



# Electroless plating of copper layer on surfaces of urea–formaldehyde microcapsule particles containing paraffin for low infrared emissivity



Xi Zhou, Jian Mao\*, Zhen Qiao

College of Materials Science and Engineering, Sichuan University, No. 24, South Section 1, Yihuan Road, Chengdu 610064, Sichuan, China

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## ABSTRACT

A copper coating was deposited by electroless plating on the surfaces of urea–formaldehyde microcapsules containing paraffin (UFP) particles. This composite microcapsule structure had low infrared (IR) emissivity and maintained a constant temperature, and could be used in IR stealth applications. The electroless copper layer formation and its micro-appearance, and the effect of the copper layer on the IR emissivity and thermal properties of the composite microcapsules were investigated. The IR emissivity of the composite microcapsules at wavelengths of 1–14  $\mu\text{m}$  gradually decreased with increasing copper mass on the surface. After formation of an integrated copper layer, the rate of IR emissivity decrease was lower. This is because the copper coating improves the surface conductivity of the UFP; a high conductivity results in high reflectivity, which leads to a decrease in IR emissivity. The lowest IR emissivity achieved was 0.68. The phase-change enthalpy of the composite microcapsules decreased with increasing amount of copper coated on the surface because of the high density of copper. When the mass increase of the UFP after electroless copper plating was about 300%, the composite microcapsules had low IR emissivity (about 0.8) and a high phase-change enthalpy (80 J/g).

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## Introduction

Phase-change materials (PCMs) change their state within a certain temperature range and can store and release large amounts of energy during phase changes (Abhat, 1983; Kenisarin & Mahkamov, 2007). Microencapsulated PCMs (MEPCMs), which consist of a PCM core and a polymeric or inorganic shell (Lan, Tan, Zou, Sun, & Zhang, 2004; Li, Zhang, Wang, & Niu, 2007), are promising because they maintain their shape and prevent PCMs leaking during phase changes (Zou, Tan, Lan, Sun, & Zhang, 2004; Ozonur, Mazman, Paksoy, & Evliya, 2006; Zhang, Lin, Yang, Zhang, & Zhang, 2007; Hawlader, Uddin, & Khin, 2003). Paraffin is a traditional PCM and is generally used as the core material in MEPCMs because of its high enthalpy and variable phase-change temperature, and urea–formaldehyde (UF) resin is usually selected as the shell material (Zhang, Fan, Tao, & Yick, 2005; Frere, Danicher, & Gramain, 1998; Mao, Yang, & Zhou, 2012). UF microcapsules containing paraffin (UFP) can be used in infrared (IR) shielding coatings to maintain a stable temperature at around the melting temperature

when the inner temperature increases or decreases, so they have potential applications in IR stealth. This is a new idea in both the IR stealth and UFP application fields. However, paraffin and UF resin both have high IR emissivity, which restricts the application of UFPs to IR stealth.

According to the Stefan–Boltzmann law, the IR radiation energy of an object is  $M = \varepsilon\sigma T^4$ , where  $M$  is the radiant emittance,  $\sigma$  is the Boltzmann constant,  $\varepsilon$  is the IR emissivity, and  $T$  is the absolute temperature. For opaque objects, the IR emissivity  $\varepsilon$  can be expressed as (Yuste et al., 2010)

$$\varepsilon = 1 - R, \quad (1)$$

where  $R$  is the reflectivity of an opaque object. Usually, a metal has a high reflectivity because of its high conductivity, so it has a low IR emissivity; for example, coatings consisting of metallic materials such as copper or aluminum powder have low IR emissivities (Yu, Xu, Luo, Shao, & Tang, 2009a; Yu, Xu, Shen, Yan, & Cheng, 2009b; Yu et al., 2009c; Hu, Xu, & Shen, 2009; Yan & Xu, 2010). Based on this, we investigated the use of a metal copper layer prepared by electroless plating on the surfaces of UFP to decrease the IR emissivity, for the production of a new type of IR stealth material. In traditional PCM applications, a copper layer improves the

\* Corresponding author. Tel.: +86 28 85404370.  
E-mail address: [maojian@scu.edu.cn](mailto:maojian@scu.edu.cn) (J. Mao).

low heat conductivity of UFP particles, which is necessary for PCM applications.

## Materials and methods

### Materials

Paraffin (with a solid–liquid phase-change temperature range from 55 to 60 °C), purchased from the Shanghai Hualing Rehabilitation Equipment Factory (China), was used as the core material. Formaldehyde (37 wt% aqueous solution) and urea were used as precursors for the shell material. Triethanolamine (TEA) and 10 wt% hydrochloric acid solution were used to control the solution pH. The electroless copper-plating bath contained CuSO<sub>4</sub>, NaOH, NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, Na<sub>2</sub>EDTA (ethylene diamine tetraacetic acid), and HCHO. All chemicals used were of analytical purity and purchased from the Chengdu Kelong Chemical Plant (China), unless otherwise stated.

### UFP preparation

Urea (180.0 g) and formaldehyde (366.0 g) were mixed in an aqueous solution (about 400 mL), the pH was adjusted to 8.5 with TEA, and the mixture was stirred at 70 °C for 1.5 h. The solution was cooled to ambient temperature and diluted with water (about 450 mL), to give the precursor solution (about 900 mL).

Paraffin encapsulation was performed by *in situ* polymerization, using a previously reported method (Mao et al., 2012). Precursor solution (100 mL) was removed, the pH was adjusted to 5.5, and it was then heated to 75 °C. This was solution A. Solution B was prepared by adding NaCl (15 g) to deionized water (400 mL). Solutions A and B were mixed, and the pH was adjusted to about 4.0. The mixture was heated to 60 °C and kept at that temperature. Paraffin (22.5 g) was dispersed in this solution, using a homogenizer at a stirring speed of 10 000 rpm to form an oil-in-water dispersion. The pH was then reduced to 2.0 at a rate of 0.5 units per 10 min. The resultant dispersion was cooled to ambient temperature. The UFP particles were obtained by sequential filtration, washing, and drying.

### Deposition of electroless plating copper layer

The surfaces of the UFP particles were clean and rough, therefore pre-preparation by washing and etching were not necessary. Surface sensitization was conducted by immersing the UFP particles in an aqueous solution containing 10 g/L SnCl<sub>2</sub> and 40 mL/L 38 vol% HCl at room temperature for 5 min. The UFP particles were then rinsed with deionized water and immediately immersed in an activating solution containing 2.0 g/L AgNO<sub>3</sub> at room temperature for 5 min. The UFP particles were then rinsed with a large volume of deionized water before immersion in the electroless copper-plating bath. The bath contained 16.0 g/L CuSO<sub>4</sub>, 25.0 g/L Na<sub>2</sub>EDTA, 12.0 g/L NaOH, 14.0 g/L NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, and 15.0 mL/L HCHO. The pH of the plating bath was adjusted to 12.5; the temperature was 30 °C. To avoid nonhomogeneous coating of copper caused by sedimentation of UFP particles, an agitator was used during the electroless plating process. The prepared samples were rinsed with deionized water, and dried at room temperature in a vacuum oven.

### Characterization

The surface morphology of the prepared samples was investigated using field-emission scanning electron microscopy (FE-SEM; S4800, Japan) and SEM with energy-dispersive spectrometer (EDS; JSM-5910LV, JEOL, Japan). The crystal structure was determined by

powder X-ray diffraction (XRD) using a Rigaku Dmax 2000 (Japan) diffractometer, with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm), operated at 40 kV and 250 mA. The IR emissivity at wavelengths of 1–14  $\mu$ m was measured using an IR-2 IR-emissivity-measuring instrument (Shanghai Institute of Technological Physics, China), with an accuracy of 0.01. Fourier-transform IR (FT-IR) transmittance spectra of the prepared samples were obtained with a NEXUS 670 FT-IR spectrometer (Thermo Electron Corporation, USA), using KBr pellets. Enthalpy measurements were performed using differential scanning calorimetry (DSC, Netzsch 204 F1, Germany) in the range 0–100 °C at a heating rate of 10 °C/min. The measurement accuracies of heat flux and temperature are  $\pm 1\%$  and  $\pm 0.1$  °C, respectively.

The mass increase (%) of the UFP particles ( $M_{in}$ ) after electroless copper plating was calculated using the following equation:

$$M_{in} = \frac{M_{Cu}}{M_{UFPs}} \times 100\%, \quad (2)$$

where  $M_{Cu}$  is the mass of copper deposited on the UFP particles and  $M_{UFPs}$  is the mass of UFP particles.

## Results and discussion

### Characterization of prepared samples

Fig. 1 shows SEM images of the UFP particles at different stages during electroless copper plating. The average particle size of the original UFPs is about 12.3  $\mu$ m (Fig. 1(a)). The surfaces of the UFP particles after surface sensitization and activation are rough (Fig. 1(b)) and contain silver particles (indicated by arrows). Surface sensitization resulted in Sn<sup>2+</sup> adsorption on the surfaces of the UFP particles, and during the subsequent activation process, silver ions were reduced to silver particles by Sn<sup>2+</sup> ions on the surface:



These reduced silver particles form the cores of the electroless copper plating process. Fig. 1(c) shows the appearance of the UFP particles after electroless copper plating for 10 min; hundreds of small particles appear on the surfaces of the UFP particles, but these particles still do not cover the surface completely. These small particles were identified as copper particles by EDS analysis (Fig. 1(e); the C element peak is from the UFP particle surfaces). Fig. 1(d) shows the UFP particles after electroless copper plating for about 60 min. There is an integrated copper coating on the UFP particle surfaces. Fig. 1(f) shows uniform UFP particles after electroless copper plating for about 60 min, and the average particle size is about 14.5  $\mu$ m.

Fig. 2 shows the FT-IR transmittance spectra of the samples. The UFP spectrum (line a in Fig. 2) is used as a control. The multiple absorption peaks at around 2919 and 2850 cm<sup>-1</sup> are associated with the aliphatic C–H stretching vibration. The absorption peak at 1467 cm<sup>-1</sup> is attributed to C–H bending, and the absorption peak at 724 cm<sup>-1</sup> is assigned to the CH<sub>2</sub> in-plane vibration. These characteristic peaks come from the paraffin core material. The absorption peak at 1641 cm<sup>-1</sup> is attributed to the –C=O stretching vibration, and the absorption peak at 1560 cm<sup>-1</sup> is assigned to the –C–N– stretching vibration. These are the characteristic peaks of the UF resin shell material. As Fig. 2 shows, the intensities of the characteristic peaks in line c decrease significantly compared with those in lines a and b, because the sample corresponding to line c has a complete copper layer covering the surface.

The minimum transmittance peaks in line c in the wavenumber range 1250–714.3 cm<sup>-1</sup> show the lowest vibration intensities. This wavenumber range corresponds to an IR wavelength of 8–14  $\mu$ m. A low vibration intensity means low IR emission.

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