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Fabrication of novel slurry containing graphene oxide-modified microencapsulated phase change material for direct absorption solar collector

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ABSTRACT

In this study, a new microencapsulated phase change material, paraffin@titania (TiO_2)/graphene oxide (GO), was prepared by in-situ hydrolysis and polycondensation of tetrabutyl titanate and the modification of GO on the TiO_2 shell. The paraffin@TiO_2/GO composite consisted of spherical particles with the diameters of 2–5 µm. Raman spectra analysis confirmed the compound of GO with the TiO_2 shell. The melting temperature and latent heat of the paraffin@TiO_2/GO composite were 60.04 °C and 74.99 J g^{-1}, respectively, in which the encapsulation efficiency of paraffin was calculated to be 37.93%. It was noteworthy that the paraffin@TiO_2/GO composite displayed better thermal stability than paraffin due to the shell material. Most of all, the novel heat transfer slurry prepared by dispersing the paraffin@TiO_2/GO composite into water exhibited higher thermal conductivity, specific heat and light absorption properties along with outstanding photo-thermal conversion performance. The prepared paraffin@TiO_2/GO composite with high heat storage capability and excellent photo-thermal conversion performance enable it to be a promising candidate in direct absorption solar collector for solar energy storage.

1. Introduction

Solar energy is one of the best renewable and sustainable sources with least environmental impact for replacing fossil fuels to save the energy crisis and environment problems [1]. Solar thermal collector, a device collecting and converting solar radiation into heat energy, is the most important technology for solar utilization system [2]. However, the poor collection and conversion efficiency of the conventional flat plate solar collector are greatly restricting the utilization of solar energy. In 1970s, Minardi and Chuang proposed the concept of direct absorption solar collector (DASC), where the internal working fluid directly absorbed the solar radiation and converted the energy to thermal [3]. This new kind of solar collector has higher receive efficiency of solar energy than the conventional solar collector since it can reduce the radiant heat loss and avoid the temperature difference between the surface of solar collector and the inside heat transfer fluid [4]. The receive efficiency of solar utilization system is dominated directly by the optical and thermo-physical properties of heat transfer fluid. Therefore, in order to acquire the high-efficiency DASC, it is significant to develop novel heat transfer fluid with the excellent thermo-physical properties and photo-thermal conversion performance.

The conventional heat transfer fluids: water, ethylene glycol, propylene glycol, thermal oil (Therminol VP-1) and the molten salt were widely used in solar thermal utilization system [5–8]. However, these fluids have low absorption properties in the visible spectrum, which contains 44% of the solar radiation energy. So there were many attempts to improve the optical absorption properties and thermo-physical performance by adding micron or nano-sized metal, metal oxide and carbon nano-materials into the based fluid to form the two-phase slurry, among these materials, the carbon nano-materials exhibited great promotion to be applied to heat transfer slurry for DASC due to their black body with high absorption coefficient and thermal conductivity. Karami et al. [9] dispersed the alkaline functional carbon nanotube (f-CNT) into water to form heat transfer slurry and investigated the optical properties and thermal conductivity. They found that adding 150 ppm of f-CNT greatly increased the extinction coefficient and enhanced 32.2% of thermal conductivity of the prepared slurry compared to pure water. Vakili et al. [10] prepared the working fluid containing graphene nanoplateles on the basis of water for DASC. They found that an increase in weight percent of graphene

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nanoplatelets improved both the absorption coefficient and thermal conductivity of the fluid. However, this kind of heat transfer slurry stored energy by the sensible heat storage mode depending on the low specific heat of the based fluid, which is greatly limited to store larger solar energy [11].

In recent years, the carrier fluid incorporated with phase change materials (PCMs) as the latent functional heat fluid (LFTF) has attracted much attention [12–14]. The PCMs can store and release large amount of latent heat during the phase transition process with nearly constant temperature, which contributes the LFTF to have high latent heat storage capacity and excellent heat transfer performance leading to outstanding heat storage rate over natural convection [15]. Moreover, the microencapsulated phase change material slurry (MPCMS) is considered as the most proposed LFTF which is fabricated by encapsulating organic PCMs as the core into organic or inorganic shell and then the microencapsulated PCMs (Micro-PCMs) particles are dispersed into the based fluid. The microencapsulation technology can effectively prevent bulk PCMs leaking from solid to liquid, improve the heat transfer efficiency, reduce the effect of external environment and enhance the thermal conductivity of PCMs [16]. The traditional Micro-PCMs were almost synthesized by polymer shell such as polymethyl methacrylate (PMMA) [17], melamine formaldehyde resin [18], urea formaldehyde [19], and polyurethane [20] by in-situ polymerization, interfacial polymerization or suspension polymerization. Paraffin, the most widely used organic PCMs, has many advantages in thermal energy storage, such as high latent heat, wide range of melting point, stable chemical properties, and reasonable price. Therefore, there were many studies focused on microencapsulating paraffin with polymer shell in recent years. Sánchez et al. [21] prepared the paraffin wax microcapsules with a polystyrene shell by suspension-like polymerization. The paraffin microcapsule has high latent heat of 153.5 J g^{-1} which is very suitable for thermal energy storage application. Ma et al. [22] developed a fast microencapsulated method to synthesize the PMMA/paraffin microcapsules by introducing UV irradiation with the emulsion polymerization.

However, these microcapsules with polymer shell have several intrinsic drawbacks such as low thermal conductivity, poor chemical stability, low mechanical strength and flammability. There is no doubt that the inorganic material has higher mechanical strength and thermal conductivity compared to polymer material. Therefore, using inorganic materials as shell not only can increase the working reliability but also improve the heat transfer performance of Micro-PCMs [23], which has become a new trend for searching better performance of Micro-PCMs and MPCMS [24]. Wang et al. [25] first reported the preparation of encapsulating PCMs into silica shell by sol-gel method in oil in water (O/W) emulsion and expounded the formation mechanism of silica shell. Pan et al. [26] proposed a method of preparing the palmitic acid microcapsules with AlOOH shell through in-situ interfacial polycondensation. The latest several studies indicated that the calcium carbonate, zinc oxide and titania could be utilized as inorganic shell materials for microencapsulation of PCMs as well [27–29]. However, the aforementioned inorganic shell microcapsules usually are white powder which has poor optical absorption properties of visible light, resulting 44% of solar radiation energy cannot be effectively used for solar collector. In order to improve the optical absorption properties and thermal performance, it is obvious that compounding PCMs microcapsule with carbon material is the best method. Chen et al. [30] prepared a Micro-PCM containing the n-dodecanol core with graphene oxide-modified poly(melamine-formaldehyde) shell by in-situ polymerization. They found the thermal conductivity of Micro-PCM was greatly increased by the modification of graphene oxide. Graphene oxide as a two-dimensional carbon nanomaterial can be easily compounded well with other materials by its numerous oxide-containing functional groups. However, the photo-thermal conversion performance of these Micro-PCMs for DASC has not been investigated yet.

Usually, the Micro-PCMs were synthesized in the O/W emulsion using water as the aqueous phase through a sol-gel process. However, it is difficult to control the hydrolysis rate of organic precursors in that aqueous O/W emulsion system causing the poor structure and surface of the resultant microcapsules. Formamide was considered as the closet polar solvent to replace water in emulsification [31]. Therefore, we used formamide as aqueous phase to create a nonaqueous O/W emulsion which made the formation of TiO_2 shell more stable through the in-situ hydrolysis and polycondensation of tetrabutyl titanate in the nonaqueous emulsion. The resultant microcapsules presented well-defined core-shell structure with smooth and compact surface. According to the literature survey, there was no report about the fabrication and properties of the paraffin@TiO_2/GO composite used for DASC system.

In this paper, we prepared a novel heat transfer slurry containing paraffin@TiO_2/GO microcapsules to improve the effective receiver efficiency of DASC system for solar energy storage. The microcapsule in which paraffin as the core and TiO_2 as the shell material was synthesized by in-situ hydrolysis and polycondensation of tetrabutyl titanate, and the graphene oxide was compounded with the TiO_2 shell by self-assembled process to enhance the visible light absorption capability and thermal transfer performance. The paraffin@TiO_2/GO composite exhibited high thermal energy storage capability, outstanding thermal stability and efficient photo-thermal conversion performance. The Micro-PCM compounded with graphene oxide was dispersed into water to form a new kind of heat transfer slurry with enhanced thermo-physical properties and photo-thermal conversion performance, which can be a potential candidate in DASC for solar energy storage.

2. Experimental section

2.1. Materials and reagents

Paraffin (melting point 56–58 °C) was purchased from Shanghai Hualing rehabilitation equipment factory. Sodium dodecyl sulfate (SDS, AR) and Hexadecyl trimethyl ammonium bromide (CTAB) was obtained from Shanghai Aladdin Reagent Co., Ltd. Tetrabutyl titanate (TBT, CP), formamide (AR) and acetic acid (AR) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Deionized water was homemade. Anhydrous ethanol (AR) was purchased from Anhui Ante Food Co., Ltd. Graphene oxide (GO) dispersion solution was purchased from Nanjing XFNANO Materials Tech Co., Ltd.

2.2. Synthesis

The procedure for microencapsulated paraffin was mainly composed of two parts. The first part of the procedure was to prepare a nonaqueous O/W emulsion, and the second part was the formation of the shell material with the modification of graphene oxide. The typical experiment was as follow: 10 g of paraffin and 3.3 g SDS was mixed to form the oil phase of the emulsion under a constant temperature of 70 °C; 70 mL of formamide as the aqueous phase was added into the oil phase mixture with a stirring rate of 750 rpm for 2.5 h to obtain the stable nonaqueous O/W emulsion. Then, 10 g of TBT was added into the prepared nonaqueous emulsion with the same agitation rate for 40 min. After that, 0.2 g of acetic acid was added into the emulsion system with a mild agitation for 5 min, and then 5 g of deionized water and 30 mL of formamide were mixed and added into the mixture dropwise to trigger the hydrolysis and polycondensation of TBT. Meanwhile, the stirring rate decreased to 500 rpm at a same temperature of 70 °C for 3 h. After the reaction, 15 mL of 2 mg/mL graphene oxide dispersion solution was added into the reaction mixture drop by drop with stirring rate of 500 rpm for 2 h at 70 °C, when the gray precipitate was obtained. The resultant paraffin@TiO_2/GO composite were collected by centrifugation and washed with deionized water and anhydrous ethanol for three times, and then the paraffin@TiO_2/GO composite was dried in a vacuum oven at 50 °C for 24 h for further characterization. For comparison, the paraffin@TiO_2 sample was synthesized by the same process