

Research Article

Encapsulation of Phase Change Materials Using Layer-by-Layer Assembled Polyelectrolytes

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Phase change materials absorb the thermal energy when changing their phases (e.g., solid-to-liquid) at constant temperatures to achieve the latent heat storage. The major drawbacks such as limited thermal conductivity and leakage prevent the PCMs from wide application in desired areas. In this work, an environmentally friendly and low cost approach, layer-by-layer (LbL) assembly technique, was applied to build up ultrathin shells to encapsulate the PCMs and therefore to regulate their changes in volume when the phase change occurs. Generally, the oppositely charged strong polyelectrolytes Poly(diallyldimethylammonium chloride) (PDADMAC) and Poly(4-styrenesulfonic acid) sodium salt (PSS) were employed to fabricate multilayer shells on emulsified octadecane droplets using either bovine serum albumin (BSA) or sodium dodecyl sulfate (SDS) as surfactant. Specifically, using BSA as the surfactant, polyelectrolyte encapsulated octadecane spheres in size of ~500 nm were obtained, with good shell integrity, high octadecane content (91.3% by mass), and good thermal stability after cycles of thermal treatments.

1. Introduction

The most efficient way to store thermal energy is the latent heat storage, which provides much higher storage density with a smaller temperature difference between heat storage and release [1]. As a form of latent heat storage system, the large numbers of phase change materials (PCMs) melt and solidify at a wide range of temperatures, making them attractive candidates to extensive applications in varied areas such as solar energy storage, heat exchangers, and thermal-regulated building strategies [1]. The most commonly used PCMs, for example, the cheap paraffin waxes (general formula C_nH_{2n+2}), are promising materials being employed for thermal-related activities because of their moderate thermal energy storage density. However, as a bulk material, PCM exhibits low thermal conductivity and extends to leak in the melted state; thus its wide application has been significantly limited [2]. One strategy to overcome this problem is to encapsulate these PCMs. In theory, encapsulated PCM materials as micro/nanoparticles could reduce their reactivity towards the outside environments, generate larger heat

transfer surface, and most importantly could govern their changes in volume as thermal-related phase change occurs.

Previous research works have established a few approaches to encapsulate PCMs by forming different shells on PCM colloidal surfaces; typical examples are sol-gel method [3], colloid method [4], and *in situ* polymerization [5]. The potential of encapsulated PCMs possessing high energy storage and release capacity depends on the core (PCM) to shell ratio. As reported, these above-mentioned methods commonly use a high component ratio of PCM: shell material, for example, approximately 3:1 (w/w) [2]. Consequently, the obtained shells possessing poor heat storage capability take up a large percentage (e.g., 25% (w/w)) of the mass of encapsulated PCM spheres and therefore decrease potential latent heat storage of the polymer-PCM system. Considering the practical matter, for an ideal PCM system, a shell layer has a good mechanical property, protects the inner PCM from leakage, and also takes up lower percentage of the whole system which is preferred to achieve a better heat storage efficiency.

Based on above considerations, here we introduce a new method to fabricate ultrathin polymeric shells on PCM colloidal surfaces using the layer-by-layer (LbL) assembly technique. The LbL assembly technique has exhibited its enormous potential to fabricate ultrathin (\sim nm) multilayer shells with desired chemical components and architectures, using the electrostatic interactions of oppositely charged complementary polyelectrolytes/components as the main driving force [6]. When the LbL assembly is applied onto colloidal particles, this technique permits a rapid and experimentally efficient way to fabricate steady composite core-shell spheres; typical examples have been carried out on a large variety of templates, such as silica microparticles [7], gold nanoparticles [8], living cells [9], oil emulsion [10], and the metastable air bubbles [11]. This technique allows a feasible strategy to prepare the multilayer shells with tunable structure and shape as well as mechanical properties [12] and thus could greatly realize our research purpose of this study.

Here, in this work, we are aiming at developing new approach to fabricate octadecane-encapsulated spheres through an environmental friendly and low cost approach process using the LbL assembly technique. We propose that the LbL assembly of PDADMAC/PSS multilayers on emulsified octadecane droplets would give the polyelectrolyte-PCM spheres not only steady entrapment but also a low shell ratio of the sphere system, providing an increased latent heat storage density compared to the pure octadecane.

2. Materials and Methods

2.1. Materials. Poly(diallyldimethylammonium chloride) (PDADMAC, 20 wt% in water, 200 k-350 kDa), Poly(4-styrenesulfonic acid) sodium salt (PSS, 70 kDa), octadecane (C_{18}), bovine serum albumin (BSA, 66 kDa), and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. All the aqueous solutions were prepared by using Milli-Q deionized water, the specific electric conductivity of which was 18.2 M Ω -cm.

2.2. Methods

2.2.1. Emulsion Preparation and LbL Assembly. SDS and BSA were used as the surfactants to fabricate the oil-in-water preemulsion. Briefly, 2 g of prewarmed octadecane was suspended in 8 mL BSA (4 mg/mL) or 2% SDS and sonicated for 2 min at 20 kHz (750 Watt \times 40%, pulse on 3 s, pulse off 2 s), resulting in a milky-white primary emulsion. Then equal volume of PDADMAC (2 mg/mL in 0.15 M NaCl) was added to the primary emulsion and sonicated for another 1 min at 20 kHz (750 Watt \times 40%, pulse on 3 s, pulse off 2 s) to make a secondary emulsion. Equal volume of the PSS and PDADMAC solutions (2 mg/mL in 0.15 M NaCl) was added to the secondary emulsion alternatively and stirred for 10 min with a magnet. To prevent the crystallization of octadecane, a water bath (35°C) was applied. After the first two polymer adsorption procedures, obtained mixture was centrifuged at 8000 rpm for 5 min. The aqueous phase was

removed by inserting a syringe needle through the oil phase. Then the LbL assembly was carried out in a 2 mL eppendorf tube, and the intermediate product was consecutively treated with PSS and PDADMAC with shaking, followed by 3 wash steps. At last, the PCM spheres with structure of C_{18} -Surfactant/(PDADMAC/PSS)₃ were obtained.

2.2.2. Characterization. The size distributions of obtained emulsions and polyelectrolyte-assembled octadecane particles were determined by dynamic light scattering (DLS) measurements. Generally, a small portion of the sample suspension was transferred into a transparent cuvette, diluted with water, and placed in the thermostated cavity of a Malvern Nano ZS zetasizer (Malvern Instruments Ltd, UK) for tests with at least 13 runs per sample.

Polyelectrolyte encapsulated octadecane suspension was observed by optical microscope. To ensure the homogeneity of the sample suspension, the samples were gently stirred before analysis. A drop of sample was then placed on a glass microslide and covered by a coverslip. The microstructure of selected samples was determined using conventional optical microscopy. The images were acquired using a CCD camera connected to Visicam Image Analyser (VWR International, UK) software installed on a computer.

Morphologies of encapsulated octadecane particles were characterized by scanning electron microscopy (SEM) (FEI Inspect-F). Diluted suspension was dropped on silicon wafer, air-dried, and coated with gold. SEM observation was carried out using an accelerating voltage of 10 kV, a spot size of 3.5, and a working distance of approximately 10 mm.

Thermal properties of pure octadecane and the polyelectrolyte encapsulated octadecane (freeze-dried) were measured by the differential scanning calorimeter (DSC) at temperature ramp rate of 10°C/min. Five heating-freezing cycles within a temperature range of -30°C to 45°C were run to determine the stability of the samples.

3. Results and Discussion

In this study, the octadecane ($C_{18}H_{38}$, mp = 26–29°C) possessing thermal-dependent phase change ability was studied as the core material; and the strong polyelectrolytes PDADMAC and PSS were used to fabricate shell layers on emulsified octadecane droplets. Briefly, 3 PDADMAC/PSS bilayers were studied as typical example here to encapsulate the C_{18} -Surfactant droplets. As revealed by the previous studies, the mean shell thickness of multilayers composed of strong polyelectrolytes is 1–2 nm per single polyelectrolyte layer [13, 14]. Therefore, 3 PDADMAC/PSS bilayers would construct shells with average thickness of \sim 10 nm. On one hand, this design was supposed to fabricate ultrathin shells with good mechanical property without generation of potential patch structures [15]; on the other hand, an even number of the layers would avoid thermal-related shell swelling due to the possible “odd-even effect” [16] when the heat exchange occurred. After the LbL assembly, encapsulated octadecane particles were obtained. As shown in Figure 1, resuspending these encapsulated octadecane particles in water made

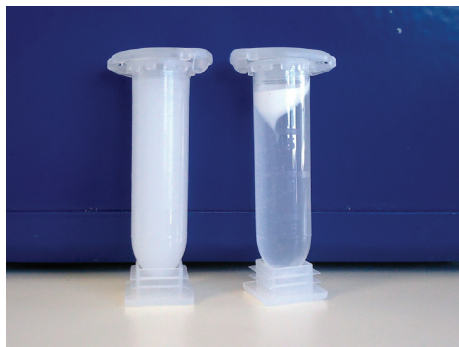


FIGURE 1: Image of the polyelectrolyte encapsulated octadecane suspension before (left) and after (right) centrifugation.

a milky-white suspension (left); after centrifugation, these octadecane particles with low density (density of pure octadecane = 0.777 g/mL at 25°C) tended to float on water (right).

To make the oil-in-water emulsion, two surfactants, SDS ($M_w = 288.38$) and BSA ($M_w = 66$ kDa) with significant different molecular weights, were used. Due to their different ability to stabilize the octadecane droplets in water, the obtained preemulsions exhibited varied size distribution and morphologies. As shown in Figure 2, using SDS as surfactant, the encapsulated octadecane particles showed larger size. After LbL deposition of four PDADMAC/PSS layers, encapsulated octadecane spheres showed an average diameter of 3831 ± 380 nm (Figure 2(a)). In contrast, using large molecular BSA as surfactant, the size of obtained polyelectrolyte-octadecane particles decreased dramatically, exhibiting an average diameter of 508 ± 177 nm (Figure 2(b)). Comparing with these ones prepared with SDS (Figure 2(a)), these octadecane particles with several hundred nanometers in size can only be seen as small black dots under microscopy observation at the same magnification (Figure 2(b)).

Application of different surfactants in this system not only influences the size distribution of prepared emulsion and encapsulated octadecane, but also affects their morphologies. As shown in Figure 3, using either SDS or BSA as surfactant, octadecane was already encapsulated by these polyelectrolyte layers, demonstrating as spherical particles. The size distribution of these fabricated octadecane particles was in high accordance with the DLS analysis and optical microscopy observation in Figure 2. By using SDS as surfactant, large particles with several micrometers in size have been fabricated, although these encapsulated octadecane particles were seen as spherical shells with obvious defects on the shells; moreover, some of them were observed as hollow structures (Figures 3(a) and 3(b)). The possible reasons can be used to explain this phenomenon: after the same emulsification treatment, small molecular SDS only exhibited limited ability to stabilize the octadecane droplets. When shaking and wash steps were carried out, these metastable small oil droplets tended to aggregate together to form larger ones, leading to obtained microspheres consequently. On the other side, high

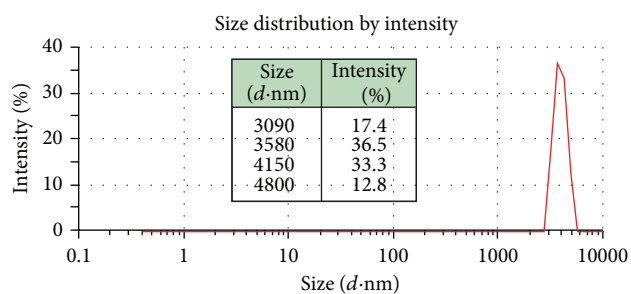
speed centrifugation (8000 rpm) during LbL assembly process would destroy the weakly connected SDS layer, therefore making damage on assembled polyelectrolyte layers, resulting in encapsulated octadecane leakage. Despite all this, the existence of these defective polyelectrolyte shells also proved the successful stepwise deposition of PDADMAC/PSS bilayers on the octadecane droplets. Unlike SDS, BSA consisting of long molecular chains showed good ability to stabilize octadecane droplets, restricting their size growth. As a result, polyelectrolyte encapsulated octadecane spheres with average diameter approximately 500 nm were made; these ones using BSA as surfactant had smooth and compact surfaces without edges or obvious sharp defects (Figures 3(c) and 3(d)). In particular, some encapsulated spheres were exhibited as oval-shaped and dumbbell-shaped particles under SEM observation (as pointed out by the arrows). This result, supported by our discussion above, verified the fact that BSA had better ability to stabilize the emulsified octadecane droplets and to prevent them from aggregation than the SDS.

To detect the thermal stability and thermal conductivity of encapsulated octadecane, 5 heating-freezing cycles in the temperature range of -30°C to 45°C were performed. These temperature cycles were designed to close around the melting point of octadecane. The sample containing better polyelectrolyte shells (using BSA as surfactant) was freeze-dried and studied here. Figure 4 showed DSC curves of pure octadecane (black curves) and polyelectrolyte encapsulated octadecane (red curves) (Figure 4(a)). In the DSC measurements, as shown in Figure 4(a), for the pure octadecane, the first heating-freezing curve was slightly different from the other four cycles, which could be attributed to the enthalpy relaxation of the material itself. The other four heating-freezing curves were almost overlapped, which indicated the same thermal status of the materials when undergoing the same thermal process. Likewise, the overlap of the five curves of the encapsulated octadecane evidenced the same status of the polyelectrolyte encapsulated octadecane spheres after thermal process, illustrating that the LbL assembled polyelectrolyte shells well stabilized the PCM (octadecane) studied in our work.

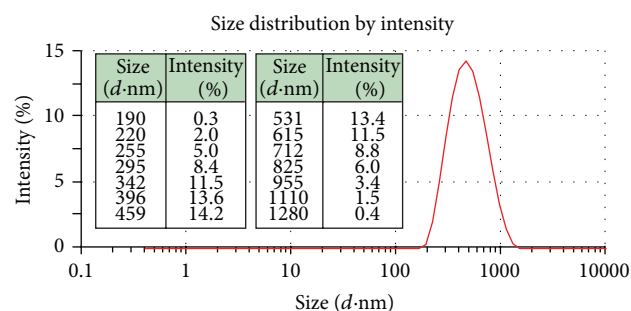
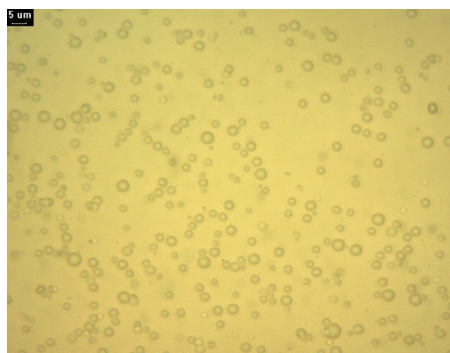
According to the DSC curves (Figure 4(b)), the melting point temperatures were detected to be 28.22°C and 29.31°C , respectively, for the octadecane before (blue) and after (green) encapsulation. After encapsulation, the enthalpy of phase change was derived as 544.44 J/g from the area of melting peak, which was lower than that of the pure octadecane (605.48 J/g). In our work, the difference was attributed to the presence of PDADMAC and PSS polyelectrolytes with higher melting points (mp: $>150^\circ\text{C}$ for PDADMAC [17], 460°C for PSS (data provided by Sigma-Aldrich)). Comparing the enthalpy data, the encapsulated octadecane content was nearly 91.3% (by mass), which was calculated by the following formula:

$$\text{octadecane content} = \frac{(\Delta H_{m,C18} + \Delta H_{c,C18})}{(\Delta H_{m,pC18} + \Delta H_{c,pC18})}, \quad (1)$$

where $\Delta H_{m,C18}$ and $\Delta H_{c,C18}$ are melting enthalpy and crystallization enthalpy of pure octadecane, respectively;



(a)



(b)

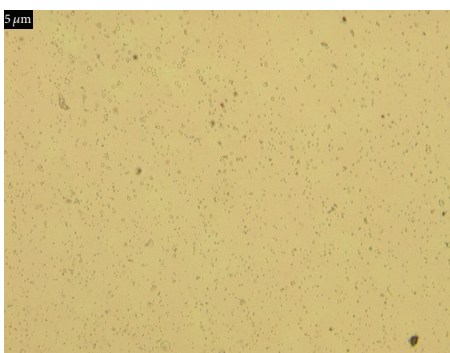


FIGURE 2: DLS measurements (left) and optical microscopy observation (right) of polyelectrolyte encapsulated octadecane using SDS (a) and BSA (b) as surfactants, respectively.

$\Delta H_{m,pC18}$ and $\Delta H_{c,pC18}$ are melting enthalpy and crystallization enthalpy of polyelectrolyte encapsulated octadecane, respectively.

The percentage of octadecane in polyelectrolyte encapsulated octadecane spheres was the key factor of the sphere system. It determined enthalpy and energy storage efficiency of the sphere system directly. In this study, 91.3% of loading ratio demonstrated that the fabricated polyelectrolyte shell was ultrathin and the whole encapsulated octadecane sphere system would achieve a good thermal storage capacity.

Repeated heating and cooling gave a stuck wax appearance of the free octadecane, as shown in Figure 5(a). On the contrary, encapsulated octadecane spheres were exhibited as dispersive white powder (Figure 5(b)). These results indicated that there was no obvious leakage of the octadecane from the polyelectrolyte-PCM spheres, verifying the successful encapsulation of the octadecane using the PDADMAC and PSS polyelectrolytes in this work.

4. Conclusions

Polyelectrolytes PDADMAC and PSS were used to encapsulate the organic phase change material octadecane through

the LbL assembly procedure. Surfactants used in this work, BSA and SDS to be specific, were found to be able to influence the morphologies and size distributions of fabricated polyelectrolyte-PCM spheres. In particular, using BSA as the surfactant, encapsulated octadecane spheres with small size and good shell integrity were obtained. Moreover, DSC test revealed that the octadecane content of the encapsulated sphere system was 91.3% by mass using BSA as surfactant. Repeated thermal treatments also verified good thermal stability of this polyelectrolyte-PCM system.

As a preliminary study, we demonstrated the possibility of using LbL assembly technique to encapsulate the PCM, offering a simple yet efficient approach to engineering steady PCM systems with good thermal energy storage capacity. Hopefully, this method could be broadened to entrap other organic PCMs for potential uses in the areas of latent energy storage use and to increase thermal stability and prevent leakage and agglomeration of molten phase change materials to be specific. Furthermore, heat transfer test of the PCM slurry in heating and cooling cycling circulation, which closes to the practical application, will be investigated in our future work. Besides, thermal-related multilayer shell integrity change will also be studied.

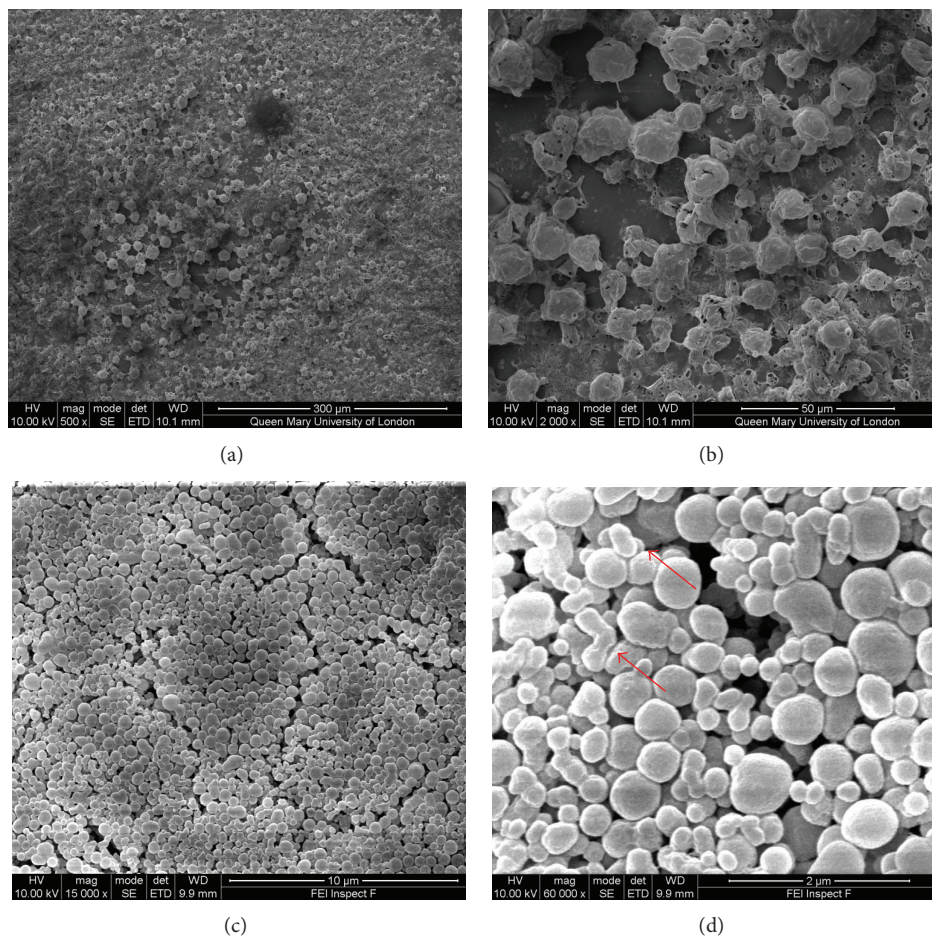


FIGURE 3: SEM images of encapsulated octadecane particles using (a, b) SDS and (c, d) BSA as surfactants, respectively. * Particle diameter and distribution expressed as mean \pm SD of at least 50 particles per sample of random measurement of SEM images. The symbols (\curvearrowright) pointed out the spheres with irregular shape.

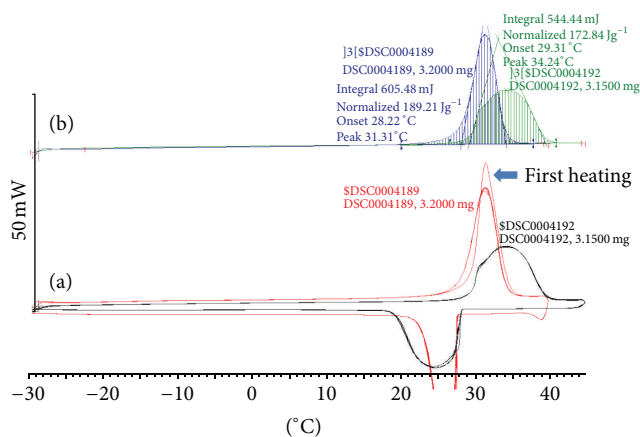


FIGURE 4: DSC curves of octadecane with (black) and without polymer coating (red) (a) and analysis of related curves (b).

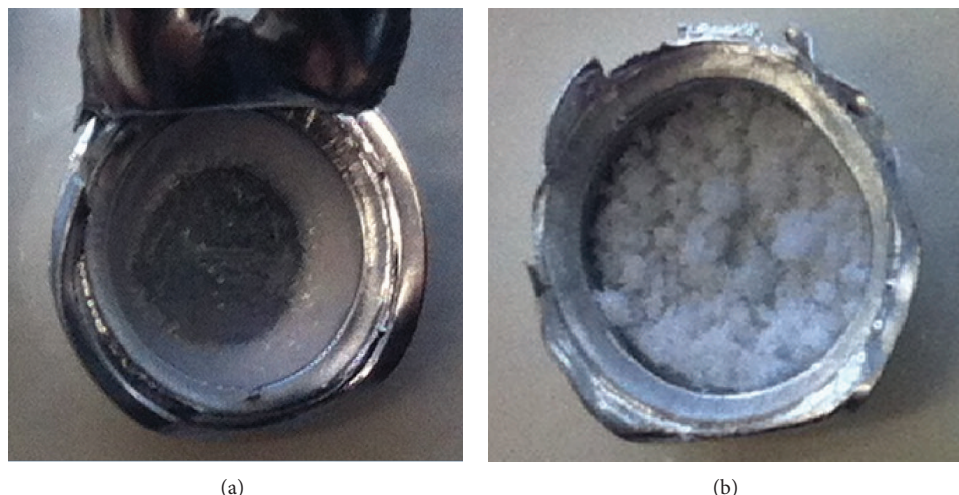


FIGURE 5: Images of the free octadecane (a) and encapsulated octadecane (b) after DSC treatments.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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