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# Synthesis of novel microencapsulated phase change materials with copper and copper oxide for solar energy storage and photo-thermal conversion

Bin Xu[a], Jing Zhou[a], Zhongjin Ni[b,*], Caixia Zhang[a], Congda Lu[c]

[a] College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China
[b] College of Engineering, Zhejiang Agriculture and Forestry University, Linan 311300, China
[c] College of Mechanical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

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## ABSTRACT

In this study, a novel microencapsulated phase change material, paraffin@Cu-$Cu_2O$, was prepared by a hydrothermal method. The diameters of the microcapsules were 600–900 nm. The micro morphology, chemical compositions, phase change properties, and thermal stability of the products were characterized. It was calculated that the encapsulation efficiency of the microencapsulated paraffin@Cu-$Cu_2O$ composite was 62.79%. The melting temperature and freezing temperature of products were close to those of paraffin, but the products had better thermal stability and higher thermal conductivity because of the metal shell materials. Additionally, we compared the paraffin@Cu-$Cu_2O$ slurry with paraffin emulsion, and we found that the slurry had better light absorbing properties, thermal conductivity, and photo-thermal conversion performance. The developed material is a promising candidate for application in direct absorption solar collector systems.

## 1. Introduction

The energy crisis and the environmental crisis are increasingly urgent. Solar energy will become the new energy industry and the key area of development planning [1]. In the 1970s, Minardi proposed a direct absorption solar collector (DASC). The working fluid in the device can absorb solar radiation directly and convert it into heat energy [2]. This can effectively reduce the radiant heat loss and avoid the presence of thermal resistance between the heat-absorbing surface and the working fluid. The photo-thermal conversion performance of the working fluid affects the efficiency of the DASC system directly. Therefore, finding a new type of nanofluid with high photo-thermal conversion performance and excellent thermophysical properties is the key to improving the efficiency of DASC systems. In recent years, the working fluids of DASC systems have usually been nanofluids based on water and ionic liquids mixed with nanoparticles or carbon nanotubes [3–5]. Due to the presence of nanoparticles, the working fluid has different optical properties—including light absorption, transmission, and scattering of solar radiation—than ordinary fluids. It can absorb light directly or selectively in some wavelengths of the solar radiation [6].

However, the photo-thermal conversion property of nanofluids is related to not only optical properties but also thermal storage capacity [7]. The working fluid of DASC can store solar energy by absorbing radiation. In general, nanofluids have lower specific heat. Therefore, the sensible heat storage mode makes it difficult to store large amounts of solar radiation energy. This means that the working fluid can only achieve high effective receiver efficiency at high levels of radiation. In recent years, phase change materials (PCM) have been widely used in heat transfer fluids because they can absorb large amounts of energy during a phase change process. Compared with the ordinary single-phase heat transfer fluid, phase change material particles in the solid-liquid phase change process will absorb or release latent heat. This new fluid is composed of a phase change material and a single phase heat transfer fluid, which has a greater apparent specific heat in the phase transition temperature. At the same time, because of the influence of phase change particles on fluid flow and heat transfer, the heat transfer capability of the fluid can be significantly increased. Wang et al. [8] used paraffin/water emulsions as photo-thermal conversion fluids. The melting enthalpy and apparent specific heat of 20 wt% paraffin/water emulsion were $39.2\ J\ g^{-1}$ and $9.105\ J\ g^{-1}\ K^{-1}$. The emulsion has great potential for application in a DASC system, but previous experiments indicate that maintaining a stable emulsion above melting temperature is difficult as instabilities could appear during phase change. Paraffin droplets will form greater droplets, and finally, less dense paraffin will move upwards to form a layer, which leads to a stratification problem [9]. In microencapsulated PCM slurries, the PCM is microencapsulated and dispersed in water. Microencapsulation could be a good solution to

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[*] Corresponding author.
*E-mail address:* zafu_neezj@163.com (Z. Ni).

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the stratification problem [10,11]. As an efficient heat transfer medium, not only can microcapsules of PCM effectively prevent stratification of phase change materials but also greatly increase the specific heat and heat transfer performance of the fluid and significantly reduce the size of the pipeline and reduce its transmission power consumption. At the same time, microcapsules of PCM can also be used as energy storage media to integrate energy storage and transport media [12]. Among numerous organic PCMs, paraffin has the advantages of high latent heat, wide melting point range, no cooling and precipitation, stable performance, and low price. As a novel latent heat functional fluid, paraffin phase change microcapsule slurry is attracting more attention [13].

In a recent study, more than 54% of phase change microcapsules were made of melamine resin, urea formaldehyde resin, and urea-modified melamine resin as shell materials, and the encapsulation ratio of PCM was as high as 70–87% [14]. The dispersion, toughness, and heat resistance of these microcapsules were good. Zhang et al. [15] encapsulated paraffin with urea-modified melamine. After adding a certain amount of urea, the thermostability of the microcapsule was increased by 5–11°C. However, the microcapsule with polymer shell has many disadvantages, such as low mechanical strength, poor chemical stability and low thermal conductivity [16].

In order to overcome these defects, Li et al. [17] introduced a method of preparing PCM microcapsules with a silica dioxide ($SiO_2$) shell. Wang et al. [18] proposed a method of preparing PCM microcapsules with a calcium carbonate ($CaCO_3$) shell. The tests showed that the mechanical strength and thermal conductivity of these microcapsules with inorganic shells were improved. However, the products prepared were usually white powder, and the absorption of visible light was poor; visible light accounts for 44% of solar radiation, so this limits the further development of the DASC system. Therefore, it is necessary to use high optical absorption and high thermal conductivity nanoparticles, such as graphene, carbon nanotubes, and metal nanoparticles, to modify the shell. However, this will greatly increase the complexity of the process and the size of PCM microcapsules. Research shows that with an increase of the particle size of the microcapsules, the fragmentation rate during the pump cycling increases, and the suspension stability in the slurry decreases [19].

Compared with polymers and inorganic materials, metals not only have the advantages of high strength and high thermal stability but also high thermal conductivity. Copper (Cu), the most common industrial raw material, has a thermal conductivity of 401 $Wm^{-1} K^{-1}$ [20], which is much higher than that of liquid paraffin (0.22 $Wm^{-1} K^{-1}$) and solid paraffin (0.28 $Wm^{-1} K^{-1}$). At the same time, nanoscale copper has the basic characteristics, such as size effect, surface effect, and quantum effect. It has unique physical and chemical properties that are different from those of macroscopic metal bulk materials. Cuprous oxide ($Cu_2O$) is a p-type semiconductor (direct bandgap ~ 2.17 eV), and P-type semiconductors have excellent optical properties due to their typically localized surface plasmon resonances (LSPR) [21]. To put it clearly, when the frequency of incident photons match the frequency of electron conduction of the entire semiconductor, the semiconductor will have a strong effect on the photon absorption and transform solar energy into heat energy. $Cu_2O$ has unique optical, electronic, and magnetic properties and is widely used in photocatalysis, solar energy conversion, antifouling coatings, and gas sensors [22–24]. Zhang et al. [25] have synthesized hollow $Cu_2O$ microcrystals, and their experiments show that they have good optical resonance capability in the visible region.

In this paper, the aim was to create a new kind of heat transfer fluid to store solar energy and improve the effective receiver efficiency of the DASC system. PCM microcapsules were prepared by a reduction method with paraffin as the core and Cu-$Cu_2O$ as the shell material in the emulsion system. This was expected to improve the optical performance and thermal performance of paraffin simultaneously due to the high light absorption ability of $Cu_2O$ and high thermal conductivity of Cu. The microencapsulated PCMs were then dispersed in water to form a new kind of heat transfer fluid, and the fluid was tested for photo-thermal performance.

## 2. Materials and methods

### 2.1. Materials and reagents

Paraffin (melting point 60–62 °C) was purchased from Shanghai Hua Ling rehabilitation equipment factory. $Cu(HCOO)_2{\cdot}4H_2O$ was purchased from Guanghua Chemical Co., Ltd. Oleylamine (OLA, AR) was obtained from Hangzhou Shuanglin Chemical Reagent Factory. $C_6H_{12}O_6$(Glu) was purchased from Sinopharm chemical reagent Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Shanghai Aladdin Reagent Co., Ltd. Deionized water was homemade.

### 2.2. Synthesis

The procedure for microencapsulated paraffin included two main parts. The first part of the procedure was the preparation of the paraffin emulsion, and the second part was the formation of a shell material. In a typical experiment, 0.8 g of $Cu(HCOO)_2{\cdot}4H_2O$ and 1.6 g of $C_6H_{12}O_6$ (Glu) were dissolved in 80 mL of deionized water to obtain the aqueous phase; 1.6 g of paraffin and 1.6 g of Oleylamine(OLA) were mixed to form the oil phase of emulsion, and the mixture was heated to 80 °C with a mechanical agitation. The aqueous phase was added to the oil phase drop by drop with a vigorous agitation for 30 min to form a stable O/W emulsion. Then the emulsion was quickly transferred to 100 mL Teflon-lined autoclave and sealed for 12 h at 120 °C. After the reaction, the autoclave was cooled to room temperature in air. Finally, the microcapsules with paraffin core and Cu-$Cu_2O$ shell were obtained by centrifugation. The collected products were washed with deionized water and ethanol solution several times and dried at 50 °C for 24 h for further characterization.

The microencapsulated paraffin@Cu-$Cu_2O$ composite was synthesized by self-assembled method in emulsion; the schematic fabrication is presented in Fig. 1. OLA was used as the emulsifier, and after being mixed with paraffin, the aqueous phase with $Cu(HCOO)_2{\cdot}4H_2O$ and Glu was added to the oil phase drop by drop with a mechanical agitation to form a stable emulsion. Alkylamines can coordinate with metal cations to form complexes [26], therefore, OLA and $Cu^{2+}$ can form the Cu-amine complex on the surface of paraffin droplet. Under hydrothermal conditions, the Cu-amine complex is reduced by Glu to form Cu nanoparticle at the interface [27]. With the process of reaction, a part of Cu nanoparticles was oxidized to $Cu_2O$. The Cu and $Cu_2O$ nanoparticle gradually became a layer of shell on the surface of paraffin droplet and capsulated paraffin completely.

### 2.3. Characterization

#### 2.3.1. Scanning electron microscopy (SEM)

The surface morphology of the MicroPCM (micro-encapsulated phase change material) was investigated using a ZEISS ΣIGMA scanning electron microscope with 15-kV acceleration voltage.

#### 2.3.2. Transmission electron microscopy (TEM)

The microstructures of the MicroPCM were determined with a FEI TecnaiG2 F30 transmission electron microscope. The samples were dispersed in ethanol solution by ultrasonicator and randomly collected on carbon-coated copper grids for observation.

#### 2.3.3. Fourier transform–infrared spectroscopy (FTIR)

The FTIR spectra were obtained using a Thermo Nicolet 6700 Fourier Transform Infrared Spectro instrument on a KBr disk at room temperature. The specimen, contrasting with paraffin, was mixed with KBr sheets and the wave number ranging from 4000–400 $cm^{-1}$.