The effect of different nanoshells on the solar–thermal conversion of microencapsulated phase-change material

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Solar-absorbing metamaterial can be used as an outside surface shell of microcapsules of phase-change materials (PCMs), to manipulate thermoregulation through solar–thermal conversion for heating up the PCM while taking advantage of latent heat that can be stored or released from the PCM over a tunable temperature range. To enable further modification of the performance of microencapsulated PCM for different applications, this paper presents a new design with one more layer of the shell added between the metamaterial outer surface and the PCM. The added shell can be made with Mg (AZ31), Ti-6Al-4V, Al, Cu or SS304. The effect of these different shell materials on the solar–thermal conversion of microencapsulated PCM is analysed and demonstrated. Different shell materials can be chosen to enhance high temperature-resistance, corrosion resistance, thermal conductivity and flame retardant capability in thermoregulating structures and in a variety of solar energy applications for such areas as construction, transportation and textiles. Such micro-microencapsulated PCMs may open up new routes to modify thermoregulating structures with novel properties and added value, and represent a breakthrough concept in solar energy conversion, thermal storage and novel thermoregulating technologies.

Keywords: microencapsulation, phase-change material, solar-absorbing metamaterial, solar–thermal conversion, thermal energy storage, thermoregulation

I. Introduction

Solar power is a sustainable and foremost resource for clean, renewable energy.[1] As the arrival of solar radiation on Earth is discontinuous with time and environmental conditions, however, storage methods are needed for exploiting solar energy effectively and flexibly. One of the most

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[1] D.Y. Goswami, F. Kreith and J. Kreider, *Principles of Solar Engineering*. New York: Taylor and Francis (2000).

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effective of the many energy storage techniques is thermal energy storage with encapsulated phase-change materials (PCMs).[2] Microencapsulation, the formation of microcapsules, is usually carried out by coating individual PCM particles with a continuous film forming a shell to produce capsules that are a micrometre to a millimetre in size;[3] that is, they have a PCM as a core and a shell forming the PCM container. The PCM can store and release significant amounts of energy when undergoing phase change through melting and solidifying at a nearly constant temperature or in a designed operating temperature range. With proper selection of the shell materials, microencapsulation of PCMs can be an effective technique for enhancing thermal transfer, resisting interaction with the surrounding environment, and preventing leakage during the melting process.[2] The microencapsulated PCM can be used for various applications in buildings, vehicles, heat pumps, thermal protection, air-conditioning, thermoregulating textiles and other heating systems.[4]

This paper evaluates an innovative structure for the microencapsulated PCMs: a three-layer nanostructured metal–dielectric–metal metamaterial thin film as the outside shell of a PCM microcore, which is firstly coated with an inner shell made with Mg (AZ31), Ti-6Al-4V, Al, Cu, or SS304. The metamaterial outer shell acts as a solar thermal resource for heating up the PCM microcore. The metal inner shell enhances the high temperature and corrosion resistances, and controls the thermal profile and thermoregulating behaviour. This paper emphasizes the effect of different shells on the solar–thermal conversion behaviour of microencapsulated PCM. Such microencapsulated PCMs with a multifunctional shell structure may open up a way to revolutionize the design and enhance the performance of solar-powered thermal storage systems and thermoregulating structures.

2. Structuring and modeling microencapsulated PCMs with multilayer shells

Fig.1 demonstrates the design of a microencapsulated PCM coated with an outer shell of tungsten–silica–tungsten metamaterial laminated over an inner metal shell.[5, 6] The metamaterial is composed of nanostructures having subwavelength planar tungsten stacks of height h on a tungsten film with a silica dielectric spacer of thickness t in between. By exciting plasmonic resonances at particular wavelengths between the planar tungsten stack and the tungsten film of the metamaterial structure, the metamaterial outer shell of the encapsulated PCM can selectively absorb solar radiation in three different wavelength regions, including the visual region from 0.4–0.7 μm, the solar region from 0.3–3.0 μm; and the thermal region with

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[2] A. Jamekhorshid, S.M. Sadrameli and M. Farid, A review of microencapsulation methods of phase-change materials (PCMs) as a thermal energy storage (TES) medium. *Renewable and Sustainable Energy Reviews* **31** (2014) 531–542.

[3] V.V. Tyagi, S.C. Kanshik, S.K. Tyagi and T. Akiyama, Development of phase-change material-based on microencapsulated technology for buildings: A review. *Renewable and Sustainable Energy Reviews* **15** (2011) 1373–1391.

[4] Z. Jin, Y. Wang, J. Liu and Z. Yang, Synthesis and properties of paraffin capsules as phase change materials. *Polymer* **49** (2008) 2903–2910.

[5] H. Wang and L. Wang, Perfect selective metamaterial solar absorbers. *Optics Express* **21** (2013) A1078–A1093.

[6] W. Tong, Formulation of nano- and micro-encapsulated phase change materials with a solar-absorbing metamaterial shell. *Journal of Nanoelectronics and Optoelectronics* **11** (2016) 756–761(6).

wavelengths larger than 2 µm.[7] The right insert of Fig. 1 illustrates a unit cell of the metamaterial with dual- or "double"-sized tungsten patches of different widths w_1 and w_2. Patches with the same width are arranged diagonally such that the structure behaves exactly the same at normal incidence for either TE or TM waves. Each patch is centred in its quadrant with the period $\Lambda' = 2\Lambda$.[5] The absorptance of the metamaterials with "single-sized" and "double-sized" tungsten patches was measured, using the same geometric parameters of $\Lambda = 600$ nm, $h = 150$ nm and $t = 60$ nm, but with different patch widths, namely $w_1 = 250$ nm and $w_2 = 300$ nm.[5] The "double-sized" metamaterial is preferable for the outer shell of the encapsulated PCM because of its broader absorption band compared to the "single-sized" one with $w_1 = 250$ nm; and its higher absorbance as compared to the "single-sized" one with $w_2 = 300$ nm. The calculated solar energy conversion efficiency is over 85% for these metamaterials[5] and this value will be used for solar thermal conversion analysis of the encapsulated PCM in this paper.

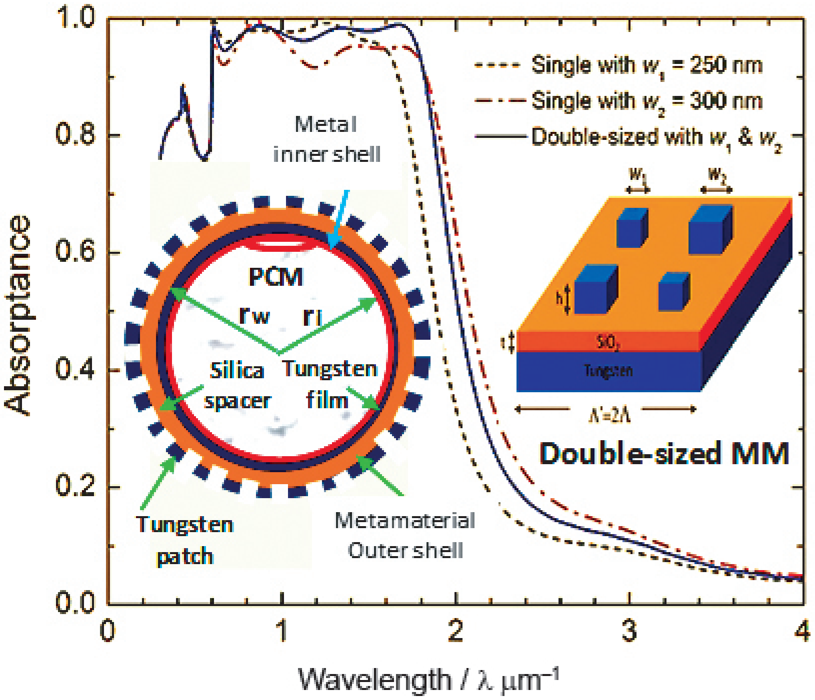

Figure 1. Schematic of solar-absorbing metamaterial–metal shells for microencapsulated PCM (left insert):[5, 6] normal absorptance in the spectral region 0.4–4 µm for a solar-absorbing metamaterial (MM) with tungsten patch widths of both $w_1 = 250$ nm and $w_2 = 300$ nm (dual- or "double"-sized), in comparison with that of single-sized with a unique tungsten patch size, w_1 or w_2. The metamaterial unit cell size $\Lambda = 600$ nm, $h = 150$ nm, and $t = 60$ nm.

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[7] K. Voss, W. Platzer and P. Robinson, Education of architects in solar energy and environment—advanced glazing [http://www.cenerg.ensmp.fr/ease/glazing_overheads.pdf] (2014) .

The inner metal shell and outer tungsten–silica–tungsten metamaterial shell can be coated onto a PCM using closed-field magnetron (CFM) sputtering, which can be carried out at room temperature, allowing different layered materials, like the metal and metamaterial multishells, to be coated in the same batch.[8] The encapsulated PCM can be used for solar energy storage through sensible heating and latent heating of the PCM.[9] As the outer metamaterial shell is much thinner than that of the inner metal shell, it is assumed that the temperature distribution in the metamaterial shell is uniform. Therefore, thermal equilibrium between the metamaterial heat absorption Q_A, heat loss from the metamaterial shell surface Q_L, and the latent heat storage capacity of the PCM Q_P, can be expressed as[9]

$$Q_A - Q_L = Q_P. \tag{1}$$

For an exactly spherical encapsulated PCM, the ratio of PCM volume to the inner volume of the shell container being φ, eqn (1) can be rewritten as

$$\begin{aligned}&4\pi r_w^2 (J_s t_d \eta\alpha - h_c(T_c - T_a)) = m_c C_c (T_f - T_i) + m_{\mathrm{PCM}}[C_{sp}(T_m - T_i) + \alpha_m \Delta h_m + C_{lp}(T_f - T_m)] = \\ &\frac{4}{3}\pi(r_w^3 - r_i^3) d_c C_c (T_f - T_i) + \frac{4}{3}\pi\varphi r_i^3 [d_{sp} C_{sp}(T_m - T_i) + d_{lp}\alpha_m \Delta h_m + d_{lp} C_{lp}(T_f - T_m)],\end{aligned} \tag{2}$$

where r_w is the radius of the outside surface of the metal shell, r_i the radius of the PCM particle, h_c the air convective transfer coefficient on the metamaterial shell surface, J_s standard solar radiation at the earth's surface (1000 W/m^2),[7] t_d the number of working hours per day of the solar-absorbing metamaterial shell, η the thermal efficiency of the solar-absorbing metamaterial shell, here taken as 85%, α a coefficient that gives the fraction of the surface of the metamaterial shell able to receive sunlight (it is mainly influenced by the angle of incidence of the light and transparency of the medium around the metamaterial PCM microcapsules; here it is taken as 0.5, assuming half of the metamaterial shell surface can receive sunlight and the medium around the shell is totally transparent), T_c the surface temperature of the metamaterial shell, T_a the environmental temperature around the metamaterial shell, α_m the fraction of PCM that is melted (taken as 1), Δh_m the heat of fusion per unit mass of PCM, m_c the mass of the metamaterial shell, m_{PCM} the mass of the PCM, d_c the density of the metamaterial shell, d_{lp} the density of liquid PCM, d_{sp} the density of solid PCM, C_c the average specific heat of the metamaterial shell, C_{sp} the average specific heat of the PCM between T_i and T_m, C_{lp} the average specific heat of the PCM between T_m and T_f, T_i the initial temperature of the PCM, T_m the melting temperature of the PCM, and T_f the final temperature of the PCM.

When the ratio φ → 1 (i.e., assuming the microsized PCM particles almost fully fill each metamaterial shell) while the heat transfer reaches an equilibrium state, the following equation could be written:

$$4\pi r_w r_i k(T_f - T_c)/(r_w - r_i) = 4\pi r_w^2 h_c (T_c - T_a), \tag{3}$$

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[8] D.R. Gibson, I. Brinkley, G.W. Hall, E.M. Waddell and J.M. Walls, Deposition of multilayer optical coatings using closed-field magnetron sputtering. *Proc. SPIE* **6286** (*Advances in Thin-Film Coatings for Optical Applications III*) (2006) 628601.

[9] A. Sharma, V.V. Tyagi, C.R. Chen and D. Buddhi, Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews* **13** (2009) 318–345.

where k is the average thermal conductivity of the shell. From eqn (3), T_c can be expressed as:

$$T_c = \frac{r_i k T_f + (r_w - r_i) r_w h_c T_a}{r_i k T_f + (r_w - r_i) r_w h_c} . \tag{4}$$

Replacing T_c in eqn (2) with eqn (4), and when $T_f \geqslant T_m$, assuming $T_a = T_i$, the PCM final temperature T_f could be derived from eqns (2) and (4) (we shall assume $h_c = 10\ \mathrm{W\ m^{-2}\ K^{-1}}$):

$$T_f = \frac{3 J_s t_d \eta \alpha r_w^2 + [(r_w^3 - r_i^3) d_c C_c 3 r_w^3 h_c^2 (r_w - r_i)/R + 3 r_w^2 h_c] T_i - \varphi r_i^3 S}{3 r_w^2 r_i h_c k / R + (r_w^3 - r_i^3) d_c C_c + \varphi r_i^3 d_{lp} C_{lp}} , \tag{5}$$

where

$$R = r_i k + (r_w - r_i) r_w h_c \tag{6}$$

and

$$S = d_{sp} C_{sp} (T_m - T_i) + d_{lp} \alpha_m \Delta h_m - d_{lp} C_{lp} T_m . \tag{7}$$

Based on eqns (1–5), the microencapsulated PCM with multishells can be manipulated as exceptional solar energy storage materials that store energy as sensible heat with no change in phase) and as latent heat. Starting with a solid PCM at ambient temperature, the addition of heat through the outer solar-absorbing metamaterial shell and inner metal shell to the PCM first causes sensible heating of the solid, followed by a solid-to-liquid phase change at almost constant temperature with the absorption of latent heat, and subsequently sensible heating of the liquid. The inverse process occurs with release of (latent) heat during the cooling process as the liquid converts into solid in the absence of solar radiation.[3] The metamaterial and metal multishells provide exceptional advantages over other shells, such as relatively high thermal conductivity, high temperature resistance and thermal stability, good corrosion resistance, and stability under a variety of environmental conditions, as well as the capability of providing solar thermal power. Therefore, the encapsulated PCM with metamaterial and metal multishells could revolutionize the design of solar energy conversion systems for a wide range of applications, including thermoregulating textiles, buildings and vehicles.

3. Effect of different metal shells on the thermal behaviour of microencapsulated PCM

To illustrate the effect of different shell materials on the solar–thermal conversion behaviour indicated by eqn (5), C_{13}–C_{24} alkanes were selected as the PCM and Mg-Al (AZ31), Ti-6Al-4V, Al, Cu or stainless steel 304 was chosen as the inner shell. Metamaterial tungsten film (thickness 150 nm) was used as the outer shell. Table 1 shows the physical properties of selected PCM and metal shells.[10,11]

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[10] A. Abhat, Low-temperature latent heat thermal energy storage: heat storage materials. *Solar Energy* **30** (1983) 313–332.

[11] D. Zhou, C.-Y. Zhao and Y. Tian, Review on thermal energy storage with phase-change materials (PCMs) in building applications. *Applied Energy* **92** (2012) 593–605.

Table 1. Physical properties of selected PCM and metal shells.[10, 11]

Material type	Chemical name	Melting point / °C	Density / kg m^{-3}		Specific heat / J kg^{-1} K^{-1}		Latent heat / kJ kg^{-1}	Thermal conductivity / W m^{-1} K^{-1}	
			Solid	Liquid	Solid	Liquid		Solid	Liquid
PCM	Paraffin C_{13}–C_{24}	22–24	900	760	2900	2100	189	–	0.21
Metal shell	Mg-Al (AZ31)	605–630	1780	–	1005.9	–	–	84.7	–
	Ti-6Al-4V	1878–3020	4430	–	526.3	–	–	6.7	–
	Aluminum	660	2700	–	896	–	–	235	–
	Copper	1085	8933	–	385	–	–	399	–
	Stainless steel 304	1399–1454	8000	–	500	–	–	16.2	–
	Metamaterial tungsten film	3422	19000	–	132	–	–	173	–

The results calculated according to eqn (5) are shown in Fig. 2 for solar-absorbing microencapsulated C_{13}–C_{24} paraffin with different inner metal shells. The final temperature of the encapsulated PCM varies with solar absorption time for different PCM particle sizes according to different initial temperatures. For example, for a typical PCM particle radius range of 10–20 μm, the metamaterial microcapsules need to be exposed to sunlight for more than 2–4 h to bring the PCM final temperature above the PCM melting point of 23 °C from the initial environmental temperature of –10 °C (Fig. 2a). The smaller the capsule radius, the shorter the sunlight exposure time needed to raise the PCM to the final temperature, although very small sizes may create fabrication challenges with present-day technology. Moreover, the extent of the effect of different metal shells on the solar–thermal conversion lies in the order Mg-Al (AZ31) > stainless steel 304 (close to Al) > Cu > Ti-6Al-4V; the higher the temperature rises, the bigger the difference of the effect. As a starting point, this analysis provides a basic guideline for choosing shell materials when designing thermoregulating structures.

The encapsulated C_{13}–C_{24} paraffin PCM can typically be used for low-temperature thermal energy storage and thermoregulation below about 100 °C. The feasibility of integrating microencapsulated paraffin with textiles has been demonstrated; one obtains unique thermoregulation properties and the microencapsulated paraffin keeps its geometrical profile and heat capacity after 1000 cycles.[12, 13] With the solar-absorbing metamaterial shell and the unique inner metal shell, these kinds of paraffin microcapsules may open up new ways for realizing thermoregulating textiles, as well as buildings and vehicles with advanced thermal properties. Potential applications for these microcapsules in textiles include complex life support and healthcare systems, specialized military uniforms and high-performance sportswear.[14] For buildings and vehicles, potential applications include solar-powered thermoregulating walls, ceiling boards, shutters and energy-saving air conditioning systems, as well as energy-saving and frost-resistant windows.

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[12] M. N. Hawlader, M.S. Uddin and H.J. Zhu, Encapsulated phase-change materials for thermal energy storage: experiments and simulation. *International Journal of Energy Research* **26** (2002) 159–171.

[13] M. Silakhori, M.S. Naghavi, H.S.C. Metselaar, T.M.I. Mahlia, H. Fauzi and M. Mehrali, Accelerated thermal cycling test of microencapsulated paraffin wax/polyaniline made by a simple preparation method for solar thermal energy storage. *Materials* **6** (2013) 1608–1620.

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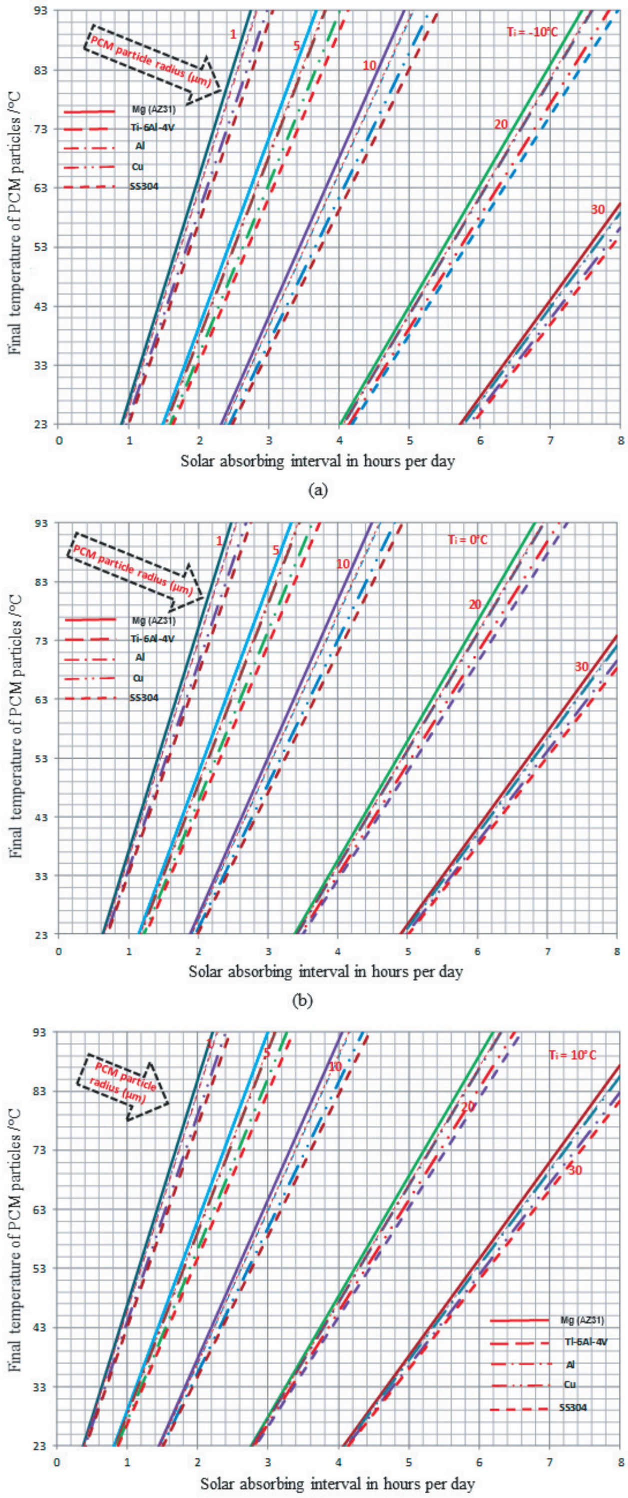

(a)

(b)

(c)

Figure 2. Solar–thermal conversion of microencapsulated C_{13}–C_{24} paraffin with different metal shells when the PCM particle radius is 1 µm and over—the PCM final temperature varies with solar absorption time for different PCM particle sizes according to different initial temperatures: (a) –10 °C; (b) 0 °C; and (c) 10 °C.

In addition, the microencapsulated PCM with a solar-absorbing metamaterial outer shell and metal inner shell has great potential for overcoming the problems or challenges facing conventional PCM smart textiles[15] with exceptional advantages, such as: (a) significantly enhanced thermal conductivity of the encapsulated PCM, because the thermal conductivity of the metal shell is much higher than that of the polymers used hitherto to microencapsulate PCM; (b) excellent flame-retardant capabilities, superior to those of conventional polymer-microencapsulated PCM; (c) metamaterial microencapsulation can directly provide solar thermal power and can be incorporated with micro- or nanoscale thermoelectric modules to generate electrical power for smart textile structures.

4. Conclusion

In this paper, the effect of different shell materials on the solar-thermal conversion behaviour of microencapsulated PCM has been analysed. The sunlight exposure time required to raise the PCM temperature is closely dependent on the radius of the microencapsulates under a given weather environment. The extent of the effect of different metal shells on the solar-thermal conversion exhibits in the order of Mg-Al (AZ31) > stainless steel 304 (close to Al) > Cu > Ti-6Al-4V; the high the temperature rise, the bigger the difference of the effect. These different shell materials can be chosen to enhance the high temperature resistance, corrosion resistance, thermal conductivity or flame retardant capability in thermoregulating structures and in a variety of solar energy applications for such sectors as construction, transportation and textiles. Such micromicroencapsulated PCMs may open up new routes to modify thermoregulating structures with novel properties and added value, and represent a breakthrough concept in solar energy conversion, thermal storage and novel thermoregulating technologies.

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