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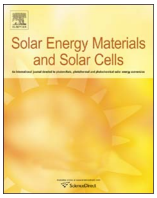

# Design and fabrication of bifunctional microcapsules for solar thermal energy storage and solar photocatalysis by encapsulating paraffin phase change material into cuprous oxide

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## ABSTRACT

This article reported the design and fabrication of bifunctional microcapsules for solar photocatalysis and solar thermal energy storage by using cuprous oxide ($Cu_2O$) as an inorganic shell to encapsulate a paraffin-type phase change material (PCM), *n*-eicosane. Such a new type of microcapsules was synthesized successfully by using an emulsion templating self-assembly method along with *in-situ* precipitation. The chemical structures of the resultant microcapsules were determined by *Fourier*-transform infrared spectroscopy, and the elemental distributions of microcapsule shell were confirmed by *X*–ray photoelectron spectroscopy and energy-dispersive *X*–ray spectroscopy. The scanning and transmission electronic microscopic observations demonstrated that the microstructures and morphologies of microcapsules were influenced significantly by the surfactant and alkali concentrations as well as the portion of cupper source for the synthesis. After the synthetic condition was optimized, the obtained microcapsules exhibited an interesting octahedral morphology and a typical core-shell structure. The thermal analysis results suggested that the microcapsules synthesized at the optimum condition not only obtained high encapsulation and energy-storage efficiencies but also presented a high thermal stability and phase-change reliability. Most of all, the microcapsules obtained a solar thermal energy-storage capability through solar photothermal conversion and also exhibited a high solar photocatalytic activity to organic dyes under the sunlight illumination. In addition, the microcapsules showed a gas-sensitive feature to some harmful organic gases in the presence of $Cu_2O$ shell. The microcapsules developed by this work indeed reveal a bifunctional feature derived from both the core and the shell materials and thus show a great potential for industrial and domestic applications due to their extended functions.

## 1. Introduction

Phase change materials (PCMs) are a class of substances which are capable of absorbing and releasing latent heat through phase transitions [1]. Different from conventional thermal energy-storage materials, PCMs can absorb large amounts of thermal energy at a certain temperature without getting hotter. On the other hand, PCMs will solidify with a decline in ambient temperature around them and release their stored latent heat accordingly [2]. With rapid growth of the consumption of fossil fuels followed by a serious environmental impact as well as a shortage of fossil energy resources, a great deal of attention has been paid recently to the improvement of energy utilization efficiency and the development of renewable energy by both scientific societies and industrial communities [3]. PCMs have been recognized as a class of renewable energy materials with a high energy-utilization efficiency, and the latent heat storage by use of PCMs is also considered as one of the most important thermal energy-storage technologies [4]. Nowadays, PCMs have received wide applications in various areas like energy-saving building materials, collection and reutilization of solar thermal energy, smart fibers and textiles with a temperature-regulating function, cooling systems of electronic components and apparatuses, industrial waste water recovery, refrigerated transportation units, etc [5]. Wu et al. [6] reported the application of PCMs as a thermal storage medium for the biofuel micro trigeneration prototype. Ma et al. [7] presented a detailed literature review on the use of PCMs for the thermal regulation and electrical efficiency improvement of photovoltaic modules. Wang et al. [8] provided a detailed introduction on the application of solar water heating system with PCMs. Sun et al. [9] introduced a free-air cooling system using PCMs as a nature cool source for space cooling in telecommunication bases. Sahoo et al. [10] summarized the applications of PCMs in heat sinks for cooling of electronic components. Taking into account the boom in industrial and

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domestic fields, there is no doubt that PCMs will play a key role in renewable resources for green growth and sustainable development in the future.

PCMs can usually be arranged into three categories: organic PCMs, inorganic PCMs and eutectic PCMs. Inorganic PCMs primarily include molten salts and salt hydrates [11]. As the most commonly used PCMs, the organic PCMs tend to be oligomers or polymers with long molecular chains consisting mainly of hydrogen and carbon, including aliphatic acids, fatty acid ester, paraffin waxes and polyglycols. They usually show high orders of crystallinity when solidifying and mostly change the phase above 0 °C [12]. Within the human comfort and electronic device tolerance range of 25–37 °C, organic paraffin waxes are very effective to store large amounts of latent heat energy and then release them controllably in such a narrow temperature range without substantial density change during the phase transition. Therefore, paraffin-based PCMs are promising candidates for thermal energy storage in the low-to-moderate temperature range and have been broadly used for solar domestic hot water heating systems, passive solar space heating–cooling systems for day/night temperature equalization in domestic buildings, thermal enclosures like Basic Telecom Shelters, and smart thermal regulating fibers and textiles [13–15]. For example, a paraffin-PCM-based solar domestic hot water system can provide more cumulative and life cycle savings than the conventional one and will continue to perform efficiently even after 15 years due to application of non-metallic tank [14]. Although the paraffin waxes are cheap comparatively, the packaging and processing necessary to obtain acceptable performance from them is really expensive and complicated. They cannot offer a reliable pattern of releasing latent heat with the chemicals in PCMs separating and stratifying when in the liquid state. Moreover, these PCMs cannot always perform re-solidification in a proper way, or they did not solidify completely with a decline of temperature, thus resulting in the reduction of their capacity to store latent heat. In addition, the molten paraffin waxes have a mobile feature and thus easily flow away when used with other supporting materials [16]. These problems have been addressed by packaging PCMs in thin or shallow containers and by adding clumping agents [17].

Microencapsulation is a physical or chemical process to engulf small liquid or solid particles of 1–100 μm diameter by a solid shell and is considered as a good solution to overcome the defects in organic PCMs. Through the microencapsulation of organic PCMs with an inert material, the resulting microcapsules are able to keep a macroscopic solid form when the PCM core is molten [18]. Furthermore, the microencapsulation of organic PCMs not only enhances the ease of handling but also provides a large specific surface area for PCMs, which allows an effective heat transfer [19]. The microencapsulation of paraffin waxes has been well developed as an important packing technology for the solid–liquid organic PCMs in the past decade. There are a large number of studies reporting the synthetic techniques and performance investigations of microencapsulated paraffin waxes with various polymeric shells through chemical methods such as complex coacervation, *in-situ* polymerization, interfacial polycondensation and suspension polymerization [20,21]. The typical polymers used as shell materials include polystyrene [22], polyurea-formaldehyde resin [23], poly(methyl methacrylate) [24], melamine-formaldehyde resin [25], poly(butyl acrylate) [26], polyurethane [27], and even the bio-based materials like silk fibroin [28] and gelatin/Arabic gum [29]. Considering the superiority of inorganic materials over the polymeric ones in nonflammability, mechanical strength, thermal conductivity, and thermal and chemical stabilities, an increasing number of studies have been conducted on the synthetic technologies associated with the microencapsulation of organic PCMs with an inorganic shell or inorganic/organic hybrid shell [30]. The most recent publications indicated that some inorganic chemicals such as $SiO_2$ [31], $Al(OH)_3$ [32], $CaCO_3$ [33], and amorphous $TiO_2$ [34] were employed successfully as wall materials to encapsulate organic PCMs through the self-assembly method. The resultant microcapsules not only exhibit a good phase-change thermal performance resulting from the enhancement of thermal conduction but also gain a higher thermal stability, longer durability, and better sealing tightness and anti-permeability due to the encapsulation by a rigid and compact inorganic shell [35].

There is no doubt that most of the studies on the development of microencapsulated organic PCMs either with polymeric shells or with the inorganic ones unexceptionally concerned the monofunctional issue of latent heat storage. Taking account of the functional diversity of inorganic materials, it is expected that, if organic PCMs are encapsulated into the specified inorganic shell, some specific physical or chemical functions are possible to be imparted to the resulting microcapsules. In this case, the diverse design and fabrication of bi- or multi-functional microcapsules were proposed as a new design idea for the preparation of microencapsulated organic PCMs in our previous studies. With such a design concept in mind, we have made great efforts to design and fabricate the microencapsulated paraffin waxes with various inorganic functional shells and have already succeed in the fabrication of microencapsulated PCMs with crystalline ZnO [36], $TiO_2$ [37], $ZrO_2$ [38,39], $SiO_2/Fe_3O_4$ hybrid [40,41] and $SiO_2$/Ag doubled-layered shells [42]. These microencapsulated PCMs all exhibited a variety of functions such as photocatalysis, magnetic effectiveness, photoluminescence, antibacterial action and electrical conduction in addition to the thermal energy-storage capability, indicating a bi- or multi-functional feature. It should be emphasized that each type of these microencapsulated PCMs was prepared on the basis on the different reaction mechanisms, synthetic pathways, and respective technique know-how as described in the relevant publications. For example, the microencapsulated PCMs with a ZnO shell were formed through interfacial precipitation along with a series of aging reactions [36]. For the microencapsulated PCMs with a $TiO_2$ or $ZrO_2$ shells, a non-aqueous oil-in-water emulsion templating system was designed to conduct a self-assembly polycondensation of inorganic precursors on the PCM core, and a crystallization promoter was utilized to promote the formation of crystalline $TiO_2$ or $ZrO_2$ shells with various functions [37–39]. As regards the microencapsulated PCMs with a $SiO_2/Fe_3O_4$ hybrid shell, a Pickering emulsion templating system was first established, in which magnetic $Fe_3O_4$ nanoparticles were used as a Pickering stabilizer, and then a self-assemble process of silica precursors followed by *in-situ* polycondensation was conducted to fabricate a $SiO_2/Fe_3O_4$ hybrid shell on the surface of PCM core [40]. In the case of the microencapsulated PCMs with a $SiO_2$/Ag doubled-layered shell, a thiol-functional silica inner layer was first fabricated onto the surface of PCM core, and the a silver outer layer was formed through surface assembly of silver ions with the aid of thiol groups followed by a reduction reaction [40]. It is evident that the fabrication of these bi- or multi-functional microencapsulated PCMs required significant breakthroughs from traditional synthetic techniques, although their syntheses were followed with some general principles like emulsion templating and interfacial self-assembly.

In this study, we reported the design and synthesis of a new type of bifunctional microcapsules based on the paraffin core and cuprous oxide ($Cu_2O$) shell. As a typical *p*-type semiconductive material with a direct bandgap of 2.0–2.2 eV, $Cu_2O$ has attracted an intense interest for its various characteristic properties in recent years, and it has obtained wide applications for solar photocatalysis, photoelectrolytic cells, solar energy conversion, antifouling coatings, and water-splitting materials [43]. $Cu_2O$ is especially characteristic of its high photocatalytic activity under the visible light illumination, low toxicity and good environmental acceptability [44]. Therefore, it is anticipative that, by encapsulating organic PCMs into a $Cu_2O$ shell, the resulting microcapsules achieve a solar photocatalytic function as well as a latent heat-storage capability. Such a novel type of microencapsulated PCMs is especially applicable for the disinfection of water supply accompanied by outdoor solar thermal energy collection or the decontamination and waste heat recovery of industrial wastewater [45]. It may also have great potential