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Synthesis and properties of microencapsulated stearic acid/silica composites with graphene oxide for improving thermal conductivity as novel solar thermal storage materials

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ABSTRACT

Phase change materials (PCM) have stable operation temperature and large storage capacity. However, PCM have problems of leakage and low thermal conductivity. For improving performances of PCM, stearic acid (SA) was encapsulated in silica shell by sol-gel method to form microencapsulated phase change materials (MPCM), and graphene oxide (GO) was attached to surface of silica by a self-assembly process to form GO@MPCM, so as to further improve performances of MPCM. The morphology of MPCM was observed through a scanning electronic microscope (SEM). The chemical structure and crystal phase of MPCM were measured by Fourier transformation infrared spectroscope (FT–IR) and X–ray diffractometer (XRD). Raman spectrometer was used to further verify that GO was attached to the MPCM. Thermogravimetric analyzer (TGA) analysis confirmed that MPCM have good thermal stability. Thermal properties of MPCM were measured by Differential scanning calorimeter (DSC), where melting temperature and latent heat of MPCM2 is 67.78 °C and 179.29 J/g. The melting temperature of GO@MPCM is similar to that of MPCM2, and the melting latent heat of GO1 @MPCM and GO2@MPCM is 146.72 J/g and 134.42 J/g, respectively. Besides, thermal conductivity of MPCM with GO is higher than that of pure SA.

1. Introduction

Energy is the material basis for the existence and development of human society. Especially in the past 200 years, the energy system based on fossil fuels such as coal, oil and natural gas has greatly promoted the progress and development of human society. However, the reserves of fossil fuels on the earth are very limited, and their extractions and emissions are also one of the major causes of ecological and environmental problems [1,2]. Therefore, improving the effective utilization of energy and reducing emissions have important implications for energy conservation and environmental protection. In addition, the development and utilization of renewable energy sources including solar energy, geothermal energy, nuclear fusion energy, etc. are an inevitable trend for future development, due to the fact that they are pollution–free and inexhaustible. However, most of the renewable energy sources are fluctuant and intermittent, which limits their applications. For example, solar energy exists only during sunny days, so it is impossible to achieve sustainable energy supply [3]. Therefore, the thermal energy storage system (TESS) highlights an important position in the energy structure. It can store heat including excess heat, waste heat, etc., and replace energy source at an appropriate time to provide thermal energy, thus solving the problem of sustainability of renewable energy sources and improving the effective utilization of energy [4,5]. In other words, the TESS is beneficial for reducing the imbalance between energy supply and demand and decreasing energy consumption.

The types of thermal energy storage mainly refer to sensible heat storage, latent heat storage and chemical reaction heat storage, in which latent heat storage is the most popular in recent years because of higher heat storage capacity and better controllability compared with other two heat storage methods [6]. At present, PCMs are considered as widely used renewable energy materials with high latent heat storage density and constant phase change temperature and are the most commonly used heat storage media for latent heat storage [7]. Besides, PCMs include organic, inorganic and mixed materials with different phase change temperature. However, most of the pure PCMs have the defects of leakage and low thermal conductivity, making the effect of PCMs in practical applications less than expected effect. Microencapsulated PCM means that the PCM is wrapped in a tiny container with a hard shell, and the container can withstand the phase change and volume change of the PCM, which is an effective way to improve

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the thermal properties of PCMs [8]. The superiorities of MPCMs are preventing leakage of melted PCMs, enhancing heat transfer rate and thermal conductivity, increasing thermal stability, controlling the volume change of phase change, maintaining morphological stability, and improving compatibility in applications [9–11].

The shell for encapsulating PCMs may be organic materials, inorganic materials or mixed materials, but all of them possess the common characteristics: good thermal and chemical stability, no reactions between shell and PCM and the higher melting point than PCM [12]. Currently, the extensively used organic shells are polymers containing poly (methyl methacrylate) (PMMA) [13–15], melamine–-formaldehyde [16], Poly (melamine–urea–formaldehyde) [17], etc., which possess good sealing properties and thermal and chemical stability [9]. Nevertheless, organic shells usually suffer from toxicity and flammability. As compared with inorganic shells, they have weaker mechanical strength, lower thermal conductivity, poorer thermal stability and weaker compatibility with building materials [9,18,19]. So inorganic shells have also been developed and studied, such as silica, titania [20,21], calcium carbonate [22], etc., and the study of the silica shells is relatively extensive. Liang et al. [23] used tetraethyl orthosilicate (TEOS) as a raw material to prepare MPCMs containing *n*–octadecane core and silica shell by interfacial hydrolysis and polymerization in miniemulsion. Zhu et al. [24] used TEOS as raw material and introduced methacryloxypropyl and methyl groups to fabricate organosilica shell by interface co–hydrolysis and co–polycondensation technique. Wu et al. [25] used sol–gel method to prepare MPCMs with Na_2SO_4 core and silica shell for high temperature thermal energy storage, and the TEOS was selected as silica precursor. In addition, TEOS was also used as a precursor of silica and combined with organic matter to prepare organic–inorganic hybrid shells [26–28]. Another commonly used silica precursor is sodium silicate, He et al. [29] used sodium silicate as a precursor to prepare a series of MCPMs with silica shell and n–alkanes core by sol–gel method. However, in many previous studies, MTES has rarely been used as a precursor to silica. Therefore, this article uses MTES as a precursor to provide a new way to prepare silica.

Increasing the thermal conductivity of the energy storage media helps to improve the thermal efficiency of the entire energy storage system. Therefore, some work has been done to further enhance its thermal conductivity on the basis of MPCM. Yuan et al. [7] prepared MPCM with silica shell and MPCM with silica–grafted GO shell, where the core material was paraffin wax. The results showed that both silica and GO can enhance the thermal conductivity of paraffin. Liu et al. [30] improved the thermal conductivity of *n*–dodecanol/melamine resin microcapsules with different degrees of oxidation of GO. It was found that GO contributes to the improvement of the thermal conductivity of microcapsules, but it is affected by the degree of oxidation of GO. Wang et al. [31] added expanded graphite (EG) into the microcapsule phase change material with paraffin core and calcium carbonate shell to form a composite material. Experiments have confirmed that the composite with 24 wt% of expanded graphite has a denser carbon network structure, thereby increasing the thermal conductivity. In addition to carbon-based materials, other materials were also used to enhance the thermal conductivity of microcapsules, such as nano-alumina [32] and silver [9].

Fatty acid is one of the organic phase change materials. Compared with other PCMs, it has some outstanding advantages: (1) Fatty acids are mainly derived from common vegetable and animal oils, making them cheap and easy to obtain. (2) Fatty acids have considerable latent heat storage density and an appropriate phase transition temperature range. (3) Fatty acids possess stable performances and congruent melting. (4) Fatty acids are environmentally friendly and safe materials [33]. Thereby, SA with the latent heat of 216.14 J/g and phase change temperature of 69.51 °C was selected as PCM for storing thermal energy in solar thermal conversion systems. Besides, the MPCMs encapsulated with SA were prepared by a sol–gel method using methyl triethoxysilane (MTES) as a raw material to synthetize silica shell. It is known that the preparation of silica by the sol–gel method usually requires the addition of an alkaline substance to promote the polymerization process, but the SA is acidic and can react with the alkali. Therefore, in this type of researches, more neutral materials such as paraffin were selected as the PCMs. The choices of fatty acids were rare yet. Furthermore, in the past studies, the precursor for the preparation of silica was generally tetraethoxysilane (TEOS) instead of MTES. In order to further improve the thermal conductivity of MPCMs, graphene oxide is coated on the surface of silica by self–assembly. To the best of our knowledge, the researches of GO–coated MPCMs obtained from such materials and methods are innovative. This work is aimed to investigate the properties of the novel MPCM with GO layer, and a series of measurements were performed including the chemical structure, crystal phase, morphology, thermal properties, thermal stability and thermal conductivity.

The microcapsule PCM with phase change temperature of about 67 °C can be applied to low–temperature solar energy systems, such as solar thermal collectors, solar heating systems, solar heat pump, solar dryer, to overcome the intermittence and fluctuation defects of solar energy, so that the supply of solar energy becomes stable and sustainable.

2. Experimental

2.1. Materials

Stearic acid (SA, $C_{18}H_{36}O_2$, octadecanoic acid, melting point: 67.0–70.0 °C, analytical reagent) is used as PCM in this work for thermal energy storage, which was purchased from Sinopharm Chemical Reagent Co., Ltd. Methyl triethoxysilane (MTES, $C_7H_{18}O_3Si$, reagent grade) was bought from Adamas Reagent Co., Ltd. for fabricating silica. Deionized water (homemade) and anhydrous ethanol (Reagent grade, Sinopharm Chemical Reagent Co., Ltd) are employed as the solvent. Sodium dodecyl sulfate (SDS; Reagent grade, Shanghai Chemical Reagent Co., Ltd.) acts as emulsifier to prepare stable oil–-water emulsion. Hydrochloric acid (Reagent grade, Nanjing Chemical Reagent Co., Ltd.) is used to adjust the PH value. Graphene oxide (GO) dispersion solution (Concentration: 2 mg/ml, Nanjing XFNANO Materials Tech Co., Ltd.) is used to improve the thermal conductivity.

2.2. Preparation of the SA oil–water emulsion

The raw materials for the preparation of the SA oil–water emulsion were 20 g of SA, 1.3 g of SDS and 200 ml of deionized water. The operation is as follows: SA and SDS were added to deionized water, and then which was stirred by a magnetic stirrer with the speed rate of 800 rpm for 60 min at a temperature of 80 °C. During this process, the lipophilic group of the surfactant SDS is directed toward the SA oil droplets, and the hydrophilic group binds to the water molecules, thereby forming a surfactant layer on the outer layer of the SA oil droplets. Ultimately, a stable oil–water emulsion in which SA was uniformly dispersed in deionized water was formed. It should be noted that it is usually to adjust the pH of the emulsion to 9–10 to promote polymerization when preparing silica by the sol–gel method and the pH value of the emulsion can be adjusted by adding alkaline solution such as ammonia [18]. However, the PCM used in this work was a fatty acid that reacts with alkali to form soap solution [34]. Therefore, the step of adjusting the pH value of the emulsion was omitted in this work and the pH value of the emulsion was around 6.

2.3. Preparation of the MPCM

As shown in Table 1, the MPCM with three different core–shell ratios were prepared by sol–gel technique and named as MPCM1, MPCM2 and MPCM3, respectively. The first step was the hydrolysis of the MTES, and the process is as follows: (1) Absolute ethanol and deionized