF35/PDMS mat (20 × 1.5 cm^2) in the untwisted deformation and twisted states was measured at a fixed voltage of 35 V. It is shown in Fig. 9 that the strip is twisted by 360°, but the time depend temperature curves remained almost unchanged, which means that bending has no obvious effect on the temperature increase of as-prepared CF/PDMS mats. Both the untwisted and twisted mat showed well-distributed temperature, which was ascribed to the homogeneous property and the stable structural feature of the compound mat, and can be seen in the inlet infrared images. It means that the G-CF/PDMS mats have very reliable and stable electrical heating performance which was attributed to strong bonding strength between graphene coated carbon fiber and polymer matrix.

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Table 2
Characteristic parameters relating to temperature response rapidity and energy efficiency.

Sample codes	Voltage(V)	τ_g	τ_d	Heating rate (°Cs^{-1})	maximum temperatures (°C)	Power density (kw m^{-2})	h$_{r+c}$ (mW/°C)
CF20	65V	100	113	0.85	201.7	2.71	0.63
CF20	50V	94	108	0.57	114.7	1.61	0.71
CF20	35V	110	60	0.2	63.1	0.78	0.80
G-CF20	65V	96	102	1.7	285.1	6.60	1.15
G-CF20	50V	88	93	1.41	177.1	3.91	1.12
G-CF20	35V	90	41	0.45	107.9	1.91	1.15
CF35	65V	120	127	1.25	232	4.01	0.8
CF35	50V	99	123	0.52	102	2.37	1.58
CF35	35V	110	111	0.08	48	1.16	2.74
G-CF35	65V	118	95	2.37	297.4	11.11	2.42
G-CF35	50V	89	90	1.72	281.3	6.57	1.49
G-CF35	35V	100	89	0.77	164.3	3.23	1.38
CF55	65V	98	129	1.08	241.5	5.50	0.66
CF55	50V	98	132	0.68	145.3	3.25	0.73
CF55	35V	100	124	0.38	88.7	1.59	0.70
G-CF55	65V	95	109	1.65	292.9	11.23	1.66
G-CF55	50 V	93	120	1.02	221	6.65	0.98
G-CF55	35V	97	116	0.75	134.1	3.25	1.17

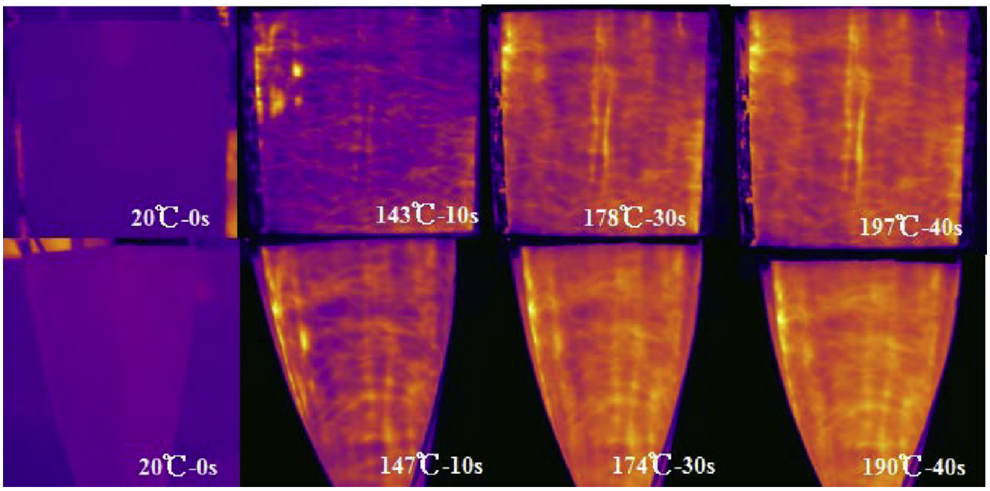

Fig. 7. Temperature distribution of G-CF35/PDMS with different time at 35 V voltage for flat and bending state.

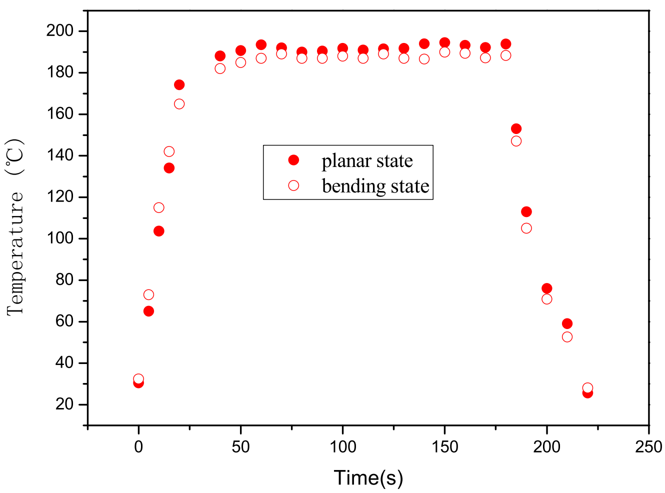

Fig. 8. Time dependent temperature profiles of G-CF35/PDMS mat tested by IR.

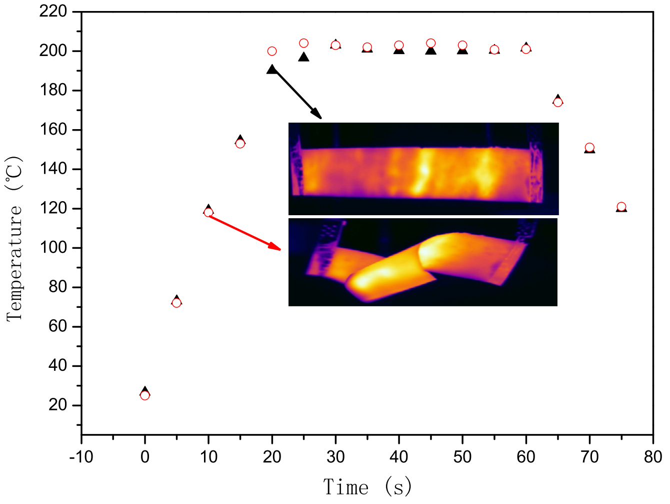

Fig. 9. Electric heating behavior of the G-CF35/PDMS mat (20 × 1.5 cm^2) under the untwisted and twisted states.

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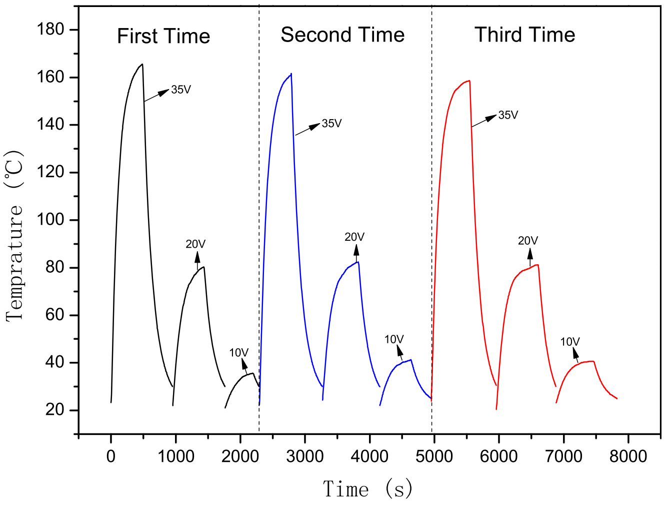

Fig. 10. Cyclic electric heating-cooling tests of G-CF35/PDMS mat for 3 cycles.

Good reproducibility is a very important performance for electric heating devices or materials. In order to evaluate the stability and sensitivity of G-CF/PDMS mat after repeatedly heating and cooling application, periodical electric heating-cooling experiment was carried out to illustrate the reproducibility of electrothermal mat. In this research, the time depend temperature curves of the sample were recorded under a cyclic inputting voltage of 35, 20 and 10 V for 3 continuous heating-cooling cycles. Fig. 10 shows the electrothermal performance curves of G-CF35/PDMS mat for 3 continuous cycles. Each voltage was applied for 15 min and shut off until the temperature decrease to the room temperature. The electric heating performance, such as stead-state maximum temperature and temperature response rapidity, remained almost the same. Moreover, the maximum balanced temperatures at a given voltage remained stable and constant no matter high or low applied voltage. It indicates that the electric thermal performance of the mat is not influenced by the heating history of repeated electric heating and cooling course, which is attributed to the excellent thermo-mechanical stability of graphene coated carbon fiber and PDMS composites.

4. Conclusions

Flexible electrothermal mats with rapid temperature responsiveness, because of the synergistic electrothermal effect of carbon fiber and graphene nanoplates, were fabricated by a sample and feasible method without needing expensive equipments. The graphene nanoplates (GNP) acetone dispersion was spray-coated on the surface of carbon fiber veil and followed by brushing and curing of polydimethylsiloxane (PDMS) on the mats. The pristine graphene nanoplates were deposited and wrapped around the surface of carbon fiber and insert into the interspace between carbon fibers resulting in volume resistance decreased substantially. With the aid of the graphene nanoplate's excellent conductor of both heat and electricity, the electric heating behavior of graphene-coated carbon fiber/PDMS mats show excellent heating properties, such as the stead-state maximum temperature reaches 297 °C, the maximum heating rate reaches 5°Cs^{-1}, with respond time only 40s, tested by an infrared camera, the maximum power density reaches 11.11 kw m^{-2}. The maximum temperature of the mats could be finely controllable by adjusting applied electric power or voltage. The G-CF/PDMS mats retain stable electrical heating performance at continuous stepwise voltage changes, even under high twisting or bending state. The G-CF/PDMS mats can be used as electric heating elements because of easy process ability, flexibility and rapid heating, especially suitable for anti-icing/deicing devices, or for other advanced fields such as personal care apparatus and flexible wearable electronics.

Conflicts of interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijlmm.2019.04.002.

References

[1] D. Janas, K.K. Koziol, A review of production methods of carbon nanotube and graphene thin films for electrothermal applications, Nanoscale 6 (2014) 3037–3045.

[2] J. Yan, Y.G. Jeong, Multiwalled carbon nanotube/polydimethylsiloxane composite films as high performance flexible electric heating elements, Appl. Phys. Lett. 105 (2014) 051907.

[3] M. Mohseni, A. Amirfazli, A novel electro-thermal anti-icing system for fiber-reinforced polymer composite airfoils, Cold Reg. Sci. Technol. 87 (2013) 47–58.

[4] Hongyan Sun, Ding Chen, Chen Ye, Xinming Li, Dan Dai, Qilong Yuan, Kuan W.A. Chee, Pei Zhao, Nan Jiang, Cheng-Te Lin, Large-area self-assembled reduced graphene oxide/electrochemically exfoliated graphene hybrid films for transparent electrothermal heaters, Appl. Surf. Sci. 435 (2018) 809–814.

[5] C. Li, Y.T. Xu, B. Zhao, L. Jiang, S.G. Chen, J.B. Xu, X.Z. Fu, R. Sun, C.P. Wong, Flexible graphene electrothermal films made from electrochemically exfoliated graphite, J. Mater. Sci. 51 (2) (2015) 1043–1051.

[6] Taejin Kim, D.D.L. Chung, Carbon fiber mats as resistive heating elements, Carbon 41 (2003) 2427–2451.

[7] Fei-Fei Chen, Ying-Jie Zhu, Zhi-Chao Xiong, Li-Ying Dong, Feng Chen, Bing-Qiang Lu, Ri-Long Yang, Hydroxyapatite nanowire-based all-weather flexible electrically conductive paper with superhydrophobic and flame-retardant properties, Appl. Mater. Interfaces 9 (45) (2017) 39534–39548.

[8] S. Sharma, B.P. Singh, S.S. Chauhan, Enhanced thermomechanical and electrical properties of multiwalled carbon nanotube paper reinforced epoxy laminar composites, Compos. Appl. Sci. Manuf. 104 (2017).

[9] Dawid Janas, Krzysztof K. Koziol, Rapid electrothermal response of high-temperature carbon nanotube film heaters, Carbon 59 (2013) 457–461.

[10] G. Xin, H. Sun, T. Hu, Large-area freestanding graphene paper for superior thermal management, Adv. Mater. 26 (26) (2014) 4521–4526.

[11] Qiangqiang Zhang, Yikang Yu, Kaichun Yang, Baoqiang Zhang, Keren Zhao, Guoping Xiong, Xingyi Zhang, Mechanically robust and electrically conductive graphene-paper/glass-fibers/epoxy composites for stimuli-responsive sensors and joule heating deicers, Carbon 124 (2017) 296–307.

[12] Long Chen, Yidu Zhang, Qiong Wu, Effect of graphene coating on the heat transfer performance of a composite anti-/deicing component, Coatings 7 (10) (2017) 158.

[13] Yang Guo, Chaochao Dun, Junwei Xu, Jiuke Mu, Peiyun Li, Liwen Gu, Chengyi Hou, Corey A. Hewitt, Qinghong Zhang, Yaogang Li, David L. Carroll, Hongzhi Wang, Ultrathin, washable, and large-area graphene papers for personal thermal management, Small 13 (44) (2017) 1702645.

[14] T.Y. Zhang, H.M. Zhao, D.Y. Wang, A super flexible and custom-shaped graphene heater, Nanoscale 9 (38) (2017) 14357.

[15] K.S. Novoselov, V.I. FalKo, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene, Nature 490 (7419) (2012) 192–200.

[16] J.W. Jiang, J.S. Wang, Joule heating and thermoelectric properties in short single-walled carbon nanotubes: electron– phonon interaction effect, J. Appl. Phys. 110 (12) (2011) 124319.

[17] Han Jiang, Huatao Wang, Ge Liu, Zhiwei Su, Jianfeng Wu, Junpeng Liu, Xinni Zhang, Youqiang Chen, Weiwei Zhou, Light-weight, flexible, low-voltage electro-thermal film using graphite nanoplatelets for wearable/

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smart electronics and deicing devices, J. Alloy. Comp. 699 (2017) 1049–1056.
[18] A.R. Raji, T. Varadhachary, K. Nan, T. Wang, J. Lin, Y. Ji, Composites of graphene nanoribbon stacks and epoxy for joule heating and deicing of surfaces, Appl. Mater. Interfaces 8 (5) (2016) 3551.
[19] J. Luo, H. Lu, Q. Zhang, Y. Yao, M. Chen, Q. Li, Flexible carbon nanotube/polyurethane electrothermal films, Carbon 110 (2016) 343–349.
[20] Taejin Kim, D.D.L. Chung, Carbon fiber mats as resistive heating elements, Carbon 41 (2013) 2427–2451.
[21] Jing Yan, Young Gyu Jeong, Highly elastic and transparent multiwalled carbon nanotube/polydimethylsiloxane bilayer films as electric heating materials, Mater. Des. 86 (2015) 72–79.
[22] D. Kongahage, J. Foroughi, S. Gambhir, Fabrication of a graphene coated nonwoven textile for industrial applications, RSC Adv. 6 (86) (2016), 82685-82685.
[23] Xudan Yao, Stephen C. Hawkins, Brian G. Falzon, An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs, Carbon 136 (2018) 130–138.
[24] D. Sui, Y. Huang, L. Huang, Flexible and transparent electrothermal film heaters based on graphene materials, Small 7 (22) (2011) 3186–3192.
[25] J. Bustillos, C. Zhang, B. Boesl, A. Agarwal, Three-dimensional graphene foam–polymer composite with superior deicing efficiency and strength, ACS Appl. Mater. Interfaces 10 (5) (2018) 5022–5024.
[26] Sijie Wan, Shaoli Fang, Lei Jiang, Qunfeng Cheng, H. Ray, Baughman, strong, conductive, foldable graphene sheets by sequential ionic and π bridging, Adv. Mater. 30 (36) (2018) 1802733.
[27] Pingan Song, Zhiguang Xu, Yuanpeng Wu, Qunfeng Cheng, Qipeng Guo, Hao Wang, Super-tough artificial nacre based on graphene oxide via synergistic interface interactions of π-π stacking and hydrogen bonding, Carbon 111 (2017) 807–812.

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