

Research Paper

Surface/interface influence on specific heat capacity of solid, shell and core-shell nanoparticles

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HIGHLIGHTS

- Heat capacity models for shell and core-shell structures are established.
- Heat capacity of carbon shell can be 30 times that of the carbon bulk.
- Influence of the interface on heat capacity is negligible at a low temperature.
- Interface greatly reduces the heat capacity of a core-shell structure at a high temperature.

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ABSTRACT

In this paper, we firstly develop the shell and core-shell HC models for the first time. Then, the differential scanning calorimeter (DSC) method is applied to measure HCs of copper nanoparticles, carbon shells and core-shell/Cu-C nanoparticles. Results show that the HC of a carbon shell can be even enlarged more than 30 times than that of the carbon bulk. Comparing experimental results with that predicted by our models, it turns out that our shell HC model could capture the experimental result well, and there is a good agreement between our core-shell HC model and experiments at a low temperature (< 460 K in this paper) where the influence of the interface can be neglected, while the interface greatly reduces the HC of a core-shell structure at a high temperature. This work is expected to provide some information about the influence of surface/interface on the HC of the shell and core-shell structures for their potential applications in energy storage systems, and also provide some physical insights into the HC of a complex nanostructure.

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1. Introduction

Nanoparticles have already been widely used to enhance the thermal conductivity of thermal interface materials [1,2] and polymer-based nanoparticle composites [3–5] for improving their performance in heat dissipation application. Additionally, the nanoparticles also attract extensive attention in tuning the latent heat, melting point and specific heat capacity (HC) of phase change materials (PCM) for energy storage application [6–9]. The incorporation of nanoparticles in a composite usually brings in a large number of interfaces or surfaces, and the surface/interface in nanoscale could exert a significant influence on material thermophysical properties because of the large surface-volume ratio.

In the thermophysical domain, the effect of surface/interface on the thermal conductivity has already been widely probed with a theoretical [10–14] and/or an experimental [15–18] approach, and a good understanding of the phonon-scattering mechanism at interface has been obtained [11,19]. However, the research concerning the influence of interface on latent heat, melting point and HC is still limited, especially the influence of interface on HC. In the previous works, the method by incorporating nanoparticles in a composite has been applied to enhance the HC according to the fact that a nanoparticle usually possesses a higher HC than that of the matrix material [20,21], although it is believed that the suppressed vibration of interfacial atoms between the nanoparticles and matrix can reduce the HC [22,23]. Considering the still unclear effect of interface on HC of a composite, a further research is desirable. The knowledge about this effect is not only significant to supply some information for the preparation of energy storage materials (ESM), but also to provide physical insights into the HC of a complex nanostructure.

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To reveal the effect of surface/interface on the HC, the copper nanoparticles, carbon shells and core-shell/Cu-C (copper nanoparticles coated with carbon shells) nanoparticles are investigated respectively in this work. Firstly, the HC models for the shell and core-shell structures are respectively established. Secondly, applying the differential scanning calorimeter (DSC) method, the HCs of copper nanoparticles, carbon shells and core-shell/Cu-C are measured. Thirdly, our HC models are tested by experiments, and results of HC of copper nanoparticles, carbon shells and core-shell/Cu-C are discussed. Finally, the influence of the interface on the HC of a core-shell structure is discussed. Results show that our model could give a good prediction of HC and the influence of interfaces can be neglected at a low temperature, while they can greatly reduce the HC of a core-shell structure at a high temperature.

2. Material characterization and HC measurement method

Copper nanoparticles with a diameter of 50 nm, carbon shells with an inner diameter of 100 nm and a thickness of 10 nm, and the core-shell nanoparticles composed of 50 nm copper core coated with a 5 or 30 nm carbon shells are commercially obtained from Beijing DK Nano Technology Co., Ltd. The structure schematic diagram of a core-shell nanoparticle is shown in Fig. 1(a) and microstructures of shell and core-shell nanoparticles observed by transmission electron microscopy (TEM) method using a Tecnai G2 F20 instrument (FEI Co., USA) with an accelerating voltage of 80 kV, and scanning electron microscope (SEM) method using a QuantaTM-250 instrument (FEI Co., USA) with an accelerating voltage of 25 kV, are also shown in Fig. 1. It shows that the shell and core-shell nanoparticles are approximately uniform, and the structure of the interface is clear.

The HC is measured by a DSC thermal analyzer (produced by Switzerland Mettler Toledo). The calibration of the equipment is carried out with indium as the reference material. In the measurement, samples with a weight of 10 ± 0.1 mg are heated with a heating rates of 10 K/min from room temperature to 800 K under the protection of nitrogen atmosphere. Based on the definition, the

HC of samples is calculated from the heat flux density curve. The HC of every sample are measured more than two times and a mean value is calculated with an error less than 3%. Considering uniform nanoparticles shown in Fig. 1, the relative error of HC caused by the size deviation of nanoparticles from the mean value is negligible.

3. Establishment of specific heat capacity models

In this part, the shell and core-shell HC models are respectively established for theoretical predictions in Part 4.

3.1. Shell specific heat capacity model

The shell HC model including the size effect of the shell thickness and inner diameter is established in this part. This model will be tested by the experimental results of a carbon shell with an inner diameter of 100 nm and a thickness of 10 nm in Part 4.2.

Considering the shell can be thought as an elastic continuum due to the large size of inner diameter and shell thickness (larger than 5 nm in this paper) [13,24–27], the Debye model is applied here to describe the HC [28],

$$C = \frac{12\pi^4 N \kappa_B}{5} \left(\frac{T}{\theta}\right)^3 \quad (1)$$

where T is temperature, κ_B is the Boltzmann constant, N is the number of atoms, θ is the Debye temperature. Based on Lindemann's criterion, the Debye temperature in nanoscale can be expressed as a function of mean square displacement (MSD) of atoms [29–32],

$$\frac{\theta^2}{\theta_\infty^2} = \frac{\sigma_\infty^2}{\sigma^2} = \exp[-(\alpha - 1)x] \quad (2)$$

here θ_∞ is the Debye temperatures of the corresponding bulk, σ is the root of MSD, σ_∞ is the root of the MSD of the corresponding bulk, α is the MSD ratio between the surface atom and the volume atom (the α calculation will be given later), and x is the surface-volume ratio.

Combining Eqs. (1) and (2), the dimensionless HC can be rewritten as,

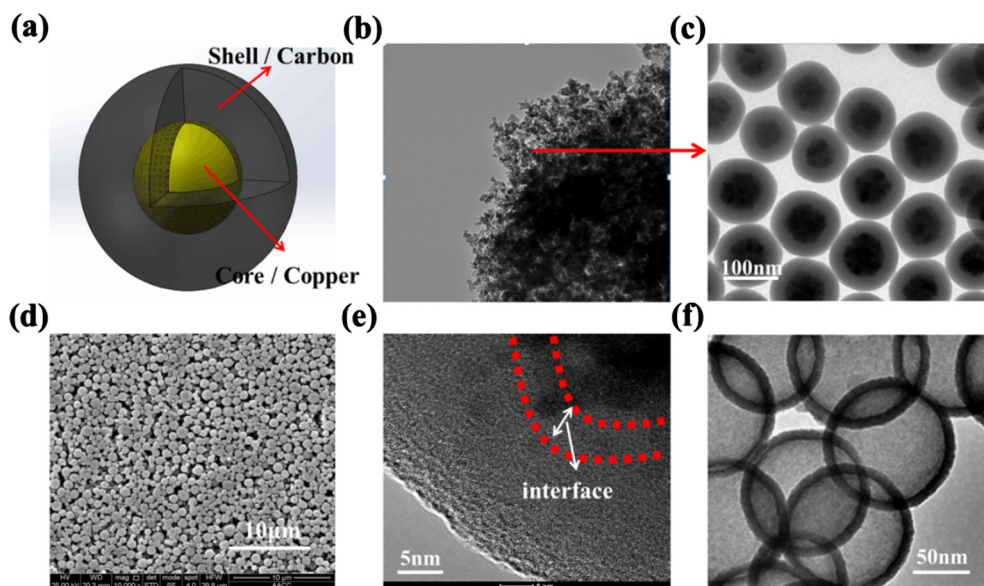


Fig. 1. Micro-structures of the carbon shell and the core-shell/Cu-C nanoparticles. (a) Schematic diagram of a core-shell/Cu-C nanoparticle; (b) core-shell nanoparticles observed by TEM; (c) enlarged structure view of core-shell/Cu-C nanoparticles; (d) core-shell nanoparticles observed by scanning electron microscope (SEM); (e) interface observed by high-resolution TEM (HRTEM); (f) carbon shell observed by TEM.

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