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Smart design and construction of nanoflake-like MnO_2/SiO_2 hierarchical microcapsules containing phase change material for *in-situ* thermal management of supercapacitors

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ABSTRACT

Phase change materials (PCMs) have been widely applied for thermal energy storage and thermoregulation. This paper reported a smart design and construction of nanoflake-like MnO_2/SiO_2 hierarchical microcapsules containing *n*-docosane PCM for *in-situ* thermal management of supercapacitors. The microcapsules based on an *n*-docosane core and SiO_2 shell were first synthesized through interfacial polycondensation, and then a mesoporous nanoflake-like MnO_2 layer was fabricated onto the surface of SiO_2 shell through template-directed self-assembly. The chemical compositions of the resultant microcapsules were confirmed by energy dispersive *X*-ray, *X*-ray photoelectron and *Fourier*-transform infrared spectroscopy, and their nanoflake-like hierarchical morphology and well-defined core–shell structure were identified by scanning and transmission electron microscopy. The mesoporous architecture of nanoflake-like MnO_2 outer layer was determined by nitrogen adsorption–desorption isotherm. The obtained microcapsules exhibited high phase-change enthalpies, high encapsulation efficiency, good phase-change and anti-osmosis performance and an effective thermoregulation capability. Most of all, these microcapsules demonstrated a higher specific capacitance than traditional MnO_2/SiO_2 solid particles at operation temperatures higher than 45 °C due to *in-situ* thermal management by the *n*-docosane core. They not only achieved a high specific capacitance of 312.2F/g at 45 °C with a current density of 1.0 A/g due to the mesoporous architecture of MnO_2 layer, but also presented a superior long-term cycling stability with high capacitance retention of 94.7% after 1000 charging/discharging cycles. With the above-mentioned superiorities, the microcapsules developed by this work will be a good candidate as an electrode material for supercapacitors. This study opens a new pathway for the development and applications of microencapsulated PCMs in the thermoregulatory electrode system of supercapacitors and Li-ions battery cells.

1. Introduction

Nowadays, with an increasing concern for a series of global issues such as fossil energy shortage, environmental pollution, CO_2 emission, climate change and global warming, sustainability has become one of the most important principles meeting the objectives of human being's development because of these enormous challenges in our social and environmental resources [1]. Most of all, the requirement of energy is considered as a perquisite of human survival and social development, and however the rapid growth of population and global economy has resulted in a significant increase in demand for energy consumption. Meanwhile, the expanding use of fossil energy sources has brought an environmental impact to us and resulted in a shortage of fossil fuels as well. In this case, the development and expansion of the use of clean and renewable energy sources will continuously play a key role in realizing sustainable development for mankind [2]. For example, the industry is committed to make an utmost effort to develop hydroelectric, geothermal, solar, wind and biomass energy, which are all clean and renewable [3]. However, the energy supplied by these green sources is intermittent and weather-dependent, and it is vital to store the energy generated from the above-mentioned sources for continuous supply. Therefore, the enhancement of energy utilization efficiency, or called "efficient energy use", is also considered as an effective means to realize the sustainable development, because it not only can save energy but also can reduce CO_2 emissions and environmental pollution [4]. Phase change materials (PCMs) are a class of thermal energy-storage materials, which can store huge amounts of latent heat through physical phase transitions and controllably release them afterwards with a very small variation in temperature on the basis of thermal energy demand. In this case, the introduction of PCMs into energy

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consumption systems can improve energy efficiency effectively and avoid energy waste by bridging the gap between the availability and use of thermal energy. As a result, PCMs have been definitely recognized as a type of renewable and sustainable energy materials.

The developments and applications of PCMs for thermal energy storage and thermal management have attracted a great deal of attention in recent years. For example, a solar thermal energy-storage technique through incorporating PCMs into building materials was reported [5], which can prove a feasible option for economical improvement of energy efficiency in the buildings. Tyagi et al. [6] introduced the technological development in the microencapsulation of PCMs for buildings, and they declared that the construction of thermal energy-storage systems with PCMs was one of the most prospective energy technologies for enhancing energy efficiency and sustainability of buildings. Sun et al. [7] introduced the application of PCMs as a natural cold source for space air cooler in some telecommunications base stations, and they confirmed that the free-air cooling system using PCMs could be applied for the base stations to significantly reduce the amount of their energy consumed in space cooling. Cui et al. [8] designed a novel concentrating photovoltaic-thermoelectric systems by incorporation of PCMs and found that the performance of such a system was superior to single photovoltaic cell and/or classical photovoltaic-thermoelectric systems. Sahoo et al. [9] reported the applications of PCMs-based heat sinks for cooling of electronic components and devices. Wang et al. [10] reported a new type of solar air collection-storage thermal system with PCMs and found that this system achieved high collection efficiency with short charging and discharging time. Park et al. [11] reported a reutilizing technique for external waste heat in the diesel engine by using PCMs and found that the fuel efficiency in terms of total energy consumption could be improved and the warm-up time of the engine was reduced. Castell and Solé [12] reported an overview on design methodologies for thermal energy-storage systems based on solid–liquid PCMs and highlighted their usefulness and limitations.

Nowadays, PCMs have been broadly applied for solar thermal energy collection and storage, heat-pump systems, waste heat recovery and reuse, energy-saving buildings, photovoltaic-thermoelectric systems, pharmaceutical refrigeration, telecom shelters in tropical regions, smart fibers and textiles with a thermoregulatory function, thermal comfort in vehicles, cooling or thermal protection of electronic devices, etc [13]. However, there are some drawbacks found when PCMs are practically used. At first, most of the PCMs have to undertake repetitive solid–liquid phase transitions when conducting latent heat storage and release, which results in a handling difficulty and easy leakage. The use of bulk PCMs also suffers from a high level of supper cooling, low thermal conduction, poor heat transfer and slow thermal response to ambient temperature [14]. In this case, the microencapsulation of PCMs into inorganic or polymeric shells becomes an optimum option to overcome these drawbacks, because it not only can make PCMs stable in form for their ease of handling but also can provide a large specific surface area for them to enhance their heat transfer and thermal conductivity [15,16]. In recent decades, a large number of studies have focused on this subject, and there are lots of successful cases published for microencapsulation of PCMs with various organic or inorganic shell materials such as polyurea-formaldehyde resin [17], polyurethane [18], melamine–formaldehyde resin [19], poly(methyl methacrylate) [20], polystyrene [21], poly(butyl acrylate) [22], SiO_2 [23], $CaCO_3$ [24], TiO_2 [25], ZnO [26], Cu_2O [27], and ZrO_2 [28]. The technical implementation of microencapsulation well protects PCMs from leakage and loss during the phase-change process and also enhances their thermal performance and latent heat-storage capability effectively. Furthermore, besides thermal energy storage and thermal management, some new functions can also be introduced into the microencapsulated PCMs through wisely designing and constructing hierarchical or hybrid shells for PCMs. A series of attempts were made for this idea in our previous work, and some successful outcomes were achieved. For example, when PCMs were fabricated with a silver/silica double-layered shell, the resulting microcapsules achieved photocatalytic and antibacterial effectiveness in addition to latent heat storage [29]. The solar thermal energy-storage and solar photocatalytic functions could be achieved by microencapsulating PCMs into a graphene/TiO_2 composite shell [30]. The microencapsulation of PCMs with a Fe_3O_4/TiO_2 or Fe_3O_4/SiO_2 hybrid shell could create a type of thermoregulatory enzyme carriers for enhancing the biocatalytic effectiveness and reusability of immobilized lipases and amylases [31,32]. These smart designs may greatly extend the applicable range of microencapsulated PCMs.

The development of electrical and electrochemical energy-storage systems has been another hot research direction in recent years. The electrical and electrochemical storage technologies are not only essential for storing excess power to meet the peak electricity demand but also can meet the increasing demand for portable electronic devices and electric vehicles, and therefore, they have received tremendous interest from both scientific communities and public society [33,34]. Supercapacitors and Li-ion battery cells are two representative electrochemical energy-storage systems and have been extensively applied for various electronic/electric devices, industrial facilities, rail transit, aerocrafts, electric vehicles and wise industrial robots due to their prominent features such as large specific energy density, high specific power, low self-discharge rate and long cycle life [35,36]. However, there are some vital defects found for the development and applications of supercapacitors and Li-ion battery cells such as overheating. Because the charge and discharge of supercapacitors and Li-ion batteries are highly exothermic processes due to various electrochemical reactions, a great amount of heat is continuously produced and then accumulated inside the supercapacitors and battery cells during the charging and discharging processes [37]. This evidently results in an instability and unreliability in electrochemical systems, thermal runway and safety problems as well as a decrease in lifespan [38]. In this case, a high efficient and low-cost thermal management system is necessary for supercapacitors or battery systems to preserve an optimum working temperature range. The classical thermal management systems for supercapacitors and Li-ion battery cells include liquid- and air-based systems, and they can generate a good cooling effect if the system is designed reasonably [39]. Recently, some of new cooling systems such as PCMs-based and heat-pipe-based thermal management systems have attracted a great deal of interest from industry and academia [40,41]. Rao et al. [42] made a numerical investigation on the thermal performance of a PCMs/mini-channel-coupled battery thermal management system, and the results indicated that this system could perform thermal management more effectively to the power battery pack in electric verticals. Wu et al. [43] reported the design and application of a heat pipe-assisted thermal management system for the Li-ion battery by using PCMs as a heat transfer medium and found that the technical combination of PCMs and heat pipe could generate an excellent cooling effect on the battery pack. Yan et al. [44] reported an investigation on the application of PCMs for the dynamic cycling of Li-ion battery cells and found that the PCMs-based system exhibited better cooling performance than natural convection systems especially at a high discharge rate. Moraga et al. [45] reported a numerical study on the cooling performance of multiple PCMs toward the Li-ion battery pack of a racing solar car, and the results showed that the seven arrays of PCMs located in one or three layers surrounding the battery cell could effectively reduce the temperature inside the battery pack during the discharging process. Nevertheless, these PCMs-based thermal management systems unexceptionally involve the heat transfer and heat exchange devices. This not only brings inconvenience to the use of PCMs but also increases the relative expense for battery thermal management systems.

In the present work, we reported an innovative design of nanoflake-like MnO_2/SiO_2 hierarchical microcapsules containing PCMs for *in-situ* thermal management and thermoregulation of supercapacitors. We first