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Storing solar energy within Ag-Paraffin@Halloysite microspheres as a novel self-heating catalyst

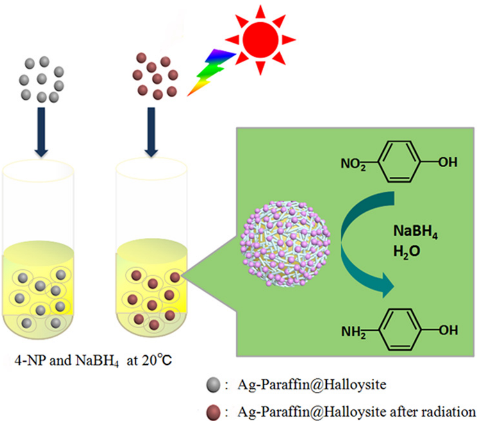
Yafei Zhao[a], Weixiao Kong[a], Zunlong Jin[a], Ye Fu[b], Wencai Wang[b], Yatao Zhang[a], Jindun Liu[a], Bing Zhang[a,*]

[a] *School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China*
[b] *Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China*

HIGHLIGHTS

- A novel self-heating catalyst Ag-Paraffin@Halloysite microsphere was prepared.
- Ag-Paraffin@Halloysite exhibits excellent heat storage/release capacity.
- It shows faster transient thermal response compared with paraffin.
- It displays much better catalytic activity after heat storage.
- This work may open up a new avenue of utilization of solar energy.

GRAPHICAL ABSTRACT



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ABSTRACT

With the rapid depletion of fossil fuels and the associated environmental issues, solar energy is identified as one of the most promising pollution-free and renewable resource. Herein, we prepared a novel Ag-Paraffin@Halloysite microsphere with the integrated abilities of storing solar energy and catalytic function by self-assembly method. The results show that Ag-Paraffin@Halloysite microsphere has a core-shell structure with paraffin as core and halloysite as shell, and Ag nanoparticles are dispersed uniformly on the surface of the microspheres. The high thermal storage capability, encapsulation ratio and encapsulation efficiency of Ag-Paraffin@Halloysite indicate that it can be used as an ideal heat storage material. Compared with pure paraffin, Ag-Paraffin@Halloysite has higher thermal conductivity, excellent thermal storage capacity, and faster transient thermal response. After heat storage, Ag-Paraffin@Halloysite shows much better catalytic activity (95.3% of conversion in 6 min) compared with the one without heat storage (71.1% of conversion in 6 min) for catalytic reduction of 4-nitrophenol. This result suggests its potential to be used as a self-heating catalyst for storing/releasing thermal energy during catalytic reactions. This work may offer a general and innovative approach to couple phase change materials with catalyst and open up a new avenue for utilization of solar energy in the fields of chemistry and chemical engineering.

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[*] Corresponding author.
E-mail address: zhangb@zzu.edu.cn (B. Zhang).

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1. Introduction

Energy and environment are the two major issues facing human beings today. An enormous increase in energy consumption has been occurred due to the rapid industrial development, population boom and ever-increasing human reliance on energy-based appliances in the past few centuries, and it was estimated that the world will need to double its energy supply by 2050 [1]. Fossil fuels including coal, petroleum oil and natural gas are accounted for the most significant portion of energy supply [2]. However, the rapid depletion of fossil fuels brings energy crisis, and the associated environmental issues including pollution and global warming stemmed from greenhouse gas carbon dioxide, leading to an urgent demand for hunting of secure, sustainable and renewable clean energy resources instead of fossil fuels [3]. As a pollution-free and renewable resource, solar energy has received increasing attention and is an effective way to relieve the issues of fossil fuel crisis and global warming [4,5].

Chemical reactions, especially catalytic reactions, account for the majority of energy consumption as most of the reactions perform with feeding of thermal energy (*e.g.* endothermic reactions) to guarantee an optimal yield. To meet energy and environmental demands, it would be desirable to take advantage of solar energy rather than heat to drive the catalytic reactions. On this account, efforts have been made to integrate solar energy with various catalytic reactions by utilizing photocatalysts (TiO_2, ZnO, SnO_2 and etc.) in the fields of photodegradation, photocatalytic water splitting and dye-sensitized solar cells [6–9]. The photocatalytic properties of photocatalysts are stemmed from the formation of photo-generated charge carriers (hole and electron) which happens upon the absorption of ultraviolet or visible light corresponding to the band gap [10]. Nevertheless, on one hand, many of the photocatalysts are only active under ultraviolet light due to their large band gaps, which leads to the utilization of less than 4% of the energy of natural solar light [11]. Considering that 50% of the solar energy comes from visible light, it is extremely crucial and of scientific dream to develop new catalysts to efficiently harvest the natural sunlight in visible light region. On the other hand, the energy demand and supply in different time/season and place is inconsistent. For this reason, it is necessary to construct solar energy storage systems to alleviate the mismatch between energy supply and demand [6,7]. For example, the spare electricity/heat can be stored during non-peak period and released during peak time, which will relieve the burden on the electricity/heat supply and boost the electricity/heat utilization efficiency [12].

Various materials have been investigated as media in solar energy storage systems for storage and retrieval of solar energy. The employment of organic phase change materials (PCMs) such as paraffin and fatty acids is believed to be an effective way to enhance the energy storage capacity because they have great capacities to absorb natural sunlight in both ultraviolet and visible light regions, and can store and release large amounts of latent heat within a slight temperature change [7,13–16]. The restrictions of direct utilization of these organic PCMs, such as leakage in the melted state, chemical instability, incompatibility with polar materials, low thermal conductivity, and large volume change during the phase change, can be lessened by encapsulation into various shell materials [16,17]. Most previous reports have shown that inorganic shell materials, such as SiO_2, TiO_2, $CaCO_3$, exhibit higher durability, thermal conductivity, and mechanical strength than the organic shell materials like polyurea, polycarbonate, polystyrene and etc. [7,18–22]. Halloysite nanotubes, natural and environmentally friendly low-cost aluminosilicate clay materials, have been used as promising materials in various areas including biomedicine, environment, catalysis, and etc. due to its hollow tubular structure, high surface area and good polymer mixability [23–25]. It has been reported that halloysite nanotubes are promising mesoporous supports for catalytic nanoparticles, which can be seeded/immobilized on the tube surface or synthesized exclusively in the lumens with enhanced catalytic properties [23,26]. It is also suggested that halloysite can be served as “skeleton” in PCMs to maintain composite structure even above the PCMs melting temperature with good thermal stability, high thermal conductivity and excellent anti-flammability [23,27–29]. Moreover, some researchers have successfully fabricated bi- or multi-functional thermal energy-storage systems using inorganic shells for the specified applications, such as PCM@TiO_2, PCM@ZrO_2, PCM@Fe_3O_4, PCM@Ag/SiO_2, and these bi- or multi-functional microencapsulated PCMs not only possess thermal energy-storage capability but also exhibit photocatalytic, fluorescent, magnetic, and electrical conductive functions [30].

Herein, we put forward a new proposal to synthesize a solar energy storage self-heating catalyst (Ag-Paraffin@Halloysite) through encapsulation paraffin into halloysite shell, modification with polydopamine and deposition of Ag nanoparticles. Upon solar irradiation, the new Ag-Paraffin@Halloysite composites are able to perform rapid sunlight-harvesting (visible light) and light-thermal conversion. Simultaneously, the generated thermal energy was stored in the Ag-Paraffin@Halloysite by a form-stable phase transition and retrieved in the subsequent model catalytic reaction (4-nitrophenol to 4-aminophenol) to quantify the catalytic activity of Ag-Paraffin@Halloysite [31,32]. To the best of our knowledge, this is the first time to couple solar energy with phase change materials and catalysis. The as-prepared Ag-Paraffin@Halloysite microcapsule catalyst would be a potential candidate as solar thermal energy storage self-heating catalyst, and this work may pioneer a general and innovative approach to integrate phase change materials with solar energy and catalyst and open a new avenue for utilizing solar energy, which extends their potential applications in renewable and clean energy sources.

2. Experimental

2.1. Materials

Halloysite were milled and sieved to obtain fine power (Henan, China). Paraffin and dopamine hydrochloride (98%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Tris (hydroxymethyl) aminomethane, L-Ascorbic acid (> 99.8%), polyvinylpyrrolidone (MW40,000 g/mol, PVP) and $NaBH_4$ (≥ 97.0%) were obtained from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Silver nitrate was from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ammonia hydroxide solution (25–28% NH_3 basis) was obtained from Luoyang chemical reagent Co. Ltd. (Luoyang, China). 4-nitrophenol (≥ 99.7%) was purchased from Macklin Biochemical Co. Ltd. All the chemicals and materials were used as received.

2.2. Preparation of Ag-Paraffin@Halloysite

The preparation of Ag-Paraffin@Halloysite microspheres includes three steps (Fig. 1). (i) Preparation of Paraffin@Halloysite: Oil phase mixture dispersion was prepared by adding 0.5 g of halloysite to 10 g of melted paraffin, followed by stirring for 30 min at 80 °C to obtain a homogeneous mixture. Then, 30 mL of pre-heated deionized water was poured into the above halloysite/melted paraffin mixture, and the Pickering emulsion was formed by stirring the mixture vigorously for 5 min at 80 °C. Paraffin@Halloysite spheres were obtained by cooling the Pickering emulsion in an ice bath and then washing with deionized water. (ii) Modification of Paraffin@Halloysite with dopamine: Surface modification of Paraffin@Halloysite spheres was carried out by oxidant induced surface self-polymerization of dopamine. Typically, 1.5 g of Paraffin@Halloysite spheres were dispersed in 100 mL of dopamine (2 mg/mL) tris (hydroxymethyl) aminomethane solution and kept in incubator shaker for 24 h at 25 °C. Then the pH of the above solution was adjusted to 8.5 by adding hydrochloric acid solution (5 M) gradually in order to initiate the polymerization of dopamine. Polydopamine was deposited on the surface of Paraffin@Halloysite as an adherent coating