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Phase change material filled hybrid 2D / 3D graphene structure with ultra-high thermal effusivity for effective thermal management



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A R T I C L E I N F O

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ABSTRACT

Graphene-based energy storage and renewable material has increasingly attracted research interest, due to its high thermal conductivity and light weight. Researchers fill phase change material (PCM) into three-dimensional graphene foam, to obtain a composite with high energy storage capability and moderate thermal conductivity. However, heat transfer mode of this kind of composite is single and cannot maximize the advantages of graphene. Herein, a stearic acid filled graphene-foam composite (GFSAC) connected with graphene paper (GP) through gravity-assisted wetting attaching process is demonstrated. The GP/GFSAC/GP composite possesses a high thermal conductivity of 1.72 Wm⁻¹K⁻¹ (with 0.53 wt % graphene loading), and an excellent effective thermal effusivity of 18.45 Jcm^{-3/2}m^{-1/2}s^{-1/2} $^{2K^{-1/2}}$. The GP/GFSAC/GP composite is shown to be an ideal material for thermal energy storage and renewable. Additionally, the low thermal resistance connection is achieved between 3D GFSAC and 2D GP, which plays a key role in the improvement of the composite is significantly lower and its temperature uniformity is much better, under the same heating condition. More importantly, after stop heating, the GP/GFSAC/GP composite shows the best temperature maintenance capacity.

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1. Introduction

Flexible electronics assembled in artificial intelligence (AI) devices play a vital role in the industry development, and their thermal management such as equipment heat dissipation and thermal protection has attracted more and more attention [1–5]. The operating temperature of most electronic devices must be strictly controlled within a certain range to insure the normal operation. For instance, when the temperature falls below 10 °C, the efficiency of lithium ion battery will be greatly affected, while when the temperature is over 75 °C, the service life and reliability of transistors assembled in CPU will be dramatically reduced [6–8]. At present, due to the continuing miniaturization and increase of power density in electronic devices, plenty of research studies pay attention to the overheating problem. Researchers have developed a series of thermal management materials, including highly

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thermal conductive graphene materials, phase change materials (PCMs) and thermal interface materials (TIMs) [9–13]. Through transferring, storing or dissipating heat from the electronic devices, the overheating problem can be solved. Meanwhile, considering the equipment used in harsh environment, such as deep sea, deep space or earth pole, the problem of overcooling can also affect the normal operation of these electronic devices. As a result, many thermal control strategies such as carbon-based film heaters and metal-based film heaters have been developed [12–14]. Through controlling the Joule heat generated from the film heater, the overcooling problem can be avoided. However, under certain circumstances, temperature sensitive electronic devices, such as CPUs, batteries and LEDs, can experience both overheating and overcooling, when they are integrated in the equipment to perform missions in harsh environment [15–19]. For example, when one side of the deep space exploring equipment is exposed to cosmic rays, its temperature rises immediately, while the temperature of the other side remains a low level. Additionally, electric energy is a kind of extremely precious source in deep space exploring, so it is almost impossible to divert excess power for electric heaters.



Therefore, exploring a thermal management method, which can handle both overheating and overcooling problems, and has low energy consumption or even no energy consumption, is of great significance for the further development of special electronic devices.

Graphene-based highly thermal conductive materials, such as two-dimensional (2D) graphene paper (GP) and three-dimensional (3D) graphene foam (GF), have made progress in maximizing their thermal conductivity by CVD growing, chemical reduction, thermal annealing, microstructure design and in-situ crosslinking, showing broad application prospects in thermal management, sensors and electrochemistry [20-26]. The GF skeleton has outstanding selfsupporting ability and excellent 3D thermal conductivity [21]. After being filled with PCM, the GF/PCM composite has good internal temperature uniformity, which will improve the thermal energy storage performance of PCM and control the composite temperature within a certain range [7,21,27-31]. Recently, Wu and coworkers have designed a novel graphene nanosheets/GF/natural rubber composite (with 6.2 vol% graphene loading) [32]. This composite possesses a thermal conductivity of 10.64 Wm⁻¹K⁻¹ at room temperature (RT), showing the highest thermal conductivity enhancement (TCE) of 8100% among those reported in literature. However, though the thermal conductivity of the composite has been greatly improved by the addition of graphene, the heat transfer mode is still single. Hence, the energy storage capacity of PCM cannot be fully utilized, especially when the composite is subjected to a point-heat-source (PHS) with high energy density. Besides, the graphene loading is relatively high, which will reduce the energy storage capacity of the composite.

Hence, we propose to combine the 2D GP and the PCM (stearic acid (SA)) filled 3D GF composite (GFSAC). The combined GP/GFSAC/GP hybrid composite can fully utilize the excellent in-plane thermal conductivity of GP, as well as the good through-thickness thermal conductivity and energy storage ability of GFSAC. In particular, a novel gravity-assisted wetting-attaching process was developed to achieve a low thermal resistance connection between the GP and the GFSAC, which could be a potential connection strategy in other thermal management application.

2. Experimental section

2.1. Materials

The GO aqueous solution is purchased from GaoxiTech Company, Hangzhou, China. The SA is purchased from Xinkang Company, Tianmen, China. The heat-conducting glue is KP98, produced by Kerafol, Germany.

2.2. Preparation of GP

The GP is prepared by annealing graphene oxide (GO) paper at 2600 °C. Firstly, we used 8 mg/ml GO aqueous solution to prepare GO paper on copper foil through casting method [33,34]. And the thickness of the paper can be effectively controlled by adjusting the moving speed of the blade and the distance between the blade and the copper foil. Then, the GO paper was reduced to GP through a two-step thermal annealing method. First, it was annealed at 1100 °C to get reduced graphene oxide (rGO) paper, and then graphitized at 2600 °C to obtain GP. In order to improve the density and thermal conductivity of GP, the GP obtained by annealing was pressed at 20 MPa for 5 min.

2.3. Preparation of GFSAC

Firstly, polyurethane (PU) foam was chosen as the template and

repeatedly impregnated in the GO aqueous solution under vacuum. Next, the two-step thermal annealing method was also used to remove the PU and reduce the GO foam to GF at the same time. Finally, the GF was fully impregnated into SA under vacuum to prepare GFSAC.

2.4. PHS heat experiment

A temperature constant PHS, which was about 0.5 mm above the surface of samples, was used to heat the sample surface, and two thermocouples were used to collect temperature signals from the sample bottom and the environment, respectively. GP/GFSAC/ GP composite, G- GP/GFSAC/GP composite, GFSAC, aluminum heat fin and SA block were tested. Unfortunately, the SA block melted and the overall structure collapsed after heating for 10 s, so its temperature signals could not be taken.

2.5. Characterization

Scanning electron microscope (SEM, JEOL JSM-7800F) was used to observe the morphologies of GP, GFSAC and GP/GFSAC/GP composites. Optical microscope images were taken by BX41M-LED, OLYMPUS. Raman spectra of GO paper, r-GO paper and GP were collected on a Renishaw inVia Raman microscope at a laser excitation wavelength of 633 nm. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max 2500 X-ray Diffractometer with a Cu Ka radiation of 0.154 nm at a generator voltage of 40 kV. The chemical compositions of GO paper, r-GO paper and GP were measured by a Nicolet iS50 Fourier transform infrared spectroscopy (FT-IR). Thermal conductivity (k) was calculated using the formula of $k = \alpha \times C_p \times \rho$, where α is the thermal diffusivity, C_p is the specific heat capacity, and ρ is the density of a composite. The inplane and through-thickness thermal diffusivities of composites were measured on a Netzsch LFA467 NanoFlash light flash apparatus at 25 °C. The specimens for in-plane (\$\$\phi25.4 mm\$) and through-thickness (ϕ 12.7 mm) tests were made by first cutting the composites, and then surface polishing. Specific heat capacity was measured by a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC) at a scanning rate of 10 °Cmin⁻¹. TGA test was conducted by a TGA 2 (SF), METTLER TOLEDO.

3. Results and discussion

3.1. Graphene paper

The GP/GFSAC/GP composite is a sandwich-like structure consisted of two parts, as shown in Fig. S1. The GPs on both sides are prepared according to the steps shown in Fig. 1a. The first step is to prepare GO paper by casting method. Then in order to obtain a high in-plane thermal conductivity, thermal annealing at different temperatures is applied on pristine GO papers followed by mechanical press. After that, a highly oriented graphite-layer-texture is created in GP (the inset of Step 5 in Fig. 1b), and the in-plane thermal conductivity of GP reaches 938 Wm⁻¹K⁻¹. The highly oriented graphene structure within GP contributes significantly to the high in-plane thermal conductivity. For carbon materials, phonon transport from lattice vibration of the covalent sp² bonding network plays an irreplaceable role in heat conduction. Thermal annealing heals defects in the lattice structure and removes functional oxygen groups and thus reduces the number of effective phonon scattering centers, leading to dramatic improvement of thermal properties [17,35].

Raman spectra, XRD and FT-IR spectra are performed to confirm the reduction of defects and functional groups and the improvement of crystallinity in the GP during thermal annealing. The



Fig. 1. Preparation process of GP. a) The manufacturing process of GP, and the insets show the microstructure change with the increase of annealing temperature. b) Raman spectra of GO paper, rGO paper and graphene paper. (A colour version of this figure can be viewed online.)

Raman spectra results are plotted in Fig. 1b. For pristine GO papers, lattice defects and oxygen functional groups are introduced during the process of graphite oxidation, as evidenced by the intense D band at near 1350 cm⁻¹ relative to the G band in the Raman spectra. Upon thermal annealing at 1100 °C, the D band has been depressed, indicating the gradual removal of defects during annealing. After being annealed at 2600 °C, the D band can no longer be identified, suggesting that the defects have been mostly removed [36,37]. Similar conclusion can also be drawn from the results of XRD and FT-IR spectra, as shown in Figs. S2a–b. Meanwhile, many gasbags are emerged in the interlayer of the GP during thermal reduction and graphitization (Figs. S2c–e), owing to the synergistic effect of gradually defects-healing, graphene sheets stacking, and gases expanding born from undocked dangling groups [15].

3.2. Stearic acid filled 3D graphene-foam composite

Through introducing nano-sized or micro-sized carbon-based fillers such as graphene nanosheets, carbon nanotubes and carbon black, the thermal conductivity of PCM (k_{PCM}) can be promoted [38,39]. Particularly, when carbon-based nanomaterials constitute a 3D continuous skeleton and form a heat transfer network, the k_{PCM} will be further improved. Here, a cost-effective template method was developed to prepare the 3D GF, as shown in Fig. 2a. Polyurethane (PU) sponge is chosen as the template material, because the sizes of its holes could be designed and PU could be completely ablated under high temperature. In Step 1, a piece of PU sponge is immersed into GO solution in vacuum, and GO nanosheets will coat onto PU skeleton, as shown in Step 2 of Fig. 2a and Fig. S3. Next, the GO coated PU foam is first heated to 1100 °C, and then graphitize at 2600 °C to finally obtain the GF, in which process PU will pyrolyze, which is also confirmed by TGA test of PU sponge (shown in Fig. S4). From the insets of Step 3, the dense and uniform holes varying from 550 µm to 600 µm, and the continuous skeleton of the GF can be clearly identified. In order to effectively store thermal energy, filling PCM into GF is a simple but effective solution. SA is chosen as the filling PCM, due to its relatively stable phase change temperature (T*) around 70 °C, which is close to the

limited operating temperatures of most electronic devices. Thus, it can not only prevent electronic devices from overheating, but also can ensure that lots of thermal energy will be stored as well. Thanks to the open holes and continuous graphene skeleton, when GF is immersed into the melt SA liquid, the liquid is able to thoroughly infiltrate into GF. At the same time, the GF can maintain its morphology and microstructure. In the final GFSAC, the holes of GF are full with SA which can be distinctly observed from the insets of Step 4 in Fig. 2a.

Mathematically, the thermal effusivity e is related to the thermal conductivity k and volumetric heat capacity C, as shown in Equation 1.

$$\mathbf{e} \cdot = \cdot \left(\mathbf{k} \mathbf{C} \right)^{1/2} \cdot = \cdot \left(\mathbf{k} \mathbf{p} \mathbf{C}_{\mathbf{p}} \right)^{1/2} \tag{1}$$

where ρ is the density and C_p is the specific heat. If PCM works at its phase change temperature, effective thermal effusivity, e_{eff} , could be defined as: $e_{eff} = (k\rho h)^{1/2}$, where *h* is the latent heat per unit mass.

1100 °C annealed rGO-foam and 2600 °C annealed GF were used to prepare the rGO-foam/SA composite and GFSAC. For GFSAC, the mass fraction of graphene is only 0.48%, while its thermal conductivity increases to 1.38 $Wm^{-1}K^{-1}$ for GFSAC at RT, as shown in Fig. 2b. DSC tests are conduted on SA and GFSAC to investigate their thermal stability, as shown in Fig. S5. The phase change temperature range of SA is 67.3 °C–72.1 °C, and the phase change enthalpy is 196.7 J/g. After the introduction of GF, the phase change temperature range of GFSAC has a small increase to 66.8 °C-73.2 °C, while the phase change enthalpy is reduced to 184 J/g. The decrease of phase enthalpy of the GFSAC is caused by the voids and gaps within the GFSAC, as shown in Fig. S6. The composite's e_{eff} is greatly improved from 4.15 Jcm^{-3/2}m^{-1/2}s^{-1/2}K^{-1/2} for SA to 15.93 Jcm^{-3/2} $^{2}m^{-1/2}s^{-1/2}K^{-1/2}$, illustrating the GFSAC possesses outstanding thermal energy storage capacity. Additionally, as shown in Fig. 2b-d, with the gradual removal of defects and recovery of crystallinity in GF, the thermal properties of GFSAC shows obvious improvement, compared with that of rGO-foam. This result proves that the GF skeleton plays an irreplaceable role in heat conduction



Fig. 2. Experimental procedure of GFSAC and thermal properties tests. a) Preparation process of GFSAC. b-d) Through-thickness thermal conductivity, phase change enthalpy and effective thermal effusivity of SA, rGO-foam/SA composite, GFSAC, GP/GFSAC/GP, G-GP/GFSAC/GP. (A colour version of this figure can be viewed online.)

and storage for this composite, although the mass fraction of graphene is very low. With reference to the TGA test at 30 °C–150 °C, shown in Fig. S5, it can be found that both SA and GFSAC exhibit good temperature stability in this temperature range without mass change, illustrating the GFSAC can work stablely in this designed temperature range. Furthermore, the thermal stability and reliability of GFSAC are evaluated through circle DSC test, as shown in Fig. S7. It can be found that the GFSAC possesses good thermal stability and its phase change temperature and phase change enthalpy have hardly changed after 60 phase transitions.

3.3. GP/GFSAC/GP composite

GP possesses a high in-plane thermal conductivity, which can effectively conduct the heat from the overheating point to the surrounding low-temperature region. GF/PCM composite has excellent capability to maintain structure temperature in a certain range, and can be developed as the energy storage and renewable material. Therefore, the combination of GP and GF/PCM composite is a potentially useful method to overcome overheating and overcooling problem at the same time with the least electric energy consumption.

At present, different parts of a thermal management structure are usually connected by heat-conducting glue or just simply by physical contact, which often brings problems such as high interfacial thermal resistance and reduced structure mechanical performance [15,20,24,40,41]. In order to obtain lower interfacial thermal resistance, a new method has been developed to connect GP and GFSAC, as shown in Fig. 3a. In detail, a piece of GP is placed at the bottom of the GFSAC and the structure is heated to the melting point of SA under vacuum condition. When SA is melted, the SA liquid in GFSAC will have a downward penetration tendency under the influence of gravity. The liquid SA will enrich at the bottom of the GFSAC, forming a convex liquid level, as shown in the insets of Fig. 3a. Once the liquid SA contacts GP at the bottom of GFSAC, the capillary force will drive SA liquid to fill the gap between GP and GFSAC. The good wetting properties between SA and GP (the average wetting angle is 70.06°, as shown in Fig. 3b), will allow SA liquid to fully wet GP. When the GP was replaced by graphite paper, SA liquid cannot fully wet its surface, and the average wetting angle between SA and graphite paper is 98.04°, as shown in Fig. S8. After SA is solidified, the GP and GFSAC are tightly connected with each other, and then, the GP on the other side is connected to the GFSAC through the same method. A feasible experiment has been designed to illustrate the necessity of gravity induced SA downward penetration for tight connection, as shown in Fig. S9 and movie 1, proving that GP and GFSAC can form effective connection through gravity-assisted wetting attaching process.

After combining with GP, the through-thickness thermal conductivity of GP/GFSAC/GP is further improved, from 1.38 Wm⁻¹K⁻¹ to $1.72 \text{ Wm}^{-1}\text{K}^{-1}$, as shown in Fig. 2b. This improvement is hypothesized to be related to the novel heat transfer mechanism of GP/GFSAC/GP composite, as shown in Fig. 3c-d. The thermal conductivity testing principle is shown in Fig. S10. When the heat flux reaches the bottom surface of GFSAC, as the thermal conductivity of surface is the same with that of internal, heat is transferred to the upper surface and diffused to the surroundings at the same speed. For the GP/GFSAC/GP composite, when the heat flow reaches the bottom surface, heat spreads more quickly along the GP, and transfers upward simultaneously with a much slower rate. The heat flow transfer mode of GP/GFSAC/GP composite allows more GF skeleton and PCM to participate in heat conduction, thus the structural temperature uniformity is improved. That means under the same intensity of pulse laser heating, GP/GFSAC/GP composite takes less time to reach the equilibrium temperature, so its measured through-thickness thermal conductivity is higher. In order to explore the synergy between 2D GP and 3D GFSAC on thermal conducting mechanism, GPs with different thicknesses of $3 \mu m$, $8 \mu m$ and $13 \mu m$ (measured by micrometer screw gauge) have been fabricated, numbered as GP1, GP2 and GP3. As the thickness increases, the thermal conductivity of GP decreases gradually, as shown in Fig. 3e. Next, GP1/GFSAC/GP1, GP2/GFSAC/GP2 and GP3/

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Fig. 3. Preparation process of GP/GFSAC/GP composite and thermal property tests at RT. a) Combination of GP and GFSAC to fabricate GP/GFSAC/GP composite, while the insets illustrate the mechanism of this process. b) The contact angle between GP and SA liquid. c-d) Heat transfer mechanism of GP/GFSAC/GP composite and GFSAC. e) In-plane thermal conductivities of GP1, GP2 and GP3, f) Through-thickness thermal conductivities of GP1/GFSAC/GP1, GP2/GFSAC/GP2 and GP3/GFSAC/GP3. (A colour version of this figure can be viewed online.)

GFSAC/GP3 have been prepared, and their through-thickness thermal conductivity has been tested, as shown in Fig. 3f. With the increase of the in-plane thermal conductivity of the 2D GP, the through-thickness thermal conductivity of GP/GFSAC/GP composite also increases, indicating that rapid in-plane heat conduction will indeed shorten the time for the structure to reach temperature equilibrium and improve the thermal management capacity.

In order to evaluate the thermal performance of GP/GFSAC/GP composite, heat-conducting glue is also used to connect GP and GFSAC, and the glue connected GP/GFSAC/GP (G-GP/GFSAC/GP) composite is prepared as a comparison. Interestingly, though the heat-conducting glue has a higher thermal conductivity (6 $Wm^{-1}K^{-1}$) than that of SA (0.13 $Wm^{-1}K^{-1}$), the through-thickness thermal conductivity of the G-GP/GFSAC/GP composite is only 0.53 $Wm^{-1}K^{-1}$, which is much lower than that of GP/GFSAC/GP

composite. The density of G-GP/GFSAC/GP composite is 1.02 g/ cm⁻³, which is a little higher than that of GP/GFSAC/GP composite (0.94 g/cm⁻³). The microstructure of GP/GFSAC/GP composite and G-GP/GFSAC/GP composite are further characterized. As shown in Fig. 4b and Figs. S11b and a thick bonding phase forms between the GP and GFSAC in G-GP/GFSAC/GP composite, which could greatly increase the thermal resistance during the through-thickness thermal conduction. Moreover, when connected with GP, the heat-conducting glue forms some mountain-like protrusions, as shown in Fig. 4d, indicating that the GP doesn't form complete connection with heat-conducting glue, but with many gaps, which will have adverse effect on heat conduction. However, for GP/ GFSAC/GP composite, a thin bonding phase forms during the gravity-assistant wetting-attaching process, which can be observed from Fig. 4a and Fig. S11a. After tearing the GP from GP/GFSAC/GP,



Fig. 4. The difference in bonding phase between GP/GFSAC/GP composite and G-GP/GFSAC/GP composite. a) Optical microscope images and SEM images of the connections between GP and GFSAC in GP/GFSAC/GP composite. b) SEM images of the connection between GP and GFSAC in G-GP/GFSAC/GP composite. c) SEM image of GP/GFSAC/GP composite surface after removing GP. e-f) The interface sketch of G-GP/GFSAC/GP composite and GP/GFSAC/GP composite. (A colour version of this figure can be viewed online.)

amounts of exposed GF skeleton and damaged SA (in the red circle of Fig. 4c) are found, which means under the help of this unique infiltration process, the GF skeleton in GFSAC could have many physical contacts with the GP, as shown in Fig. 4c. Meanwhile, it can also be seen in Fig. S12b that there are some SA residues on the torn surface of GP, indicating that GFSAC has formed a tight connection with GP.

When the electronic devices operate missions in harsh environment, they may experience repeated overheating and overcooling, thus the stability of their thermal management materials is particularly important. The samples of GP/GFSAC/GP and G-GP/GPSAC/GP are put into an oven together, and then heated to 90 °C with a heating rate of 5 °C/min. After being kept at 90 °C for 5 min, the samples are cooled down to 50 °C, and kept for another 5 min. After repeating the procedure 100 times, GP is still tightly connected to GFSAC (Fig. 4a), and the thermal conductivity only slightly decreases by 3.1% to 1.56 Wm⁻¹K⁻¹, exhibiting excellent reuse stability. However, for G-GP/GFSAC/GP composite, after undergoing 100 times repeated heating and cooling cycles, there appear obvious delaminations between the GP and GFSAC, as shown in Fig. 4b, causing a reduction in thermal conductivity, from 0.53 Wm⁻¹K⁻¹ to 0.36 Wm⁻¹K⁻¹. During the repeated heating and

cooling cycles, SA will undergo repetitive melting-solidification process and produce huge volume change. The bonding phase of GP/GFSAC/GP composite is relatively thin and flexible; thus, it could deform along with the volume change of the SA to ensure that GP is tightly connected to GFSAC. The higher thickness and rigidity of the bonding phase in G-GP/GFSAC/GP composite make it less flexible. Therefore, the G-GP/GFSAC/GP composite could not meet the deformation requirement of SA volume change.

The main difference between G-GP/GFSAC/GP composite and GP/GFSAC/GP composite is the connection, so the reason why their thermal performance difference is so large should also be the connection. Hence, in order to better explain this, a simple but useful heat transfer model according to the law of minimum resistance of heat transfer has been established to calculate the thermal resistance (R_b) of bonding phase. For G-GP/GFSAC/GP composite, as shown in Fig. 4e, it is composed of GP, GFSAC and bonding phase. With the addition of heat-conducting glue, two new interfaces appear, namely the interface between GP and heat-conducting glue, and the interface between heat-conducting glue and GFSAC. Therefore, the additional thermal resistance (R_{b1}) of G-GP/GFSAC/GP composite could be divided into three parts: 1) interfacial thermal resistance between GP and bonding phase (R_{CP})

_{BP}), 2) thermal resistance of bonding phase (R_G), and 3) interfacial thermal resistance between bonding phase and GFSAC ($R_{BP-GFSAC}$). For GP/GFSAC/GP composite, as shown in Fig. 4f, it also consists of GP, GFSAC and bonding phase, but there is only a new interface appearing, namely the interface between GP and bonding phase. That is because the bonding phase is grown from GFSAC, so there is no interface between bonding phase and GFSAC. The additional resistance (R_{b2}) of GP/GFSAC/GP composite only consists of two parts: 1) interfacial thermal resistance between GP and bonding phase (R_{GP-BP}), and 2) thermal resistance of the bonding phase (\overline{R}). Separately, the surface characteristic based model is applied to analyze the interfacial thermal resistance, and the law of minimum thermal resistance is used to calculate the material thermal resistance, as shown in Equation (2) [42].

$$\begin{cases} R_{i} = \frac{k_{1} + k_{2}}{2k_{1}k_{2}} \left(\frac{A_{n}}{A_{r}}\right)\sigma \\ R_{t} = \frac{I}{(A \cdot k)} \end{cases}$$
(2)

Where R_i is the interfacial thermal resistance, and R_t is the thermal resistance of material, k_1 , k_2 represent the thermal conductivity of the materials on two sides of the interface. σ is the roughness of the interface, A_n is the nominal area of interface, and A_r is the actual microscopic area of contact. *I*, *A* and *k* represent the thickness, area and thermal conductivity, respectively.

The thickness of bonding phase is tested through SEM. The thickness of bonding phase is 163.95 µm for G-GP/GFSAC/GP composite, and 17.66 µm for GP/GFSAC/GP composite. The average thermal conductivity \overline{k} of bonding phase in GP/GFSAC/GP composite is 233.86 $Wm^{-1}K^{-1}$, calculated by the law of minimum thermal resistance (Supplementary Discussion 1). Additionally, it is assumed that different parts are ideally connected, and A_n is equal to A_r . Thus, according to Equation (2), $R_{b1} = (3.036 + 0.085\sigma_{GP} + 0.446\sigma_{GFSAC})$ KW⁻¹, and $R_{b2} = (0.008 + 0.003\sigma_{GP})$ KW⁻¹, which is much lower than R_{b1} . As the value of σ_{GP} and σ_{GFSAC} is relatively small, the thermal conductivity can be roughly calculated after ignoring the effect of interface roughness on thermal resistance, the thermal conductivity of GP/ GFSAC/GP composite is 1.03 Wm⁻¹K⁻¹, and the thermal conductivity of G-GP/GFSAC/GP composite is 0.15 $Wm^{-1}K^{-1}$ (Supplementary Discussion 2). The theoretical calculation results are consistent with the test results, proving that the GP/GFSAC/GP composite prepared by gravity-assisted wetting-attaching process has much more excellent heat conduction capabilities, and providing a prerequisite for further exerting the thermal energy storage advantages of GP/GFSAC/GP composite. The e_{eff} of GP/GFSAC/GP composite reaches 18.45 Jcm^{-3/2}m^{-1/2}s^{-1/2}K^{-1/2}, while that of G- G/GFSAC/GP composite is only 8.34 Jcm^{-3/2}m^{-1/2}s^{-1/} ${}^{2}K^{-1/2}$. Therefore, through properly connecting 2D GP and 3D GFSAC, it can effectively reduce the thermal resistance and improve the thermal performance of composite. Comparison of the e_{eff} of GP/GFSAC/GP composite with the previous literature is made and shown in Fig. 5. The materials is Fig. 5 are isotropic and used to store energy (Supplementary Table 1), so the T* is chosen between 60 °C and 80 °C. As it can be seen from Fig. 5, the energy storage capacity of GP/GFSAC/GP composite reaches a relatively high level. Besides, among these reports, GP/GFSAC/GP composite has the lowest filler content.

3.4. Thermal management capability

To evaluate the structure's heat management capability, PHS heating method and plate source heating method are applied. The

PHS heating method is shown in Fig. 6a and Fig. S13. It can be found from Fig. 6b that the RT maintains at about 19.8 °C, while the temperature of the PHS stabilizes near 203 °C. With the heating time increasing, the bottom temperature (BT) of samples continues to increase, and the increasing rates of GP/GFSAC/GP composite and aluminum fin are higher than others, indicating better throughthickness thermal transfer capability. In addition, the increasing rate of temperature gradually decreases, for GP/GFSAC/GP composite, G-GP/GFSAC/GP composite and GFSAC. This is because that with the heat transferring, more and more PCM takes part in heat absorption, and the thermal energy is stored as latent heat of PCM. For aluminum fin, as the temperature rises, the radiative dissipation capability increases fastly, balancing heat absorption and heat dissipation. After heating for 180s, the BT of GP/GFSAC/GP composite reaches 40.8 °C, which is comparable to that of aluminum fin (39.8 °C), while the BTs of GFSAC and G-GP/GFSAC/GP are both below 39 °C. Besides, after stop heating, the aluminum fin only takes 238 s to cool down to RT, while the GP/GFSAC/GP composite can maintain the temperature above RT even after 420 s. The GP/ GFSAC/GP composite has not only great through-thickness thermal transfer ability, but also good heat preservation ability, which is extremely important to temperature sensitive devices which have to work in a permit temperature range. When these devices are in operation state, the composite can store excess heat to avoid exceeding the upper temperature limit. When the devices are in standby mode, the composite can release thermal energy stored in the PCM to prevent the temperature falling below the lower temperature limit.

After heating for 180s, the temperature field information is collected by the infrared camera (Fig. 6c–f). The maximum temperature on the top surface of the GP/GFSAC/GP composite is 42.6 °C, while the minimum temperature is 35.4 °C, the temperature difference on its top surface is only 7.2 °C. For GFSAC, the maximum temperature of its top surface is 89.9 °C, which is much higher than the melting point of SA, and there exists a huge temperature difference of 56.2 °C between different regions on the surface of GFSAC. An obvious melting mark could be observed on the surface of GFSAC, while this could not be found on the GP/GFSAC/GP composite, as shown in Fig. 6g–h, proving the GP on the surface of the GP/GFSAC/GP composite does efficiently transfer the heat of the PHS to the surrounding region, reduce the temperature at the heat concentration point, and greatly improve the temperature uniformity of the structure.

It's worth to mention that the surface temperature field of G-GP/ GFSAC/GP composite is not as uniform as that of GP/GFSAC/GP composite. The surface peak temperature of G-GP/GFSAC/GP composite reaches 90.2 °C, which is far above the phase change temperature of SA. However, its bottom temperature is only 37.4 °C, showing a huge temperature gradient across the composite. Additionally, from the side IR photographs, it could be observed that GP/ GFSAC/GP composite shows the most uniform distribution. It's because that huge amount of highly concentrated thermal energy at the point is quickly transferred to the entire composite by the GP skeleton. As a result, its internal temperature field possesses excellent uniformity, and the thermal energy storage capability of SA is fully utilized.

The GP/GFSAC/GP composite's thermal management capability under plate heating is also measured, as shown in Fig. S14. The difference between PHS and plate heating is that a thermostatic heating plate is used to heat the lower surfaces of all the samples at the same time in plate heating. All samples are in RT of 19 °C before heating. After the plate is heated for 5 min, the bottom of the SA melts, and some SA liquid leaks from the bottom of the GFSAC, while the GP/GFSAC/GP composite maintains its structure. Through the IR photographs, it can be found that the temperature



Fig. 5. Comparison of effective thermal effusivity. Comparison of effective thermal effusivity for phase change materials measured in the literature and this work (references [2,10,40,43–45]). The two data lines enclosed in the rectangle refer to this work for GFSAC and GP/GFSAC/GP composite. (A colour version of this figure can be viewed online.)



Fig. 6. PHS heat experiment. a) Sketch of the PHS heat experiment. b) Temperature change of different samples, a PHS was used to heat at the center of the sample, after heating for 3 min, PHS was removed and sample cooled naturally. c-f) Infrared photograph of GP/GFSAC/GP composite, G-GP/GFSAC/GP composite, GFSAC and aluminum fin. g-h) Optical photograph of GP/GFSAC/GP composite and GFSAC after heating. (A colour version of this figure can be viewed online.)

distribution of the GP/GFSAC/GP composite is the most uniform (about 60 $^{\circ}$ C) and there is no heat accumulation. However, there exists obvious heat accumulation at the bottom of the GFSAC, which is harmful to PCM storing energy. Although the aluminum

fin maintains a relative low temperature level of about 53 °C, its temperature rapidly reduces to room temperature after stopping heating for 1.5 min. While the GP/GFSAC/GP composite can keep its temperature above 25 °C after stopping heating for 7 min.

4. Conclusion

In summary, a novel method to achieve high TCE and $e_{\rm eff}$ in graphene-based thermal management structure by combining 2D GP and 3D GFSAC is demonstrated. The thermally conductive GP is constructed by highly oriented graphene nanosheets, so it possesses excellent in-plane thermal conductivity and can effectively transfer the highly concentrated heat to the surrounding lowtemperature region. Additionally, the GF skeleton in GFSAC not only provides a network channel for heat transfer, but also acts as a self-supporting structure to prevent leakage of SA. In the final graphene-based thermal management structure, GP and GFSAC achieve a low thermal resistance connection through the gravityassistant wetting-attaching method, and the mass fraction of graphene accounts for only 0.53%, which can maximize the energy storage performance of the composite. As a result, GP/GFSAC/GP composite can not only prevent electronic devices from overheating, but also avoid problems due to overcooling at the same time.

CRediT authorship contribution statement

Gengyuan Liang: Conceptualization, Methodology, Software, Formal analysis, Writing - original draft. Jianwei Zhang: Writing review & editing, Project administration, Funding acquisition. Shaohang An: Investigation, Resources. Jun Tang: Visualization, Data curation. Su Ju: Validation. Shuxin Bai: Supervision. Dazhi Jiang: Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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