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Largely enhanced thermal conductivity of poly (ethylene glycol)/boron nitride composite phase change materials for solar-thermal-electric energy conversion and storage with very low content of graphene nanoplatelets

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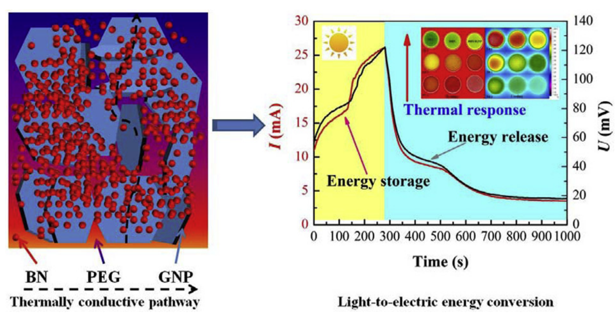
HIGHLIGHTS

- Very low content of GNP is introduced into PEG/BN composite PCMs.
- Thermal conductivity and photoabsorption ability of composite PCMs are enhanced.
- GNP contributes to the perfect conductive network and sunlight harvesting ability.
- Solar-to-thermal & solar-to-electric energy conversion and storage are realized.

GRAPHICAL ABSTRACT



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ABSTRACT

Phase change materials (PCMs) with high thermal conductivity and efficient solar energy conversion have recently attracted much attention. However, a facile strategy to enhance thermal conductivity and realize energy conversion and storage is still eagerly desired. In this work, a very low content of graphene nanoplatelets (GNP) is introduced into poly (ethylene glycol) (PEG)/boron nitride (BN) composite PCMs, resulting in great improvement in thermal conductivity and photoabsorption ability via a facile solution blending process. The presence of GNP contributes to enhancing thermal conductivity and realizing efficient solar energy conversion (including solar-to-thermal and solar-to-electric energy conversion) for the PEG/BN/GNP composite PCMs owing to the formation of improved BN/GNP thermally conductive network and the improvement of sunlight harvesting ability, respectively. Thermophysical properties demonstrate that compared with PEG/BN composite PCMs at the same BN content, PEG/BN/GNP composite PCMs containing a low GNP content maintain comparable energy storage density. The study sheds light on the realization of solar energy utilization and storage of the organic PCMs requiring high thermal conductivity.

1. Introduction

As economics and population grow, the problem of energy supply becomes increasingly prominent. On the one hand, solar energy, as the most abundant and available renewable energy resource, is expected to replace fossil fuels and reduce the mismatch between energy supply and demand via developing reliable and efficient energy conversion and storage devices and systems.

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On the other hand, the collection and utilization of thermal energy from the solar irradiance can be also of critical importance for a greener and sustainable energy future [1–5]. One of the most promising ways to convert, store and utilize solar energy and thermal energy is developing phase change materials (PCMs) which can provide a high energy storage density, absorb and release thermal energy at a constant temperature during phase transitions in the form of melting or solidification [3,6–9].

Organic PCMs including poly (ethylene glycol) (PEG), paraffin wax (or n-alkanes) and fatty acids, have been studied extensively owing to their high energy storage density, wide melting temperatures for convenient use, low or negligible supercooling degree, desirable chemical and thermal stability, and abundance in natural resources [1,7–19]. However, directly realizing efficient solar energy conversion, storage and utilization for the organic PCMs has been hindered owing to the weak photoabsorption ability [3,20]. Consequently, studies on the solar energy conversion, storage and utilization of PCMs have attracted a great deal of interest in recent years. Light-to-heat, electric-to-thermal, magnetic-to-thermal and heat-to-electric routes have been proved to be able to efficiently realize energy conversion, storage and release [3–5,9,20–27]. However, only few attempts have been made to directly realize light-to-electric energy conversion, storage and utilization that is of critical importance and value for the organic PCMs [28].

In addition, most PCMs exhibit inherently low thermal conductivity (~0.2 W m^{-1} K^{-1}), which in turn leads to slow thermal charging/discharging rates [1,6,9,21,29,30]. Great efforts have been dedicated to fabricating PCMs with improved thermal conductivity by incorporating thermally conductive fillers [31]. Boron nitride (BN) and carbon materials with high intrinsic thermal conductivity have been identified to effectively perform in improving the thermal conductivity of PCMs [1,2,10,32,33]. Compared with the expensive carbon nanotubes (CNTs) and graphene exhibiting higher thermal conductivity (about 2000–6000 and 5000 W m^{-1} K^{-1} in theory, respectively) [12,34–38], BN (with a thermal conductivity of about 250–300 W m^{-1} K^{-1}) [39] has great potentials in serving as fillers for fabricating highly conductive composites owing to the high performance and relatively low cost. Therefore, BN and derivatives have been widely used as a thermally conductive filler for plastics [40–47], rubbers [48,49], etc [50]. It should be noted that only a few attempts on introducing BN into PCMs to enhance thermal conductivity have been carried out [2], because the required large amounts of fillers replace the working substance, which leads to the significant decrease of the energy storage density of PCMs [29,51–53]. In order to make full use of thermally conductive fillers, two or more fillers were used together to further enhance the thermal conductivity of the composites [34,39,54–60].

In this work, to improve the thermal conductivity and photoabsorption ability of PEG based PCMs, hybrid fillers comprising of BN and a very low amount of graphene nanoplatelets (GNP) were introduced into PEG by a facile solution blending process, and the solar-to-thermal and solar-to-electric energy conversion, storage and utilization were realized. The introduction of 1 wt% GNP in PEG/BN composite PCMs helps to form an improved and perfect thermally conductive pathway of BN to synergistically enhance the thermal conductivity. Additionally, the presence of GNP contributes to improving the ability for photoabsorpsion and has a negligible effect on the melting and crystalline properties and energy storage density of the PEG/BN composite PCMs. The high thermal conductivity and improved photoabsorption ability of PCMs are very important for the effective light harvesting of solar irradiation and solar energy conversion, storage and utilization.

2. Experimental

2.1. Materials

Hexagonal BN powder with a density of 2.29 g cm^{-3} and a purity of 99.9% and PEG (Mn = 10,000) were purchased from Aladdin Reagent (Shanghai, China). GNP nanosheets (cz-030, ~40 μm) and absolute ethanol (AR) were obtained from Xiamen Knano Graphene Technology Co Ltd and Shanghai Fine Chemical Reagent Co., Ltd., respectively. For all experiments, the materials were used as received without further purification, and distilled water was also used.

2.2. Preparation of composite phase change materials

The composite PCMs were prepared by a facile solution blending method. GNP was first dispersed in ethanol with ultrasonic bath treatment for 20 min. Then a certain amount of BN powder was added in under vigorously stirring for 1 h at 90 °C, and more attention should be paid to avoiding excessive evaporation of the solvent during this process. PEG was then introduced to the hybrid filler solution followed by vigorously stirring to evaporate almost all of the solvent for 4 h. Finally, the samples were dried in vacuum oven to constant weight at 40 °C. The GNP content was maintained as 1 wt% for each sample and BN content was 5 wt%, 10 wt%, 20 wt %, 30 wt%, and the obtained PEG/BN/GNP composite PCM samples with different BN mass content were labeled as 5BN/1GNP, 10BN/1GNP, 20BN/1GNP and 30BN/1GNP, respectively. For comparison, pure PEG, PEG/GNP and PEG/BN composite PCM samples were also prepared in the same way, and the obtained PEG/GNP and PEG/BN composite PCM samples were marked as 1GNP and 5BN, 10BN, 20BN, 30BN, respectively.

2.3. Characterization

The morphologies of the bulk fillers and composite PCMs were visually characterized with a JEOL JSM-5900LV field-emission scanning electron microscopy (SEM) instrument (Japan) with energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 20 kV. The X-ray diffraction (XRD) patterns in the range of diffraction angle 2θ = 5–50° at a scanning speed of 3 ° min^{-1} at room temperature and Fourier transform infrared (FTIR) spectroscopy patterns over the wavenumber range of 4000–400 cm^{-1} of the samples were obtained by using a DX-1000 diffractometer with Cu K α radiation (λ = 0.154 nm) at a voltage of 40 kV and a current of 40 mA and a Nicolet 6700 FTIR spectrometer (Nicolet Instrument Company, USA) with a resolution of 4 cm^{-1} in transmission mode, respectively.

An Ultraviolet–Visible Near-Infrared (UV–vis-NIR) spectrophotometer (UV3600, Shimadzu, Japan) was used to study the optical properties of PEG and the composite PCMs. The photo-to-thermal energy conversion test was carried out under simulated sunlight provided by a CEL-HXUV300 xenon lamp (CEAULIGHT, China) with an AM 1.5 filter, and a CEL-NP2000 optical power meter (CEAULIGHT, China) was used to verify the light irradiation power, and temperature of the sample was recorded using a paperless recorder with thermocouples (OMEGA). The light-to-electric energy conversion and collection were performed with a CEL-HXUV300 xenon lamp (CEAULIGHT, China), a commercial Seeback thermoelectric device and a Keithley electrometer (2400, Cleveland, Ohio, USA). The thermal conductivity was tested using a Hot Disk Thermal Constant Analyzer (TPS 2500, Hot Disk AB Company, Sweden) by a transient plane heat source method. Furthermore, to evaluate the thermal responses of PCMs, a photo shot was taken by an infrared thermal imager (Fluke Ti27) to record the temperature