1. Background and Objectives

Phase change or phase transition, as one of the most common phenomena that occurs every second in our planet, was used to describe transitions between solid, liquid, gaseous states as well as plasma of matters. Phase change materials (PCMs) are recognized as the materials that use phase transitions to achieve certain designed functions. Using latent heat in PCMs is one of the most efficient ways of storing thermal energy and it has received wide attention in decades. Among PCMs based on different phase change processes, solid-liquid PCMs are the most studied and used storage medium of thermal energy due to the high enthalpy of fusion and small volume expansion. Various types of solid-liquid PCMs were developed including both organic compounds (e.g., paraffin waxes, fatty acids, esters and other organic compounds) and inorganic compounds (e.g., salt hydrates, molten salts, metals and alloys). However, the biggest historical drawback of using conventional PCMs, like the low thermal conductivity of organic materials and inorganic salts, large volume changes of inorganic salts during melting and high corrosion from inorganic salts and metals. Those give limitations for their wider applications.

Metals and their alloys can overcome the problems existing in organic compounds and inorganic salts as mentioned above. Low melting point metals are promising materials that can be used as PCM for heat storage and thermal management in wider working conditions. Due to the high thermal conductivity, the metallic heat storage media shows rapid thermal energy transfer. In addition, the high density of the metals also contributes to the high volumetric density of heat storage. Based on these advantages, the low melting point metals can be applied in the thermal energy storage system in concentrated solar power (CSP) station. It also could be used for chip cooling in USB flash memory, smartphones and other high power density devices.

However, as a high performance PCM in thermal energy storage and management, the low melting point metals or alloys still in demand of efforts to be modified for practical applications. First, due to the corrosive characteristics of metals in liquid state, the compatibility between low melting point metal PCM and its container should be guaranteed. The bad compatibility between liquid metals and container, seriously limited their applications. Moreover, the sintering of liquid metal particles in low melting point metal PCMs may lead to the changes in as-designed structure or morphology during operation, deteriorating their sustainable usage in the form of nanofluids or slurry. Therefore, the structure design for encapsulating in micro or nano-sized low melting point metal PCMs in need for improving their utility.

The aims of this dissertation are to explore various synthetic methods, to create unique micro/nanostructures, thus, to make the best use of the high thermal conductivity of low melting
point metal PCMs, isolate them from outside environment for protection and also seek the novel methods for the further morphology control of related PCMs. Silica (SiO$_2$) and alumina (Al$_2$O$_3$) were chosen as the encapsulation materials due to their good physical and chemical stability.

Until now, only a few examples have been reported to achieve using SiO$_2$ and Al$_2$O$_3$ to coat low-melting-point metal for thermal energy storage. Compared to them, in this dissertation, more facile and more customized methods were used, and the PCMs with unique structures named Sn NPs@p-SiO$_2$ and Sn@Al$_2$O$_3$ with good thermal cyclic stability were fabricated. In the case of using SiO$_2$ to encapsulate Sn NPs, a novel transformation from Sn@SiO$_2$ core-shell NPs to Sn@SiO$_2$ yolk-shell NPs and SnO$_2$@SiO$_2$ hollow NPs were observed, based on which the nanostructure control via liquid metal diffusion was first time realized.

2. Materials and Methods

2.1 Synthesis of Sn NPs@p-SiO$_2$

![Scheme 1](image1.png)

Scheme 1. Preparation of Sn NPs@p-SiO$_2$. Step 1: Synthesis of p-SiO$_2$ spheres as structure matrix; Step 2: Impregnation of the Sn precursor; Step 3: Reduction of the Sn precursor inside the SiO$_2$ matrix to obtain Sn NPs embedded into p-SiO$_2$.

Porous p-SiO$_2$ spheres were first prepared by the hydrolysis and condensation of TEOS triggered by ammonia in the mixture of ethanol and H$_2$O with the existence of CTAB. The obtained p-SiO$_2$ spheres were purified and vacuum-dried overnight then used as matrix and dispersed in SnCl$_2$ solution for loading Sn precursor. After removing the unabsorbed Sn precursor by purification and drying in vacuum, the powder was reduced by thermal annealing in a mixed H$_2$/N$_2$ (3:97) gas flow at 550°C for 6 h in a tube furnace. Finally, Sn NPs@p-SiO$_2$ was obtained as a black powder.

2.2 Synthesis of Sn@Al$_2$O$_3$

![Scheme 2](image2.png)

Scheme 2. Synthesis process of Sn@Al$_2$O$_3$ spheres.
First, SnO\textsubscript{2} spheres were prepared by a solvothermal method from SnCl\textsubscript{2} precursor in a Teflon-lined stainless-steel autoclave. Then, the SnO\textsubscript{2} spheres were dispersed in a pre-prepared boehmite solution and refluxed for 12 h. After purification with deionized water and 1-propanol, and drying in vacuum, the powder was calcined at 1000°C in the air in a tube furnace for 30 min, and finally reduced by a mixed H\textsubscript{2}/N\textsubscript{2} (3:97) gas flow at 560°C for 6 h. The final product, Sn@Al\textsubscript{2}O\textsubscript{3}, was obtained as a black powder.

2.3 Synthesis of Sn@SiO\textsubscript{2}

The Sn NPs were synthesized using a well-developed hot-injection method. Developed method. To encapsulate Sn NPs with uniform SiO\textsubscript{2} shell, a modified reversed micro-emulsion method was used. Sn nanoparticle-dispersed stock solution (in hexane) was mixed with polyethylene glycol mono-4-nonylphenyl ether and deionized water to make emulsion by sonication. Afterward, TEOS were added, and the hydrolysis and condensation of TEOS were triggered by injection of ammonia solution for making the SiO\textsubscript{2} encapsulation on Sn NPs. The thickness of SiO\textsubscript{2} shell can be easily tuned by changing the concentration of Sn nanoparticle-dispersed stock solution.

2.4 In-situ Transmission Electron Microscopy (TEM) Observation of the Transformation of Sn@SiO\textsubscript{2} Core-Shell NPs to Yolk-Shell NPs and Hollow NPs

In situ TEM observations were carried out using a dedicated 1000 kV JEM-1000K RS TEM (JEOL, Tokyo, Japan) operated at 1000 kV. A wire-type heating holder (JEOL, EM-ZO81834SWHH, Tokyo, Japan) was used. The powder samples (Sn@SiO\textsubscript{2}) were loaded on a tungsten wire and heated up to 300°C under vacuum. TEM images were recorded with a charge-coupled device with an exposure time of typically 0.5 s and 5 s. The electron beam current flux for strong electron beam condition was 37.3 pA·cm\textsuperscript{-2}, and for weak electron beam condition was 2.7 pA·cm\textsuperscript{-2}, as measured with a Faraday gauge.

3. Results and Discussion

3.1 Sn Nanoparticles Confined in Porous Silica Spheres for Enhanced Thermal Cyclic Stability

In this part (Chapter 2), Sn NPs@p-SiO\textsubscript{2} spheres with the diameter of ca. 400 nm was successfully synthesized. The size of Sn NPs distributed inside p-SiO\textsubscript{2} is ca. 30 nm in diameter. The structure of Sn NPs@p-SiO\textsubscript{2} was investigated by using TEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) depth profile techniques. X-ray fluorescence spectrometry (XRF) was used to estimate the elemental composition. The results show that Sn NPs are uniformly embedded inside the p-SiO\textsubscript{2} spheres (Figure 1A). The formation mechanism of Sn NPs@p-SiO\textsubscript{2} was discussed. First, Sn precursors (main composition: Sn\textsubscript{2}Cl\textsubscript{6}(OH)\textsubscript{4}O\textsubscript{6}) are absorbed into p-SiO\textsubscript{2} spheres after the impregnation of the SnCl\textsubscript{2} precursor. Then, amorphous Sn precursor is formed after annealing at a temperature below 260°C. After that, crystal Sn oxides (SnO\textsubscript{x}, x = 1, 2) form at ca. 330°C with a change in the pore structure of the p-SiO\textsubscript{2} spheres. Finally, SnO\textsubscript{x} is reduced and Sn NPs are formed inside the p-SiO\textsubscript{2} spheres with the ability to further expand the pores inside the p-SiO\textsubscript{2} spheres (Figure 1B).

To investigate the stability of the separated distribution of Sn NPs inside p-SiO\textsubscript{2}, 100 melt–freeze thermal cycles were performed in the 100–250°C range. The results show a good
long-term thermal stability and decreased melting temperature of Sn which is corresponding to the nanoscale characteristic (Figure 1C). No morphology changes were observed before and after cycling according to the TEM images.

![Figure 1](image)

**Figure 1.** (A): (a, b) TEM images of (a) as-synthesized p-SiO$_2$ spheres and (b) Sn NPs@p-SiO$_2$. (c) SAED pattern of Sn NPs@p-SiO$_2$. (d) Size histogram of Sn NPs in p-SiO$_2$; (B): Illustration of the mechanism of Sn NPs@p-SiO$_2$ formation; (C): (a) DSC results for 100 melt–freeze cycles for Sn NPs@p-SiO$_2$. (b) Enthalpy of melting vs cycle number. (c) Enlarged DSC curves in the 220–245°C range during 100 cycles. (d) Melting temperature of Sn NPs confined into p-SiO$_2$ (blue spheres) at each cycle compared with the melting temperature of bulk Sn (red dashed line).

3.2 Size-Tunable Alumina-Encapsulated Sn-Based Phase Change Materials for Thermal Energy Storage

In this part (Chapter 3), Sn@Al$_2$O$_3$ was examined by TEM, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and XRD, in which a big spherical Sn core (1–2 μm) and many small Sn spheres (50–250 nm) were encapsulated by a thick Al$_2$O$_3$ shell (100–700 nm) (Figure 2A). The obtained Sn@Al$_2$O$_3$ particles not only have high PCM content (92.37 wt %) but also show a stable thermal behavior and morphology during 100 melt–freeze cycles in the air atmosphere (Figure 2B, C).

To investigate the formation mechanism of Sn@Al$_2$O$_3$, the intermediate SnO$_2$@Al$_2$O$_3$ was checked by TEM, XRD, SEM, focused ion beam (FIB) cross-section imagine and XPS. It was found that the boehmite treatment, in which the penetration of aluminum species into SnO$_2$ spheres played an important role, was found to be responsible for the unique structure formation of final Sn@Al$_2$O$_3$. To test this finding above, the Sn@Al$_2$O$_3$ samples with different sizes from ∼600 to ∼60 nm were synthesized for comparison with Sn@Al$_2$O$_3$ obtained from the standard synthesis, showing a good control in size of Sn@Al$_2$O$_3$ (Figure 3). The understanding
of structure formation mechanism gives the possibilities of a new facile way for the synthesis of metal nanoparticles and particle-distributed nanostructures.

Figure 2. (A): TEM (a) and SEM (b) images of Sn@Al₂O₃ particles. SAED patterns of black cores inside shell of Sn@Al₂O₃ (c) and shell with light contrast (d). (e) XRD pattern of as-prepared Sn@Al₂O₃ particle powder; (B): Relative melting enthalpy in 100 melt–freeze cycles of Sn@Al₂O₃-1600 compared with bulk Sn (ΔH/ΔH₀) during melt–freeze cycles (red spheres) where ΔH and ΔH₀ are enthalpy of melting of Sn@Al₂O₃-1600 and that of bulk Sn, respectively. The relative melting enthalpies of Sn@Al₂O₃-60 and Sn NPs@p-SiO₂ are labeled with green and blue spheres, respectively; (C): TEM and SEM images of Sn@Al₂O₃-1600 after 100 melt–freeze cycles in the air.
Figure 3. TEM images of (c–h) Sn@Al₂O₃ with different morphologies (c: Sn@Al₂O₃-1600; f: Sn@Al₂O₃-600; g: Sn@Al₂O₃-350; h: Sn@Al₂O₃-60) reduced from the corresponding (a–d) SnO₂@Al₂O₃ (a: SnO₂@Al₂O₃-1600; b: SnO₂@Al₂O₃-600; c: SnO₂@Al₂O₃-350; d: SnO₂@Al₂O₃-60) prepared by using SnO₂ with various sizes, i.e., (a) ~1.6 μm, (b) ~600 nm, (c) ~350 nm, and (d) ~60 nm. (i–l) The corresponding scheme for the formation of Sn@Al₂O₃. All scale bars are 500 nm.

3.3 From Core-Shell to Yolk-Shell and Hollow: Controllable Nanostructure via Liquid Metal Diffusions

In this part (Chapter 4), Sn NPs were encapsulated with SiO₂ shell to form Sn@SiO₂ core-shell NPs, then loaded on a TEM holder with heating function and heated to 300°C in vacuum with in-situ TEM observation. It was observed that hollow NPs formed after heating. During real-time observation at 300°C, it was found that, under strong electron beam condition (37.3 pA·cm⁻²), Sn cores in Sn@SiO₂ move dynamically with deformation of encapsulating SiO₂ structure. The disappearance of liquid state Sn cores occurs in both strong (37.3 pA·cm⁻²) and weak (2.7 pA·cm⁻²) electron beam conditions, but in different modes. Combined above results with the observed Ostwald ripening inside SiO₂ during heating, it is believed that the diffusion of Sn occurs which contributes to the formation of hollow nanostructure.

With this understanding, controllable nanostructures from core-shell NPs to yolk-shell NPs and hollow NPs were synthesized by tuning the core-shell volumetric ratio of starting Sn@SiO₂ core-shell NPs with annealing in a sealed pan in a differential scanning calorimeter (DSC) in sequence. By measuring the volume of remained Sn core and the diameter of original Sn core from more than 200 yolk-shell and hollow NPs, it was found that the amorphous SiO₂ shell that fabricated in this case provides space with a certain capacity for Sn species to stay after heating and diffusion. The diffused Sn may interact with the dangling bonding in SiO₂, making the Sn stay as the state of SnOₓ, and leaving hollow space in the center, thus creating the hollow structure. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and EDS mapping of obtained hollow NPs show that the Sn element was distributed inside the SiO₂ shell, giving evidence to the Sn diffusion.

4. Conclusion and Prospective

- A nanostructure in which phase-change Sn NPs were confined inside p-SiO₂ spheres was synthesized through a facile method utilizing common starting chemicals. The p-SiO₂ spheres effectively stabilized the embedded Sn NPs during cyclic melting–cooling. The melting depression phenomenon of the Sn NPs expands the application window of phase-change thermal energy storage using low-melting-temperature metals. The formation of voids inside Sn NPs@p-SiO₂ was investigated for the first time. The transformation of the Sn precursor occurred and included the formation and decomposition of the amorphous Sn precursor, formation and reduction of crystal Sn oxides, and interactions between Sn NPs and SiO₂ during annealing in a 3% H₂/N₂ atmosphere. It is believed that the transformation of the Sn precursor during annealing accompanied by the modification of the formed Sn NPs led to the formation of big voids inside p-SiO₂ spheres, which gives inspiration for new strategies for the synthesis of hollow SiO₂ spheres and yolk–shell SiO₂ structures.
- Alumina-encapsulated Sn particles (Sn@Al₂O₃) were successfully prepared and used as PCMs. The fabrication process consisted of a surfactant-free solvothermal synthesis of SnO₂ spheres, boehmite treatment on SnO₂ spheres, calcination in the air, and the final
hydrogen reduction to transform SnO$_2$ to metallic Sn. All the steps of fabrication are facile and low-cost which can be simply applied to the mass production. The as-obtained Sn@Al$_2$O$_3$ particles with a high PCM content (92.37 wt %) showed a stable thermal behavior and morphology during 100 melt–freeze cycles in the air atmosphere. The Sn@Al$_2$O$_3$ shows a core–shell structure with small Sn nanoparticles dispersed in the shell. The formation of Sn@Al$_2$O$_3$ structure is a result of boehmite treatment on SnO$_2$ spheres for the involvement of aluminum. The penetration of boehmite sol (AlOOH) into the SnO$_2$ spheres contributes to the formation of the thick alumina shell, which plays a key role in the thermal storage stability. This result also provided the possibility for a facile method for designing new metal nanoparticles with a particle-distributed nanostructure. These results also demonstrate the great potential of Sn@Al$_2$O$_3$ particles in the applications as a thermal energy storage material in high-temperature conditions which are not suitable for organic PCMs.

- A novel design of controllable nanostructure of Sn@SiO$_2$ from core-shell to yolk-shell and hollow has been achieved through a liquid metal diffusion process. The transformation of Sn@SiO$_2$ core-shell nanoparticles into hollow SiO$_2$ nanostructure by diffusion of liquid Sn cores inside Sn@SiO$_2$ was real-time observed via in-situ TEM. The diffusion of liquid state Sn acts as the role for removing the cores thus creating the cavity for hollow nanostructure. Importantly, based on these findings, the control over the morphologies of hollow/yolk-shell Sn@SiO$_2$ nanostructures was demonstrated by adjusting the volume ratio between core and shell of starting Sn@SiO$_2$ core-shell nanoparticle precursors. Furthermore, these findings provide valuable knowledge of diffusion of liquid state metal inside SiO$_2$ structure, as well as a novel tool in designing complicated hollow nanostructures in future studies.

References