Solar Energy Materials and Solar Cells 176 (2018) 212–221

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Novel metal coated nanoencapsulated phase change materials with high thermal conductivity for thermal energy storage

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ARTICLE INFO

Keywords:
Phase change materials
Nanocapsules
Polydopamine modification
Electroless plating
Thermal conductivity

ABSTRACT

Fast heat transfer is very important for practical application of phase change materials. Herein, a novel kind of silver coated nanoencapsulated phase change materials (NanoPCMs) with high thermal conductivity were prepared, and their properties were examined. Dopamine surface activation was carried out on silica nanocapsules containing n-octadecane, followed by electroless plating in Tollen's reagent. Chemical composition and crystallinity of the original silica nanocapsules, polydopamine modified NanoPCMs, and silver coated NanoPCMs were characterized by FT-IR, XPS, and XRD methods. Microstructure and morphology of these NanoPCMs were observed by SEM and TEM. Phase change property, thermal stability, thermal reliability, and thermal conductivity of these NanoPCMs were measured by DSC, TG, thermal cycling test, and laser flash methods, respectively. Although the mass-based latent heats decline obviously after silver plating due to high density of metallic Ag, the volume-based latent heats only exhibit minor decrease. These NanoPCMs crystallize mainly based on heterogeneous nucleation and show low supercooling, by introducing n-octacosane as nucleating agent. Moreover, they can keep constant phase change properties during multiple melting/solidifying thermal cycles. Most importantly, the apparent thermal conductivity of the silver coated NanoPCMs increases significantly from 0.246 to 1.346 W/m K. Owing to these excellent properties, the silver coated NanoPCMs are promising for thermal energy storage and thermo-regulation applications.

1. Introduction

Phase change materials (PCMs) are capable of storing and releasing large amounts of latent heat by melting and solidifying at near constant temperatures, so they are very useful in thermal energy storage and thermo-regulation fields. As a result, PCMs can reduce the dependency on fossil fuels, contribute to highly efficient energy utilization, and reduce green house gas emission [1]. In order to prevent leakage and erosion of melted PCMs to surrounding environment, and increase the heat transfer area, PCMs can be enwrapped by shell materials and converted to encapsulated PCMs. According to their sizes, encapsulated PCMs are classified into macrocapsules (> 1 mm), microcapsules (MicroPCMs, 1–1000 μm) and nanocapsules (NanoPCMs, < 1 μm) [2]. By encapsulation, the application fields of PCMs have been largely extended, such as solar energy storage [3,4], energy efficient buildings [5], and thermo-regulated garments [6,7], etc.

For latent heat storage with PCMs, fast heat transfer is very important in practical applications, because it implies high thermal energy charging/discharging rates [8,9]. In order to improve the heat transfer properties of encapsulated PCMs, adoption of highly thermal conductive shell materials as well as decrease of capsule sizes are two key factors.

Traditionally, various organic polymers were utilized to encapsulate PCMs, such as melamine-formaldehyde (M-F) resin [10,11], polystyrene (PS) [12], polymethylmethacrylate (PMMA) [13,14], and so on [15,16]. These shell materials possess desirable sealing characteristics and good chemical and thermal stability, but the thermal conductivity is fairly low. Inorganic materials including silica [17–19], TiO_2 [20–22], $CaCO_3$ [23,24], and ZrO_2 [25] received much attention in recent years, because they are more thermal conductive and possess better thermal stability than organic polymers. However, currently available inorganic shell materials prepared through sol-gel process often exhibit mesoporous structure and poor mechanical strength. Alternatively, it is an efficient way to enhance the thermal conductivity and thermal stability of micro/nano encapsulated PCMs by incorporating some highly thermal conductive additives, such as silica

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https://doi.org/10.1016/j.solmat.2017.12.006
Received 18 July 2017; Received in revised form 17 October 2017; Accepted 6 December 2017

[26–28], graphene [29–31], graphite [3], Al_2O_3 [32], Si_3N_4 [4], and metals [33–35], into organic polymer shell materials. Zhang et al. [31] microencapsulated n-hexadecane with double-walled shells (polystyrene/graphene oxide) from Pickering emulsion templating, and achieved high encapsulation ratio and good thermal stability. Wu et al. [30] synthesized microcapsules containing n-hexadecane with a melamine-urea-formaldehyde (MUF) shell incorporating different amount of graphene by emulsion polymerization. The results indicated that heat enthalpy of the microcapsules gradually decreases with the rising addition of graphene, but the heat transfer performance and thermal stabilities are enhanced. Dao et al. [29] prepared stearic acid (SA)/graphene composite microcapsules, which possessed high latent heat and improved thermal conductivity from 0.205 to 0.335 W/m K. Liu et al. [3] prepared microencapsulated phase change composite, with paraffin as core material and graphite nanoparticles embedded M-F resin as shell material. Jiang et al. [32] synthesized new MicroPCMs based on paraffin wax core and poly(methyl methacrylate-co-methyl acrylate) shell with nano-Al_2O_3 inlay via emulsion polymerization. The thermal conductivity of the paraffin microcapsules was improved from 0.244 to 0.382 W/m K. Yang et al. [4] synthesized PCMs microcapsules based on n-octadecane (n-OD) core and PMMA shell supplemented with modified Si_3N_4 powders, and the thermal conductivity was enhanced from 0.231 to 0.363 W/m K. Song et al. [33] reported MicroPCMs incorporated with silver nanoparticles by in situ polymerization, and found that the microcapsules exhibited increased shell toughness and thermal stability. Al-Shannaq et al. [34] developed a new method for coating PMMA microcapsules containing PCMs with silver metal, by using dopamine surface activation followed by electroless plating. The apparent thermal conductivity of the MicroPCMs increased significantly by metal coating from 0.189 to 2.41 W/m K. Zhang et al. [35] synthesized microcapsules containing n-eicosane as core with silver/silica double-layered shell for thermal energy storage, electrical conduction and antimicrobial effectiveness, through interfacial polycondensation followed by sliver reduction.

On the other hand, smaller capsule size of encapsulated PCMs can greatly benefit the heat transfer properties. Especially, nanometer sized NanoPCMs have much larger specific surface area than macro or micro encapsulated PCMs, which can result in much faster thermal energy storage/release. In addition, when applied in latent functionally thermal fluid (LFTF), NanoPCMs do not fracture easily in the course of flow [17]. Therefore, NanoPCMs have attracted much interest and significant development has been achieved [2]. Sarı et al. [36] and Chen et al. [14] synthesized nanocapsules with PMMA as shell containing n-octacosane and n-dodecanol as core, respectively, by miniemulsion polymerization method. Zhang et al. [37] and Tumirah et al. [38] synthesized nanocapsules containing n-OD as core, with poly(ethyl methacrylate), PMMA, and poly(styrene-*co*-methyl methacrylate) shells, respectively. Fang et al. [12] reported PS nanoencapsulated n-tetradecane for cold thermal energy storage. Latibari et al. [22] focused on NanoPCMs containing fatty acids (palmitic acid, stearic acid) as core and inorganic materials (SiO_2, TiO_2) as shell for thermal energy storage applications. We [39,40] previously reported nanocapsules containing n-OD as core with organosilica shells achieved by facile interfacial hydrolysis-condensation reaction in miniemulsion, and studied the morphological control and thermal properties of these NanoPCMs.

It is desirable to integrate the advantages of both highly thermal conductive shell materials and small capsule size of NanoPCMs, for improvement of heat transfer properties. Metal is a kind of materials with excellent thermal conductive and mechanical properties. However, utilization of metal on encapsulation of PCMs was challenging, thus only few works [33–35] were reported previously, and these works were limited to MicroPCMs (their sizes are in the micrometer scale, > 1 μm). To the best of our knowledge, metal coating of NanoPCMs has not been reported in literatures to date. Compared with metal plating on micrometer sized capsules, it is more difficult to coat a metal layer on nanometer sized capsules, which demand better control on the electroless plating process. In order to alleviate the negative effect (drop of latent heat) resulted from the additional metal layer, the metal layer should be as thin as possible. In recent years, surface modification by polydopamine (PDA) achieved many successes on a variety of materials [41,42], and it provided an excellent platform to deposit metal coatings onto lots of substrates including some nanoparticles [42,43]. Therefore, we herein report the preparation of a novel kind of silver coated NanoPCMs, on the basis of silica nanocapsules containing n-OD, by using dopamine surface activation followed by electroless plating. In addition, previously reported metal coating on MicroPCMs was mostly based on organic polymer shell materials like PMMA. Contrarily, in this work, we conduct metal coating based on an inorganic silica shell material. The electroless plating process has been optimized for successful preparation of the silver coated NanoPCMs with good surface morphology. Moreover, the chemical and crystal structure, morphologies, and thermal properties of the as-prepared NanoPCMs were thoroughly investigated. This novel kind of silver coated NanoPCMs with enhanced thermal conductivity and mechanical strength will benefit their application in thermal energy storage, thermo-regulation, and slurries for cooling of electronic devices [44].

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), anhydrous ethanol, $AgNO_3$, $NH_3{\cdot}H_2O$ (25 wt%), and HCl (37 wt%) were purchased from Sinopharm Chemical Reagents Company. Cetyltrimethylammonium bromide (CTAB) was commercially supplied by Tianjin Kermal Chemical Reagents Company. Methyltrimethoxysilane (MTMS), n-OD (90 wt%), and n-octacosane were purchased from Alfa Aesar. Dopamine hydrochloride and polyvinylpyrrolidone (PVP, M.W. 40,000 g/mol) were purchased from Sigma-Aldrich. Tris(hydroxymethyl)aminomethane (Tris) and D-(+)-glucose were supplied by Aladdin Co. Ltd. All chemicals were of reagent quality and used without further purification.

2.2. Preparation of NanoPCMs with silica shell (n-OD@silica)

Nanoencapsulated n-OD with silica shell was prepared through interfacial co-hydrolysis and condensation of TEOS and MTMS in miniemulsion, according to our previously reported method [40] with some modification. Briefly, n-OD (11.4 g), n-octacosane (0.6 g, serving as a nucleating agent to suppress supercooling of the NanoPCMs [45]), MTMS (6.0 mL) and TEOS (12.0 mL) were mixed in a beaker (500 mL), to form a clear solution. Then, CTAB (1.968 g), deionized H_2O (171 mL) and anhydrous ethanol (85.2 mL) were added into the beaker in turn. The mixture was heated to 68 °C, and homogenized (FA25 high shearing homogenizer, Fluke) at the rate of 13,000 rpm for 5 min, followed by sonication (VCX 750 ultrasonic processor, Sonics & Materials) for 10 min, to form a stable miniemulsion. The mixture was transferred into a three necked flask (500 mL) equipped with a mechanical stirrer and thermo stated in an oil bath (68 °C). Aqueous ammonia (25 wt%, 1.56 mL) was added to the flask and the reaction proceeded with gentle stirring (300 rpm) for 16 h. Finally, white powder-like products (Fig. 1) were collected after filtration, washing with deionized water, and freeze drying.

2.3. Preparation of PDA modified NanoPCMs (n-OD@silica-PDA)

PDA modified NanoPCMs were prepared by oxidative self-polymerization of dopamine in buffered solution (Scheme 1a). Typically, n-OD@silica (0.80 g) were dispersed in Tris-HCl buffered solution (pH = 8.5, 50 mM, 100 mL) in a three necked flask (250 mL) by magnetically stirring (1000 rpm, 30 min) and sonication (KQ-400KDB, 100% amplitude, 10 min) at 25 °C. Dopamine hydrochloride (0.40 g) was added into the flask and the reaction proceeded in the presence of air at 25 °C