Synergistic Enhancement of Phase Change Materials through Three-Dimensional Macropore Lamellar Structured MOF/EG Composite for Solar Energy Storage and Beyond

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April 25, 2023

Abstract

Phase change materials (PCMs) have gained significant attention as thermal energy storage materials for reducing dependence on fossil fuels. However, the leakage caused by long-term molecular motion has become a bottleneck for the further advances of energy storage density and application value. Herein, a novel PCM composite with good shape stability, thermal conductivity and photothermal conversion capability was designed. Given the synergistic or hybridization effect between metal-organic frameworks (MOFs) and expanded graphite (EG) components offered the composite unique capabilities, even with the merits of both. The combination of ZIF-67 and EG in a hybrid structure can effectively prevent particle agglomeration, while simultaneously providing a high specific surface area and pore volume for the adsorption of paraffin wax. Compared to pristine unsupported PCMs, the as-obtained PCM composite possesses a 3-fold enhancement in thermal conductivity, 95.56% photothermal conversion efficiency and excellent shape stability. It demonstrates the potential of MOFs-enhanced PCM composites for thermal energy storage and highlight the importance of synergistic or hybridization strategies in the development of advanced materials for sustainable energy applications.

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Abstract: Phase change materials (PCMs) have gained significant attention as thermal energy storage materials for reducing dependence on fossil fuels. However, the leakage caused by long-term molecular motion has become a bottleneck for the further advances of energy storage density and application value. Herein, a novel PCM composite with good shape stability, thermal conductivity and photothermal conversion capability was designed. Given the synergistic or hybridization effect between metal-organic frameworks (MOFs) and expanded graphite (EG) components offered the composite unique capabilities, even with the merits of both. The combination of ZIF-67 and EG in a hybrid structure can effectively prevent particle agglomeration, while simultaneously providing a high specific surface area and pore volume for the adsorption of paraffin wax. Compared to pristine unsupported PCMs, the as-obtained PCM composite possesses a 3-fold enhancement in thermal conductivity, 95.56% photothermal conversion efficiency and excellent shape stability. It demonstrates the potential of MOFs-enhanced PCM composites for thermal energy storage and highlight the importance of synergistic or hybridization strategies in the development of advanced materials for sustainable energy applications.
Keywords: High thermal conductivity; Phase change materials; Metal-organic frameworks; Photothermal conversion; Expanded graphite

1. Introduction

The demand for sustainable energy storage and thermal management systems has been rapidly increasing in recent years due to the ever-growing energy consumption and environmental concerns.\cite{11, 2} Despite their low carbon footprint and environmental benefits, renewable energy sources suffer from intermittency and instability during the energy conversion process.\cite{13, 4} Phase change thermal storage technology can improve the efficiency of energy systems by time-shifting or reducing peak thermal loads.\cite{10} It has emerged as a promising solution to these challenges, offering high energy density, long-term storage capability, and affordable.\cite{6-8}

Phase change materials (PCMs) can be categorized into solid-solid, solid-gas, liquid-gas, or solid-liquid PCM categories depending on their phase change mechanism.\cite{9} Among these, solid-liquid PCMs are considered the most practical due to their high latent heat, negligible volume, and pressure change during the phase change process.\cite{10} However, solid-liquid PCMs are prone to leakage during phase change process and have poor thermal conductivity, limiting their practical applications.\cite{11, 12} As a result, to be viable for use, solid-liquid PCMs must be encapsulated and enhanced.\cite{13}

It is reassuring to know that metal-organic frameworks (MOFs) can offer an amicable solution to a continuity issue for growing demand for multifunctionality in PCMs. MOFs are crystalline materials composed of metal ions or clusters and organic ligands.\cite{14, 15} They possess highly controllable pore structures and surface chemical properties, making them widely applicable in various fields, such as gas adsorption, catalysis, sensing, and drug delivery.\cite{16-18} The unique structure of MOFs enables them to exhibit excellent optical, electrical, magnetic, and photocatalytic properties, making them useful in energy conversion, storage, and transmission applications.\cite{19} Xu et al.\cite{20} reported on an unprecedented nanocomposite PCM, which utilizes non-flammable, non-toxic, and high latent heat sugar alcohols encapsulated in an easily synthesized zeolitic imidazole framework (ZIF) crystals. The phase change temperature and latent heat of the composites were 19.8°C and 285 J/g, respectively. Zhang et al.\cite{21} successfully encapsulated the phytochemicals curcumin and indocyanine green in zeolitic imidazole framework-8/polyactic acid (ZIF-8/PLA) electrospinning fibrous membrane nanocarriers, which were further encapsulated with PCM by non-covalent interactions. The obtained composites exhibit a desirable biocompatibility and potent antibacterial activity through photothermal/photodynamic/chemo-killing effects. Despite the promising potential of MOFs in energy storage applications, they are often hindered by issues such as structural instability and aggregation.\cite{22} A promising approach to address this challenge is to combine MOFs derivatives with carbonaceous materials.\cite{23-25} This strategy not only enhances the pore volume and surface area of the resulting hybrids, but also imparts superior dispersion and thermal properties.\cite{26-28} By addressing the limitations of MOFs derived materials, this approach enables their full utilization in energy storage applications. Wang et al.\cite{29} selected ZIF-8 as the representative of organometallic frameworks to obtain porous polyhedral ZnO, which was attached to expanded graphite (EG) flakes to form a ZnO/EG layered porous hybrid structure. The synergistic effect of porous ZnO and EG can significantly enhance the heat transfer efficiency of composites, while also preventing the leakage of molten palmitic acid. Li et al.\cite{24} successfully synthesized hierarchical three-dimensional reduced graphene porous carbon support PCMs oxide@MOF templates by carbonizing graphene, while achieving large phase change enthalpy (168.7 J/g) and high thermal conductivity (0.60 W·m⁻¹·K⁻¹) simultaneously. As a result, the integration of MOF and porous carbon is a viable strategy to synergistically enhance the performance of materials by leveraging their respective strengths.

In this work, a novel three-dimensional macropore lamellar structured MOF/EG composite was developed to enhance the performance of PCMs. The MOF not only serves as a support material for EG pores, but also exhibits excellent photothermal conversion ability (Fig 1), enabling efficient utilization of the composite for latent heat storage technology in solar energy applications. The synergistic mechanism between MOF and EG significantly enhances the thermal conductivity and shape stability of PCM. The results show that the photothermal conversion efficiency of PCM composites reaches 95.56% with a latent heat of 159.16 J/g. Furthermore, the thermal conductivity of the PCM composites reaches 3 times that of paraffin wax (PW).
2. Experiments

2.1 Materials

Cobalt nitrate hexahydrate, 2-methylimidazole, methanol, and petroleum ether were obtained from Shanghai Titan technology Co., LTD (Shanghai, China). EG was supplied by Qingdao Graphite Co., Ltd (Qingdao, China), the average particle size of the selected EG was 150 µm, and its expansion ratio was 270 mL g⁻¹. PW was supplied by Shanghai Joule Wax Co. LTD (Shanghai, China). All reagents used without further purification and no processing of raw materials was required.

2.2 Synthesis of EG@ZIF-67

Our work commenced with the homogeneous dispersion of cobalt nitrate hexahydrate, 2-methylimidazole, and EG in methanol solution. The reaction was carried out by blending the methanolic solution of cobalt nitrate hexahydrate and EG with the methanolic solution of 2-methylimidazole. The reaction was conducted at room temperature and 500 r/min for 2 h and left for 24 h. In this case, the generated ZIF-67 was purple and attached to the surface of the EG, resulting in a purple color of the solution, while part of the EG precipitated. The solution was extracted and dried, and the remaining solid material was the EG@ZIF-67 composite. The proportion of EG and ZIF-67 was facilely tuned by the amount of several different starting materials. The mass ratio of cobalt nitrate hexahydrate, 2-methylimidazole and EG was shown in Table 1.

2.3 Synthesis of PW/EG@ZIF-67

Composite materials were prepared by a simple physical blending method. PW dissolved in petroleum ether was encapsulated in the EG-skeleton by vacuum impregnation. The composite materials were obtained by evaporation of petroleum-ether. To facilitate the optimization process, we fixed the mass ratio of PW and support skeleton to investigate the effect of different EG@ZIF-67 on the composite (Table 2).

3. Results and Discussion

Initially, the microstructure of the composite was studied. The FEI Sirion 200 field emission scanning electron microscopy (SEM) was used to characterize the structure and morphology of EG@ZIF-67 and PW/EG@ZIF-67 to verify the microstructure and size. The synthesized ZIF-67 particles had a regular truncated rhombic dodecahedron shape (Fig. 2a), which was consistent with the reported results, and proved that ZIF-67 particulates were synthesized successfully. The Fig. 2b clearly reveals continuous heat bridge structure of the EG. The SEM analysis results of different MOF/EG composites are shown in Fig 2c—h. As seen from the 0.4MOF/0.6EG and 0.5MOF/0.5EG samples, MOF particles were attached to the EG, which is consistent with the expected results. And the MOF particles in the 0.6MOF/0.4EG sample stacked on EG, forming a stacked particle structure. After encapsulation the PW, the ZIF-67 particles were fully blended with the PW, but failed to encapsulate the PW completely due to the small pore size of ZIF-67 (Fig. 2i). Enhanced by EG, PW was homogeneously adsorbed or attached to the MOF/EG backbone, indicating good compatibility between PW and support materials (Fig 2j, Fig 2k, and Fig 2l).

Fourier-transform infrared spectra (FT-IR) were recorded using the Bruker VERTEX 70 FT-IR as KBr discs to evaluate the synthesis of EG@ZIF-67 and PW/EG@ZIF-67. The FT-IR spectra of ZIF-67, EG, and PCM composites at the wavenumbers between 3500 cm⁻¹ and 600 cm⁻¹ are shown in Fig 3a. The peaks at 2921 cm⁻¹ and 1143 cm⁻¹ were from the stretching vibration of N–H and C–N. The peaks at 1307 cm⁻¹ was attributed to the plane vibration of the imidazole ring, while the stretching vibrations of the imidazole ring and C=N bonding appeared at 1425 cm⁻¹ and 1585 cm⁻¹, indicating that the ZIF-67 was successfully synthesized. The characteristic peaks became more pronounced with the increase of MOF ratio. In addition, no significant new peaks were observed, indicating the absence of impurities generation. As shown in Fig 3b, FT-IR analysis showed that the main response in the PW/EG@ZIF-67 composites was from PW, as evidenced by the peaks at around 2920 cm⁻¹ and 2850 cm⁻¹, which were ascribed to the –CH₃ asymmetrical stretching vibration and –CH₂ symmetrical stretching vibration, respectively. The peaks near the wavelengths of 1465 cm⁻¹ and 720 cm⁻¹ represented the rocking vibration of the –CH₂ group, while the peak at 1376 cm⁻¹ was the result of the deformation vibration of –CH₃. No significant
new peaks were observed except for some slight shifts, indicating that there was no chemical reaction between ZIF-67 and PW. X-ray diffraction (XRD) patterns were recorded on a diffractometer (D8 ADVANCE, BRUKER) with Co Kα radiation at a tube current of 30 mA and a generator voltage of 35 kV and performed from 4 to 50° of 2θ. In Fig. 3c, the XRD pattern exhibits diffraction peaks at 2θ values of 7.35°, 10.40°, 12.74°, 14.71°, 16.46°, 18.06°, 22.13°, 24.53°, 26.71°, and 29.69° corresponding to (001), (002), (112), (022), (013), (222), (114), (233), (134) and (044) planes of ZIF-67 single crystal. In addition, the XRD diffraction peaks of the prepared ZIF-67 were relatively high and sharp, which indicates its high crystallinity. The XRD patterns of PCM composites show that the main response of the PCM composites derives from PW (Fig. 3d). The sharp diffraction peaks representing the crystallization of pure PW were attributed to the diffractions of (110), (200) and other crystal planes. The absence of additional peaks besides the expected peaks for PW, MOF, and EG indicates that no chemical reaction occurred among these three components and no new material was produced.

Although organic PCMs have excellent energy storage density, they inevitably face application challenges caused by leakage during phase change processes. Therefore, we investigate leakage as one of the main properties of the samples. To investigate the shape stability of each sample and observe the leakage using infrared thermography, the samples were placed at 55°C until the pure PW melted completely after the pressing process. In addition, the mass loss of the samples after testing was recorded and the leakage rate was calculated for each sample. The results of the leakage proof are shown in Fig 4a. When PW uses only EG as the support material, the leakage rate of the PW/EG sample is 7.5% (Fig 4b). At the same time, the infrared thermography showed consistency with the results recorded by the digital camera, as well as the quantitative calculations of leakage. After ZIF-67 enhancement, the leakage rates of the composites were significantly reduced, the leakage rate of samples 0.05MOF/0.95EG-PCM and 0.1MOF/0.9EG-PCM being 6.9% and 4.6%, respectively, and the leakage rate of sample 0.2MOF/0.8EG was only 1.4%, which demonstrated the positive effect of ZIF-67 on the shape stability of the composites. However, the leakage of the composites deteriorated with further increase in the mass fraction of ZIF-67, with 5.1% and 13.4% for samples 0.4MOF/0.6EG and 0.6MOF/0.4EG, respectively. It can be explained that ZIF-67 can transform the lamellar EG into a three-dimensional structure with large pores. When less ZIF-67 is added, the support effect is not obvious, while too much ZIF-67 will block the pores, resulting in smaller pore size and thus inhibiting the generation of porous structures. Therefore, the mass ratio of EG and ZIF-67 in the composite should be balanced. The best shape stability was achieved when the mass fraction ratio of EG and ZIF-67 was 2:8, in which case the leakage rate of the composite was 1.4%.

Thermal conductivity is an essential factor in evaluating PCM composites as it relates to heat transfer efficiency and response time in solid-liquid transition. EG is an excellent choice for enhancing the thermal conductivity of PCM owing to its continuous heat bridge structure. The thermal conductivity of each sample was measured at different temperatures and the results are shown in Fig 4c. The thermal conductivity of the samples showed an increasing trend with increasing mass fraction of EG, which is consistent with the theory. The sample with the best shape stability (0.2MOF/0.8EG-PCM) had a thermal conductivity of 0.93 W·m⁻¹·K⁻¹ at 40°C, which is approximately three times higher than the thermal conductivity of pure PW (0.32 W·m⁻¹·K⁻¹). In addition, the thermal conductivity of the samples was also correlated with the operating temperature. The thermal conductivity was positively correlated with temperature before the phase change occurred. However, it decreased significantly after the PCM composite underwent the solid-liquid transition, which can be explained by the fact that PW in liquid form has lower thermal conductivity than in solid form.

The latent heat value of PCM composites is the most significant thermal property, as it determines the energy storage density. The energy-storage properties of PCM samples, including phase change temperature and latent heat of phase change, were measured by differential scanning calorimetry (DSC). DSC was performed in a TA Q200 (Thermal Analysis Corporation, USA) at a heating/cooling rate of 2°C min⁻¹ under a nitrogen atmosphere. All the samples were heated to 75°C, then cooled to 5°C and equilibrated for 1 min. The results are shown in Fig 5a. The latent heat values of the samples increased with PW loading. As the sample 0.2MOF/0.8EG-PCM had the lowest leakage rate, the loaded PW mass fraction was the highest.
and its latent heat of phase change was also the highest, with latent heat of melting and crystallization of 159.16 J/g and 156.55 J/g, respectively. In addition, the latent heats of melting and crystallization of PW were 169.01 J/g and 172.92 J/g, respectively, and according to the calculation, the theoretical enthalpies of the samples were 153.64 J/g and 157.20 J/g, respectively, which were close to the actual situation and proved that there was no latent heat loss of PW in the sample. The performance of the sample 0.2MOF/0.8EG after long-term thermal cycling was simulated by heating-cooling cycle, and the results are shown in Fig 5b. After 500 heating and cooling cycles, the DSC curves of the samples remained almost constant, demonstrating the excellent long-term recyclability of the composite. It can be used as an excellent heat storage medium in various fields, especially for practical scenarios with long-term needs.

4. Applications

Solar energy is a sustainable and clean energy source. However, the temporal instability of solar energy severely limits its practical application. Latent heat storage technology offers an alternative way of solar energy harvesting, mainly thanks to its low cost, ease of preparation and simplicity of operation; therefore the photothermal energy conversion properties of composite was investigated for potential applications in the field of solar energy harvesting. As shown in Fig 6a, the photothermal experimental platform consists of a simulated light source with a constant light intensity of 120 mW·cm⁻², a foam box, a data acquisition unit and a data analysis unit constructed. The PCM composite samples underwent a complete phase change process under the continuous irradiation of a simulated solar light source and were cooled to room temperature after the light source was turned off. The change in temperature of the sample with time was recorded throughout the process.

As shown in Fig 6b, the temperature of the samples increased rapidly in the initial stage of illumination, followed by a stage of temperature plateau, which was the phase change process of the sample. The MOF-PCM showed the fastest heating rate among all samples, proving its excellent photothermal conversion ability. The absorption of ZIF-67 in the near-infrared region (near 1125 nm) is significantly enhanced by the energy level transition of the d-d transition (4A₂ - 4T₁ (F)) of the tetrahedral cobalt (II) ions, while the absorption of yellow-green light (near 580 nm) is enhanced by the energy level of the d-d transition (4A₂ - 4T₁ (P)) of the cobalt (II) ions. In addition, ZIF-67 has excellent optical performance at 1 µm and 1.34 µm excitation wavelengths, with a two-photon absorption cross sectional area at 85×10⁵ GM, demonstrating its excellent two-photon absorption capability, so the composite material with ZIF-67 has a faster response rate to sunlight. The photothermal conversion efficiency (η) can be calculated using the following equation:

\[ \eta = \frac{m \times \Delta H}{I \times S \times (T_f - T_s)} \times 100\% \] (1)

In the aforementioned equation, \( \eta \) is the light-thermal conversion efficiency, \( m \) represents the mass of the sample, \( \Delta H \) is the latent heat of phase change, \( S \) is the radiated area, \( I \) represents the optical power density, \( T_s \) represents the starting time points of the phase change during the heating process, and \( T_f \) represents the ending time points of that. After ZIF-67 enhancement, the photothermal conversion efficiency of sample MOF-PCM can achieve 95.56\%, while sample 0.2MOF/0.8EG-PCM can also achieve 79.71\%, which is much higher than that of the EG enhancement (62.75\%). The results demonstrate that MOF has great potential to enhance the photothermal energy conversion performance of PCM composites and can be effectively used in latent heat storage technology for solar energy.

5. Conclusion

In this work, we developed a three-dimensional macropore lamellar structured MOF/EG composite via in situ generated MOF to encapsulate and enhance the performance of PCMs. The MOF not only serve as a support material for EG pores, but also exhibits excellent photothermal conversion ability, making the composites ideal for latent heat storage technology in solar energy applications. Furthermore, the thermal conductivity and shape stability of the PCM are significantly improved due to the synergistic effect of MOF and EG. Further studies showed that the photothermal conversion efficiency of the PCM composites could
reach 95.56% and the latent heat was 159.16 J/g. Moreover, the thermal conductivity of the MOF/EG-PCM composite was three times higher than that of pure PCM. However, MOF has broad application prospects in various fields such as catalysis, sensing, battery, gas adsorption, and biomedicine. Therefore, the development of multifunctional materials combining the heat storage and temperature control function of PCMs is an essential direction for further research to explore more potential applications of composite materials. Overall, the strategies for enhancing PCMs with MOFs can effectively improve the performance of PCMs and expand their applications. However, it is essential to balance performance optimization with cost considerations to ensure the feasibility and sustainability of these materials in practical applications.

**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.

**Acknowledgments**

This work was supported by the National Natural Science Foundation of China (No. 51906252), Natural Science Foundation of Jiangsu Province (No. BK20190632), and China Postdoctoral Science Foundation (No. 2019M661980). The authors also thank Dr. Hua Wei and Dr. Rui Zhou at Advanced Analysis & Computation Center of CUMT for their assistance with chemical analysis.

**References**


Table 1 Scale strategy of MOF/EG composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cobalt nitrate hexahydrate (g)</th>
<th>2-methylimidazole (g)</th>
<th>EG (g)</th>
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</thead>
<tbody>
<tr>
<td>EG</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.05MOF/0.95EG</td>
<td>0.233</td>
<td>0.263</td>
<td>0.95</td>
</tr>
<tr>
<td>0.1MOF/0.9EG</td>
<td>0.466</td>
<td>0.525</td>
<td>0.9</td>
</tr>
<tr>
<td>0.2MOF/0.8EG</td>
<td>0.931</td>
<td>1.051</td>
<td>0.8</td>
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<tr>
<td>0.4MOF/0.6EG</td>
<td>1.862</td>
<td>2.102</td>
<td>0.6</td>
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<td>2.627</td>
<td>0.5</td>
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<td>MOF</td>
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Table 2 Composition of MOF/EG-PCM composites

<table>
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<th>Sample</th>
<th>ZIF-67 (g)</th>
<th>EG (g)</th>
<th>PW (g)</th>
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<td>10</td>
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