



Construction of CNT@Cr-MIL-101-NH₂ hybrid composite for shape-stabilized phase change materials with enhanced thermal conductivity

Jingjing Wang, Xiubing Huang*, Hongyi Gao*, Ang Li, Chen Wang

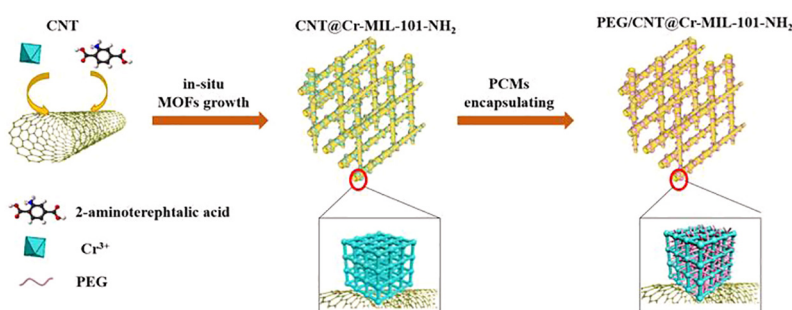
Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China



HIGHLIGHTS

- PEG was stabilized by MOFs through capillary force and hydrogen bond interaction.
- CNTs provided uniform and continuous heat transfer channels.
- Close integration between CNTs and MOFs could reduce the interfacial thermal resistance.
- Thermal conductivity of PCM composite was improved by 100.9%.

GRAPHICAL ABSTRACT



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ABSTRACT

The leakage of the liquid phase above the melting point and the low thermal conductivity of phase change materials (PCMs), are the major barriers that currently prevent the practical applications of organic PCMs. In this work, a novel supporting material with mutual interpenetrating network structure was developed by the heterogeneous decorations of Cr-MIL-101-NH₂ metal-organic frameworks (MOFs) nanoparticles on the surfaces of carbon nanotubes (CNTs). PCMs, absorbed by capillary force of porous structure and anchored by hydrogen bond interaction of amino groups, were stabilized by the MOFs nanoparticles. The close integration between CNTs and MOFs nanoparticles was conducive to the construction of three-dimensional (3D) and mutual interpenetrating network structured supporting material, which provided continuous heat transfer paths, increased mean free paths for phonons transmission and promoted effectively the reduction of interfacial thermal resistance between the PCM molecules and supporting materials. The thermal conductivity of PEG2000/CNT@Cr-MIL-101-NH₂ shape-stabilized PCM composite was improved by 100.9% over PEG2000/Cr-MIL-101-NH₂ PCM composite. Furthermore, the obtained PEG/CNT@Cr-MIL-101-NH₂ PCM composite showed large phase change enthalpy, good chemical stability and excellent thermal cycling stability.

1. Introduction

Phase change materials as thermophysical energy storage materials have received renewed emphasis in the sustainable use of energy, including solar energy harvesting, thermal management of electronic

devices, and buildings' heating and cooling [1–5]. Recently, the coupled cooling system based on the PCMs unit was completely developed to the cooling of the underground mine refuge chamber [6]. Organic solid-liquid PCMs have been studied extensively owing to their moderate phase change enthalpies, wide melting temperatures for

* Corresponding authors.

E-mail addresses: xiubinghuang@ustb.edu.cn (X. Huang), hygao2009@163.com (H. Gao).

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convenient use, excellent chemical stability, and abundance in natural resources [7–9]. However, two major drawbacks that seriously limit the application of PCMs in the latent heat thermal energy storage system are low thermal conductivity and liquid leakage [1,10,11]. Considerable efforts have been devoted to introducing new supporting materials to development of shape-stabilized solid-liquid PCMs to address these technical issues.

Impregnation of PCMs into porous materials with high thermal conductivity to obtain the shape-stabilized PCMs has been developed because of higher magnitude of thermal conductivity of the porous material than the pure PCMs [12]. The most widely porous materials used as thermal conductivity enhancers were graphite matrix (such as expanded graphite [13,14], graphene oxide [10]), metal matrix (such as Al [15], Cu [16] or Ni [17] foam). Recently, Min et al. used the biological porous carbon which was derived from potatoes and white radishes by the high-temperature carbonization method as the support to load PEG. The obtained PCM composite showed the highest thermal conductivity of 4.5 W/m K, which was about 10 times higher than the pristine PEG [18]. On the other hand, significant progresses on simultaneously introducing of high conductivity nano-materials and porous supporting materials into PCMs to prepare shape-stabilized PCMs have been achieved recently. The porous materials possessing high porosity and low density were used as carriers to maintain the form-stable effects. Nano-materials as additives were embedded into conventional PCMs to increase thermal conductivity of shape-stabilized PCMs. This includes the use of nanopowders (such as Ag [19], Cu [20], Al [21], TiO₂ [22], β -AlN [23]), nanowires (Ag [24,25], Cu [26], carbon fibers [27]), and nanotubes (CNTs [28–34]).

CNTs possess high thermal conductivity in the axis direction and an individual multi-walled CNT can be as high as 2000–6000 W m⁻¹ K⁻¹ in thermal conductivity [11,35]. With their high thermal conductivity and light weight, CNTs received considerable attentions as additives to enhance the thermal conductivity of PCM composites for heat transfer applications [28,29]. Tang et al. reported a novel hybrid material based on single-walled CNTs and form-stable polymer PCMs, which processed the UV-vis sunlight harvesting, light-thermal conversion, thermal energy storage and form-stable effects [36]. Karaipekli et al. worked for the enhanced thermal conductivity of expanded perlite/paraffin PCM composite with CNTs. Compared to perlite/paraffin composite, the application of CNTs has an apparent improving effect for the thermal conductivity without considerably affecting the compatibility of components and thermal stability [30]. Huang et al. introduced CNTs as filler for enhancing the thermal conductivity of paraffin/expanded perlite form-stable PCM composite [31]. Their results showed that the form-stable PCM composite could exhibit satisfactory thermal conductivity while maintaining reasonable latent heat by adjusting the CNTs mass fraction. Tang et al. reported the CNTs/PEG/SiO₂ shape-stabilized PCM composite, in which inorganic SiO₂ net served as the supporting material to maintain the form-stable performance and CNTs as high conductive additive to enhance the energy utilization efficiency during heat charging and discharging processes [32]. Compared with pure PEG and PEG/SiO₂ composite, the thermal conductivities of CNTs/PEG/SiO₂ composite were enhanced by 53.1% and 26.7%, respectively. In another study, a ternary montmorillonite/paraffin/CNT PCM composite was synthesized, and the thermal conductivity of the montmorillonite/paraffin/CNT PCM composite increased 34% relative to that of montmorillonite/paraffin [33]. The thermal conductivity of above PCMs composites could be slightly improved by introducing of CNTs, which may be due to that the CNTs were hydrophobic and preferentially aggregate and entangle together. It was quite difficult to achieve effective dispersion of CNTs due to the high surface energy and their high aspect ratio. Therefore, how to combine CNTs and porous materials to construct novel supporting material with uniform and dispersed heat transfer channels is still a challenge.

Metal-organic frameworks (MOFs) with extremely-high surface areas caused by the three-dimensional porous structures including

metal centers and organic linkers have emerged as one of the most promising supporting materials for heterogeneous catalysis [37,38], drug delivery [39,40], and gas storage and separations [41–43]. Although unfavorable thermal conductivity of MOFs, there is interest in the incorporation of PCMs into nanochannels of MOFs by taking advantages of the high pore volume, high surface area, and tunable nature of MOFs [44]. Herein, a novel high thermally-conductive supporting material with mutual interpenetrating network structure was developed by the heterogeneous decorations of amino-functionalized MOFs nanoparticles on the surfaces of CNTs. The PEG/CNT@Cr-MIL-101-NH₂ shape-stabilized PCMs composites with high PEG loading, large phase change latent heat and good thermal cycling stability as well as improved thermal conductivity were achieved. This PCM composite material provides a novel approach for accessing shape-stabilized composite PCMs with good thermal conductivity, which overcomes a problem found in some PCM composites where the introducing of high thermal conductive additive was not highly dispersed.

2. Experimental section

2.1. Materials

Multi-walled carbon nanotubes (CNTs, Diameter: 30–50 nm, Length: 10–20 μ m) were purchased from Chengdu Organic Chemicals Co. Ltd. at the price of around 5.0 RMB/g. Chromic nitrate hydrate, 2-aminoterephthalic acid, sodium hydroxide and polyvinylpyrrolidone (PVP) (Mw: ~58 000) were purchased from Alfa Aesar. Chemically pure polyethylene glycol with different molecular weight (Mw = 2000, 4000, 6000, 8000 and 10,000) was purchased from Alfa Aesar. All other reagents were used as received without further purification.

2.2. Synthesis of CNT@Cr-MIL-101-NH₂ hybrid composite

Composite of CNTs with the Cr-MIL-101-NH₂ were fabricated by the following in situ Cr-MIL-101-NH₂ synthesis. The CNTs were added to a PVP aqueous solution (2 mg mL⁻¹, 30 mL), then sonicated for 1 h. After centrifugation, the supernatant was removed, the precipitates were re-dispersed in deionized water (15 mL) to which chromic nitrate hydrate (0.8 g, 2 mmol), 2-aminoterephthalic acid (0.36 g, 2 mmol) and sodium hydroxide (0.2 g, 5 mmol) were added. The mixed solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and kept at 150 °C for 12 h. The generated precipitates were collected after centrifugation, then washed with dimethyl formamide and methanol. Finally, the products were dried overnight at 120 °C in a vacuum. The amounts of CNTs in the precursors were adjusted to obtain the CNT@Cr-MIL-101-NH₂ hybrid composites with different CNTs contents of 4.9, 9.4, 13.5, 17.2 and 23.5 wt%, respectively. These CNT@Cr-MIL-101-NH₂ hybrid composites were named as A1, A2, A3, A4 and A5, respectively. Pure Cr-MIL-101-NH₂ MOF nanoparticles were synthesized under the same conditions without adding CNTs. The mass percentage of CNTs in the CNT@Cr-MIL-101-NH₂ hybrid composite was shown in Table S1 (Supporting information).

2.3. Preparation of PEG/CNT@Cr-MIL-101-NH₂ PCM composites

The PEG/CNT@Cr-MIL-101-NH₂ PCM composites were fabricated by a physical blending and impregnating method. Firstly, PEG was dissolved in absolute ethanol. Then, CNT@Cr-MIL-101-NH₂ was added to the PEG solution and the resulting solution was stirred vigorously for 4 h. Finally, the mixture was dried at 80 °C for overnight until the ethanol solvent was completely evaporated. Furthermore, PCM composites with various PEG contents were prepared and tested to evaluate the stability of PCM composites.

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