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# Thermal conductivity enhancement of Ag nanowires on an organic phase change material

J. L. Zeng · Z. Cao · D. W. Yang · L. X. Sun ·
L. Zhang

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**Abstract** One of the greatest challenges in the application of organic phase change materials (PCMs) is to increase their thermal conductivity while maintaining high phase change enthalpy. 1-Tetradecanol/Ag nanowires composite PCM containing 62.73 wt% (about 11.8 vol%) of Ag nanowires showed remarkably high thermal conductivity (1.46 W $m^{-1}$ $K^{-1}$) and reasonably high phase change enthalpy (76.5 J $g^{-1}$). This behavior was attributed to the high aspect ratio of Ag nanowires, few thermal conduct interfaces, and high interface thermal conductivity of Ag nanowires in the composite PCM. These results indicated that Ag nanowires might be strong candidates for thermal conductivity enhancement of organic PCMs.

**Keywords** Silver nanowires · Composites materials · Nanocomposites · Thermal conductivity · Phase change materials

## Introduction

Organic phase change materials (PCMs) can store and release thermal energy in much higher storage density by liquefying and solidifying within a small temperature difference, making them very attractive in thermal energy storage and thermal protection [1–5]. Besides, they can also be used as thermal interface materials, which are indispensable in thermal management of micro-electronics [6], since organic PCMs in their liquid state can fill small air gaps that existed between two solid surfaces in contact. Organic PCMs possess the merits of chemical and thermal stable, low or no sub-cooling, and no corrosive [3]. However, the main drawback that hinders the application of organic PCMs is their unacceptably low thermal conductivity. Great efforts, such as improving encapsulation structure [7], dispersing high conductive fillers in organic PCMs matrixes [8–12], and dispersing organic PCMs in high conductive matrixes [13, 14], have been devoted to improve the thermal conductivity of organic PCMs. However, few organic PCMs have attained satisfactory thermal conductivity while maintaining reasonable thermal energy storage density. Hong et al. [15] improved the thermal performance of paraffin by applying open-cell aluminum foams as matrix. However, the thermal conductivity was not reported, and such structures cannot be used as thermal interface materials. Mills et al. [16] improved the thermal conductivity of paraffin by impregnating porous graphite matrix with paraffin. However, the obtained composite PCM showed considerable anisotropy with respect to the thermal conductivity.

As a famously known one-dimensional nano-structured material, carbon nanotubes have been widely researched as thermal conductivity filler [10, 11, 17]. However, the low interface thermal conductance of carbon nanotubes shows a fatal problem [18]. Ag nanowires (NWs) are another kind of one-dimensional nano-structured materials. Numerous methods [19–21] have been proposed to prepare Ag NWs by virtue of its highest electrical and thermal conductivity among all the metals. If the thermal conductivity can be

J. L. Zeng (✉) · Z. Cao · D. W. Yang · L. Zhang
School of Chemistry and Biological Engineering, Changsha University of Science & Technology, Changsha 410004, People's Republic of China
e-mail: julan_zeng@yahoo.com.cn

L. X. Sun (✉)
Materials & Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China
e-mail: lxsun@dicp.ac.cn

improved effectively by Ag NWs, organic PCMs will have a bright future in thermal energy storage and thermal protection, as well as thermal interface materials. However, to the best of our knowledge, no experimental study about the improvement of thermal conductivity of the organic PCMs using Ag NWs has been reported. In this regard, this article presents the thermal properties of Ag NWs/1-tetradecanol (TD) composite PCM.

## Experimental

### Materials

All the reagents were of analytical grade and were used without further purification. Ag NWs were prepared according to a reported procedure [21].

### Preparation of composite PCMs

Ag NWs, TD, and anhydrous ethanol were mixed in test tubes. The mixtures were ultrasonicated at 343 K for 10 min and allowed to remain at room temperature to evaporate most of ethanol naturally. Then, the mixtures were ultrasonicated at 343 K for 1 h. After being cooled to room temperature, the mixtures were dried in vacuum at room temperature for 24 h and then ground. The ratios of raw materials of composite PCMs are listed in Table 1.

### Characterization

Infrared spectra were recorded on a BRUKER EQUINOX 55 FT-IR spectrometer using KBr pellet (400–4,000 $cm^{-1}$). Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku D/max-$\gamma$b X-ray diffractometer with monochromatic detector. Copper K$\alpha$ radiation was used, with a power setting of 50 kV and 200 mA, and a scan rate of 5° $min^{-1}$. The samples were sputtered with gold, and then the surface morphology of the composites was investigated by scanning electron microscope (SEM, JEOL/EO JSM-6360).

Differential scanning calorimeter (DSC, DSC141 SETARAM) was used to investigate the energy storage properties of the composite PCMs from 273 to 333 K with the heating rate of 10 K $min^{-1}$ in nitrogen atmosphere. Thermogravimetry (TG) measurements were performed on a Cahn TherMax 500 TGA system from room temperature to 773 K with the heating rate of 10 K $min^{-1}$ and $N_2$ as carrier gas. The ground composite PCMs were pressed under 20 MPa to obtain two cylinders ($\varnothing = 13$ mm). A Hot Disc thermal constant analyzer was used to obtain the thermal conductivity of the composites at room temperature with a sensor diameter of 2.001 mm. The sensor was sandwiched by two cylinders and fixed by a clamp.

**Table 1** Raw materials ration of composite PCMs

| Sample | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Weight of Ag NWs/g | 0.101 | 0.303 | 0.602 | 0.863 | 1.01 |
| Weight of TD/g | 1.01 | 1.01 | 1.00 | 1.01 | 0.60 |
| Mass fraction of Ag NWs/% | 9.09 | 23.08 | 37.58 | 46.08 | 62.73 |

## Results and discussion

### Structure and morphology investigations

The IR spectra of the selected composite PCMs and TD were shown in Fig. 1. The figure shows that these IR spectra are similar. The absorption bands in each spectrum were at the same site: the broad band in the range of 3,200–3,500 $cm^{-1}$ was assigned to the stretching vibration of hydroxyl group of the alcohol. The $\nu$ (CH) and $\delta$ (CH) absorption bands were exhibited at 2917, 2846 $cm^{-1}$ and 1465, 721 $cm^{-1}$, respectively. The stretching vibration of C–O of primary alcohol could be seen at 1,062 $cm^{-1}$. This result demonstrates that no strong interaction existed between the Ag NWs and TD.

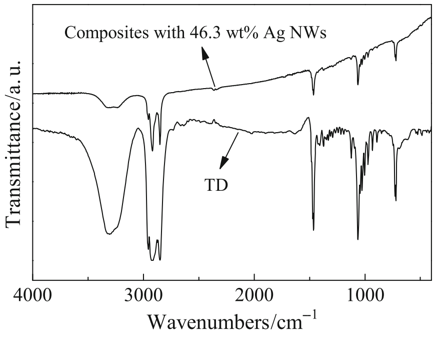


**Fig. 1** IR spectra of composites PCM containing 46.08 wt% Ag NWs and TD

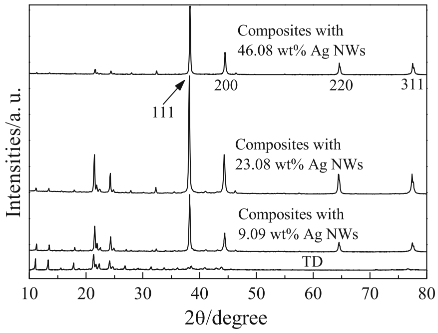


**Fig. 2** XRD patterns of composites PCMs and TD

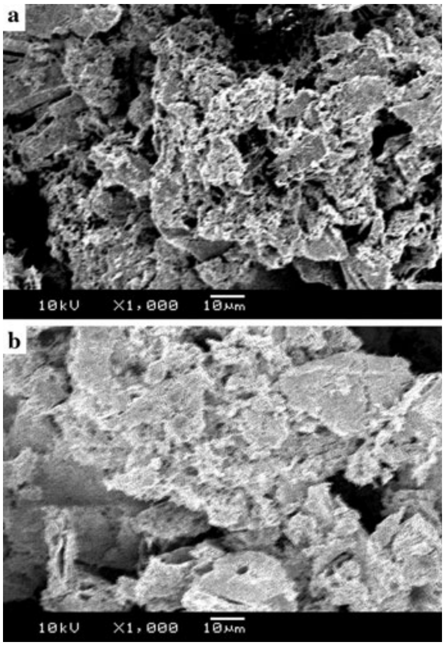


**Fig. 3** SEM images of composites with 23.08 wt% (**a**) and 62.73 wt% (**b**) Ag NWs

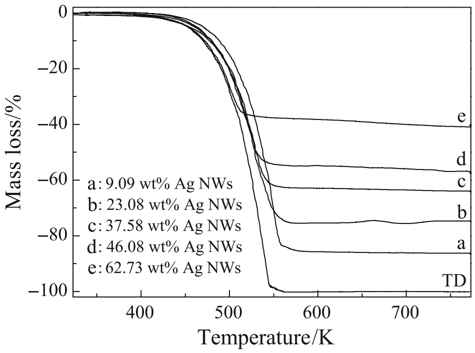


**Fig. 4** TG curves of the composites PCMs and TD

The XRD patterns of the composite materials and pure TD were shown in Fig. 2. The peaks appeared at $2\theta > 35°$ could be assigned to the diffraction of (111), (200), (220), and (311) planes of silver (PCPDF No. 040783) and agreed well with the reference [21]. The result indicated that Ag NWs were successfully prepared and that no diffraction peak of silver oxide existed, indicating that Ag NWs were stable in the composite PCMs. The SEM images of the composite PCMs (Fig. 3) show that the Ag NWs were coated with a layer of TD. The Ag NWs were dispersed randomly in the TD matrix. When the Ag NWs contents were low, there were blocks of TD exhibited (Fig. 3a). However, when the Ag NWs contents increased to 62.73 wt% (Fig. 3b), the networks of Ag NWs were formed and the blocks of TD disappeared, indicating that the composite PCM might have good thermal conductivity.

## Thermal properties

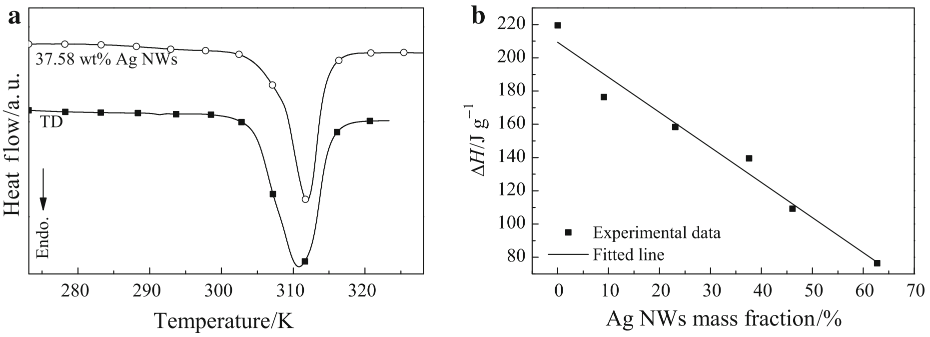
The thermal stability of composite PCMs was similar to that of TD (Fig. 4). The composite PCMs and TD went through a one-step weight loss, corresponding to the evaporating of TD during the heating process. The figure also showed that the residue of composite PCMs agreed well with the Ag NWs contents in the corresponding composite PCMs, indicating that Ag NWs and TD were just physically mixed.

The DSC curves of all the composite PCMs were similar. Figure 5a shows the DSC curves of TD and the composite PCM containing 37.58 wt% Ag NWs. It could be seen that the solid–liquid phase change feature of TD in the composite PCMs was not affected by Ag NWs. The phase change enthalpy ($\Delta H$) of TD and composite PCMs obtained from DSC experiments are depicted in Fig. 5b. In general, the $\Delta H$ of the composite PCMs decreased linearly as the loading of Ag NWs increased. The $\Delta H$ of the composite PCM containing 62.73 wt% of Ag NWs was 76.5 J $\text{g}^{-1}$. This value is close to the $\Delta H$ of some reported PCMs [22, 23], indicating that reasonably high phase change enthalpy was maintained in the composite PCM.

## Thermal conductivities

Figure 6 shows that the thermal conductivity of the composite PCMs increased linearly with the loading of Ag NWs. The thermal conductivity of TD was

**Fig. 5** Heat storage of the composite PCM and TD. **a** DSC curves; **b** relationship between $\Delta H$ and Ag NWs loading



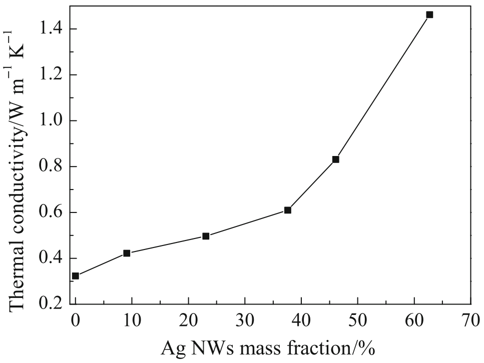


**Fig. 6** Thermal conductivity of the composites

0.32 W m$^{-1}$ K$^{-1}$. However, the thermal conductivity of the composite PCM containing 62.73 wt% (about 11.8 vol%) of Ag NWs was increased to 1.46 W m$^{-1}$ K$^{-1}$. It is much higher than that of some reported composite PCMs. Taking into account of its $\Delta H$ (76.5 J g$^{-1}$), the composite could be regarded as a novel organic composite PCM with remarkably high thermal conductivity and reasonably good energy storage density.

It has been reported that the thermal conductivity of composite materials containing about 10 vol% of metal powder was just slightly improved compared to matrix materials [24–27]. Hence, the result of our research indicated that Ag NWs possess much stronger ability to enhance the thermal conductivity of composite materials than metal powder. We ascribed this enhancement to the much high aspect ratio of Ag NWs, hence to the few thermal conductivity interfaces. We also noted that the thermal conductivity of Ag NWs/TD composite PCMs was even higher than CNTs/TD composite PCMs [11, 12]. CNTs could only moderately improve the thermal conductivity of composite materials due to the low interface thermal conductivity [18]. As a result, we believe that the higher thermal conductivity of Ag NWs/TD composite PCMs also originated from the high interface thermal conductivity of Ag NWs. It was reported that the thermal conductivity of paraffin could be greatly improved by applying expanded graphite as matrix. However, serious anisotropy on the thermal conductivity of such composite PCM also existed [16]. As a result, it can be concluded that the Ag NWs can be considered as strong candidates to improve thermal conductivity of organic PCMs, which are used as thermal energy storage materials, as well as thermal interface materials.

## Conclusions

(1) Ag NWs were applied to improve the thermal conductivity of PCM for the first time;
(2) The thermal conductivity of the composite PCM containing 62.73 wt% (about 11.8 vol%) of Ag NWs was 1.46 W m$^{-1}$ K$^{-1}$ while its phase change enthalpy was 76.5 J g$^{-1}$;
(3) The strong ability of Ag NWs to improve the thermal conductivity of composite PCMs originated from its high aspect ratio, few thermal conductivity interfaces, and high interface thermal conductivity;
(4) AgNWs might be strong candidates for thermal conductivity enhancement of organic PCMs, which might be prospectively utilized in thermal energy storage and thermal protection, as well as thermal interface materials.

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