Materials Research Express

PAPER

Synthesis of novel microencapsulated phase change material with SnO₂/CNTs shell for solar energy storage and photo-thermal conversion

Xiaochun Ma 1, Han Liu 1, Chen Chen 1, Yanjun Liu 1, Lin Zhang 1, Bin Xu 1, 2 and Fan Xiao 1, 2

1 Institute of Material Forming and Control Engineering, Zhejiang University of Technology, Hangzhou 310014, People’s Republic of China
2 Key Laboratory of Mechanical Engineering, Zhejiang University of Technology, Hangzhou 310014, People’s Republic of China

Authors to whom any correspondence should be addressed.

E-mail: sub@zjut.edu.cn and xiaofan@zjut.edu.cn

Keywords: microcapsules, carbon nanotubes, phase change materials, photo-thermal conversion, tin dioxide

Abstract

In this study, In-situ precipitation reaction was used to prepare paraffin@SnO₂/CNTs composite phase change materials. The paraffin@SnO₂/CNTs composites material were prepared by using paraffin as a phase change core material, and tin dioxide and carbon nanotubes as composite shell materials. The microstructure, chemical composition and crystal phase structure of the composites were analyzed by Scanning electron microscope (SEM), Fourier infrared spectrum (FT-IR) and X-ray diffraction (XRD). The thermal performance and thermal stability of phase change materials were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The microcapsule has a core–shell structure with a diameter of 2–5 μm. The encapsulation efficiency of the paraffin@SnO₂/CNTs composite was calculated to be 42.94%. The slurry is formed by dispersing microcapsules in water, which not only greatly improves the specific heat capacity, thermal conductivity, visible light absorption, but also makes the effective receiving efficiency reach 91.79% at 40°C, indicating that it is a promising heat transfer working slurry in the field of Direct Absorption Solar Collectors (DASC) system.

1. Introduction

As a renewable, clean and abundant energy, solar energy is the most ideal energy to replace the traditional fossil fuels [1]. Solar thermal energy utilization system can make full use of solar energy [2]. Solar collector is the key component of solar energy utilization system, which can convert solar radiation into heat energy. Furthermore, the problem of solar radiation irradiation discontinuity can be solved by some corresponding energy storage technologies to promote the development of solar energy. The concept of Direct Absorption Solar Collectors (DASC) was proposed by Minardi in the 1970s [3]. The DASC system, which has no high temperature absorption surface and absorbs solar radiation directly by heat transfer fluid (HTF), can avoid the heat resistance between the absorption surface and the medium, thus effectively reducing the radiation heat loss [4]. The receiving efficiency of DASCs is influenced by the photoabsorption and thermophysical properties of HTF [5]. In order to obtain efficient receiving efficiency, it has become urgent to prepare a novel slurry having good optical and thermophysical properties.

In recent years, some studies have shown that the dispersion of metal nanoparticles [6] and carbon-based composites [7] into heat transfer fluids can improve the optical absorption properties of working fluids. However, the specific heat capacity of such a working fluid is so small that it is impossible to store too much energy, resulting in inefficient reception efficiency. Since the phase change materials (PCMs) has a large specific heat capacity, it has been found that dispersing the phase change materials into the heat transfer carrier fluid to obtain the latent functional heat fluid (LFTF) can greatly improve the thermal energy storage capacity of the
working fluid [8, 9]. As the LFTF, it can not only make full use of the latent heat of phase change materials, but also have good fluidity to carry out heat transfer, so as to realize the integration of energy storage and transportation and improve the receiving efficiency of DASC system. However, the PCMs is directly mixed with the base fluid, and a phase change occurs due to heat absorption, thereby causing delamination. The research of Microencapsulated phase change materials (Micro-PCMs) can solve the problem of stratification caused by the leakage of PCMs, which is formed by the application of microcapsule technology to phase change materials [10]. The Micro-PCMs are composite phase change materials that use a microencapsulation technique to form a core–shell structure by concentrating a shell material on the surface of PCMs, which can also enhance the heat transfer capacity of phase change materials [11, 12]. The microcapsule slurry was obtained by dispersing the Micro-PCMs in the base fluid. Because paraffin have the characteristics of low price, large latent heat and stable chemical properties, the application of paraffin in microcapsule slurry has received extensive attention. For example, Yuan et al successfully synthesized paraffin@SiO2/graphene oxide (GO) composite, which produces microcapsule slurry exhibiting excellent photo-thermal conversion efficiency [13]. Liu et al reported a new type of microencapsulated paraffin@melamine–formaldehyde (MF)/graphite microcapsules, which was dispersed into ionic liquids to obtain microcapsule slurry that exhibited excellent photothermal conversion properties [14].

The first step in preparing a phase change slurry with good photothermal performance is to synthesize phase change microcapsules with excellent thermophysical properties. The preparation of conventional microencapsulated PCM uses polymer wall materials such as urea-formaldehyde Resin, polyurethane, polymethyl methacrylate [15–17]. However, the flammability, low thermal conductivity and poor thermal stability of polymer shell materials severely limit the application of Micro-PCMs [18, 19]. The wall material of Inorganic microcapsule has high mechanical strength, flame Retardancy, heat resistance and thermal conductivity, which can enhance the heat transfer performance of PCM, durability and working reliability of microcapsule [8, 20]. Some research groups have successfully reported the synthesis of silica phase change microcapsules and found that the thermal properties of microcapsules have been significantly improved [21, 22]. Xu et al reported a method for preparing a microcapsule material using Cu–Cu2O as the shell material [23]. Li et al reported a method for preparing a multifunctional n-eicosane@ZnO composite materials via the in situ precipitation [24]. These studies have shown that the thermal conductivity of microcapsules has increased to some extent. However, the commonly prepared inorganic microcapsule powder is usually white, and the inability to effectively absorb solar radiation limits the application in solar collectors. Modification of microcapsules with carbon-based materials not only improves thermal conductivity but also solves the problem of light absorption performance. Liu et al introduced a microcapsules composite material of dodecyl alcohol as core material and MF resin modified with GO and CNTs as shell material, which not only greatly improved the thermal conductivity of the materials, but also the photothermal conversion performance of the prepared slurry has been greatly improved [25]. In addition, we have successfully prepared paraffin@TiO2/GO, and paraffin@Cu–Cu2O/CNTs microcapsules, which have greatly improved in terms of photothermal properties as compared to unmodified materials [26, 27]. According to the literature, tin dioxide (SnO2) is an inorganic material with high thermal conductivity and good thermal stability [28, 29]. Kalaiselvam et al introduced a bifunctional phase change microcapsule with SiO2/SnO2 as its shell material. Its results show that the addition of SnO2 greatly improves its thermal conductivity [30]. The purpose of this paper is to prepare a high performance photothermal conversion functional slurry to improve the receiving efficiency of the DASC system. The heat transfer slurry prepared by the paraffin@SnO2/CNTs composite phase change materials not only has good heat transfer capacity and heat storage capacity, but also has good visible light absorption performance, thereby exhibiting excellent photothermal conversion performance. Hence, this new type of slurry with good thermophysical properties and photothermal conversion performance has broad application prospects in the field of solar collectors.

2. Experimental

2.1. Materials
Paraffin as a phase change core material was supplied by Shanghai Hualing Machinery Equipment Co., Ltd; Sodium dodecyl sulfate (SDS) as an emulsifier was purchased from Shanghai Aladdin Reagent Co., Ltd; The acetic acid to adjust the pH value was provided by Shanghai Lingfeng Chemical Reagent Co., Ltd; Tin tetrachloride pentahydrate (SnCl4·5H2O, AR) as a source of tin was supplied by Shanghai Maclean Biochemical Technology Co., Ltd; Urea(CH2N2O,AR) as a precipitant was purchased from Sinopharm Group Chemical Reagent Co., Ltd; Absolute ethanol (CH3COOH,AR) was purchased from Anhui Ante Food Co., Ltd; Carboxylated carbon nanotubes (CNTs, purity >95%) was commercially obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences.
2.2. Synthesis of paraffin@SnO2/CNTs

Paraffin@SnO2/CNTs microcapsules were synthesized via in situ precipitation reaction. The mechanism of microcapsules formation is shown in figure 1. In a typical synthesis process, 6 g of sliced paraffin is melted at 75 ºC, then 2 g SDS and 40 ml of deionized water are added to obtain paraffin emulsion through emulsification for 2 h with a rate of 750 rpm. The mixture of 4 g Tin tetrachloride pentahydrate, 4.28 g urea and 0.3 g acetic acid were dissolved in 30 ml anhydrous ethanol, slowly added to the flask, and the reaction was maintained at 500 rpm for 40 min. 3 g carbon nanotubes (CNTs) and 15 ml anhydrous ethanol were mixed in another beaker to form a solution which was added dropwise into the paraffin emulsion with stirring at 500 rpm for 40 min. After that, the above mixture was transferred to a polytetrafluoroethylene reactor and hydrothermally treated at 90 ºC for 4 h, and centrifuged to obtain a dark precipitate, which was washed with deionized water and anhydrous ethanol to obtain the paraffin@SnO2/CNTs microcapsules. Microcapsule slurry was obtained by dispersing paraffin@SnO2 and paraffin@SnO2/CNTs microcapsules into deionized water, respectively.

In the initial stage of emulsification, SDS is an emulsifier in which the oleophilic and hydrophilic ends are inserted into the paraffinic oil phase and the aqueous phase, respectively, to form an oil-in-water emulsion. Since the SnCl4 · 5H2O has strong amphiphilic property, it is captured by the emulsifier molecules on the surface of the paraffin, and at the same time, more tin ions are aggregated around the paraffin due to electrostatic ion adsorption. A large amount of urea begins to be thermally decomposed and reacted with tin tetrachloride, so tin ions begin to form SnO2 nanoparticles deposited on the paraffin surface. Furthermore, Tin ions will attract carboxylated carbon nanotubes to form new microcapsule composites by coordination adsorption with carboxyl groups. After the hydrothermal treatment, the reaction product is paraffin@SnO2/CNTs composite.

2.3. Characterization of paraffin@SnO2/CNTs

The surface microstructure of paraffin@SnO2/CNTs microcapsules was observed on field emission scanning electron microscopy (SEM, Nova Nano SEM 450). The chemical structure of paraffin@SnO2/CNTs microcapsules was determined by Fourier transform infrared spectroscopy (Thermo Nicolet 6700 FT-IR spectrophotometer) using KBr pellets in the wave ranges of 4000–400 cm⁻¹. And the crystal structure of the microcapsules was determined by x-ray diffraction (Panalytical XPERT PRO diffractometer), using Ni-filtered Cu Kα radiation (λ = 0.1541 nm). The phase change properties of the products were measured by Differential scanning calorimetry (DSC, Mettler Toledo DSC with STARe System) at a scanning rate of 10 ºC min⁻¹ under nitrogen atmosphere. Thermogravimetric analysis (TGA) used the SDT Q5000 thermal gravimetric analyzer to determine the thermal stability of the paraffin@SnO2/CNTs microcapsules under a nitrogen atmosphere at a heating rate of 10 ºC min⁻¹. XIATECH Hot Disk thermal conductivity meter (TC-3000) were used to measure the thermal conductivity of the samples, which is obtained by averaging after five measurements. The UV–vis spectroscopy was performed by UV–vis spectrophotometer (UV-2450, SHIMADZU).

2.4. Photothermal analysis of slurry

In order to analyze the photothermal conversion performance of the microcapsule dispersion slurry, the measurement method is as follows. Paraffin@SnO2 and paraffin@SnO2/CNTs microcapsules microcapsules were dispersed into deionized water and 0.1 wt% SDS was added to obtain two stable slurries. The thermal conductivity meter and DSC were used to determine the specific heat capacity and thermal conductivity of the above slurry. A photothermal conversion device as displayed in figure 2 was made to analyze the photothermal conversion performance of the dispersion slurry. The device includes solar radiant energy simulation system consisting of four 60 W lamps, thermal insulation system and data collection system. The effective receiving efficiency of the prepared dispersion slurry can be calculated according to the following equation (1) [13]:

Figure 1. Schematic diagram of the paraffin@SnO2/CNTs microcapsules.
Where \( \eta \) refers receiver efficiency; \( m \) refers the mass of the heat transfer slurry; \( C_P \) refers the specific heat capacity; \( G_S \) represents solar radiation intensity; \( A \) refers the area of the energy received by the light source, \( T \) refers the real-time temperature of the microcapsule slurry, and \( t \) is the irradiation time of the sample. The \( G_SAt \) of the equation (1) represents the heat of the sample to be tested received by the simulated light source, and the \( m \int C_P(T) dT \) of the formula represents the heat actually absorbed by the irradiation to increase the temperature. The ratio of the two results is the effective receiving efficiency. In these test, the weight of the test slurry is 8 g, the received light area is \( 4 \pi \text{ cm}^2 \), and the solar simulated irradiance is 1000 W m\(^{-2}\).

3. Results and discussion

3.1. Morphology of paraffin@SnO\_2/CNTs microcapsules

The microstructure of the paraffin@SnO\_2/CNTs microcapsules composite is displayed in figure 3. It can be clearly found that all the microcapsules have a quasi-spherical structure with diameter of 1–5 \( \mu \text{m} \). As shown in...
Figure 3(a), some small tin oxide particles on the surface of the microcapsules result in a rough surface morphology, which can be attributed to the free deposition of tin oxide nanoparticles. When the carbon nanotubes are added for modification, the surface of the microcapsules becomes smoother because the addition of carbon nanotubes slows down the self-polymerization of the tin oxide particles, and the precipitated tin oxide can cover the paraffin surface more uniformly, as displayed in figures 3(b), (c). Figure 3(d) is a further enlarged image showing the carboxylated carbon nanotubes entangled on the surface of paraffin@SnO2/CNTs microcapsules, and the illustration in the upper right corner is broken microcapsules, from which the core–shell structure can be clearly observed.

3.2. Characterization of paraffin@SnO2/CNTs microcapsules

The FT-IR spectra of paraffin, SnO2, paraffin@SnO2 and paraffin@SnO2/CNTs are displayed in figure 4(a). The absorption peaks at 2918 cm⁻¹ and 2849 cm⁻¹ ascribe to the stretching vibration of −CH₃ and −CH₂ in the spectrum of paraffin, while the absorption peaks at 1463 cm⁻¹ and 1377 cm⁻¹ represent the in-plane bending vibration of −CH₃ and −CH₂. These peaks are typical infrared characteristic peaks of paraffin. In the spectrum of the SnO₂, the vibrational bands at 1638 and 3453 cm⁻¹ can be correspond to the bending vibration and stretching vibration of hydroxyl group, respectively. The band at 1058 cm⁻¹ is observed due to the vibration of different types of surface hydroxyl groups, and the absorption peak at 562 cm⁻¹ belongs to the variable angle vibration of the Sn–O–Sn. Compared with the infrared absorption curve of SnO₂ and paraffin, it can be found that the paraffin@SnO₂ microcapsules have all the absorption peaks of SnO₂ and paraffin, indicating that the microcapsules contain SnO₂ and paraffin. There is no new peak in the composite phase change material, which shows that all parts of the material combine in physical way. In addition, the absorption peaks of paraffin@SnO₂
microcapsules and paraffin@SnO$_2$/CNTs composites are similar, and no absorption peaks of CNTs are observed, which may be due to the low concentration of carbon nanotubes, resulting in too weak absorption peaks.

The crystal structure is determined by XRD, as shown in figure 4(b). The diffraction peaks at 21.48°, 23.86°, 36.09° and 40.50° can be allocated to the plane (110), (200), (210) and (310), respectively, according to JCPDF No. 0401995. There are five broad diffraction peak at 26.5°, 33.7°, 37.2°, 51.9° and 65.4°, which demonstrate the amorphous structure of SnO$_2$. Both the paraffin@SnO$_2$ microcapsules and paraffin@SnO$_2$/CNTs composites contain all XRD characteristic peaks of paraffin and SnO$_2$, which confirms that the paraffin is successfully encapsulated in the SnO$_2$ shell. Because there are fewer carbon nanotubes in the microcapsule composite, the diffraction peak intensity of the carbon nanotube is so weak that it cannot be observed in XRD diffraction, but the SEM can clearly observe its existence.

3.3. Thermal properties

The phase-change property of paraffin@SnO$_2$ microcapsules and paraffin@SnO$_2$/CNTs composites were investigated by the dynamic DSC. The DSC thermograms of paraffin, paraffin@SnO$_2$ microcapsules and paraffin@SnO$_2$/CNTs composites were shown in figure 5. In addition, the thermal conductivities of the product were measured by a transient hot-wire method using XIATECH Hot Disk thermal conductivity meter (TC-3000). The relevant parameters were listed in table 1. The DSC curve shows that there are a large amount of endothermic and exothermic in two temperature ranges, which can be ascribed to the solid-solid phase transition and solid-liquid phase change of paraffin, respectively. The phase change characteristics of paraffin@SnO$_2$ microcapsules and paraffin@SnO$_2$/CNTs composites are similar to those of paraffin because...
parafin does not chemically react with the shell material during microcapsule preparation. Based on the DSC curve, it can be found that crystallization temperature and melting temperature of parafin are determined to be 56.48 and 61.45 °C, and its enthalpy is at 203.07 and 197.89 J g⁻¹, respectively. The parafin@SnO₂ microcapsules melt at 61.63 °C and freezing at 56.31 °C with latent heat of 133.08 and 132.17 J g⁻¹, respectively.

The CNTs were added to modify the microcapsules, and the formed parafin@SnO₂/CNTs composites melt at 61.43 °C and crystallizes at 55.39 °C with a latent heat of 86.50 and 85.67 J g⁻¹, respectively. It can be found that the crystallization temperature of parafin@SnO₂ microcapsules and parafin@SnO₂/CNTs composites is somewhat reduced compared to pure parafin, which can be ascribe to the heterogeneous nucleation of parafin encapsulated in tiny spaces [31]. Based on the above data, the encapsulation efficiency (E) of product is calculated by equation (2) [32]:

\[ E = \frac{\Delta H_{\text{f,paraffin}} + \Delta H_{\text{m,paraffin}}}{\Delta H_{\text{f,microcapsules}} + \Delta H_{\text{m,microcapsules}}} \times 100\% \]

In order to obtain high efficiency thermal energy storage, the most important factors are the heat transfer efficiency and the loading of phase change material in the micro-capsule or the encapsulation efficiency (E) of PCMs. The phase change materials microcapsules with the inorganic shell like SnO₂ shell or Carbon nanotube modified composite shell are the best choice to improve the thermal conductivity and high en-capsulation efficiency, which is contributed to obtain high efficiency thermal energy storage system. Where \( \Delta H_{\text{f,microcapsules}} \) and \( \Delta H_{\text{m,microcapsules}} \) are the crystallization and melting latent heats of the product, respectively; \( \Delta H_{\text{f,paraffin}} \) and \( \Delta H_{\text{m,paraffin}} \) represent crystallization and melting latent heats of the pure paraffin, respectively. According to the enthalpy of phase change microcapsules and paraffin, the paraffin encapsulation efficiency of microcapsules can be calculated. The encapsulation efficiency of the paraffin@SnO₂ microcapsules is calculated as 66.15%, and the encapsulation efficiency of the paraffin@SnO₂/CNTs composites is 42.94%.

3.4. Thermal stability of paraffin@SnO₂/CNTs microcapsules

The TGA curve of paraffin, paraffin@SnO₂ and paraffin@SnO₂/CNTs composites are displayed in figure 6. The thermal decomposition process of paraffin is only one step, occurring at 250–340 °C, in which the paraffin is completely decomposed. For paraffin@SnO₂ and paraffin@SnO₂/CNTs composites, the thermal

![Figure 6. TGA thermograms of paraffin, paraffin@SnO₂ microcapsules and paraffin@SnO₂/CNTs composites.](image)

### Table 1. Phase-change performance of paraffin, paraffin@SnO₂ and paraffin@SnO₂/CNTs.

| Samples                  | \( T_f \) (°C) | \( T_m \) (°C) | \( \Delta H_f \) (J g⁻¹) | \( \Delta H_m \) (J g⁻¹) | E (%) | Thermal conductivity (W m⁻¹ K⁻¹) |
|--------------------------|----------------|----------------|--------------------------|--------------------------|-------|---------------------------------|
| paraffin                 | 56.48          | 61.45          | 203.07                   | 197.89                   | —     | 0.25                            |
| paraffin@SnO₂            | 56.31          | 61.63          | 133.08                   | 132.17                   | 66.15 | 0.69                            |
| paraffin@SnO₂/CNTs       | 55.39          | 61.43          | 86.50                    | 85.67                    | 42.94 | 0.77                            |
decomposition of paraffin phase change materials is significantly slowed down, which can be ascribe to the protective effect of SnO$_2$ shell materials. The above results illustrate that the thermal stability of microcapsules encapsulated paraffin can be significantly enhanced. Due to the good thermal properties of the above microcapsule composite, making it possible to be applied in the DASC system.

3.5. Thermophysical properties and photo-thermal conversion performance of slurry
A photograph of a 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs dispersion slurry is shown in figure 7(a). Since the carbon nanotubes are attached to the microcapsules, the color of the slurry is significantly darkened, which can effectively enhance the absorption efficiency of solar radiation. As the fluid temperature ranges from 30 to 80 °C, the thermal conductivity of water, 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs slurry as displayed in figure 7(b) increases from 0.6136, 0.6394 and 0.6417 W m$^{-1}$ K$^{-1}$ to 0.669, 0.7003 and
0.7095 W m$^{-1}$ K$^{-1}$, respectively. It can be found that the thermal conductivity of the heat transfer slurry containing 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs are enhanced by 4.03%, 4.37% compared with the based fluid at 30 °C. This increase in thermal conductivity is due to the high thermal conductivity tin oxide shell material and the carbon nanotube modified composite shell material, which provides a possibility for the application of the heat transfer slurry in the DASC system. Figure 7(c) is the specific heat of deionized water, 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs slurry. For the microcapsules slurry, its specific heat capacity is larger than water from 40 to 50 °C, especially at about 60 °C, the specific heat capacity of the slurry is significantly increased, which can be attributed to the solid-liquid phase change in paraffin, since paraffin can absorb a large amount of heat during the phase change process. The difference in specific heat capacity of the slurry is due to the difference in latent heat of the dispersed sample. The larger the latent heat value of the microcapsule sample, the larger the specific heat capacity. This shows that the addition of phase change microcapsules in conventional fluids can increase the specific heat capacity to enhance the solar heat storage capacity of heat transfer working fluids. The relationship between temperature and irradiation time curve of water, 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs slurry is shown in figure 7(d). After all the samples were exposed to the simulated light source for 3000 s, the temperature of the 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs slurry gradually increased to 82.5 and 90.2 °C, respectively, while the water temperature only reached 75.6 °C, suggesting the excellent photothermal conversion performance of paraffin@SnO$_2$/CNTs slurry. This can be attributed to the carbon nanotube-modified slurry having a darker color as shown in figure 7(a), thereby facilitating visible light absorption. According to equation (1), the effective receiving efficiency of water, 5 wt% paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs slurry can be calculated as displayed in figure 7(e). The results show that the prepared slurry has high photothermal conversion efficiency as compared to the based fluid. The optical properties of the paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs composites were determined by UV-visible spectroscopy as shown in figure 7(f). The absorbance of the paraffin@SnO$_2$/CNTs composites in the visible region is three times that of the paraffin@SnO$_2$ microcapsules, indicating that the modified CNTs on the microcapsule shell can significantly improve the optical absorption. In addition, since the microcapsules have a large thermal conductivity as displayed in table 1, the absorbed solar radiation can be efficiently transferred to the phase change material for storage. The above results indicate that the carbon nanotube-modified microcapsules have high thermal conductivity and light absorption properties, so that the slurry dispersed under appropriate loading conditions has high thermal conductivity, large specific heat capacity and good photo-thermal conversion performance, indicating that the prepared new slurry has broad prospects in the field of DASC system.

4. Conclusions

A new type of paraffin@SnO$_2$/CNTs microcapsules were successfully synthesized by an in situ precipitation reaction approach. According to the results of SEM, FT-IR and XRD, it can be found that the pure paraffin is well encapsulated in a tin oxide shell, and the paraffin@SnO$_2$/CNTs microcapsules have a quasi-spherical structure with a diameter of 1–5 μm. Based on DSC data, the encapsulation efficiency of paraffin@SnO$_2$ and paraffin@SnO$_2$/CNTs composites was 66.15 and 42.94%, respectively, which illustrates that phase change microcapsules have good thermal storage performance. The TGA curve shows that paraffin has excellent thermal stability under the protection of the shell material. The thermal conductivity of paraffin@SnO$_2$/CNTs microcapsule slurry increased by 4.38% compared with the base fluid. In addition, not only the visible light absorption performance of paraffin@SnO$_2$/CNTs microcapsule slurry has been significantly improved, but also the photothermal conversion efficiency can reach 91.79%, indicating that the microcapsule slurry is a potential heat transfer fluid in DASC.

Acknowledgments

The authors gratefully acknowledge the financial supports from Natural Science Foundation of Zhejiang Province (No. Y4110505) and National Natural Science Foundation of China (No. 51201152).

ORCID iDs

Xiaochun Ma  https://orcid.org/0000-0002-9348-1872
Lin Zhang  https://orcid.org/0000-0001-9647-8110
Bin Xu  https://orcid.org/0000-0001-5253-3640
Fan Xiao  https://orcid.org/0000-0002-4048-2425
References

[1] Vakili M, Hosseinalipour SM, Delfani S and Khojastepour S 2016 Photothermal properties of graphene nanoplatelets nanofluid for low-temperature direct absorption solar collectors Sol. Energy Mater. Sol. Cells 152 187–91

[2] Gupta HK, Agrawal GS and Das Mathur J 2015 An experimental investigation of a low temperature Al2O3–H2O nanofluid based direct absorption solar collector Sol. Energy 118 390–6

[3] Minardi IE and Chuang HN 1975 Performance of a ‘black’ liquid flat-plate solar collector Sol. Energy 17 179–83

[4] Otanicar T P and Golden J S 2009 Comparative environmental and economic analysis of conventional and nanofluid solar hot water technologies Environ. Sci. Technol. 43 6082–7

[5] Delgado M, Lazaro A, Mazo J and Zalba B 2012 Review on phase change material emulsions and microencapsulated phase change material slurries: materials, heat transfer studies and applications Renew. Sustain. Energy Rev. 16 253–73

[6] Karimi M, Akhavan-Bahabadi M A, Delfani S and Raisee M 2015 Experimental investigation of CuO nanofluid-based direct absorption solar collector for residential applications Renew. Sustain. Energy Rev. 52 793–801

[7] Karimi M, Bahabadi M A A, Delfani S and Ghozatloo A 2014 A new application of carbon nanotubes nanofluid as working fluid of low-temperature direct absorption solar collector Sol. Energy Mater. Sol. Cells 121 114–8

[8] Jamekhoshid A, Sadrameli S M and Farid M 2014 A Review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium Renew. Sustain. Energy Rev. 31 531–42

[9] Liu C, Rao Z, Zhao J, Huo Y and Li Y 2015 Review on nanoencapsulated phase change materials: preparation, characterization and heat transfer enhancement Nano Energy. 13 814–26

[10] Royon L, Perrot P, Guiffrit G and Frauza S 1998 Physical properties and thermorheological behaviour of a dispersion having cold latent heat-storage material Energy Convers. Manag. 39 1529–35

[11] Chen Z, Wang J, Fei Y, Zhang Z and Gao X 2015 Preparation and properties of graphene oxide-modified poly(melamine-formaldehyde) microcapsules containing phase change material n-dodecane for thermal energy storage J. Mater. Chem. A 3 11624–30

[12] Wang X, Li C and Zhao T 2018 Fabrication and characterization of poly(melamine-formaldehyde)/silicon carbide hybrid microencapsulated phase change materials with enhanced thermal conductivity and light-heat performance Sol. Energy Mater. Sol. Cells 183 82–91

[13] Yuan K, Wang H, Jian L, Fang X and Zhang Z 2015 Novel slurry containing graphene oxide-grafted microencapsulated phase change material with enhanced thermo-physical properties and photo-thermal performance Sol. Energy Mater. Sol. Cells 143 29–37

[14] Jian L, Chen L, Fang X and Zhang Z 2017 Preparation of graphite nanoparticle-modified phase change microcapsules and their dispersed slurry for direct absorption solar collectors Sol. Energy Mater. Sol. Cells 159 159–66

[15] Yuan K, Wang H, Jian L and Yang Z 2008 Synthesis and properties of paraffin capsules as phase change materials Polymer (Guildf) 49 2903–10

[16] Ji L, Tai Q, Lu H, Yuan H and Lei S 2010 Microencapsulated ammonium polyphosphate with polyurethane shell: preparation, characterization, and its flame retardant in polyurethane Polym. Adv. Technol. 21 392–400

[17] Sari A, Alkan C, Karapırelli A and Uzun O 2009 Microencapsulated octacosane as phase change material for thermal energy storage Sol. Energy 83 1757–63

[18] Yi J, Lee W, Musina Z and Ding Y 2010 A one-step method for producing microencapsulated phase change materials Particuology. 8 588–90

[19] Zhou D and Zhao CY 2011 Experimental investigations on heat transfer in phase change materials (PCMs) embedded in porous materials Appl. Therm. Eng. 31 978–7

[20] Yin D, Li M, Liu J and Zhang Q 2014 Pickering emulsion: a novel template for microencapsulated phase change materials with polymer–silica hybrid shell Energy. 64 575–81

[21] Fang G, Zhi C and Hui L 2010 Synthesis and properties of microencapsulated paraffin composites with SiO2 shell as thermal energy storage materials Chem. Eng. J. 163 154–9

[22] Li B, Liu T, Hu L, Wang Y and Gao L 2013 Fabrication and properties of microencapsulated paraffin@SiO2 phase change composite for thermal energy storage ACS Sustain. Chem. Eng. 1 374–80

[23] Xu B, Zhou J, Ni Z, Zhang C and Lu C 2018 Synthesis of novel microencapsulated phase change materials with copper and copper oxide for solar energy storage and photo-thermal conversion Sol. Energy Mater. Sol. Cells 179 87–94

[24] Li F, Wang X and Wu D 2015 Fabrication of multifunctional microcapsules containing n-eicosane core and zinc oxide shell for low-temperature energy storage, photocatalysis, and antibiosis Energy Convers. Manag. 106 837–85

[25] Liu Z, Chen Z and Yu F 2019 Enhanced thermal conductivity of microencapsulated phase change materials based on graphite oxide and carbon nanotube hybrid filler Sol. Energy Mater. Sol. Cells 192 72–80

[26] Ma X, Liu Y, Liu H, Zhang L, Xu B and Xiao F 2018 Fabrication of novel slurry containing graphite oxide-modified microencapsulated phase change material for direct absorption solar collector Sol. Energy Mater. Sol. Cells 188 73–80

[27] Xu B, Chen C, Zhou J, Ni Z and Ma X 2019 Preparation of novel microencapsulated phase change material with Cu–Cu2O/CNTs as the shell and their dispersed slurry for direct absorption solar collectors Sol. Energy Mater. Sol. Cells 200 109980

[28] Habibzadeh S, Kazemi-Beydokhti A, Khodadadi A A, Mortazavi Y, Omanovic S and Shariat-Niasar M 2010 Stability and thermal conductivity of nanofluids of tin dioxide synthesized via microwave-induced combustion route Chem. Eng. J. 156 671–8

[29] Turkes P, Plunkett C and Helbig R 2000 Thermal conductivity of SnO2 single crystals J. Phys. C: Solid State Phys. 13 4941–51

[30] Imran Hussain S, Ameelia Roseline A and Kalaiselvam S 2018 Bifunctional microencapsulated eutectic phase change material with SiO2/SnO2 nanosphere shell for thermal and electrical energy storage Mater. Des. 154 291–301

[31] Cao F and Rao Y 2014 Supercooling suppression of microencapsulated phase change materials by optimizing shell composition and structure Appl. Energy 113 1512–8

[32] Latibari S T, Mehrali M, Mehrali M, Mahlia T M J and Metselaar H S C 2013 Synthesis, characterization and thermal properties of microencapsulated phase change materials via sol–gel method Energy 61 664–72