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Novel slurry containing graphene oxide-grafted microencapsulated phase change material with enhanced thermo-physical properties and photo-thermal performance

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ABSTRACT

In this work, a new microencapsulated phase change material, paraffin@ silica (SiO_2)/graphene oxide (GO), is prepared by two steps: engulfing paraffin with silica by in situ hydrolysis and poly condensation of tetraethoxysilane and the modification of the SiO_2 shell with GO. The paraffin@SiO_2/GO composite is composed of spherical capsules with diameters of ~20 um. Raman spectrometer analysis verifies the embedding of GO in the SiO_2 shell. The melting and freezing temperatures of the composite are very close to those of paraffin. Based on the melting and freezing enthalpy of the composite, the encapsulation ratio of paraffin is calculated to be 50.8% in the paraffin@SiO_2 composite and 49.6% in the paraffin@SiO_2/GO composite. It is shown that the paraffin@SiO_2/GO composite exhibits enhanced thermal stability and excellent thermal reliability. The phase change slurry prepared by dispersing the paraffin@SiO_2/GO composite in water shows higher thermal conductivity and heat capacity along with remarkable photo-thermal conversion performance, making it potential for use as the heat transfer fluid in direct absorption solar collectors. The high heat storage capability and excellent photo-thermal conversion performance of the paraffin@SiO_2/GO composite enable it to be a potential material to store solar energy in practical applications.

1. Introduction

Solar thermal utilization, a technology for efficiently utilizing solar radiation, has attracted a great deal of interest [1]. Solar collector, a device absorbing the solar radiative energy and store as thermal energy, is the crucial component of any solar utilization systems. The performance of solar collectors directly determines the efficiency of the solar thermal utilization systems. In 1970s, the concept of direct absorption solar collector (DASC) was proposed [2] where the heat transfer flow directly absorbed the solar energy and transform it to the thermal energy. This new kind of solar collectors is proved to have the relatively higher receive efficiency than traditional solar collectors, since the temperature difference between the surface and the fluid is lower than the traditional solar collectors [3]. It is no doubt that the heat transfer fluid plays a key role in the DASC. Therefore, novel heat transfer fluids with excellent thermophysical property and photo-thermal conversion performance are highly desirable for the development of high-efficiency DASCs.

The original heat transfer fluids are water, ethylene glycol and other media [4]. Some other heat transfer fluids like thermal oil [5] and fused salt [6] are currently widely used in solar thermal power generation system. However, the traditional heat transfer fluids have intrinsic drawbacks including decreasing their receiver efficiency and limiting their industrial utilization. For instance, most of the heat transfer fluids have poor absorptive property in the visible light, which counts 44% of the solar spectrum energy. The thermal oil not only has a certain vapor pressure, but also is easily decomposed and carbonized, decreasing the heat transfer performance and the safety of the systems. Although inorganic fused salt is resistant to high temperature, it is easy to plug the pipelines in using process and needs additional heating system, which increases the complexity and cost of systems and brings the difficulty of maintenance. Moreover, the traditional heat transfer fluids storage the solar energy as the sensible heat, which is determined by the specific heat of the fluids. Usually, the sensible heat of the heat transfer fluids is limited to storage large solar heat

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flux. Therefore, traditional heat transfer fluid and thermal storage materials with various defects result in low solar thermal efficiency, which limits the further development of solar technology. Developing a new kind of fluid with high energy storage capacity and excellent photo-thermal performance is pivotal.

The term phase change materials (PCMs) generally refer to materials absorbing or releasing a large amount of latent heat during its phase transitions [7]. Since the phase change technology was utilized in the 1970s by NASA, PCMs had been considered as one of the widely used renewable energy materials in solar energy utilization. In general, PCMs can be broadly classified into two types: organic and inorganic. Organic PCMs such as paraffin waxes, fatty acids, and fatty alcohols, have high phase change enthalpies between 150 and 240 $J\,g^{-1}$ [8]. However, the bulk PCMs suffer leakage in the melting process, hence it requires a packaging technology to hold the PCMs within containers [9]. Microcapsules are these tiny little containers packing the core material individually with a robust shell, which tolerate phase changes including volume changes in their cores [10]. This technique can engulf small solid or liquid particles with a solid shell so that it can avoid the leakage of PCMs from their location, reduce the interference of the external environment on the phase change behavior, increase the heat-transfer area, and permit the shell material to withstand frequent volume changes of the storage material when the phase change occurs [11]. In recent years, there are many studies reported on the PCMs concerning the microencapsulation technique for developing microencapsulated paraffin PCMs. The conventional microcapsules of paraffin PCMs usually employed polymers as shell materials. Sánchez et al. [12] developed a cheap and feasible pathway for the microencapsulation of PCMs with a polystyrene shell by suspension polymerization. Onder et al. [13] investigated the encapsulation technology of paraffin waxes with natural and biodegradable polymers, achieving high heat-storage capacities by the complex coacervation method. Zhang et al. [14,15] introduced the synthesis of the PCMs microcapsules with a resorcinol-modified melamine–formaldehyde shell and polyuria-shells containing different soft segments through in situ polymerization and interfacial polymerization. However, those polymeric wall materials have the common drawbacks, such as flammability, low mechanical strength, poor thermal and chemical stability, and low thermal conductivities. Most of inorganic materials show a better rigidity and strength than the polymeric ones, and therefore, a high-strength inorganic shell material not only improves the thermal transfer performance of a PCM system but also increases the durability and working reliability of microencapsulated PCMs [16]. Some attempts have recently been taken to enhance the thermal conductivity of the microcapsule shell by encapsulating PCMs into inorganic silica. Wang et al. [17] firstly reported the preparation method of inorganic microcapsules by encapsulating PCMs with silica in an oil-in-water emulsion. Shi et al. [18] reported the synthesis of microencapsulated paraffin composites with a silica shell as thermal-energy-storage materials via a sol–gel process. Nevertheless, the aforementioned silica microencapsulated PCMs were white powders, which have weak optical absorption property in the solar thermal utilization systems. The visible light which accounts for approximately 44% of solar radiation almost cannot be directly or effectively utilized by the white microencapsulation due to the poor visible light absorptivity. Therefore, the wall materials were modified by high absorptive materials such as carbon materials, thus greatly improve the optical absorption performance of microencapsulated PCMs. Graphene oxide, a carbon material contains myriad oxide functionalities (predominately alcohols and epoxides), but retains a stacked structure similar to graphite, [19] is easily compounded with other materials. Zhang et al. [20] introduced the synthesis of the PCMs microcapsules with the n-hexadecane shell and double-walled shells (polystyrene/graphene oxide) through Pickering emulsion template.

The phase change slurry, formed by adding phase change material into the base fluid, is a kind of promising medium for thermal energy storage and management [21]. The addition of phase change materials can obviously strengthen the heat capacity of the fluid and thus enhance the heat transfer performance. The high viscosity and the big flow resistance mainly exist in the phase change emulsion, but these defects can be improved in the suspending liquid with microencapsulated phase change materials [22]. The work by Siddiqui et al. demonstrated that the phase change slurry based solar collector has higher efficiency that normal fluids, implying that the phase change slurry has great potential to be used as heat transfer fluid in the direct solar thermal collectors [23]. The performance of heat transfer of the fluid will be greatly improved by adding the graphene oxide with a high thermal conductivity into the latent functional thermal fluid.

In this paper, in order to develop new phase change slurry for DASCs, a microencapsulated PCM with paraffin as core and SiO_2 as shell material was prepared, and the graphene oxide was induced into the SiO_2 shell to improve the efficiency of solar energy utilization. The paraffin@SiO_2/GO composite have a high thermal storage capability and good thermal stability, and the new material can absorb visible light and convert it to thermal energy more effectively compared with traditional organic PCMs. The microencapsulated PCMs containing graphene oxide was dispersed in water, which shows excellent photo-thermal performance. Therefore, we developed a new kind of phase change slurry with enhanced thermal property and photo-thermal performance, which is promising to store solar thermal energy in practical application.

2. Experimental section

2.1. Materials and reagents

Paraffin (melting point 60–62 °C) was purchased from Huayong Paraffin Co., Ltd. Span80 (CP) was purchased from Tianjin Fu Chen Chemical Reagents. Tween80 (CP) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Polyvinyl alcohol (PVA, AH-26, GR) and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetra ethoxysilane (TEOS, CP) and glacial acetic acid were purchased from Guangzhou Chemical Reagent Factory and Shanghai Richjoint Chemical Reagents Co., Ltd, respectively. Graphene oxide (GO) dispersion solution was purchased from Nanjing XFNANO Materials Tech Co., Ltd.

2.2. Synthesis

The procedure for microencapsulating paraffin included the preparation of an emulsion and the formation of a shell material, as shown in Fig. 1. The emulsion was prepared by dispersing paraffin in PVA aqueous solution with the aid of Tween80 and Span80. The SiO_2 shell material was formed through the interfacial hydrolysis and condensation of TEOS. A typical synthesis of the paraffin@SiO_2/GO composite was carried out as follows. 1.5 g of PVA was dissolved in 98.5 mL of distilled water to obtain a PVA aqueous solution; 9.2 g of paraffin and 3.0 g of mixed surfactants (the mass ratio of Span80 to Tween80 is 0.45–0.55) were mixed to form an organic solution; the aqueous PVA solution was added to the organic solution, and the mixture was emulsified mechanically at a stirring rate of 600 r/min to form an O/W emulsion; while stirring, 2.0 g of sodium chloride solution (2.5 M) was added into the emulsion; after stirring for 30 min, 15 g of TEOS and 0.2 g of acetate acid solution (10.0 mass%) were added drop by drop into