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Preparation of graphite nanoparticles-modified phase change microcapsules and their dispersed slurry for direct absorption solar collectors

Jian Liu, Leilei Chen, Xiaoming Fang*, Zhengguo Zhang*

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

A microencapsulated phase change composite, in which paraffin as the core and graphite nanoparticles embedded melamine–formaldehyde (MF) as the shell, has been prepared and characterized. The paraffin@MF/graphite composite is composed of spherical particles with diameters ranging from hundreds of nanometers to several micrometers. Raman spectroscopy analyses confirm the existence of graphite on the shell of the paraffin@MF/graphite composite. DSC results indicate that the melting temperature and latent heat of the paraffin@MF/graphite composite are 50.5 °C and 90.8 J g^{-1}, respectively, in which the mass ratio of paraffin is calculated to be 51.1%. The paraffin@MF/graphite composite can be dispersed into the ionic liquid to form a novel latent functional thermal fluid (LFTF). It is found that the temperature of the LFTF can increase from 30 to 113 °C under irradiation, indicating its remarkable photo-thermal conversion performance. The thermal storage capacity of this new kind of heat transfer fluid (HTF) is twice larger than pure ionic liquid. The high heat storage capability and excellent photo-thermal conversion performance enable the paraffin@MF/graphite composite as a potential material for solar energy utilization.

1. Introduction

Solar energy utilization is one of the most promising ways to replace fossil fuels since harnessing solar energy is carbon-neutral and renewable [1]. Solar thermal utilization, which is a direct and efficient application of solar radiation, has attracted a great deal of interest [2]. In the solar thermal energy utilization systems, solar collectors are the key component because the solar thermal utilization efficiency is largely dependent on the receiver efficiency. Direct absorption solar collectors(DASCs), where the heat transfer fluids (HTFs) directly absorb and convert solar energy to thermal energy, have been proved to have higher receiver efficiency, since it was proposed in the 1970 s [3]. In the DASCs, the receiver efficiency and the whole system efficiency were greatly limited by the optical absorption and thermo-physical properties of HTFs. Therefore, it is crucial to develop novel HTFs with excellent extinction and thermo-physical properties for high-efficiency DASCs.

In recent years, nanofluids, a kind of uniform suspensions prepared by dispersing nanosized materials into liquids such as water, ethylene glycol, thermal oil and ionic liquids [4–7], have been used as working HTFs for DASCs [8–14]. Theoretical predictions and experimental investigations have proven that the receiver efficiency of the nanofluid-based DASCs is superior to that of the flat-plate collectors [8,15], which can be attributed to the enhanced thermo-physical and optical properties of those nanofluids [16]. Among all kinds of nanoadditives composed of metal, metal oxide and carbon, carbon nanomaterials show great promise for use in preparing the nanofluids for DASCs due to their black color and high thermal conductivity [17–19]. Sani et al. [17] dispersed single-wall carbon nanohorns (SWCNHs) and carbon black into ethylene glycol to form nanofluids and investigated optical properties of the nanofluids; They found that the SWCNHs and carbon black dispersed nanofluids exhibited excellent optical absorption properties as compared with pure ethylene glycol. Otanicar et al. [8] numerically and experimentally investigated the photo-thermal performance of the nano-graphite dispersed nanofluids; The obtained results showed an improvement in receiver efficiency of up to 5% even the volume fraction of the nano-graphite is as low as 0.5%. Wang et al. [18,19] numerically and experimentally investigated the photo-thermal performance of the

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* Corresponding authors.
E-mail addresses: cexmfang@scut.edu.cn (X. Fang), cezhang@scut.edu.cn (Z. Zhang).

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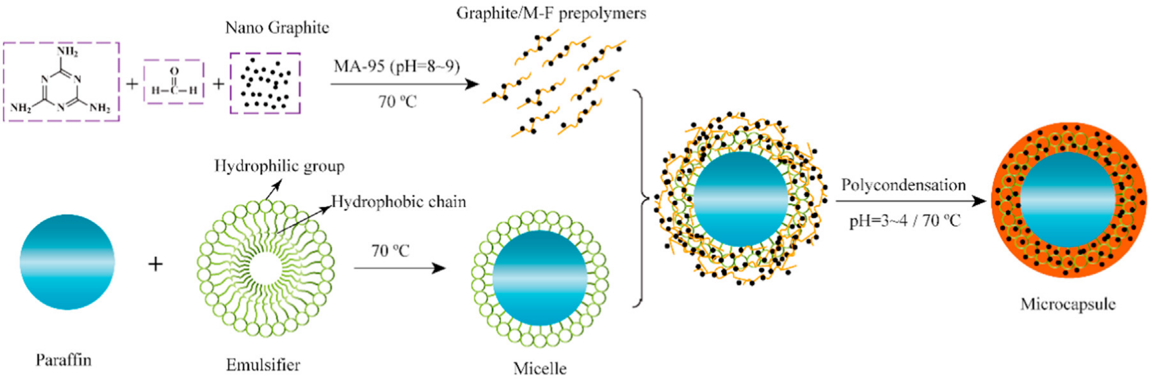

Fig. 1. Scheme of preparing the paraffin@MF/graphite composite.

carbon-coated cobalt nanoparticles/Terminol®VP-1 nanofluid; the obtained results indicated that the total efficiency of the new nanofluid-based DASC is as high as 35%, meaning that the nanofluid based DASCs are capable of replacing the fossil fuel in thermal energy utilization.

Moreover, the incorporation of phase change materials (PCMs) into conventional HTFs to prepare latent functional thermal fluids (LFTFs), has been proven to be an effective way for achieving heat transfer enhancement by increasing the apparent specific heat of the HTFs, owing to the latent heat absorbed or released by the PCMs during their phase-changing process. Microencapsulated PCM slurry is a kind of LFTFs, which can be prepared by encapsulating PCMs with organic or/and inorganic shells followed by dispersing into conventional HTFs. Several theoretical and experimental studies [20,21] revealed that the phase change slurries exhibited an enhancement in convective heat transfer performance. Also, the numerical investigation by Siddiqui et al. [22] demonstrated that the phase change slurry based solar collector has higher efficiency than the one based on the normal fluids owing to the superior effective specific heat of the phase change slurry over that of the normal fluids, suggesting that the LFTFs has great potential to be used as HTFs in the DASCs. In addition, in order to improve the thermal conductivity of the microencapaluated PCMs (Micro-PCMs) with organic shells, graphene oxide, a kind of two-dimensional carbon nanomaterials, has been used to modify the polymer shells. Chen et al. [23] fabricated a Micro-PCM with n-dodecanol as the core and graphene oxide modified melamine-formaldehyde (MF) resin as the shell; They found that the graphene oxide modified Micro-PCM has higher thermal conductivity than the unmodified one indicating the modification with carbon nanomaterials has the function of enhancing heat transfer characteristic. Wang et al. [24] successfully prepared a Micro-PCM with a high microencapsulation ratio of PCM (78%) and a double-walled shell by Pickering emulsion templating, in which n-hexadecane was used as the core, polystyrene as the interior shell and graphene oxide as the exterior shell. The obtained results showed that the graphene oxide was in favor of stabilizing the Micro-PCM dispersed phase change slurry. Based on the above researches, one can expect that the slurries containing the carbon nanomaterials modified Micro-PCMs should exhibit enhanced thermal conductivity and high specific heat, making them very promising working fluids for DASCs. However, no work has been done on the optical property and photo-thermal performance of these slurries yet.

In this study, graphite nanoparticles were used to modify a Micro-PCM that is composed of paraffin as the core and the MF resin as the shell. The morphology, structure and thermal properties of the graphite nanoparticles modified Micro-PCM were characterized. And then, the modified Micro-PCM was dispersed into an ionic liquid ([BMIM]BF_4) to obtain a novel LFTF, with the purpose of developing a suitable working fluid for medium-temperature DASCs. The thermal conductivity, specific heat and photo-thermal performance of the novel LFTF were investigated. It is found that the LFTF exhibits enhanced thermal conductivity and high photo-thermal performance, making it an applicative HTF in DASCs.

2. Experimental section

2.1. Materials and reagent

Paraffin was purchased from Huayong Paraffin Co, Ltd. Melamine and formaldehyde (AR 99%) were purchased from Tianjin Fu Chen Chemical Reagents. Polyving akohol, citric acid, ethanol, the surfactant SMA1000HNa and the emulsifier MA-95 were purchased from Aladdin Reagent (Shanghai) Co., Ltd. 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) was purchased from Lanzhou institute of chemical physics, China. Nano graphite was purchased from Nanjing XFNANO Materials Tech Co, Ltd.

2.2. Synthesis

The procedure for microencapsulating paraffin was similar to that of the previously reported method [23] with some modifications, which includes the synthesis of a MF prepolymer solution, the preparation of an emulsion, and the formation of the shell material modified with graphite nanoparticles, as shown in Fig. 1. The pre-polymer solution was synthesized by mixing 20 g of melamine, 43 g of formaldehyde (37%), 0.2 g of graphite and 20 g of distilled water. The pH of the obtained mixture was adjusted to 8.5 with MA-95 under stirring at 70 °C for 3 h. 10 g of paraffin, 1 g of SMA1000HNa, 0.1 g of polyving akohol and 80 ml of distilled water were emulsified mechanically at 65 °C with a stirring rate of 1500 rpm for 1 h. The prepolymer solution was added dropwise into the emulsion under stirring, and then the emulsion was adjusted to pH 3.4 with a citric acid solution. After the mixed system was continuously stirred at 70 °C with a rate of 800 rpm for 3 h, the shell material was formed. Finally, the resultant microcapsules were filtered and washed with ethanol and distilled water for several times at approximately 60 °C. The wet powder was dried in a vacuum oven at 60 °C for 24 h to remove water. The obtained sample was donated as paraffin@MF/graphite. For comparison purpose, the Micro-PCM with the MF shell were synthesized by the same process without adding the graphite nanoparticles and donated as paraffin@MF. In addition, a MF sample was synthesized by a similar process without adding any paraffin.

Phase change slurries were prepared by dispersing paraffin@MF and paraffin@MF/graphite at different mass fractions into the ionic liquid ([BMIM]BF_4), respectively.