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Research Paper

Tailoring of bifunctional microencapsulated phase change materials with CdS/SiO_2 double-layered shell for solar photocatalysis and solar thermal energy storage

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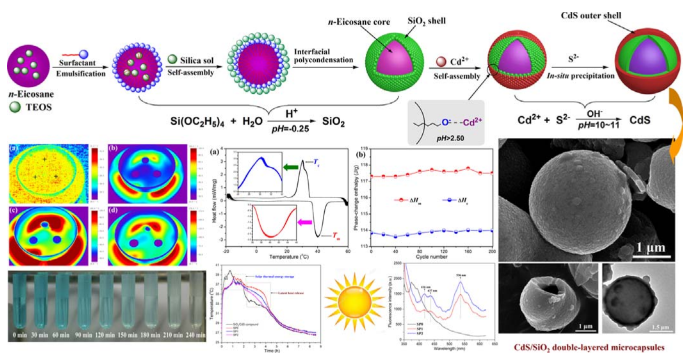
HIGHLIGHTS

- A new type of microencapsulated PCMs was tailored with a CdS/SiO_2 double-layered shell.
- The microcapsules show a spherical morphology and well-defined core-shell structure.
- The microcapsules achieved dual functions derived from PCM core and CdS layer.
- The microcapsules can serve for solar photocatalysis and solar thermal energy storage.
- The microcapsules exhibit an interesting photoluminescence feature.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel type of bifunctional microcapsules was tailored by encapsulating an *n*-eicosane phase-change material (PCM) into a CdS/SiO_2 hybrid via the interfacial polycondensation of silica precursors, followed by an *in-situ* precipitation between Cd^{2+} and S^{2-} ions. Structural characterizations indicated that a double-layered shell based on an amorphous SiO_2 inner layer and a crystalline CdS outer layer was fabricated successfully onto the *n*-eicosane core. Transmission and scanning electron microscopy demonstrated that the *n*-eicosane@SiO_2/CdS double-layered microcapsules had a regularly spherical morphology with a perfect core-shell structure. Thermal analysis revealed that the *n*-eicosane@SiO_2/CdS microcapsules achieved high energy-storage efficiency and reliable phase-change properties. Most of all, the *n*-eicosane@SiO_2/CdS microcapsules not only exhibited good solar thermal energy-storage and thermoregulatory capabilities but also showed a high solar photocatalytic activity to organic dyes under the natural sunlight. Additionally, the microcapsules presented a fluorescent function due to the CdS outer layer. With these unique bifunctional characteristics, the *n*-eicosane@SiO_2/CdS double-layered microcapsules developed by this work can serve for energy efficiency, sustainable chemistry and green processes, and therefore they exhibit an application potential for solar thermal energy collection and storage, solar photocatalytic depuration of industrial waste water, the solar photochemical detoxification of organic water pollutants, etc.

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1. Introduction

Sustainable development calls for an improvement in the quality of life without increasing the use of our natural resources beyond the carrying capacity of the earth, which suggests that the domains of sustainability are dependent upon the relationship between the social and the natural. In this case, sustainable development becomes one of the largest concerns in the world due to enormous challenges in our social and environmental resources, and 2015 was hence marked as a defining year for sustainable development worldwide [1]. Nevertheless, energy and environment have become the two major problems threatening the sustainable development of human beings. The excessive reliance on fossil fuels leads to greenhouse gas emissions and a wide variety of harsh environmental impacts, followed by the impending exhaustion of fossil resources in daily lives and industry. As predicted by "World Energy Outlook 2013", the global energy demand will increase by one third from 2011 to 2035, and energy-related CO_2 emission will rise by 20% to 37.2 gigaton if fossil fuels are used as usual [2]. This inevitably brings a serious impact to human survival overall the world. To resolve the relevant environmental problems, the reduction of the use of fossil fuels by developing more cost-effective renewable and sustainable energy technologies becomes more and more imperative [3]. In current years, the thermal energy storage technologies have attracted a great deal of attention of scientist for their exceptional behaviors, which would result in a reduction in the overall energy demand. For example, the storage and utilization of solar power are one of the most promising large-scale sustainable energy technologies to meet the requirement of rapidly growing energy demand with a low cost and almost zero environmental impact [4,5]. Latent heat storage is one of the widely available thermal energy storages, which can be easily implemented by utilizing the phase transitions of a material. It can provide a much higher energy-storage density with a smaller temperature difference between latent heat storage and release. Therefore, the utilization of latent heat is considered as one of the most efficient means for thermal energy storage and use [6]. Latent heat storage is a relatively new area in sustainable energy utilization and high energy efficiency, which was pioneered by Dr. Telkes in the 1940s [7]. However, such an issue had not received much attention until the energy crisis of late 1970s, and then it was extensively researched for the use in solar heating systems [8].

As a family of latent-heat storage materials, phase change materials (PCMs) can absorb and release large amounts of thermal energy through phase transition when freezing and melting. Solid-solid PCMs have exhibited many desirable characteristics, for example, no liquid or gas generation, no leakage, small volume change and easily being processed into expected shape [9–11]. However, there are several deficiencies such as low transition enthalpy, high transition temperature, unstable thermal property and high cost in most of the solid-solid PCMs. All these disadvantages dramatically limit their applications. Solid-liquid PCMs have the weakness of low thermal conductivity and liquid leakage when undergoing the solid-liquid phase changes. Nevertheless, they show the advantages of high transition enthalpy, suitable phase-change temperature, small volume change and moderate cost and thus are the most studied and most commonly available [12,13]. There are a number of organic and inorganic compounds that could be employed as solid-liquid PCMs, including organic fatty acids and paraffin waxes, inorganic salt hydrates and eutectic [14–16]. Among these solid-liquid PCMs, paraffin waxes exhibit chemically stable, well-defined melting points and no trend to segregate, and therefore, they are considered as the most promising solid-liquid PCMs [17–19].

To overcome the leakage problem when solid-liquid PCMs in a liquid state and also to increase the heat transfer area, the microencapsulation techniques have been developed to hold the PCMs in a sealed container over fifty years [20]. Microencapsulated PCMs are expected to possess some certain characteristics such as required morphology, uniform diameter, high thermal stability, high shell strength, and good penetration resistance [21]. Microencapsulation of PCMs can normally be implemented by several physical or chemical processes such as coacervation [22], emulsion [23], suspension [24], polyaddition polymerization [25] and *in-situ* polymerization [26]. The open publications indicated that more than fifteen polymers could be used as shell materials to encapsulating PCMs, which included melamine-formaldehyde resin, polystyrene, poly(methyl methacrylate), polyurea, polystyrene, poly(butyl acrylate), polyurethanes and so more [27,28]. These polymer shells hold the PCMs in a liquid state successfully and can prevent the leakage of PCMs, and their sufficient mechanical strength also can ensure a structural stability for the microcapsule system. However, it is unavoidable to bring a low thermal conductivity and flammability due to the nature of polymeric materials, resulting in the hysteresis of thermal response and heat transfer during the thermal regulating process [29]. Considering the characteristics of high thermal conductivity, long-term durability and non-flammability for inorganic materials, it is expected that the energy-storage capability and thermal performance of PCMs can be enhanced by combination of organic PCMs with inorganic shell materials [30]. In this case, the microencapsulation of organic PCMs with an inorganic shell has attracted great attention in recent years, and there are numerous studies focusing on this issue as searched from relevant references [31,32]. In our previous studies, we have successfully developed a series of microencapsulated paraffin PCMs with different inorganic shells, which included $CaCO_3$ [33], ZrO_2 [34], TiO_2 [35], ZnO [36], Fe_3O_4/SiO_2 [37] and Ag/SiO_2 hybrid materials [38]. These microcapsules all achieved good phase-change performance, high thermal conductivity and excellent long-term durability. Some of them also exhibited photocatalytic, fluorescent, magnetic, and antibacterial effectiveness due to the introduction of functionalized inorganic shells.

In the current work, we designed and tailored a novel type of bifunctional microcapsules composed of a paraffin core and an SiO_2/CdS double-layered shell for solar photocatalysis and solar thermal energy-storage applications. CdS is one of the earliest discovered semiconductor material with a relatively narrow band gap, and it has gained broad applications for thin-film transistors, field-effect transistors, photodetectors, photosensors and photovoltaic elements [39,40]. More of all, as a semiconductor-type photocatalyst, CdS can be activated by visible light and thus has a high photocatalytic activity to decompose water pollutants and to photoreductively degrade the halogenated benzene derivatives and toxic metal ions, which was considered as a green process for water detoxification [41]. Based on these specific characteristics, we attended to encapsulate the paraffin core with a CdS/SiO_2 double-layered shell. It is believed that such a design can endow the microencapsulated PCMs with some new functions, and the obtained microcapsules have a potential for water-pollution control as well as solar thermal energy collection. The purpose of the current work is to develop a fabricating technology for these new microcapsules and also to investigate their thermal performance, solar thermal energy-storage capability and photocatalytic activity.

2. Experimental

2.1. Chemicals

n-Eicosane used as a core material was purchased from Acros Organics Company, USA. Tetraethyl orthosilicate (TEOS) was commercially obtained from Sinopharm Chemical Reagent Co., Ltd., China. Cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$) and thiourea (CH_4N_2S) were supplied by Adamas Reagent Co., Ltd., China. Formamide, ammonia ($NH_3 \cdot H_2O$,