

Overcoming the supercooling of hydrated salts: three-dimensional graphene composite PCMs

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Novel composite phase change materials (PCMs) based on three-dimensional reduced graphene oxide (3D-rGO) were fabricated. Both borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and 3D-rGO were used to reduce the supercooling degree of sodium sulphate decahydrate. The T-history method was used in studying the effect of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 3D-rGO on supercooling of PCM. It was found that both borax and 3D-rGO can reduce the supercooling degree of the composite PCMs, and the positive synergy effect between 3D-rGO and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is significant. These results provide valuable guidance for improving the phase transition properties of hydrated salts.

1. Introduction: In recent years, phase change material (PCM) has become the focus of energy utilisation and material science [1, 2]. Phase change energy storage technology as an approach to solving the contradiction between supply and demand of energy is studied by the researchers in various countries around the world. During the phase change, PCM can store and release a large amount of latent heat by exchanging energy with the surrounding environment. Hydrated salts such as low-temperature PCMs exhibit many advantages such as low-phase transition temperature, large latent heat storage, small volume change, low pollution and so on. Sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is a typical hydrated salt, whose latent heat-storage density is larger than that of most organic PCMs and has a suitable phase transition temperature [3, 4]. However, its intrinsic large supercooling, a status where melted $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ solidifies below its normal freezing point, makes it difficult to release the stored latent heat within the operating temperature range. Supercooling degree is a measure of the substance supercooling, which is the difference between the theoretical and actual crystallisation temperature of the material. The theoretical temperature of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 32.4°C [5]. To promote the widespread use of low-temperature PCM, it is necessary to reduce the supercooling degree of hydrated salts.

According to the existing research, the supercooling degree of hydrated salt can be reduced by adding nucleating agents such as borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), acidified copper powder, aluminium oxide and silicon dioxide [6]. Xu and Ke [7] verified that using $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ as a nucleating agent is an effective way to reduce the supercooling degree of sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$). Other studies have found that the addition of 2–3 wt.% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ can reduce the supercooling degree to below 3°C . However, the nucleating agents always distribute inhomogeneously inside PCMs, which lead to an inadequate reduction of supercooling degree. In this Letter, we continue to adopt $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ as a nucleating agent and introduced three-dimensional reduced graphene oxide (3D-rGO) as a supporting material of PCM and a nucleating agent.

Graphene offers some outstanding properties due to its particular structure with the large surface area, high porosity, low density and stable mechanical properties [8]. Different 3D-graphene-based structures have been fabricated recently and have attracted a great deal of attention [9]. Wang and Ellsworth [10] demonstrated the creation of 3D-graphene aerogel (GA) by freeze drying. Zhao *et al.* [11] developed a novel architecture called graphene sponge (GS), which was assembled of GO sheets by hydrothermal

treatment with the assistance of thiourea. The GS exhibits adjustable pore structure and surface property, and are mechanically strong. Chen *et al.* [12] proposed a direct synthesis method of template-guided chemical vapour deposition of 3D-graphene foam. In this work, graphite oxide was reduced and 3D-graphene hydrogel was synthesised during the hydrothermal reaction. 3D-GA was prepared by vacuum freeze drying the 3D-graphene hydrogel.

Nowadays, 3D-rGO has been introduced to improve the shortcomings of functional materials, which is identified as a promising practical solution [13–15]. However, no study on 3D-rGO binding to inorganic hydrated salts is found. In this Letter, a novel composite PCMs with excellent heat-storage properties has been synthesised based on 3D-rGO and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

2. Experimental

2.1. Materials: Natural flake graphite (–200 mesh) was purchased from Shanghai YiFan Graphite Co. Ltd. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ were supplied by Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Preparation of 3D-rGO: In this Letter, graphite oxide was prepared by modified Hummers method [16]. On this basis, the 3D-graphene hydrogel was fabricated by a hydrothermal reduction reaction, and the multilayer 3D-rGO was obtained by vacuum freeze drying.

After 1 h of ultrasonic dispersion, 60 ml of GO suspension was placed in a hydrothermal reactor (100 ml) at 180°C for 16 h. During the hydrothermal reaction, GO was reduced and 3D-graphene hydrogel was synthesised. After pre-freezing at -30°C for 4 h, vacuum freeze dried to obtain a 3D-rGO having a large specific surface and a high porosity.

2.3. Preparation of composite PCMs: An excess of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with different $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content was heated in a vacuum oven at 70°C for 2 h and the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was completely melted. Mix the molten salt and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ until well blended by a high-speed mixer before proceeding to the next process. The prepared 3D-rGO was then completely immersed in the molten salt in a vacuum chamber for 2 h to fill the cellular skeleton with molten $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

For the composite PCMs containing 3D-rGO, the content of 3D-rGO is 2 wt.%, the content of nucleating agent is 0, 0.5, 1, 2 and 3 wt.%, the content of hydrated salt is 98, 97.5, 97, 96 and

95 wt.%. For the composite PCMs without 3D-rGO, the content of nucleating agent is 0, 0.5, 1, 2 and 3 wt.%, the content of hydrated salt is 100, 99.5, 99, 98 and 97 wt.%. Subsequently, the sample was cooled to room temperature and then kept in an incubator chamber. Fig. 1 shows the sample preparation procedure.

2.4. Characterisation: The cross-sectional morphology of the samples was observed using a field-emission scanning electron microscopy (SEM) (Quanta 200FEG, FEI Company). The T-history curves of the composite PCMs were obtained using four-channel data logger thermometer (Center 309, CENTER Technology Corp.) [17, 18]. In the experiments, samples were sealed in the test tubes, as shown in Fig. 2, and then placed into a water bath.

T-history curves of difference samples during the cooling process are shown in Fig. 3. The supercooling degree calculating formula is

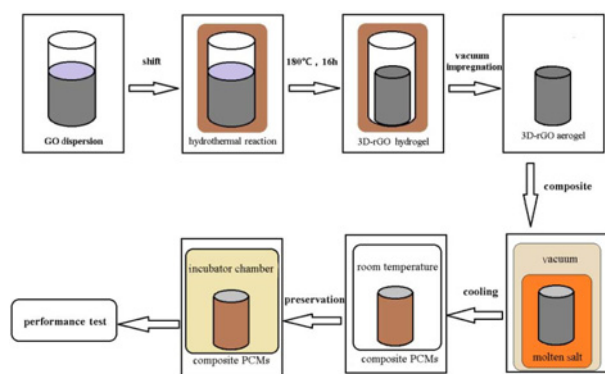


Fig. 1 Schematic diagram of fabrication of composite PCMs

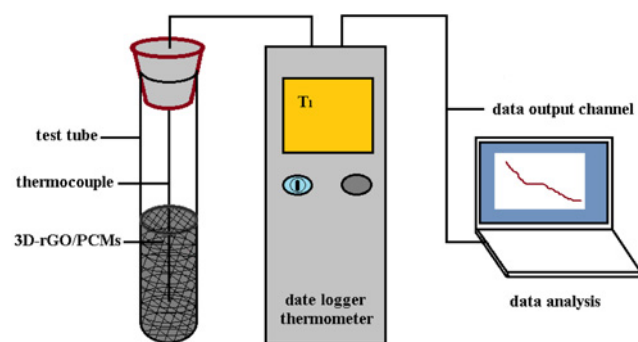


Fig. 2 Schematic diagram of the experimental rig

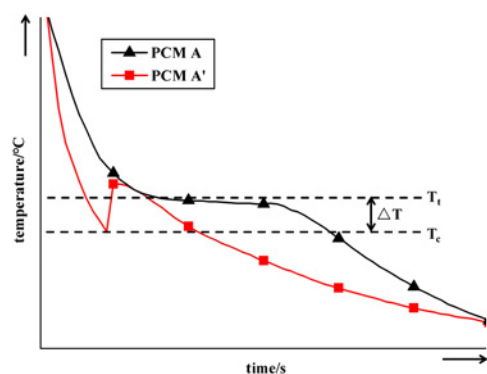


Fig. 3 T-history curve of PCM

as follows:

$$\Delta T = T_t - T_c \quad (1)$$

where ΔT is a supercooling degree of PCM, T_t is the theoretical crystallisation temperature and T_c is the actual crystallisation temperature of PCM. T_t of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 32.4°C .

3. Results and discussion: Fig. 4a shows that $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ as a nucleating agent can reduce the supercooling degree of PCM during the cooling process. For pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, there is no explicit phase change temperature on the T-history curve. The latent heat is released rapidly at 20.7°C , and the system temperature can reach to about 32.6°C . The T-history curves of PCM containing $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ become relatively smooth and the supercooling degree of PCM has been reduced to some extent. Fig. 4b shows the joint effect of 3D-rGO and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ on the supercooling degree of the composite PCMs. The T-history curve of the composite PCMs is smoother than PCM curve without 3D-rGO. The crystallisation temperature is more obvious, indicating that the phase change process is more stabilised.

Supercooling degree and supercooling degree reduction rate, as shown in Fig. 5, were obtained from analysis of the T-history curves in Fig. 4. The supercooling degree reduction rate (R) is defined as the reduction percentage in material supercooling degree between theoretical crystallisation temperature of the pure hydrated salt and actual crystallisation temperature of PCM containing $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, as shown below:

$$R = \frac{(T_t - T_c)}{T_t \times 100\%} \quad (2)$$

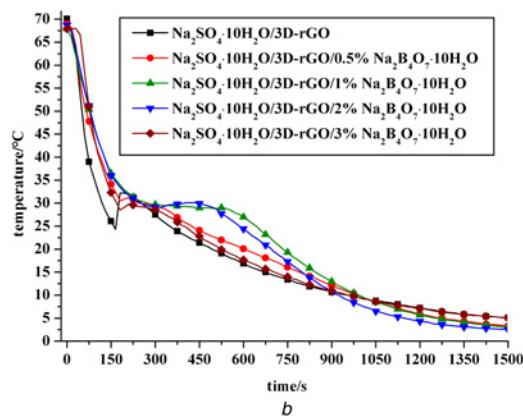
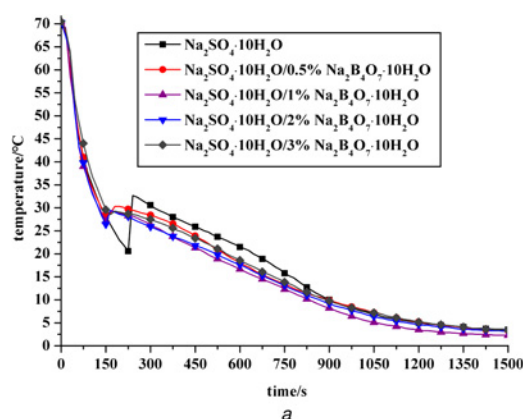


Fig. 4 Results and discussion

a T-history curves of PCM with different $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ contents
b T-history curves of PCM containing 3D-rGO with different $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ contents

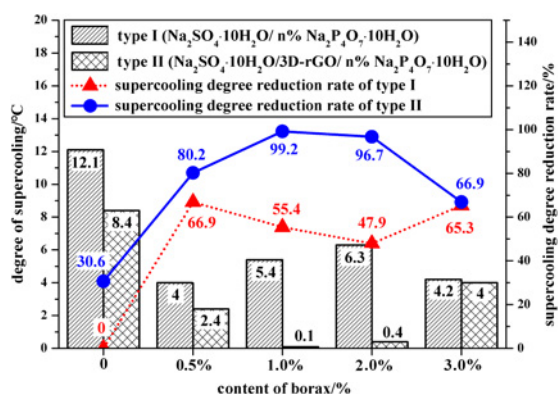


Fig. 5 3D-rGO influence on the supercooling degree and curves of supercooling degree reduction rate

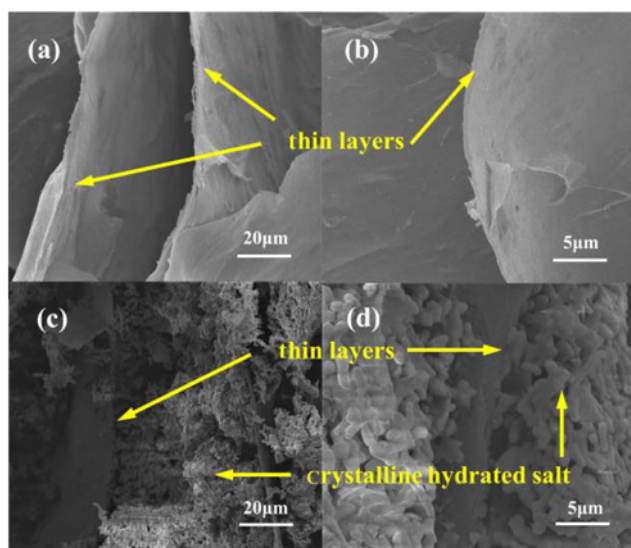


Fig. 6 PCM with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is uniformly dispersed in the layer-separated space of the 3D-rGO network
a, b SEM photographs of multilayer 3D-rGO
c, d Composite PCMs

With the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content of 0.5%, the supercooling degree of PCM can be reduced to 4°C, the reduction rate is 66.9%. However, the supercooling degree cannot be reduced further by adding a more nucleating agent. A possible reason may be that nucleating agent is hard to be distributed uniformly inside PCM, which weakens the nucleating effect though sufficient nucleating agent is added in PCM. For the composite PCMs with 3D-rGO but without $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, the supercooling degree can be reduced to 8.4°C. In composite PCMs with a $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content of 1 and 2%, the supercooling degree can be nearly eliminated with the help of 3D-rGO.

More visually, the highest reduction rate appears at 1% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content. At the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content of 1%, the supercooling degree of composite PCMs with the addition of 3D-rGO can be reduced by 99.2%, the PCM containing only $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ can be reduced by 55.4%. The biggest reduction rate gap appears at the 2% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content, the supercooling degree of composite PCMs with the addition of 3D-rGO can be reduced by 96.7%, the PCM containing $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ only can be reduced by 47.9%. This illustrates that the positive synergy effect of 3D-rGO and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is significant in reducing the supercooling degree. At an $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content of more than 2% and <1%; however, the effect is less significant.

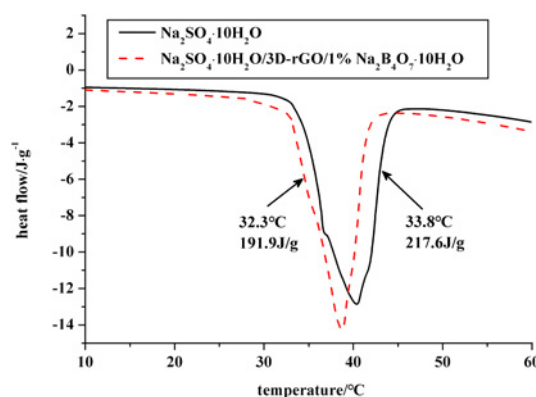


Fig. 7 DSC heating curve of composite PCMs and pure hydrated salt

As a supporting framework material, 3D-rGO with high porosity and the large specific surface area provides enough loading space and attachment locations for PCM. At the same time, many tiny spaces separated by graphene layers may help reduce phase separation during phase transitions. PCM with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is uniformly dispersed in the layer-separated space of the 3D-rGO network, which means that the nucleating agent can facilitate the crystallisation of the molten PCM effectively, as shown in Fig. 6. Figs. 6a and b show a unique multilayer morphology consisting of great numbers of gaps and dense graphene sheets that tend to be oriented vertically. Figs. 6c and d show the fine and uniform crystal substance of PCM and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ fulfilled in the pore space between graphene layers, which is the internal reason for reducing the supercooling degree of composite PCM. Fig. 7 shows an endothermic peak appearing near 32.3°C in the Differential Scanning Calorimetry (DSC) curve of the composite PCM of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} / 3\text{D-rGO} / 1\% \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, the DSC curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is taken as a reference. The latent heat of composite PCM is about 191.9 J/g, which is determined by the area of endothermic melting peaks.

4. Conclusion: In this Letter, graphite oxide was prepared by modified Hummers method. On this basis, the 3D-graphene hydrogel was fabricated by a hydrothermal reduction reaction, and the multilayer 3D-rGO was obtained by vacuum freeze drying. Hydrated salts composite PCMs based on 3D-rGO and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ were synthesised by vacuum impregnation. From the analysis and study of the thermal characteristics of hydrated salts composite PCMs, main conclusions are as follows:

- Compared to the traditional modification method, the supercooling degree can be further greatly reduced in composite PCMs with 3D-rGO. With the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ content of 1%, the supercooling degree of PCM with 3D-rGO is reduced to 0.1°C, the reduction rate is 99.2% compared with the pure hydrated salt PCM.
- Compared to PCM containing only $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, the difference of supercooling is obvious in composite PCMs prepared with or without adding 3D-rGO. The internal reason is a nucleating agent that can be uniformly dispersed in the composite PCMs containing 3D-rGO, so as to improve the use ratio of nucleating agent and the crystallisation effect.

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6 References

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