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Preparation a three-dimensional hierarchical graphene/stearic acid as a phase change materials for thermal energy storage

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Abstract

Three-dimensional hierarchical graphene (3DHG) was compounded with stearic acid (SA) to obtain SA/3DHG composite phase change materials (PCMs). The specific surface area and pore volume of 3DHG are 393 m$^2$ g$^{-1}$ and 0.57 m$^3$ g$^{-1}$. The phase-transition temperatures of SA/3DHG composites keep at 69 ± 1 °C with different adding amounts of 3DHG, meanwhile SA/3DHG-3 possesses the melting enthalpy of 189.7 J g$^{-1}$ and solidifying enthalpy of 188.8 J g$^{-1}$. 3DHG shows significant enhancement on the thermal properties and shape stability of SA. The thermal conductivity of SA/3DHG-3 reaches to 0.93 W m$^{-1}$ K$^{-1}$, which is as high as 2.8 times of pure SA (0.33 W m$^{-1}$ K$^{-1}$). The investigations of XRD and FTIR indicate that no chemical but physical combination occurs between SA and graphene. 3DHG has substantial meso-porous/macro-porous structure for packaging SA to form the irregular core–shell structure. The hierarchical pores are also beneficial to the graded thermal transfer inside SA/3DHG composite PCMs. The efficiency of heating process from 25 °C to 90 °C was improved by about 57%. Furthermore, the 3D network skeleton built up by graphene sheets can form an effective and connected heat transfer paths for SA, thus improves the endothermic and exothermic efficiency of SA/3DHG composite PCMs. This work emphasizes the 3D hierarchical structure of graphene and provides a promising way to prepare composite PCMs with high large storage density and heat transfer efficiency.

1. Introduction

Solar energy is a promising thermal source to meet energy demand without harmful effects to environment, thus it plays an important role for energy sustainable development. In order to reduce the imbalance of thermal energy and improve the utilization level of solar energy, developing efficient energy storage devices and systems is an effective solution [1–3]. Thermal storage technology acts a pivotal part in the application of heat storage and transformation. Latent heat phase change materials (PCMs) possesses excellent thermal storage capacity, preferable thermal stability and constant storage temperature, which have been studied extensively [4–6].

Organic PCMs have good chemical and physical stability, small volume variation, and negligible supercooling [7, 8], thus they were utilized wildly in the fields of solar energy storage [9], building energy efficiency [10–12], intelligent textiles [13, 14], and electronics [15]. Stearic acid (SA) has suitable phase transition temperature (69 ± 1 °C) and large latent heat (200 ± 2 J g$^{-1}$) and can melt with most other fatty acids forming multi-component eutectic mixture to adjust the melting temperature [16, 17]. However, the low thermal conductivity and leakage, as common disadvantages of all organic PCMs, limit the applications of SA in some cases [18, 19]. The feasible preparation of composite PCMs using carbon materials, such as expanded graphite [20, 21], carbon nanospheres [22, 23], graphene oxide (GO) [24], and carbon nanotubes [25] have been investigated. The additives supply a black surface and thermal transfer ways in PCM matrix to enhance its
thermal conductivity. Chen et al. [26] used porous carbon spheres as a supporting material to polyethylene glycol, which had large melting enthalpy of 112.08 J g⁻¹ and solidification enthalpy of 107.34 J g⁻¹. Wang et al. [27] fabricated a flexible carbon foam (CF)-based PCMs, which has great leakage-proof ability and thermal stability. Unfortunately, most of researches show the poor adsorption capacity of carbon additives, which results in the significant reduction of the phase change enthalpy. Therefore, it is an important issue for future research to investigate high thermal conductivity additives with superior adsorption performance. Porous carbon materials supply large porosity and surface area as well as a well-interconnected network to PCMs. Porous carbon/PCM composites can maximizes its thermal conductivity at the minimum sacrifice of thermal enthalpy.

Graphene has single-atom thick and flexible sheet structure made of hexagonal arrangement of bonded carbon atoms. Owing to its large surface area and high aspect ratio, graphene possess excellent electrical, electrochemical, thermal and mechanical properties [28–30]. A large amount of work indicates that graphene and chemically modified graphene has potential application prospects in the fields of electro catalysis, field effect devices, chemical and biological sensors, polymer composites, and energy storage materials [31, 32]. Li and Wang [33] studied a composite PCMs made up of polyethylene glycol (PEG) and GO, which has a strong visible light collection capacity and stored heat 80 kJ kg⁻¹. Atinafu et al. [34] prepared a Multifunctional composite PCMs prepared by in situ synthesis. The thermal storage capacity of the composite phase change material is as high as 101.4% and the photo thermal conversion capacity is as high as 78%. In order to discover the effect of graphene, Yu exhibited the thermal and electrical analyses of PEG/Graphene composite materials and found the significantly enhancement in both capacity.Remarkably, the combination of graphene and PCMs has advantages of synergistic growth in the thermal properties [35]. Graphene sheets possess high specific surface, excellent thermal conductivity and the ability to spontaneously assemble into a 3D structure, which is an excellent material for thermal conductivity enhancement. Therefore, the development and preparation of graphene-based composite PCMs is an effective solution to meet the demanding of energy storage and conversion applications.

In this paper, the preparation and thermal properties of SA/three-dimensional hierarchical graphene (3DHG) composite PCMs are presented. 3DHG were reduced from graphene oxide by adding ascorbic acid and freeze drying treatment. The 3DHG was integrated with SA via vacuum impregnation to obtain SA/3DHG composite PCMs. The porous structure of 3DHG can absorb and fully contact with melted SA due to its high specific surface area and large pore volume. Simultaneously, the 3DHG constructed by continuous graphene skeletons serve as heat transfer fins in the SA/3DHG composite PCMs. Consequently, the 3DHG equipped the SA/3DHG composite PCMs with superior thermal performance and negligible decrease on phase transition enthalpy for low-temperature thermal storage.

2. Experimental

2.1. Materials

Stearic acid (SA, CH₃(CH₂)₁₄COOH, analytically pure), graphite (C), sulfuric acid (H₂SO₄, ≥98%), potassium permanganate (KMnO₄, analytically pure), hydrogen peroxide (H₂O₂, 30%), hydrochloric acid (HCl, 10%), Sodium nitrate (NaNO₃, analytical reagent) and L-ascorbic acid (C₆H₈O₆, analytically pure) were supplied by Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of graphene oxide, 3DHG and SA/graphene composite PCMs

Modified Hummers method was adopted to prepare GO using natural flake graphite [36]. Firstly, natural flake graphite (1 g) were blended with H₂SO₄ (23 ml) in a beaker by agitating magnetically at 30 °C for 24 h to guarantee the uniformity, then adding NaNO₃ (0.1 g) and stirring for 5 min. The obtained mixture was oxidized by 3 g KMnO₄ under an icy bath for 0.5 h. The oxidation process was terminated with adding H₂O₂ (10 ml) slowly. Then adding 120 ml deionized water and 10 ml HCl were used in metal removal. Subsequently, the blend was filtered and rinsed with deionized water until pH was neutral. Afterwards, exfoliation was performed by ultrasonic for 1 h, and the centrifugation at 5000 rpm for 30 min was adopted to remove unexfoliated GO layers. According to the electrostatic repulsive forces formed by ionization of carboxylic groups [37, 38], GO sheets dispersed stably in aqueous solution. Finally, GO were collected after placing the supernatant in a freeze-drying oven for 23 h.

3DHG was synthesized facilely and rapidly. 5 mg GO was distributed into 20 ml deionized water, followed by ultrasonication for 2 h. The process of reducing of GO and self-assembling of graphene were prompted by adding 10 mL ascorbic acid (10 g L⁻¹) with oil bath at 95 °C for 2.5 h. The product was washed by deionized water and alcohol. Finally, the 3DHG was dried by freeze drying for 23 h. For comparison, RGO sheets were prepared by adding ascorbic acid to GO solution with ultrasonic dispersion treatment.
The synthesis of composite PCMs was done by a vacuum impregnation method. The corresponding mass ratio of 3DHG was slowly added to the melted SA in water bath with magnetic stirring for 1 h. Subsequently, the preparation was completed after treating the samples with vacuum adsorption for 6 h. Composite PCMs with 1 wt.%, 2 wt.% and 3 wt.% of 3DHG are labeled as SA/3DHG-1, SA/3DHG-2, and SA/3DHG-3. The 1 wt.% graphene oxide and 1 wt.% RGO were also compounded with SA followed by the above steps to make the SA/GO-1 and SA/RGO-1 composite PCMs, respectively.

2.3. Experiment instruments
The micro-morphology of samples was observed using emission scanning electron microscopy (SEM, JEOL, Japan) and JEM-2100F transmission electron microscopy (TEM, JEOL, Japan). The reduction of GO is determined by x-ray diffractometer (XRD, Japan) with Cu Kα irradiation (λ = 0.154 06 nm) and the x-ray photoelectron diffraction energy spectrometer (XPS, ESCALAB, USA) which testing the combined state of the samples. In order to measure the chemical compatibility of composites, fourier transform infrared spectroscopy (FTIR, Nicolet 6700, USA) was adopted at the range of 400–4000 cm⁻¹. N₂ adsorption-desorption isotherms were conducted by the accelerated surface area and porosimetry system (ASAP 2020, USA) to investigate the specific surface area and pore-size distribution of samples. Multi-point BET (Brunauer–Emmett–Teller) was applied to calculate the specific surface area of the sample (SBET) with the range of 0.05–1.0 relative pressure (P/P0). The phase change temperatures and enthalpies of composite PCMs were acquired by differential scanning calorimetry (DSC 3500, UAS) from 20 °C ~ 100 °C at a heating and cooling rate of 5 °C min⁻¹ under nitrogen atmosphere. Hot disk constant analyzer (TPS2500S, Hot Disk, Sweden) was utilized to measure the thermal conductivity of samples using transient plane heat source method. The charging and exothermic properties were collected by a data recorder (NHR-8700B, China) between 25 °C ~ 90 °C. Thermal stability of the samples were tested by thermal gravimetric analyzer (Discovery TGA, USA) under nitrogen atmosphere with heating rate of 10 °C min⁻¹.

3. Results and discussions
3.1. Microstructure of SA/3DHG composite PCMs
The microstructures of 3DHG and SA/3DHG-3 composite PCM were showed in figure 1. Figures 1(a) and (b) are SEM and TEM images of 3DHG, respectively. 3DHG has abundant graded pores with irregular folds caused by its ultrathin feature, which can package SA to form the irregular core–shell structure. The overlapping and interlocking graphene sheets with flexibility built up the connected 3D structure of 3DHG, which can provide continuous thermal conductive channels for heat transport inside the SA/3DHG composite PCMs. Figures 1(c) and (d) are SEM images of SA/3DHG-3 composite PCMs. Obviously, SA is adsorbed and filled in the pores by
the capillarity of 3DHG, and the 3D skeleton constructed by 3DHG nano-graphite sheets is covered. The boundary surfaces between SA and graphene sheets combined compactly because of the hydrophobic and high contact area formed from the 2D lamellar structure of graphene, which to some extent can prevent the leakage and fluidity of melted SA. The graphene sheets of 3DHG is still connected to each other in SA/3DHG-3 sample, and the three-dimensional heat transfer network structure is still constructed, which can improve the efficiency of heat transition in the exothermic/endothermic process of SA. In order to test the thermal conductivity, the samples were pressed in a mould at 10 MPa pressure for 10 min. Figure 2 displays the images of SA/GO-1, SA/RGO-1, and SA/3DHG-1 composite PCMs from left to right. The darkest color of SA/3DHG-1 sample indicates the best compatibility of SA and 3DHG.

3.2. Components of SA/graphene composite PCMs
The XRD patterns of GO, RGO, and 3DHG are depicted in figure 3(a), which can characterize the differences in phase structure and crystallinity of the samples. It can be seen that a characteristic diffraction peak of GO lies at 12.5° (001), which signifying the formation of oxygen functional groups of GO resulted by the drastic oxidation reaction and the intercalation of water molecules [39]. RGO exhibits a broad diffraction peak at 18°–28°, and the disappearance of the primary peak at 12.5°, both meaning the successful reduction of GO using L-ascorbic acid [40]. In addition, 3DHG shows a similar XRD pattern with RGO. XRD spectra were also used to observe the phase change of SA before and after compounding with additives, and to determine the type of reaction in the compounding process. Figure 3(b) shows the XRD spectra of SA, SA/GO, SA/RGO and SA/3DHG composite PCMs. The sharp and intense diffraction peaks at 6.8°, 11.2°, 21.6° and 23.2° are the characteristic peaks of SA [41], which still existed in the XRD spectra of SA/GO, SA/RGO and SA/3DHG composite PCMs. Besides, the crystallinity of SA changes slightly with the addition of graphene, and the intensity of diffraction peak also changes. However, the diffraction peak of SA composite PCMs is only the superposition of the diffraction peak of SA and graphene, and no new diffraction peak is produced. As a consequence, the process of preparing the composite PCMs is a physical combination, and composite PCMs still retain the original composition and thermophysical properties of SA.

Figure 4 displays the FTIR diagrams of SA, SA/GO, SA/RGO and SA/3DHG composite PCMs, which is adopted to investigate the chemical compatibility between SA and the high thermal conductivity additives. For pure SA, the peaks set at 2920 and 2839 cm⁻¹, which manifest the asymmetric and symmetric stretching vibration of –CH₂ group, respectively. The peak at 719 cm⁻¹ states the in-plane oscillation of the –CH₂ functional group. The absorption peak at 1703 cm⁻¹ is the stretching vibration of C=O group [42]. The wide peak around 2500–3200 cm⁻¹ implies the stretching vibration of –OH group. In the spectra of composite PCMs, the major peaks of composite PCMs were consistent to that of SA. In addition, the infrared spectra composite PCMs show that the absorption peaks of 2500–3200 cm⁻¹ are broadened due to the superposition of the absorption peaks of SA and graphene. The above results indicate that there is no chemical reaction and only physical bonding in the composite process, which also approves the results of XRD analysis.

3.3. Chemical states of elements
The XPS spectrum of the 3DHG in figure 5(a) present the peaks belong to C–1s ≈ 283.8 eV, 286.1 eV and 288.7 eV, corresponding to C–C, C–O and O=C–O bonds, respectively. It is obviously that the intensity of C–C bond peaks are significantly higher than those at C–O and O=C–O, which means that the oxygen-containing groups on the surface of the 3DHG are reduced by ascorbic acid during heating process. Figure 5(b) displays the
Figure 3. XRD patterns of (a) GO, RGO and 3DHG (b) SA, SA/GO, SA/RGO and SA/3DHG composite PCMs.

Figure 4. FTIR spectra of SA, SA/GO, SA/RGO and SA/3DHG composite PCMs.
high resolution spectrum of O 1 s of 3DHG. It can be seen that the chemical state of O on the surface of 3DHG is mainly adsorbed water (H 2ads, binding energy is 533.2 eV), and a small amount of hydroxyl (–OH, binding energy is 531.2 eV), which further indicate that the oxygen-containing groups of 3DHG were mostly reduced. These results confirm that the 3DHG are successfully prepared, which is coincident with the XRD results (figure 3).

3.4. BET surface area and pore distribution of 3DHG

N2 adsorption–desorption isotherms were measured to study the specific surface area and pore-size distribution of RGO and 3DHG. Clearly, the pore-size distribution curves have a form of IV hysteresis loop in figure 6, signifying the presence of mesopores and macropores in samples. The average pore size of 3DHG is mainly distributed between 10 nm–100 nm, while the pore size distribution of RGO is mainly concentrated between 2 nm–10 nm. Furthermore, 3DHG possesses a BET surface area about 393 m² g⁻¹ and the pore volume of 0.57 m³ g⁻¹ in table 1, what are larger about 3 times of those RGO (133 m² g⁻¹, 0.32 m³ g⁻¹). The 3DHG with higher area and porosity can improve the adsorption rate to reserve more melted SA in composite PCMs. In addition, the mesoporous and macropores in 3DHG contribute to the formation of efficient thermal transfer skeleton. Therefore, the 3DHG facilitates improving the thermal conductivity of composite PCMs.
3.5. Latent heat, initial temperature and melting temperature of SA/graphene composite PCMs

The phase change temperature and enthalpy play a decisive role to estimate the thermal performance of PCMs, which reflect the quality of heat storage capacity. Figure 7 displays the DSC graph of SA, SA/3DHG composite PCMs, and two primary phase transition peaks are observed distinctly. The peaks are created by the heterogeneously nucleated rotator-liquid phase transformation, which signifies the solid–liquid phase transition of SA. The thermal energy storage date of SA, SA/GO, SA/RGO, and SA/3DHG composite PCMs with various contents of corresponding additives are summarized in table 2. It can be found that the melting and solidification temperatures of pure SA are 69.85 °C and 67.53 °C, respectively. A slight change in the phase change temperatures of composite PCMs are observed, which indicates that the carbon additives have negligible effect on phase change temperature. According to table 2, SA demonstrates a high thermal energy storage density with the melting and solidifying enthalpies of 223.63 J g⁻¹ and 225.67 J g⁻¹. Moreover, SA/3DHG-3 possesses the melting latent heat of 189.7 J g⁻¹ and solidifying latent heat of 188.8 J g⁻¹. The phase change latent heat of SA/3DHG composite PCMs decline with the rise of graphene mass fraction on account of the increasing substitute of the working substance with fillers. Generally, the SA/3DHG composite PCMs are good choice for thermal storage because of its small addition and little reduction in latent heat of composites.

| Samples | S_{BET}(m² g⁻¹) | V_{pore}(m³ g⁻¹) | d_{pore}(nm) |
|---------|----------------|-----------------|--------------|
| RGO     | 133            | 0.32            | 11.8         |
| 3DHG    | 393            | 0.57            | 5.8          |

Table 1. BET data of RGO and 3DHG.

![DSC curves of SA/3DHG composite PCMs.](image)

Table 2. Phase change temperatures and phase change enthalpies of SA, SA/GO, SA/RGO and SA/3DHG composite PCMs.

| Sample        | T_m(°C) | ΔH_m(J·g⁻¹) | T_s(°C) | ΔH_s(J·g⁻¹) |
|---------------|---------|-------------|---------|-------------|
| SA            | 69.9    | 223.6       | 67.5    | 225.7       |
| SA/GO-1       | 69.4    | 223.9       | 68.4    | 225.4       |
| SA/GO-2       | 70.2    | 223.4       | 68.5    | 225.2       |
| SA/GO-3       | 69.7    | 215.3       | 68.4    | 213.9       |
| SA/RGO-1      | 69.7    | 220.3       | 68.4    | 220.9       |
| SA/RGO-2      | 69.8    | 206.4       | 68.2    | 210.9       |
| SA/RGO-3      | 69.9    | 189.1       | 63.7    | 185.1       |
| SA/3DHG-1     | 69.4    | 215.9       | 68.3    | 217.5       |
| SA/3DHG-2     | 69.5    | 205.9       | 68.4    | 211.1       |
| SA/3DHG-3     | 69.3    | 189.7       | 63.6    | 188.8       |

Figure 7. DSC curves of SA/3DHG composite PCMs.
3.6. Thermal conductivity of SA/graphene composite PCMs

Thermal conductivity is a crucial parameter to measure the performance of thermal storage materials. Figure 8 lists the thermal conductivity of SA and composite PCMs. The thermal conductivity of SA is 0.33 W m$^{-1}$ K$^{-1}$, which curbs the utilization of SA in thermal storage and transmission [43]. Furthermore, the thermal conductivity of SA/GO-3 and SA/RGO-3 composite PCMs rises to 0.45 W m$^{-1}$ K$^{-1}$ and 0.59 W m$^{-1}$ K$^{-1}$ after introducing GO and RGO, respectively. For SA/3DHG composite PCMs, the improvement of thermal conductivity is much dependent on the additive contents of 3DHG. It is notable that SA/3DGH-3 composite PCMs possesses a thermal conductivity at up to 0.93 W m$^{-1}$ K$^{-1}$, which is increased by 281% compared with pure SA. The 3DHG has large specific surface area and meso-porous/macro-porous structure, which is easy to expand the contact area with SA. In addition, the three-dimensional network skeleton structure constructed by graphene sheets can form an effective and connected heat transfer channel in SA, and improve the endothermic and exothermic efficiency of SA PCMs. Therefore, SA/3DHG composite PCMs have a good enhancement on the thermal conductivity, which can significantly increase the endothermic and exothermic efficiency.

3.7. Thermal storage and release efficiency of SA/graphene composite PCMs

Charging and exothermic properties of pure SA, SA/GO, SA/RGO and SA/3DHG composite PCMs are collected by a data logger, which are the most intuitive manifestation of heat transfer performance for PCMs. Figure 9 displays the thermal storage and release curves of pure SA and SA/GO, SA/RGO and SA/3D RGO composite PCMs. From figure 9(a), it can be observed that the temperatures of SA composite PCMs rise gradually with heating time elapse, and SA composite PCMs have a larger slope in the heating curve than pure SA at the beginning of heating, which corresponds to a faster heating rate. The order of the heating rate from room
temperature to 90 °C is SA/3DHG > SA/RGO > SA/GO > pure SA, which further proves that the filling of carbon materials improves the thermal properties of SA, and 3DHG has optimization influence on thermal performance. The heating time of pure SA from 25 °C to 90 °C is 1783 s, while that of SA/3DHG is only 767 s, which is 1016 s less than that of pure SA. In order to further reflect the modification and optimization of composite PCMs, the exothermic curves were collected in figure 9(b). The excellent thermal charging and releasing properties of SA/3DHG composite PCMs can be attributed to those two reasons. (1) Three-dimensional continuous graphene skeleton in 3DHG can provide a good heat transfer channel for the adsorbed SA, making the heat storage and release faster. (2) Micro porous and high specific surface area of 3DHG can increase the adsorption mass and contact area with SA, then the heat transfer of composite PCMs was improved. The above results indicate that 3DHG can be used as an effective PCM filler, which can greatly increase the endothermic and exothermic rates of pure PCMs, and also prove its practical significance in wide application.

### 3.8. Thermal stability of SA/graphene composite PCMs

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of SA/3DHG composite PCMs and pure SA were measured by STA 2500 thermogravimetric analyzer. Figures 10(a) and (b) are TG and DTG results of pure SA and SA/3DHG composite PCMs, respectively. Combining the TG and DTG curves of SA, it can be found that the SA only has a single thermogravimetric process, which is the volatilization of SA fat chain when it is heated from 100 °C to 500 °C. The process of thermal weightlessness can be reflected directly in the DTG curves. The DTG curve vertex of SA/3DHG composite PCMs obviously moves towards higher temperature than that of pure SA. The $T_{\text{max}}$ mass loss rate of SA is 260 °C, while that of SA/3DHG composite PCMs is 275 °C, which increases by 16 °C. The results manifest that 3DHG can retard the vaporization of SA, which could improve the thermostability of SA.

In order to better understand the advantages of SA/3DHG composite PCMs, the comparison of thermal properties with different filler from recently literatures are listed in table 3. It can be clearly seen that SA/3DHG composite PCMs prepared in this work exhibit high thermal enthalpy, suit phase change temperature and high conductivity with the minimal amount of filler among the organic composite thermal storage materials. Those

| References | Filler          | Matrix          | Filler content wt% | $T_m$ (°C) | Thermal enthalpy (kJ kg$^{-1}$) | Thermal conductivity (W m$^{-1}$ K$^{-1}$) |
|------------|-----------------|-----------------|-------------------|------------|---------------------------------|---------------------------------------------|
| [42]       | Graphene aerogel| Palmitic acid   | 2                 | 64.7       | 198.0                           | 0.41                                        |
| [44]       | porous carbonized woods | Lauric acid | 18.9             | 41.0       | 177.9                           | 0.23                                        |
| [45]       | Graphene       | OD              | 4                 | 56.8       | 181.5                           | 0.91                                        |
| [46]       | CNT            | Steric acid     | 7                 | 70.8       | 186.6                           | 0.51                                        |
| [47]       | Expanded vermiculite | Lauric acid | 30                | 41.0       | 126.8                           | 0.49                                        |
| [48]       | CNT/expanded perlite | Paraffin | 15                | 43.7       | 95.98                           | 0.51                                        |
| present work | SA/3DHG     | SA              | 3                 | 69.3       | 189.7                           | 0.93                                        |
excellent thermal properties can significant increase the energy storage efficiency and reduce the size of heat storage devices.

4. Conclusions

3DHG was successfully reduced from two-dimensional graphene oxide by adding ascorbic acid and heating treatment. The uniform and stable SA/3DHG composite PCMs were obtained by melt blending and vacuum adsorption methods. The 3DHG shows large specific area of 393 m² g⁻¹ and pore volume of 0.57 m³ g⁻¹. Meanwhile, the abundant meso-porous and macro-porous structure can increase the capillary of 3DHG to keep the melted SA filled in the graded porous structure. There is no chemical reaction in the preparation of the composites, and the XRD spectra of samples show the doubling of the characteristic peaks of graphene and pure SA. The impact of graphene on the phase transition temperature of SA is small, but the measured phase change enthalpy is slightly lower than the theoretical value because of the abnormal interaction between pore structure and surface of 3DHG and SA. The melting and solidifying enthalpies of SA/3DHG-3 are 189.7 J g⁻¹ and 188.8 J g⁻¹. SA/3DHG-1 composite PCMs show that the heat charging time was 1016 s less and the heat releasing time was 2376 s less than that of pure SA. The TG and DTA data signify that SA/3DHG composite PCMs exhibits better thermal stability than SA. The thermal conductivity of SA/3DHG is 0.93 W m⁻¹ K⁻¹. The three-dimensional network skeleton constructed by graphene sheets can form an effective and connected heat transfer channel in SA, and improve the endothermic and exothermic efficiency and thermal stability of SA PCMs. SA/3DHG composite PCMs can be used for heat dissipation and temperature control of small high precision instruments to make them have the best working efficiency. In order to promote the wide application of composite PCMs, it is necessary to simplify the preparation process, control the pore size of graphene and further improve the thermal conductivity. This method could be expanded by other organic PCMs with the hierarchical 3D network structure graphene and adopted in the application for thermal energy storage and transmission.

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